Crystal Growth for **Beginners**

Fundamentals of Nucleation, Crystal Growth, and Epitaxy

3rd Edition

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Preface to the Third Edition

In the last decades, we have witnessed very intensive studies of the growth and physical properties of low-dimensional structures such as quantum dots, quantum wires, quantum wells and quantum wells superlattices, nanowires, nanobelts and nanoflowers, fullerenes and carbon nanotubes, graphene sheets, and many others, because of their unique properties for electronic and optoelectronic applications. In fact, a whole new physics developed before our eyes on the base of nucleation and growth phenomena. Hundreds of review papers, books, and conference proceedings were devoted to these problems (Farrow *et al.*, 1987; Singh 2003; Barnham and Vvedensky 2001). The growth of low-dimensional structures was not treated in this textbook with the only exception of the growth of quantum dots by the Stranski–Krastanov mechanism of growth. As for the very fashionable epitaxial growth of graphene on metal substrates such as Ru(0 0 0 1), Cu(1 1 1), Ni(1 1 1), my impression is that it is too early to include it in a textbook for beginners. Although there are excellent review papers and monographs on the growth of nanowires by vapor–liquid–solid mechanism of growth as the one by Dubrovskii (2014), I decided to include a brief chapter on this topic in order to cover the basics of the process. Various materials such as Si, Ge, III-V, and II-VI compounds have been grown successfully by this method. On the other hand, the growth of such nanowires (nanorods or whiskers) represents a beautiful illustration of the growth by two-dimensional (2D) nucleation in its limiting cases of mononuclear and polynuclear layer-by-layer growth which is in fact described in detail in the book.

There is, however, one more reason to accept the offer of the publishing house to prepare a third edition and it is not purely

scientific. In the last years, I have become more and more interested in the stories of the people who introduced the most important ideas and concepts in crystal growth. About 10 years ago, I asked a younger colleague of mine what is the nationality of Wulff. "German, of course," he immediately replied. I was horrified. Then I decided to prepare a talk about the life of J. W. Gibbs, G. V. Wulff, M. Volmer, I. N. Stranski, L. Krastanov, R. Kaischew, F. C. Frank, N. Cabrera, J. H. van der Merwe, Ya. I. Frenkel, and Ya. B. Zeldovich. I tried to present not only their scientific achievements but also the historic background and the scientific atmosphere in which they lived and worked, and to give interesting events from their life which to give an impression of their personalities. In fact, I have made an attempt to show them as living people with their passions, weaknesses, problems, decisions they had to make in different moments of their respective life. The talk was welcome with great interest not only in my institute where half of the staff worked in one or another aspect of phase transitions but also in the Department of Condensed Matter Physics of the Autonomous University of Madrid. This was the reason to include at the end of the textbook a brief chapter with short biographical texts of the above scientists with suitable photographs which to show them where possible in the time when they made their most important contributions or in significant moments in their life. A big problem was the balance between the historic and scientific background. When I finished writing and read the chapter, I had the impression that I have gone too far with the history and the text reads to me more like a historical rather than a scientific one. Anyway, it is up to the readers to decide if the text is interesting to them, and more importantly, if they enjoy it. The separate texts unavoidably differ in length and details. The main reason is the scarcity of records for ones and abundance of information (recollections of contemporaries, memories of former students and relatives) for others.

I am very grateful to Juan Jose de Miguel for his help in writing the biography of Cabrera and, in particular, to Javier García Sanz for the beautiful narrative of the atmosphere in the Autonomous University of Madrid during the first years of the stay there of Nicolás

Cabrera. A text from Sebastian Vieira written on the occasion of the centenary of the birth of Nicolás Cabrera served as a basis for his biography. The biography of J. H. van der Merwe was written mostly based on the paper of F. R. N. Nabarro (2002). I am greatly indebted to A. A. Chernov for the critical reading of the texts and for his advice to avoid panegyrics. I am also very thankful to the colleagues of mine who read the text and encouraged me to include it in the textbook.

In addition, I tried to make the text more readable by including new figures in order to better illustrate some parts of the text which looked to me a bit more difficult to grasp the essential physics. The text itself was also updated and made more easily understandable in many places.

I would like to express my gratitude to D. Kashchiev for the critical reading of the chapter devoted to the vapor–liquid–solid mechanism of growth of nanowires and who gave me his kind permission to reproduce a figure from a paper of his and supplied me with the corresponding file. In particular I am greatly indebted to Dr. Niall McEvoy from AMBER (Advanced Materials and BioEngineering Research) and School of Chemistry in Trinity College Dublin, for his kindness to grant me his permission to use his beautiful SEM micrograph of ZnO nanorods for the cover of the book.

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Preface to the Second Edition

Although published in 1995 the main body of the first edition was in fact written in 1990. The only exception was the chapter devoted to the one-dimensional nucleation which I wrote two years later during my stay in the National Tsing Hua University in Taiwan. It so happened that in 1989–1990 two new phenomena with great potential for industrial application were discovered — the effect of surface active species (surfactants) on the mode of growth of semiconductor epilayers by Copel *et al.* [1989], and the formation of coherent (dislocation-free) three-dimensional islands in Stranski–Krastanov growth mode by Eaglesham and Cerullo [1900]. In addition, the last decade has seen the beginning of intensive studies of the effect of the additional barrier to down-step diffusion (discovered by Ehrlich more than thirty years ago) on the morphology of growing surfaces. These studies were connected with a dramatic development of the surface analytical tools. As a result of these developments in fact the whole theory of nucleation and growth had to be rewritten taking into account the Ehrlich–Schwoebel barrier.

The idea to update the book taking into account the discoveries mentioned above was the first reason to prepare a second revised edition of this textbook. The second reason was related to the book itself. Many colleagues told me that the book is not easy for reading. Nearly the same number of colleagues told me the opposite. After some years I understood the reason for this distribution of opinions. I myself liked one half of the book and disliked the other one. I found very interesting the fact that my favorite parts were those in which I did not feel as an expert (one cannot be an expert in everything) and vice versa, I disliked those parts in which I had made

contributions myself. So I decided to make an attempt to rectify this inconsistency. The first logical step was to delete most of the contributions of my own. This was easy. The second part, namely writing on what other people have recently done, was really a heavy task for one obvious reason. I had to "decide what will remain in science and what will be forgotten". To solve the problem, I simply decided to write what I liked most. As a result, I deleted the section of the effect of non-convexity of the interatomic potentials on the structure of epitaxial interfaces, and added two new sections on the effect of Ehrlich–Schwoebel barrier and surfactants on the surface morphology. Although the two factors affect both the crystal and epitaxial growth I decided to put the first section in Chap. 3, and the second in Chap. 4. Significant changes have also been made in the sections dealing with the atomistic rate of nucleation and the saturation nucleus density. Moreover, I have looked for a long time for a more elegant way to introduce the criterion of stability of planar adsorbates against clustering. I was so fascinated by the approach of Sir Rudolf Peierls that I decided to reproduce the whole derivation from his brilliant three-page paper. This in turn led to a complete reshaping of the chapter dealing with the thermodynamic criterion of the mechanism of epitaxial growth.

Concerning the readability, a friend of mine told me that a textbook in physics is not a thriller, and the reader should make some effort to grasp the essence. Although I know some textbooks on solid state physics and statistical thermodynamics that read like thrillers to me, I decided to agree with him. Nevertheless, I tried to correct the text where, in my opinion, the latter was clumsy, or the problem ill-defined. So, I do hope that I have succeeded, at least partially, in updating the text in the right direction and making it more readable.

I would like to express my gratitude to G. H. Gilmer, T. T. Tsong, Th. Michely, M. Horn-von Hoegen and B. Voigtländer who gave me their kind permission to reproduce figures from their papers and supplied me with the corresponding files. Particularly, I am greatly indebted to B. Voigtländer for his kindness to grant me his permission

to use the beautiful STM micrograph of “hut” clusters of Ge on Si(001) for the cover of this book. I would like also to thank J. E. Prieto for the critical reading of Chap. 4.

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Preface to the First Edition

The idea to write this book is not totally mine. It belongs partly to Dr. Svetoslav D. Toschev, a colleague and friend of mine, with whom I worked together on the kinetics of electrochemical nucleation of metals. Unfortunately, his untimely death in 1971 prevented him to carry out this project. The idea to write such a book arose out of the long experience we had at the Institute of Physical Chemistry in the theories and experiments on nucleation, crystal growth and epitaxy. In fact, the first paper on crystal growth was published in Bulgaria in as early as 1927 by Ivan Stranski, who introduced the concept of half-crystal position simultaneously with W. Kossel. This turned out to be the most important concept in nucleation and crystal growth. Using this concept Stranski considered, two years later, together with K. Kuleliev the stability of the first several monolayers deposited on a foreign substrate. This work served as a basis for the later treatment by Stranski and Krastanov of the mechanism of epitaxial growth of a monovalent ionic crystal on the surface of a bivalent ionic crystal. This system was chosen because of the easier evaluation of the interatomic forces at that time. Stranski and his coworkers were the first to realise that the thickness variation of the chemical potential in ultrathin epitaxial films determines the mechanism of growth. Now the mechanism of epitaxial growth by formation of several complete monolayers followed by the growth of isolated 3D islands named after Stranski and Krastanov is well known to all researchers involved in epitaxial growth. In fact the work of Stranski and Kuleliev was the first theoretical study of epitaxial growth. In the early thirties Stranski and Kaischew introduced the concept of mean separation work in order to describe the equilibrium of small three-dimensional and

two-dimensional crystals with the parent phase. This allowed them to describe the kinetics of crystal nucleation and 2D growth of perfect crystals in a quantitative way. Today these early papers are almost forgotten but they inspired further research in the field by many authors, like R. Becker and W. Döring, Max Volmer, W. K. Burton, N. Cabrera and F. C. Frank, and many others.

I got the idea to write this book when I was reading a course on Nucleation, Crystal Growth and Epitaxy at the Institute of Microelectronics and Optoelectronics in Botevgrad, Bulgaria. I was surprised to find that so many people involved de facto in growth and characterization of advanced materials by CVD, LPE, MOCVD, MBE, etc. have no basic knowledge in crystal growth and epitaxy. Although they were good specialists in high vacuum, surface and bulk materials characterization, device construction, etc., they did not understand the elementary processes which form the basis of the fabrication of these devices. I was further convinced to write this book after I had read a similar course of lectures at the University of Dresden a year later and after many discussions with colleagues of mine.

There are many excellent monographs, treatises and review papers on different aspects of nucleation, crystal growth and epitaxy. Most of them are listed in the reference list. I would like to bring the reader's attention to the monographs of Max Volmer, Kinetik der Phasenbildung, and Y. Frenkel, Kinetic Theory of Liquids. The only books which cover an appreciable part of the problems treated in this are the monograph of A. A. Chernov in Vol. 3 of Modern Crystallography and The Theory of Transformations in Metals and Alloys, 2nd edition, by J. W. Christian, which I read with great pleasure. All these books are, however, aimed more or less at researchers with some preliminary knowledge of the matter. It turned out that there was not a textbook which could give the basic knowledge on nucleation, crystal growth and epitaxy from a unified point of view and on a level accessible to graduate students or even undergraduate students who have just begun to do research. The reader will need some knowledge in elementary crystallography and chemical thermodynamics. The mathematical description should not give trouble at all even

to undergraduate students. In fact, in all cases in which more complicated mathematical treatment is required, problems with lower dimensionality are considered instead. Thus the mathematical treatment is considerably simplified and the physical meaning is easier to grasp. A typical case is the consideration of Herring's formula. In some cases, the use of some specific mathematical methods like the Euler equation in Chap. 1 and special functions like the Bessel functions and the elliptic integrals could not be avoided. However, the reader should not accept them with "grief". Any good textbook will be able to help the reader who is unfamiliar with the mathematical methods. All of the above is what determined the title of the book.

The book is naturally divided into four chapters: Equilibrium, Nucleation, Crystal Growth and Epitaxial Growth. In the first chapter all the information necessary to understand the material in the remaining chapters is given. Thus the mean separation work which determines the equilibrium of a 2D island with the parent phase is defined in Chap. 1 and is used in Chap. 3 to derive an expression for the rate of propagation of curved steps. The second chapter deals with all the problems connected with nucleation. The only exception is the theory of one-dimensional nucleation which is included in Chap. 3 because it is intimately connected with the propagation of single height steps. The concept which unifies the whole presentation is that of the separation work from a half-crystal (kink) position. One could think of it as the chemical potential of the particular crystal of a monolayer of the deposit (taken with negative sign). By using this concept, it is shown that the only difference between crystal growth and epitaxial growth is of a thermodynamic nature. The chemical potential in ultrathin epitaxial films differs from that of the crystal. The kinetics of growth of both single crystals and epitaxial films are one and the same.

I did not discuss the text with any of my colleagues. That is why I take the sole responsibility for any misinterpretations or errors and I will be very grateful to anybody who detects them and brings them to my notice. On the other hand, I am extremely grateful to V. Bostanov, A. Milchev, P. F. James, H. Böttner, T. Sakamoto and S. Balibar who gave me their kind permission to reproduce

figures from their papers and supplied me with the corresponding photographs. I am also greatly indebted to Professor D. D. Vvedensky from the Imperial College, London, for his kindness to grant me his permission to use the beautiful picture of a Monte Carlo simulation of Si(001) growth for the cover of the book. The book has been written at the Institute of Physical Chemistry of the Bulgarian Academy of Sciences with the only exception of Sec. 3.2.4, which deals with the growth of Si(001) vicinal surfaces by step flow. I decided to include this section in order to illustrate the propagation of single height steps by one-dimensional nucleation. This section was written during my stay at the Department of Materials Science and Engineering of the National Tsing Hua University in Hsinchu, Taiwan, Republic of China, where I was invited as a visiting professor. The final preparation of the manuscript was also carried out at the National Tsing Hua University. I would like to express my sincere gratitude to Professor L. J. Chen and the staff of the department for their kind hospitality and assistance. In this respect I would also like to acknowledge the financial support of the Science Council of the Republic of China.

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Chapter 1

Crystal–Ambient Phase Equilibrium

1.1 Equilibrium of Infinitely Large Phases

The equilibrium between two infinitely large phases α and β is determined by the equality of their chemical potentials μ_α and μ_β. The latter represent the derivatives of the Gibbs free energies with respect to the number of particles in the system at constant pressure P and temperature T, $\mu = (\partial G/\partial n)_{P,T}$, or, in other words, the work which has to be done in order to change the number of particles in the phase by unity. In the simplest case of a single-component system, we have

$$\mu_\alpha(P,T) = \mu_\beta(P,T). \tag{1.1}$$

The above equation means that the pressures and the temperatures in both phases are equal. The requirement $P_\alpha = P_\beta = P$ is equivalent to the condition that the boundary dividing both phases is flat or, in other words, that the phases are infinitely large. This question will be clarified in the next section where the equilibrium of phases with finite sizes will be considered.

Let us assume now that the pressure and the temperature are infinitesimally changed in such a way that the two phases remain in equilibrium, i.e.,

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta. \tag{1.2}$$

It follows from (1.1) and (1.2) that

$$d\mu_\alpha(P,T) = d\mu_\beta(P,T). \tag{1.3}$$

Recalling the properties of the Gibbs free energy ($dG = VdP - SdT$), we can rewrite (1.3) in the form

$$-s_\alpha dT + v_\alpha dP = -s_\beta dT + v_\beta dP, \tag{1.4}$$

where s_α and s_β are the molar entropies, and v_α and v_β are the molar volumes of the two phases in equilibrium with each other.

Rearranging (1.4) gives the well-known Equation of *Clapeyron*

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T\Delta v}, \tag{1.5}$$

where $\Delta s = s_\alpha - s_\beta$, $\Delta v = v_\alpha - v_\beta$, and $\Delta h = h_\alpha - h_\beta$ is the enthalpy of the corresponding phase transition.

Let us consider first the case when the phase β is one of the condensed phases, say, the liquid phase and the phase α is the vapor phase. Then the enthalpy change Δh will be the enthalpy of evaporation $\Delta h_{\text{ev}} = h_v - h_l$ and v_l and v_v will be the molar volumes of the liquid and the vapor phases, respectively. The enthalpy of evaporation is always positive and the molar volume of the vapor v_v is usually much greater than that of liquid v_l. In other words, the slope dP/dT will be positive. We can neglect the molar volume of the crystal with respect to that of the vapor and assume that the vapor behaves as an ideal gas, i.e., $P = RT/v_v$. Then Eq. (1.5) attains the form

$$\frac{d\ln P}{dT} = \frac{\Delta h_{\text{ev}}}{RT^2}, \tag{1.6}$$

which is well known as the Equation of *Clapeyron–Clausius.* Replacing Δh_{ev} with the enthalpy of sublimation Δh_{sub}, we obtain the equation which describes the crystal–vapor equilibrium.

Assuming Δh_{ev} (or Δh_{sub}) does not depend on the temperature, Eq. (1.6) can be easily integrated to

$$\frac{P}{P_0} = \exp\left[-\frac{\Delta h_{\text{ev}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{1.7}$$

where P_0 is the equilibrium pressure at some temperature T_0.

In the case of the crystal–melt equilibrium, the enthalpy Δh is equal to the enthalpy of melting Δh_m which is always positive and the equilibrium temperature is the melting point T_m.

Figure 1.1: Phase diagram of a single-component system in P–T coordinates. O and O' denote the triple point and the critical point, respectively. The vapor pressure becomes supersaturated or undercooled with respect to the crystalline phase if one moves along the line AA′ or AA″. The liquid phase becomes undercooled with respect to the crystalline phase if one moves along the line BB″. ΔP and ΔT are the supersaturation and undercooling, respectively.

As a result of the above considerations, we can construct the phase diagram of our single-component system in coordinates P and T (Fig. 1.1). The enthalpy of sublimation of crystals Δh_{sub} is greater than the enthalpy of evaporation Δh_{ev} of liquid, and hence the slope of the curve in the phase diagram giving the crystal–vapor equilibrium is greater than the slope of the curve of the liquid–vapor equilibrium. On the other hand, the molar volume v_l of the liquid phase is usually greater than that of the crystal phase v_c (with some very rare but important exceptions, for example, in the cases of water and bismuth), but the difference is small so that the slope dP/dT is great, in fact, much greater than that of the other two cases and is also positive with the exception of the cases mentioned above. Thus, the P–T space is divided into three parts. The crystal phase is thermodynamically favored at high pressures and low temperatures. The liquid phase is stable at high temperatures and high pressures, and the vapor phase is stable at high temperatures and low pressures. Two phases are in equilibrium along the lines and the three phases

are simultaneously in equilibrium at the so-called triple point 0. The liquid–vapor line terminates at the so-called critical point 0′ beyond which the liquid phase does not exist any more because the surface energy of the liquid becomes equal to zero and the phase boundary between both phases disappears.

1.2 Supersaturation

When moving along the dividing lines, the corresponding phases are in equilibrium, i.e., Eq. (1.1) is strictly fulfilled. If the pressure or the temperature is changed in such a way that we deviate from the lines of the phase equilibrium one or another phase becomes stable. This means that its chemical potential becomes smaller than the chemical potentials of the phases in the other regions. Any change of the temperature and/or pressure which leads to change of the region of stability leads in turn to transition from one phase to another. Thus, the decrease of the temperature or the increase of the pressure leads to crystallization or liquefaction of the vapor, the decrease of the temperature leads to solidification of the liquids. Figure 1.2 shows the variation of the chemical potentials of the crystal and vapor phases with the pressure at a constant temperature. The chemical potential of the vapor increases with the pressure following the logarithmic law which corresponds to a shift along the line AA′ in Fig. 1.1. At the same time, the chemical potential of the crystal phase is a linear function of the pressure, its slope being given by the molecular volume v_c. Both curves intersect at the equilibrium pressure P_0. At pressures smaller than P_0, the chemical potential of the crystal is greater than that of the vapor and the crystal should sublimate. In the opposite case $P > P_0$, the vapor should crystallize. The difference of the chemical potentials, which is a function of the pressure, represents the thermodynamic driving force for crystallization to occur. It is called a *supersaturation* and is defined as the *difference of the chemical potentials* $\Delta\mu$ *of the infinitely large mother and new phases* at the particular value of the temperature. In other words, we have (Fig. 1.2)

$$\Delta\mu = \mu_v(P) - \mu_c(P). \tag{1.8}$$

Figure 1.2: Dependence of the chemical potentials of the vapor, μ_v, and the crystal, μ_c on the pressure when one moves along the line AA′ in Fig. 1.1. P_0 denotes the equilibrium pressure.

As written above, the expression for the supersaturation is incorrect. The correct way of writing is just the opposite. The supersaturation should be equal to the chemical potential of the new phase relative to the chemical potential of the mother phase, i.e., $\Delta\mu = \mu_c(P) - \mu_v(P)$. However, we have to remember that the chemical potentials are always negative quantities and smaller chemical potential means more negative chemical potential. This is clearly seen in Eq. (1.58) where the chemical potential of the infinitely large crystal (at 0 K) is equal to the energy required to evaporate an atom (which is a positive quantity) taken with a negative sign. Then the difference $\mu_c - \mu_v$ will be negative. To avoid confusion with signs, we usually define $\Delta\mu$ as in Eq. (1.8). That is why when writing the expression for the work for nucleus formation (Eq. (2.3)), we put a minus sign before the term that includes the supersaturation.

Bearing in mind Eq. (1.1), or $\mu_v(P_0) = \mu_c(P_0)$, we can rewrite Eq. (1.8) in the form

$$\Delta\mu = [\mu_v(P) - \mu_v(P_0)] - [\mu_c(P) - \mu_c(P_0)].$$

For small deviations from equilibrium, the above equation turns into

$$\Delta\mu \cong \int_{P_0}^{P} \frac{\partial \mu_v}{\partial P} dP - \int_{P_0}^{P} \frac{\partial \mu_c}{\partial P} dP = \int_{P_0}^{P} (v_v - v_c) dP \cong \int_{P_0}^{P} v_v dP.$$

Treating the vapor as an ideal gas ($v_v = kT/P$), we obtain upon integration

$$\Delta\mu = kT \ln \frac{P}{P_0}, \tag{1.9}$$

where P_0 is the equilibrium vapor pressure of the infinitely large crystal phase at the given temperature.

Without going into details, we can write an expression for the supersaturation in the case of crystallization from solution, when the solution is treated as ideal, in the form

$$\Delta\mu = kT \ln \frac{C}{C_0}, \tag{1.10}$$

where C and C_0 are, respectively, the real and the equilibrium concentrations of the solute. In fact, a more rigorous treatment requires the consideration of multicomponent systems. For more details, see Chernov (1980).

Figure 1.3 shows the variation of the chemical potentials of the crystal and liquid phases with the temperature at a constant pressure (the line BB'' in Fig. 1.1). The supersaturation which in this case is frequently called *undercooling* is again defined as the difference of the chemical potentials of the infinitely large liquid and crystal phases, μ_l and μ_c, respectively, at a given temperature

$$\Delta\mu = \mu_l(T) - \mu_c(T). \tag{1.11}$$

Following the same procedure as above, we obtain

$$\begin{aligned}\Delta\mu &= [\mu_l(T) - \mu_l(T_m)] - [\mu_c(T) - \mu_c(T_m)] \\ &\cong \int_{T_m}^{T} \frac{\partial \mu_l}{\partial T} dT - \int_{T_m}^{T} \frac{\partial \mu_c}{\partial T} dT = \int_{T}^{T_m} \Delta s_m dT.\end{aligned}$$

Figure 1.3: Dependence of the chemical potentials of the liquid phase, μ_l, and the crystal phase, μ_c, on the temperature when one moves along the line BB″ in Fig. 1.1. The melting point is denoted by T_m.

Assuming the entropy of melting $\Delta s_m = s_l - s_c$ is independent of the temperature, one obtains after integration

$$\Delta\mu = \Delta s_m(T_m - T) = \frac{\Delta h_m}{T_m}\Delta T. \tag{1.12}$$

Obviously, Eq. (1.12) is also applicable to the case of crystallization of undercooled vapor after the enthalpy of melting is replaced by the enthalpy of sublimation (the line AA'' in Fig. 1.1).

Finally, in the particular case of electrocrystallization of metals, the supersaturation is given by

$$\Delta\mu = ze\eta, \tag{1.13}$$

where z denotes the valence of the neutralizing ions, $e = 1.60219 \times 10^{-19}$C is the elementary electric charge, and $\eta = E - E_0$ is the so-called *overvoltage or overpotential* given by the difference of the equilibrium potential E_0 of the deposited metal in the solution and the electrical potential E applied from outside (Kaischew 1946, 1947).

Let us now compare the supersaturation for growth from vapor and the undercooling for growth from melt of such a "simple" crystal as Si. The Si vapor consists of Si, Si_2, and Si_3, but the concentration

of the monomer is many orders of magnitude larger than that of polymer molecules and the latter can be neglected. The growth from vapor very often takes place at a temperature of about 600 K and the atom arrival rate $\Re$ is usually of the order of one monolayer (ML) per minute or approximately 1.1×10^{13} cm^{-2} s^{-1} (Voigtländer 2001). The equilibrium vapor pressure of Si at 600 K is $P_e = 1.3 \times 10^{-32}$ atm or 1.3×10^{-27} N m^{-2}. The flux of atoms which arrive per second on unit area of 1 cm^2 is given by $\Re_e = P_e(2\pi mkT)^{-1/2}$ (see Eq. (2.56)) where $m \approx 4.66 \times 10^{-26}$ kg is the mass of a single atom, $k = 1.38 \times 10^{-23}$ J K^{-1} is the Boltzmann constant. Then $\Re_e \approx 6.5 \times 10^{-8}$ cm^{-2}s^{-1} and $\Delta\mu = kT \ln(\Re/\Re_e) \approx 2.5$ eV. Repeating the same calculations at higher temperatures (the equilibrium vapor pressure increases exponentially with temperature, see Eq. (1.58)), we find that $\Delta\mu = 1.2$ eV at 1000 K and becomes negative $\Delta\mu = -0.2$ eV at 1400 K. In other words, at about 1300 K, the Si crystal begins to evaporate rather than to grow at the above atom arrival rate. We calculate now the undercooling in Si melt. With $\Delta s_m = 30$ J mol^{-1} (Hultgren *et al.*, 1973), we find $\Delta\mu \approx 3$ meV ($\Delta T = 10$ K). Comparing both estimates, we reach the following very important conclusion. Under typical conditions (comparatively low temperatures in vapor growth and close to the melting point in growth from melts), the growth from vapor takes place very far from equilibrium compared with the growth from melt.

It was Max Volmer (1939) who introduced the term "Überschreitung" or "step across" for both the supersaturation and the undercooling to denote the transition through the line of co-existence of the two phases. Thus, the difference of the chemical potentials of the infinitely large new and mother phases appears as a measure of deviation from the phase equilibrium and determines the rate of the transition from one phase to another.

1.3 Equilibrium of Finite Phases

In the previous section, we considered the equilibrium of two phases in a single-component system assuming that the phases are sufficiently (or infinitely) large or, in other words, the phase boundary

between them is flat. This is not obviously the case at the beginning of the process of phase transition which is of interest to us. Thus, in the cases of transition from vapor to crystal, from vapor to liquid, or from liquid to vapor phases, the process of formation of the new phase always goes through the formation of small crystallites, droplets, or bubbles. In this section, we will clarify two questions: (i) the mechanical equilibrium of small particles with their ambient phase or, in other words, the interrelation of the pressures in the two phases when the phase boundary is not flat, and (ii) the thermodynamic equilibrium of small particles or their equilibrium vapor pressure as a function of their size. In fact, we will derive and interprete the equations of Laplace and Thomson–Gibbs.

1.3.1 *Equation of Laplace*

We consider a vessel with a constant volume V containing vapor with pressure P_v and a liquid droplet with a radius r, and an inner pressure P_l both at one and the same constant temperature T (see Fig. 1.4). The condition for equilibrium is given by the minimization of the Helmholz free energy of the system $F(V,T)$

$$dF = -P_v dV_v - P_l dV_l + \sigma dS = 0, \tag{1.14}$$

where V_v and V_l are the volumes of the vapor phase and the droplet, σ is the surface tension of the liquid, and S is the droplet surface area. The value of the surface tension of the infinitely large liquid phase is usually taken for σ. As $V = V_v + V_l = \text{const}$ and $dV_v = -dV_l$,

Figure 1.4: To the derivation of the equation of Laplace.

Eq. (1.14) can be rewritten after rearrangement in the form

$$P_l - P_v = \sigma \frac{dS}{dV_l}.$$

Bearing in mind that $S = 4\pi r^2$ and $V_l = 4\pi r^3/3$,

$$\frac{dS}{dV_l} = \frac{d(4\pi r^2)}{d(4\pi r^3/3)} = \frac{2}{r},$$

and the above equation turns into

$$P_l - P_v = \frac{2\sigma}{r}, \tag{1.15}$$

which is known as the *Laplace* equation. The latter states that the pressure in a small droplet is always higher than the pressure of the surrounding vapor. The difference $2\sigma/r$ is called the *Laplace* or *capillary pressure* and is equal to zero when the phase boundary is flat ($r \to \infty$). Then, $P_l = P_v = P_\infty$ as stated in Sec. 1.1. Here the notation P_∞ for the equilibrium pressure is used instead P_0 to emphasize the fact that the dividing surface is flat, i.e., it has an infinite radius of curvature.

The physical meaning of Eq. (1.15) becomes more clear if we derive it from the balance of forces. The overall force exerted on the droplet from outside is a sum of the force $4\pi r^2 P_v$ exerted from the vapor phase and the force $8\pi r\sigma$ due to the surface tension. It is equal to the force due to the internal pressure $4\pi r^2 P_l$, i.e.,

$$4\pi r^2 P_v + 8\pi r\sigma = 4\pi r^2 P_l$$

and Eq. (1.15) results. Thus, the Laplace pressure is clearly due to the surface tension of the small droplet.

In the case of the arbitrary surface with the principal radii of curvature r_1 and r_2, Eq. (1.15) reads

$$P_l - P_v = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right). \tag{1.16}$$

Let us estimate as an example the pressure in a water droplet in a fog. The typical size of the droplets is about 1 μm = 1×10^{-6} m. The surface tension of the water is 75 erg cm^{-2} = 0.075 J m^{-2}.

Figure 1.5: To the derivation of the equation of Thomson–Gibbs.

Then, $2\sigma/r = 150\,000$ N m^{-2} = 1.5 atm. If the outside pressure is 1 atm, we obtain that the inner pressure is 2.5 times higher than the outer pressure.

1.3.2 *Equation of Thomson–Gibbs*

In order to solve the problem of the thermodynamic equilibrium, we consider the same system as before at constant pressure P and temperature T (Fig. 1.5). In this case, the variation of the Gibbs free energy $G(P, T, n_v, n_l, S)$ of the system reads ($dP = dT = 0$)

$$\Delta G = \mu_v dn_v + \mu_l dn_l + \sigma dS = 0, \tag{1.17}$$

where n_v and n_l are the number of moles in the vapor and liquid phases, respectively.

When writing the expression for the Gibbs free energy, we take for the chemical potential of the atoms in the small droplet the value which is valid for the bulk phase and compensate the difference between the bulk liquid and the small droplet by the surface energy σS. Besides, we again ascribe to the surface tension its bulk value. As the system is closed, $n_v + n_l = \text{const}$ and $dn_v + dn_l = 0$. Solving (1.17) together with $dn_v = -dn_l$ gives

$$\mu_v - \mu_l = \sigma \frac{dS}{dn_l}.$$

With $n_l = 4\pi r^3/3v_l$, it turns into the famous equation of *Thomson–Gibbs*

$$\mu_v - \mu_l = \frac{2\sigma v_l}{r}. \tag{1.18}$$

Comparing Eqs. (1.15) and (1.18), it becomes immediately clear that the product $(P_l - P_v)V_l = n\Delta\mu$ is just equal to the work gained when a liquid droplet is formed from the unstable vapor phase or, in other words, when $n = V_l/v_l$ atoms or molecules are transferred from the vapor phase with a higher chemical potential to the liquid phase with a lower chemical potential (Gibbs 1928).

As μ_l is the chemical potential of the bulk liquid phase, the difference $\mu_v - \mu_l$ is just equal to the supersaturation $\Delta\mu$ (see Eq. (1.9)) and

$$P_r = P_\infty \exp\left(\frac{2\sigma v_l}{rkT}\right). \tag{1.19}$$

The latter states that the equilibrium vapor pressure of a small liquid droplet with a radius r is higher than that of the infinitely large liquid with a flat surface. The physical reason is easy to understand if we imagine that an atom on a curved convex surface is more weakly bound to the remaining atoms than in the case of an atom on a flat surface.

Obviously, we have the opposite case when considering a vapor bubble with a radius r in an overheated liquid. Following a similar procedure, we find

$$P_r = P_\infty \exp\left(-\frac{2\sigma v_l}{rkT}\right). \tag{1.20}$$

The dependence of the equilibrium vapor pressures of a liquid droplet and a gas bubble on their size is shown in Fig. 1.6.

In order to derive an analogous equation for a small crystallite, we have to know its equilibrium shape. The latter is defined as the shape at which the crystal has a minimal surface energy at a given constant volume. For a liquid droplet, the equilibrium shape is obviously a sphere. We will accept by now that Eq. (1.19) is valid for small crystallites with the only exception that the radius of the droplet is replaced by the radius of the sphere inscribed in the crystallite.

Let us now evaluate the effect of the droplet size on the equilibrium vapor pressure. We consider again a small water droplet with a radius of 1 μm. Such a droplet contains 1.4×10^{11} molecules

Figure 1.6: Dependence of the equilibrium vapor pressures of a small liquid droplet (curve 1, Eq. (1.19)) and in a vapor bubble in an overheated liquid (curve 2, Eq. (1.20)). P_∞ denotes the equilibrium vapor pressure of the infinitely large liquid phase.

($v_l = 3 \times 10^{-23}$ cm^3). For such a large droplet, we can take again the surface tension of the infinitely large liquid phase $\sigma = 75$ dyne cm^{-1}. Then Eq. (1.19) yields $P_r/P_\infty = 1.001$ and the Thomson–Gibbs effect can be neglected. However, for smaller droplets with a radius of the order of 10 Å, which contain 140 molecules, $P_r/P_\infty = 3.3$. We point out that for such small droplets, the surface tension should be smaller than that of the infinitely large liquid phase as suggested by Kirkwood and Buff (1949) and by Tolman (1949). It is of interest to estimate the temperature of melting of small crystallite by using Eqs. (1.12) and (1.18). We consider as an example a small Ge crystal with a radius of 10 Å and containing about 200 atoms in its melt. With the values for the surface energy at the crystal–melt boundary $\sigma = 250$ erg cm^{-2} (Skripov 1977), the entropy of melting $\Delta s_m = 30.55$ J K^{-1} mol, and $v_c = 2.3 \times 10^{-23}$ cm^3, we obtain $T_m - T = 220$ K. The latter means that, whereas the bulk Ge melts at 1210 K, the small Ge crystallite melts below 1000 K. As seen from the above, we can introduce a crystal size, which is usually called a Thomson–Gibbs size, under which the Thomson–Gibbs effects play

a significant role. As will be shown in the following, this characteristic size differs for three-dimensional (3D) and two-dimensional (2D) crystals.

1.4 Equilibrium Shape of Crystals

When considering the equilibrium of a small crystal with its ambient phase (vapor, solution, or melt), there exists obviously a shape which is the most favorable from a thermodynamic point of view in the sense that the work of formation of such a crystal is the minimal one at the given crystal volume. The work of formation of a small crystal consists of two parts: a volume part $(P_c - P_v)V_c = n(\mu_v - \mu_c)$ which is gained when transferring n atoms or molecules from the ambient (vapor) phase with a chemical potential μ_v to the crystal phase with a lower bulk chemical potential μ_c when the crystal phase is the stable one ($\mu_c < \mu_v$), and a surface part σS which is spent to create a new phase-dividing surface. The volume part depends obviously only on the volume of the crystal or on the number of the atoms transferred. At a constant volume, the surface part depends only on the crystal shape. Then the condition for the minimum of the Gibbs free energy change connected with the crystal formation at a constant volume which determines the equilibrium shape is reduced to the minimum of the surface energy. The equilibrium shape of a liquid droplet is evidently a sphere. The case of a crystal is more complicated as the latter is confined by crystal faces with different crystallographic orientations and, respectively, different specific surface energies. This means that the surface energy depends on the crystallographic orientation and in that sense it is anisotropic.

In general, there are three ways to create a new surface. In the first one, two homogeneous phases are cut (or cleaved) into two parts each, and then the different halves are put into contact. New surface can be formed also by the transfer of atoms from one phase to another forming convex (during growth) or concave (during evaporation or dissolution) form. Finally, new surface can be created by stretching out an old one (by stretching out the bulk crystal). When two

liquid phases are involved, the above three methods do not differ. The work spent to create reversibly and isothermally a unit area of a new surface is called *specific surface free energy.* When a new surface is formed by the two first methods, chemical bonds are broken or created. Thus, the work for the creation of a new surface or, in other words, the specific surface free energy, is equal as a first approximation to the sum of the energies of the broken bonds per unit area. When applying the third method, the number of the broken bonds remains unchanged, but the surface area per dangling bond is changed, which in turn leads to a change of the surface energy.

It follows from the above that, the more closely packed the given crystal face, the smaller is the density of the unsaturated bonds and thus its specific surface free energy. Let us consider, for example, the specific surface free energies of the faces of a crystal with a simple cubic lattice. The latter does not exist in nature, with the only exception being one of the crystal modifications of the metal polonium, but is widely used in theoretical considerations. It is well known under the name *Kossel crystal.* When determining the specific surface energy, we will take into account the bonds between first, second, and third-nearest neighbor atoms. The procedure of determination of σ of the face (hkl) involves a construction of a column in the shape of a prism with a form of the base which follows, for convenience, the symmetry of the crystal face, i.e., square on $(1\,0\,0)$, hexagonal on $(1\,1\,1)$ faces of cubic crystals, etc. (Honnigmann 1958). Then the energy necessary for the detachment of this column from the crystal face Ψ_{hkl} is divided by the doubled area Σ_{hkl} of the contact because two surfaces are involved. Thus, $\sigma_{hkl} = \Psi_{hkl}/2\Sigma_{hkl}$. Following Fig. 1.7(a), a column of atoms with a square base is detached from the $(1\,0\,0)$ face of a Kossel crystal and two surfaces are created. The value of the surface energy is then

$$\sigma_{1\,0\,0} = \frac{\psi_1 + 4\psi_2 + 4\psi_3}{2b^2} = \frac{1}{b^2}\left(\frac{1}{2}\psi_1 + 2\psi_2 + 2\psi_3\right),$$

where ψ_1, ψ_2, and ψ_3 are the works required to break the bonds between the first, second, and third neighbors, respectively, and b^2 is the area per atom, b being the interatomic distance.

Figure 1.7: For the determination of the specific surface energies σ_{hkl} of the faces (a) (1 0 0) and (b) (1 1 0) of a crystal with simple cubic lattice.

For the rhombohedral face (1 1 0) (see Fig. 1.7(b)), the column has a rectangular base and

$$\sigma_{1\,1\,0} = \frac{2\psi_1 + 6\psi_2 + 4\psi_3}{2b^2\sqrt{2}} = \frac{1}{b^2}\left(\frac{1}{\sqrt{2}}\psi_1 + \frac{3}{\sqrt{2}}\psi_2 + \sqrt{2}\psi_3\right).$$

The shortest first neighbor bonds have the greatest contribution to the energy. The energies of the second neighbor bonds are probably not greater than 10% of the energies of the first neighbor bonds for metallic and covalent bonds. The contribution of the third neighbor bonds could be neglected. It follows from above that $\sigma_{1\,0\,0} < \sigma_{1\,1\,0}$. Performing the same calculations for the faces (1 1 1) and (2 1 1), we will find that $\sigma_{1\,0\,0} < \sigma_{1\,1\,0} < \sigma_{1\,1\,1} < \sigma_{2\,1\,1}$, etc.

1.4.1 *Theorem of Gibbs–Curie–Wulff*

1.4.1.1 *Crystal in a 3D medium*

We consider first the simpler case of a crystal in a 3D homogeneous medium (vapor, solution, or melt). Following Gibbs (1878) and Curie (1885), we derive an expression for the equilibrium shape of a single-crystal proceeding from the general condition of the minimum of the Helmholz free energy of the system at $T = \text{const}$ and $V = \text{const}$:

$$dF = 0, \qquad dV = 0. \tag{1.21}$$

We assume first that the crystal is a polyhedron confined by a limited number of different crystal faces with areas Σ_n to which a series of *discrete* values of the specific surface energies σ_n correspond. Then the equilibrium condition (1.21) reads

$$dF = -P_v dV_v - P_c dV_c + \sum_n \sigma_n d\Sigma_n = 0, \tag{1.22}$$

where P_c is the inner pressure of the crystal and P_v is the pressure of the vapor phase, and V_v and V_c are the volumes of the vapor phase and the crystal, respectively.

Bearing in mind that $V = V_v + V_c = \text{const}$ or $dV_v = -dV_c$, the above equation is reduced to

$$-(P_c - P_v)dV_c + \sum_n \sigma_n d\Sigma_n = 0. \tag{1.23}$$

The volume of the crystal can be considered as a sum of the volumes of pyramids constructed on the crystal faces with a common apex in an arbitrary point within the crystal. Then

$$V_c = \frac{1}{3}\sum_n h_n \Sigma_n$$

and

$$dV_c = \frac{1}{3}\sum_n \big(\Sigma_n dh_n + h_n d\Sigma_n\big),$$

where h_n are the heights of the pyramids.

On the other hand, every change of the volume with accuracy to infinitesimals of second order is equal to the shift of the surfaces Σ_n by a distance dh_n so that (Fig. 1.8)

$$dV_c = \sum_n \Sigma_n dh_n.$$

Figure 1.8: To the derivation of the equilibrium shape of a 3D crystal.

Combining the last two equations gives

$$dV_c = \frac{1}{2}\sum_n h_n d\Sigma_n. \tag{1.24}$$

Substituting (1.24) in (1.23) gives

$$\sum_n \left[\sigma_n - \frac{1}{2}(P_c - P_v)h_n\right] d\Sigma_n = 0.$$

As the changes $d\Sigma_n$ are independent from each other, every term in the brackets is equal to zero and

$$P_c - P_v = 2\frac{\sigma_n}{h_n}. \tag{1.25}$$

The difference $P_c - P_v$ does not depend on the crystallographic orientation and for the equilibrium shape one obtains

$$\frac{\sigma_n}{h_n} = \text{const}, \tag{1.26}$$

or

$$\sigma_1 : \sigma_2 : \sigma_3 : \cdots = h_1 : h_2 : h_3 : \cdots . \tag{1.26$'$}$$

The relationship (1.26) expresses the geometrical interpretation given later by Wulff (1901) known as the *Wulff's rule* or *Gibbs–Curie–Wulff's theorem*, or very often *Wulff construction*. It states that *in equilibrium the distances of the crystal faces from a point within the crystal (called a Wulff's point) are proportional to the corresponding specific surface energies of these faces* (see Fig. 1.10). According to this rule, we can construct the equilibrium shape by the following procedure: we draw vectors normal to all possible

Figure 1.9: For the determination of the specific energy of the interface between two isomorphic crystals A and B (after Kern *et al.*, 1979).

crystallographic faces from an arbitrary point. Then distances proportional to the corresponding values of the specific surface energies σ_n are marked on the vectors and planes normal to the vectors are constructed through the marks. The resulting closed polyhedron is the equilibrium shape. Crystal faces with the lowest surface energies belong to it. Crystal faces which only touch the apexes of this polyhedron or are situated even further do not belong to the equilibrium form.

The proportionality constant in (1.26) is determined by the difference of the pressures in both phases. As shown in the previous section $(P_c - P_v)v_c = \Delta\mu$, where $v_c = V_c/n_c$ is the molar volume of the crystal phase. The condition $P_c - P_v = \text{const}$ is thus equivalent to the statement that the difference of the chemical potentials, or in other words, the supersaturation $\Delta\mu = \mu_v - \mu_c$ has one and the same value all over the crystal surface. Then

$$\Delta\mu = \frac{2\sigma_n v_c}{h_n} \tag{1.27}$$

Figure 1.10: Equilibrium shape of a crystal on a foreign substrate. Wulff's point is denoted by O. The distance from Wulff's point to the contact plane is denoted by h_m. The distances h_1 and h_2 to the free surfaces remain the same as in a free polyhedron. The equilibrium shape in the absence of a foreign substrate is shown by the additional dashed line.

and hence the supersaturation determines the scale or the size of the crystal. As seen, Eq. (1.27) has the familiar form of the Thomson–Gibbs equation. As Wulff's point has been arbitrarily chosen, we can take it in the center of the crystal.

1.4.1.2 *Crystal on a surface*

In the same way, we can derive Gibbs–Curie–Wulff's theorem for a crystal formed on a foreign substrate (Fig. 1.10) (Kaischew 1950, 1951, 1960). In this, case the crystal lies with one of its faces with specific surface energy σ_m on the substrate, the latter having a specific surface energy σ_s. An interfacial boundary is formed between the crystal and the substrate. In order to find its specific energy, we will perform the following imaginary experiment.

Relation of Dupré: We consider two crystals A (substrate) and B (deposit) of equal dimensions (Fig. 1.9) (Kern *et al.*, 1979). We cleave them reversibly and isothermally and produce two surfaces of A, each one with area Σ_{A}, and two surfaces of B, each one with area

$\Sigma_{\mathrm{B}} = \Sigma_{\mathrm{A}}$. In doing so, we expend energies U_{AA} and U_{BB}. We then put the two halves of A in contact with the two halves of B and produce two interfacial boundaries AB, each one with area $\Sigma_{\mathrm{AB}} = \Sigma_{\mathrm{B}} = \Sigma_{\mathrm{A}}$. The work gained is $-2U_{\mathrm{AB}}$. The excess energy of the boundary AB required to balance the energy change accompanying the above process is $2U_i$. Thus, we have

$$2U_i = U_{\mathrm{AA}} + U_{\mathrm{BB}} - 2U_{\mathrm{AB}}.$$

Clearly, when the two crystals are indistinguishable from each other, $U_{\mathrm{AA}} = U_{\mathrm{BB}} = U_{\mathrm{AB}}$ and the excess energy $U_i = 0$. Using the definition of the specific surface energy ($\sigma_{hkl} = U_{hkl}/2\Sigma_{hkl}$), one obtains the well-known relation of *Dupré* (1869)

$$\sigma_i = \sigma_{\mathrm{A}} + \sigma_{\mathrm{B}} - \beta, \tag{1.28}$$

where the specific interfacial energy $\sigma_i = U_i/\Sigma_{\mathrm{AB}}$ is defined as the excess energy of the boundary per unit area, and the specific adhesion energy $\beta = U_{\mathrm{AB}}/\Sigma_{\mathrm{AB}}$ is defined as the energy per unit area to disjoin two different crystals. Note that β accounts for the binding between the two crystals and does not depend on the lattice misfit. The latter will be taken into account when considering the epitaxial growth of thin films.

Equilibrium Shape: When a crystal is formed on a foreign substrate, a surface energy $\sigma_s\Sigma_m$ is lost and a surface energy $\sigma_i\Sigma_m$ is gained, Σ_m being the area of the contact. Then instead of (1.22), one has to write

$$dF = -P_v dV_v - P_c dV_c + \sum_{n\neq m} \sigma_n d\Sigma_n + (\sigma_i - \sigma_s)d\Sigma_m = 0. \tag{1.29}$$

Following the same procedure as above, we find the relation known in the literature as Wulff–Kaischew theorem (Kaischew 1950; Müller and Kern 2000)

$$\frac{\sigma_n}{h_n} = \frac{\sigma_m - \beta}{h_m} = \mathrm{const} \tag{1.30}$$

or

$$\sigma_1 : \sigma_2 : \sigma_3 : \cdots : \sigma_m - \beta = h_1 : h_2 : h_3 : \cdots : h_m, \tag{1.30$'$}$$

where h_m is the distance from the Wulff point to the contact plane (Fig. 1.10).

It follows that the distance h_m from Wulff's point to the contact plane is proportional to the difference of the corresponding specific surface energy and the specific adhesion energy. Obviously, when the substrate catalytic potency is equal to zero, $\beta = 0$, the distance h_m will have its "homogeneous" value in the absence of a substrate. In this case, we speak of *complete nonwetting*. At the other extreme $\beta = \sigma_A + \sigma_B = 2\sigma$ ($\sigma_A = \sigma_B = \sigma$), we have the case of *complete wetting* and the crystal will be reduced to a 2D ML island. In all intermediate cases $0 < \beta < 2\sigma$, we have *incomplete wetting* and the height of the crystal will be smaller than its lateral size. The effect of the wetting on the equilibrium shape of a crystal on a foreign substrate is demonstrated in Fig. 1.11.

1.4.2 *Polar diagram of the surface energy*

We have considered by now a crystal confined to discrete faces with small Miller indices. Let us now imagine a crystal face which is

Figure 1.11: Equilibrium shape of a crystals on an unlike substrate. The distances h_1 and h_2 in the free polyhedron (a) are proportional to the specific free energies σ_1 and σ_2 according to the Gibbs–Curie–Wulff theorem (1.26). In the presence of an unlike substrate, the distances to free surfaces remain the same as in the free polyhedron. The distance h_i to the plane of contact is determined by the difference $\sigma_i - \beta$ according to the Wulff–Kaischew theorem (1.30). (b) Shows complete nonwetting ($\beta = 0$), (c) and (d) show different degrees of incomplete wetting (note that in the latter case the vector h_i is negative), (e) shows complete wetting ($\beta = 2\sigma_i$).

(a)

(b)

Figure 1.12: Vicinal surfaces deviated by an angle (a) θ and (b) $-\theta$ from a small index (singular) face.

slightly deviated (by a small angle θ) from one of the small index faces, say, the cubic one (1 0 0) of a Kossel crystal as shown in Fig. 1.12(a). Such a face is called *vicinal*. It is clear for geometrical reasons that it consists of terraces and steps. For simplicity, we accept that the steps are monoatomic and equidistant. The specific surface energy of such a face is a sum of the surface energy of the terraces σ_0 and of the energy of the steps or the edge energy $\varkappa \cong b\sigma_0$ which can be evaluated in the same way as the surface energy, just by counting the number of the broken bonds per unit length. If one neglects the interaction between the steps as a first approximation for the specific surface energy of such a vicinal face, one obtains (Landau 1969)

$$\sigma(\theta) = \frac{\varkappa}{b}\sin(\theta) + \sigma_0\cos(\theta). \tag{1.31}$$

We consider now a vicinal face which is symmetric to the first one, i.e., tilted by an angle of $-\theta$ (Fig. 1.12(b)). Its surface energy is

$$\sigma(-\theta) = -\frac{\varkappa}{b}\sin(\theta) + \sigma_0\cos(\theta). \tag{1.32}$$

Figure 1.13: Polar diagram of the specific surface energy-dependence of the surface energy on angle θ in (a) orthogonal coordinates, (b) polar coordinates (2D representation) and (c) spherical coordinates (3D representation). First neighbor interactions only are taken into account (after Chernov 1984).

Graphic representations of the $\sigma(\theta)$ functions (1.31) and (1.32) are given in Fig. 1.13(a). As seen, they are continuous everywhere with the exception of the point $\theta = 0$, where $(d\sigma/d\theta)_{\theta\geq 0} = \varkappa/b$ and $(d\sigma/d\theta)_{\theta\leq 0} = -\varkappa/\mathrm{b}$. In other words, the $\sigma(\theta)$ dependence has a *singular* point at $\theta = 0$ its derivative making a jump of $2\varkappa/b$. The same singular points exist at $\theta = \pm\pi/2, \pm\pi$, etc. In Fig. 1.13(b), the same functions are plotted in polar coordinates. A contour consisting of circular segments and possessing singular points at $\theta = 0, \pi/2$, and $3\pi/2$ results. In the 3D case (Fig. 1.13(c)), a body is obtained which consists of eight spherical segments and has six sharp singular points. This plot is called a *polar diagram* of the surface energy.

Figure 1.14: Polar diagram of the specific surface energy (the outermost contour denoted by $\Psi_1 + \Psi_2$, (2D representation) taking into account the first (Ψ_1) and second (Ψ_2) nearest neighbor interactions. The contours denoted by Ψ_1 and Ψ_2 give the polar diagrams as calculated by taking into account separately the first and the second nearest neighbors. The closed contour consisting of straight lines drawn through the singular points of the contour $\Psi_1 + \Psi_2$ gives the equilibrium shape of the crystal.

When constructing the above polar diagram, only the bonds between the first neighbor atoms have been taken into account. The bonds between the second neighbors in the Kossel crystal are directed at angle $\pi/4$ with respect to the first neighbor bonds. We can perform the same considerations as above (Chernov 1984) accounting for the second neighbor bonds only. Thus, a polar diagram which is inscribed in the first one (the second neighbor bonds are much weaker than the first neighbor ones) and is rotated at an angle of $\pi/4$ with respect to the latter is obtained (Fig. 1.14). The sum of the two curves gives the polar diagram when accounting simultaneously for both the first and the second neighbors. As seen, new shallower minima appear which correspond to faces which are analogous to the (1 1 0) faces in the 3D Kossel crystal. The contribution of the third neighbor bonds is insignificant and will not affect considerably the shape of the polar diagram. In any case, accounting for the more

distant neighbors always leads to more complicated polar diagrams and equilibrium shapes.

1.4.3 *Herring's formula*

Let us now derive the condition for the equilibrium shape of the crystal accounting for the anisotropy of the surface energy, or in other words, the $\sigma(\theta)$ dependence. This is a question of utmost importance as it is unambiguously connected with the problem of the equilibrium structure (the roughness) of the crystal surfaces. The 3D problem is somewhat complicated from the mathematical point of view and for this reason we will consider the simpler case of a two-dimensional (2D) crystal which represents a cross-section of the 3D one. On the other hand, the 2D case is very important for the understanding of the 2D nucleation and, in turn, the layer growth of smooth crystal faces.

When treating the problem, we will follow exactly the approach of Burton, Cabrera and Frank (1951). The crystal volume V_c will be replaced by the crystal surface area S_c and the specific surface energy $\sigma(\theta)$ by the specific edge energy $\varkappa(\theta)$. Then, instead of (1.21), we write

$$\Phi = \min, \qquad S_c = \text{const}, \tag{1.33}$$

where

$$\Phi = \int_{\mathrm{L}} \varkappa(\theta) dl \tag{1.34}$$

is the edge energy of the "2D crystal", the integration being carried out over the whole periphery L of the latter, and

$$S_c = \int_S ds \tag{1.35}$$

is the surface area of the crystal where ds is the surface area of a curvilinear sector.

Let r and φ be the polar coordinates of a point M of the crystal boundary L (Fig. 1.15) and x and y be the corresponding orthogonal coordinates. We construct a tangent T to the crystal boundary L at the point M and a perpendicular ON with length n from the origin

Figure 1.15: The derivation of the Herring's formula in the 2D case. L and T denote the crystal boundary and the tangent to it at a point M, r, and φ are the polar coordinates of a point M of the crystal surface, and n and θ are the polar coordinates of the point N belonging to the polar diagram $\varkappa(\theta)$ (after Burton, Cabrera and Frank 1951).

O to the tangent. The latter makes an angle θ with the abscissa. The line element of the crystal boundary in a parametric form $x = x(t)$ and $y = y(t)$ reads

$$dl = (x'^2 + y'^2)^{1/2} dt,$$

where $x' = dx/dt$ and $y' = dy/\mathrm{dt}$.

By the same way, the area of the curvilinear sector ds is

$$ds = \frac{1}{2}(xy' - yx')dt.$$

If we choose the angle θ as the parameter, the integrals (1.34) and (1.35) can then be rewritten in the form

$$\Phi = \int_0^{2\pi} \varkappa(\theta)(x'^2 + y'^2)^{\frac{1}{2}} d\theta, \tag{1.36}$$

$$S_c = \frac{1}{2}\int_0^{2\pi} (xy' - yx')d\theta. \tag{1.37}$$

From Fig. 1.15, we find that the perpendicular n from the origin to the tangent T is given by

$$n = x\cos\theta + y\sin\theta.$$

Then, we can find the point N for any point M of the crystal boundary. Conversely, making use of the transformations

$$x = n\cos\theta - n'\sin\theta, \tag{1.38a}$$

$$y = n\sin\theta + n'\cos\theta, \tag{1.38b}$$

we can construct the crystal contour if we know $n(\theta), (n' = dn/d\theta)$.

Then Eqs. (1.36) and (1.37) can be written in terms of $n(\theta)$:

$$\Phi = \int_0^{2\pi} \varkappa(\theta)(n + n'')d\theta = \min, \tag{1.39}$$

$$S_c = \frac{1}{2}\int_0^{2\pi} n(n + n'']d\theta = \text{const}, \tag{1.40}$$

where $n'' = d^2n/d\theta^2$.

Following the method of Lagrange, we multiply Eq. (1.40) by an indefinite scalar $-\lambda$ and sum up both equations to obtain

$$\int_0^{2\pi} \left[\varkappa(\theta)(n + n'') - \frac{1}{2}\lambda n(n + n'')\right]d\theta = \min. \tag{1.41}$$

The condition for a minimum is still preserved as we multiplied by a constant and added a constant. The solution of (1.41) will give us a function $n = n(\theta)$ which satisfies both conditions $\Phi = \min$ and $S_c = \text{const}$. To solve the problem, we will use the method of Euler for finding of an extremum (Zeldovich and Myshkis 1967; Arfken 1973). It states that if we have a functional of the kind

$$\int_a^b F(x, y, y', y'')dx = \min,$$

where $y = y(x), y' = dy/dx, y'' = d^2y/dx^2$, the equation which satisfies it has the form

$$\frac{\partial F}{\partial y} - \frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y'}\right) + \frac{\partial^2}{\partial x^2}\left(\frac{\partial F}{\partial y''}\right) = 0,$$

where the functions y, y', and y'' are taken upon differentiation as independent variables without accounting for their dependence on x.

Applying the above method from (1.41), one obtains

$$\frac{\partial^2}{\partial\theta^2}[\varkappa(\theta) - \lambda n(\theta)] + [\varkappa(\theta) - \lambda n(\theta)] = 0. \tag{1.42}$$

Thus, the equilibrium shape of the crystal is governed by a nonlinear equation of second order which satisfies the conditions $\Phi = \min$ and $S_c = \text{const}$. Its solution $n(\theta)$ will give us the rule for constructing the equilibrium shape of our 2D crystal (the crystal contour) on the base of the polar diagram of the edge energy and making use of Eq. (1.38). In fact, we have to solve the much simpler linear differential equation of second order. With the substitution $u = \varkappa(\theta) - \lambda n(\theta)$, Eq. (1.42) turns into $u'' + u = 0$. Its solution reads (Kamke 1959)

$$u = C\sin(x - \phi)$$

or

$$n(\theta) = \frac{1}{\lambda}\varkappa(\theta) - C\sin(\theta - \phi),$$

where C and ϕ are constants. The second term on the right-hand side is a periodic function with a period 2π. However, different crystals have different symmetries and thus different periods. For example, cubic crystals have a period of $\pi/2$, hexagonal crystals have a period $\pi/3$, etc. In order to get rid of this restriction, we put $C = 0$ and obtain

$$n(\theta) = \frac{1}{\lambda}\varkappa(\theta). \tag{1.43}$$

By analogy with the previous case, the proportionality constant multiplies the crystal volume $\lambda = \Delta\mu/s_c$, where s_c is the area of an atom in the 2D crystal and

$$\Delta\mu = \frac{\varkappa(\theta)s_c}{n(\theta)}. \tag{1.44}$$

Equation (1.44) which appears as a generalized Thomson–Gibbs equation is the Gibbs–Curie–Wulff theorem for 2D crystals in which $n(\theta)$ is the radius vector of the polar diagram $\varkappa(\theta)$.

Carrying out the differentiation in Eq. (1.42) gives

$$n + n'' = \frac{1}{\lambda}[\varkappa(\theta) + \varkappa''(\theta)],$$

where $\varkappa''(\theta) = d^2\varkappa(\theta)/d\theta^2$.

Realizing that

$$n + n'' = \frac{(x'^2 + y'^2)^{3/2}}{x'y'' - y'x''} = R,$$

is, in fact, the principal radius of the curvature of the crystal contour, R, with $\lambda = \Delta\mu/s_c$, one obtains

$$\Delta\mu = \frac{s_c}{R}\left[\varkappa(\theta) + \frac{d^2\varkappa(\theta)}{d\theta^2}\right].$$

By analogy, for a 3D crystal with principal radii of curvatures R_1 and R_2 and polar angles θ_1 and θ_2, for the equilibrium shape, one obtains an expression with s_c and $\varkappa(\theta)$, respectively, replaced by v_c and $\sigma(\theta)$ (for more rigorous derivation, see Chernov 1984), which is known as the formula of *Herring* (Herring 1951, 1953)

$$\Delta\mu = \frac{v_c}{R_1}\left(\sigma + \frac{d^2\sigma}{d\theta_1^2}\right) + \frac{v_c}{R_2}\left(\sigma + \frac{d^2\sigma}{d\theta_2^2}\right). \tag{1.45}$$

In the same way, the generalized Gibbs–Curie–Wulff theorem for the 3D crystals reads

$$\Delta\mu = \frac{2\sigma(\theta)v_c}{n(\theta)}. \tag{1.46}$$

Equations (1.44) and (1.46) give us the practical rule for the construction of the equilibrium shape. First, we ascribe a particular value to the scale parameter $\Delta\mu/2v_c$ which determines the size of the crystal. Then, we draw the radius vector $n(\theta)$ from the central point at an arbitrary selected crystallographic direction θ and find the cross-sectional point with the polar diagram (Fig. 1.16). We then construct through it a plane normal to $n(\theta)$ and repeat this procedure for the whole contour of the diagram. A family of planes results, and its inner envelope is, in fact, the equilibrium shape of the crystal.

Let us go back to the Herring formula (1.45) and consider more closely the quantity $\sigma_n^* = \sigma + d^2\sigma/d\theta_n^2$ $(n = 1, 2)$, which is usually

Figure 1.16: Construction of the equilibrium shape based on the polar diagram of the surface energy following Eq. (1.46).

called the *surface stiffness*. At the singular points, the first derivatives of σ with respect to θ experience a jump (equal to $2\varkappa/b$ in the above oversimplified case). Hence, the second derivatives and, in turn, the surface stiffnesses σ_n^* have infinitely large values. The left-hand side of Eq. (1.45) has a finite value and obviously the right-hand side to have a finite value the principal radii R_1 and R_2 should be infinitely large. Hence, at the singular points, the curvature of the corresponding crystal faces will be equal to zero or, in other words, the crystal faces will be flat. This is the reason the flat faces are often called *singular faces*. Immediately, aside of the singular points, the second derivatives of σ and, in turn, the surface stiffnesses σ_n^* acquire finite positive values and so do the radii R_1 and R_2. Therefore, the crystal surface will be rounded. It will consist of terraces and steps or, in other words, it will be atomically rough. Finally, there are regions where $\sigma_n^* = 0$ and so are the radii R_1 and R_2 (the ratios σ_n^*/R_n having again finite values). These are obviously the edges and the apexes of the crystal. Negative values of the surface stiffnesses have no physical meaning as this means negative radii R_1 and R_2 and hence concave regions which cannot exist on the equilibrium shape.

As discussed above, the supersaturation must have one and the same value over every point of the surface of a crystal with an equilibrium shape. It follows that the supersaturation around a crystal without an equilibrium shape will differ from one point to another. Facets with areas smaller than required by the equilibrium condition will have larger chemical potential and, hence, the supersaturation over them will be lower than the current one in the system and *vice versa*. If such a crystal is immersed into a supersaturated ambient phase and given enough time to equilibrate, smaller facets will dissolve to become larger facets, and larger facets will grow to become smaller facets up to the moment the supersaturation attains one and the same value all over the crystal surface and the equilibrium shape is reached. As will be shown in the following, the above conclusion is valid for crystallites sufficiently small ($kTR_n/\sigma_n^* v_c \ll 1$) so that the supersaturation difference which is the driving force for the equilibration to be reached is sufficiently large.

Finally, Eq. (1.45) can be expressed in the form

$$\Delta\mu = v_c \left(\frac{\sigma_1^*}{R_1} + \frac{\sigma_2^*}{R_2} \right) \tag{1.47}$$

or

$$P_c - P_v = \frac{\sigma_1^*}{R_1} + \frac{\sigma_2^*}{R_2}. \tag{1.48}$$

We conclude that the Herring formula is a generalization for finite crystallites of Laplace's Equation (1.16) which relates the liquid surface tension to the pressure difference on both sides of the curved liquid surface. The Laplace pressure is determined in this case by the surface stiffnesses which govern the crystal curvature rather than by the specific surface energies. Thus, Eq. (1.48) explains the term surface stiffness. It is a measure of resistivity of the crystal faces against bending (roughening) when a pressure (force per unit area) is applied on them. Flat facets require infinitely high pressures in order to be "bent".

1.4.4 *Stability of crystal surfaces*

In fact, we have just concluded that the structure of a given crystal surface is determined by the corresponding value of the surface stiffness. When the latter is infinite, the corresponding crystal face is flat and atomically smooth. When the surface stiffness has some finite positive value, the crystal surfaces are rounded and in the near vicinity of the singular faces should consist of terraces divided by steps. We accepted that the steps are of monomolecular height. The width of the terraces or the density of the steps depends on the value of the polar angle. However, we can have different structures of a vicinal face at one and the same value of the polar angle. Thus, if the steps are with double height, the terraces should be twice as wide, when the steps have a triple height the terraces will have a triple width, etc., at one and the same value of the polar angle (Fig. 1.17(b)). So one cannot determine unambiguously the real structure of the corresponding vicinal surface on geometrical reasons only. Moreover, under real conditions, the surface energy and, in turn, the surface stiffness can change their values. This is usually the case when some impurity atoms are adsorbed on the crystal surface. The impurity atoms saturate the unsaturated dangling bonds on the crystal surface and decrease the surface energy. The larger the concentration of the impurity atoms, the smaller will be the specific energy of a particular crystal surface (Szyszkowski 1908; Moelwin-Hughes 1961; Mutaftschiev 2001). Another reason for changing of the surface energy is the surface reconstruction (Mönch 1979). As a result, the structure of the crystal surface should change. So our next task is to find the real structure of the crystal surfaces or, in other words, the condition of the stability of a given crystal surface. The problem of the stability of the crystal surfaces was first considered by Chernov (1961) and discussed later by Cabrera and Coleman (1963). In this chapter, we follow the presentation of the latter.

We consider an infinite vicinal crystal surface inclined to the nearest singular face by an angle θ (Fig. 1.17) and consisting of terraces and monomolecular steps. It is easy to realize such a face bearing in

Figure 1.17: A scheme illustrating the stability of a vicinal crystal surface against faceting: (a) Schematic view in terms of the slope $p = \tan\theta$ of the original vicinal face which breaks down into facets with slopes $p_1 = \tan\theta_1$ and $p_2 = \tan\theta_2$. The dashed lines with slopes p_1' and p_2' give possible deviations from the faceted surface with slopes p_1 and p_2, respectively (see text). (b) Side view of a vicinal surface of a Kossel crystal whose slope is accommodated either by single height steps or by facets (after Cabrera and Coleman 1963).

mind that single-crystal wafers which are cut and polished under the crystallographic orientation of one of the singular faces are always inclined to the latter at some very small angle. In general, such a face can be represented by $z = z(x, y)$, where $z = 0$ determines the singular face. Then, the orientation at a point (x, y) will be determined by two independent components $p = -dz/dx$ and $q = -dz/dy$. We consider for simplicity the case in which the steps are parallel to the y axis (which is, thus, normal to the surface of the sheet), i.e., $q = 0$ and the vicinal face is described by $z = z_0 - px$ where $p = \tan\theta$. Let the face area be denoted by Σ_0. Then, the area of the reference singular face is $\Sigma = \Sigma_0 \cos\theta$.

The surface energy of the face Σ_0 is $\Phi_0 = \sigma(\theta)\Sigma_0$. In terms of the component p, it can be written as

$$\Phi_0 = \sigma(\theta)\Sigma_0 = \sigma(p)(1+p^2)^{1/2}\Sigma = \xi(p)\Sigma, \tag{1.49}$$

where $(1+p^2)^{1/2} = 1/\cos\theta$ and $\xi(p) = \sigma(p)(1+p^2)^{1/2}$.

Let us now assume that two new faces with slightly different orientations

$$p_1 = p + \delta p_1 \qquad \text{and} \qquad p_2 = p + \delta p_2 \tag{1.50}$$

are formed. The total projected areas of these faces are Σ_1 and Σ_2, respectively. If the face Σ_0 is the stable one, its surface energy Φ_0 should be smaller than the surface energy of the newly formed profile $\Phi = \xi(p_1)\Sigma_1 + \xi(p_2)\Sigma_2$ at constant volume. In other words, the condition $\Delta\Phi = \Phi - \Phi_0 > 0$ should be fulfilled. The condition of constant volume is reduced in our case to that of a constant area of the cross-section shown in Fig. 1.17(a). It can be easily obtained from $\Delta S = S_1 - S_2 = 0$, where S_1 and S_2 are the areas under the profiles, with slopes p_1 and p_2, respectively. One obtains

$$p_1\Sigma_1 + p_2\Sigma_2 = p\Sigma. \tag{1.51}$$

Substituting (1.50) in (1.51) and making use of the relation

$$\Sigma_1 + \Sigma_2 = \Sigma, \tag{1.52}$$

the condition for constant volume $\Delta S = 0$ turns into

$$\Sigma_1\delta p_1 + \Sigma_2\delta p_2 = 0. \tag{1.53}$$

The functions $\xi(p_i)$ $(i = 1, 2)$ can be expanded in the Taylor series up to the parabolic terms

$$\xi(p_i) = \xi(p) + \xi'(p)\delta p_i + \frac{1}{2}\xi''(p)(\delta p_i)^2, \tag{1.54}$$

where $\xi'(p) = d\xi/dp$ and $\xi''(p) = d^2\xi/dp^2$.

Substituting (1.54) in the expression for $\Delta\Phi$ and making use of (1.52) and (1.53) give

$$\Delta\Phi = \frac{1}{2}\xi''(p)\big[\Sigma_1(\delta p_1)^2 + \Sigma_2(\delta p_2)^2\big]. \tag{1.55}$$

The term in the square brackets is always positive and the condition $\Delta\Phi > 0$ is satisfied when

$$\xi''(p) > 0. \tag{1.56}$$

Bearing in mind that $d\sigma/dp = (d\sigma/d\theta)(d\theta/dp)$, $\theta = \tan^{-1}(p)$, $d\theta/dp = -1/(1+p^2)$, and $\xi''(p) = \sigma^*/(1+p^2)^{3/2}$, the condition (1.56) reduces to

$$\sigma^* = \sigma + \frac{d^2\sigma}{d\theta^2} > 0. \tag{1.56$'$}$$

It follows that when the surface stiffness of the original vicinal face which consists of terraces divided by monomolecular steps is positive, it will be stable. Otherwise, it will break down into terraces divided by macrosteps, or in the limiting case, into separate crystal faces preserving the overall slope of the original face with respect to the singular face.

A schematic plot of $\xi(p)$ is given in Fig. 1.18. We have, in principle, three possibilities. In the first one (Fig. 1.18(a)), the second derivative of $\xi(p)$ is everywhere positive between the singular minima at $p = 0$ and $p = p_0$. This means that all possible surfaces between $p = 0$ and $p = p_0$ will be stable and will not break into facets as long as the there are no species adsorbed on them. In the second case (Fig. 1.18(b)),

Figure 1.18: Schematic plot of the parameter $\xi(p) = \sigma(p)(1+p^2)^{1/2}$ vs the slope p: (a) $\xi''(p) > 0$, (b) $\xi''(p) < 0$, (c) $\xi''(p) > 0$ between p_1 and p_2 and $\xi''(p) < 0$ between 0 and p_1 and between p_2 and p_0 (after Cabrera and Coleman 1963).

the second derivative of $\xi(p)$ is everywhere negative. This means that only the singular surfaces with the orientations p and p_0 will be stable. If a surface with orientation p such that $0 < p < p_0$ is formed, it will break down into facets with the orientations $p = 0$ and $p = p_0$. In the general case (Fig. 1.18(c)), in between 0 and p_0, there are regions with $\xi''(p) > 0$ and $\xi''(p) < 0$. It follows that only the surfaces at the singular minima whose orientations are between p_1 and p_2, where the condition $\xi''(p) > 0$ is fulfilled, can exist on the crystal surface. All others are not stable and should break down into facets.

The physical meaning of this result is simple. If the new crystal surfaces with orientations p_1 and p_2 have smaller specific surface energies than the original face with orientation p and a decrease of the surface energy overcompensates the increase of the surface area, the crystal surface will break down into facets. In the reverse case, it will be stable.

The stability of the facets can be examined by the same way as for the original surface. In this case, we allow two new surfaces with orientations $p_1' = p_1 + \delta p_1$ and $p_2' = p_2 + \delta p_2$ to form (Fig. 1.17(a)). From the condition of the positive change of the surface energy at constant volume, we find that the facets will be stable when the corresponding surface stiffnesses σ_1^* and σ_2^* of the facets are positive. Thus, an unstable smooth surface with negative surface stiffness should break down into facets with positive surface stiffnesses.

Faceting of crystal surfaces was observed long ago. Early works are reviewed by Moore (Moore 1963). In principle, faceting could be caused by any reason which diminishes the specific surface energy. In particular, this is the adsorption of surface active species. Thus, the adsorption of Ag on the stepped Ge(1 1 1) surfaces leads to the formation of (5 4 4) and (1 1 1) facets at Ag coverage of about 0.2 MLs at $T \cong 400°$C (Suliga and Henzler 1983). At an increased coverage of Ag greater than 0.7 MLs, (2 1 1) facets are formed. The above results were refined in a later paper (Henzler, Busch and Friese 1990). A Ge crystal has been cut and polished with 3° misorientation ($p = 0.0524$) with respect to the (1 1 1) surface. Vicinal surfaces with monoatomic steps and 18 atomic spacings wide terraces were obtained which can

be described by Miller indices (19,17,17). Silver was then deposited at room temperature and the crystal was annealed at 400°C for 10 min. After cooling down to room temperature again, the following changes were observed. At a coverage of the Ag atoms of 1/4 ML (with respect to the surface coverage of Ge(1 1 1)), the initial (19,17,17) surface broke down to facets (13,11,11) with greater slopes and narrower terraces and flat wider portions with (1 1 1) orientation. The fractions of the overall surface of both facets were estimated to be 0.75 and 0.25, respectively. At the Ag coverage of 1/2 ML, half of the surface was found to have (10,8,8) orientation and the other half (1 1 1) orientation. After the desorption of the silver and the annealing of the Ge crystal, the initial orientation (19,17,17) was recovered.

Clean Si(1 0 0) surfaces misoriented by 5° in the [0 1 1] direction contain steps of average spacing 29 Å and height 2.7 Å (double steps). After a deposition of As beyond a critical surface coverage of 0.38 MLs, which is independent of the temperature, the terraces become about 100 Å wide and the steps are 9 Å (six MLs) high (Ohno and Williams 1989(a)). The process is reversible. After the desorption of the arsenic, the surface recovers its initial structure. The same is observed for Si(1 1 1) surfaces misoriented by 6° in the $[1\,\bar{1}\,0]$, $[2\,\bar{1}\,\bar{1}]$, and $[\bar{2}\,1\,1]$ directions. At coverages of As higher than a critical one of 0.16 MLs, the single steps turn into double steps (Ohno and Williams 1989b).

Besides, it was found that Si(1 1 2) surfaces are stable when heated up to 800°C regardless of carbon contamination and break down to (1 1 1), (1 1 3), (5 2 5), and (2 5 5) surfaces when heated between 950 and 1150°C in the presence of carbon on the crystal surface. The extent of faceting increases if carbon is introduced before heating beyond 950°C. Annealing at 1250°C removes the carbon and restores the initial surface structure (Yang and Williams 1989).

It is worth noting that the As-induced faceting of the Si(1 0 0) and (1 1 1) surfaces takes place at As_2 pressures comparable to those used when GaAs is grown on Si single-crystal wafers. It is, thus, unsafe to assume that the surface of the substrate preserves its stepped structure under the conditions of the experiment. The same is valid when the necessary precautions to lower the carbon contaminations

in the vacuum chamber are not taken into account. Works on faceting of metal surfaces are summarized by Somorjai and van Hove (1989).

1.5 Atomistic Views on Crystal Growth

1.5.1 *Equilibrium of infinitely large crystal with the ambient phase — the concept of half-crystal position*

The above considerations were purely macroscopic in the sense that thermodynamic macroquantities have been used for the description of the equilibrium between different phases. Moreover, the elementary processes of attachment and detachment of individual building units (atoms, ions or molecules) to and from the growing particles of the new phase have not been taken into account. This is one of the reasons the earlier ideas and statements of Gibbs have not been fully comprehended until 1927 when simultaneously Kossel (1927) and Stranski (1927, 1928) introduced the concept of work of separation of a building unit from the so-called *half-crystal position*. In this chapter, we will consider the problem on a microscopic atomic level.

Let us consider, for example, the cubic face (1 0 0) of a Kossel crystal containing one monoatomic step (Fig. 1.19). The step can be defined as the boundary between some region of the surface and an adjacent region whose height differs by one interplanar spacing.

Figure 1.19: The most important sites an atom can occupy on a crystal surface: 1 — atom embedded into the outermost crystal plane, 2 — atom embedded into the step edge, 3 — atom in a half-crystal (kink) position, 4 — atom adsorbed at the step, 5 — atom adsorbed on the crystal face.

Atoms can occupy different sites on this surface, incorporated into the face (site 1), the step (site 2), into the corner position 3, or adsorbed at the step (site 4), or on the crystal surface (site 5). Depending on their positions, the atoms are differently bound to the crystal surface. Thus, an atom adsorbed on the crystal surface is bound by one bond with the crystal and has five unsaturated dangling bonds. On the contrary, an atom incorporated into the face has five bonds saturated and one unsaturated. Moreover, the detachment of these atoms leads to the change of the number of the unsaturated dangling bonds, or in other words, to the specific surface energy. The only exception is the atom in position 3 which has an equal number of saturated and unsaturated bonds. Then no change of the specific surface energy will take place when the latter is detached from this peculiar position. As seen, an atom in this position is bound to a half atomic row, half-crystal plane and a half-crystal block. This is the reason this position is called *a half-crystal* or *kink* position. By repetitive attachment or detachment of atoms to and from this position, the whole crystal (if it is large enough to exclude the size effects) can be built up or disintegrated into single atoms.

The work $\varphi_{1/2}$ necessary to detach an atom from a half-crystal position depends on the symmetry of the crystal lattice (Table 1.1) but is always equal to the work required to break half of the bonds of an atom situated in the bulk of the crystal. Thus, for a Kossel crystal

$$\varphi_{1/2} = 3\psi_1 + 6\psi_2 + 4\psi_3.$$

Table 1.1: The number of the first, second and third neighbors of an atom in a half-crystal position.

	Number of neighbors		
Crystal lattice	First	Second	Third
Simple cubic	3	6	4
Face-centered cubic	6	3	12
Body-centered cubic	4	3	6
Hexagonal closed packed	6	3	1
Diamond	2	6	6

If we denote by Z_1, Z_2, and Z_3 the coordination numbers of the first, second, and third coordination spheres, respectively, in the corresponding crystal lattice, then

$$\varphi_{1/2} = \frac{1}{2}(Z_1\psi_1 + Z_2\psi_2 + Z_3\psi_3). \tag{1.57}$$

When a sufficiently large crystal is in equilibrium with the ambient phase, the half-crystal position is statistically occupied and unoccupied with equal frequency. This means that the probability of the attachment of atoms from the ambient phase to the kink position is equal to the probability of their detachment. It follows that the equilibrium of the infinitely large crystal with the ambient phase is determined by the half-crystal position and $\varphi_{1/2}$ may be taken as approximately equal to the enthalpy of evaporation Δh_{ev}. In other words, it is namely the work of separation from the half-crystal (kink) position which determines the equilibrium vapor pressure of an infinitely large crystal and, in turn, its chemical potential. Thus, for simple crystal with monoatomic vapor which behaves as an ideal gas (Stern 1919; Stranski and Kaischew 1934a; Kaischew 1936) holds

$$\mu_c^{\infty} = kT \ln P_{\infty} = -\varphi_{1/2} + kT \ln[(2\pi m)^{3/2}(kT)^{5/2}/h^3], \tag{1.58}$$

where m is the atomic mass and h is Plank's constant.

As can be seen from Eq. (1.58), at $T = 0$, the chemical potential is equal to the separation work from the half-crystal position taken with an opposite sign. It is namely this property of the half-crystal position which makes it unique in the theory of crystal growth. For the history of discovery of the half-crystal position, the reader is referred to the historical review of Kaischew (1981).

The second very important property of the half-crystal position becomes evident if we write the expression for the work of separation from it in the form

$$\varphi_{1/2} = \varphi_{\mathrm{lat}} + \varphi_{\mathrm{nor}},$$

where φ_{lat} denotes the lateral bonding with the half-crystal plane and half-atomic row, and φ_{nor} denotes the normal bonding with the underlying half-crystal block.

This division has two advantages. First, it reflects the properties of the particular crystal face. Let us consider, for example, the most closely packed faces (1 1 1) and (1 0 0) of the fcc lattice. We will restrict ourselves to first neighbor interactions. In order to detach an atom from a half-crystal position on the (1 1 1) face we have to break three lateral bonds and three normal bonds, whereas on the (1 0 0) face, we have to break two lateral bonds and four normal bonds. In both cases, we have to break six bonds, but we could conclude that the (1 0 0) face has a greater adsorption potential than the (1 1 1) face.

Another very important consequence of this division is connected with the epitaxial growth of thin films. In fact, if we replace the underlying crystal block by another block of different material, the lateral bonding will remain approximately the same if we assume the additivity of the bond energies. However, the normal bonding or the bonding across the interface will change (Stranski and Kuleliev 1929). Then, for a Kossel crystal, the separation work from the half-crystal position will be ($\psi_1 \equiv \psi$)

$$\varphi'_{1/2} = 2\psi + \psi' = 3\psi - (\psi - \psi')$$

or

$$\varphi'_{1/2} = \varphi_{1/2} - (\psi - \psi'), \tag{1.59}$$

where ψ' is the energy to break a bond between unlike atoms.

It is immediately seen that when $\psi < \psi'$, $\varphi'_{1/2} > \varphi_{1/2}$, and the equilibrium vapor pressure of the first ML on the foreign substrate is smaller than the equilibrium vapor pressure of the bulk crystal, i.e., $P'_\infty(1) < P_\infty$, then at least one ML can be deposited at any vapor pressure higher than $P'_\infty(1)$. This means that a deposition will take place even when $P'_\infty(1) < P < P_\infty$, i.e., at undersaturation with respect to the bulk crystal. In the opposite case ($\psi > \psi'$), $\varphi'_{1/2} < \varphi_{1/2}$, and $P'_\infty(1) > P_\infty$. This means that the deposition requires the existence of a supersaturation in the system. The atoms of the second ML feel more weakly the energetic influence of the substrate and the latter will have a negligible effect on the atoms of the third ML. It follows that, in this particular case, the chemical

potential is not constant but depends on the number of the monolayer, or, in other words, on the film thickness. In this case, we speak of epitaxy which will be considered in more detail in Chapter 4. It will be shown that the thickness dependence of the chemical potential can be easily derived assuming that the lateral bonding remains the same and accounting only for the difference in bonding across the interface. As will be discussed in Chapter 4, the latter leads to different modes of growth of the thin epitaxial films (for a review, see Markov and Stoyanov 1987).

And finally, one more very important conclusion follows from Eq. (1.57). If we assume that half of each bond of an atom to the neighboring atoms in the bulk of the crystal belongs to the atom, then the sum $\sum_i Z_i(\psi_i/2)$ gives the cohesive energy of the crystal. In other words, the energy of bonding of an atom in the half-crystal position equals the cohesive energy of the crystal. Thus, the chemical potential of the crystal is a bulk characteristic of the latter. This is the reason why the chemical potential of a given crystal does not depend on the adsorption of impurities on the crystal surface.

1.5.2 *Equilibrium finite crystal–ambient phase — the concept of mean separation work*

As was mentioned above, we can build up or dissolve a crystal by repetitive attachment or detachment of building units only when the crystal is large enough so that the role of the edges can be ignored. If this is not the case, it is clear that the half-crystal position is no longer a repetitive step and it does not determine the equilibrium of the finite size crystal with its vapor phase. To solve this problem, Stranski and Kaischew (1934a,1934b,1934c,1934d) considered the dynamic equilibrium of a small crystal with its vapor and concluded that for a small particle to be in equilibrium with its own ambient phase, the probability of building up a whole new crystal plane should be equal to the probability of its dissolution. So as a measure of the equilibrium of a finite crystal with its surrounding, they introduced the so-called mean separation work which is defined as the energy per atom of disintegration of a whole crystal plane into

Figure 1.20: For the evaluation of the mean separation work $\bar{\varphi}_3$ which determines the equilibrium of a finite 3D crystal with the vapor phase according to Stranski and Kaischew (1934b). First, (a) $(n-1)^2$ are detached in such a way that two rows of atoms are left. The detachment of each atom requires the breaking of three bonds, then (b) the two remaining rows of atoms, each consisting of $n-1$ atoms, are detached with the exception of the corner atom. The detachment of the atoms requires the breaking of two bonds per atom, and finally (c) the last atom at the corner is detached which requires the breaking of only one bond (after Stranski and Kaischew 1934b).

single atoms. This quantity must have one and the same value for all crystal planes belonging to the equilibrium form.

Consider, for example, a Kossel crystal with edge length $l_3 = n_3 a$, where n_3 is the number of atoms in the edge of the 3D crystal and a is the atomic spacing. The energy per atom for the disintegration of a whole lattice plane into single atoms will be (following Figs. 1.20(a)–(c))

$$\bar{\varphi}_3 = [3\psi(n_3-1)^2 + 4\psi(n_3-1) + \psi]/n_3^2 = 3\psi - \frac{2\psi}{n_3}.$$

On the other hand, $3\psi = \varphi_{1/2}$ (Table 1.1) so that

$$\bar{\varphi}_3 = \varphi_{1/2} - \frac{2\psi}{n_3}. \tag{1.60}$$

It follows that the mean work of separation goes asymptotically to the work of separation from kink position as the crystal size is increased. Then, a crystal can be considered large enough if $n_3 > 70$ or $l_3 > 2 \times 10^{-6}$cm ($a = 3 \times 10^{-8}$cm).

As $\bar{\varphi}_3$ determines the equilibrium with the vapor phase, we can write in analogy with Eq. (1.58)

$$\mu_c = \mu_v = kT \ln P_c = -\bar{\varphi}_3 + kT \ln[(2\pi m)^{3/2}(kT)^{5/2}/h^3], \qquad (1.61)$$

where the chemical potential of the small crystallite is equal to the chemical potential of the vapor.

Then,

$$\Delta\mu = \mu_v - \mu_c^\infty = kT \ln(P_c/P_\infty) = \varphi_{1/2} - \bar{\varphi}_3 = 2\psi/n_3. \quad (1.62)$$

Obviously, this is the same Thomson–Gibbs equation (1.19). We can define the specific surface energy of the Kossel crystal confining ourselves to first neighbor interactions as the energy to create two surfaces of area a^2 each

$$\sigma = \psi/2a^2. \qquad (1.63)$$

Substituting for ψ from Eq. (1.63) into (1.62), one obtains

$$\Delta\mu = 4\sigma v_c/l_3, \qquad (1.64)$$

which is exactly the Thomson–Gibbs equation as given by (1.19) ($l_3 = 2r$ and $v_c = a^3$ for a Kossel crystal). Thus, Stranski and Kaischew (1934a) derived a purely thermodynamic equation by making use of a kinetic approach.

1.5.3 *Equilibrium 2D crystal–ambient phase*

Stranski and Kaischew further considered the case when a 2D crystal formed on one of the faces of a 3D crystal is in equilibrium with the ambient phase. In analogy with the 3D case, they suggested that the probability of building up a whole new atomic row with a length $l_2 = n_2 a$ (Fig. 1.21) should be equal to the probability of its disintegration into single atoms. The equilibrium 2D crystal–vapor phase is now determined by the corresponding *mean work of separation* $\bar{\varphi}_2$, which in this particular case is equal to the energy per atom for the disintegration of a whole edge row of atoms. Assuming, for simplicity, a square-shaped crystal with n_2 atoms in the edge, the mean work of separation reads

$$\bar{\varphi}_2 = 3\psi - \psi/n_2 = \varphi_{1/2} - \frac{\psi}{n_2}. \qquad (1.65)$$

Figure 1.21: For the evaluation of the mean separation work $\bar{\varphi}_2$ which determines the equilibrium with the ambient phase of a finite 2D crystal with edge length l_2 on the surface of a 3D crystal with edge length l_3. n_2 and n_3 denote the numbers of atoms in the edges of the 2D and 3D crystals, respectively (after Stranski and Kaischew 1934b).

Then, the supersaturation required for the formation of a 2D crystal on the surface of a 3D crystal is

$$\Delta\mu = kT \ln\left(\frac{P}{P_\infty}\right) = \frac{\psi}{n_2}. \tag{1.66}$$

Using the definition of the specific edge energy

$$\varkappa = \psi/2a, \tag{1.67}$$

one obtains the familiar equation of Thomson–Gibbs for the 2D case,

$$\Delta\mu = \frac{2\varkappa a^2}{l_2}. \tag{1.66$'$}$$

Comparing Eqs. (1.64) and (1.66), ($\varkappa = \sigma a$) leads to the conclusion that in equilibrium the edge length of the 2D crystal should be shorter than that of the 3D one by a factor of 2 at one and the same supersaturation, i.e., $l_2 = l_3/2$.

1.5.4 *Equilibrium shape of crystals — atomistic approach*

The introduction of the mean works of separation enabled Stranski and Kaischew (1935) to give a new atomistic approach for the determination of the equilibrium shape of the crystals. The basic idea is that atoms whose energy of binding with the crystal is smaller than the mean work of separation cannot belong to the equilibrium shape

because the corresponding vapor pressure will be higher than the equilibrium vapor pressure in the system. Then, in order to derive the equilibrium shape one starts from a crystal with an arbitrary simple form and all atoms whose separation work is smaller than $\varphi_{1/2}$ are successively removed from the crystal surface. Precisely at that moment, all crystal faces belonging to the equilibrium shape appear. Then, the areas of the faces are varied (whole crystal planes are removed or added) up to the moment when the mean separation works $\bar{\varphi}_3$ of all the crystal planes have one and the same value. During the last operation, all faces which do not belong to the equilibrium form disappear (see Honnigmann 1958).

Taking into account more distant neighbor atoms in the calculation of the mean separation works, facets with higher specific surface energy appear on the equilibrium shape, as shown in Fig. 1.14. Thus, when accounting only for the first neighbors in a Kossel crystal, the equilibrium shape consists only of the cubic faces (1 0 0). Taking into account the second neighbors leads to the appearance of the (1 1 0) and (1 1 1) faces in addition to (1 0 0) faces. Then, by comparing the theoretical predictions with experimental observations, one can make conclusions concerning the influence of the radius of action of the interatomic forces on the equilibrium shape.

The atomistic approach of Stranski and Kaischew can be illustrated by finding of the equilibrium shape of a 3D crystal lying on a foreign substrate. We consider for simplicity a cubic crystal with a square base with a lateral edge $l = na$ and height $h = n'a$, where n and n' are the numbers of atoms in the horizontal and vertical edges (Fig. 1.22). Following the above procedure, the mean separation work calculated from the side crystal face is

$$\bar{\varphi}_3' = 3\psi - \frac{\psi - \psi'}{n'} - \frac{\psi}{n}. \tag{1.68}$$

The mean separation work calculated from the upper base is given by Eq. (1.60). The condition for the equilibrium shape is that the chemical potentials of the different faces, or in other words, their mean separation works have to be equal ($\bar{\varphi}_3' = \bar{\varphi}_3$). The latter leads

Figure 1.22: A cubic crystal of lateral extent l and height h on a foreign substrate. The specific surface energies of the substrate, σ_s, the upper and the lateral faces of the deposit crystal, σ, and the substrate — deposit interface, σ_i, determine the equilibrium shape ratio h/l.

to the relation (Kaischew 1950)

$$\frac{h}{l} = \frac{n'}{n} = 1 - \frac{\psi'}{\psi}. \tag{1.69}$$

Substituting ψ and ψ' by the specific surface energy and the specific adhesion energy gives

$$\frac{h}{l} = 1 - \frac{\beta}{2\sigma} = \frac{\sigma + \sigma_i - \sigma_s}{2\sigma}, \tag{1.70}$$

where σ_i is the specific interfacial energy expressed by the relation of Dupré (1.28). The same result can be obtained if one starts from the classical thermodynamic conditions $\Phi = l^2(\sigma + \sigma_i - \sigma_s) + 4lh\sigma = \min$ and $V_c = l^2 h = \text{const}$ (Bauer 1958).

1.5.5 *Equilibrium vapor pressure of a 2D crystal on a foreign substrate*

It is also of interest to treat the question of equilibrium vapor pressure of a 2D crystal formed on the surface of a crystal of different material. Assuming, for simplicity, a square shape, the mean separation work estimated from the crystal edge reads

$$\bar{\varphi}'_2 = 2\psi + \psi' - \frac{\psi}{n_2} = \varphi'_{1/2} - \frac{\psi}{n_2},$$

where the term $\varphi'_2 = 2\psi + \psi'$ is, in fact, the work of separation of an atom from the half-crystal position of the semi-infinite adlayer on the foreign substrate (Stranski and Kuleliev 1929).

Bearing in mind that $\varphi_{1/2} = 3\psi$ for the supersaturation and hence for the equilibrium vapor pressure, one finds

$$\Delta\mu = kT \ln\left(\frac{P}{P_\infty}\right) = \psi - \psi' + \frac{\psi}{n_2}.$$

The difference $\varphi_{1/2} - \varphi'_{1/2} = \psi - \psi'$ of the binding energies can be either positive ($\psi > \psi'$) or negative ($\psi < \psi'$) as discussed earlier. This means that the equilibrium vapor pressure of the 2D crystal can be either higher or lower than the equilibrium vapor pressure of the bulk crystal and the deposition can be carried out at supersaturation or undersaturation, respectively.

1.6 Equilibrium Structure of Crystal Surfaces

1.6.1 *Classification of crystal surfaces*

The process of growth of crystals takes place at the crystal–ambient phase interface where the latter can be vapor, melt, or solution. Obviously, the equilibrium structure of this interface, or in other words, its roughness determines the crystal shape, on one hand, and the mechanism of growth and in turn its rate of growth, on the other.

Let us consider, for example, an atomically smooth crystal face belonging to a perfect defectless crystal. The formation of a new lattice plane requires the existence of monoatomic steps which offers half-crystal positions. Randomly appearing 2D formations of the new lattice layer with closed contours can serve as a source of such steps with closed contours. Initially, they are unstable and have the tendency to dissolve into the mother phase. When such formations serve as "2D nuclei" of the new layer exceed some critical size, their further growth is thermodynamically favored and they cover completely the crystal face. After that the steps vanish and the initial state is restored. Then, the formation of new lattice plane requires the formation of new 2D nuclei and the process is repeated. Hence, the growth of a defectless atomically smooth crystal face is a periodic process involving successive 2D nucleation and lateral growth (Fig. 3.17) which is usually observed in the crystal growth by molecular beam epitaxy (MBE) (Harris, Joyce and Dobson 1981a, 1981b;

Neave, Joyce, Dobson and Norton 1983). The formation of 2D nuclei is connected, however, with definite energetic difficulties and requires the overcoming of a critical supersaturation. Then the rate of growth of a defectless crystal surface will be a nonlinear (in fact, exponential) function of the supersaturation.

However, experimental data showed that crystals can grow at supersaturations as low as 0.01% in marked discrepancy with the nucleation theory of crystal growth. The problem was solved in 1949 when at the discussion meeting of the Faraday Society in Bristol, Frank (1949) proposed the *spiral mechanism* of crystal growth. He suggested that the continuous growth of crystals at low supersaturation can be attributed to the presence of crystal defects, particularly screw dislocations (see Fig. 3.10). The latter offer nonvanishing monoatomic steps with kink positions along them, thus making the 2D nucleation unnecessary. In 1951, Burton, Cabrera and Frank published their famous paper "The growth of crystals and the equilibrium structure of their surfaces" (Burton *et al.*, 1951). Considering the growth of a crystal face in the presence of screw dislocations, they found that the distance between the consecutive coils of the spiral is directly proportional to the linear size of the critical 2D nucleus which is determined by the existing supersaturation. Then, the slopes of the growth pyramids which are formed at the emergency points of the screw dislocations are directly proportional to the supersaturation. One can conclude that, in general, the growth rate will be again a nonlinear function of the supersaturation.

Finally, if the crystal face is atomically rough, it offers a great number of kink positions. Building particles arriving from the mother phase can be incorporated to the crystal lattice practically at any place which makes the 2D nucleation as well as the presence of screw dislocations unnecessary. No thermodynamic hindrance exist any more, the process is fast, and the growth rate is simply proportional to the flux of atoms from the ambient phase and thus should be a linear function of the supersaturation.

Thus, the crystal growth means the incorporation of building units which arrive from the ambient phase to the half-crystal positions. Then, the rate of growth of a given crystal face in a direction

normal to its surface is proportional to the density of growth sites (half-crystal or kink positions) which the face offers to the building units from the ambient phase. This density depends on the crystallographic orientation of the face, on the one hand, and temperature, on the other.

Burton and Cabrera (1949) classified the crystal surfaces with respect to their capability of growth into *close packed* and *nonclose packed* or *stepped* surfaces. The question has been further elucidated by Hartman (1973) and others (Honigmann 1958; Cabrera and Coleman 1963).

The crystal surfaces are, thus, divided into three groups: F (*flat*), S (*stepped*), and K (*kinked*) surfaces, depending on whether they are parallel to at least two most dense rows of atoms, one most dense row of atoms, or are not parallel to most dense rows of atoms at all, respectively (Hartman 1973). F faces are, for example, the (1 0 0) face of Kossel crystals and fcc crystals which are parallel to two most dense rows of atoms, the (1 1 1) face of fcc and the (0 0 0 1) face of hcp crystals which are parallel to three most dense rows of atoms, etc. (see Fig. 1.23). Typical examples of S and K faces are the (1 1 0) and (1 1 1) faces of a Kossel crystal. It is clear that when a crystal face is parallel to more than one most dense row of atoms, the number of saturated shortest and hence strongest chemical bonds parallel to the crystal surface is greatest. The number of the unsaturated bonds is minimal and so is the specific free energy of the face (see the arrows in Fig. 1.23). When the crystal face is parallel to one most dense row of atoms only, it intersects other one and all chemical bonds parallel to the latter become unsaturated. Thus, the number of the unsaturated bonds reaches its highest value when the crystal face intersects all most dense rows of atoms and, hence, such a face offers more growth sites (kink positions) than the S and F faces.

As the K faces offer kink sites with much greater density than the S and F faces, they will grow faster than the latter. The S faces also offer kink sites along the steps but their density is smaller than that on the K faces. Finally, the F faces of perfect crystals do not offer kink sites at all. Then, at small enough supersaturations to prevent 2D nucleation, the rate of growth in a direction normal to

Figure 1.23: A schematic representation of a Kossel crystal illustrating F (flat) and S (stepped) surfaces depending on whether they are parallel to two and one most dense rows of atoms, respectively, and a K (kinked) surface which is not parallel to a most dense row of atoms at all. The long arrows give the directions of the most dense rows of atoms (the directions of the first neighbor bonds). The short arrows represent the unsaturated first neighbor bonds of an atom belonging to the corresponding crystal face (after Hartman 1973).

the particular faces will be highest for the K faces, smaller for the S faces, and zero for the F faces. It follows that the K faces should disappear first, followed by the S faces and finally the crystal will be enclosed during growth by the F faces only and will cease to grow at all at small enough supersaturation.

As has been shown in the previous section, the crystal faces can be divided also in singular and vicinal faces. Singular minima correspond to the singular faces, and the latter can be any of the low index faces irrespective of whether they are F, S, or K faces. Finally, the vicinal faces which are slightly tilted with respect to one of the main (singular) crystal planes offer to the arriving building units a train of parallel steps divided by smooth terraces. This classification is of practical interest. When crystals are cut for the preparation of substrates for epitaxial growth with particular crystallographic orientations, the angle of cutting with respect to the orientation selected is

never equal to zero. Thus, crystals wafers prepared by cutting always offer vicinal surfaces for crystal growth. Besides, during spiral growth (Fig. 3.10), the side faces of the growth pyramids represent, in fact, vicinal surfaces. The same is the case when the crystal face grows through the formation and growth of 2D nuclei. Pyramids of growth are formed by the successive formation of 2D nuclei one on top of the other and their side faces represent again vicinal surfaces (see Fig. 3.2). This is the reason why we consider first the equilibrium structure of single height steps.

1.6.2 *Equilibrium structure of a step*

We consider for simplicity a single step of monoatomic height and infinite length on the surface of a simple cubic crystal. At $T = 0$, the step will be perfectly straight. As the temperature is increased, kinks separated by smooth parts will begin to appear. The kinks can be conventionally divided into *positive* and *negative* depending on whether a new row of atoms begins or ends (Fig. 1.24). If the step follows in average the direction of the most dense row of atoms, the number of positive and negative kinks will be equal. The total

Figure 1.24: Positive K^+ and negative K^- kinks along a step at $T \neq 0$. Overhang is also shown.

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Figure 1.25: For the determination of the activation energy of formation of a kink: (a) First we transfer an atom embedded into the step (site 2 in Fig. 1.19) to an adsorption position at the step (site 4 in Fig. 1.19). A hole and an adatom are formed. (b) The hole is widened by removing a second atom and transferring it next to the first one. As a result four kinks, two positive and two negative, are formed (after Burton and Cabrera 1949).

number of kinks increases when the step deviates from this direction. The kinks can be monoatomic as well as polyatomic. For simplicity, we consider the first monoatomic kinks only. We rule out also the so-called overhangs (Fig. 1.24).

The energy required to form a kink is $\omega = \psi/2$. Indeed, as shown in Fig. 1.25, in order to produce a hole and an adsorbed atom in the initially straight step, we break three lateral bonds and create one bond, thus spending a net amount of energy 2ψ. The transfer of the next atom (to separate the kinks by a smooth part) is not connected with a change of energy. Thus, we spend energy 2ψ to form four kinks (two positive and two negative) or $\omega = \psi/2$ per kink. This holds for the crystal–vapor interface. If the ambient phase is the melt, we can calculate the energy to form a kink on the base of the so-called lattice model of the melt. It is assumed that the atoms in the liquid form the same lattice as in the crystal, but the energies to disrupt the bonds between two neighboring atoms in the crystal ψ_c, in the melt ψ_m, and belonging to both the crystal and the melt ψ_{cm}, are different. We perform the same considerations as before but now we add the

energy to transfer two liquid atoms from the melt into the created holes in the step. Then, the energy ω to form a kink per crystal–melt bond ψ_{cm} is

$$\omega = \frac{1}{2}(\psi_c + \psi_m) - \psi_{\mathrm{cm}}. \tag{1.71}$$

In the case of the crystal–vapor interface $\psi_m = \psi_{\mathrm{cm}} = 0$ and $\omega = \psi_c/2 \equiv \psi/2$.

It is worth noting that the work to create a kink is, in fact, the work to create one more dangling bond or, in other words, to elongate the step by one interatomic spacing. Thus, the creation of kinks leads to the change of the specific edge energy of the step or of the surface energy of the crystal face.

We denote by n_+ and n_- the number of single positive and negative kinks, respectively, and by n_0 the number of smooth parts where there are no jumps at all. Their sum

$$n_+ + n_- + n_0 = n = 1/a \tag{1.72}$$

is just equal to the number of atoms per unit length of the step where a is the first neighbor distance.

If the energy to form a kink is $\omega = \psi/2$, we can write (Burton, Cabrera and Frank 1951)

$$\frac{n_+}{n_0} = \frac{n_-}{n_0} = \eta$$

or

$$\frac{n_+ n_-}{n_0^2} = \eta^2, \qquad \eta = \exp[-\omega/kT] = \exp[-\psi/2kT]. \tag{1.73}$$

If the average orientation of the step deviates from the direction of the most dense row of atoms by a small angle φ, then

$$n_+ - n_- = \varphi/a. \tag{1.74}$$

By solving the system (1.72)–(1.74) at $\varphi = 0$ for the mean distance between the kinks δ_0, one obtains

$$\delta_0 = \frac{1}{n_+ + n_-} = a\left(1 + \frac{1}{2\eta}\right) = a\left(1 + \frac{1}{2}\exp(\omega/kT)\right). \tag{1.75}$$

Let us evaluate this quantity. The enthalpy of evaporation of, say, silver is $\Delta H_e = 60\,720$ cal mol^{-1}; $\psi = \Delta H_e/6$ or $\omega = \Delta H_e/12$. At $T = 1000$ K, $\omega/kT = 2.53$, and $\delta_0 = 7a$. In other words, at the crystal–vapor interface of silver, we have kinks of any sign, on average, at every 7 atomic distances, i.e., the step will be rough. In the case of Si crystal–melt interface at the temperature of melting, $T_m = 1685$ K, $\Delta H_m/kT_m = 3.3$, $\omega/kT_m = 1.66$, and $\delta_0 = 3.5$a. An interesting example is the vicinal surface of Si(0 0 1). As will be shown in section 3.2.4, steps called S_{A} and S_{B} with $\omega = 0.15$ eV and 0.01 eV, respectively, alternate. Using Eq. (1.75), we find that very rough and very smooth steps coexist on the Si(0 0 1) vicinal surface.

Contrariwise, one can use Eq. (1.75) in order to evaluate ω and in turn the bond strength ψ, by measurements of δ_0, as this was done by Swartzentruber *et al.* (1990) in the case of Si(0 0 1). Yau *et al.* (2000) used this method to estimate the bond between the molecules of the protein apoferritin which has been grown in an aqueous solution. The latter has a face-centered cubic lattice with a lattice parameter $a_0 = 184$ Å. With the help of atomic force microscope (AFM), the authors measured $\delta_0 \approx 3.5a$ from which the values of $\omega = 1.6\,kT$ and $\psi = 0.082$ eV have been estimated ($T = 296$ K). Let us check if this value for ψ is reasonable. For this purpose, we calculate the surface energy of the protein (1 1 1) crystal surface and compare it with the surface energies of other fcc crystals compiled and discussed by Bonzel (1995). The formula $\sigma_{111} = 3\psi/2\Sigma_{111}$, where $\Sigma_{111} = a_0^2\sqrt{3}/4$ is the area occupied by a molecule (see Sec. 1.4), gives 0.3 erg cm^{-2} or 0.02 meV Å^{-2}. The surface energy of the softest fcc metal Pb is 610 erg cm^{-2} = 38 meV Å^{-2}. Having in mind that the amount of water bound to 1g of a globular protein in an aqueous solution varies from 0.2 to 0.5 g, we can expect that the energy of the protein–aqueous solution interface is at least 1000 times lesser than that of the interface metal vacuum. We conclude that the value of ψ deduced by Yau *et al.* is not unreasonable.

All this means that, whereas at $T = 0$, the step is perfectly straight without kinks of any sign, at any temperature higher than zero, it will contain kinks, or in other words, it will be rough. This is due to the decrease of the Gibbs free energy of the step with

increasing temperature owing to the increase of entropy. For the Gibbs free energy of the step, we can write the usual expression (we neglect the PV term)

$$G_{\mathrm{st}} = U_{\mathrm{st}} - TS_{\mathrm{st}}, \tag{1.76}$$

where

$$U_{\mathrm{st}} = (n + n_+ + n_-)\psi/2. \tag{1.77}$$

is the potential energy of the unsaturated bonds at the step (n is the number of the unsaturated bonds in a direction normal to that of the step and n_+ and n_- are the numbers of the unsaturated bonds parallel to the step, every unsaturated bond having energy $\omega = \psi/2$).

The entropy is determined by the number of the possible ways of distribution of the kinks and the smooth parts so that (if we neglect the kink-kink interaction)

$$S_{\mathrm{st}} = k \ln \left(\frac{n!}{n_+! n_-! n_0!} \right). \tag{1.78}$$

Solving again the system (1.72)–(1.74) for the simpler case of a step parallel to the direction of the most dense atomic row ($\varphi = 0$), we obtain

$$\frac{n_+}{n} = \frac{n_-}{n} = \frac{\eta}{1 + 2\eta}, \qquad \frac{n_0}{n} = \frac{1}{1 + 2\eta}. \tag{1.79}$$

Substituting (1.79) in (1.76), (1.77), and (1.78) and using the Stirling formula $\ln N! = N \ln N - N$ give

$$G_{\mathrm{st}} = -nkT \ln[\eta(1 + 2\eta)]. \tag{1.80}$$

This expression was obtained under the assumption that the kinks are monoatomic. If we relax this restriction for G_{st}, one obtains (Burton, Cabrera and Frank 1951)

$$G_{\mathrm{st}} = -nkT \ln \left(\eta \frac{1 + \eta}{1 - \eta} \right). \tag{1.81}$$

It is easy to see that $G_{\mathrm{st}} > 0$ when η is greater than some critical value $\eta_r = \sqrt{2} - 1$. Beyond this value, $G_{\mathrm{st}} < 0$. This means that a

critical temperature determined by the condition $\Delta G_{\rm st} = 0$ exists:

$$\frac{kT_r}{\psi} = 0.57 \qquad \text{or} \qquad \frac{\Delta H_e}{kT_r} = 0.88Z \tag{1.82}$$

below which the steps are rough but still exist. Bearing in mind that the step divides a half-crystal plane (with vacancies in it) from a dilute adlayer, it is clear that, at temperatures higher than T_r, both regions are mutually dissolved, the steps no longer exist, and the surface of the face becomes atomically rough. This phenomenon is similar to the mutual dissolution of a liquid and a vapor phase at the critical point at which the phase boundary between them disappears.

Figure 1.26 shows the results of a Monte Carlo simulation of the structure of a (1 0 0) face of a Kossel crystal containing steps (Leamy, Gilmer and Jackson 1975). At low temperature $T = 0.427\psi/k < T_r$ ($\omega/kT = 1.17$), two steps are clearly visible together with a small number of adatoms and advacancies. At high temperature $T = 0.667\psi/k > T_r$ ($\omega/kT = 0.75$), steps are no longer distinguishable.

1.6.3 *Equilibrium structure of F faces*

We have seen in the previous section that the disappearance of a monoatomic step leads to the roughening of the stepped surface. So the next logical question is: Can F faces roughen if steps are not initially present? The answer is *yes*, but the problem is much more complicated.

The roughness of a crystal face can be defined as

$$R = \frac{U - U_0}{U_0}, \tag{1.83}$$

where U_0 is the internal (potential) energy of the reference flat face at $T = 0$, which is proportional to the number of the unsaturated bonds normal to the face ($U_0 = \psi/2$ per atom), and U is the internal energy of the face at $T > 0$. The latter is proportional to the number of both normal and lateral bonds. Thus, the roughness is given by the ratio of the unsaturated lateral and normal bonds. If we exclude the overhangs from our considerations (this is the well-known solid-on-solid or SOS model), the number of the normal bonds does not change upon roughening and $U_0 = \text{const}$.

Figure 1.26: Atomic structure of a singular crystal face with square lattice containing steps as a function of the temperature. The figures give the value of ω/kT (H. J. Leamy, G. H. Gilmer and K. A. Jackson, in *Surface Physics of Materials*, Vol. 1, ed. J. P. Blakeley, (Academic Press, 1975), p. 121. By permission of Academic Press and courtesy of George Gilmer.)

At $T = 0$, the face is atomically smooth and all surface atoms are at the same level. Unsaturated lateral bonds do not exist, and $R = 0$. At $T > 0$, some atoms can leave the uppermost atomic plane leaving vacancies in it and adsorb on it, thus giving rise to the appearance of unsaturated lateral bonds and hence to some degree of roughness. When there are atoms on different levels, jumps analogous to the kinks in the step appear. In the case of the steps, however, the problem is much simpler because the total number of kinks and smooth parts is equal to the number of bonds per unit length of the step, and the appearance of a kink or a smooth part at any particular point does not depend on the situation in the neighboring points. In the 2D

case of a crystal surface, the situation is completely different. If we consider, for example, the (1 0 0) face of a Kossel crystal, we will see that the number of the lateral bonds is twice greater than the number of atoms per unit area. Hence, the number of the jumps between atoms on different levels is greater than the number of the atoms. This means that the existence of a jump at a given site depends on the existence of jumps in neighboring sites, although the existence of atoms on different levels is independent. As we are interested in the number and distribution of jumps or unsaturated lateral bonds, we have to deal with this *cooperative* phenomenon which means that the appearance of jumps between atoms on different levels is interdependent. This is quite a difficult problem, and exact solution exists for the simplest case of a surface with a square atomic mesh and atoms on two levels only. More general solutions can be found if some approximations are used.

Burton, Cabrera and Frank (1951) first realized that the two-level problem is analogous to the 2D Ising model in the theory of ferromagnetism. The latter deals with a square mesh of spins which can be directed either up or down (Fig. 1.27). The energy of interaction of two neighboring spins can be taken either +1 or −1 depending on whether they are parallel or antiparallel, respectively. Such a system

Figure 1.27: A square mesh of spins as an illustration of the 2D Ising model at a temperatures (a) higher and (b) lower than the critical temperature T_c.

shows critical behavior in the sense that beyond some critical temperature (the well-known temperature of Curie) all spins are randomly oriented (Fig. 1.27(a)). At lower temperatures all, spins are equally directed, thus giving rise to a ferromagnetic state (Fig. 1.27(b)).

Consider now a crystal face with atoms on two levels. If an atom has a neighbor on the same level, the energy of interaction between them will be $-\psi$. Otherwise, the bond will be unsaturated and the energy of interaction will be zero. This is equivalent to parallel and antiparallel spins, respectively. Hence, if all atoms are situated on one end the same level and the face is atomically smooth, all lateral bonds are saturated and this state is equivalent to the ferromagnetic one. Obviously, a critical temperature analogous to that of Curie will exist, above which approximately half of the atoms will be on the upper level and the other half on the lower level. Using the exact solution of Onsager (1944) for this "simple" case, Burton, Cabrera, and Frank deduced that the critical temperature is given by

$$\exp(-\psi/2kT_r) = \sqrt{2} - 1 \qquad \text{or} \qquad kT_r/\psi = 0.57 \tag{1.84}$$

for the (0 0 1) face of a Kossel crystal.

Obviously, the roughening of a crystal face taking place on more than two levels and without square symmetry cannot be treated in this way. Some approximation should be used. So we consider first the two-level model of Jackson (1958), and then we treat by the same way the multilevel model of Temkin (1964) (see also Bennema and Gilmer 1973).

1.6.3.1 *Model of Jackson*

We consider a flat, atomically smooth face with N adsorption sites per unit area at the equilibrium temperature T_e. Let N_A atoms be adsorbed on this face so that the surface coverage is $\theta = N_\mathrm{A}/N$. Every atom has Z_1 lateral bonds. For instance, $Z_1 = 4$ for the (1 0 0) face of Kossel and fcc crystals, $Z_1 = 6$ for the (1 1 1) face of fcc crystal, etc.

The relative Gibbs free energy of the system is (The PV term is again neglected)

$$\Delta G_f = \Delta U_f - T\Delta S_f, \tag{1.85}$$

where ΔU_f is again the internal energy due to the unsaturated lateral bonds and ΔS_f is the configurational entropy of the distribution of N_A atoms over N adsorption sites ($S_f(T = 0) = 0$). In order to calculate ΔU_f we use the so-called approximation of Bragg–Williams known also as "mean-field" approximation. In this particular case, the latter consists of the following. An adatom on the surface can have $1, 2, 3, \ldots, Z_1$ first neighbors. If we assume that the atoms are randomly distributed and clustering is ruled out, we can accept that approximately every adatom will have on average $Z_1\theta$ first neighbors and, respectively $Z_1(1-\theta)$ unsaturated bonds. Then,

$$\Delta U_f = N_\mathrm{A} Z_1 (1-\theta)\frac{\psi}{2} = N Z_1 \theta (1-\theta)\frac{\psi}{2}. \tag{1.86}$$

The entropy can be calculated in the usual way

$$\Delta S_f = k \ln\left(\frac{N!}{N_\mathrm{A}!(N-N_\mathrm{A})!}\right) = -kN\theta\ln\theta - kN(1-\theta)\ln(1-\theta), \tag{1.87}$$

where we again made use of the Stirling formula.

Then, for the Gibbs free energy, one obtains

$$\Delta G_f/NkT_e = \alpha\theta(1-\theta) + \theta\ln\theta + (1-\theta)\ln(1-\theta). \tag{1.88}$$

A graphical representation of $\Delta G_f/NkT_e$ is given in Fig. 1.28 for different values of the parameter α:

$$\alpha = \frac{Z_1\psi}{2kT_e} = \frac{Z\psi}{2kT_e}\frac{Z_1}{Z} = \frac{\Delta H_e Z_1}{kT_e Z} = \frac{\Delta S_e}{k}\frac{Z_1}{Z}, \tag{1.89}$$

where Z is the coordination number of an atom in the bulk crystal.

As can be seen, all curves are symmetric and have a maximum or a minimum at $\theta = 1/2$. The second derivative

$$\frac{d^2}{d\theta^2}\frac{\Delta G_f}{NkT_e} = -2\alpha + \frac{1}{\theta} + \frac{1}{1-\theta}$$

Figure 1.28: Dependence of the relative Gibbs free surface energy $\Delta G_f/NkT_e$ on the surface coverage θ at different values of the parameter α denoted by the figure at each curve (after Jackson 1958).

is negative at $\theta = 1/2$ when $\alpha > 2$ and positive when $\alpha < 2$. This means that at $\alpha < 2$, the Gibbs free energy has a minimum at $\theta = 1/2$. On the contrary, at $\alpha > 2$, the Gibbs free energy has a maximum at $\theta = 1/2$, and two equally deep minima at values of θ very close to 0 and 1. The two minima correspond to two equivalent configurations — the first one ($\theta \cong 0$) consisting of a small density of adatoms on a flat crystal face and the second one ($\theta \cong 1$) representing a flat crystal face with a few vacancies in it. If we accept that the maximum surface roughness is defined by $\theta = 1/2$, the crystal face will be rough at $\alpha < 2$ and smooth at $\alpha > 2$.

We can now answer the question what the structure of the crystal — ambient phase interface will be at the temperature of transition — melting or sublimation. For many metals, the entropy of melting $\Delta S_m/R$ has a typical value around 1.2 and their surfaces will be rough at T_m or near to it. The different crystal faces will have nearly one and the same density of kinks and the crystals will grow

rounded from their melts. On the other hand, the relative entropy of evaporation $\Delta S_e/R$ has a typical value over 10. The F faces will be smooth and the crystals will grow well polygonized from the vapor phase. The above refers to metals. In the case of some organic crystals, the entropy of melting is large and they grow polygonized from their melts.

The model of Jackson was further generalized by Chen, Ming, and Rosenberger (1986) to account for the nonlinear behavior of energy to break a bond between the first neighbors due to many-body interactions with more distant neighbors. The analysis leads to lower values of the α factor for a series of metals (Cu, Pb, Zn), thus increasing the tendency to roughening at temperatures lower than predicted by the Jackson model.

1.6.3.2 *Model of Temkin*

The main shortcomings of the Jackson model aside from the use of the mean-field approximation is that the roughness of the face is restricted to two levels only and the result is applicable only at the equilibrium temperature. This is the reason Temkin (1964, 1968) developed further this approach, allowing the crystal face to roughen at an arbitrary depth and arbitrary temperature, i.e., during the processes of growth and dissolution ($\Delta\mu \neq 0$).

The Bragg–Williams approximation again permits one to solve the more general case of multilevel roughening (Temkin 1964; Bennema and Gilmer 1973). At $T = 0$, the crystal face is completely smooth as shown in Fig. 1.29(a). At some higher temperature, the face is rough and the roughness is not confined to two levels as in the Jackson model but can go from $-\infty$ to $+\infty$. In fact, we consider the SOS model ruling out the overhangs (Fig. 1.29(b)). Every crystal layer (with number n) consists of N_{ns} solid atoms belonging to the crystal and N_{nf} atoms belonging to the fluid phase. Then

$$N_{\mathrm{ns}} + N_{\mathrm{nf}} = N = \text{const.} \tag{1.90}$$

We define the corresponding surface coverages as before

$$\theta_n = \frac{N_{\mathrm{ns}}}{N} \qquad \text{and} \qquad 1 - \theta_n = \frac{N_{\mathrm{nf}}}{N}. \tag{1.91}$$

Figure 1.29: Schematic representation of the SOS (solid-on-solid) model of an F face: (a) smooth face at $T = 0$, (b) rough face at $T > 0$. Overhangs as shown by the shadowed block are forbidden. The figures denote the number of the corresponding crystal layer.

Then the fraction of fluid atoms is $1 - \theta_n$. As n varies from $-\infty$ to $+\infty$, the problem of finding all the θ_n is subject to the boundary conditions

$$\theta_{-\infty} = 1 \quad \text{and} \quad \theta_{+\infty} = 0. \tag{1.92}$$

As we exclude the overhangs from consideration and hence $\theta_n \leq \theta_{n-1}$, (1.92) means that we go from completely solid phase to completely fluid phase. In order to find a solution for θ_n, we will follow the approach of Mutaftschiev (Mutaftschiev 1965; Bennema and Gilmer 1973).

The Gibbs free energy of a rough surface with respect to the smooth one is given by (Mutaftschiev 1965)

$$\Delta G_f = \Delta G_v + \Delta U_f + T\Delta S_f. \tag{1.93}$$

The first term accounts for the interchange of atoms between the crystal and fluid phases. This interchange is connected with the difference of the chemical potentials of the atoms in the crystal, μ_c, and that in the fluid μ_f: $\Delta\mu = \mu_c - \mu_f$ which is just the supersaturation. Then, for ΔG_v, we can write (see Eq. (1.91))

$$\begin{aligned}\Delta G_v &= (\mu_c - \mu_f)\sum_{-\infty}^{0} N_{\text{nf}} + (\mu_f - \mu_c)\sum_{1}^{\infty} N_{\text{ns}} \\ &= N\Delta\mu\left(\sum_{-\infty}^{0}(1-\theta_n) - \sum_{1}^{\infty}\theta_n\right),\end{aligned}$$

with the term in the brackets giving the net amount of atoms leaving the crystal or joining the crystal from the ambient phase. If the roughening takes place without the interchange of atoms between both phases, then both sums cancel each other, and $\Delta G_v = 0$. This is strictly valid only at the equilibrium temperature $T = T_e$ or, in other words, at $\Delta\mu = 0$.

The second term in (1.93) is completely analogous to the internal energy in Jackson's model and gives simply the number of the unsaturated lateral bonds. Then,

$$\Delta U_f = Z_1 N \frac{\psi}{2} \sum_{-\infty}^{\infty} \theta_n (1 - \theta_n).$$

It is immediately seen that in the case of a two-level model, the sum is reduced to one term only which is precisely equal to the first term in Jackson's expression (1.86).

The configurational entropy ΔS_f can be calculated by the same way as in the Jackson model:

$$\Delta S_f = k \ln \prod_{-\infty}^{\infty} \frac{(N\theta_n)!}{(N\theta_{n+1})!(N\theta_n - N\theta_{n+1})!}.$$

Using the boundary conditions (1.92) and the Stirling formula, an expression completely analogous to that of Jackson is obtained:

$$T\Delta S_f = -kTN \sum_{-\infty}^{\infty} (\theta_n - \theta_{n+1}) \ln(\theta_n - \theta_{n+1}).$$

Then, for the relative Gibbs free energy $\Delta G_f / NkT$, one obtains

$$\frac{\Delta G_f}{NkT} = \beta \left(\sum_{-\infty}^{0} (1 - \theta_n) - \sum_{1}^{\infty} \theta_n \right) + \alpha \sum_{-\infty}^{\infty} \theta_n (1 - \theta_n)$$
$$+ \sum_{-\infty}^{\infty} (\theta_n - \theta_{n+1}) \ln(\theta_n - \theta_{n+1}), \tag{1.94}$$

where

$$\beta = \frac{\Delta\mu}{kT} \tag{1.95}$$

and α is again given by (1.89) in which T_e is replaced by T.

This expression is not simply the generalization of Jackson's for the case of many levels, although it is immediately seen that Jackson's expression is automatically obtained if we put $\beta = 0, \theta_{-1} = 1, \theta_0 = \theta$, and $\theta_{+1} = 0$. The roughness of the crystal face is considered in a *nonconservative* system as we do not keep the number of the solid atoms constant but allow interchange between phases. Thus, although the Temkin model is a static thermodynamic model, it considers the surface roughening in the process of growth or dissolution of the crystal, whereas Jackson considers the system at equilibrium ($T = T_e$ and, hence, $\beta = 0$).

The stability of the crystal–fluid interface is determined by the condition of minimum of the Gibbs free energy

$$\frac{\partial}{\partial \theta_n}\left(\frac{\Delta G}{NkT}\right) = 0,$$

which leads to the following master equation for θ_n:

$$\frac{\theta_n - \theta_{n+1}}{\theta_{n-1} - \theta_n} = \exp(2\alpha\theta_n - \alpha + \beta). \tag{1.96}$$

Using the substitution $z_n = 2\alpha\theta_n - \alpha + \beta$, Eq. (1.96) turns into

$$\frac{z_n - z_{n+1}}{z_{n-1} - z_n} = \exp(z_n). \tag{1.97}$$

Expressing $z_{n-1} - z_n$ through $z_n - z_{n+1}$ and substituting the latter into the equation for z_n, (1.97) can be written in the form

$$z_{n+1} = z_n - (z_0 - z_1)\exp\left(\sum_{\mathrm{m}=1}^{n} z_m\right), \tag{1.98a}$$

$$z_{-(n+1)} = z_{-n} + (z_0 - z_1)\exp\left(-\sum_{\mathrm{m}=0}^{n} z_{-\mathrm{m}}\right). \tag{1.98b}$$

The boundary conditions $\theta_{-\infty} = 1$ and $\theta_\infty = 0$ turn into

$$z_{-\infty} = \beta - \alpha, \qquad z_\infty = \beta + \alpha. \tag{1.99}$$

Let us consider first the simpler case of $\beta = 0$, i.e., the multilevel generalization of Jackson's model. Two symmetric solutions of

Eq. (1.98) subject to the boundary conditions (1.99) are possible (Temkin 1968). The first solution is

$$z_0 = -z_1, \qquad z_{-1} = -z_2, \qquad z_{-2} = -z_3, \qquad \text{etc.}, \quad (1.100)$$

which corresponds to

$$\theta_0 = 1 - \theta_1, \qquad \theta_{-1} = 1 - \theta_2, \qquad \theta_{-2} = 1 - \theta_3, \qquad \text{etc.}$$

The second solution is

$$z_0 = 0, \qquad z_{-1} = -z_1, \qquad z_{-2} = -z_2, \qquad \text{etc.}, \quad (1.101)$$

which corresponds to

$$\theta_0 = 1/2, \qquad \theta_{-1} = 1 - \theta_1, \qquad \theta_{-2} = 1 - \theta_2, \qquad \text{etc.}$$

Comparing both solutions, it is immediately seen that the second one (1.101) corresponds to a higher value of the Gibbs free energy as $\theta_0 = 1/2$ and some degree of roughness always exists, whereas the first solution (1.100) permits θ_0 to be close to unity and θ_1 to be close to zero. Hence, the solution (1.100) provides a minimum in the surface energy whereas solution (1.101) corresponds to an inflection point. If we go back to the Jackson model for which $\theta_{-1}, \theta_{-2}, \theta_{-3} = 1$, and $\theta_1, \theta_2, \theta_3 = 0$, we will see that the second solution $\theta_0 \equiv \theta \cong 0.5$ corresponds to the maximum of the relative Gibbs free energy at values of the parameter α greater than 2. The first solution $\theta_0 = 1 - \theta_1$ corresponds to either a flat face with the negligible density of adatoms ($\theta \cong 0$) or a flat face with the negligible density of vacancies ($\theta \cong 1$).

Figure 1.30 shows the dependence of θ_n on n for different values of the parameter α. As can be seen, the interface becomes more and more smeared with decreasing α. On the contrary, when $\alpha = 3.31$, the interface consists of one layer with some vacancies in it and a few adatoms on top of it. In other words, at $\alpha > 3.3$, the interface is flat and atomically smooth.

We consider further the more general case of $\beta \neq 0$ and construct a plot of $\ln \beta$ vs α (Fig. 1.31). As can be seen, the whole field is divided into two parts: A and B. In part A, Eq. (1.96) has two solutions: one ground state solution (1.100) and one saddle point solution (1.101).

Figure 1.30: Dependence of the surface coverage on the number n of the layer at different values of the parameter α denoted by the figure at each curve at equilibrium ($\beta = 0$) (after Temkin 1964, 1968).

Figure 1.31: Phase diagram in coordinates $\ln \beta$ and α showing the state of the crystal surface as follows from the model of Temkin. In the region denoted by A the system of Eq. (1.96) has two solutions, one of which is the ground state solution corresponding to a smooth surface and the other is a saddle point. Both solutions coincide on the dividing line, and in the region denoted by B no solution exists. The latter can be interpreted as disappearance of the crystallographic orientation of the face or roughening of the face (after Temkin 1964, 1968).

On the dividing line, both solutions coincide. In region B, the master Eq. (1.96) has no solution at all which is interpreted as a loss of the crystallographic orientation of the crystal face. In other words, it becomes so rough that it cannot be distinguished as a crystal face with definite crystallographic orientation any more. The latter means that, under conditions of region B, the atoms arriving from the ambient phase can be incorporated at any site of the crystal surface without the necessity to overcome a thermodynamic energy barrier. At values of α and β, such that we are in region A, the ground state is a more or less flat surface and its growth requires the formation of 2D nuclei or the presence of screw dislocations.

Figure 1.32 (Leamy, Gilmer and Jackson 1975) demonstrates a Monte Carlo simulation of a roughening of a crystal face with increasing temperature. As can be seen, the latter leads to an increase of the thermal fluctuations of the heights of the atomic columns.

1.6.3.3 *Criterion of Fisher and Weeks*

Although the models of Jackson and Temkin predict the roughening of the crystal surfaces above some critical temperature, they do not correctly account for the thermal fluctuations in the system because of the mean-field approximation used.

As shown above, the model of Temkin predicts that under conditions of region B in Fig. 1.31 the crystal surface cannot be distinguished any more as having a definite crystallographic orientation. In other words, the crystal surface becomes delocalized with respect to the crystal lattice. This statement contains in itself the main difference between a liquid and a crystal surface. The flat crystal surface has a definite crystallographic orientation and is said that to be *localized* or *immobile*. On the contrary, the liquid surface is delocalized in the sense that it has not a definite crystallographic orientation. At low enough temperatures, the crystal surfaces are more or less smooth and so are the steps on them. At higher temperatures, thermal fluctuations become important and the steps become more and more rough and the Gibbs free energy G_{st} tends to zero. As shown, by Swendsen (1978), Weeks (1980), Fisher and Weeks (1983), Jayaprakash, Saam and Teitel (1983), G_{st} vanishes with the temperature following the

Figure 1.32: Atomic structure of a singular crystal face with square lattice without steps as a function of the temperature. The figures give the value of ω/kT. (H. J. Leamy, G. H. Gilmer and K. A. Jackson, in: Surface Physics of Materials, Vol. 1, ed. J. P. Blakeley, (Academic Press 1975), p. 121. By permission of Academic Press and courtesy of George Gilmer.)

law

$$G_{\mathrm{st}} \propto \exp\left(-\frac{C}{(T_r - T)^{1/2}}\right), \tag{1.102}$$

i.e., in a very (infinitely) smooth manner.

The step free energy G_{st} is closely connected with the specific surface energy and, thus, with the surface stiffness. It has been shown in the previous section that the surface stiffness is infinite for a flat crystal surface, whereas it has a finite value for a rounded "rough" surface. Theoretical treatment of the temperature behavior of the surface stiffness (Chui and Weeks 1978; Fisher and Weeks 1983)

resulted in an expression for the roughening temperature which naturally connects the latter with the surface stiffness

$$kT_r = \frac{2}{\pi}\sigma^*(T_r)d_{hkl}^2, \tag{1.103}$$

where $\sigma^*(T_r)$ is the surface stiffness at the transition temperature and d_{hkl} is the interplanar distance parallel to the interface. The more closely packed a given crystal face is, the larger the interplanar distance and the higher the roughening temperature will be. Thus, for an fcc lattice $d_{111} = a_0/\sqrt{3}$, $d_{100} = a_0/2$ and $(d_{111}/d_{100})^2 = 4/3 = 1.33$. Hence, in equilibrium, at some finite temperature, the most close packed surfaces will be flat, whereas others will be rounded. Slight deviation from equilibrium will lead to the growth of the rounded regions and their subsequent disappearance. The crystal will be confined by low index planes only. If again equilibrated, the rounded regions should reappear.

The theoretical criterion (1.103) has been experimentally verified in the case of ^{4}He crystals (Wolf *et al.*, 1985; Keshishev *et al.*, 1981; Babkin *et al.*, 1984; Avron *et al.*, 1980; Gallet *et al.*, 1986, 1987; Nozières and Gallet 1987) which is the ideal choice for such kind of investigations. The main advantages are the following. The liquid helium–4 is superfluid below 1.76 K, i.e., its viscosity is nearly zero. Moreover, its thermal conductivity is practically infinite. Besides, helium can be easily purified, the impurity concentration being as low as 1×10^{-9} at %. The latter is of utmost importance as the adsorption of impurities changes drastically the surface energy. Crystal helium has a very high thermal conductivity also. Thus, in contrast to other crystals, the heat and mass transport are very fast. Then, the equilibrium shape is reached in a very short time.

As mentioned above, the structure of the crystal surface affects the mechanism of growth. Wolf *et al.* (1985) investigated the latter and found that at temperatures beyond 1.232 K, the dependence of the growth rate R on $\Delta\mu$ is linear, which can be considered as a direct indication of atomically rough surface. On the contrary, at temperatures below 1.232 K a nonlinear dependence is established which proved to be exponential as required by the 2D nucleation mechanism of growth (Fig. 1.33). The slope of the logarithmic plot gives directly

Figure 1.33: Semi-logarithmic plot of the ratio of the rate of growth V in (0001) direction and the level difference H (the latter is proportional to the supersaturation $\Delta\mu$), as a function of the reciprocal supersaturation $1/H \propto 1/\Delta\mu$ for various temperatures. The straight lines show that $V \propto \Delta\mu \exp(-K_2/\Delta\mu)$ and hence the growth takes place by 2D nucleation (see Chapter 2). The slopes of the straight lines give in fact the squares of the specific edge energies of the steps surrounding the 2D nuclei. As seen the slope becomes equal to zero at $T = 1.232$ K which shows that the specific energy of the steps also becomes equal to zero. The latter means that the crystal surface is no longer smooth but rough. (P. E. Wolf, F. Gallet, S. Balibar, E. Rolley and P. Nozières, *J. Phys.* **46**, 1987 (1985). By permission of Les Editions de Physique and courtesy of S. Balibar.)

the energetic barrier for 2D nucleus formation, and at $T = 1.232$ K, it becomes equal to zero. The latter means that the free energy of the steps becomes equal to zero, the surface becomes atomically rough, and 2D nucleation is no more necessary for the crystals to grow. What is more interesting is that the dependence of the Gibbs free energy of the steps (estimated from growth experiments) on the temperatures decays exponentially, going smoothly to the roughening temperature T_r (Fig. 1.34). Thus, an excellent quantitative agreement between theory and experiment is achieved.

Figure 1.34: Variation of the step free energy with temperature as deduced from plots shown in Fig. 1.33. As seen the step free energy vanishes within the experimental accuracy near $T = T_r = 1.28$ K. (F. Gallet, S. Balibar and E. Rolley, *J. Phys.* **48**, 369 (1987). By permission of Les Editions de Physique and courtesy of S. Balibar.)

Let us consider Eq. (1.103) in more detail. The interplanar distance d_{hkl} can be identified as the step height. Then, the product $\sigma^*(T_r)d_{hkl}$ can be treated as the energy of the step and the product $\sigma^*(T_r)d_{hkl}^2$ as the energy to form a kink or, the energy ω to form a dangling bond (Chernov 1989). Assuming $\sigma^* \cong \sigma$ as a first approximation, one can now use Eq. (1.103) to find the critical temperature T_r and to predict the mechanism of growth. Thus, for Ge(1 1 1), the surface energy of the crystal–melt interface as found from nucleation experiments is equal to 251 erg cm^{-2} (Skripov 1977) and that of the crystal–vapor interface is equal to 1100 erg cm^{-2} (Swalin 1972; see also Kern *et al.*, 1979). Then, with $d_{hkl} = 3.26 \times 10^{-8}$ cm for the critical temperatures for roughening, T_r, the values 1150 K and 5000 K for the crystal–melt and crystal–vapor interfaces, respectively, are obtained. Bearing in mind that the melting point of Ge is $T_m = 1210$ K, it follows that the most closely packed surface (1 1 1) and, hence, all the other surfaces of Ge should be rough when in contact with the melt below the melting point and Ge crystals should grow rounded from melt. In the other case, the roughening

temperature is well above the melting point and the Ge crystals should grow well polygonized from a vapor phase.

1.6.4 *Kinetic roughness*

All criteria of surface structure derived so far are of thermodynamic nature. The roughness of the crystal face is due to entropy effects which decrease the Gibbs free energy of the crystal surface. However, there can be the so-called *kinetic* roughness which can take place at temperatures below the thermodynamic critical temperature. When the supersaturation is high enough, the rate of formation of 2D nuclei becomes very large so that new nuclei can be formed before the complete coverage of the crystal face by the preceding one. Several layers grow simultaneously and we observe what is called a *multilayer* growth. Then, if the density of 2D nuclei is very large, it may happen that the mean distance between their edges (which in turn are rough) becomes comparable with the interatomic distance (Chernov 1973). Arriving atoms can, thus, be incorporated practically at any site. Obviously, kinetic roughness can be observed when the specific edge-free energy, and respectively, the work of formation of 2D nuclei are very small. This question will be considered in more detail in Chapter 3.

Chapter 2

Nucleation

2.1 Thermodynamics

Gibbs was the first to realize that the formation of the new phase requires as a necessary prerequisite the appearance of small clusters of building units (atoms or molecules) in the volume of the supersaturated ambient phase (vapor, melt or solution). He considered these nuclei as small liquid droplets, vapor bubbles, or small crystallites, or, in other words, as small complexes of atoms or molecules which have the same properties as the corresponding bulk phases with the only exception being their small linear sizes. Although oversimplified, this picture has been a significant step towards the understanding of the transitions between different states of aggregation, because when phases with small sizes are involved, the surface-to-volume ratio turns out to be large compared with that of macroscopic entities. Then the fraction of the Gibbs free energy of systems containing small particles which is due to the surface energy becomes considerable. Moreover, this approach allows the description of the phases with finite sizes in terms of such macroscopic thermodynamic quantities as specific surface and edge energies, pressure, etc. That is why the theory of the formation of the new phase as developed by Gibbs (1928), Volmer (1926, 1939), Farkas (1927), Stranski and Kaischew (1934), Becker and Döring (1935), Frenkel (1955), and others is known as *capillary* or *classical* theory of nucleation. As will be shown in this chapter, the classical theory is valid at small or moderate supersaturations, in contrast to the atomistic theory which is applicable at extremely

high supersaturations where the nuclei consist of very small number of building units of the order of unity.

In any thermodynamic system, even the stable ones, local deviations from the normal state or *fluctuations* should have place which are less probable in the sense that they increase the thermodynamic potential of the system. If one considers a homogeneous molecular system (liquid or vapor), there are always small fluctuations of the density in the sense of small molecular aggregates which are well compatible with the given state of aggregation. Such density fluctuations can be called after Frenkel (1955) "homophase" fluctuations. On the other hand, there might be the so-called heterophase fluctuations which could lead to visible transition to another state of aggregation (Fig. 2.1). Their concentration should increase considerably near the phase equilibrium determined by the equality of the chemical potentials $\mu_\alpha = \mu_\beta$. If the initial bulk phase α is the stable one ($\mu_\alpha < \mu_\beta$), these density fluctuations are "lifeless" in the sense that they grow to negligible sizes and decay without revealing a tendency to unlimited growth. If, however, the initial phase α is unstable ($\mu_\alpha > \mu_\beta$), the tendency to growth prevails after exceeding a certain critical size. It is just these density fluctuations or clusters that are called critical

Figure 2.1: A fluctuation of the density in a supersaturated vapor. The circle gives an impression of the phase dividing surface.

nuclei of the new phase. In order to form such clusters, a free energy should be expended. In other words, the system should overcome an activation barrier whose height is given by the work of formation of the critical nuclei.

When considering the change of the thermodynamic potential connected with the formation of nuclei of the new phase, one assumes that the shape of the nuclei is just the equilibrium shape as determined in the previous chapter. Arbitrary shapes could be accounted for as well, but it is the equilibrium shape that ensures a minimal work for nucleus formation and, thus, determines the most probable path. Moreover, when one considers the transition from one condensed phase to another, say, crystalline from crystalline or amorphous ones, the formation of the nuclei will be accompanied by the appearance of elastic stresses due to the different molar volumes of both phases. The contribution of these stresses could be significant (Hilliard 1966; Christian 1981) and often greater than the contribution due to the nucleus shape. In the following presentation, the contribution of these strains will not be accounted for. For more detail, the reader is referred to the monograph of Christian (1981). In the case of epitaxial growth of thin films, however, the substrate and deposit crystals have, as a rule, different lattice parameters, and lateral stresses in both crystals appear as a consequence. The contributions due to these elastic strains cannot be avoided if we want to understand the phenomenon and should be added to the change of the thermodynamic potential in addition to the volume and surface terms discussed in the previous chapter.

In the present chapter, the nucleation of single-component systems will be considered. The nucleation in binary systems was first treated by Reiss (1950) following the approach of Frenkel (1955). The problem was considered further by many authors (Wilemski 1975a, 1975b; Temkin and Shevelev 1981, 1984; Shi and Seinfeld 1990; Zeng and Oxtoby 1991) and the interested reader is referred to the original papers. Cahn and Hilliard (1958, 1959) considered the nucleation in a two-component incompressible fluid and found that at small supersaturations, the classical theory results. However, on approaching the spinodal, the work for nucleus formation tends to zero as the energy

of the interface between the nucleus and the ambient phase vanishes at the spinodal. The radius of the critical nucleus tends to infinity, but the density of the nucleus tends to that of the ambient phase. The theory of Cahn and Hilliard was further developed by Hoyt (1990) to the case of multicomponent systems. For a review, see Uhlmann and Chalmers (1966).

The problems of nucleation, both thermodynamic and kinetic, are considered in numerous monographs and review papers (Volmer 1939; Defay *et al.*, 1966; Kaischew 1980; Turnbull 1956; Frenkel 1955; Dunning 1955; Hirth and Pound 1963; Nielsen 1964; Hollomon and Turnbull 1953; Toschev 1973; Stoyanov and Kashchiev 1981; Stoyanov 1979; Zettlemoyer 1969; Nucleation Phenomena 1966, 1977; Skripov 1977; James 1982; Christian 1981; Oxtoby 1992; Kashchiev 2000; Mutaftschiev 2001; Dubrovskii 2014) and the reader interested in different aspects of particular phase transitions is referred to them.

2.1.1 *Homogeneous formation of 3D nuclei*

We consider first the simplest case of formation of liquid nuclei in the bulk of a vapor phase. The simplicity is obviously due to the isotropic surface tension σ of the liquid which leads to the spherical equilibrium shape of the small liquid entities. We consider a volume containing n_v molecules of a vapor with the chemical potential μ_v which is a function of the temperature T and pressure P (see Fig. 1.5). The thermodynamic potential of the initial state of the system at $T = \text{const}$ and $P = \text{const}$ is, thus, given by (the interested reader is referred to the excellent review paper of Milchev 1991)

$$G_1 = n_v \mu_v.$$

A droplet of a liquid with the bulk chemical potential μ_l is formed from n molecules of the vapor phase and the thermodynamic potential of the system vapor–liquid droplet reads

$$G_2 = (n_v - n)\mu_v + G(n),$$

where $G(n)$ is the thermodynamic potential of a cluster containing n molecules. The work of formation of a cluster consisting of n atoms

is then given by the difference $\Delta G(n) = G_2 - G_1$:

$$\Delta G(n) = G(n) - n\mu_v. \tag{2.1}$$

It follows that the work of formation of the cluster represents the difference of the thermodynamic potential of the cluster and the thermodynamic potential of the same amount of material (number of moles or molecules) but in the mother (vapor) phase. This is the most general definition of the nucleation work. As will be shown in the following, it can be used for the derivation of both the classical and the atomistic theories of nucleation.

In the capillary theory of nucleation, the thermodynamic potential of the liquid droplet is given by the sum of the chemical potential of the constituent atoms in the infinitely large liquid phase $n\mu_l$ and the surface energy $4\pi r^2\sigma$ of the droplet

$$G(n) = n\mu_l + 4\pi r^2\sigma. \tag{2.2}$$

In this equation, σ is the surface energy of the flat surface. The dependence of the surface energy on the droplet size has been discussed by Kirkwood and Buff (1949) and by Tolman (1949). They found that the surface energy should, in general, decrease with decreasing droplet size. Assuming Lennard–Jones interatomic forces, Benson and Shuttleworth (1951) have found a decrease of 15% for the surface energy of a close-packed cluster consisting of 13 atoms in comparison with the energy of a flat surface. The physics behind this result is simple. The decrease of the surface tension with the droplet size is due to the loss of the long-range part (the more distant neighbors) of the attractive energy for atoms far from the droplet surface. The cohesive energy is reduced and according to the definition of the surface energy (see Sec. 1.4), the surface tension is also lowered. In the analysis that follows, we will neglect the curvature dependence of the surface energy.

The change of the Gibbs free energy upon the formation of the droplet is then

$$\Delta G = -n(\mu_v - \mu_l) + 4\pi r^2\sigma.$$

Figure 2.2: Dependence on the droplet radius of the Gibbs free energy change ΔG connected with the formation of liquid nuclei from a supersaturated vapor phase. When the liquid phase is stable ($\mu_l < \mu_v$) ΔG displays a maximum at some critical radius $r = r^*$. Beyond this size, the growth of the nucleus leads to a decrease of the Gibbs free energy of the system. The maximum Gibbs free energy ΔG^* is the work of formation of the critical nucleus. When the vapor phase is stable $\mu_v < \mu_l$, both terms in Eq. (2.3) are positive and the formation of nuclei capable of unlimited growth is thermodynamically prohibited as it leads to an infinite increase of the Gibbs free energy.

Bearing in mind that $n = 4\pi r^3/3v_l$ (v_l being the molecular volume of the liquid), one obtains

$$\Delta G(r) = -\frac{4}{3}\frac{\pi r^3}{v_l}\Delta\mu + 4\pi r^2\sigma, \tag{2.3}$$

where $\Delta\mu = \mu_v - \mu_l$ is the supersaturation (Eq. (1.9)). The $\Delta G(r)$ dependence is plotted in Fig. 2.2.

Thus, in the simplest case of a droplet formation in vapor, ΔG consists of two terms: the volume term $4\pi r^3\Delta\mu/3v_l = (4\pi r^3/3)(P_l - P_v)$ and the surface term $4\pi r^2\sigma$. The minus before the volume term reflects the fact that energy is gained when the liquid phase is thermodynamically stable ($\mu_l < \mu_v$). The increase of the thermodynamic potential of the system is due to the formation of a dividing surface. Then, ΔG displays a maximum at some critical size r^* given

by (Fig. 2.2)

$$r^* = \frac{2\sigma v_l}{\Delta\mu}. \tag{2.4}$$

Equation (2.4) is in fact the equation of Thomson–Gibbs (1.18) and gives the condition for the equilibrium of the nucleus with the ambient phase. Note, however, that *this equilibrium is unstable*. Indeed, if some more atoms join the critical nucleus, its radius increases and, in turn, its equilibrium vapor pressure becomes smaller than the one available in the system (Eq. (1.19)). Then, the probability of decay becomes smaller than the probability of growth and it should grow further. In the opposite case, its equilibrium vapor pressure becomes greater than the one available in the system and the nucleus reveals a tendency for further decay. In other words, any infinitesimal deviation of the size of the nucleus from the critical one leads to the decrease of the thermodynamic potential of the system. In this sense, the cluster with a size r^* is a critical nucleus of the new phase.

The maximal value of ΔG which is obtained by substitution of r^* into Eq. (2.3)

$$\Delta G^* = \frac{16\pi}{3}\frac{\sigma^3 v_l^2}{\Delta\mu^2} \tag{2.5}$$

gives the height of the energy barrier which should be overcome for condensation to take place. It is inversely proportional to the square of the supersaturation (a result which is obtained for the first time by Gibbs 1878) and increases steeply near the phase equilibrium (i.e., at small supersaturations), thus imposing great difficulties for the phase transition to occur.

When the ambient phase is stable ($\mu_v < \mu_l$), both terms in Eq. (2.3) are positive and ΔG tends to infinity (see Fig. 2.2), thus reflecting the fact that the heterophase density fluctuations at undersaturation are thermodynamically unfavored.

Substituting the supersaturation $\Delta\mu$ into (2.5) by the radius r^* of the critical nucleus from the Thomson–Gibbs Equation (2.4) gives

$$\Delta G^* = \frac{1}{3}4\pi r^{*2}\sigma = \frac{1}{3}\sigma\Sigma. \tag{2.6}$$

As seen, the Gibbs free energy required to form a critical nucleus of the new phase with equilibrium shape is precisely equal to one-third of the surface energy $\sigma\Sigma$, a result obtained for the first time by Gibbs (1878).

Useful expressions for $\Delta G(r)$ could be obtained if we substitute the supersaturation from the Thomson–Gibbs Equation (2.4) into (2.3) in terms of the radius r^* of the critical nucleus

$$\Delta G(r) = \Delta G^* \left[3\left(\frac{r}{r^*}\right)^2 - 2\left(\frac{r}{r^*}\right)^3\right] \tag{2.7}$$

or in terms of the number n^* of atoms in the nucleus (from $v_c n = 4\pi r^3/3$):

$$\Delta G(n) = \Delta G^* \left[3\left(\frac{n}{n^*}\right)^{2/3} - 2\left(\frac{n}{n^*}\right)\right], \tag{2.8}$$

where ΔG^* is given by (2.6). We will use the set of Eqs. (2.7) and (2.8) when deriving an expression for the rate of nucleation.

The result (2.6) is a universal one. It does not depend on the state of aggregation of the nucleus and can be easily obtained for crystalline nuclei in a general form. Indeed, in this case,

$$\Delta G^* = -\frac{V^*}{v_c}\Delta\mu + \sum_n \sigma_n \Sigma_n,$$

where V^* is the volume of the critical nucleus and v_c is the volume of one building unit in the crystal phase. Bearing in mind (see Chapter 1, Sec. 1.4.1)

$$V^* = \frac{1}{3}\sum_n h_n \Sigma_n,$$

and Eq. (1.27) for the equilibrium shape

$$\frac{h_n}{\sigma_n} = \frac{2v_c}{\Delta\mu},$$

one obtains

$$\Delta G^* = \frac{1}{3}\sum_n \sigma_n \Sigma_n. \tag{2.9}$$

One can use this expression to obtain the work of formation of crystalline nuclei with an arbitrary symmetry and radius of action of

the interatomic forces. In the simplest case of a nucleus of a Kossel crystal with first neighbor interactions, the (1 0 0) faces appear only on the equilibrium shape. Then,

$$\Delta G^* = 2l^{*2}\sigma = \frac{32\sigma^3 v_c^2}{\Delta\mu^2}. \tag{2.10}$$

Under the same condition (first neighbor interactions), the equilibrium shape of a crystal with face centered cubic (fcc) lattice has the form of a truncated octahedron and consists of six square faces (1 0 0) and eight hexagonal (1 1 1) faces with equal edge lengths (Markov and Kaischew 1976b). Then,

$$\Delta G^* = \frac{1}{3}\left(6l^{*2}\sigma_{1\ 0\ 0} + 8\frac{3\sqrt{3}}{2}l^{*2}\sigma_{1\ 1\ 1}\right).$$

From the equilibrium shape condition $h_{1\ 1\ 1} : h_{1\ 0\ 0} = \sigma_{1\ 1\ 1} : \sigma_{1\ 0\ 0}$ with the first neighbor model relation $\sigma_{1\ 1\ 1}/\sigma_{1\ 0\ 0} = \sqrt{3}/2$, it follows

$$l^* = \frac{\sigma_{1\ 0\ 0} v_c}{\Delta\mu} = \frac{2\sigma_{1\ 1\ 1} v_c}{\Delta\mu\sqrt{3}}$$

and

$$\Delta G^* = \frac{1}{3}\frac{v_c^2}{\Delta\mu^2}\left(6\sigma_{1\ 0\ 0}^3 + 16\sqrt{3}\sigma_{1\ 1\ 1}^3\right) = \frac{8\sigma_{1\ 0\ 0}^3 v_c^2}{\Delta\mu^2}. \tag{2.11}$$

Equations (2.5), (2.10), or (2.11) are applicable for nucleation from any supersaturated (undercooled) phase (vapor, liquid or solution). For this aim, the corresponding differences of the chemical potentials $\Delta\mu$ (Eqs. (1.9), (1.10), or (1.12)) and the specific energies of the corresponding interfaces (crystal–vapor, crystal–melt, or crystal–solution) should be taken into account.

2.1.2 *Heterogeneous formation of 3D nuclei*

The process of nucleation is stimulated by the presence of impurity particles, ions, or foreign surfaces. Nuclei are usually formed on the walls of the reaction vessels. While these effects are usually undesirable, the process of nucleation on foreign substrates is essential for the epitaxial deposition of thin films. We will illustrate this problem

Figure 2.3: For the determination of the concept of a structureless substrate which is very convenient for studying the catalytic potency of the substrate on the nucleus formation. (a) shows the energetic profile of a single crystal substrate, where E_{sd} and E_{des} are the activation energies for surface diffusion and desorption, respectively. In (b) the surface potential is no longer a periodic function ($E_{sd} = 0$). This simplification excludes the effect of the lattice misfit but permits the study of the effect of $E_{des} \neq 0$.

with the formation of a liquid droplet on the so-called structureless substrate (Volmer 1939). But before doing that, we have to clarify what "structureless substrate" means.

A single-crystal substrate exerts on the particles of the mother phase a periodic potential which is characterized by a period equal to the interatomic spacing and overall amplitude equal to the activation energy for surface diffusion (Frenkel and Kontorova 1938). In the simplest case, it can be presented by a sinusoide (Fig. 2.3a). If a nucleus is formed onto such a surface, it should be elastically strained to fit the substrate. Then the energy of the elastic strains should be added to the change of the thermodynamic potential. In order to simplify the problem, we assume that the modulation of the periodic potential is equal to zero. The hypothetical structureless substrate

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(Fig. 2.3b) is the result which gives the possibility of studying the effect of the interatomic forces on the process of nucleation, neglecting the lattice mismatch as a first approximation. Then, we can make the necessary correction for the latter.

When considering the homogeneous formation of liquid droplets from a vapor phase, we assumed that the equilibrium shape of the droplet is a sphere. We also assumed that the shape of the crystalline nuclei is the equilibrium one in order to derive the expression for the Gibbs energy change of their formation. Obviously, we should first derive an expression for the equilibrium shape of a droplet on a foreign substrate.

We consider a liquid droplet on a smooth structureless substrate (Fig. 2.4). It represents a segment of a sphere with the radius of curvature r and projected radius $r \sin\theta$, where θ is the so-called wetting angle. The latter characterizes the energetic influence of the substrate. We denote the specific surface energies of the free surfaces of the droplet and the substrate, and of the substrate–droplet interface by σ, σ_s, and σ_i, respectively. Then, the condition of equilibrium is expressed by the well-known relation of Young (1805) (see also

Figure 2.4: Equilibrium shape of a liquid droplet with a radius of curvature r on a structureless substrate. The latter is characterized by the wetting angle θ between the substrate plane and the tangent to the droplet surface. The wetting angle is determined through the Young equation from the specific surface energies of the interfaces between the liquid droplet and the solid substrate and the vapor phase, and between the substrate and the liquid droplet, denoted by σ, σ_s, and σ_i, respectively.

Adam 1968):

$$\sigma_s = \sigma_i + \sigma \cos\theta, \tag{2.12}$$

which is an analog of the relation of Dupré (1869) (Eq. (1.28)) for the case of liquid droplet on a solid surface.

The Young relation is easy to derive following the approach given in Chapter 1. We have to find as before the minimum of the surface energy Φ of the liquid droplet at constant volume V_l of the segment. Bearing in mind that the area of the free surface and the area of the contact are given by

$$\Sigma = 2\pi r^2(1 - \cos\theta)$$

and

$$\Sigma_i = \pi r^2 \sin^2\theta,$$

respectively, the surface energy Φ of the liquid droplet reads

$$\Phi = 2\pi r^2(1 - \cos\theta)\sigma + \pi r^2 \sin^2\theta(\sigma_i - \sigma_s). \tag{2.13}$$

The volume of the segment is

$$V_l = \frac{4}{3}\pi r^3 \frac{(1 - \cos\theta)^2(2 + \cos\theta)}{4}. \tag{2.14}$$

From $dV_l = 0$, we find

$$dr = -\frac{(1 + \cos\theta)\sin\theta}{(1 - \cos\theta)(2 + \cos\theta)} r d\theta.$$

Substituting it in $d\Phi = 0$ results in Eq. (2.12).

The change of the thermodynamic potential upon the formation of the droplet is given by

$$\Delta G = -\frac{V_l}{v_l}\Delta\mu + \Phi,$$

where V_l and Φ are given by (2.14) and (2.13), respectively.

Substituting $\sigma_i - \sigma_s = -\sigma\cos\theta$ from the equation of the equilibrium shape (2.12) in the expression for ΔG gives

$$\Delta G = \frac{4}{3}\pi r^3 \frac{(1 - \cos\theta)^2(2 + \cos\theta)}{4}\frac{\Delta\mu}{v_l} + 2\pi r^2\sigma(1 - \cos\theta) - \pi r^2\sigma\sin^2\theta\cos\theta.$$

Following the same procedure as before, we find that the change of the thermodynamic potential reaches a maximum at a critical size

$$r^* = \frac{2\sigma v_l}{\Delta\mu},$$

which does not depend on the wetting angle. The latter clearly recalls that the equilibrium vapor pressure depends only on the curvature but not on whether the droplet is a complete sphere or not.

Then, for the work for nucleus formation, one obtains

$$\Delta G^*_{\text{het}} = \frac{16\pi}{3}\frac{\sigma^3 v_l^2}{\Delta\mu^2}\phi(\theta) = \Delta G^*_{\text{hom}}\phi(\theta), \tag{2.15}$$

where

$$\phi(\theta) = \frac{1}{4}(1-\cos\theta)^2(2+\cos\theta) \tag{2.16}$$

is a function of the wetting angle and accounts for the catalytic potency of the substrate with respect to the nucleus formation.

A graphic representation of $\phi(\theta)$ is given in Fig. 2.5. As seen, it varies from 0 to 1 when θ varies from 0 to π. In other words, in the case of complete wetting, $(\phi(\theta = 0) = 0)$, $\Delta G^*_{\text{het}} = 0$, the formation of three-dimensional (3D) droplets is thermodynamically

Figure 2.5: Plot of the wetting function $\phi = (1-\cos\theta)^2(2+\cos\theta)/4$ vs the wetting angle θ. It varies from zero to unity when θ varies from 0 (complete wetting) to π (complete nonwetting).

unfavored and the liquid has the tendency to spread over the substrate as a continuous film. In the other extreme (complete nonwetting $\phi(\theta = \pi) = 1$), $\Delta G^*_{\text{het}} = \Delta G^*_{\text{hom}}$, which means that the substrate does not exert any energetic influence on the nucleus formation and the nucleus has the shape of a complete sphere, that is, we have in practice homogeneous nucleation. It should be noted, however, that in the case of complete wetting ($\theta = 0$), the formation of the new phase still requires overcoming an energetic barrier which is connected with the formation of a two-dimensional (2D) nucleus. The increase of the Gibbs free energy in this case is due to the formation of a single height step surrounding the nucleus.

Comparing the wetting function $\phi(\theta)$ with the volume of the segment, it becomes immediately clear that $\phi(\theta) = V^*/V_0$, where V_0 is the volume of the complete sphere. Then,

$$\Delta G^*_{\text{het}} = \Delta G^*_{\text{hom}} \frac{V^*}{V_0}, \tag{2.17}$$

that is, the ratio of the works for heterogeneous and homogeneous formations of nuclei at one and the same supersaturation is simply equal to the ratio of the corresponding volumes of the nuclei. As will be shown in the following, this is also a universal result which depends neither on the state of aggregation of the nucleus nor on its crystal lattice.

Indeed, the work of the homogeneous formation of a crystalline nucleus in a general form is

$$\Delta G^*_{\text{hom}} = -\frac{V_0}{v_c}\Delta\mu + \sum_n \sigma_n \Sigma_n,$$

where V_0 is the volume of the homogeneously formed critical nucleus.

Substituting σ_n from the Gibbs–Curie–Wulff theorem (Eq. (1.27)) into the surface energy term gives

$$\Delta G^*_{\text{hom}} = \frac{1}{2}\frac{V_0^*}{v_c}\Delta\mu, \tag{2.18}$$

that is, the work of nucleus formation is equal to one-half of the volume work which is required to transfer $n = V_0^*/v_c$ atoms from the parent to the new phase.

The work of heterogeneous formation of a 3D nucleus is

$$\Delta G^*_{\text{het}} = -\frac{V^*}{v_c}\Delta\mu + \sum_{n\neq m}\sigma_n\Sigma_n + (\sigma_m - \beta)\Sigma_i,$$

where V^* is the volume of the critical nucleus formed on a foreign substrate and $\sigma_m - \beta = \sigma_i - \sigma_s$ follows from the relation of Dupré.

Substituting again σ_n and $\sigma_m - \beta$ from the Gibbs–Curie–Wulff theorem valid for the heterogeneous case (Eq. (1.30)) gives

$$\Delta G^*_{\text{het}} = \frac{1}{2}\frac{V^*}{v_c}\Delta\mu. \tag{2.19}$$

Equation (2.17) follows from (2.18) and (2.19).

Equations (2.18) and (2.19) can be written in the form

$$n^* = \frac{2\Delta G^*}{\Delta\mu}, \tag{2.20}$$

where $n^* = V^*/v_c$ is the number of atoms in the critical nucleus.

It follows that in all cases, the number of atoms in the critical nucleus is equal to the doubled work for nucleus formation divided by the supersaturation. Bearing in mind that the work of nucleus formation is inversely proportional to the square of the supersaturation (Eq. (2.5)), we find that the number of atoms in the critical nucleus decreases with the cube of the supersaturation.

Equation (2.19) allows us to calculate easily the work for the nucleus formation of a, say, cubic nucleus on a foreign substrate (Fig. 1.22). With $V^* = l^{*2}h^*$, the condition for the equilibrium shape $h^*/l^* = (\sigma + \sigma_i - \sigma_s)/2\sigma = \Delta\sigma/2\sigma$ (Eq. (1.69)) and the Thomson–Gibbs equation $l^* = 4\sigma v_c/\Delta\mu$, one obtains

$$\Delta G^*_{\text{het}} = \frac{32\sigma^3 v_c^2}{\Delta\mu^2}\frac{(\sigma + \sigma_i - \sigma_s)}{2\sigma} = \Delta G^*_{\text{hom}}\frac{\Delta\sigma}{2\sigma}, \tag{2.21}$$

where $\Delta\sigma/2\sigma = h^*/l^* = h^* l^{*2}/l^{*3} = V^*/V_0^*$. Equation (2.21) can be easily obtained also combining Eqs. (2.10), (2.17), and (1.70).

It appears (Eqs. (1.70) and (2.16)) as if the foreign substrate "cuts" the homogeneous nucleus at a height determined by the equilibrium shape, or in other words, by the ratio of the interatomic forces. The latter is given by the wetting function $\phi(\theta)$ for liquid

droplets or the equivalent expression $(\sigma + \sigma_i - \sigma_s)/2\sigma = 1 - \psi'/\psi$ valid for crystals.

2.1.3 *Heterogeneous formation of elastically strained 3D nuclei*

The problem of formation of nuclei on single-crystal substrates is much more complicated and can be solved more or less approximately. The main difficulty arises from the fact that the strains are anisotropic. There are lateral strains due to the tendency of the nuclei to fit the substrate and normal strains with an opposite sign due to the Poisson effect. (The latter accounts for the transverse deformations of the crystal lattice which appear as a result of longitudinal strains.)

The strain affects both the volume and the surface parts of the work expanded to form a nucleus. The strain energy per atom should be added to the change of the thermodynamic potential and, thus, should be obviously accounted for in the volume term. This is the same if we state that the strains change the strength of the lateral chemical bonds between the atoms and, thus, the chemical potential of the crystal.

The role of the elastic strain on the surface energy term is twofold. As mentioned in Chapter 1, a new surface can be created by stretching out an old one (when stretching out the whole crystal). Thus, if the crystal is laterally strained in both orthogonal directions parallel to the substrate surface, the upper crystal surface will be "isotropically" strained in two directions. As a result, its specific energy will be changed. On the other hand, the lateral deformation of the crystal leads to a strong anisotropic change of the specific energy of the side faces. Bearing in mind the Poisson effect, the chemical bonds will be stretched out in directions parallel to the substrate surface but compressed in the normal direction and vice versa. As a result, the specific energy of the side crystal faces will be changed in a very peculiar way. In addition, the strain in a direction normal to the substrate surface is not constant but gradually decreases from the bottom to the top surface of the nucleus. The latter is due to the free side surfaces where the strains can partially relax. And finally,

the elastic strains should affect the bonding between the substrate and deposit atoms and, in turn, the specific energy of the interfacial boundary, or in other words, the wetting of the substrate by the strained 3D islands. The contribution of the strains to the specific surface energies should be added to the surface term.

That is why in this section the problem will be qualitatively considered mostly as an illustration of the atomistic approach developed by Kossel, Stranski, and Kaischew (see Sec. 1.4). A more rigorous treatment has been recently performed by Müller and Kern (1998, 2000), Tersoff and Tromp (1993), Tersoff and LeGoues (1994), Shchukin *et al.* (1995), Yu and Madhukar (1997), Duport *et al.* (1998), Politi *et al.* (2000), and others. The interest to this problem comes from the formation of coherently strained 3D islands in highly mismatched epitaxy of semiconductor materials that have possible application as quantum dots in optoelectronics.

A Kossel crystal is adopted for simplicity. We confine ourselves to first neighbor interactions and neglect the Poisson effect. We assume further that the lattice misfit is accommodated completely by homogeneous elastic strain, the misfit dislocations being ruled out. The atomistic approach has, in this case, one important advantage. It permits one to account for the effect of the strains on the specific surface energies in an implicit form without entering into sophisticated details.

The change of the thermodynamic potential when a nucleus of the new phase is formed in a general form reads

$$\Delta G = -n\Delta\mu + \Phi, \tag{2.22}$$

where n is the number of building units and Φ is the surface energy. According to the definition of Stranski (1936/1937), the latter is given by

$$\Phi = n\varphi_{1/2} - U_n, \tag{2.23}$$

where U_n is the energy of disintegration of the whole crystal into single atoms. In fact, this quantity taken with a negative sign, $-U_n$, is the potential (binding) energy of the chemical bonds of the crystal. Equation (2.23) can be easily understood. The first term on the right-hand side gives the energy of the bonds as if all atoms are in the

bulk of the crystal. The second term gives the energy of the bonds between the atoms of the cluster and, hence, the difference is simply the number of the unsaturated dangling bonds on the cluster "surface" multiplied by the energy required to break a bond. Note that Φ can be expressed in terms of surface, edge, and apex energies in the case of large enough crystals, but, as written above, is applicable for arbitrarily small clusters. It is also very important to note that, whereas the first term is only a function of the crystal volume, the second one is additionally a function of the crystal shape.

As shown in Chapter 1, the equation of Thomson–Gibbs (1.62) in atomistic terms reads

$$\Delta\mu = \varphi_{1/2} - \bar{\varphi}_3, \tag{2.24}$$

where $\bar{\varphi}_3$ (Eq. (1.60)) is the mean work of separation representing the energy of disintegration per atom of a whole uppermost lattice plane of the crystal and which must have one and the same value for all crystal faces belonging to the equilibrium shape.

Substituting Eq. (2.24) into Eq. (2.23) gives the work of formation of the critical nucleus in the atomistic approach as

$$\Delta G^* = n^* \bar{\varphi}_3 - U_{n^*}. \tag{2.25}$$

We have to account now for the effect of the elastic strain on the energy of the first-neighbor bonds. We consider the harmonic approximation of the interatomic potential which is usually represented by a Lennard–Jones or Morse potential. As shown in Fig. 2.6, the work necessary to disrupt a strained bond will be equal to $\psi - \varepsilon$, where ψ is the work to break an unstrained bond and ε is the strain energy of a bond. The latter is given by

$$\varepsilon = \frac{1}{2}\gamma(a-b)^2,$$

where γ is the elastic constant of the first-neighbor bond, and a and b are the natural interatomic spacings of the substrate and nucleus crystals, respectively.

The nucleus of our model is shown in Fig. 2.7. It can be imagined as consisting of blocks having the shape of square-based prisms (rather than cubes) with thickness smaller or larger than the lateral size, thus reflecting the fact that the lateral bonds are strained,

Figure 2.6: Schematic representation of the change of the interatomic bond strength with the bond strain. The solid line shows the elastic (Hookean) approximation to a pairwise interatomic potential given by the dashed line. The work to break an unstrained bond is ψ. The work to break an elastically strained bond is $\psi - \varepsilon$, where ε is the strain energy per bond.

Figure 2.7: Part of a nucleus of a Kossel crystal formed on a single-crystal substrate with quadratic symmetry. The nucleus is homogeneously strained in both lateral directions to fit the substrate. The lateral bonds are equally strained and the work to break them is equal to $\psi - \varepsilon$. The normal bonds remain unchanged if the Poisson effect is neglected. Then the work to break a bond perpendicular to the substrate surface is equal to ψ.

whereas the normal bonds preserve their length (the Poisson effect is neglected). Then the energy to break a lateral bond will be $\psi - \varepsilon$ and that of a normal one, ψ. The numbers of atoms in the lateral and normal edges are n_e and n'_e, respectively.

The mean works of separation calculated from the upper (subscript u) and side (subscript s) faces read

$$\bar{\varphi}_{\mathrm{u}} = 3\psi - 2\varepsilon - 2\frac{\psi - \varepsilon}{n_e} \tag{2.26a}$$

and

$$\bar{\varphi}_s = 3\psi - 2\varepsilon - \frac{\psi - \varepsilon}{n_e} - \frac{\psi - \psi'}{n'_e}, \tag{2.26b}$$

respectively. The condition $\bar{\varphi}_{\mathrm{u}} = \bar{\varphi}_s$ gives for the equilibrium shape the following expression:

$$\frac{n'_e}{n_e} = \left(1 - \frac{\psi'}{\psi}\right)\left(1 - \frac{\varepsilon}{\psi}\right)^{-1}. \tag{2.27}$$

Bearing in mind that the condition for the equilibrium shape of unstrained nucleus is given by (Eq. (1.69))

$$\frac{n'}{n} = 1 - \frac{\psi'}{\psi},$$

it follows that

$$\frac{n'_e}{n_e} = \frac{n'}{n}\left(1 - \frac{\varepsilon}{\psi}\right)^{-1},$$

i.e., an elastically strained nucleus consists of a larger number of lattice planes than the unstrained one.

From Eqs. (2.24) and (2.26), recalling that $\varphi_{1/2} = 3\psi$ for a Kossel crystal for the supersaturation, one obtains

$$\Delta\mu = 2\frac{\psi}{n_e^*} + 2\varepsilon\left(1 - \frac{1}{n_e^*}\right), \tag{2.28}$$

where n_e^* is the number of the atoms in the lateral edge of the strained critical nucleus. Rearranging (2.28) gives for the latter

$$n_e^* = \frac{2(\psi - \varepsilon)}{\Delta\mu - 2\varepsilon} = n^*\left(1 - \frac{\varepsilon}{\psi}\right)\left(1 - n^*\frac{\varepsilon}{\psi}\right)^{-1}, \tag{2.28$'$}$$

where $n^* = 2\psi/\Delta\mu$ is the number of atoms in the edge of the unstrained critical nucleus ($\varepsilon = 0$) at the same value of the supersaturation. As seen, n_e^* is inversely proportional to the difference $\Delta\mu_e = \Delta\mu - 2\varepsilon$, which reflects the increase of the chemical potential of the strained nucleus due to the strain energy per atom, 2ε. (We recall that $\Delta\mu = \mu_v - \mu_c$ so that the chemical potential of the strained island is $\mu_c^e = \mu_c + 2\varepsilon$.) An inspection of Eq. (2.28′) shows that $n_e^* > n^*$ and the difference increases sharply with the increase of the strain energy per bond, ε. Hence, we have both $n_e'^* > n'^*$ and $n_e^* > n^*$, i.e., the laterally strained nucleus is larger than the unstrained in both height and width at one and the same supersaturation.

The equilibrium vapor pressure of an unstrained nucleus is $kT\ln(P/P_\infty) = \Delta\mu = 2\psi/n^*$ and then the analogous quantity for a strained nucleus reads

$$P_e = P\exp\left(\frac{2\varepsilon}{kT}\right). \tag{2.29}$$

We obtained the important result that the equilibrium vapor pressure of a laterally strained small crystal formed on a foreign single-crystal substrate is higher than that of the unstrained one due to its increased chemical potential as a consequence of the elastic strain.

Making use of Eqs. (2.24), (2.27), and (2.28′) and counting the bonds between the atoms in the nucleus gives for the work of elastically strained nucleus

$$\Delta G_e^* = n_e^{*2}\psi\left(1 - \frac{\psi'}{\psi}\right) = \frac{4\psi(\psi-\varepsilon)^2}{(\Delta\mu - 2\varepsilon)^2}\left(1 - \frac{\psi'}{\psi}\right). \tag{2.30}$$

In other words,

$$\Delta G_e^* = \Delta G^*\left(1 - \frac{\varepsilon}{\psi}\right)^2\left(1 - \frac{2\varepsilon}{\Delta\mu}\right)^{-2}, \tag{2.31}$$

where ΔG^* is the work of formation of the unstrained nucleus ($\varepsilon = 0$) given by Eq. (2.21).

ΔG_e^* and ΔG^* are plotted against supersaturation in Fig. 2.8. As seen, ΔG_e^* is larger than ΔG^* and tends asymptotically to infinity when $\Delta\mu$ tends to 2ε, whereas ΔG^* still has a finite value. It follows that the formation of elastically strained nuclei requires supersaturation which is higher than the strain energy per bond.

Figure 2.8: Dependence of the Gibbs free energy ΔG_e^*, of formation of an elastically strained 3D nucleus on a foreign single crystal substrate on the supersaturation. A critical supersaturation $\Delta\mu = n\varepsilon$ should be exceeded which is equal to the strain energy per atom. The Gibbs free energy ΔG^* of formation of elastically unstrained 3D nucleus is also given for comparison. As seen, ΔG_e^* is greater than ΔG^* and the formation of elastically strained nucleus requires higher supersaturation.

2.1.4 *Formation of 2D nuclei*

It was Brandes (1927) who first considered the possibility of the formation of 2D nuclei on the surface of a foreign substrate. He found that the Gibbs free energy of formation of such nuclei is precisely equal to one-half of their edge energy

$$\Delta G_2^* = \frac{1}{2}\sum_n \varkappa_n l_n, \tag{2.32}$$

where $\varkappa_n$ is the specific edge energy of the nth edge and l_n is its length. The similarity of Eqs. (2.32) and (2.9) is apparent.

Following the same procedure as before, one can derive an expression for the work of formation of 2D nuclei. The more general case of nucleation on a foreign substrate will be treated first.

We consider a cluster with square equilibrium shape (the equilibrium shape has to be, in principle, determined beforehand, making use of the Gibbs–Curie–Wulff theorem for the 2D case (Eq. (1.44)). In the simplest case of a Kossel crystal with first neighbor interactions only, the equilibrium shape is a square with edge length l formed on the surface of a foreign structureless substrate. The variation of the Gibbs free energy reads

$$\Delta G = -\frac{l^2}{s_c}\Delta\mu + l^2(\sigma + \sigma_i - \sigma_s) + 4l\varkappa, \tag{2.33}$$

where $n = l^2/s_c$ is the number of the atoms in the cluster. The dependence of ΔG on l is similar to that shown in Fig. 2.2. It displays a maximum at a critical edge length

$$l^* = \frac{2\varkappa s_c}{\Delta\mu - s_c(\sigma + \sigma_i - \sigma_s)}. \tag{2.34}$$

Then the work of formation of a critical 2D nucleus is

$$\Delta G_2^* = \frac{4\varkappa^2 s_c}{\Delta\mu - s_c(\sigma + \sigma_i - \sigma_s)}. \tag{2.35}$$

Substituting $\Delta\mu$ from the Thomson–Gibbs Equation (2.34) into (2.35), one obtains $\Delta G_2^* = 2l^*\varkappa$, which is identical to (2.32). The latter can be easily obtained following the procedure applied for the 3D case.

Without going into details and following the same procedure as above, one can treat the problem of formation of elastically strained 2D nuclei. For the corresponding work of formation, one obtains (Markov *et al.*, 1978)

$$\Delta G_{e2}^* = \frac{(\psi - \varepsilon)^2}{(\Delta\mu - 2\varepsilon) - (\psi - \psi')}$$

or

$$\Delta G_{e2}^* = \frac{4\varkappa_e^2 s_c}{(\Delta\mu - 2\varepsilon) - s_c(\sigma + \sigma_i - \sigma_s)}, \tag{2.36}$$

where now the specific edge energy $\varkappa_e = (\psi - \varepsilon)/2a$ accounts for the elastic strain and $s_c = a^2$ is the area occupied by a surface atom.

In the case of nucleation on the surface of the same crystal ($\varepsilon = 0$, $\sigma_i = 0$, $\sigma_s = \sigma$ and $\sigma + \sigma_i - \sigma_s = 0$),

$$l^* = \frac{2\varkappa s_c}{\Delta\mu} \tag{2.37}$$

and

$$\Delta G_2^* = \frac{4\varkappa^2 s_c}{\Delta\mu}. \tag{2.38}$$

The number of atoms in the critical nucleus is given by $n^* = l^{*2}/s_c$. Substituting l^* from (2.37) and the result into (2.38) yields

$$\Delta G_2^* = n^* \Delta\mu, \tag{2.39}$$

which is the 2D analog of Eq. (2.20). As will be shown in the following, Eqs. (2.20) and (2.39) can be used to determine the limits of applicability of the classical nucleation theory.

Equations (2.35), (2.36), and (2.38) are valid for polygonized square nuclei without rounded regions at finite temperatures as required by Herring's formula, i.e., when the steps, which appeared as a result of the nucleus formation, are straight. If the steps are roughened to some extent below the roughening temperature T_r, the equilibrium shape will be more or less circular, and instead of Eqs. (2.37) and (2.38), we have

$$r^* = \frac{\varkappa s_c}{\Delta\mu} \tag{2.40}$$

and

$$\Delta G_2^* = \frac{\pi\varkappa^2 s_c}{\Delta\mu}, \tag{2.41}$$

where r^* is the radius of the critical nucleus. Note that in this case $\varkappa$ will have a value different (smaller) than that in Eq. (2.38), which is valid for straight steps without kinks. For more details concerning the formation of 2D nuclei, the reader is referred to the work of Burton, Cabrera and Frank (1951).

In some cases of technological importance as the growth of Si single crystals, the shape of the 2D islands is not isometric but rectangular. As shown in Chapter 3, Sec. 3.3.2, the surface of Si(0 0 1) is reconstructed in such a way that parallel rows of dimers are

formed which rotate by 90° on every next terrace. This is the reason two different kinds of steps, one straight S_A and the other rough S_B, alternate on a vicinal surface which is tilted by a small degree with respect to Si(0 0 1) (see Fig. 3.46). For the same reason, a 2D island on a terrace will be enclosed by two S_A and two S_B steps. The edge energy of the S_A steps is about 10 times smaller than that of the S_B steps (Chadi 1987); from what follows that the equilibrium shape of such an island will be rectangular rather than quadratic with an aspect ratio $\alpha \approx 0.1$. We can easily convince ourselves that the work of formation of such rectangular nuclei is given by the same expression (2.38) in which the geometric coefficient 4 is replaced by a function $(1+\alpha)^2/\alpha$ of the aspect ratio. It follows that the more elongated nucleus requires larger work of formation. It is easy to show that Eq. (2.39) is valid in this case also.

2.1.5 *Mode of nucleation on a foreign substrate*

We discuss in this section the question as to which mode of nucleation, 2D or 3D, is thermodynamically preferred as a function of the supersaturation depending on the difference of the cohesion and adhesion energies $\Delta\sigma = \sigma + \sigma_i - \sigma_s = 2\sigma - \beta = (\psi - \psi')/b^2$, on one hand, and the strain energy ε, on the other.

Let us consider first the case of $\Delta\sigma < 0$, i.e., when the attractive forces exerted by the substrate on the deposit atoms are stronger than the forces between the deposit atoms. As follows from the above considerations, 3D nucleation is thermodynamically prohibited ($\Delta G_3^* = 0$) and only 2D nuclei can be formed. Under this condition, the quantity in the denominator of Eq. (2.35) is positive and ΔG_2^* has a finite value at $\Delta\mu = 0$ and even at undersaturation $\Delta\mu < 0$. Thus, in this case (Fig. 2.9), 2D nuclei of at least the first monolayer can be formed in an undersaturated system, an idea introduced in the theory of the epitaxial crystal growth by Stranski and Krastanov (1938). Obviously, ΔG_2^* tends to infinity at an undersaturation $-\Delta\mu = s_c\Delta\sigma$, which determines the equilibrium vapor pressure of an adlayer under stronger forces across the interface.

We have practically the same case when $\Delta\sigma = 0$. In fact, this condition means that the 2D nuclei are formed on the surface of the

Figure 2.9: Dependence of the Gibbs free energies of formation of 2D and 3D nuclei on the supersaturation for different values of the surface energy change $\Delta\sigma = \sigma + \sigma_i - \sigma_s = (\psi - \psi')/b^2$. 2D nucleation is only possible at complete wetting $\Delta\sigma < 0$ or $\Delta\sigma = 0$. In the case of $\Delta\sigma < 0$, 2D nucleation can take place even at undersaturation as discussed in Chapter 1, whereas at $\Delta\sigma = 0$, 2D nucleation always requires supersaturation. In the case of incomplete wetting, $\Delta\sigma > 0$, 2D and 3D nucleation can occur, 3D nucleation being always more probable than 2D nucleation. 2D nucleation occurs at supersaturations higher than some value $\Delta\mu_0 = s_c\Delta\sigma = \psi - \psi'$ determined by the difference in bonding. At a critical supersaturation $\Delta\mu_{\rm cr} = 2\Delta\mu_0$, the 3D nucleus transforms into 2D nucleus (Fig. 2.10) and 3D nucleation is no longer possible. This is the reason why the corresponding curves for ΔG_3 are given by dashed lines at $\Delta\mu > \Delta\mu_{\rm cr}$. In this interval, only 2D nucleation is possible. The critical supersaturations $\Delta\mu_0^e$ and $\Delta\mu_{\rm cr}^e$ for formation of strained nuclei are shifted to greater values by the strain energy per atom $n\varepsilon$(the straight dashed lines).

same crystal, only in this case σ_i is precisely equal to zero and $\sigma = \sigma_s$. 3D nucleation is again prohibited (the wetting is complete) and 2D nuclei can be formed only in a supersaturated system $\Delta\mu > 0$.

The case of the positive surface energy change, $\Delta\sigma > 0$, offers greater variety — 3D nuclei can be formed as well in addition to 2D nuclei. We consider first the case when the strain energy $\varepsilon = 0$. 3D nuclei can be formed only in a supersaturated system $\Delta\mu > 0$, and

Figure 2.10: Transformation of a 3D into a 2D nucleus with increasing supersaturation assuming the equilibrium shape $h/l = \Delta\sigma/2\sigma$ is preserved (after Toschev, Paunov and Kaischew 1968).

ΔG_3^* decreases with the square of the supersaturation (Eq. 2.16). 2D nuclei, however, can be formed at positive supersaturations higher than a critical one:

$$\Delta\mu_0 = s_c(\sigma + \sigma_i - \sigma_s), \tag{2.42}$$

which determines the equilibrium vapor pressure (or solubility) of the adlayer.

Beyond this value, ΔG_2^* decreases with the supersaturation, and at some critical supersaturation,

$$\Delta\mu_{\mathrm{cr}} = 2s_c(\sigma + \sigma_i - \sigma_s) = 2\Delta\mu_0 \tag{2.43}$$

becomes equal to ΔG_3^*. Obviously, the condition $\Delta G_2^* = \Delta G_3^*$ means that the height of the 3D nucleus becomes equal to that of one monolayer or, in other words, the 3D nuclei turn into 2D ones (Fig. 2.10). This is easy to understand bearing in mind the assumption made in the beginning of this section that the nuclei retain the equilibrium shape. Therefore, when the supersaturation increases, the 3D nuclei preserve their height-to-width ratio h/l and, as a result, they turn into 2D nuclei at $\Delta\mu_c$ (Lacmann 1961; Toschev, Paunov and Kaischew 1968).

In the same way, one can consider the case of elastically strained ($\varepsilon \neq 0$) 2D and 3D nuclei. 3D nuclei can be formed at supersaturations $\Delta\mu$ higher than the strain energy per atom, $n\varepsilon$, where n is the number of lateral bonds per atom in the nucleus ($n = 2$ and $n = 3$ for the square and hexagonal meshes of the substrate surface,

respectively). 2D nuclei can be formed at supersaturations higher than

$$\Delta\mu_0^e = n\varepsilon + s_c(\sigma + \sigma_i - \sigma_s). \tag{2.44}$$

The critical supersaturation $\Delta\mu_{\rm cr}^e$ at which the 3D nuclei turn into 2D nuclei is shifted by $n\varepsilon$ with respect to $\Delta\mu_{\rm cr}$ and reads

$$\Delta\mu_{\rm cr}^e = n\varepsilon + 2s_c(\sigma + \sigma_i - \sigma_s) = \Delta\mu_{\rm cr} + n\varepsilon. \tag{2.45}$$

It follows that at supersaturations in the interval $\Delta\mu_0$ to $\Delta\mu_{\rm cr}$ or, correspondingly, $\Delta\mu_0^e$ to $\Delta\mu_{\rm cr}^e$, 3D nucleation is thermodynamically favored, although 2D nucleation is, in principle, also possible. Beyond $\Delta\mu_{\rm cr}$ respectively, $\Delta\mu_{\rm cr}^e$, only 2D nucleation is possible.

Rearranging (2.45) gives the following criterion for the mode of nucleation on a foreign substrate (Markov and Kaischew 1976a, 1976b). 3D nucleation is energetically favored when

$$\sigma_s < \sigma + \sigma_i - \frac{\Delta\mu - n\varepsilon}{2s_c}. \tag{2.46}$$

2D nucleation will take place when

$$\sigma_s \geq \sigma + \sigma_i - \frac{\Delta\mu - n\varepsilon}{2s_c}. \tag{2.47}$$

The above criterion can be easily generalized for crystals with other lattices and orientations (Markov and Kaischew 1976a, 1976b).

We can rewrite Eqs. (2.46) and (2.47) in the form

$$\sigma_s \lesseqgtr \sigma + \sigma_i^* - \frac{\Delta\mu}{2s_c}, \tag{2.48}$$

where $\sigma_i^* = \sigma_i + n\varepsilon/2s_c$ is the specific energy of the interface accounting not only for the different interaction energies but also for the homogeneous strains at the interface (for more detail, see Chapter 4).

One concludes that the mode of nucleation in one and the same system can be varied by changing the supersaturation. Thus, at high enough supersaturations, 2D nucleation is only possible from the point of view of the classical thermodynamics, whereas at lower supersaturations the 3D nucleation prevails.

2.2 Rate of Nucleation

In this chapter, the classical (capillary) theory of nucleation will be considered first, treating consecutively the cases of homogeneous and heterogeneous nucleation and the formation of 3D and 2D nuclei in the latter case. Then, we will treat in some detail the atomistic theory of heterogeneous nucleation which plays an important role in deposition of thin films at high supersaturations. At the end of this chapter, the nonsteady state effects in nucleation as well as the saturation of the nucleus density will be briefly considered. Ostwald's step rule when nuclei of thermodynamically less stable phase are initially formed will be briefly discussed.

2.2.1 *General formulation*

As mentioned at the beginning of the previous section, the nuclei of the new phase appear in the bulk of the ambient one as heterophase fluctuations of the density, i.e., the nucleation is a random process. The number of nuclei formed in a fixed interval of time is a random quantity and is subject to statistical laws (Toschev 1973). The average values, however, can be calculated and are subject to the kinetic theory of nucleation. Thus, the aim of this chapter is the calculation of the rate of nucleation or, in other words, the average number of nuclei formed per unit time and volume (or unit area of the substrate in the heterogeneous case) of the ambient phase.

We will follow the approach of developed by Becker and Döring (1935). In fact, the first treatment of the problem was given by Volmer and Weber (1926). The latter was further elaborated by Farkas (1927), Stranski and Kaischew (1934), Frenkel (1939), Zeldovich (1942) (for a review, see Christian 1981).

We treat first the rate of formation of liquid droplets in vapors. We consider a vessel with a volume V containing supersaturated vapor with pressure P and temperature T. The following simplifying assumptions are adopted:

1. The growing clusters preserve a constant geometrical shape (spherical in the particular case) which coincides with the

equilibrium one. As mentioned in the previous chapter, it ensures minimal free energy.

2. Clusters consisting of N atoms (N being greater enough than the critical number n^*) are removed from the system and replaced by an equivalent number of single atoms, thus ensuring a constant supersaturation in the system.
3. The nucleation process is considered as a series of consecutive bimolecular reactions (a scheme proposed by Leo Szillard) (see Benson 1960)

$$\mathcal{A}_1 + \mathcal{A}_1 \underset{\omega_2^-}{\overset{\omega_1^+}{\rightleftarrows}} \mathcal{A}_2$$

$$\mathcal{A}_2 + \mathcal{A}_1 \underset{\omega_3^-}{\overset{\omega_2^+}{\rightleftarrows}} \mathcal{A}_3$$

$$\cdots$$

$$\mathcal{A}_n + \mathcal{A}_1 \underset{\omega_{\mathrm{n+1}}^-}{\overset{\omega_n^+}{\rightleftarrows}} \mathcal{A}_{n+1}$$

$$\cdots$$

in which the growth and the decay of the clusters take place by the attachment and detachment of single atoms. Triple and multiple collisions are ruled out as less probable. ω_n^+ and ω_n^- denote the rate constants of the direct and the reverse reactions, respectively. Here, $\mathcal{A}$ is used as a chemical symbol.

Clusters consisting of n atoms (to be called clusters of class n) are formed by the growth of clusters of class $n-1$ and the decay of clusters of class $n+1$ (birth processes) and disappear by the growth and decay into clusters of classes $n+1$ and $n-1$ (death processes), respectively. Then, the change of the concentration $Z_n(t)$ of clusters of class n with time is given by (Zeldovich 1942)

$$\frac{dZ_n(t)}{dt} = \omega_{n-1}^+ Z_{n-1}(t) - \omega_n^- Z_n(t) - \omega_n^+ Z_n(t) + \omega_{n+1}^- Z_{n+1}(t). \tag{2.49}$$

Introducing the net flux of clusters through the size n,

$$J_n(t) = \omega_{n-1}^+ Z_{n-1}(t) - \omega_n^- Z_n(t), \tag{2.50}$$

turns Eq. (2.49) into

$$\frac{dZ_n(t)}{dt} = J_n(t) - J_{n+1}(t). \tag{2.51}$$

In the steady state $dZ_n(t)/dt = 0$ and

$$J_n(t) = J_{n+1}(t) = J_0, \tag{2.52}$$

where we denote by J_0 the steady state rate or the frequency of formation of clusters of any class which obviously does not depend on the cluster size n. Hence, J_0 is also equal to the rate of formation of the clusters with the critical size n^*. In other words, in the steady state

$$\begin{aligned} J_0 &= \omega_1^+ Z_1 - \omega_2^- Z_2, \\ J_0 &= \omega_2^+ Z_2 - \omega_3^- Z_3, \\ &\ldots \\ J_0 &= \omega_n^+ Z_n - \omega_{n+1}^- Z_{n+1}, \\ &\ldots \\ J_0 &= \omega_{s-1}^+ Z_{n-1}, \end{aligned} \tag{2.52$'$}$$

where $Z_N = 0$ as accepted at point 2.

Following Becker and Döring, we multiply each equation by a ratio of the rate constants. The first equation is multiplied by $1/\omega_1^+$, the second by $\omega_2^-/\omega_1^+\omega_2^+$, the nth by $\omega_2^-\omega_3^- \ldots \omega_n^-/\omega_1^+\omega_2^+ \ldots \omega_n^+$, etc. Then we sum up the equations and obtain after rearrangement (Becker and Döring 1935)

$$J_0 = Z_1 \left[\sum_{n=1}^{N-1} \left(\frac{1}{\omega_n^+} \frac{\omega_2^- \omega_3^- \ldots \omega_n^-}{\omega_1^+ \omega_2^+ \ldots \omega_{n-1}^+} \right) \right]^{-1}. \tag{2.53}$$

This is the general expression for the steady state rate of nucleation. It is applicable to any case of nucleation (homogeneous or heterogeneous, 3D or 2D, or even one-dimensional (1D)) taking the appropriate expressions for the rate constants ω_n^+ and ω_n^-. Moreover, it allows the derivation of equations for the classical as well as the

atomistic nucleation rate at small and high supersaturations as limiting cases. We will consider in more detail the classical (capillary) theory of homogeneous nucleation. The corresponding equations for the heterogeneous formation of 2D and 3D nuclei will be then written down by analogy without derivation. Finally, the atomistic theory of nucleation will be treated on the base of Eq. (2.53). The 1D nucleation which takes place when smooth single height steps propagate will be considered in Chapter 3.

2.2.2 *The equilibrium state*

Before going further, it is instructive to consider the equilibrium state. In an undersaturated system, the equilibrium state gives the equilibrium distribution of the homophase density fluctuations (Frenkel 1955). In a supersaturated system, the equilibrium state can be realized near enough to the phase equilibrium. Obviously, the latter will be a metastable equilibrium and will give the equilibrium distribution of the heterophase fluctuations. Far from the line of the phase equilibrium ($\mu_\alpha = \mu_\beta$), an equilibrium state cannot be realized. However, we can write an expression even in this case which will serve as a convenient reference.

Under the condition $J_0 = 0$, from (2.50) follows

$$\omega_{n-1}^{+} N_{n-1} = \omega_n^{-} N_n, \tag{2.54}$$

where N_n denote now the equilibrium concentrations of clusters of class n in the absence of molecular flux in the system.

Equation (2.54) is known as the equation of the *detailed balance* (Zeldovich 1942). It can be rewritten in the form

$$\frac{N_n}{N_{n-1}} = \frac{\omega_{n-1}^{+}}{\omega_n^{-}}.$$

Multiplying the ratios N_n/N_{n-1} from $n = 2$ to n gives

$$\frac{N_n}{N_1} = \prod_{i=2}^{n} \left(\frac{\omega_{i-1}^{+}}{\omega_i^{-}} \right) = \left(\frac{\omega_2^{-} \omega_3^{-} \ldots \omega_n^{-}}{\omega_1^{+} \omega_2^{+} \ldots \omega_{n-1}^{+}} \right)^{-1}. \tag{2.55}$$

As seen, the rate constant ratio on the right-hand side appears in the expressions for both the equilibrium concentration of clusters N_n of class n and the steady-state rate of nucleation (2.53). Obviously, the problem is reduced to finding expressions for the rate constants ω_n^+ and ω_n^-. We will do that for the simplest case of homogeneous formation of liquid nuclei in supersaturated vapors adopting the idea of Gibbs that the nuclei represent small liquid droplets.

The rate constant of the growth reactions ω_n^+ is given by the number of collisions of atoms from the vapor phase on the surface of the droplets. Then for the rate constant of growth of a cluster of class $n-1$ to form cluster of class n, we have

$$\omega_{n-1}^+ = \frac{P}{(2\pi mkT)^{1/2}} \Sigma_{n-1}, \tag{2.56}$$

where $P/(2\pi mkT)^{1/2}$ is the number of collisions per unit area, P is the vapor pressure available in the system, and Σ_{n-1} is the surface area of a cluster of class $n-1$.

The rate constant of the reverse reaction of decay of a cluster of class n to form a cluster of class $n-1$ can be evaluated as follows (Volmer 1939). In equilibrium with the vapor phase, the number of atoms leaving the cluster in a fixed interval of time is equal to the number of atoms arriving at its surface. Hence, the flux of atoms leaving the cluster is equal to the equilibrium flux of atoms arriving at its surface. On the other hand, condensation takes place when the center of mass of the molecule joining the droplet crosses the sphere of action of the interatomic forces (Fig. 2.11). The radius of the droplet increases just after that event. The evaporation of a molecule is the reverse process. When it leaves the droplet, its center of mass should cross the same sphere of action and, at that moment, the droplet shrinks and its surface area becomes equal to Σ_{n-1}. This area namely should be taken into account when considering the rate constant of the reverse reaction and

$$\omega_n^- = \frac{P_n}{(2\pi mkT)^{1/2}} \Sigma_{n-1}, \tag{2.57}$$

where P_n is the equilibrium vapor pressure of cluster of class n.

Figure 2.11: For the determination of the surface area of a liquid droplet containing n molecules upon detachment of a single molecule shown by the small circle. The molecule leaves the droplet when its center of mass crosses the surface of action of the intermolecular forces given by the dashed circle. Precisely at that moment, the surface area of the droplet is Σ_{n-1} as given by the solid circle (after Volmer 1939).

The pressures P and P_n can be expressed through the Thomson–Gibbs equation

$$kT \ln \frac{P}{P_\infty} = \frac{2\sigma v_l}{r^*}$$

and

$$kT \ln \frac{P_n}{P_\infty} = \frac{2\sigma v_l}{r_n},$$

where r_n is the radius of a droplet consisting of n molecules. Then,

$$\frac{\omega_n^-}{\omega_{n-1}^+} = \frac{P_n}{P} = \exp\left[\frac{2\sigma v_l}{kT}\left(\frac{1}{r_n} - \frac{1}{r^*}\right)\right].$$

We replace then the radii r_n and r^* by the number of atoms through $nv_l = 4\pi r^3/3$ and for every term in (2.55) (and also in the sum of (2.53)), one obtains

$$\frac{\omega_2^-\omega_3^-\ldots\omega_n^-}{\omega_1^+\omega_2^+\ldots\omega_{n-1}^+} = \exp\left[\frac{2\sigma}{kT}\left(\frac{4\pi v_l^2}{3}\right)^{1/3}\sum_1^n\left(\frac{1}{n^{1/3}} - \frac{1}{n^{*1/3}}\right)\right].$$

Assuming $n^* \gg 1$ (the capillary approximation), we replace the sum by an integral and carrying out the integration yields

$$\frac{\omega_2^-\omega_3^-\ldots\omega_n^-}{\omega_1^+\omega_2^+\ldots\omega_{n-1}^+} = \exp\left\{\frac{\sigma}{kT}\left(\frac{4\pi v_l^2 n^{*2}}{3}\right)^{1/3}\left[3\left(\frac{n}{n^*}\right)^{2/3} - 2\left(\frac{n}{n^*}\right)\right]\right\}.$$

A comparison of the above equation with Eqs. (2.8) and (2.6) shows immediately that the expression in the curly brackets on the right-hand side is simply the function $\Delta G(n)/kT$. Hence,

$$\frac{\omega_2^- \omega_3^- \ldots \omega_n^-}{\omega_1^+ \omega_2^+ \ldots \omega_{n-1}^+} = \exp\left(\frac{\Delta G(n)}{kT}\right) \tag{2.58}$$

or

$$\frac{\omega_2^- \omega_3^- \ldots \omega_n^-}{\omega_1^+ \omega_2^+ \ldots \omega_{n-1}^+} = \exp\left\{\frac{\Delta G^*}{kT}\left[3\left(\frac{n}{n^*}\right)^{2/3} - 2\left(\frac{n}{n^*}\right)\right]\right\}, \tag{2.58$'$}$$

i.e., every term in the sum in the denominator of (2.53) represents one point of the dependence $\exp[\Delta G(n)/kT]$.

Substituting (2.58) into (2.55) gives, for the equilibrium concentration of clusters of class n,

$$N_n = N_1 \exp\left(-\frac{\Delta G(n)}{kT}\right). \tag{2.59}$$

The reader can find a more rigorous derivation of (2.59) in the monograph of Frenkel (1955) (see also Toschev 1973).

2.2.3 *Steady-state nucleation rate*

Replacing the sum in the denominator of Eq.(2.53) by an integral gives

$$\sum_{n=1}^{n-1}\left(\frac{1}{\omega_n^+}\frac{\omega_2^- \omega_3^- \ldots \omega_n^-}{\omega_1^+ \omega_2^+ \ldots \omega_{n-1}^+}\right) \cong \int_1^N \frac{1}{\omega_n^+}\exp\left\{\frac{\Delta G^*}{kT}\left[3\left(\frac{n}{n^*}\right)^{2/3} - 2\left(\frac{n}{n^*}\right)\right]\right\} dn.$$

The function in the exponential on the right-hand side displays a maximum at $n = n^*$ (Fig. 2.2) and can be expanded in the Taylor series in the vicinity of the maximum

$$\Delta G(n) = \Delta G^*\left[3\left(\frac{n}{n^*}\right)^{2/3} - 2\left(\frac{n}{n^*}\right)\right] \cong \Delta G^*\left(1 - \frac{1}{3n^{*2}}(n-n^*)^2\right) \tag{2.60}$$

Figure 2.12: Dependence of the Gibbs free energy change $\Delta G(n)/kT$ (dashed line), $\exp[\Delta G(n)/kT]$ and the reciprocal of the rate constant of the forward reaction on the cluster size. As seen, $\exp[\Delta G(n)/kT]$ displays a sharp maximum and its width is confined in the near vicinity of the critical size. The reciprocal of the rate constant $1/\omega_n^+$ is a weak function of n and can be taken as a constant at the critical size.

Then, the sum attains the form

$$\exp\left(\frac{\Delta G^*}{kT}\right)\int_1^N \frac{1}{\omega_n^+}\exp\left(-\frac{\Delta G^*}{kT}\frac{1}{3n^{*2}}(n-n^*)^2\right)dn.$$

In order to carry out the integration, we make the following approximations. As shown in Fig. 2.12, the exponential under the integral displays a sharp maximum in the vicinity of n^* and the limits of integration can be extended to $-\infty$ and $+\infty$ without making a significant error. Second, the rate constant ω_n^+ is not a sensitive function of n and can be replaced by $\omega_{n^*}^+ \equiv \omega^* =$ const. and then taken out before the integral.

Finally, carrying out the integration from minus infinity to plus infinity, one obtains for the steady-state nucleation rate

$$J_0 = \omega^* \Gamma Z_1 \exp\left(-\frac{\Delta G^*}{kT}\right), \tag{2.61}$$

where Z_1 is the steady-state concentration of single molecules in the vapor phase and ω^* is the frequency of the attachment of molecules to the critical nucleus.

The parameter Γ in expression (2.61) for the steady-state nucleation rate

$$\Gamma = \left(\frac{\Delta G^*}{3\pi kTn^{*2}}\right)^{1/2} \tag{2.62}$$

is known in the literature as a factor of Zeldovich (1942) (see also Frenkel 1955). In fact, it was derived for the first time by Farkas (1927). Its physical meaning can be revealed if one inspects more closely the definition of the steady-state nucleation rate (2.53). Zeldovich (1942) argued that the steady-state distribution function Z_n deviates perceptibly from the equilibrium one, N_n, only in the vicinity of the critical size n^*. In other words, the processes taking place in an interval $\Delta n^* = n_r - n_l$ (Fig. 2.13) around the critical size determine the overall rate of nucleation. In this interval, the clusters perform Brownian motion in the space of the size n and part of the clusters can dissolve back into the mother phase. According to Zeldovich, the width of this interval is determined by the condition that the free-energy change $\Delta G(n)$ varies by kT around the maximum, (at $n \leq n_l, Z_n \cong N_n$ and at $n \geq n_r = N$, $Z_n = 0$), i.e.,

$$\Delta G^* - \Delta G(n = n_l, n_r) = kT.$$

Bearing in mind (2.60), it follows that the width of the interval Δn^* reads

$$\Delta n^* = 2\left(\frac{3kTn^{*2}}{\Delta G^*}\right)^{1/2} = \frac{2}{\Gamma\sqrt{\pi}}. \tag{2.63}$$

In other words, the factor of Zeldovich is simply a reciprocal of Δn^* and, thus, accounts for the deviation of the system from the equilibrium state. A more rigorous treatment of this problem is given by Kashchiev (1969).

Figure 2.13: For the determination of the interval $\Delta n^* = n_r - n_l$ around the critical size. According to Zeldovich (1942), the processes which takes place in this interval determine the overall rate of nucleation. The width of the interval is in fact the reciprocal to the nonequilibrium Zeldovich factor Γ.

Bearing in mind Eqs. (2.4) and (2.5), it turns out that Γ is directly proportional to the square of the supersaturation $\Gamma = \Delta\mu^2/8\pi v_l(\sigma^3 kT)^{1/2}$. In other words, $\Gamma = 0$ at the phase equilibrium ($\Delta\mu = 0$) and increases steeply when deviating from it. In the case of water condensation from the vapor ($\sigma = 70$ erg cm^{-2}) in the range of P/P_∞ from 2 to 6, n^* varies from 470 to 30 and correspondingly Γ increases from 0.004 to 0.054 (Toschev 1973). Thus, the Zeldovich factor is usually of the order of 1×10^{-2} in the case of homogeneous nucleation.

The steady-state rate of nucleation (2.61) can be rewritten in the form ($Z_1 \cong N_1$)

$$J_0 = \omega^* \Gamma N^*, \tag{2.64}$$

i.e., it is a product of the equilibrium concentration of critical nuclei,

$$N^* = N_1 \exp\left(-\frac{\Delta G^*}{kT}\right), \tag{2.65}$$

the Zeldovich factor Γ, and the frequency of attachment of building units to the critical nucleus ω^*. It can be easily proved that this is a

general expression valid for all possible cases of nucleation and can be used in any particular case.

2.2.4 *Nucleation of liquids from vapors*

In this particular case, the surface of the nucleus is given by $4\pi r^{*2}$ and

$$\omega^* = P(2\pi mkT)^{-1/2} 4\pi r^{*2}. \tag{2.66}$$

Then

$$J_0 = \frac{P}{\sqrt{2\pi mkT}} 4\pi r^{*2} \frac{\Delta\mu^2}{8\pi v_l \sigma \sqrt{\sigma kT}} \frac{P}{kT} \exp\left(-\frac{16\pi\sigma^3 v_l^2}{3kT\Delta\mu^2}\right), \tag{2.67}$$

where $P/kT = N_1$ assuming the vapor phase behaves as an ideal gas. Recalling the Thomson–Gibbs Equation (2.4) for the critical radius, Eq. (2.67) turns into

$$J_0 = \left(\frac{P}{kT}\right)^2 \frac{2\sigma^{1/2} v_l}{\sqrt{2\pi m}} \exp\left(-\frac{16\pi\sigma^3 v_l^2}{3(kT)^3[\ln(P/P\infty)]^2}\right). \tag{2.68}$$

A closer inspection of Eq. (2.68) shows that the pre-exponential $K_1 = \omega^* \Gamma Z_1$ is not very sensitive to the supersaturation in comparison with $\exp[-\Delta G^*/kT] = \exp[-K_2/\Delta\mu^2]$. Therefore, one can accept that K_1 is approximately a constant, i.e.,

$$J_0 = K_1 \exp\left(-\frac{K_2}{\Delta\mu^2}\right), \tag{2.69}$$

where $K_2 = 16\pi\sigma^3 v_l^2/3kT$. With typical values of the quantities involved, one finds that K_1 is of order of 1×10^{25} cm^{-3}s^{-1}.

Equation (2.69) is demonstrated in Fig. 2.14. As seen, there exists a critical supersaturation $\Delta\mu_c$ below which the nucleation rate is practically equal to zero and increases steeply beyond it. The critical supersaturation can be determined by the condition $J_0 = 1$ cm^{-3}s^{-1}. After taking the logarithm of J_0 in (2.69), we find

$$\Delta\mu_c = \left(\frac{K_2}{\ln K_1}\right)^{1/2}. \tag{2.70}$$

Figure 2.14: Plot of the nucleation rate vs the supersaturation. The nucleation rate is practically equal to zero up to a critical supersaturation $\Delta\mu_c$. Beyond this value the rate of nucleation increases sharply by many orders of magnitude. This is the reason why the nucleation rate can be measured in a very narrow interval of supersaturations.

In the case of nucleation in water vapors at a temperature $T = 275$ K, $K_1 \cong 1 \times 10^{25}$ cm^{-3}s^{-1}, $\sigma = 75.2$ erg cm^2, $v_l = 3 \times 10^{-23}$ cm^3, $\Delta\mu_c = 5.42 \times 10^{-14}$ erg or $P_c/P_\infty = 4.16$ which is in excellent agreement with the value 4.21 experimentally found by Volmer and Flood (Volmer 1939).

The existence of critical supersaturation leads to the conclusion that the condensation of vapors will be experimentally observed only at $P > P_c$. In the opposite case, the vapors will be in a metastable state, i.e., due to kinetic reasons no condensation will take place for the time of the experiment. Thus, we identify the critical supersaturation with the *limit of metastability* of the ambient phase. Recalling the phase diagram (Fig. 1.1) of a single-component system, the existence of such a limit of metastability means that observable phase transitions will not occur when the lines of the phase equilibrium (determined by the equality of the chemical potentials) are crossed. For this purpose, the limits of metastability should be crossed and they lie to the left of the phase equilibrium lines. It should be pointed

out that the metastability limits are very sensitive to the values of the specific surface energies of the corresponding phase boundaries. In general, the metastability limits will be smaller for the liquid–crystal transition than for the vapor–liquid transition due to the smaller surface energy between condensed phases. The presence of impurity particles, ions, or foreign substrates will reduce the metastability limit with the square root of the wetting function. Besides, the presence of surfactants (substances which once adsorbed at the phase boundaries change drastically the surface energies) will also reduce the values of the specific surface energies and in turn the metastability limit.

2.2.5 *Statistical contributions*

Later theoretical studies showed, however, that the above agreement between theory and experiment is apparent. Lothe and Pound (1962) (see also Dunning 1969) noted that the Gibbs free energy of formation of liquid nuclei as given by Eq. (2.3) is valid for the state of rest. As discussed by Christian (1981), it gives, in fact, the free energy of formation of a liquid droplet confined in a liquid rather than a vapor. When formed in a vapor phase, the droplet must acquire the gas-like translational and rotational degrees of freedom and must loose six internal or liquid-like degrees of freedom. Then, instead of (2.3), one should write

$$\Delta G(r) = -\frac{4}{3}\frac{\pi r^3}{v_l}\Delta\mu + 4\pi r^2\sigma + \Delta G_{\mathrm{tr}} + \Delta G_{\mathrm{rot}} + \Delta G_{\mathrm{rep}},$$

where ΔG_{tr} and ΔG_{rot} must be negative and ΔG_{rep} positive.

The corresponding expressions, respectively, are (Lothe and Pound 1962)

$$\Delta G_{\mathrm{tr}} = -kT\ln\left(\frac{(2\pi n^* mkT)^{3/2}kT}{Ph^3}\right),$$

$$\Delta G_{\mathrm{rot}} = -kT\ln\left(\frac{(2kT)^{3/2}(\pi I^3)^{1/2}}{\hbar^3}\right)$$

and

$$\Delta G_{\mathrm{rep}} = \frac{1}{2}kT\ln(2\pi n^*) + Ts,$$

where $I \cong 2n^* m r^{*2}$ is the moment of inertia of the nucleus, s is the entropy of the liquid, h is the Plank's constant and $\hbar = h/2\pi$. Then, for water at $T = 300$ K, $n^* = 100$, $I = 8.6 \times 10^{-36}$ g cm^2, $P = 0.075$ atm, $m = 3 \times 10^{-23}$ g and $s = 70$ J K^{-1} mol^{-1}, $\Delta G_{\mathrm{tr}} = -24.4\ kT$, $\Delta G_{\mathrm{rot}} = -20.6\ kT$ and $\Delta G_{\mathrm{rep}} = 11.5\ kT$. As these terms for the free energy depend very weakly on the nucleus size, they contribute primarily to the pre-exponential with a total of 1×10^{17}. Then for the critical supersaturation, one obtains $P_c/P_\infty = 3.09$ in marked disagreement with the experimentally found value of 4.21. The interested reader can find more information in Feder *et al.* (1966), Lothe and Pound (1969), Reiss (1977), Nishioka and Pound (1977), Kikuchi (1977), and Christian (1981).

2.2.6 *Nucleation from solutions and melts*

In the case of solutions, the flux of building units to the critical nuclei is determined by diffusion in the bulk of the solution. On the other hand, the molecules of the solute should break the bonds with the molecules of the solvent before being attached to the nucleus. In other words, an energy barrier for desolvation should be overcome. The frequency ω^* of attachment of molecules to the critical nucleus will be proportional to the concentration of the solute C and, thus, instead of (2.66), we have

$$\omega^* = 4\pi r^{*2} C \nu \lambda \exp(-\Delta U/kT), \tag{2.71}$$

where ν is a frequency factor, ΔU is the energy of desolvation, and λ is the mean free path of particles in the liquid which is equal approximately to the atomic diameter. Then for the nucleation rate, one obtains (Walton A G 1969)

$$J_0 = 4\pi r^{*2} C^2 \nu \lambda \exp(-\Delta U/kT) \Gamma \exp[-\Delta G^*/kT], \tag{2.72}$$

in which the concentration C is expressed in the number of molecules per unit volume and the supersaturation is expressed by (1.10).

The main problem in the estimation of the pre-exponential is the lack of knowledge concerning the value of ΔU. We may assume that it is of the order of the molecular interactions, i.e., 10–20 kcal mol^{-1}.

Measurements of the critical supersaturation in the nucleation of a series of salts in aqueous solutions (Nielsen 1967; Walton 1967) gave reasonable values for the specific surface energies of the crystal–solution interface ($\cong$100 erg cm^{-2}) and for the pre-exponential factors ($\cong 10^{24}-10^{25}$ cm^{-3}s^{-1}). The values of ΔU calculated from these data vary from 7 kcal mol^{-1} for $BaSO_4$ to 14.5 kcal mol^{-1} for $PbSO_4$. Laudise determined the value 20 kcal mol^{-1} for quartz in aqueous solutions of NaOH from measurements of the rate of hydrothermal growth of the (0 0 0 1) face in the temperature interval 570–660 K (Laudise 1959) (see also Laudise 1970).

Solidification of liquids does not differ too much from the crystallization in solutions. In this case, the activation energy barrier ΔU originates from the rearrangement of the molecules in the liquids when crossing the crystal–melt boundary to occupy precise positions in the crystal lattice, i.e., from the replacement of the long–range disorder in the liquid by long-range order in the crystal. That is the reason ΔU is usually identified with the activation energy for viscous flow. The latter varies from 1 to 6 kcal mol^{-1} for metals (Grosse 1963), 10 kcal mol^{-1} for organic melts to 50–150 kcal mol^{-1} in glass-forming melts (SiO_2, GeO_2) (Mackenzie 1960; Gutzow 1975; Oqui 1990). On the other hand, there are no transport difficulties in melts and the concentration C in (2.71) and (2.72) should be replaced by the number of atoms in unit volume $1/v_l$. Then,

$$\omega^* = 4\pi r^{*2}\frac{1}{v_l}\nu\lambda\exp(-\Delta U/kT) \tag{2.73}$$

and

$$J_0 = 4\pi r^{*2}\frac{\nu\lambda}{v_l^2}\exp(-\Delta U/kT)\Gamma\exp[-\Delta G^*/kT], \tag{2.74}$$

where the supersaturation is given by (1.12)

$$\Delta\mu = \Delta h_m\frac{\Delta T}{T_m} = \Delta s_m\Delta T.$$

Assuming then spherical symmetry and isotropic interfacial tension

$$\Delta G^* = \frac{16\pi\sigma^3 v_c^2 T_m^2}{3\Delta h_m^2 (\Delta T)^2}, \tag{2.75}$$

$$\Gamma = \frac{(\Delta h_m \Delta T)^2}{8\pi v_c (\sigma^3 kT)^{1/2} T_m^2} \tag{2.76}$$

and

$$r^* = \frac{2\sigma v_c T_m}{\Delta h_m \Delta T} \tag{2.77}$$

for the pre-exponential, one obtains

$$K_1 = \frac{2\sigma^{1/2} v_c}{(kT)^{1/2}} \frac{\nu\lambda}{v_l^2} \exp(-\Delta U/kT). \tag{2.78}$$

Thus, for homogeneous nucleation in metal melts, say Ag (Turnbull and Sech 1950) with $1/v_l \cong 5 \times 10^{22}$ cm^{-3}, ($v_c \cong v_l$), $T \cong 1000$ K, $\sigma \cong 150$ erg cm^{-2}, $\nu \cong 2 \times 10^{13}$ s^{-1}, $\lambda \cong 3 \times 10^{-8}$ cm, and $\Delta U/\ kT \cong 3$ the typical value 1×10^{35} for K_1 is obtained.

Considering Eq. (2.74) more closely shows that the nucleation rate depends not only on the undercooling $\Delta T = T_m - T$ but also on the absolute value of the temperature. Hence, the temperature dependence of the nucleation rate should display a maximum as the decrease of the temperature leads to an increase of the undercooling. It is easy to find by differentiation of (2.74) that $T_{\max} > T_m/3$ ($T_{\max} = T_m/3$ when $\Delta G^* \gg \Delta U$). The physical reason for this behavior of the nucleation rate in melts, which is uncharacteristic for nucleation in vapors, consists in the competition between the inhibition of the transport processes in the melt (higher viscosity) and increasing the thermodynamic driving force for nucleation to occur. At the lower temperature side of the maximum, the viscosity becomes so large that the melt glassifies before crystallization takes place. The above behavior has been established experimentally for the first time by Tamman (1933) in the case of glycerine and piperine. Typical nucleation rate vs temperature plots are shown in Fig. 2.15 for lithium disilicate melts in the interval 425–527°C (James 1974).

The main difficulty in the experimental verification of nucleation theory in melts lies in the purification of the melts to avoid the

Figure 2.15: Experimentally measured rate of nucleation in lithium disilicate melt vs temperature. The high temperature branch is determined by the activation energy for nucleus formation. The low temperature branch is determined by the transport processes in the melt. (P. F. James, *Phys. Chem. Glasses* **15**, 95 (1974). By permission of Society of Glass Technology and courtesy of P. F. James.)

heterogeneous nucleation on impurity particles. Turnbull and Sech (1950) (see also Hollomon and Turnbull 1951) measured the critical undercooling for homogeneous nucleation to take place applying the following method. The bulk melt sample was dispersed into small droplets in an inert matrix to outnumber the impurity particles. Then the maximum undercooling measured was taken as the one for the homogeneous nucleation. Their data for a series of 17 metals are compiled in Table 2.1 (Strickland-Constable 1968;

Table 2.1: Homogeneous nucleation of metals after Turnbull and Cech (1950). $\Delta T_{\max}$ is the maximum supercooling, T_m is the melting point, $\Delta T_{\max}/T_m$ is the maximum supercooling relative to the melting point, σ is the specific surface energy at the solid–liquid boundary, σ_m is the molar surface energy, and Δh_m is the molar enthalpy of melting.

Metal	$\Delta T_{\max}$	$\frac{\Delta T_{\max}}{T_m}$	σ erg cm^{-2}	σ_m cal g atom^{-1}	$\frac{\sigma_m}{\Delta h_m}$
Mercury	58	0.247	24.4	296	0.530
Gallium	76	0.250	55.9	581	0.436
Tin	105	0.208	54.5	720	0.418
Bismuth	90	0.166	54.4	825	0.330
Lead	80	0.133	33.3	479	0.386
Antimony	135	0.150	101	1430	0.302
Aluminum	130	0.140	93	932	0.364
Germanium	227	0.184	181	2120	0.348
Silver	227	0.184	126	1240	0.457
Gold	230	0.172	132	1320	0.436
Copper	236	0.174	177	1360	0.439
Manganese	308	0.206	206	1660	0.480
Nickel	319	0.185	255	1860	0.444
Cobalt	330	0.187	234	1800	0.490
Iron	295	0.164	204	1580	0.445
Palladium	332	0.182	209	1850	0.450
Platinum	370	0.181	240	2140	0.455

Toschev 1973). An updated table to include later results of Skripov *et al.* (1970), Powell and Hogan (1968), and others is given by Chernov (1984). Turnbull (1950) correlated the experimental results with (2.74) together with (2.75) and (2.76) and found that the maximum relative undercoolings $\Delta T_{\max}/T_m$ are nearly constant for all metals investigated ($\Delta T_{\max}/T_m \cong 0.183$). The same behavior shows the ratio of the gramatomic surface energy σ_m of the crystal–melt interface and the molar enthalpy of melting Δh_m. The gramatomic surface energy is defined as $\sigma_m = \sigma N_{\mathrm{A}} v_c^{2/3}$, where N_{A} is the Avogadro number (6.023×10^{23} atoms per mol) and v_c is the volume of one building unit in the crystal. It was found that for most of the

Figure 2.16: Dependence of the molar surface energy $\sigma_m = \sigma N_A v_c^{2/3}$ on the molar enthalpy of fusion Δh_m for a series of metals. As seen, for most of the metals the ratio $\sigma_m/\Delta h_m = \text{const} \approx 0.5$ (after Turnbull 1950).

metals studied, the ratio $\sigma_m/\Delta h_m \cong 0.5$. Figure 2.16 demonstrates the plot σ_m vs Δh_m. As seen, most of the metals with the exception of Ge, Bi, and Sb follow the straight line with a slope of 0.46. The above result becomes immediately clear, bearing in mind that the enthalpy of melting is connected with the separation work from half-crystal position, i.e., it is proportional to the $Z/2$ times of the energy per bond. On the other hand, $v_c^{2/3}$ represents the area occupied by such a unit. Then, σ_m is proportional to the work to separate two nearest-neighbor atoms (Stranski, Kaischew and Krastanov 1933).

Analogous results have also been obtained for nucleation in melts of alkali halides (Buckle and Ubbelohde 1960, 1961), organic melts (Thomas and Staveley 1952; Nordwall and Staveley 1954), and polymers (Koutsky 1966; Cormia, Price and Turnbull 1962). They are reviewed by Jackson (1966) and critically analyzed by Walton (1969).

2.2.7 *Rate of heterogeneous nucleation*

As mentioned in the previous section, one of the main difficulties in the experimental verification of the theory of the homogeneous nucleation is the preferred nucleation on the walls of the reaction vessels, foreign particles, ions, etc. The rate of heterogeneous nucleation should be obviously much greater than that of the homogeneous one under the same conditions due to the wetting from the substrate. At the same time when depositing a substance on a foreign substrate, the latter is never homogeneous in the sense that there are always some defect sites with a higher chemical potential such as emerging points of screw dislocations, embedded foreign atoms, and so on, which are more active in comparison with the remaining part with respect to crystal nucleation. On the other hand, in the case of vapor condensation, the frequency of attachment of adsorbed atoms through diffusion of the latter on the substrate surface to the periphery of the growing clusters is usually much greater in comparison with volume diffusion in the vapor phase (Pound, Simnad and Yang 1954; Hirth and Pound 1963). We have the opposite case when deposition takes place from solutions and melts.

We treat first the case of vapor condensation having in mind the general expression (2.61) for the steady-state nucleation rate. Atoms arrive from the vapor phase on the substrate surface and after a thermal accommodation period which is of the order of magnitude of several atomic vibrations (Hirth and Pound 1963), begin to migrate on the surface. Then they collide with each other to produce clusters of different sizes, thus giving rise to critical nuclei. The concentration of atoms, Z_1, is now identified by the adatom concentration n_s. The latter is determined by the adsorption–desorption equilibrium and is equal to the product of the adsorption flux

$$\Re = \frac{P}{(2\pi mkT)^{1/2}} \tag{2.79}$$

and the mean residence time

$$\tau_s = \frac{1}{\nu_\perp} \exp\left(\frac{E_{\text{des}}}{kT}\right), \tag{2.80}$$

which is elapsed before re-evaporation takes place. E_{des} denotes the activation energy for desorption and $\nu_\perp$ the vibrational frequency of the adatoms in a direction normal to the surface plane. Then,

$$n_s = \frac{P}{(2\pi mkT)^{1/2}} \frac{1}{\nu_\perp} \exp\left(\frac{E_{\text{des}}}{kT}\right). \tag{2.81}$$

The flux of adatoms toward the critical nuclei along the substrate surface is

$$j_s = D_s \text{grad} n_s \cong D_s \frac{n_s}{a}, \tag{2.82}$$

where

$$D_s = a^2 \nu_= \exp\left(-\frac{E_{\text{sd}}}{kT}\right) \tag{2.83}$$

is the surface diffusion coefficient, E_{sd} is the activation energy for surface diffusion, $\nu_=$ is the vibrational frequency of the adatoms in a direction parallel to the surface plane, and a is the length of a diffusion jump.

Bearing in mind that the periphery of the critical nucleus, assuming a semispherical shape is $2\pi r^* \sin\theta$ and $\nu_\perp \cong \nu_= = \nu$, for the frequency of attachment of atoms to the latter, one obtains

$$\omega^* = 2\pi r^* a \sin\theta \frac{P}{(2\pi mkT)^{1/2}} \exp\left(\frac{E_{\text{des}} - E_{\text{sd}}}{kT}\right). \tag{2.84}$$

Finally, for the steady-state nucleation rate, one obtains

$$J_0 = 2\pi r^* \sin\theta \frac{\Re^2 a}{\nu} \Gamma \exp\left(\frac{2E_{\text{des}} - E_{\text{sd}}}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right). \tag{2.85}$$

This equation is valid for the nucleation of liquid droplets. The Zeldovich factor $\Gamma = \Delta\mu^2/8\pi v_l[\sigma^3\phi(\theta)kT]^{1/2}$ now includes the wetting function $\phi(\theta)$. In the case of crystal nucleation, the periphery of the nucleus $4l^*$ should be inserted instead of $2\pi r^* \sin\theta$ and for the ΔG^* the corresponding expression (2.18) must be taken.

In the case of heterogeneous nucleation, there is a statistical contribution to the work of nucleus formation which is independent of the nucleus size (Lothe and Pound 1962; see also Sigsbee 1969) which accounts for the distribution of the clusters and the single adatoms

among the adsorption sites of density N_0 ($\cong 1 \times 10^{15}$ cm^{-2}). Assuming the density of clusters is negligible compared with the adatom concentration

$$\Delta G_{\text{conf}} \cong -kT \ln\left(\frac{N_0}{n_s}\right). \tag{2.86}$$

As a result, the adatom concentration n_s is replaced by the density of the adsorption sites N_0, and the following expression for the nucleation rate is obtained

$$J_0 = 2\pi r^* \sin\theta \Re a \Gamma N_0 \exp\left(\frac{E_{\text{des}} - E_{\text{sd}}}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right). \tag{2.87}$$

In the case of nucleation in condensed phases (solutions or melts), the expression for the steady-state rate is easy to obtain taking the frequency of attachment of atoms ω^* as that given by Eqs. (2.65) or (2.67) and replacing the surface area of the critical nucleus $4\pi r^{*2}$ by the area of the segment $4\pi r^{*2}(1 - \cos\theta)$.

2.2.8 *Rate of 2D nucleation*

The 2D nucleation kinetics can be treated by the same way as the 3D one. Following the procedure outlined in Sec. 2.1, we find

$$\frac{\omega_2^- \omega_3^- \ldots \omega_n^-}{\omega_1^+ \omega_2^+ \ldots \omega_{n-1}^+} = \exp\left\{\frac{\Delta G_2^*}{kT}\left[2\left(\frac{n}{n^*}\right)^{1/2} - \frac{n}{n^*}\right]\right\}.$$

After expanding the function in the exponent in the Taylor series up to the parabolic term and replacing the sum in Eq. (2.53) by an integral with limits of integration extended to $-\infty$ and $+\infty$, we obtain

$$\sum_{n=1}^{N-1}\left(\frac{1}{\omega_n^+}\frac{\omega_2^- \omega_3^- \ldots \omega_n^-}{\omega_1^+ \omega_2^+ \ldots \omega_{n-1}^+}\right) \cong \frac{1}{\omega^*}\left(\frac{4\pi kT n^{*2}}{\Delta G_2^*}\right)^{1/2} \exp\left(\frac{\Delta G_2^*}{kT}\right).$$

Then, expression (2.64) results, in which the Zeldovich factor is given by

$$\Gamma = \left(\frac{\Delta G_2^*}{4\pi kT n^{*2}}\right)^{1/2}. \tag{2.88}$$

2.2.8.1 *Rate of 2D nucleation from vapors*

The frequency of attachment of single atoms to the periphery of the critical nucleus to produce a cluster with a supercritical size is given by

$$\omega^* = 4l^* a \frac{P}{(2\pi mkT)^{1/2}} \exp\left(\frac{E_{\text{des}} - E_{\text{sd}}}{kT}\right),$$

and for the nucleation rate, one obtains

$$J_0(2D) = 4l^* a \Re \Gamma N_0 \exp\left(\frac{E_{\text{des}} - E_{\text{sd}}}{kT}\right) \exp\left(\frac{\Delta G_2^*}{kT}\right), \quad (2.89)$$

where Γ, l^*, and ΔG_2^* are given by Eqs. (2.88), (2.34), and (2.35). The same expression is valid for the case of 2D nucleation on the same substrate ($\Delta\sigma = 0$) by taking expressions (2.37) and (2.38) for l^* and ΔG_2^*, respectively. There the values for the activation energies for surface self-diffusion and desorption from the same substrate should be taken.

2.2.8.2 *Rate of 2D nucleation from solutions*

When considering the solution and melt growth of crystals through the formation and lateral propagation of 2D nuclei, we will need expressions for the rate of 2D nucleation. In the first case, the flux of arrival of molecules of the solute ($\text{cm}^{-2}\text{s}^{-1}$) is given by $a\nu C \exp(-\Delta U/kT)$ (Eq. (2.71)), and the frequency of arrival of molecules per molecular site will be

$$j_+ = a^3 \nu C \exp\left(-\frac{\Delta U}{kT}\right) = \nu C v_c \exp\left(-\frac{\Delta U}{kT}\right). \quad (2.90)$$

The number of sites available for the attachment of molecules along the perimeter of the 2D nucleus is $2\pi r^*/a$ and

$$\omega^* = 2\pi \frac{r^*}{a} C v_c \nu \exp\left(-\frac{\Delta U}{kT}\right). \quad (2.91)$$

Bearing in mind Eqs. (2.40), (2.41), (2.64), (2.88), and (2.91), the rate of 2D nucleation reads

$$J_0(\text{2D}) = \nu C v_c \left(\frac{\Delta\mu}{kT}\right)^{1/2} \exp\left(-\frac{\Delta U}{kT}\right) N_0 \exp\left(-\frac{\pi \varkappa^2 a^2}{kT\Delta\mu}\right), \quad (2.92)$$

where $\Delta\mu$ is given by Eq. (1.10). For typical values of the quantities involved, $\nu \cong 1 \times 10^{13}$ s^{-1}, $Cv_c \cong 0.1$ (10% concentration of the solute), $\Delta\mu/kT \cong 0.04$, $\Delta U = 10$ kcal mol^{-1}, $N_0 = 1 \times 10^{15}$ cm^{-2}, and $T = 300$ K, the pre-exponential factor has a value $K_1 \cong 1 \times 10^{19}$ cm^{-2} s^{-1}.

2.2.8.3 *Rate of 2D nucleation in melts*

In order to calculate the rate of 2D nucleation in melts, our first task is to find an expression for the frequency of attachment of building units to the critical nucleus. The flux of atoms which cross the phase boundary to be incorporated into the crystal lattice is given by

$$j_+ = k_+ \exp\left(-\frac{\Delta U}{kT}\right). \tag{2.93}$$

The corresponding reverse flux is given by

$$j_- = k_- \exp\left(-\frac{\Delta h_m + \Delta U}{kT}\right), \tag{2.94}$$

where k_+ and k_- are the rate constants.

At the phase equilibrium $T = T_m$, both fluxes are equal and

$$k_+ = k_- \exp\left(-\frac{\Delta h_m}{kT_m}\right) = k_- \exp\left(-\frac{\Delta s_m}{k}\right). \tag{2.95}$$

The reverse rate constant can be identified with the vibration frequency of the surface atoms $k_- = \nu$ and

$$j_+ = \nu \exp\left(-\frac{\Delta s_m}{k}\right) \exp\left(-\frac{\Delta U}{kT}\right), \tag{2.96}$$

$$j_- = \nu \exp\left(-\frac{\Delta h_m + \Delta U}{kT}\right). \tag{2.97}$$

Making use of (2.96) gives

$$\omega^* = 2\pi \frac{r^*}{a} \nu \exp\left(-\frac{\Delta s_m}{k}\right) \exp\left(-\frac{\Delta U}{kT}\right) \tag{2.98}$$

and

$$J_0 = \nu N_0 \left(\frac{\Delta s_m \Delta T}{kT}\right)^{1/2} \exp\left(-\frac{\Delta s_m}{k}\right) \exp\left(-\frac{\Delta U}{kT}\right)$$
$$\times \exp\left(-\frac{\pi \varkappa^2 a^2}{\Delta s_m \Delta T k T}\right). \tag{2.99}$$

An estimate in the case of formation of 2D nuclei on the (1 1 1) face of Si growing at a temperature which is 1 K under the melting point $T_m = 1685$ K, with $\nu = 3\times10^{13}$ s^{-1}, $\Delta s_m/k = 3.6$, $\Delta U/kT = 3$, and $N_0 \cong 1 \times 10^{15}$ cm^{-2}, gives for the pre-exponential the value $K_1 = 2 \times 10^{22}$ cm^{-2}s^{-1}.

2.2.9 *Atomistic theory of nucleation*

Experimental investigations of the heterogeneous nucleation showed that the number of atoms constituting the critical nucleus is very small (Robinson and Robins 1970, 1974; Paunov and Harsdorff 1974; Toschev and Markov 1969; Müller *et al.*, 1996). It does not exceed several atoms and, in some particular cases of nucleation on active sites, this number is equal to zero. This means physically that the adatom is so strongly bound to the active site that the combination active site–atom is a stable configuration. It is, thus, obvious that the quantities used by the phenomenological thermodynamics such as specific surface energies, equilibrium shape, even state of aggregation (we cannot say whether a cluster of 4–5 atoms is solid or liquid as we do not know the long-range order), cannot be defined. That is why the atomistic approach which excludes the use of such quantities has been developed (Walton D 1962, 1969).

In order to understand the atomistic approach, we should establish the limits of validity of the classical theory of nucleation. For this aim, we should consider the equilibrium of small particles of the new phase, or in other words, we should go back to the equation of Thomson–Gibbs (1.19) represented graphically in Fig. 1.6. But before going to thermodynamics, let us study the kinetic region of validity of the classical nucleation theory (see Milchev 1991). For this aim, we will carry out a simple estimation of the nucleation rate

in the familiar case of the formation of 2D nuclei on the surface of Si(0 0 1). As discussed in Sec. 2.1.4, the nuclei should be elongated owing to the reconstruction (2×1) characteristic for this surface (for more details, see Chapter 3). We will calculate the time elapsed to the appearance of the first nucleus on a terrace with a typical width 1000 Å (tilt angle 0.1°). This time τ should be reciprocal of the nucleation frequency on an area S of 1000×1000 Å. The latter is defined as $\Omega = J_0 S$ or $\tau = 1/\Omega$. The nucleation rate is given by $J_0 = K_1 \exp(-\Delta G_2^*/kT)$, where the pre-exponential K_1 has a typical value of 1×10^{20} cm^{-2} s^{-1} for nucleation on surfaces and $\Delta G_2^* = n^* \Delta\mu$ as given by Eq. (2.39). We calculate the supersaturation at high temperature where the classical nucleation theory is expected to be valid. Following the same procedure as in Chapter 1, Sec. 1.2, we find $\Delta\mu = 0.23$ eV at 1200 K. Assuming now $n^* = 20$ ($\Delta G_2^*/kT = 46$, $kT = 0.1$ eV), we obtain that the experimentalist should wait in average 300 years in order to register a nucleation event. As noted by Dash (1977), although on the base of an incorrect formula, "the characteristic times for nucleation on an ideal surface are astronomically large". Reasonable values for τ of the order of seconds are obtained for $n^* < 10$ or $\Delta G_2^*/kT < 20$. This very long time for nucleation to occur even for comparatively small nuclei is due to the critical behavior of the nucleation rate as shown in Fig. 2.14. The nucleation rate is practically equal to zero up to a critical value $\Delta\mu_c$ and increases sharply beyond it. We conclude further that at small supersaturations (large nuclei) the classical nucleation theory is valid but the rate of nucleation is so small that nucleation events never happen. Thus, the kinetics also appear as a limitation to the applicability of the classical nucleation theory.

It is seen, however, that the classical theory describes qualitatively well the phenomena. The reason becomes clear if we consider in more detail Eq. (1.19) of Thomson–Gibbs. We replace the radius of the particle in the equation of Thomson–Gibbs by the number of atoms in it and obtain

$$\frac{P_n}{P_\infty} = \exp\left(\frac{2\sigma b v_l^{2/3}}{kTn^{1/3}}\right),$$

where P_n is the equilibrium vapor pressure of a cluster consisting of n atoms or molecules and b is a geometrical factor equal to $(4\pi/3)^{1/3}$ for a spherical droplet.

It is immediately seen that the left-hand side of the equation (the ratio of the equilibrium vapor pressures) is a continuous quantity, whereas the right-hand side is a discrete function of the number of molecules. In other words, a fixed value of the vapor pressure or of the chemical potential corresponds to each number n of the molecules. At the same time, there are intermediate values of the vapor pressure to which correspond values of the number of molecules which are not integers. This situation is represented graphically in Fig. 2.17 (Milchev and Malinowski 1985). The value P_2 of the vapor pressure corresponds to two-atom clusters, P_3 to three-atom clusters, etc. If the actual vapor pressure $P = P_2$, a pair of atoms is precisely in equilibrium with the vapor phase (the critical nucleus) and the three-atom cluster is stable as the vapor phase is supersaturated with respect to it and it can grow further. If $P = P_3$, the three-atom cluster is the critical nucleus and the four-atom cluster is stable. However, if $P_3 < P < P_2$, the pair of atoms becomes unstable as the vapor phase is undersaturated with respect to it and it should decay. At the same time, the three-atom cluster is still stable and will remain stable as long as the vapor pressure is higher than P_3. It follows that, contrary to the classical concept, a cluster with a fixed size is stable in an interval of supersaturation which is as larger as the cluster size is smaller. The increase of the cluster size leads to a sharp decrease of the width of the intervals and the discrete dependence can be approximated by a smooth curve. In other words, the classical approach becomes applicable. For small clusters, however, the latter is very rough approximation, although the tendency remains the same. Thus, the fundamental difference between the classical and the atomistic considerations is that a single nucleus size should be operative over a range of temperatures or atom arrival rates.

2.2.9.1 *The equilibrium state*

We calculate first the steady-state concentration of clusters consisting of n atoms as in the classical case. We consider a vessel with a

Figure 2.17: Dependence of the equilibrium vapor pressure of atomic clusters on the number of atoms in the clusters. Clusters of a given size are stable in intervals of supersaturation given by the bars. The classical Thomson–Gibbs equation is plotted as a solid line. As seen, it is a good approximation for large clusters (after Milchev and Malinowski 1985).

volume V containing a crystal of the material to be deposited with a chemical potential μ_c^∞, n_v molecules of vapor with a chemical potential μ_v, and a substrate with an adlayer on top of its surface which consists of a population of single atoms and clusters of class n with density N_n ($n = 1, 2, 3,...$). If the clusters are small, we cannot use anymore Eq. (2.2) which divides the thermodynamic potential into volume and surface parts. Instead, we will use the atomistic approach introduced by Stranski and Kaischew which has the advantage that it avoids the use of macroscopic quantities. In terms of this approach

(see Sec. 2.1.3) instead of (2.2), the Gibbs free energy $G(n)$ of a cluster consisting of n atoms reads

$$G(n) = n\mu_c^\infty + \Phi, \tag{2.100}$$

where $\Phi = n\varphi_{1/2} - U_n$ (see Eq. (2.23)) accounts for the surface (nonvolume) part of the energy in complete analogy with Eq. (2.2).

Substituting (2.100) into (2.1) and accounting for Eq. (2.23) give

$$\Delta G(n) = G(n) - n\mu_v = n(\varphi_{1/2} - \Delta\mu) - U_n, \tag{2.101}$$

where $\Delta\mu = \mu_v - \mu_c^\infty$.

We accept for simplicity that the adlayer is a 2D ideal gas (Stoyanov 1979). The latter means that the population of any class n of clusters is also an ideal gas. In doing that, we implicitly assume that the configurational entropy of distribution of N_n clusters amongst N_0 adsorption sites does not take into account the adsorption sites occupied by clusters of other classes. We also assume implicitly that a cluster consisting of n atoms occupies only one adsorption site. This approximation, which is strictly valid when N_n is much smaller than the density N_0 ($\approx 1 \times 10^{15}$ cm^{-2}) of the adsorption sites, allows us to restrict ourselves to one class n of clusters only, instead of considering the whole population of clusters.

The thermodynamic potential of N_n clusters of class n is

$$\mathcal{G}(N_n) = N_n G(n) - kT \ln\left(\frac{N_0!}{(N_0 - N_n)!N_n!}\right),$$

where the second term gives the configurational entropy of distribution of N_n clusters amongst N_0 adsorption sites.

The chemical potential of a 2D ideal gas of clusters of class n then is

$$\mu_n = \frac{\partial \mathcal{G}(N_n)}{\partial N_n} = G(n) - kT \ln\left(\frac{N_0}{N_n}\right). \tag{2.102}$$

We consider first the case of true equilibrium in our system. The chemical potential, μ_n, of the ideal 2D gas of clusters of class n in the adlayer is equal to the chemical potential of n atoms in the vapor $n\mu_v$, which in turn is equal to the chemical potential $n\mu_c$ of the same number of atoms in the bulk crystal. As discussed in the beginning of this book, the chemical potential is, in fact, the work which has

to be done in order to change the number of particles in the phase by unity. Then, μ_n is the work required to remove or add a whole cluster of class n from or to the adlayer. In equilibrium, this work has to be equal to the work required to evaporate or incorporate the same number n of atoms from or to the crystal. In other words,

$$\mu_n = n\mu_v = n\mu_c^\infty.$$

Using the above equality and rearranging (2.102) give the equilibrium concentration of n-atomic clusters

$$\frac{N_n^e}{N_0} = \exp\left(-\frac{G(n) - n\mu_c^\infty}{kT}\right).$$

Let us now assume as before that we deviate from equilibrium, i.e., $\mu_v > \mu_c^\infty$, but the nucleation rate $J_0 = 0$. The equilibrium concentration N_n^e tends to the steady-state concentration Z_n, and

$$\frac{Z_n}{N_0} = \exp\left(-\frac{G(n) - n\mu_v}{kT}\right).$$

Substituting in the above equation $G(n) - n\mu_v$ from (2.101) yields

$$\frac{Z_n}{N_0} = \exp\left(-\frac{n\varphi_{1/2} - n\Delta\mu - U_n}{kT}\right). \tag{2.103}$$

If $n = 1$, for the density of the monomers, one obtains

$$\frac{Z_1}{N_0} = \exp\left(-\frac{\varphi_{1/2} - \Delta\mu - U_1}{kT}\right)$$

or, taking the nth power

$$\left(\frac{Z_1}{N_0}\right)^n = \exp\left(-\frac{n\varphi_{1/2} - n\Delta\mu - nU_1}{kT}\right). \tag{2.104}$$

Dividing (2.103) and (2.104), and bearing in mind that $U_n - nU_1$ is equal to the energy E_n required to disintegrate the cluster into single adatoms, gives for the equilibrium density of clusters consisting of n atoms the expression

$$\frac{Z_n}{N_0} = \left(\frac{Z_1}{N_0}\right)^n \exp\left(\frac{E_n}{kT}\right), \tag{2.105}$$

which was obtained for the first time by Derek Walton (1962).

2.2.9.2 *Steady-state nucleation rate*

At small enough supersaturations, n is large and the $\Delta G(n)$ dependence resembles very much the classical one as shown in Fig. 2.2 given in terms of n instead of r. This is not the case, however, when the supersaturation is large. As shown in Fig. 2.18(a), $\Delta G(n)$ is a discrete function of n and displays a highest value at a certain value of $n = n^*$. In the particular case of $\Delta\mu/\psi = 3.25$, the cluster with a highest ΔG value consists of two atoms, and the equilibrium vapor pressure is determined by the breaking of one lateral bond. The equilibrium vapor pressure of the three-atom cluster is lower than that of the atom pair as it is determined by the breaking of two bonds per atom. Hence, the latter is more stable than the pair, which, thus, plays the role of the critical nucleus. Analogously, in the case of $\Delta\mu/\psi = 2.75$, the cluster with a maximum value of ΔG consists of six atoms and the equilibrium vapor pressure is determined by the breaking of two bonds per atom, whereas the equilibrium vapor pressure of seven atom cluster is determined by the breaking of three bonds per atom.

It follows from above that, when the size of the critical nucleus is small, its geometrical shape does not remain constant as adopted by the classical theory. No analytical expression can be derived for n^* and its structure should be determined by a trial-and-error procedure estimating the binding energy of each configuration. It turns out, for example (Stoyanov 1979), that small clusters with a fivefold symmetry have lower potential energy than clusters with the normal fcc lattice with (1 1 1) orientation.

In order to calculate the steady-state rate of nucleation, we make use of the general expression (2.53) derived by Becker and Döring (Stoyanov 1973). As was shown, each term in the denominator of (2.53) represents one point of the dependence $\exp[\Delta G(n)/kT]$ (Eq. (2.58)). For n sufficiently large, the latter is more or less a smooth function of n, which justifies the replacement of the sum by an integral (see Sec. 2.1; Fig. 2.18(b)). At small value of n, this procedure is obviously unapplicable. The $\exp[\Delta G(n)/kT]$ vs n dependence, normalized to $\exp[\Delta G(n^*)/kT]$, is shown in Fig. 2.18(b)

Figure 2.18: Dependence of (a) the Gibbs free energy change $\Delta G(n)/\psi$ in units of the work ψ to break a first neighbor bond and (b) $\exp[\Delta G(n)/kT]$ on the number of atoms n in the cluster at different values of the supersaturation. At small supersaturations ($\Delta\mu = 0.02\psi$), the number of atoms in the critical nucleus is large ($\approx$1 0 0) and it can be described within the framework of the classical thermodynamics. The corresponding curves are fluent and the summation of Eq. (2.53) can be replaced by integration. At extremely large supersaturations ($\Delta\mu = 3.25\psi$ and $\Delta\mu = 2.75\psi$), the critical nucleus consists of two and six atoms, respectively. The $\Delta G(n)/\psi$ and $\exp[\Delta G(n)/kT]$ dependences are represented by broken lines, and the integration of $\exp[\Delta G(n)/kT]$ is no longer possible. Instead, the value $\exp[\Delta G(n^*)/kT]$ is taken with the contribution of the remaining terms being neglected.

for two different values of supersaturation. As seen, $\exp[\Delta G(n)/kT]$ displays a sharp maximum at $n = n^*$, all other terms in the sum of the denominator being negligible. Obviously, the term corresponding to the critical size gives the main contribution to the sum. The latter constitutes the main difference between the classical and the atomistic approaches to nucleation. In the former case, we have to sum up (or integrate) over a large number of terms, whereas in the latter case, we just take one of them corresponding to the critical nucleus and neglect all the others.

Hence,

$$\sum_{n=1}^{N-1}\left(\frac{1}{\omega_n^+}\frac{\omega_2^-\omega_3^-\ldots\omega_n^-}{\omega_1^+\omega_2^+\ldots\omega_{n-1}^+}\right) \cong \frac{1}{\omega^*}\gamma\exp\left(\frac{\Delta G^*}{kT}\right), \tag{2.106}$$

where $\Gamma = 1/\gamma$ is the Zeldovich factor which accounts for the remaining smaller terms in the sum and in this case is of the order of unity. $\omega_n^+ \cong \omega^* = \text{const}$ as before.

Then, bearing in mind (2.22) that with $n = n^*$,

$$\Delta G^* = -n^*\Delta\mu + \Phi,$$

and for the nucleation rate, one obtains

$$J_0 = \omega^*\Gamma n_s \exp\left(-\frac{\Phi}{kT}\right)\exp\left(\frac{\Delta\mu}{kT}n^*\right). \tag{2.107}$$

The logarithm of the steady-state nucleation rate is plotted against the supersaturation in Fig. 2.19. It represents a broken line when the experimental data cover more than one supersaturation interval. This is easy to understand recalling that the size of the critical nucleus remains constant in more or less wide intervals of the supersaturation (Stoyanov 1979) and so is its geometrical shape and in turn its "surface energy" Φ. The slopes of the straight lines give directly the number of the atoms in the critical nuclei which can be evaluated from comparison with experimental data. Figure 2.20 represents experimental data for the nucleation rate in electrodeposition of mercury on platinum single-crystal spheres (Toschev and Markov 1969) interpreted in terms of the atomistic theory by Milchev and

Figure 2.19: Dependence of the logarithm of the nucleation rate on the supersaturation $\Delta\mu$. At high supersaturations the dependence is represented by a broken line reflecting the real dependence of the supersaturation on the cluster size. $\Delta\mu_1$ and $\Delta\mu_2$ denote the critical supersaturations at which the number of atoms in the critical nucleus from one integer value to another. At small supersaturations the broken line turns gradually into a fluent curve due to the decrease of the widths of the cluster stability intervals (see Fig. 2.17). Thus the classical nucleation theory appears to be a good approximation at small supersaturations (after Milchev *et al.*, 1974).

Stoyanov (1976). The values for $n^* = 6$ and 10 have been found from the slopes of both parts of the plot. The same values ($n^* = 2$ and 5) have been also obtained in the electrolytic nucleation of silver on platinum single-crystal spheres in the solution of $AgNO_3$ in fused salts at high temperatures (Toschev *et al.*, 1969).

Expression (2.107) does not give explicitly the dependence of the nucleation rate on the atom arrival rate and the temperature in deposition from vapor, and in this sense is not suitable for, interpretation of the experimental data in this particular case. For this purpose, we have to derive expressions for the growth and decay frequencies specific for the case under consideration and to insert them into Eq. (2.53).

Figure 2.20: Experimental data for the nucleation rate as a function of the overpotential η in the case of electrochemical nucleation of mercury on platinum single crystals (Toschev and Markov 1969). The data are plotted in "atomistic" coordinates $\ln J_0$ vs η. As seen, the number of atoms in the critical nucleus changes at about 0.096 V. (A. Milchev and S. Stoyanov, *J. Electroanal. Chem.* **72**, 33 (1976). By the permission of S.A. Elsevier Sequoia and courtesy of A. Milchev.)

In the capillary approach,

$$\omega_n^+ = P_n D_s \mathrm{grad} n_s \cong P_n D_s \frac{n_s}{a} = \frac{P_n}{a} D_s n_s,$$

where P_n is the perimeter of the cluster and P_n/a is, in fact, the number of the lateral unsaturated bonds.

In the atomistic approach (Stoyanov 1973),

$$\omega_n^+ = \alpha_n D_s n_s, \tag{2.108}$$

where α_n, in complete analogy with the capillary model (P_n/a), gives the number of ways of formation of a cluster of size $n+1$ by joining an adatom to a cluster of size n, or in other words, the number of the adsorption sides neighboring a cluster of n atoms.

The decay constant reads

$$\omega_n^- = \beta_n \nu \exp\left(-\frac{E_n - E_{n-1} + E_{\mathrm{sd}}}{kT}\right), \tag{2.109}$$

where E_n is the energy to disintegrate a cluster of size n into single atoms. The difference $E_n - E_{n-1}$ gives the energy of detachment of an atom from the cluster of size n. E_{sd} is the activation energy for surface diffusion and β_n is the number of ways of detachment of single atoms from a cluster of size n. A one-to-one correspondence exists between each decay process $n+1 \to n$ and each growth process $n \to n+1$ and, hence,

$$\alpha_n = \beta_{n+1}. \tag{2.110}$$

Recalling the expression for the surface diffusion coefficient, Eq. (2.109) can be rewritten in the form

$$\omega_n^- = \beta_n D_s N_0 \exp\left(-\frac{E_n - E_{n-1}}{kT}\right), \tag{2.111}$$

where $N_0 \cong a^{-2}$ is the density of the adsorption sites on the substrate surface.

Equation (2.53) can be rewritten in the form

$$J_0 = \omega_1^+ n_s \left(1 + \frac{\omega_2^-}{\omega_2^+} + \frac{\omega_2^- \omega_3^-}{\omega_2^+ \omega_3^+} + \frac{\omega_2^- \omega_3^- \omega_4^-}{\omega_2^+ \omega_3^+ \omega_4^+} + \cdots\right)^{-1}. \tag{2.112}$$

Assuming $n^* = 1$ (all terms in the denominator are much smaller than the unity and $E_1 = 0$) with (2.108), one obtains

$$J_0 = \alpha_1 D_s n_s^2 = \alpha_1 \frac{\Re^2}{\nu N_0} \exp\left(\frac{2E_{\mathrm{des}} - E_{\mathrm{sd}}}{kT}\right). \tag{2.113}$$

For $n^* = 2$ ($\omega_2^-/\omega_2^+ \gg 1$ and $\omega_2^-/\omega_2^+ \gg \omega_2^- \omega_3^-/\omega_2^+ \omega_3^+$),

$$J_0 = \alpha_2 D_s^2 n_s^3 \nu^{-1} \exp\left(\frac{E_2 + E_{\mathrm{sd}}}{kT}\right)$$

or

$$J_0 = \alpha_2 \frac{\Re^3}{\nu^2 N_0^2} \exp\left(\frac{3E_{\text{des}} - E_{\text{sd}}}{kT}\right) \exp\left(\frac{E_2}{kT}\right). \tag{2.114}$$

Respectively, for $n^* = 6$,

$$J_0 = \alpha_6 D_s^6 n_s^7 \nu^{-5} \exp\left(\frac{E_6 + 5E_{\text{sd}}}{kT}\right)$$

or

$$J_0 = \alpha_6 \frac{\Re^7}{\nu^6 N_0^6} \exp\left(\frac{7E_{\text{des}} - E_{\text{sd}}}{kT}\right) \exp\left(\frac{E_6}{kT}\right). \tag{2.115}$$

Then, in the general case,

$$J_0 = \alpha^* D_s^{n^*} n_s^{n^*+1} \nu^{-(n^*-1)} \exp\left(\frac{E^* + (n^* - 1)E_{\text{sd}}}{kT}\right)$$

or

$$J_0 = \alpha^* \Re \left(\frac{\Re}{\nu N_0}\right)^{n^*} \exp\left(\frac{E^* + (n^* + 1)E_{\text{des}} - E_{\text{sd}}}{kT}\right), \tag{2.116}$$

where $\alpha^* \equiv \alpha(n^*)$ and $E^* \equiv E(n^*)$.

Equation (2.116) can also be written in terms of the adatom concentration in the form

$$J_0 = \alpha^* D_s \frac{n_s^{n^*+1}}{N_0^{n^*-1}} \exp\left(\frac{E^*}{kT}\right), \tag{2.117}$$

which will be used when considering the 2D nucleation growth of crystals from vapors in Chapter 3.

The critical nucleus size can change by an integer number of atoms. For example, a clear evidence for a transition from 1 to 3 atoms in the critical nucleus has been reported by Müller *et al.* (1996) in the case of nucleation of Cu on Ni(0 0 1). Thus, a single nucleus size is operative over a temperature interval. The latter can be defined as follows. Let us consider, for example, the nucleation on Ag (1 1 1) surface. At extremely low temperatures, a single atom will be a critical nucleus. Above some temperature T_1, the critical nucleus will be a pair of atoms, and the cluster of three atoms, each one situated at the apex of a triangle, will be a stable configuration so that two chemical bonds correspond to each atom. Above some other critical

temperature $T_2 > T_1$, the six-atom cluster will be a critical nucleus and the seven-atom cluster with three bonds per atom will be stable. We can easily calculate T_2 and T_1 and determine the interval of the stability of the two-atom nucleus. The left-hand limit of the interval T_1 is determined from the condition $\omega_2^- / \omega_2^+ = 1$:

$$T_1 = \frac{E_2 + E_{\mathrm{des}}}{k \ln(\beta_2 N_0 \nu / \alpha_2 \Re)}.$$

By the same way, we find

$$T_2 = \frac{E_6 - E_2 + 4E_{\mathrm{des}}}{k \ln(\beta_3 N_0^4 \nu^4 / \alpha_6 \Re^4)}.$$

Then, for Ag(1 1 1) with $\Delta H_e = 60\,720$ cal mol^{-1}, $E_2 = \psi = \Delta H_e/6 = 10\,120$ kcal mol^{-1}, $E_6 = 9\psi$, $E_{\mathrm{des}} = 3\psi$, $N_0 \cong 1 \times 10^{15}$ cm^{-2}, $\nu \cong 1 \times 10^{13}$ s^{-1}, $\Re = 1 \times 10^{14}$ cm^{-2} s^{-1}, and neglecting the coefficients α_n and β_n for $\Delta T = T_2 - T_1$, one obtains 160 K. This means that one and the same critical size will be operative under the conditions of the experiment except for the case when we work in a temperature region around the critical temperature. This is the case in the electrolytic nucleation of mercury as shown in Fig. 2.20.

Critical nuclei consisting of zero, one and two atoms are found in the electrolytic nucleation of silver on glassy carbon (Milchev 1983). The critical size of 0 atoms is interpreted as nucleation on active sites whose binding energy $-E_0$ to the adatoms is strong enough so that the mean residence time of the atom on the site is longer than the mean time elapsed between the arrivals of two successive atoms to the site. Under such a condition, the couple adatom-active site is considered as a stable cluster because the probability of its growth is larger than the probability of its decay. If this is not the case the pair adatom-active site is no longer a stable cluster and nuclei can form also randomly on the defect-free surface. Thus, random nucleation on defect-free surface and selective nucleation on the active site can take place simultaneously. Depending on the density of the active sites and their binding energy, one or the other mechanism predominates. In the limiting case of nucleation on active sites, the

following expression is obtained (Stoyanov 1974):

$$J_0 = \alpha_1 \frac{Z_0}{N_0} \frac{\Re^2}{\nu N_0} \exp\left(\frac{E_0 + 2E_{\text{des}} - E_{\text{sd}}}{kT} \right), \tag{2.118}$$

where Z_0 is the density of the active sites.

As seen in both cases of critical sizes $n^* = 0$ and 1 (Eq. (2.113)), the nucleation rate is directly proportional to the square of the atom arrival rate. In that sense, both cases are practically undistinguishable. Really, the pre-exponential in (2.118) is smaller than that in (2.113) by $Z_0/N_0 \cong 10^{-2}$–10^{-4}, but $\exp[E_0/kT]$ overcompensates this effect.

2.2.10 *Nonsteady state nucleation*

One can assume that in the initial moment after "switching on" of the supersaturation the concentration of the homophase fluctuations given by Eq. (2.59) is negligible and $J_0 = 0$. It follows that sometime from that initial moment should pass in order that a steady-state molecular flow in the system be established, or in other words, the concentrations of the clusters attain their steady-state values Z_n. The solution of this problem attracted the attention of many authors (Zeldovich 1942; Zeldovich 1992; Kantrowitz 1951; Probstein 1951; Farley 1952; Wakeshima 1954; Collins 1955; Chakraverty 1966; Kashchiev 1969), and the problem has been experimentally studied in detail in different systems (Toschev and Markov 1968, 1969; James 1974) and reviewed extensively (Lyubov and Roitburd 1958; Toschev and Gutzow 1972; Toschev 1973). We will show in this section how the problem of the transient state can be treated and will evaluate the nonsteady-state effects for different supersaturated (undercooled) systems.

As mentioned in Sec. 2.2.1, the steady state is determined by the condition $dZ_n(t)/dt = 0$. We have now to solve the general problem as given by Eq. (2.51). In other words, as followed by Eq. (2.50) the rates of formation of clusters of different sizes are no longer equal in the time-dependent case. This is the case at least in the beginning of the process after the supersaturation is "switched on."

We mentioned that the formation of a cluster with a critical size appears as a result of fluctuations of the density in the parent phase. Let us consider this process more closely. Imagine that we have a cluster with a size n smaller than the critical one n^*. When a single atom joins the cluster, it becomes of size $n+1$. When an atom is detached from the cluster, the latter becomes of size $n-1$. The attachment and detachment of atoms are random processes and, hence, the cluster increases or decreases in size randomly. In other words, the cluster performs random walking back and forth on the axis of the sizes up to the moment it reaches the critical size. Then, the further growth is connected with the fall of the thermodynamic potential and loses its random character. We can easily prove this following the approach developed by Frenkel and Zeldovich (Frenkel 1955).

Considering n as a continuous variable Zeldovich and Frenkel replaced Eq. (2.51) by the differential equation

$$\frac{dZ(n,t)}{dt} = -\frac{dJ(n,t)}{dn}, \tag{2.119}$$

where n is now not an index to denote that it is no more a discrete variable.

The nucleation rate $J(n,t)$ is defined in the continuous case as (compare with Eq. (2.50))

$$J(n,t) = \omega_{n-1}^{+} Z(n-1,t) - \omega_n^{-} Z(n,t). \tag{2.120}$$

The expression of the detailed balance (2.54) in the absence of a molecular flux through the system now reads

$$\omega^{+}(n-1)N(n-1) = \omega^{-}(n)N(n). \tag{2.121}$$

Eliminating the decay constant $\omega^{-}(n)$ from (2.120) and (2.121) gives

$$J(n,t) = \omega^{+}(n-1)N(n-1)\left(\frac{Z(n-1,t)}{N(n-1)} - \frac{Z(n,t)}{N(n)}\right)$$

or

$$J(n,t) \cong -\omega^{+}(n)N(n)\frac{d}{dn}\left(\frac{Z(n,t)}{N(n)}\right), \tag{2.122}$$

where the approximation $\omega^+(n-1)N(n-1) \cong \omega^+(n)N(n)$ has been used.

Combining (2.119) and (2.122) gives

$$\frac{dZ(n,t)}{dt} = \frac{d}{dn}\left[\omega^+(n)N(n)\frac{d}{dn}\left(\frac{Z(n,t)}{N(n)}\right)\right]. \tag{2.123}$$

Recalling the equilibrium distribution of clusters of class n (2.59), we carry out the differentiation and obtain

$$\begin{aligned}\frac{dZ(n,t)}{N(n)dt} &= \omega^+(n)\frac{d^2}{dn^2}\left(\frac{Z(n,t)}{N(n)}\right)\\ &\quad + \left(\frac{d\omega^+(n)}{dn} - \frac{\omega^+(n)}{kT}\frac{d\Delta G(n)}{dn}\right)\frac{d}{dn}\left(\frac{Z(n,t)}{N(n)}\right).\end{aligned}$$

This equation is valid within the whole interval of n from 1 to N. In the vicinity of the critical size, it is simplified to

$$\frac{d}{dt}\left(\frac{Z(n,t)}{N(n)}\right) = \omega^+(n^*)\frac{d^2}{dn^2}\left(\frac{Z(n,t)}{N(n)}\right), \tag{2.124}$$

assuming as above that the growth coefficient is nearly a constant, $\omega^+(n) \cong \omega^+(n^*) = \text{const}$ and bearing in mind that $\Delta G(n)$ displays a maximum at $n = n^*$, i.e., $[d\Delta G(n)/dn]_{n=n^*} = 0$.

As seen, the time and size dependence of the steady-state concentration $Z(n,t)$ is governed by a partial differential equation of second order. In fact, this is the familiar diffusion equation in which the diffusion coefficient is replaced by the growth rate constant $\omega^+(n^*)$ and which reflects the random character of the growth process in the critical region Δn^*. We can, thus, envisage the growth of the clusters as a "diffusion" in the space of the size n.

Even without solving the governing Eq. (2.124), we can draw some qualitative conclusions by considering a simple analogy with the diffusion process towards some boundary. At the initial moment, the "concentration" is one and the same all over the system, which is equivalent to the homogeneous ambient phase without clusters of any size. Once we have a supersaturation, which is equivalent to the appearance of a diffusion gradient, the "concentration" in the near

vicinity of the boundary decreases and we have a "concentration" profile which changes with time up to reaching the steady state. The same happens into the supersaturated medium. Clustering begins and the concentration of clusters of a given class n gradually increases with time up to the moment it reaches the steady-state value. This picture has been directly verified by Courtney (1962) who computed the time dependence of the cluster concentrations.

To proceed further, it is necessary to define the boundary conditions. As mentioned earlier, Zeldovich and Frenkel argued that rate determining are the processes in a small region around the critical size. A detailed mathematical analysis of the problem carried out by Kashchiev (1969) has shown that this is a very good approximation. It follows that $Z(n,t)$ and $N(n)$ differ only in this region Δn^*, i.e., at $n < n_l$ (see Fig. 2.13), $Z(n,t) = N(n)$, and at $n > n_r$, $Z(n,t) = 0$ at any time t. Thus, the natural initial condition ($t = 0$) is that immediately after "switching on" the supersaturation clusters of any size are absent in the system. In other words, at the initial moment, only single molecules (monomers) are present in the system. The boundary conditions arise from point 2 in Sec. 2.2.1. At any moment, the concentration of clusters of class $N \gg n^*$ is equal to zero and the steady-state concentration of the monomer is equal to the equilibrium concentration. In other words,

$$\begin{aligned} Z(1,0) &= N(1), \quad Z(n \geq 2, 0) = 0 \\ Z(1,t) &= N(1), \quad Z(N,t) = 0. \end{aligned}$$

The solution of Eq. (2.124) subject to the above boundary conditions reads (Kashchiev 1969)

$$\frac{Z(n,t)}{N(n)} = \frac{1}{2} - \frac{n - n^*}{\Delta n^*} - \frac{2}{\pi} \sum_{i=1}^{\infty} \frac{1}{i} \sin\left(i\pi \frac{n - n^*}{\Delta n^*} + \frac{i\pi}{2}\right) \exp\left(-i^2 \frac{\pi \omega^* t}{16 \Delta n^{*2}}\right).$$

It is immediately seen that at the steady state ($t \to \infty$) the sum vanishes and for the critical nucleus, $n = n^*$, $Z(n^*) = N(n^*)/2$.

Substituting the above solution into (2.122) (the latter taken for the rate of formation of critical nuclei) gives (Kashchiev 1969)

$$J(t) = J_0 \left[1 + 2 \sum_{i=1}^{\infty} (-1)^i \exp\left(-i^2 \frac{t}{\tau} \right) \right], \tag{2.125}$$

where the parameter

$$\tau = \frac{4(\Delta n^*)^2}{\pi \omega^*} \tag{2.126}$$

is the so-called induction period.

Bearing in mind that the number of the nuclei vs time is given by the integral

$$N(t) = \int_0^t J(t) dt, \tag{2.127}$$

the integration of (2.125) gives (Kashchiev 1969)

$$N(t) = J_0 \tau \left[\frac{t}{\tau} + \frac{\pi^2}{6} - 2 \sum_{i=1}^{\infty} \frac{(-1)^i}{i^2} \exp\left(-i^2 \frac{t}{\tau} \right) \right], \tag{2.128}$$

where J_0 is given by any of the expressions derived in the previous section. As follows from (2.125) (Fig. 2.21), the steady state should be reached after a period of approximately 5τ.

We can now evaluate the induction period τ for different cases of nucleation. In the case of the formation of spherical nuclei from vapors from (2.126), (2.62), (2.63), and (1.9), one obtains

$$\tau = \frac{16}{\pi} \left(\frac{m}{kT} \right)^{1/2} \frac{\sigma}{P[\ln(P/P_\infty)]^2}. \tag{2.129}$$

Then for the homogeneous nucleation of water vapor at room temperature $T = 300\,\mathrm{K}$ with $\sigma = 75.2$ erg sm^{-2}, $P\infty \cong 20$ Torr $= 2.66 \times 10^4$ dyne cm^{-2}, $P/P\infty = 4$, $m \cong 3 \times 10^{-23}$ g, $\tau \cong 1 \times 10^{-8}$ s, i.e., the induction period is practically undetectable.

The problem differs considerably when condensed phases are involved. Making use of (2.71) for ω^* yields

$$\tau = \frac{16}{\pi} \frac{\sigma}{kT[\ln(C/C_\infty)]^2 C\nu\lambda} \exp\left(\frac{\Delta U}{kT} \right) \tag{2.130}$$

Figure 2.21: Dependences of the nonsteady state nucleation rate $J(t)$ relative to the steady state nucleation rate J_0 (curve 1, Eq. (2.125)) and the number of the nuclei (curve 2, Eq. (2.128)) on time in units of the time lag τ. As seen, the steady state rate is reached after approximately 5τ. The incubation period t_0 of the $N(t)$ curve is referred to τ by $t_0 = \pi^2\tau/6 = 1.64\tau$.

for nucleation in solutions where the concentration must be taken in the number of molecules per cubic centimeter.

Evaluation of τ shows that it varies in orders of magnitude due to the different values of the activation energy of desolvation. In any case, the value of the induction period is several orders of magnitude greater than that from vapors. Thus, for the nucleation of $BaSO_4$ in aqueous solutions (assuming for simplicity a spherical shape) with $\sigma = 116$ erg cm^{-2}, $C = 1 \times 10^{-5}$ mol l^{-1} $= 6 \times 10^{15}$ molecules cm^{-3}, $C/C\infty = 1000$, $\nu = 3 \times 10^{13}$ s^{-1}, $a \cong 4 \times 10^{-8}$ cm and $\Delta U = 7$ kcal mol^{-1} ($\Delta U/kT = 11.67$), $\tau \cong 5 \times 10^{-3}$ s. At the same time for $PbSO_4$ ($\sigma = 100$ erg cm^{-2}, $C = 8.5 \times 10^{16}$ cm^{-3}, $C/C\infty = 28$ and $\Delta U = 14.5$ kcal mol^{-1}) $\tau = 5 \times 10^2$ s, i.e., the induction period is five orders of magnitude longer.

In the case of nucleation in melts with (2.73)

$$\tau = \frac{16}{\pi}\frac{\sigma kTv_c}{\Delta s_m^2 \Delta T^2 \nu a}\exp\left(\frac{\Delta U}{kT}\right). \tag{2.131}$$

The induction period is also negligible in homogeneous nucleation in simple metal melts. Thus, in solidification of Ag with $\sigma = 150$ erg cm^{-2}, $T = 1230\,\mathrm{K}$, $\Delta T = 5\,\mathrm{K}$, $v_c = 5 \times 10^{-22}$ cm^3, $\Delta s_m = 2.19$ cal K^{-1} mol^{-1} $= 1.52{\times}10^{-16}$ erg K^{-1}, $\nu = 2{\times}10^{13}$ s^{-1} and $\Delta U/kT \cong 2.5$, $\tau \cong 2 \times 10^{-6}$ s. At the same time, for typical glass-forming melts such as SiO_2 and GeO_2 ($\Delta U/kT \cong 30 - 40$) $\tau \cong 1 \times 10^5$ s, i.e., the induction period is as long as a day and night. This means that the process of phase transition can be completed before a steady-state nucleation rate is reached. In other words, the whole crystallization process takes place in a transient regime.

Induction times of the order of tens of minutes have been observed in the nucleation of polydecamethylene terephthalate (Sharples 1962). In the case of the crystallization of Graham glass ($NaPO_3$) on artificially introduced gold and iridium particles, Toschev and Gutzow (1972) found induction periods as long as 10 h and 5 h, respectively, at about 300°C. Moreover, the induction time is a strong function of the temperature. James (1974) found that the induction periods in the crystallization of lithium disilicate melts vary from nearly 51 h at 425°C to 7 min at 489°C, i.e., more than two orders of magnitude in a temperature interval of 64°C. A value of 105 kcal mol^{-1}, or in other words, $\Delta U/kT \cong 72$, for the activation energy for viscous flow has been estimated from the data.

An expression for the induction period τ in heterogeneous nucleation from a vapor phase is easy to obtain from (2.126) and (2.84)

$$\tau = 17\left(\frac{m}{k^3T^3}\right)^{1/2}\frac{\phi(\theta)}{\sin\theta}\frac{\sigma^2 v_l}{aP[\ln(P/P_\infty)]^3}\exp\left(-\frac{E_{\mathrm{des}} - E_{\mathrm{sd}}}{kT}\right). \tag{2.132}$$

Comparing (2.132) with (2.129) gives

$$\frac{\tau(\mathrm{het})}{\tau(\mathrm{hom})} \cong \frac{\pi}{2}\frac{r^*}{a}\frac{\phi(\theta)}{\sin\theta}\exp\left(-\frac{E_{\mathrm{des}} - E_{\mathrm{sd}}}{kT}\right).$$

The pre-exponential is of the order of unity with the exception of the cases of extremely high values of the wetting angle and the ratio $\tau(\mathrm{het})/\tau(\mathrm{hom})$ is determined primarily by the activation energies for

desorption and surface diffusion. One can conclude that in the case of heterogeneous nucleation, the induction time is even smaller than that in the homogeneous case (Brune *et al.*, 1994; Bott *et al.*, 1996). This is not, however, the case when the surface of the growing crystal is covered by a monolayer (ML) of a surface active species. This layer represents obviously a barrier which inhibits the transport of the building units to the growth sites. As a result, measurable induction periods should appear. Thus, induction times of the order of seconds and minutes depending on the atom arrival rate have indeed been reported recently by Hwang *et al.* (1998) in the deposition of Ge on the Pb-precovered Si(1 1 1) surface in the submonolayer regime (see Fig. 2.22).

Bearing in mind that the Zeldovich factor is inversely proportional to the square root of the wetting function $\phi(\theta)$, we find that in

Figure 2.22: A series of number of nuclei vs time curves in the case of vapor deposition of Ge on Pb precovered Si(1 1 1). Induction periods of the order of tens of seconds are visible. The plateaus in the original data are omitted for clarity. The atom arrival rates are denoted in number of bilayers per minute by the figures at each curve. The data are from I.-S. Hwang, T.-C. Chang, and T. T. Tsong, *Phys. Rev. Lett.* **80**, 4229 (1998). By the permission and courtesy of Tien T. Tsong.

the case of nucleation in condensed phases (solutions or melts), the induction period τ in heterogeneous nucleation in condensed phases should be given by (2.130) or (2.131) but multiplied by the quantity $\phi(\theta)/(1-\cos\theta) = (1-\cos\theta)(2+\cos\theta)/4$. This function displays a maximum of 0.5625 at $\theta = 120°$. Hence, $\tau(\text{het})$ will be again smaller than $\tau(\text{hom})$ by this function.

A straightforward test of the nonsteady state effects in the theory of heterogeneous nucleation requires measurements either of the time of appearance of the first nucleus or the dependence of the number of nuclei on time at a constant supersaturation. Precise measurements of the number of nuclei vs time have been performed in the case of the electrolytic formation of metal nuclei on foreign metal substrates and the results have been compared with Eq. (2.128) (Toschev and Markov 1969). In order to separate the process of nucleation from that of the growth of the nuclei, the so-called double-pulse potentiostatic technique has been used. Π-shaped electric pulses (Fig. 2.23) have been imposed on an electrolytic cell consisting of two electrodes

Figure 2.23: Double pulse technique for investigation of the number of nuclei vs time when used to study the electrochemical nucleation of metals on foreign metal substrates. Nuclei are formed during the first pulse AB of height η. They grow to sizes visible under microscope during the second pulse BC of height η_g. The latter is lower than the critical overpotential required for nucleation to occur with a measurable rate. The number of nuclei formed during the first pulse averaged from a large number of measurements is then plotted vs the pulse duration t at a constant pulse height (S. Toschev and I. Markov, *Ber. Bunsenges. Phys. Chem.* **73**, 184 (1969)).

Figure 2.24: Micrograph showing mercury droplets (bright points) electrodeposited on a platinum single crystal sphere. Every droplet is reflected from the mirror smooth surface of the electrode and looks like a bar. The large bright spot near the middle of the electrode is a reflection of the lamp. The nuclei are formed preferably around the (1 1 1) poles of the sphere (S. Toschev and I. Markov, *Ber. Bunsenges. Phys. Chem.* **73**, 184 (1969)).

immersed in an electrolytic solution of metal ions. The height of the first pulse of duration t is a measure of the overpotential $\eta = E - E_0$ (Eq. (1.13)). The height of the second pulse is sufficiently low (in fact, lower than the critical supersaturation) so that no nuclei can be formed during it for a long enough time. The nuclei formed during the first pulse grow to visible sizes during the second one and are counted under microscope. A platinum single-crystal sphere sealed into glass capillary served as a cathode, while the anode was a sheet or a wire (or a pool of mercury in this particular case) of the metal whose ions are present into the solution. Figure 2.24 shows a typical picture of mercury droplets formed on the platinum single-crystal sphere. As seen, they are preferably formed around the (1 1 1) poles of the sphere.

Figure 2.25 shows a series of number of nuclei vs time curves for the electrodeposition of mercury nuclei at different overpotentials denoted by the figures at the curves. The transient behavior required by the nonsteady-state theory (Fig. 2.21) is clearly demonstrated. Induction periods of the order of milliseconds are observed. The validity of Eq. (2.128) is tested in Fig. 2.26. As seen, the points

Figure 2.25: A series of number of nuclei vs time curves in the case of electrochemical nucleation of mercury on platinum single crystal spheres at different overpotentials, denoted by figures in mV at the curves. The transient behavior of the nucleation process is clearly demonstrated. The curve obtained at $\eta = 0.084$ mV shows a saturation which is due to overlapping of nucleation exclusion zones (S. Toschev and I. Markov, *Ber. Bunsenges. Phys. Chem.* **73**, 184 (1969)).

fall close to the theoretical $N(t)$ curve

$$f(x) = x - \frac{1}{6}\pi^2 - 2\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp(-n^2 x) \tag{2.133}$$

in dimensionless coordinates $f(x) = N/J_0\tau$ and $x = t/\tau$.

The slopes of the linear parts of the curves in Fig. 2.25 give a straight line in logarithmic coordinates $\log J_0$ vs $1/\eta^2$ (Fig. 2.27), thus confirming qualitatively the validity of the capillary model (2.69). The number of the atoms constituting the critical nucleus can be evaluated as a function of the overpotential from the slope of the

Figure 2.26: Plot of the number of nuclei vs time from Fig. 2.25 in dimensionless coordinates $F(x) = N(t)/J_0\tau$ and $x = t/\tau$. The solid curve represents the theoretical curve (2.133) (S. Toschev and I. Markov, *Ber. Bunsenges. Phys. Chem.* **73**, 184 (1969)).

straight line, and the values from 3 to 8 have been obtained in this particular case. Obviously, the capillary model of heterogeneous nucleation, which makes use of such phenomenological quantities as the bulk surface specific energies, etc., cannot be used for a quantitative description of the process at very high supersaturations. That is the reason the data of Fig. 2.25 have been interpreted in terms of the atomistic model of nucleation (Fig. 2.20).

2.2.11 *Mass crystallization and saturation nucleus density*

As was mentioned above, the main problem in the investigation of the nucleation kinetics in melts and solutions is the presence of impurity particles which stimulate the process due to the wetting. However, the existence of impurity particles leads, in addition, to another phenomenon. It is reasonable to assume that the particles have different

Figure 2.27: Plot of the logarithm of the steady-state rate of electrolytic nucleation of mercury on platinum single-crystal spheres vs the reciprocal square of the overpotential as required by the classical theory of 3D nucleation. The rates represent, in fact, the slopes of the linear parts of the $N(t)$ curves shown in Fig. 2.25. The straight line demonstrates the qualitative validity of the classical nucleation theory, although the number of atoms in the critical nucleus is about 8 (S. Toschev and I. Markov, *Ber. Bunsenges. Phys. Chem.* **73**, 184 (1969)).

activity with respect to crystal nucleation (or different wetting angles or adhesion forces) or, in other words, a different critical supersaturation, according to Eq. (2.70), in which the wetting function $\phi(\theta)$ should enter in the case of heterogeneous nucleation. Then, the active particles will take part in the process only when the supersaturation in the system is higher than their critical supersaturation. In such a case, the number of the nuclei formed will be equal to the number of the particles whose critical supersaturation is lower than the actual value in the system. A saturation phenomenon will be observed in the sense that the number of nuclei will reach a constant value. As the particles have different critical supersaturations, the increase of the current supersaturation in the system will lead to the involvement of new particles with higher critical supersaturations and the saturation nucleus density will grow. This process will continue up to

the moment when the supersaturation exceeds the critical supersaturation for homogeneous nucleation. Then, a large number of nuclei homogeneously formed will appear. Such a saturation behavior is clearly established in the case of nucleation of polymethylene terephthalate (Sharples 1962). The author explains the phenomenon with the catalytic action of foreign particles of finite numbers and different activities in the melt.

The same picture holds for the nucleation on foreign substrates. Defect sites on the substrate surface with different critical supersaturation play the role of the foreign particles in this particular case (Robins and Rhodin 1964; Kaischew and Mutaftschiev 1965).

An expression for the time dependence of the number of nuclei can be easily derived under the simplifying assumption of equal activity (or critical supersaturation) of the defect sites (Robins and Rhodin 1964). Let us denote by N_d (cm^{-2}) the density of the defect sites and by J_0' (s^{-1}) the frequency of nucleation per active site. Then, the change of the number N of nuclei with time will be given by

$$\frac{dN}{dt} = J_0'(N_d - N), \tag{2.134}$$

where $N_d - N$ is the number of the free active sites on which nuclei are not yet formed.

The integration of (2.134) subject to the initial condition N $(t = 0) = 0$ gives

$$N = N_d[1 - \exp(-J_0' t)]. \tag{2.135}$$

As seen, at $t \to \infty$, $N \to N_d = \text{const}$. The saturation is reached in practice when $t > 5/J_0'$, where $1/J_0'$ is the time constant of the process.

This equation can be easily generalized for the case of active sites with different critical supersaturations to give (Kaischew and Mutaftschiev 1965)

$$N = \int_0^{\Delta\mu} N_d(\Delta\mu_c)\{1 - \exp[-J_0'(\Delta\mu_c)t]\}d\Delta\mu_c, \tag{2.136}$$

where $N_d(\Delta\mu_c)$ and $J_0'(\Delta\mu_c)$ are now functions of the activity or the critical supersaturation $\Delta\mu_c$. Obviously, Eq. (2.136) holds for nucleation in 3D systems (melts) as well as in 2D systems (surfaces). The main problem of such a treatment, however, is that the distributions $N_d(\Delta\mu_c)$ and $J_0'(\Delta\mu_c)$ are usually unknown.

Another reason for the saturation of the nucleus density is the appearance of *locally undersaturated* zones around growing nuclei where the nucleation rate is reduced or even equal to zero owing to the consumption of the diffusing adatoms in the case of nucleation on the substrate or accumulation of heat of crystallization in the case of nucleation in melts. Nuclei and, in turn, empty zones around them are progressively formed and grow during growth. When the zones overlap and cover the whole substrate surface or fill the whole volume of the melt, the process of nucleation is arrested and a saturation of the nucleus density is reached. The radii of the nucleation exclusion zones are defined by the intersection of the gradient of the supersaturation around the growing island and the critical supersaturation for nucleation to occur (see Fig. 2.28).

The case of solidification of melts is more complicated. If the heat conductivity of the melt is low, the temperature of the growing crystallites and their near vicinity increases as a result of accumulation of the latent heat of crystallization (Fig. 2.29). As a result, the temperature, T_i, at the solid–melt interface is high and very close to the melting point and then it smoothly goes to the bulk temperature,

Figure 2.28: To the definition of a nucleation exclusion zone. $\Delta\mu_c$ is the critical supersaturation for nucleation to take place with visible rate, r_c is the radius of the zone.

Figure 2.29: To the formation of nucleation exclusion zones in the solidification of melts. In the case of low heat conductivity of the melt, the latent heat of crystallization accumulates at the liquid–solid interface and the temperature, T_i, at the solid surface is close to the melting point. A gradient of the temperature from T_i to the bulk temperature T results (Curve 1). This leads to comparatively large radius, r_c, of the zones which is obtained by the intersection of the temperature profile with the critical temperature, T_c, for nucleation to occur. When the latent heat of crystallization is rapidly taken away from the interface, the temperature in the near vicinity of the solid surface is close to the bulk temperature far away of the crystallites (Curve 2) and nucleation exclusion zones are practically nonexistent. The crystallites themselves play the role of prohibited for nucleation zones.

T, of the melt. The intersection of the temperature profile (Curve 1) with the critical temperature, T_c, for nucleation to occur ($T_m - T_c$ is the critical undercooling), defines the radius of the zones with higher temperature or reduced undercooling around the growing crystallites in which the nucleation is more or less prohibited. When these zones overlap and fill up the whole volume of the melt, the nucleation process ceases and saturation of the nucleus density is reached (Christian 1981). Spaepen and Turnbull (1982) called this case "heat-flow control" or "soft impingement." In this case, the melt solidifies with a small number with greater size of grains.

In the case of high heat conductive melts, the temperature at the interface is low and close to the bulk temperature (Curve 2). The zones with reduced undercooling are, in fact, reduced to the growing crystallites themselves ("interface-limited growth",

"hard impingement" (Christian 1981; Spaepen and Turnbull 1982)). The final result is qualitatively the same, but a large number of smaller size grains are formed.

We have an analogous picture in deposition on substrates. Assuming that the surface diffusion of adatoms is the process which determines the rate of growth of the clusters from the gas phase, we have to account for the fact that the adatom concentration in the near vicinity of the growing nuclei is reduced and the system is *locally undersaturated.* As a result, zones with a reduced and even zero nucleation rate appear which grow together with the clusters (Lewis and Campbell 1967; Halpern 1969; Stowell 1970; Markov 1971). Sigsbee and Pound (1967) (see also Sigsbee 1969) coined the term "nucleation exclusion zones." Nucleation exclusion (also "depleted" or "denuded") zones have been easier observed in the vicinity of steps. Voigtänder *et al.* (1995) found that some surface active species (surfactants) (e.g., elements of Group III like In) increase the width of the depleted zones on the surface of Si(1 1 1), whereas the elements of Group V (As, Sb) make them narrower. When the zones overlap and cover the whole substrate surface, the nucleation ceases and the saturation nucleus density is reached. The saturation phenomenon has been observed in the case of deposition of gold on amorphous carbon films (Paunov and Harsdorff 1974), gold on cleaved surfaces of KCl, and NaF at low temperatures (Robinson and Robins 1970), etc.

In the same systems (Au/KCl(1 0 0), Au/NaF(1 0 0) but at high temperatures) Robins and Donohoe (1972) observed the appearance of maxima instead of plateaus. They explained this by the coalescence of crystallites which dominate at higher temperatures. Note that the first two reasons, namely, the presence of defect sites and the nucleation exclusion zones, lead to the appearance of saturation, whereas the coalescence leads to well-pronounced maximum.

The nucleation exclusion zones are easily visualized in the case of electrolytic nucleation of metals on inert substrates. In this case, the reduction of the supersaturation around the growing particles of the new phase is due predominantly to ohmic drop particularly in concentrated solutions of the electrolyte, but bulk diffusion toward the growing particles also takes a part particularly in dilute solutions.

Figure 2.30: Pulse train for visualization and investigation of the nucleation exclusion zones in electrodeposition of metals. The height and duration of the first pulse are chosen in such a way that only one nucleus is formed. It grows to a predetermined size during the second pulse. The height of the third pulse is chosen in such a way that the whole substrate surface is covered with metal nuclei except only for the zone around the initial droplet or small crystal. The metal coating which serves to outline the nucleation exclusion zone grows to become visible under the microscope during the fourth pulse. The sizes of the nucleation exclusion zones and the initial crystallites are then measured as functions of the duration and height of the second and third pulses. (I. Markov, A. Boynov and S. Toschev, *Electrochim. Acta* **18**, 377 (1973). By permission of Pergamon Press Ltd.)

A triple-pulse train as shown in Fig. 2.30 (Markov, Boynov and Toschev 1973; Markov and Toschev 1975) is imposed onto the cell consisting of a platinum single-crystal hemispherical cathode and an anode of the metal to be deposited, both immersed in a solution of the electrolyte. The first pulse produces a single nucleus which grows to visible size during the second pulse. The third pulse is high enough to ensure a complete coverage of the platinum sphere with the metal except for a "prohibited" area around the initial particle where the actual overpotential is insufficient to cause nucleation, thus visualizing the nucleation exclusion zones. Typical pictures of this phenomenon are shown in Fig. 2.31 in the cases of electrodeposition of mercury and silver.

The mathematical treatment of the process of overlapping of nucleation exclusion zones irrespective of the dimensionality of the system is usually carried out on the base of either the geometrical

(a)

(b)

Figure 2.31: Nucleation exclusion zones around (a) mercury droplet and (b) silver crystallites. It is clearly seen that the zones grow together with the crystallites. ((a) I. Markov, A. Boynov and S. Toschev, *Electrochim. Acta* **18**, 377 (1973). By permission of Pergamon Press Ltd. (b) By courtesy of A. Milchev.)

approach of Avrami (1939, 1940, 1941) or the probabilistic formalism developed by Kolmogorov (1937). (The problem was also independently considered by Johnson and Mehl (1939). A critical analysis has been given by Belen'ky (1980).) As shown in Fig. 2.32, the problem is reduced to the calculation of the hatched areas (or volumes) covered simultaneously by two or more circular (or spherical) regions. It can be solved geometrically (Avrami 1939, 1940, 1941), but as is well known, the area covered simultaneously by several regions is just equal to the probability of finding an arbitrary point simultaneously

Figure 2.32: A drawing illustrating the mathematical approach of Avrami (1939) and Kolmogorov (1937). In order to calculate the part of the volume (or the substrate surface) filled with circles representing the nucleation exclusion zones one has to subtract the shadowed regions covered simultaneously by two or more circles. This could be done geometrically (Avrami) or by using the probabilistic theory (Kolmogorov). It is clear that the fraction of the volume, or the surface covered by the shadowed regions, is equal to the probability of finding an arbitrary point simultaneously in two or more circles.

in all regions. That is why the probabilistic approach is much simpler and permits an easy generalization to account for the nucleation on active sites. We will give a detailed derivation of Kolmogorov's formula as we shall need it further when considering the 2D growth of crystals and epitaxial films.

As follows from the above, we have to calculate first the fraction of the surface area (or volume) of the sample which is covered by nucleation exclusion zones (in the case of soft impingement) or crystallites (in the case of hard impingement). Then, we make use of the result in order to calculate the saturation nucleus density. We emphasize that the dependence of the fraction of the volume that is solidified in a time t is a problem of the so-called mass crystallization which has an importance of its own, particularly in solidification of alloys (Christian 1981; Chernov 1984). This means that we solve in fact simultaneously two problems: mass crystallization and the saturation nucleus density.

We consider a supersaturated phase with a volume V that is sufficiently large as compared with the crystallites to be grown. Nuclei are spatially and temporally randomly formed with an average rate

$J_0 = \text{const}$. A nucleation exclusion zone with a volume V' appears and spreads around each growing nucleus. The rate of growth $v(\mathbf{n}, t)$ of the zone is a function of the direction $\mathbf{n}$ and time t and can be expressed in the form

$$v(\mathbf{n}, t) = c(\mathbf{n})k(t), \tag{2.137}$$

assuming the rate of growth $v(\mathbf{n}, t)$ follows one and the same law of growth $k(t)$ irrespective of the direction.

We introduce the quantity

$$c^3 = \frac{1}{4\pi} \int_\Sigma c^3(\mathbf{n}) d\sigma,$$

which has the sense of an average with respect to the direction and where the integration is carried out along the surface Σ of the sphere with a center in the origin of the coordinate system. Then, the volume of the zone growing around a nucleus formed at a moment t' will be at a moment $t > t'$:

$$V'(t', t) = \frac{4\pi}{3} c^3 \left(\int_{t'}^{t} k(\tau - t') d\tau \right)^3. \tag{2.138}$$

The density of nuclei N as a function of time is given by

$$\frac{dN}{dt} = J_0 \Theta(t), \tag{2.139}$$

where $\Theta(t)$ is the fraction of the volume of the system uncovered by nucleation exclusion zones. The integration of (2.139) subject to the initial condition $N(t = 0) = 0$ yields

$$N = J_0 \int_0^t \Theta(\tau) d\tau. \tag{2.140}$$

If we assume that Eq. (2.137) represents the growth low of the crystallites themselves rather than that of the nucleation exclusion zones (hard impingement or interface-limited growth), the quantity Θ will give the volume (or area) of the sample uncovered by crystallites. Then the quantity

$$\xi = \frac{V_c(t)}{V} = 1 - \Theta, \tag{2.141}$$

Figure 2.33: The calculation of the probability of finding an arbitrary chosen point P in a nucleation exclusion zone or in a crystallized volume. The necessary and sufficient condition for the point P to be in a nucleation exclusion zone at a moment t is that a nucleus is formed at a moment $t' < t$ at a point P′ which is spaced from P at a distance smaller than $r(t', t)$, i.e., in the volume outlined by the dashed line. Then, the point P will be in the nucleation exclusion zone outlined by the solid line.

where $V_c(t)$ is the crystallized volume at time t, represents the time dependence of the solidification of the sample, or the kinetics of the mass crystallization.

The fraction $\Theta(t)$ is equal to the probability, an arbitrary chosen point, P at a moment t to be outside a nucleation exclusion zone (Fig. 2.33). The necessary and sufficient condition the point P to be in a nucleation exclusion zone at a moment t is the formation of a nucleus at a moment $t' < t$ at another neighboring point P′ which is spaced from P at a distance smaller than

$$r = c \int_{t'}^{t} k(\tau - t') d\tau,$$

or in other words, the point P has to be in the volume V' given by Eq. (2.138).

The probability that at least one nucleus will form in the time interval $\Delta t'$ in a volume V' with accuracy to infinitesimals of second and higher orders is

$$J_0 V'(t', t) \Delta t'.$$

The probability that a nucleus will not form in the time interval $\Delta t'$ in the volume V' is

$$1 - J_0 V'(t', t)\Delta t'.$$

The probability for the point P to be outside a nucleation exclusion zone at a moment t from the beginning of the process is

$$\Theta(t) = \prod_{i=1}^{s} [1 - J_0 V'(t_i)\Delta t'], \tag{2.142}$$

where $t = s\Delta t'$ and $t_i = i\Delta t'$. Taking the logarithm of (2.142) yields

$$\begin{aligned} \ln \Theta(t) &= \sum_{i=1}^{s} \ln[1 - J_0 V'(t_i)\Delta t'] \cong -\sum_{i=1}^{s} J_0 V'(t_i)\Delta t' \\ &\cong -J_0 \int_0^t V'(t')dt'. \end{aligned}$$

Then the part of the volume V which is uncovered by nucleation exclusion zones is

$$\Theta(t) = \exp\left(-J_0 \int_0^t V'(t')dt'\right)$$

and

$$N = J_0 \int_0^t \exp\left(-J_0 \int_0^\tau V'(t')dt'\right) d\tau, \tag{2.143}$$

where $V'(t')$ is given by (2.138).

The saturation nucleus density N_s obtained from the condition $t \to \infty$ is

$$N_s = J_0 \int_0^\infty \exp\left(-J_0 \int_0^\tau V'(t')dt'\right) d\tau, \tag{2.144}$$

Assuming a constant rate of growth $k(t) = 1$ (the temperature does not change during the crystallization process),

$$V' = \frac{4}{3}\pi c^3 (t - t')^3$$

and (Kolmogorov 1937)

$$N(t) = J_0 \int_0^t \exp\left(-\frac{\pi}{3} J_0 c^3 t^4\right) dt.$$

Under the condition $t \to \infty$ for the saturation nucleus density, one obtains

$$N_s = 0.9 \left(\frac{J_0}{c} \right)^{3/4}.$$

The fraction ξ of the melt covered by growing crystallites (c is the rate of growth of the crystallites, "hard impingement") in time t is given by

$$\xi = 1 - \exp\left(-J_0 \int_0^t V'(t')dt' \right) = 1 - \exp\left(-\frac{\pi}{3} J_0 c^3 t^4 \right). \tag{2.145}$$

For the particular case when the nucleation process takes place in a short interval at the beginning of crystallization so that a number of nuclei, N_s, is formed at the initial moment $t = 0$, we have one integration less and, instead of the above equation, we get

$$\xi = 1 - \exp[-N_s V'(t')] = 1 - \exp\left(-\frac{4}{3} \pi N_s c^3 t^3 \right). \tag{2.146}$$

In the case of a nucleation on a surface, we have a 2D system and the volume V' (Eq. (2.138)) has to be replaced by the area of the nucleation exclusion zone

$$S'(t', t) = \pi c^2 \left(\int_{t'}^t k(\tau - t')d\tau \right)^2. \tag{2.147}$$

Then, we can consider by the same way the coverage of a crystal face by laterally growing 2D nuclei. The 2D islands themselves will play the role of nucleation exclusion zones and with a constant growth rate $k(t) = 1$ the surface coverage at a moment t will be given by

$$\xi = \frac{S_c}{S} = 1 - \exp\left(-\frac{\pi}{3} J_0 c^2 t^3 \right), \tag{2.148}$$

where c is the rate of growth of the 2D nuclei and S is the surface area of the crystal face.

Equations (2.145), (2.146), and (2.148) represent different cases of solidification kinetics. A detailed analysis of the effect of the dimensionality of the system in which the phase transformation takes place, the mechanism of nucleation, the mechanism of growth of the nuclei,

the shape of the growing crystallites, etc. have been carried out by Christian (1981). A general expression can be written in the form

$$\xi = 1 - \exp(-kt^n), \tag{2.149}$$

where the exponent n can take different values depending on the factors counted above. Thus, the value of the time exponent n could give valuable information about the kinetics of the crystallization process and can be found from the slope of the so-called log–log plot which is obtained by the linearization of the experimental $\xi(t)$ curves in coordinates $\ln[\ln(1-\xi)]$ against $\ln(t)$.

The value of the exponent n in the solidification of melts depends strongly on the mechanism of growth of the crystallites and their shape (Christian 1981). As described above (Fig. 2.29), they can grow either in a heat-flow regime (soft impingement) or in an interface-reaction regime (hard impingement). In the latter case, $n = 4$ and 3 at the constant nucleation rate and zero nucleation rate (instantaneous nucleation at $t = 0$), respectively. But n can be smaller than 3 in the case of nucleation on existing grains. In the case of the heat-flow regime, $n = 2, 5$ and 1.5 at constant and zero nucleation rate at all crystallite shapes, respectively, and to unity in the cases of growth of platelets or needles. In addition, as shown above, the kinetics of solidification is derived assuming a steady-state nucleation rate. Thus, the interpretation of the results can be confused by the transient character of nucleation which is the usual case in solidification in melts.

Figure 2.34 shows the results of solidification of amorphous thin films of $CoSi_2$ (Liang *et al.*, 1994). The average slope gives a value $n \approx 4$ which is an indication that the nucleation process takes place randomly in the bulk of the amorphous film with a constant rate (progressive nucleation). In other words, instantaneous nucleation in the beginning of the solidification (Eq. (2.146)) is ruled out and the process of nucleation is 3D irrespective of the small thickness of the film. It is also concluded that the rate of the growth of the crystallites is constant ($k(t) = 1$) which is an indication of interface-limited growth and "hard impingement" of the spherulites.

Figure 2.34: (a) ξ (t) curves and (b) log–log plot in the case of crystallization of $CoSi_2$. The S-shaped curves are clearly demonstrated. The log–log plot shows straight lines with nearly equal slope. (J.M. Liang, L.J. Chen, I. Markov, G.U. Singco, L.T. Shi, C. Farrell, K.N. Tu, *Mater. Chem. Phys.* 38, 250 (1994) By permission of Elsevier.)

The active sites and the nucleation exclusion zones usually influence simultaneously the nucleation kinetics. A general solution can be obtained by following the same procedure as above. We consider for simplicity the case of equal activity of the nucleation centers with the steady-state nucleation rate.

Nuclei are formed with a frequency $J_0(s^{-1})$ on active centers whose number is N_d. To solve the problem, we have to find the fraction of free active centers at a moment t. We consider as free those centers on which nuclei have not yet formed and which are not captured by nucleation exclusion zones. The latter means that a center on which nucleus has not yet formed can be covered by a zone originated by a nucleus growing in the near vicinity. Then, the supersaturation in its vicinity can become lower than its critical supersaturation and a nucleus cannot form anymore on it. In that sense, the center can be deactivated.

The probability of formation of at least one nucleus in the volume V' (Eq. (2.138)) within the time interval $\Delta t'$ is now given by

$$J_0 N_d [V'(t')] \Delta t',$$

where

$$N_d[V'(t')] = 1 + (N_d - 1)\frac{V'(t')}{V}$$

is the average number of the active sites in the volume $V'(t')$. This equation accounts for the fact that in the volume $V'(t')$ there is one center with a probability of unity (the center P) and the remaining $N_d - 1$ centers with a probability of $V'(t')/V$. Then, the fraction $\Theta(t)$ of the free centers on which nuclei are not yet formed and which are not covered by nucleation exclusion zones ($N_d \gg 1$) will be

$$\Theta(t) = \exp\left(-J_0 t - J_0 N_d \int_0^t \frac{V'(t')}{V} dt'\right). \tag{2.150}$$

The time dependence of the number N of nuclei formed up to time t is given by the definition equation

$$N(t) = J_0 N_d \int_0^t \Theta(\tau) d\tau$$

or

$$N(t) = J_0 N_d \int_0^t \exp\left(-J_0 \tau - J_0 N_d \int_0^\tau \frac{V'(t')}{V} dt'\right) d\tau. \tag{2.151}$$

It is immediately seen that when the zone growth rate $c = 0$, i.e., $V'(t') = 0$, Eq. (2.151) turns into Eq. (2.135). In the other extreme, when the number of the active centers is large enough or the rate of growth of the nucleation exclusion zones is sufficiently high so that the second term in the exponential is much greater than $J_0 t$, Kolmogorov's formula (2.143) results from (2.151). The physical meaning of this result is that the major part of the active centers are deactivated by nucleation exclusion zones and the latter govern the nucleation kinetics. Generalization for the time-dependent nucleation and activity distribution of the centers is easy to carry out and the interested reader is referred to the original papers (Markov and Kashchiev 1972a, 1972b, 1973).

At the end of this chapter, we consider briefly the problem of nucleus density in thin-film growth, and in particular the scaling of the nucleus density with the ratio, D/F, of the hopping frequency $D = \nu \exp(-E_{\mathrm{sd}}/kT)$ and the atom arrival rate F measured in

the number of MLs per unit time. Our considerations are based on the *rate equation approach* introduced in 1966 by Zinsmeister (1966, 1968, 1969, 1971) and elaborated further by numerous investigators (Venables 1973, 1979; Venables *et al.*, 1984; Stoyanov and Kashchiev 1981). For more recent developments of the theory, the reader is referred to the papers of Bales and Chrzan (1994), Bales and Zangwill (1997), Ratsch *et al.* (1994), Amar, Family and Lam (1994), Amar and Family (1995, 1996, 1997), and the references therein.

We assume that the critical nucleus consists of one atom, the pair of atoms being stable, or in other words, we accept that the aggregation process is irreversible. The atoms arrive at the crystal surface, diffuse on it, and meet each other to produce stable and immobile dimers. The latter grow further by the attachment of single atoms which join the clusters upon striking. This means that there is not any barrier of kinetic origin that inhibits the growth of the clusters or the nucleus formation, and the growth takes place in a diffusion regime (see Sec. 3.2.1.1). Coalescence of immobile or diffusing clusters is ruled out. Then, we can write the simplest set of rate equations in the form

$$\frac{dn_1}{dt} = F - 2Dn_1^2 - Dn_1N \tag{2.152a}$$

$$\frac{dN}{dt} = Dn_1^2, \tag{2.152b}$$

where n_1 is the density of single atoms, and

$$N = \sum_{i=2}^{\infty} n_i, \tag{2.153}$$

is the density of stable clusters. Both densities are expressed in units of the density N_0 of the adsorption sites of the surface. The second and the third terms on the right-hand side of Eq. (2.152a) accounts for the disappearance of single atoms owing to the formation of stable dimers and the growth of larger clusters, respectively. The number 2 before the second term accounts for the fact that two single atoms are consumed in order to produce a pair of atoms. Equation (2.152b) represents simply the nucleation rate as given by Eq. (2.113).

In the very beginning of deposition, most of the single atoms are consumed by dimer formation. With the progress of deposition, the density of the stable clusters increases and atoms arriving at the surface join preferentially stable clusters rather than meet each other to produce new stable dimers. A saturation is nearly reached and the nucleation term $2Dn_1^2$ becomes negligibly small as compared to the growth term Dn_1N. Assuming at this stage a steady state is reached ($dn_1/dt = 0$) gives for the density of monomers $n_1 = F/D_sN$. Substituting the latter in Eq. (2.152b) and carrying out the integration result in

$$N \propto \left(\frac{D}{F}\right)^{-1/3} \theta^{1/3}, \tag{2.154}$$

where $\theta = Ft$ is the amount of material deposited.

The above result can be easily generalized for an arbitrary size, i^*, of the critical nucleus. In other words, we accept a reversible nucleation process. Instead of the set (2.152), we make use of Eq. (2.117) and write (Venables *et al.*, 1984)

$$\frac{dn_1}{dt} = F - (i^* + 1)Dn_1^{i^*+1} - Dn_1N, \tag{2.155a}$$

$$\frac{dN}{dt} = \omega^* Dn_1^{i^*+1}, \tag{2.155b}$$

where $\omega^* = \alpha^* \exp(E^*/kT)$ (Eq. (2.117)). The second term in Eq. (2.155a) gives again the number of atoms consumed to produce a stable cluster of $i^* + 1$ atoms, and Eq. (2.155b) is again the nucleation rate as given by the general Eq. (2.117). Note that in this case N is given again by Eq. (2.153), but the summation is carried out from $i^* + 1$. We follow the same procedure as above, neglecting the nucleation term at some stage of deposition when the adatom concentration reaches a steady state. Substituting $n_1 = F/DN$ in Eq. (2.155b) gives upon integration

$$N \propto \left(\frac{D}{F}\right)^{-\chi} \theta^{1/(i^*+2)}, \tag{2.156}$$

where

$$\chi = \frac{i^*}{i^* + 2} \tag{2.157}$$

is the scaling exponent.

Kandel (1997) relaxed the condition for the diffusion regime of deposition assuming that a barrier exists which hinders the incorporation of single atoms to clusters of any size. The growth proceeds in a kinetic regime which means that the rate of crystallization is controlled by the attachment of atoms to the clusters rather than by the diffusion on the crystal surface (see Sec. 3.2.1.1). This resulted in a scaling behavior of N as before (Eq. (2.156), the exact expression will be derived in Sec. 3.2.5.2) but with a scaling exponent

$$\chi = \frac{2i^*}{i^* + 3}. \tag{2.158}$$

The scaling exponent (2.157) varies with i^* from 1/3 to 1, whereas (2.158) has values larger than unity already at $i^* > 2$. Thus, one can distinguish between diffusion and kinetic regimes of growth if χ is smaller or greater than unity. Examples of the scaling exponent (2.158) have been reported in surfactant-mediated epitaxial growth — the homoepitaxy of Si on the Sn precovered surface of Si(1 1 1) (Iwanari and Takayanagi 1992), and of Ge on the Pb precovered surface of Si(1 1 1) (Hwang *et al.*, 1998). In the latter paper a value of $\chi = 1.76$ has been found from the plot of $\ln N$ vs $\ln F$. In the case of the homoepitaxial growth of Si(1 1 1) under clean conditions, a value of $\chi = 0.85$ has been obtained from the same plot $\ln N - \ln F$ (Voigtländer *et al.*, 1995). It could be concluded that the nucleation process takes place either in a diffusion regime with $i^* = 6$ or in a kinetic regime with $i^* = 2$. The latter seems more reasonable, bearing in mind the comparatively low temperature of growth (<700 K) and that Si is a very strong bonded material. A two-atom nucleus can be thought of consisting of an atom in the lower half-layer and an atom belonging to the upper half-layer, both connected by a first-neighbor bond. The third atom that stabilizes the nucleus belongs again to the lower half-layer and is connected to two first-neighbor bonds to the upper atom and the underlying bilayer. Thus, in order to detach

an atom from the stable cluster, one has to break simultaneously two first-neighbor bonds and to spend an energy which is of the order of the latent heat of evaporation of Si — 4.2 eV (Hultgren *et al.*, 1973).

As mentioned at the beginning of this section, the coalescence of growing crystallites can also lead to the limitation of the nucleus density. The reader is referred to the numerous review papers and monographs (Stoyanov and Kashchiev 1981; Lewis and Anderson 1978) and the references therein.

2.2.12 *Ostwald's step rule*

It was found long ago that when the new phase has several (at least two) modifications, one of which is thermodynamically stable and the others are metastable, the formation of one or more metastable phases is often (but not always) observed first. A typical example is the crystallization of zeolites (for a review see Barrer 1988). It appears that the first zeolite which crystallizes is not stable when it is left for some time in the reaction vessel in contact with the solution at the temperature of growth. After some time, it dissolves in to the mother solution and a new more stable type of zeolite crystallizes at the expense of the first one. The second type can also dissolve and a third type of zeolite nucleates and grows. Thus, for example, the first type of zeolite (faujasite, pore size 7.4 Å) is replaced by mazzite (ZSM-4) which is more dense (pore size 5.8 Å). At about 100°C, the faujasite displays a maximum yield after approximately 20 h of crystallization time. The mazzite first appears at the time of the maximum of the faujasite and reaches a maximum yield after 40 h more (Rollmann 1979). If the first zeolite is isolated from the mother solution, it remains usually stable for quite a long time which is an indication that the transformation occurs through dissolution and crystallization in the mother phase. A similar step-like behavior shows the crystallization of amorphous Si–Ti alloy upon annealing at 500°C (Wang and Chen 1992). Ti_5Si_3, Ti_5Si_4, TiSi, and $TiSi_2$ nucleate and grow consecutively. After sufficiently long annealing, the thermodynamically most stable phases $TiSi_2$ and TiSi are only present.

It was Ostwald (1897) who first compiled the available observations and gave his famous empirical rule according to which the thermodynamically metastable phase should nucleate first. Then, at a later stage, the metastable phase should transform into the phase which is thermodynamically stable under the given conditions (temperature and pressure). Thus, the formation of the new stable phase should take place by consecutive steps from one phase to another with increasing thermodynamic stability. The first theoretical interpretation of this phenomenon which is known as Ostwald's step rule was given by Stranski and Totomanow (1933) in terms of the steady-state nucleation rate. They showed that more often the metastable phase should have a higher nucleation rate provided the system has not been transferred very far below the transformation point. We will repeat here in more detail their considerations.

We consider for simplicity the phase diagram given in Fig. 2.35. We know that the liquid can be undercooled to considerable temperature without visible crystallization to take place. This means that the liquid phase can, in principle, nucleate and grow from the vapor phase when the system is supersaturated (undercooled) below the triple point, i.e., along the lines AA' or AA''. The liquid phase will be metastable and should solidify at a later stage. We have to compare now the steady-state rates of nucleation of metastable liquid droplets and stable crystallites. The considerations are valid for any crystallization process which includes more than one new phase. We will assume for simplicity that the pre-exponential factors K_1 (see Eq. (2.68)) are equal. Having in mind Eq. (2.68) for the ratio of the nucleation rates holds

$$\ln\left(\frac{J_{0\mathrm{m}}}{J_{0\mathrm{s}}}\right) = \frac{b_s\sigma_s^3 v_s^2}{kT\Delta\mu_s^2} - \frac{b_m\sigma_m^3 v_m^2}{kT\Delta\mu_m^2},$$

where the subscripts s and m refer to the stable and the metastable phases, respectively, and b_s and b_m are geometric factors. It follows that the nucleation rate of the metastable phase will be higher, or in other words, Ostwald's step rule will be valid, when the first term on the right-hand side is greater than the second one.

Figure 2.35: Part of the phase diagram shown in Fig. 1.1 near the triple point O. The solid lines denoted by SV and LV give the solid–vapor and liquid–vapor equilibrium, respectively. The dashed line denoted by m is a continuation of the LV line in the region of stability of the crystal phase and gives the equilibrium between the vapor phase and the metastable liquid phase. As shown, the equilibrium vapor pressure $P_{0\mathrm{m}}$ of the metastable liquid is higher than the equilibrium vapor pressure $P_{0\mathrm{s}}$ of the stable crystal phase. It follows that at any temperature $T < T_{\mathrm{tr}}$, the supersaturation $\Delta\mu_s = kT\ln(P/P_{0\mathrm{s}})$ with respect to the stable phase will be higher than the supersaturation $\Delta\mu_m = kT\ln(P/P_{0\mathrm{m}})$ with respect to the metastable phase.

The stable phase is usually more dense so $v_s < v_m$. On the other hand, the more dense phase has greater specific surface energy than the less dense phase, i.e., $\sigma_s > \sigma_m$, as the density of unsaturated dangling bonds on the surface is greater. Near the triple point, or near any point of transformation, for which the equilibrium vapor pressures (or solubilities) are equal, i.e., $P_{0\mathrm{s}} = P_{0\mathrm{m}}$ (or $C_{0\mathrm{s}} = C_{0\mathrm{m}}$), the supersaturations $\Delta\mu_s = kT\ln(P/P_{0\mathrm{s}})$ and $\Delta\mu_m = kT\ln(P/P_{0m})$ are equal. Taking into account the third power of the surface energy and the second power of the molecular volume, one could anticipate that the specific surface energy will overcompensate the influence of

the molecular volume and the geometric factors and

$$b_s\sigma_s^3 v_s^2 > b_m\sigma_m^3 v_m^2, \tag{2.159}$$

which is the necessary and sufficient condition for Ostwald's step rule to hold.

The situation becomes more complicated far from the point of transformation. As shown in Fig. 2.35, the equilibrium vapor pressure P_{0m} of the metastable phase will be greater than $P_{0\mathrm{s}}$ of the stable phase. Then, $\Delta\mu_s > \Delta\mu_m$ at one and the same pressure in the system. Then, in order the Ostwald's step rule to hold (2.159) should be replaced by

$$\left(\frac{\Delta\mu_s}{\Delta\mu_m}\right)^2 < \frac{b_s}{b_m}\left(\frac{\sigma_s}{\sigma_m}\right)^3\left(\frac{v_s}{v_m}\right)^2, \tag{2.160}$$

where

$$\frac{\Delta\mu_s}{\Delta\mu_m} = \frac{\ln(P/P_{0\mathrm{s}})}{\ln(P/P_{0\mathrm{m}})} = \frac{\ln(P/P_{0m}) + \ln(P_{0m}/P_{0\mathrm{s}})}{\ln(P/P_{0\mathrm{m}})} > 1. \tag{2.161}$$

The ratio $\Delta\mu_s/\Delta\mu_m$ is always greater than unity as $P_{0\mathrm{m}}$ is always higher than $P_{0\mathrm{s}}$ by definition.

The physical meaning of (2.160) is immediately shown in Fig. 2.36 where the corresponding works of nucleus formation are plotted vs the actual vapor pressure in the system. The metastable phase begins to nucleate at higher vapor pressure $P_{0\mathrm{m}}$ and initially the work of formation of nuclei of the metastable phase is greater than that of the stable one. Beyond some critical pressure P_{cr}, both curves intersect each other, and the nucleation of the metastable phase becomes thermodynamically favored. When the vapor pressure is lower than P_{cr} but higher than P_{0m}, $\Delta\mu_{\mathrm{m}}$ becomes very small and the ratio $\Delta\mu_s/\Delta\mu_m$ can become large. The sign in (2.160) is changed and the stable phase will nucleate first. At very small vapor pressures such that $P_{0\mathrm{s}} < P < P_{0\mathrm{m}}$, only the stable phase will nucleate.

The main obstacle in applying Eqs. (2.159) and (2.160) is the lack of knowledge about the specific surface energies particularly at the interfaces between condensed phases. One can circumvent this obstacle in nucleation in melts by using the finding of Turnbull (1950) that the molar surface energies $\sigma_{\mathrm{mol}} = \sigma N_{\mathrm{A}} v_c^{2/3}$ of materials with the same

Figure 2.36: Plot of the works of formation of nuclei of the stable, ΔG_s^*, and metastable, ΔG_m^*, phases vs the vapor pressure. $P_{0\mathrm{s}}$ and $P_{0\mathrm{m}}$ denote the corresponding equilibrium vapor pressures. Both curves intersect at some critical vapor pressure P_{cr}, beyond which $\Delta G_m^* < \Delta G_s^*$. Nucleation of the metastable phase is expected at $P > P_{\mathrm{cr}}$.

nature of the chemical bonds are proportional to the corresponding enthalpies of melting (Jackson 1966) (see Fig. 2.29 and Table 2.1). We can assume that the proportionality constant is one and the same for the different phases and that the nuclei have one and the same shape, i.e., $b_s = b_m$. Recalling Eq. (1.12), Eq. (2.160) turns into

$$\frac{(1 - T/T_s)^2}{(1 - T/T_m)^2} < \frac{\Delta h_s}{\Delta h_m}. \tag{2.162}$$

In the case when the melting points T_m and T_s of both phases are nearly the same, Ostwald's step rule will be observed if the corresponding enthalpies of melting Δh_m and Δh_s obey the inequality

$$\Delta h_m < \Delta h_s, \tag{2.163}$$

which follows from (2.159).

The problem becomes more complicated if the transient effects in nucleation have to be accounted for. The necessity of doing that arise from the fact that if the induction period of nucleation of the metastable phase is much longer than that of the stable phase, the metastable phase will not crystallize, although its steady-state nucleation

rate could be higher. As shown above, the transient effects play a considerable role in nucleation from solutions and melts, while they can be neglected in nucleation from a vapor phase. When considering the problem, we will follow, in general, the treatment of Gutzow and Toschev (1968).

We will denote by the subscripts s and m the induction periods of the stable and metastable phases. It is seen from Eqs. (2.130) and (2.131) that τ is directly proportional to the geometric factor b and the specific surface energy σ and inversely proportional to the square of the supersaturation. Then, the condition $\tau_m < \tau_s$ leads to

$$1 < \left(\frac{\Delta\mu_s}{\Delta\mu_m}\right)^2 < \frac{b_s}{b_m}\frac{\sigma_s}{\sigma_m}. \tag{2.164}$$

Then the combination of (2.160) and (2.164) gives rise, in principle, to the following four possibilities:

1. $J_{0\mathrm{m}} > J_{0\mathrm{s}}$ and $\tau_m < \tau_s$ (Fig. 2.37(a)):

$$1 < \left(\frac{\Delta\mu_s}{\Delta\mu_m}\right)^2 < \frac{b_s}{b_m}\frac{\sigma_s}{\sigma_m} < \frac{b_s}{b_m}\left(\frac{\sigma_s}{\sigma_m}\right)^3\left(\frac{v_s}{v_m}\right)^2. \tag{2.165}$$

   The above holds when the cube of the ratio of the specific surface energies overcompensates the square of the ratio of the molecular volumes. The metastable phase will nucleate first with a higher rate.
2. $J_{0\mathrm{m}} > J_{0\mathrm{s}}$ and $\tau_m > \tau_s$ (Fig. 2.37(b)):

$$1 < \frac{b_s}{b_m}\frac{\sigma_s}{\sigma_m} < \left(\frac{\Delta\mu_s}{\Delta\mu_m}\right)^2 < \frac{b_s}{b_m}\left(\frac{\sigma_s}{\sigma_m}\right)^3\left(\frac{v_s}{v_m}\right)^2. \tag{2.166}$$

   The metastable phase will nucleate at a later stage but with a higher rate.
3. $J_{0\mathrm{m}} < J_{0\mathrm{s}}$ and $\tau_m > \tau_s$ (Fig. 2.37(c)):

$$1 < \frac{b_s}{b_m}\frac{\sigma_s}{\sigma_m} < \frac{b_s}{b_m}\left(\frac{\sigma_s}{\sigma_m}\right)^3\left(\frac{v_s}{v_m}\right)^2 < \left(\frac{\Delta\mu_s}{\Delta\mu_m}\right)^2. \tag{2.167}$$

Figure 2.37: Four possible cases of the time dependence of the nucleation rates of the stable, J_s, and the metastable, J_m, phases: (a) $J_{0\mathrm{m}} > J_{0\mathrm{s}}$, $\tau_m < \tau_s$, (b) $J_{0\mathrm{m}} > J_{0\mathrm{s}}$, $\tau_m > \tau_s$, (c) $J_{0\mathrm{m}} < J_{0\mathrm{s}}$, $\tau_m > \tau_s$, (d) $J_{0m} < J_{0s}$, $\tau_m < \tau_s$. τ_m and τ_s denote the incubation periods of the metastable and stable phases, respectively (after Gutzow and Toschev 1968).

The stable phase will nucleate first and its rate of nucleation will be greater. Ostwald's step rule will not be observed.

4. $J_{0\mathrm{m}} < J_{0\mathrm{s}}$ and $\tau_m < \tau_s$ (Fig. 2.37(d)):

$$1 < \frac{b_s}{b_m}\left(\frac{\sigma_s}{\sigma_m}\right)^3\left(\frac{v_s}{v_m}\right)^2 < \left(\frac{\Delta\mu_s}{\Delta\mu_m}\right)^2 < \frac{b_s}{b_m}\frac{\sigma_s}{\sigma_m}. \tag{2.168}$$

The metastable phase will nucleate first, but its nucleation rate will be lower. The occurrence of this case requires a drastic change in chemical bonding and should be a rare event.

The theoretical analysis presented so far leads to the conclusion that, in general, the crystallization of the thermodynamically less

stable phase is more pronounced when the square of the supersaturation ratio $\Delta\mu_m/\Delta\mu_s$ is smaller. Bearing in mind (2.161) the latter means that Ostwald's step rule will operate when crystallization takes place near the transformation temperature and/or at very high supersaturations. Going below from the transformation temperature leads to gradual transition from case 1 to case 3.

Chapter 3

Crystal Growth

One can say that the building units (atoms or molecules) become a part of the crystal when their chemical potential becomes equal to the chemical potential of the crystal. As discussed in Chapter 1, the latter is equal at absolute zero to the work necessary to detach a building unit from the half-crystal or kink position taken with a negative sign. In other words, when the atoms or the molecules are attached to kink positions or even stronger (positions 1 and 2 in Fig. 1.19) they become a part of the crystal. In any other position, they are connected more weakly to the crystal surface than atoms in the kink position and their equilibrium vapor pressure and in turn their chemical potential will differ from that of the bulk crystal. In this sense, the adsorption of atoms on the crystal surface or along the steps cannot be considered as crystal growth. All this is valid when the crystal is in contact with a supersaturated ambient phase, i.e., when the chemical potential of the latter is greater than that of the crystal. In equilibrium, the chemical potential of the adlayer will be equal to that of the crystal and of the parent phase.

The mechanism of crystal growth is unambiguously determined by the structure of the crystal surfaces. S and K faces offer kink sites enough for their growth. F faces can grow without the necessity of overcoming an energy barrier beyond the roughening temperature. Below this temperature, the F faces are smooth and their growth requires the formation of two-dimensional (2D) nuclei or the presence of screw dislocations to ensure steps with kink sites along them. In

this chapter, we consider first the growth of rough faces or the so-called *normal mechanism* of growth. Then, the growth of defectless crystal faces through formation and lateral spreading of 2D nuclei, and the *spiral growth* of F faces containing screw dislocations are considered separately. In all cases, the peculiarities of the growth from melts, solutions, and vapors are accounted for.

3.1 Normal Growth of Rough Crystal Faces

We consider in this chapter the growth of rough faces without making distinction for the reason of their roughness. The latter can be due either to the crystallographic orientation of the face or to the entropy effects at sufficiently high temperatures. In any case, the change of the energy of a building unit when shifting the latter across the phase boundary between the crystal and the ambient phase (vapor, melt, or solution) has schematically the shape shown in Fig. 3.1. The lowest energy state on the left-hand side of the boundary represents the energy of the building unit incorporated at a kink position,

Figure 3.1: Schematic variation of the free energy for the thermally activated transfer of building units across the interface between the ambient phase and the crystal. The lower state corresponds to a building unit in a half-crystal position. Δh is the corresponding enthalpy of the transition (sublimation, dissolution or fusion). ΔU is the kinetic barrier for the incorporation of the building units into the half-crystal position connected with preceding chemical reactions, desolvation in solution growth or viscous flow in growth in melts.

whereas the line on the right-hand side gives the average value of the energy of the unit in the ambient phase. The difference between both levels gives the enthalpy of the corresponding phase transition (sublimation, dissolution, or melting). The barrier at the phase boundary with a height ΔU can have different nature in different media as discussed in the previous chapter. Thus, in growth from vapors, the barrier can be due to preceding chemical reaction, such that the pyrolysis of silane (SiH_4) in chemical vapor deposition (CVD) of Si or arsine (AsH_3) in metal-organic chemical vapor deposition (MOCVD) of GaAs. More complex molecules should overcome an energetic barrier in order to occupy the correct orientation, i.e., we have a barrier of steric character. In the cases of growth in solutions and melts, the energy barrier ΔU can be identified with the energies of desolvation and viscous flow, respectively, as discussed in Chapter 2.

Experimental evidence concerning the roughening temperature shows that metallic crystals in contact with their vapors remain faceted up to the melting point. Heyraud and Metois (1980) observed (1 1 1) and (0 0 1) facets on the surface of rounded gold crystallites on graphite up to 1303 K ($T_m = 1337$ K). The same authors (Metois and Heyraud 1982; Heyraud and Metois 1983) found that with increasing temperature the (1 1 1) and (1 0 0) facets on the surface of Pb crystallites on graphite diminish in size but are still persistent at 300°C (T_m(Pb) = 327.5°C). Pavlovska *et al.* (1989) studied the equilibrium shape of small Pb crystals (10–20 μm) and found that the most closed packed (1 1 1) faces were visible up to the melting point. The less closed packed (1 1 0) face which is an S face disappears at 40 K lower than the melting temperature (Frenken and van der Veen 1985). Tin (Zhdanov 1976), zinc (Heyer, Nietruch and Stranski 1971), and copper (Stock and Menzel 1978, 1980) in contact with their vapors did not show roughening transition up to the corresponding temperatures of melting. On the contrary, vicinal surfaces of refractory metals such as Ta ($T_m = 3269$ K, (Vanselow and Li 1993)) and Rh ($T_m = 2239$K, (Vanselow and Li 1994)) showed well-pronounced roughening and sharp increase of the growth rate at temperatures of the order of 700–900 K. Well-pronounced roughening transitions below the melting point show usually organic crystals such as dyphenyl (Nenow and

Dukova 1968; Pavlovska and Nenow 1971a, 1971b; Nenow, Pavlovska and Karl 1984), naphthalene (Pavlovska and Nenow 1972), carbon tetrabromide (Pavlovska and Nenow 1977), and adamantane (Pavlovska 1979). For review, see also Nenow (1984). We can conclude that crystals of practical importance with stronger interatomic bonds in contact with their vapors should be faceted up to the melting point and should grow from vapors by the spiral or 2D nucleation mechanism, whereas organic crystals should grow by the normal mechanism at elevated temperatures and 2D nucleation or spiral mechanism at lower temperatures. We consider first the normal mechanism of growth from melts.

The rate of growth is proportional to the net flux of atoms:

$$R = a\left(\frac{a}{\delta}\right)^2 (j_+ - j_-), \tag{3.1}$$

where δ is the average spacing of the kink sites and $(a/\delta)^2$ is the geometrical probability of a building unit arriving at the crystal surface to find a kink site. j_+ and j_- are, respectively, the fluxes of attachment and detachment of building units per site of growth to and from the growing surface given by Eqs. (2.96) and (2.97). Substituting (2.96) and (2.97) into (3.1) gives

$$R = a\nu\left(\frac{a}{\delta}\right)^2 \exp\left(-\frac{\Delta s_m}{k}\right) \exp\left(-\frac{\Delta U}{kT}\right) \times \left\{1 - \exp\left[-\frac{\Delta h_m}{k}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right]\right\}.$$

The term in the square brackets is precisely equal to $\Delta\mu/kT$ (see Eq. (1.12)) and

$$R = a\nu\left(\frac{a}{\delta}\right)^2 \exp\left(-\frac{\Delta s_m}{k}\right) \exp\left(-\frac{\Delta U}{kT}\right)\left[1 - \exp\left(-\frac{\Delta\mu}{kT}\right)\right].$$

Rough faces can grow at any supersaturation higher than zero. Expanding the exponent in the Taylor series up to the linear term for small supersaturations ($\Delta\mu \ll kT$), the rate of growth becomes

directly proportional to the latter

$$R = \beta_m \Delta T, \tag{3.2}$$

where

$$\beta_m = a\nu \frac{\Delta s_m}{kT} \left(\frac{a}{\delta}\right)^2 \exp\left(-\frac{\Delta s_m}{k}\right) \exp\left(-\frac{\Delta U}{kT}\right) \tag{3.3}$$

is known as the *kinetic coefficient* for crystallization in melts (Chernov 1980). As seen, the latter depends on the entropy of the phase transition, the energy barrier ΔU, and the degree of roughness accounted for by the probability $(a/\delta)^2$ to find a kink site. When the average kink spacing δ tends to infinity, the kinetic coefficient and in turn the rate of growth go to zero, thus reflecting the simple fact that atomically smooth crystal faces cannot grow through the normal mechanism. Expressions similar to (3.2) and (3.3) have been derived by Wilson (1900) and Frenkel (1932).

As seen, the dependence of the growth rate of rough crystal faces on the supersaturation is linear for small values of the latter. In other words, the rough crystal surface behaves as the surface of a liquid. The atomically smooth crystal faces require the formation of steps to ensure kink sites along them. Then, the kink spacing δ will depend on the step density and, thus, on the rate of formation of 2D nuclei or on the distance between the consecutive coils of the growth spirals. As will be shown below, the latter is also a function of the supersaturation through the radius of the 2D nuclei which is a nonlinear function of the supersaturation. It follows that in all other cases, except for the rough surfaces, the growth rate will be a nonlinear function of the supersaturation.

The theory of normal growth from melts was extended to cover the case of growth of small rounded crystallites (Machlin 1953). The derivation is exactly the same as the one given by Burton, Cabrera, and Frank (1951) for the lateral growth of 2D islands (see Sec. 3.2.1.1). The result (see Christian 1982) is

$$R(r) = R\left(1 - \frac{r^*}{r}\right),$$

where r^* is the radius of the critical nucleus and R is given by Eq. (3.2). Obviously, this equation is valid in the initial stages of the

crystallization process when the radius of the growing crystal grain is comparable with the radius of the critical nucleus. It is important to note, however, that according to the above equation, smaller crystallites grow more slowly than larger crystallites. Besides, this equation states that the rate of growth of a crystallite whose size is equal to that of the critical nucleus is equal to zero. In other words, such a crystallite is in equilibrium with the parent phase.

For the growth of Si from its melt with $\Delta s_m/k = 3.5$, $T_m = 1685$ K, $a \cong 3 \times 10^{-8}$ cm, $\delta = 3a$, $\nu = 1 \times 10^{13}$ s^{-1}, and $\Delta U/RT_m \cong 3$, the kinetic coefficient has the value $\beta \cong 0.1$ cm s^{-1}K^{-1}. At the same time for the growth of Ag with $\Delta s_m/k = 1.2$ and $\Delta U/RT_m \cong 1$, $\beta \cong 10$ cm s^{-1}K^{-1}.

In the case of growth from solutions, the growth flux is given by

$$j_+ = \nu C v_c \exp\Big(-\frac{\Delta U}{kT}\Big), \tag{3.4}$$

where C is the concentration of the solute at the crystal–solution interface in units of number of molecules in a cubic centimeter, v_c is the volume of a building unit in the crystal phase. The product Cv_c is, thus, the probability to find an atom in the vicinity of a kink site.

The reverse flux is

$$j_- = \nu(1 - Cv_c) \exp\Big(-\frac{\Delta h_d + \Delta U}{kT}\Big), \tag{3.5}$$

where $1 - Cv_c$ is the probability the space around the kink site to be free of a solute particle and Δh_d is the enthalpy of dissolution.

In equilibrium $C = C_0$ (C_0 is the equilibrium concentration at a temperature T), both fluxes are equal and

$$\exp\Big(-\frac{\Delta h_d}{kT}\Big) = \frac{C_0 v_c}{1 - C_0 v_c}. \tag{3.6}$$

Making use of this relation and Eqs. (3.1), (3.4), and (3.5) gives for the growth rate

$$R = \beta_s v_c (C - C_0), \tag{3.7}$$

where

$$\beta_s = \frac{a\nu}{C_0 v_c}\left(\frac{a}{\delta}\right)^2 \exp\left(-\frac{\Delta h_d + \Delta U}{kT}\right) \tag{3.8}$$

is the kinetic coefficient for crystallization in solutions.

Replacing Δh_d by C_0 through (3.6) gives for β_s in the case of dilute solutions ($C_0 v_c \ll 1$)

$$\beta_s \cong a\nu\left(\frac{a}{\delta}\right)^2 \exp\left(-\frac{\Delta U}{kT}\right). \tag{3.9}$$

A classical example of normal growth in solutions is the hydrothermal growth of α-quartz (SiO_2) (Laudise 1959, 1970). Crystals of materials such as sapphire (Al_2O_3) (Laudise and Ballman 1958), ZnO, and ZnS (Kolb and Laudise 1966; Laudise and Ballman 1960), yttrium–iron garnet ($Y_3Fe_5O_{12}$) (Kolb *et al.*, 1967), and many others (Demianetz and Lobachov 1984) are also successfully grown using this method.

The growth is carried out in autoclave at high temperature under high pressure. Small pieces of the material to be grown are poured into the lower part of an autoclave in which it dissolves into the solvent. Single-crystal seeds are hanged on a wire of inert material in the upper growth zone of the autoclave. Part of the latter (usually about 80%) is filled with alkaline solution of NaOH, KOH, or K_2CO_3, which improves the solubility of the crystals. The autoclave is then put down vertically in a furnace that heats the lower part to higher temperature compared with the upper part where the growth takes place. Both dissolution and the growth zones are usually divided by a perforated metallic disk to localize the temperature gradients. Upon heating the solution fills in the whole volume of the autoclave. At temperatures 400°C and 350°C of the lower and the upper parts, respectively, the pressure usually increases up to 2000 atm. The material in the lower part dissolves into the solvent and by convection is transported into the upper part. The solution is saturated in the lower part at the higher temperature and is supersaturated at the lower temperature in the upper part. The supersaturation is, thus, determined by the difference of the solubilities C_0 and C of the material at the higher and lower temperatures, respectively. Under these conditions, the crystals grow with a rate of about 1–2 mm per day.

The interested reader can find more details in Demianetz, Kuznetzov and Lobachov (1984).

In the case of growth of α-quartz, Laudise (1959) found that the rate of growth is directly proportional to the difference of the temperatures ΔT which is, in turn, proportional to the difference of the concentrations $\Delta C = C - C_0$. At a temperature of growth 347°C and $\Delta T = 50$°C, a rate of growth as high as 2.5 mm day^{-1} has been measured. The Arrhenius plot of the slopes of the straight lines $R \div \Delta T$ vs the reciprocal temperature represents a straight line whose slope can be identified by the activation energy ΔU. The value 20 kcal mol^{-1} has been, thus, found for the growth of the (0 0 0 1) face of α-quartz. The solubilities of the α-quartz at 400°C and 347°C are found to be 2.43 and 2.28 g/100 g solvent, or 1.43×10^{20}, and 1.35×10^{20} molecules cm^{-3}. Then, for the supersaturation $\Delta C/C_0$, one obtains 0.059. Having in mind that the volume of a molecule is $v_c \cong 6 \times 10^{-23}$ cm^3, the approximation $C_0 v_c = 8.6 \times 10^{-3} \ll 1$ and Eq. (3.9) is justified. Then, with $\delta \cong 3a$, $\nu = 1 \times 10^{13}$ s^{-1} and $a \cong 4 \times 10^{-8}$ cm, $\beta_s \cong 5 \times 10^{-3}$ cm s^{-1} and $R = 2.5 \times 10^{-6}$ cm s^{-1} or 2.1 mm day^{-1}, in good agreement with the measured value.

Finally, we will derive an expression for the rate of normal growth in a vapor phase. The direct flux of atoms per kink from the vapor phase toward the growing crystal is

$$j_+ = \frac{P}{\sqrt{2\pi mkT}} a^2 \exp\Big(-\frac{\Delta U}{kT}\Big), \tag{3.10}$$

where $P/\sqrt{2\pi mkT}$ is the flux of atoms per unit area and a^2 is the area of a kink.

The reverse flux is given by

$$j_- = \nu \exp\Big(-\frac{\Delta h_s + \Delta U}{kT}\Big). \tag{3.11}$$

In equilibrium ($j_+ = j_-$), $P = P_\infty$, and

$$\frac{P_\infty}{\sqrt{2\pi mkT}} a^2 = \nu \exp\Big(-\frac{\Delta h_s}{kT}\Big). \tag{3.12}$$

Then,

$$j_- = \frac{P_\infty}{\sqrt{2\pi mkT}} a^2 \exp\Big(-\frac{\Delta U}{kT}\Big)$$

and

$$R = \beta_v \frac{P - P_\infty}{P_\infty}, \tag{3.13}$$

where

$$\begin{aligned}\beta_v &= a\nu\left(\frac{a}{\delta}\right)^2 \exp\left(-\frac{\Delta h_s + \Delta U}{kT}\right) \\ &= \left(\frac{a}{\delta}\right)^2 \frac{P_\infty a^3}{\sqrt{2\pi mkT}} \exp\left(-\frac{\Delta U}{kT}\right)\end{aligned} \tag{3.14}$$

is the kinetic coefficient in vapor. Equation (3.13) with (3.14) has been derived without the kinetic barrier ΔU and the degree of roughness $(a/\delta)^2$ as early as in the end of the 19th century (Hertz 1882) and in the beginning of the 20th century (Knudsen 1909). For dyphenyl with $\delta = 3a$, $a^3 = 2.17 \times 10^{-22}$ cm^3, $m = 2.56 \times 10^{-22}$ g, $\Delta U/kT \cong 1$, and $T = 68°$C ($T_m = 69°$C), $\beta_v = 1 \times 10^{-6}$ cm^3 s^{-1} dyne^{-1}. Then, with P_∞ ($T = 68°$C) $\cong 1$ Torr $= 1333$ dyne cm^{-2} and $P = 1343$ dyne cm^{-2}, $\Delta P = P - P_\infty = 10$ dyne cm^{-2}, and $R = 10\mu$m s^{-1}.

Comparing (3.3), (3.9), and (3.14) leads to the conclusion that in all cases the kinetic coefficient is proportional to the surface roughness in terms of the probability of finding a kink $(a/\delta)^2$ and to the exponential of the activation energy for the incorporation of a building unit into the crystal lattice ΔU. Then, the latter can be determined from an Arrhenius plot of the kinetic coefficient vs the reciprocal temperature as this is done in the case of hydrothermal growth of α-quartz. Moreover, for growth from solutions and vapors, the rates of growth are of the order of micrometers per second, whereas from melts, the growth rates are several orders of magnitude higher. A detailed analysis of the theoretical models of the normal mechanism of growth of atomically rough crystal surfaces was carried out by Rosenberger (1982) (see also Christian (1981)).

3.2 Layer Growth of Flat Faces

When the crystal face is atomically smooth, its rate of growth or, in other words, the velocity of its shift parallel to itself is determined by two independent processes: (i) formation of steps and (ii) lateral movement of these steps. One or the other of these processes

can determine the overall rate of growth. In the case of a defectless crystal face, the rate of growth is determined by the frequency of formation of 2D nuclei. The latter is an energetically activated process and a critical supersaturation should be overcome for the growth to take place. When screw dislocations are present, they represent a nonvanishing source of steps and the process of growth is not limited anymore by the step formation. Then, the rate of growth is determined by the rate of the lateral movement of the steps which, in turn, depends on their height and structure, the rate of surface diffusion, the interaction of the steps with each other, the encounter with crystal defects, impurity atoms, etc.

In the general case, any small part of the crystal surface can be considered as a vicinal face consisting of a train of parallel steps with arbitrary height divided by smooth terraces which are parallel to the nearest singular face. When the rate of growth is determined by 2D nucleation, pyramids of growth are formed during growth by the formation of 2D nuclei one upon the other (Fig. 3.2). The side surfaces of these pyramids can be considered as vicinal faces. Hillocks with vicinal side surfaces are also formed during the growth in the presence of screw dislocations (Fig. 3.10(d)). When single-crystal wafers are prepared from bulk single crystals through cutting and polishing, they can never be cut perfectly parallel to the singular faces and, thus, they offer, in fact, vicinal surfaces for further growth for geometrical reasons.

The rate of layer growth of the crystal face R in a direction normal to the singular face or to the surface of the terraces depends on the

Figure 3.2: Pyramid of growth consisting of 2D islands formed one on top of the other. The side surface of such a pyramid represents, in fact, a vicinal surface. The slope of the vicinal is determined by the rates of 2D nucleation and step propagation.

Figure 3.3: For the determination of the rate of growth R of a vicinal surface tilted by an angle θ with respect to the nearest singular face in a direction normal to the latter. The quantity $V = R\cos\theta$ is the rate of growth of the vicinal surface parallel to itself.

velocity of the step advance v and the density of the steps p,

$$R = pv, \tag{3.15}$$

where $p = h/\lambda = \tan\theta$ is the slope of the vicinal given by the ratio of the step height h and the step spacing λ (Fig. 3.3). The velocity of growth of the face V parallel to itself will be given by $V = R\cos\theta$, where θ is the angle the particular part of the crystal surface makes with the singular face.

Note that the angle θ and, in turn, the step density depend in general on the source of the steps and on the kinetics of growth, i.e., on the supersaturation. In the case of 2D nucleation growth, the step distance (Fig. 3.2) depends on the rate of 2D nucleation. The higher the supersaturation (the smaller the specific edge energy), the greater the rate of 2D nucleation will be. Then, 2D nuclei are formed at an earlier moment on top of the underlying 2D islands and the step spacing is smaller. The same is true for the case of spiral growth where the step distance is directly proportional to the radius of the 2D nucleus which is inversely proportional to the supersaturation. As will be shown in the next section, the velocity of step advance v is also a function of the step density p and it is our first task to find expressions for v in any particular case of growth from vapor, solution, or melt.

3.2.1 *Rate of advance of steps*

The height of the steps on the crystal surface can vary in general from one atomic diameter (monoatomic steps) to several atomic diameters (polyatomic steps), and finally to hundreds and thousands atomic diameters (macrosteps). In fact, the latter represent ledges or even small crystal faces which are often easily visible. The formation of macrosteps from monoatomic steps can be easily explained bearing in mind that, the higher the step, the lower its rate of advance will be. The latter is due to the fact that a polyatomic step requires higher flux of atoms in order to move with the same rate as the monoatomic step. Two monoatomic steps can meet each other as a result of local fluctuation of the supersaturation or of the concentration of impurity atoms, on the one hand, or of encountering lattice imperfections, on the other. If such an event takes place irrespective of the reason, a double step is formed whose rate of advance will be smaller than that of the monoatomic step because it requires twice as great a flux of atoms in order to move at the same rate as a monoatomic step. Then, a third monoatomic step will catch up with the double step to form a triple height step. The process continues up to the moment a macrostep is formed. Thus, the initially smooth crystal surface (or the vicinal face) can, under given conditions, break up into *hills and valleys.* These processes are described usually in terms of kinematic waves and shock waves by the kinematic theory of crystal growth (Frank 1958b; Cabrera and Vermilyea 1958; Chernov 1961). On the other hand, the macrosteps are dissipative structures in the sense that they can turn into monoatomic steps again under certain conditions (Chernov 1961; Bennema and Gilmer 1973).

In general, macrosteps are permanently present on the crystal surfaces. Their contribution to the overall rate of growth should not be great because of the smaller rate of advance. That is the reason to begin our presentation with the rate of advance of monoatomic steps. As in the case of normal growth of atomically rough faces we will consider separately the growth from different ambient phases — vapors, solutions, and melts.

3.2.1.1 *Growth from vapor phase*

Elementary Processes on Crystal Surfaces: Consider a vicinal crystal face (vicinal side of a growth hillock or a pyramid due to consecutive 2D nucleation, see Figs. 3.2 and 3.10) below the roughening temperature in contact with its own vapor. We assume that the steps are with monoatomic height. We are not interested by now in the origin of the steps — 2D nuclei or screw dislocations. The overall process of growth includes the following separate elementary processes (Fig. 3.4): (i) adsorption of atoms from the vapor on the terraces between the steps which gives rise to a population of adatoms, (ii) surface diffusion of the adatoms toward the steps, and (iii) incorporation of the adatoms in the kinks along the steps which leads to the advancement of the steps and, hence, to the growth of the crystal in a direction normal to its surface. The overall process of evaporation consists in the same elementary steps taken in an opposite order. We neglect the direct impingement of atoms on the steps from the vapor phase. It is easy to show, as in the case of heterogeneous nucleation from vapor, that the flux of atoms from the vapor phase directly to

Figure 3.4: Schematic view of an isolated single height(SH) step growing through surface diffusion. j_v is the flux of atoms from the bulk vapor phase toward the crystal surface, j_s is the flux of adatoms diffusing to the step, and δ_0 is the average spacing between kinks of any sign. λ_s is the mean distance covered by the adatoms during their life time τ_s on the surface.

the step is much smaller than the flux of atoms diffusing on the terraces to the step. (The coupled volume and surface diffusion problem has been treated by Gilmer, Ghez and Cabrera 1971).

Under the conditions of equilibrium of the crystal with its vapor phase, the fluxes of adsorption $P_\infty/(2\pi \mathrm{mkT})^{1/2}$ and desorption, n_s/τ_s, of atoms are equal so that the adatom concentration n_s has its equilibrium value

$$n_{\mathrm{se}} = \frac{P_\infty}{\sqrt{2\pi mkT}}\tau_s, \tag{3.16}$$

where P_∞ is the equilibrium vapor pressure of infinitely large crystal, m is the mass of the atoms, and τ_s is the mean time of residence of the adatoms on the crystal surface before being re-evaporated and is given by

$$\tau_s = \frac{1}{\nu_\perp}\exp\Big(\frac{E_{\mathrm{des}}}{kT}\Big), \tag{3.17}$$

where $\nu_\perp$ is the vibrational frequency of the adatoms normal to the surface and E_{des} is the activation energy for the desorption of an adatom from the crystal surface.

Substituting P_∞ from (1.58) and τ_s from (3.17) into (3.16) for n_{se}, one obtains

$$n_{\mathrm{se}} = N_0 \exp\Big(-\frac{\varphi_{1/2} - E_{\mathrm{des}}}{kT}\Big), \tag{3.18}$$

where N_0 combines the entropy factors in (1.58) but for simple crystals is of the order of the number $N_0 \cong 1/a^2$ per unit area of adsorption sites on the crystal surface ($\approx 1 \times 10^{15}$ cm^{-2}), a being the mean distance between the adsorption sites. The difference $\varphi_{1/2} - E_{\mathrm{des}}$ gives the energy to transfer an atom from a kink position on the flat surface. In other words, Eq. (3.18) expresses also the equilibrium kinks–adlayer as at equilibrium the fluxes from the adlayer to and from the kinks are equal.

The mean distance the adatoms can cover during their lifetime on the surface is

$$\lambda_s = \sqrt{D_s\tau_s}, \tag{3.19}$$

where D_s is the surface diffusion coefficient:

$$D_s = a^2 \nu_= \exp\Big(-\frac{E_{\rm sd}}{kT}\Big). \tag{3.20}$$

Here, $E_{\rm sd}$ is the activation energy for surface diffusion and $\nu_=$ is the vibrational frequency of the adatoms parallel to the crystal surface. Assuming $\nu_\perp = \nu_= = \nu$,

$$\lambda_s = a \exp\Big(\frac{E_{\rm des} - E_{\rm sd}}{2kT}\Big). \tag{3.21}$$

The desorption energy $E_{\rm des}$ is always greater than the diffusion energy barrier $E_{\rm sd}$ ($E_{\rm des} = 3\psi$ for the (1 1 1) face and $E_{\rm des} = 4\psi$ for the (1 0 0) face of fcc crystals, whereas $E_{\rm sd} < \psi$). Then, $\lambda_s \gg a$. In order to evaluate λ_s we neglect $E_{\rm sd}$ in comparison with $E_{\rm des}$. Considering the case of Ag at 1000 K ($\psi/kT = 5$), we find $\lambda_s(1\,1\,1) = 2 \times 10^3 a$ and $\lambda_s(1\,0\,0) = 2 \times 10^4 a$. We see that λ_s is much greater than the mean distance between the kinks $\delta_0 = 7a$ under the same conditions. For the (1 1 1) face of Si at the melting temperature, $\lambda_s = 2 \times 10^2 a \gg \delta_0 = 3.5a$. As seen, the more closely packed the surface is, the smaller is λ_s and the smaller is the equilibrium adatom concentration $n_{\rm se}$. Thus, for Ag, $n_{\rm se}(1\,0\,0) = 2 \times 10^{-5} N_0$, but $n_{\rm se}(1\,1\,1) = 2 \times 10^{-7} N_0$.

Kinetic Coefficient of a Step: We will perform the same considerations concerning a single step as for a rough crystal face. Going back to Fig. 3.1, we identify the left-hand energetic level with the energy of an atom in a kink position as before. The upper right-hand side level is identified this time with the energy of an atom adsorbed on the smooth part of the crystal face. Then, the difference between both levels $\Delta h = \Delta W = \varphi_{1/2} - E_{\rm des}$ gives the energy required to transfer an atom from a kink position on the flat surface. The energy barrier ΔU has the same meaning as before.

The flux of adatoms related to a kink site ($\rm s^{-1}$) toward the step is

$$j_+ = \nu n_{\rm st} a^2 \exp\Big(-\frac{\Delta U}{kT}\Big), \tag{3.22}$$

where $n_{\rm st}$ is the adatom concentration in the step's vicinity and a^2 is the area of a kink site.

The flux of atoms leaving the kink sites to be adsorbed on the terrace is

$$j_- = \nu \exp\Big(-\frac{\Delta W + \Delta U}{kT}\Big). \tag{3.23}$$

In equilibrium ($j_+ = j_-$), the adatom concentration attains its equilibrium value $n_{\rm se}$ given by Eq. (3.18).

The rate of the step advance is given by

$$v_\infty = a\frac{a}{\delta_0}(j_+ - j_-), \tag{3.24}$$

where a/δ_0 is the probability of finding a kink site and δ_0 is the kink spacing defined by Eq. (1.75).

Substituting j_+ and j_- from (3.22) and (3.23) into (3.24), for v_∞, one obtains

$$v_\infty = 2a^2\beta_{\rm st}(n_{\rm st} - n_{\rm se}), \tag{3.25}$$

where the factor 2 accounts for the arrival of atoms from both lower and upper terraces to the step and

$$\beta_{\rm st} = a\nu\frac{a}{\delta_0}\exp\Big(-\frac{\Delta U}{kT}\Big) \tag{3.26}$$

is the *kinetic coefficient of the step* or the rate of crystallization in complete analogy with the kinetic coefficient of the crystal face (3.14).

We define the rate of diffusion as the mean distance λ_s divided by the mean residence time τ_s:

$$\frac{\lambda_s}{\tau_s} = \frac{D_s}{\lambda_s} = a\nu\exp\Big(-\frac{E_{\rm des} + E_{\rm sd}}{2kT}\Big). \tag{3.27}$$

Obviously, when the rate of diffusion is much lower than the kinetic coefficient of the step,

$$\frac{D_s}{\lambda_s} \ll \beta_{\rm st}, \tag{3.28}$$

which is equivalent to $E_{\rm des} + E_{\rm sd} > 2\Delta U + 2\omega$, the velocity of the step advance will be determined by the process of surface diffusion. In other words, the surface diffusion is the rate-controlling process.

Figure 3.5: Illustration of the regimes of growth of a train of parallel equidistant steps. In a diffusion regime, (a) the adatom concentration has a profile of inverse parabola with a maximum over the middle of the terrace. In a kinetic regime, (b) the diffusion of the adatoms is fast and the profile of the adatom concentration is represented by a straight line. The steps do not interact through the diffusion fields.

It is said that the crystal grows in a *diffusion regime*. If this is not the case, i.e., when

$$\frac{D_s}{\lambda_s} \gg \beta_{\mathrm{st}}, \tag{3.29}$$

or $E_{\mathrm{des}} + E_{\mathrm{sd}} < 2\Delta U + 2\omega$, the processes taking part when the building units are incorporated into the kink sites determine the rate of the step advancement and the crystal face grows in a *kinetic regime.*

The regimes of growth are illustrated in Fig. 3.5. As will be shown in the following in the diffusion regime, the incorporation of adatoms in the steps is fast and the adatom concentration has a maximum in the middle of the terrace. Around the steps, there are diffusion fields which can overlap if the steps are sufficiently close. Then, the steps will interact with each other. On the contrary, in a kinetic regime, the diffusion is fast and flattens the adatom concentration. The latter is represented by a straight line. There are no more diffusion fields and the neighboring steps do not interact with each other.

Rate of Advance of a Single Step: We consider a part of the crystal face containing a single monoatomic step confined between two infinitely wide terraces (Fig. 3.4). The vapor pressure is $P > P_\infty$ and the supersaturation is given by

$$\sigma = \frac{\Delta\mu}{kT} = \ln\left(\frac{P}{P_\infty}\right) \approx \frac{P}{P_\infty} - 1 = \alpha - 1 \tag{3.30}$$

for P slightly greater than P_∞ ($\alpha = P/P_\infty$).

The adatom population in equilibrium with the vapor phase with pressure P is

$$n_s = \frac{P\tau_s}{\sqrt{2\pi mkT}} = \alpha n_{\mathrm{se}}. \tag{3.31}$$

The supersaturation in the adlayer is defined as

$$\sigma_s = \frac{n_s}{n_{\mathrm{se}}} - 1 = \alpha_s - 1, \tag{3.32}$$

where $\alpha_s = n_s/n_{\mathrm{se}}$.

Note that σ_s is a function of the distance y normal to the step (Fig. 3.4), whereas σ is constant all over the surface.

The flux of atoms diffusing on the surface towards the step is

$$j_s = -D_s\frac{dn_s}{dy} = -D_s n_{\mathrm{se}}\frac{d\alpha_s}{dy}.$$

We introduce the potential function $\Psi = \sigma - \sigma_s = \alpha - \alpha_s$. Then, the surface flux reads

$$j_s = D_s n_{\mathrm{se}}\frac{d\Psi}{dy}$$

or, in a more general form,

$$j_s = D_s n_{\mathrm{se}}\mathrm{grad}\Psi. \tag{3.33}$$

The net flux of atoms arriving from the vapor phase on the crystal surface is

$$j_v = \frac{P}{\sqrt{2\pi mkT}} - \frac{n_s}{\tau_s} = \frac{n_{\mathrm{se}}}{\tau_s}\Psi. \tag{3.34}$$

Assuming the movement of the step can be neglected in diffusion problems (the justification will be given below), the equation of continuity of Ψ reads

$$\mathrm{div} j_s = j_v, \tag{3.35}$$

which in the case of diffusion in one direction is equivalent to

$$\frac{dj_s(y)}{dy} = j_v.$$

The latter is simply the condition for the adatom concentration at a given distance y from the step to have a time-independent (steady-state) value. In other words, the difference of the surface fluxes to

and from a strip parallel to the step with a width from y to $y + dy$ must be compensated by the arrival of atoms from the vapor phase.

Then,

$$D_s n_{\mathrm{se}} \mathrm{div}(\mathrm{grad}\Psi) = \frac{n_{\mathrm{se}}}{\tau_s}\Psi.$$

The latter can be rewritten in the general form (Burton, Cabrera and Frank 1951)

$$\lambda_s^2 \Delta\Psi = \Psi, \tag{3.36}$$

where the symbol Δ denotes the Laplace operator:

$$\Delta = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}. \tag{3.37}$$

Equation (3.36) is the governing equation which must be solved subject to various initial and boundary conditions for different symmetries and physical conditions.

Several physical possibilities should be considered when approaching the problem of the rate of advance of an isolated step.

(i) The mean path λ_s covered by the adatoms during their time of residence τ_s on the crystal face is much larger than the average kink spacing δ_0. Physically, this means that the step acts as a continuous trap for the adatoms. The master Eq. (3.36) is then reduced to an equation of a linear diffusion (see Fig. 3.4)

$$\lambda_s^2 \frac{d^2\Psi}{dy^2} = \Psi. \tag{3.38}$$

(ii) The mean path λ_s covered by the adatoms during their time of residence τ_s is smaller than the average kink spacing δ_0. The adatoms diffuse directly to the isolated kinks. The diffusion problem is solved in polar coordinates as the diffusion field has a circular shape. A solution in terms of Bessel functions is obtained (Burton, Cabrera and Frank 1951).

(iii) The mean path λ_s covered by the adatoms during their lifetime is again smaller than the average kink spacing δ_0, but the adatoms diffuse on the crystal surface to join the edge of the step and then

diffuse along it to be incorporated into the kinks (Burton, Cabrera and Frank 1951).

As has been shown in Chapter 1, the steps are rough long before the critical temperature is reached and the condition $\lambda_s \gg \delta_0$ is practically always fulfilled. It follows that case (i) is the most probable one. As for the remaining cases, the reader is referred for more details to the original paper (Burton, Cabrera and Frank 1951) as well as to the review paper of Bennema and Gilmer (1973).

We solve first the particular case (3.38) of linear diffusion to a single isolated straight step. In order to find a solution of the master Eq. (3.36), we have to specify the boundary conditions. At a distance large enough from the step, the adlayer is unaffected by the presence of the step and $n_s = \alpha n_{\rm se}$ (Eq. (3.31)). Then, $\sigma = \sigma_s$ and $\Psi = 0$. In the near vicinity of the step ($y \to 0$), the adatom concentration is determined by the processes of attachment and detachment of adatoms to and from the kink sites. If the activation energy ΔU is negligible, the kinetic coefficient will be large enough and (3.28) will be fulfilled. Then, the exchange of atoms between the kinks and the adlayer will be rapid enough and the concentration of adatoms in the near vicinity of the step will be equal to the equilibrium concentration $n_{\rm se}$. Then, $\sigma_s = 0$ and $\Psi = \sigma$. In the opposite case of considerable value of ΔU, the kinetic coefficient of the step will be very small and the condition (3.29) will hold.

In the general case at $y = 0$,

$$\sigma_s = \sigma_{\rm st} = \frac{n_{\rm st} - n_{\rm se}}{n_{\rm se}}. \tag{3.39}$$

Then, $\Psi = \sigma - \sigma_{\rm st} = \chi\sigma$, where (Bennema and Gilmer 1973)

$$\chi = \frac{\sigma - \sigma_{\rm st}}{\sigma}, \tag{3.40}$$

whence

$$\sigma_{\rm st} = \sigma(1 - \chi).$$

Equation (3.25) becomes

$$v_\infty = 2a^2\beta_{\rm st} n_{\rm se}\sigma(1 - \chi). \tag{3.41}$$

The solution of Eq. (3.38) subject to the boundary conditions

$$\begin{aligned} y &= 0, & \Psi &= \chi\sigma, \\ y &\to \pm\infty, & \Psi &= 0 \end{aligned}$$

reads

$$\Psi = \chi\sigma \exp\Big(\pm\frac{y}{\lambda_s}\Big), \tag{3.42}$$

where the + and − signs refer to $y < 0$ and $y > 0$, respectively.

Then, the rate of advance of the single step

$$v_\infty = \frac{j_s(y=0)}{N_0}$$

is

$$v_\infty = 2\chi\sigma a^2 n_{\mathrm{se}} \frac{D_s}{\lambda_s} = 2\chi\sigma\lambda_s\nu \exp\Big(-\frac{\varphi_{1/2}}{kT}\Big). \tag{3.43}$$

Equation (3.41) has been derived under the assumption that n_{st} is the adatom concentration in the near vicinity of the step. We did not specify what is the reason for the deviation of the concentration from its equilibrium value. Then, we can determine the parameter χ by equating the expressions (3.41) and (3.43) to obtain

$$\chi = \left(1 + \frac{D_s}{\lambda_s\beta_{\mathrm{st}}}\right)^{-1}. \tag{3.44}$$

As seen, the unknown parameter χ depends only on the ratio of the rate of diffusion D_s/λ_s and the rate of crystallization β_{st}.

Finally, for the rate of advance of a single step, one obtains

$$v_\infty = 2\sigma\lambda_s\nu \exp\Big(-\frac{\varphi_{1/2}}{kT}\Big)\left(1 + \frac{D_s}{\lambda_s\beta_{\mathrm{st}}}\right)^{-1}. \tag{3.45}$$

Applying the condition (3.28), leads to the expression

$$v_\infty = 2\sigma\lambda_s\nu \exp\Big(-\frac{\varphi_{1/2}}{kT}\Big) \tag{3.46}$$

valid for the advance of the step in a purely diffusion regime. The condition (3.29) leads to Eq. (3.41) with $\chi \to 0$:

$$v_\infty = 2a^2\beta_{\mathrm{st}} n_{\mathrm{se}}\sigma, \tag{3.41$'$}$$

which describes the behavior of the step in a kinetic regime and where the adatom concentration around the step is determined solely by the

processes taking part at the step edge. No diffusion gradient exists in this case and the adatom concentration preserves the value n_s determined by the adsorption–desorption balance all over the crystal surface except for a narrow strip around the step. It is seen, however, that in both cases the rate of advance of an isolated step is a linear function of the supersaturation σ.

The movement of the step, when solving the diffusion problem, can be obviously neglected when the mean velocity of motion of an adatom on the surface $v_{\text{diff}} = \lambda_s/\tau_s$ is much greater than the rate of advance of the step $v_\infty = 2\sigma D_s n_{\text{se}} a^2/\lambda_s$. The ratio $v_\infty/v_{\text{diff}} = 2\sigma n_{\text{se}}/N_0$ is obviously smaller than unity as the supersaturation $\sigma < 1$ and the equilibrium adatom concentration n_{se} is usually a small part of the density of the adsorption sites N_0 (Bennema and Gilmer 1973).

Rate of Advance of a Train of Parallel Steps: We consider a train of parallel equidistant steps as shown in Fig. 3.6 where y_0 is the step separation. We again assume that $\lambda_s \gg \delta_0$. Obviously, the adatom concentration has its maximum value at the middle between the steps so that $(dn_s/dy)_{y=0} = 0$ (the distance y being measured from the midpoint between the steps) or $(d\Psi/dy)_{y=0} = 0$. The concentration in the near vicinity of the steps is again equal to n_{st} and $\Psi(y \to \pm y_0/2) = \chi\sigma$. Then, the solution of Eq. (3.38) reads

$$\Psi = \chi\sigma \frac{\cosh(y/\lambda_s)}{\cosh(y_0/2\lambda_s)}, \tag{3.47}$$

Figure 3.6: Train of parallel equidistant steps spaced at a distance y_0 from each other. To solve the diffusion problem, it is convenient to consider distances from the midpoint between the steps.

and for v_∞, one obtains

$$\begin{aligned} v_\infty &= 2\chi\sigma a^2 n_{\mathrm{se}} \frac{D_s}{\lambda_s} \tanh\Big(\frac{y_0}{2\lambda_s}\Big) \\ &= 2\chi\sigma\lambda_s\nu \exp\Big(-\frac{\varphi_{1/2}}{kT}\Big) \tanh\Big(\frac{y_0}{2\lambda_s}\Big), \end{aligned} \tag{3.48}$$

which reduces to (3.43) when $y_0 \to \infty$.

Bearing in mind that in a kinetic regime the adatom concentration on the terraces between the steps is not affected by the presence of the latter and the steps do not interact with each other through the diffusion fields, we can perform the same operation as the above to find an expression for χ. Equating (3.41) and (3.48) gives

$$\chi = \Big[1 + \frac{D_s}{\lambda_s\beta_{\mathrm{st}}} \tanh\Big(\frac{y_0}{2\lambda_s}\Big)\Big]^{-1}$$

and

$$v_\infty = 2\sigma\nu\lambda_s \exp\Big(-\frac{\varphi_{1/2}}{kT}\Big) \frac{\tanh(y_0/2\lambda_s)}{1 + (D_s/\lambda_s\beta_{\mathrm{st}}) \tanh(y_0/2\lambda_s)}. \tag{3.49}$$

It is immediately seen that the condition (3.28) leads to an expression valid for the purely diffusion regime of growth

$$v_\infty = 2\sigma\lambda_s\nu \exp\Big(-\frac{\varphi_{1/2}}{kT}\Big) \tanh\Big(\frac{y_0}{2\lambda_s}\Big), \tag{3.50}$$

whereas the condition (3.29) leads again to Eq. (3.41′) for the kinetic regime of step advance.

The hyperbolic tangent $\tanh(x)$ increases initially linearly with its argument x and at large enough values of the latter ($x > 2$) it goes asymptotically to unity. So if the step distance y_0 is sufficiently larger than the mean free path λ_s of the adatoms on the crystal surface $\tanh(y_0/2\lambda_s) \to 1$ and the adatom concentration in the middle parts of the terraces far from the steps will be unaffected by the presence of the latter, i.e., it will be equal to $n_s = P\tau_s/\sqrt{2\pi mkT}$. The diffusion fields will not overlap, the steps will not interact with each other, and the rate of step advance will be equal to that of isolated steps. Equation (3.49) reduces to (3.45) and Eq. (3.50) reduces to (3.46). In the other extreme $y_0/2\lambda_s \to 0$ (it is enough if $y_0/2\lambda_s < 0.1$), the

hyperbolic tangent can be approximated by its argument and (3.50) turns into $v_\infty = \nu\sigma y_0 \exp(-\varphi_{1/2}/kT)$. As will be shown in the next chapter, the step separation y_0 is inversely proportional to the supersaturation and $v_\infty = \text{const}$. Physically, this means that the overlapping of the diffusion fields is so strong that the adatom concentration on the terraces between the steps is practically equal to the equilibrium adatom concentration n_{se} and the diffusion gradient becomes equal to zero. The steps move under conditions which are very near to equilibrium and their rate of advance ceases to depend on the supersaturation.

Rate of Advance of Curved Steps: We consider the rate of lateral growth of circular 2D cluster with radius ρ. Its shape is determined by the differences in the velocities for different orientations. If the velocity is orientationally independent, the shape will be circular.

The flux of atoms towards the curved step will be given now by

$$j_+ = \frac{2\pi\rho}{\delta_0}\nu n_{\text{st}} a^2 \exp\Big(-\frac{\Delta U}{kT}\Big), \tag{3.51}$$

where $2\pi\rho/\delta_0$ is the number of the kinks at the island's periphery.

In order to find the reverse flux, we should recall that the equilibrium of small 2D islands with the parent phase is determined not by the work of separation from the half-crystal position but by the mean separation work $\bar{\varphi}_2$ (Eq. (1.65)). Then, the work to transfer an atom from a kink position along the edge of the 2D island to the adlayer on the terrace will be given by

$$\Delta W(\rho) = \bar{\varphi}_2 - E_{\text{des}} = \varphi_{1/2} - \frac{\varkappa a^2}{\rho} - E_{\text{des}} = \Delta W - \frac{\varkappa a^2}{\rho}, \tag{3.52}$$

where $\varkappa$ is the specific edge energy of the step (Eq. (1.67)). In fact, Eq. (3.52) reflects the enhanced chemical potential of the cluster of finite size, or, in other words, the Thomson–Gibbs effect (see Eq. (1.66′)).

The reverse flux reads

$$j_- = \frac{2\pi\rho}{\delta_0}\nu \exp\Big(-\frac{\Delta W(\rho) + \Delta U}{kT}\Big). \tag{3.53}$$

At equilibrium, both fluxes are equal, $n_{\rm st} = n_{\rm se}(\rho)$, and the equation of Thomson–Gibbs for the 2D case

$$n_{\rm se}(\rho) = N_0 \exp\Big(-\frac{\Delta W(\rho)}{kT}\Big) = n_{\rm se} \exp\Big(\frac{\varkappa a^2}{\rho kT}\Big), \tag{3.54}$$

results where $n_{\rm se}$ is given by (3.18).

Assuming the 2D island is large enough (low supersaturation), the net fluxes from the upper surface of the island and the surrounding crystal face to the circular step should be equal. Then, the radial velocity of the step advance will be

$$v(\rho) = 2\frac{j_+ - j_-}{2\pi\rho N_0}$$

and

$$v(\rho) = 2a^2\beta_{\rm st}[n_{\rm st} - n_{\rm se}(\rho)], \tag{3.55}$$

where the kinetic coefficient $\beta_{\rm st}$ is again given by (3.26). As seen, (3.55) reduces to (3.25) when $\rho \to \infty$. Bearing in mind that $n_{\rm se}(\rho) > n_{\rm se}$, it follows that the velocity of advance of a curved step is smaller than the rate of advance of a straight step under the same conditions.

The difference $n_{\rm st} - n_{\rm se}(\rho)$ can be rearranged as follows:

$$\begin{aligned} n_{\rm st} - n_{\rm se}(\rho) &= n_{\rm se}\Big[\Big(\frac{n_{\rm st}}{n_{\rm se}} - 1\Big) - \Big(\frac{n_{\rm se}(\rho)}{n_{\rm se}} - 1\Big)\Big] = n_{\rm se}[\sigma_{\rm st} - \sigma(\rho)] \\ &= n_{\rm se}\{[\sigma - \sigma(\rho)] - [\sigma - \sigma_{\rm st}]\} = n_{\rm se}\sigma\Big(1 - \frac{\sigma(\rho)}{\sigma} - \chi\Big). \end{aligned}$$

The radius ρ_c of the critical radius is defined by the Thomson–Gibbs equation (1.66′)

$$\sigma = \frac{\varkappa a^2}{kT\rho_c}. \tag{3.56}$$

From (3.54) and (3.56), it follows that

$$\frac{\sigma(\rho)}{\sigma} = \frac{\rho_c}{\rho}$$

and finally

$$v(\rho) = 2a^2\beta_{\rm st}n_{\rm se}\sigma\Big(1 - \frac{\rho_c}{\rho} - \chi\Big). \tag{3.57}$$

The diffusion equation (3.36) in polar coordinates reads

$$\frac{d^2\Psi(r)}{dr^2} + \frac{1}{r}\frac{d\Psi(r)}{dr} = \frac{\Psi(r)}{\lambda_s^2}, \tag{3.58}$$

where $\Psi(r) = \sigma - \sigma_s(r)$ and is subject to the boundary conditions $\Psi(r \to \infty) = 0$, $[d\Psi(r)/dr]_{r=0} = 0$ and $\Psi(r = \rho) \equiv \Psi(\rho) = \sigma - \sigma_{\rm st}(\rho) = \chi\sigma$ ($\sigma_{\rm st}(\rho) = n_{\rm st}/n_{\rm se} - 1$). The solution of (3.58) reads

$$\Psi(r) = \Psi(\rho)\frac{I_0(r/\lambda_s)}{I_0(\rho/\lambda_s)} \qquad \text{for } r < \rho, \tag{3.59a}$$

$$\Psi(r) = \Psi(\rho)\frac{K_0(r/\lambda_s)}{K_0(\rho/\lambda_s)} \qquad \text{for } r > \rho, \tag{3.59b}$$

where $I_0(x)$ and $K_0(x)$ are the Bessel functions of first and second kind, respectively, with imaginary argument.

The flux of atoms toward the edge of the cluster is

$$j_s(\rho) = 2\pi\rho D_s n_{\rm se}\left(\frac{d\Psi}{dr}\right)_{r=\rho} = 4\pi\rho n_{\rm se}\frac{D_s}{\lambda_s}\Psi(\rho), \tag{3.60}$$

where the formulae $I_0'(x) = I_1(x)$, $K_0'(x) = -K_1(x)$, $I_1(x)K_0(x) + I_0(x)K_1(x) = 1/x$ and the approximation $I_0(x)K_0(x) = 1/2x$ valid for $x > 1$ have been used.

The radial velocity of advance of a curved step is then

$$v(\rho) = \frac{j_s(\rho)}{2\pi\rho N_0} = 2a^2 n_{\rm se}\chi\sigma\frac{D_s}{\lambda_s}. \tag{3.61}$$

From (3.57) and (3.61), one obtains

$$\chi = \left(1 - \frac{\rho_c}{\rho}\right)\left(1 + \frac{D_s}{\lambda_s\beta_{\rm st}}\right)^{-1}$$

and

$$v(\rho) = 2\sigma\lambda_s\nu\exp\left(-\frac{\varphi_{1/2}}{kT}\right)\left(1 - \frac{\rho_c}{\rho}\right)\left(1 + \frac{D_s}{\lambda_s\beta_{\rm st}}\right)^{-1}$$

or

$$v(\rho) = v_\infty\left(1 - \frac{\rho_c}{\rho}\right), \tag{3.62}$$

where v_∞ is the rate of advance of a straight step given by (3.45).

Finally, in the interesting case of growth of concentric circular clusters with edges spaced y_0 from each other, the rate of advance will be given by (see Eq. (3.49))

$$v(\rho) = 2\sigma\lambda_s\nu \exp\Big(-\frac{\varphi_{1/2}}{kT}\Big)\frac{\tanh(y_0/2\lambda_s)}{1+(D_s/\lambda_s\beta_{\rm st})\tanh(y_0/2\lambda_s)}\Big(1-\frac{\rho_c}{\rho}\Big). \tag{3.63}$$

This is a general expression for the rate of advance of monoatomic steps. All limiting cases of curved and straight steps or train of steps in both diffusion or kinetic regime of growth can be easily derived from it.

3.2.1.2 *Growth from solutions*

In the growth from solutions, the supply of growth units takes place predominantly through diffusion in the bulk of the solution (Burton, Cabrera and Frank 1951; Chernov 1961), although there is evidence that the growth units reach the growth sites at least partly by surface diffusion as well (Bennema 1974; Vekilov *et al.*, 1992; Zhang and Nancollas 1991). The problem of growth by surface diffusion resembles very much that from vapors and in the following presentation we will take into consideration the bulk diffusion only. The problem of propagation of steps simultaneously by surface and bulk diffusion has been treated theoretically by Van der Eerden (1982, 1983).

The solutions are usually stirred. If the solution is still, the exhaustion of the solution near the growing crystal gives rise to convection flows. Thus, in all cases, the solution moves with respect to the growing crystal. When a fluid moves tangentially to a plane surface, the velocity of the fluid decreases towards the surface and in the near vicinity of the latter an immobile boundary layer is formed as shown in Fig. 3.7 (Schlichting 1968). The latter is frequently called a *stagnant layer*. The thickness of the stagnant layer depends on the velocity of the fluid ϑ, its viscosity η, and density ρ, and the distance x from the leading edge of the crystal surface according to the approximate formula

$$d \cong 5\Big(\frac{x\eta}{\vartheta\rho}\Big)^{1/2}.$$

Figure 3.7: Schematic representation of the stagnant boundary layer above the surface of a crystal in a tangentially moving fluid. The arrows give an impression of the decrease of the velocity of the fluid when approaching the crystal surface. The thickness of the stagnant layer d depends on the distance x from the leading edge of the crystal face.

For values of the parameters involved, typical for aqueous solutions at room temperature, $\eta = 1 \times 10^{-2}$ g cm^{-1} s^{-1}, $\rho = 1$ g cm^{-3}, $\vartheta = 40$ cm s^{-1}, and $x = 0.1$ cm, $d \cong 0.25$ mm. The above-mentioned formula gives only a qualitative indication as the real situation in the stirred solution or around rotating crystal can be quite different. The concept of the stagnant boundary layer is also widely used for the description of the processes taking part in the reactors for CVD (Carra 1988).

It is usually assumed that, within a stagnant layer, the transport of the growth species to the surface of the crystal occurs by diffusion, whereas at the upper boundary of the layer, the concentration of the solute is maintained constant and equal to the bulk concentration C_∞. Assuming again that the rate of the movement of the steps is sufficiently smaller than the rate of diffusion, the concentration of the solute in the boundary layer is described by the equation of Laplace $\Delta C = 0$, where Δ is the Laplace operator. When considering the movement of a single step as a result of incorporation of growth units into kink sites along the step, the mean kink spacing is obviously much smaller than the thickness of the boundary layer. Then, the step acts as a linear sink for the growth units and the diffusion field

Figure 3.8: Cylindrical symmetry of the volume diffusion field around an isolated step. The distance from the step is characterized by the radius vector r.

Figure 3.9: Schematic view of a train of parallel steps along the y directions spaced at an average distance y_0. The transport of building units through bulk diffusion takes place along the solid lines. The dashed lines represent surfaces with equal solute concentration. Far from the steps at the upper boundary d of the stagnant layer the solute concentration C_∞ is equal to that of the bulk of the solution (after Chernov 1961).

has the form of a semicylinder oriented with its axis along the step (Fig. 3.8). It is, thus, convenient to express the Laplace equation in cylindrical coordinates

$$\frac{d^2C}{dr^2} + \frac{1}{r}\frac{dC}{dr} = 0,$$

where r is the radius vector. When we consider growth of a vicinal crystal face with equidistant steps we have to take into account the overlapping of the diffusion fields as this is shown in Fig. 3.9 (Chernov 1961). We will consider these two cases separately as was done above.

Rate of Advance of a Single Step: We consider this simpler case for illustrating the approach. A solution of the Laplace equation is the function (Carslaw and Jaeger 1960)

$$C(r) = A\ln(r) + B, \tag{3.64}$$

which can be verified by inspection and where A and B are constants. The latter can be found from the boundary conditions

$$r = \frac{a}{\pi}, \qquad C = C_{st}, \tag{3.65a}$$

$$r = d, \qquad C = C_{\infty}, \tag{3.65b}$$

where C_{st} and C_{∞} are the concentrations at the step vicinity and the upper boundary of the stagnant layer or in the bulk of the solution, respectively (Fig. 3.9).

The condition (3.65a) means that we approximate the step with height a by a semicylindrical surface with a radius $r = a/\pi$. The condition (3.65b), as it is written, means that the concentration has the value C_{∞} at the semicylindrical surface with a radius $r = d$. As there are no other steps nearby and, therefore, no other sinks for the solute species, this condition is a direct consequence of the assumption that the transport occurs by volume diffusion towards the sites of growth. In other words, there is no flux of atoms to other parts of the surface and the concentration far from the step is constant and equal to C_{∞} in all directions.

Then, for the concentration profile around the step, one obtains

$$C(r) = C_{\infty} - (C_{\infty} - C_{\mathrm{st}})\frac{\ln(r/d)}{\ln(a/\pi d)}. \tag{3.66}$$

The rate of the step advance is

$$v_{\infty} = v_c D\left(\frac{dC}{dr}\right)_{r=a/\pi} = \frac{\pi v_c D C_0}{a\ln(\pi(d/a))}\chi\sigma, \tag{3.67}$$

where v_c is the volume of a growth unit in the crystal, D is the bulk diffusion coefficient, C_0 is the equilibrium concentration of the solute at the given temperature. $\sigma = C_{\infty}/C_0 - 1$ is the supersaturation, $\sigma_{\mathrm{st}} = C_{\mathrm{st}}/C_0 - 1$, $\chi = (\sigma - \sigma_{\mathrm{st}})/\sigma$, and $C_{\infty} - C_{\mathrm{st}} = \chi C_0\sigma$ in complete analogy with the previous case.

On the other hand,

$$v_\infty = \beta_{\rm st} v_c (C_{\rm st} - C_0) = \beta_{\rm st} C_0 v_c \sigma_{\rm st} = \beta_{\rm st} C_0 v_c \sigma (1 - \chi), \quad (3.68)$$

where

$$\beta_{\rm st} = a\nu \frac{a}{\delta_0} \exp\Big(-\frac{\Delta U}{kT}\Big)$$

is the kinetic coefficient of the step in complete analogy with that of the crystal face (Eq. (3.9)). As seen, the only difference is in the dimensionality of the probability of finding a kink site.

Equating (3.67) with (3.68) gives

$$\chi = \frac{a\beta_{\rm st} \ln(\pi(d/a))}{\pi D + a\beta_{\rm st} \ln(\pi(d/a))}$$

and

$$v_\infty = \frac{\beta_{\rm st} C_0 v_c \sigma}{1 + (a\beta_{\rm st}/\pi D) \ln(\pi(d/a))}. \quad (3.69)$$

As before, when the rate of diffusion, $\pi D/a$, is sufficiently greater than the rate of crystallization, $\beta_{\rm st}$, the latter controls the rate of the step advance. The latter is given in the kinetic regime by

$$v_\infty = \beta_{\rm st} C_0 v_c \sigma. \quad (3.70)$$

At the other extreme of the diffusion regime ($\pi D/a \ll \beta_{\rm st}$),

$$v_\infty = \frac{\pi D C_0 v_c}{a \ln(\pi(d/a))} \sigma \quad (3.71)$$

and v_∞ is a linear function of the supersaturation as in the case of vapor growth.

Rate of Advance of a Step in a Train of Steps: This problem is solved for the first time by Chernov (1961). The solution of the Laplace equation $\Delta C = 0$ (see Fig. 3.9 for the orientation of the

coordinate system) subject to the boundary conditions

$$y = 0 \qquad \text{and} \qquad z = d, \quad C = C_\infty, \tag{3.72a}$$

$$y = 0 \qquad \text{and} \qquad z = \frac{a}{\pi}, \quad C = C_{\text{st}}, \tag{3.72b}$$

reads

$$C = A \ln\left[\sin^2\left(\frac{\pi}{y_0}y\right) + \sinh^2\left(\frac{\pi}{y_0}z\right)\right]^{1/2} + B, \tag{3.73}$$

where A and B are constants:

$$A = \frac{C_\infty - C_{\text{st}}}{\ln[\sinh(\pi d/y_0)] - \ln[\sinh(a/y_0)]} \cong \frac{C_\infty - C_{\text{st}}}{\ln[(y_0/a)\sinh(\pi d/y_0)]}, \tag{3.74}$$

$$B = C_\infty + A \ln\left[\sinh\left(\frac{\pi d}{y_0}\right)\right], \tag{3.75}$$

where the approximation $\sinh(a/y_0) \cong a/y_0$ $(a/y_0 \ll 1)$ has been used.

The function $\sin(\pi y/y_0)$ in (3.73) reflects the periodicity in C due to the sequence of equidistant steps. The hyperbolic sine $\sinh(\pi z/y_0)$ accounts for the dependence of C in a direction normal to the growing surface. It is immediately seen that (3.73) reduces to (3.64) at $y = 0$ and large distances between the steps so that $\sinh(\pi z/y_0) \cong \pi z/y_0$. Strictly speaking, the boundary condition (3.72a), $C = C_\infty$, is valid for $z = d$ at any y. As discussed by Chernov (1961), when $\pi d \gg y_0$, the concentration does not depend anymore on y for large values of z and the condition $C(0, d) = C_\infty$ becomes equivalent to $C(d) = C_\infty$. In the opposite case $\pi d \ll y_0$, we have, in fact, steps far apart and the solution for single step is valid.

In order to calculate the rate of step advance, we have to find the concentration gradient dC/dr. The latter is given by

$$\frac{dC}{dr} = \frac{dC}{dz}\frac{dz}{dr} + \frac{dC}{dy}\frac{dy}{dr},$$

where $dz/dr = r/z$, $dy/dr = r/y$, and $r = (y^2 + z^2)^{1/2}$. Making use of (3.67) and the above relations, we find that $(dC/dr)_{r=a/\pi} = \pi A/a$

and

$$v_\infty = \frac{\pi v_c D C_0 \chi \sigma}{a \ln[(y_0/a)\sinh(\pi d/y_0)]}.$$

Equating (3.68) and the above expression gives

$$\chi = \frac{a\beta_{\rm st} \ln[(y_0/a)\sinh(\pi d/y_0)]}{\pi D + a\beta_{\rm st} \ln[(y_0/a)\sinh(\pi d/y_0)]}$$

and finally

$$v_\infty = \frac{\beta_{\rm st} C_0 v_c \sigma}{1 + (a\beta_{\rm st}/\pi D)\ln[(y_0/a)\sinh(\pi d/y_0)]}. \tag{3.76}$$

It is immediately seen that the condition $\pi d/y_0 \ll 1$ reduces Eq. (3.76)–(3.69) valid for single isolated steps.

The corresponding limit cases for the diffusion and kinetic regime are easy to obtain. In the first case ($\pi D/a \ll \beta_{\rm st}$),

$$v_\infty = \frac{\pi D C_0 v_c \sigma}{a \ln[(y_0/a)\sinh(\pi d/y_0)]}, \tag{3.77}$$

whereas in the second case ($\pi D/a \gg \beta_{\rm st}$), Eq. (3.70) results.

The reciprocal of the function in the denominator in (3.77) has qualitatively the same behavior as the hyperbolic tangent. The velocity of step advance in a train is a linear function of the supersaturation in diffusion regime only when the step spacing y_0 is sufficiently larger than the thickness of the boundary layer, which means in practice isolated steps. In the other extreme $\pi d \gg y_0$, the hyperbolic sine $\sinh(x)$ can be approximated by $\exp(x)/2$ and $v_\infty \cong DC_0 v_c \sigma y_0/ad$ $=$ const ($y_0 \approx 1/\sigma$) as in the case of growth from vapors.

We consider as an example the growth of the prismatic face of $NH_4H_2PO_4$ (ADP) crystals from an aqueous solution at room temperatures (Chernov 1989). With $a \cong 4 \times 10^{-8}$ cm, $\nu \cong 1 \times 10^{13}$ s^{-1}, $\delta_0 \cong 4a$, $D \cong 1 \times 10^{-6}$ cm^2 s^{-1}, and $\Delta U \cong 10$ kcal mol^{-1}, $\beta_{\rm st} \cong 4 \times 10^{-3}$ cm s^{-1}, $a\beta_{\rm st}/\pi D \cong 5 \times 10^{-5} \ll 1$ (the logarithm can contribute no more than an order of magnitude), and the growth proceeds in the kinetic regime. The saturation concentration

$C_0 \cong 3.5$ mol l^{-1}, $C_0 v_c \cong 0.2$ and with $\sigma = 0.03$, $v_\infty \cong 2.4 \times 10^{-5}$ cm s^{-1} in good agreement with the experimentally measured value 3×10^{-5} cm s^{-1}. The reader can find more details in the excellent review paper of Chernov (1989) and the original papers quoted therein (Chernov *et al.*, 1986; Kuznetsov, Chernov and Zakharov 1986; Smol'sky, Malkin and Chernov 1986).

Another interesting example is the growth of (1 1 1) faces of $Ba(NO_3)_2$ crystals (Maiwa, Tsukamoto and Sunagawa 1990). The experimentally measured rate of step advance depends on the supersaturation linearly at high rates of flow of the solution (40 cm s^{-1}) and nonlinearly at low flow rates (5 cm s^{-1}). Assuming $\pi d/y_0 \ll 1$ at high flow rates, the rate of the step advance will be given by Eq. (3.69) which is a linear function of the supersaturation. At low flow rates, $\pi d/y_0 \gg 1$ and the hyperbolic sine can be approximated by an exponent, thus giving rise to a linear term of the supersaturation in the denominator of Eq. (3.76). The latter leads to a clear nonlinear dependence of v_∞ on σ at small supersaturations as observed in the experiment whose slope at $\sigma = 0$ is approximately equal to $\beta_{\rm st} C_0 v_c$.

3.2.1.3 *Growth from melts*

As mentioned in Chapter 1, the entropies of melting, $\Delta s_m/k$ (in terms of the Bolzmann constant), of most of the metals have an average value of about 1.2 and their surfaces near the melting point are expected to be rough according to the simplest criterion of Jackson. The $\Delta s_m/k$ values for semiconductors are usually greater — from 3.6 and 3.7 for Si and Ge to 5.7 for InP, 7.4 for InSb, 7.6 for InAs, and 8.5 for GaAs, etc. So that the surfaces of the binaries mentioned above are expected to be smooth and to grow by the layer mechanism. As for the elemental semiconductors, it is difficult to predict the structure of their surfaces with sufficient accuracy.

In general, the growth from simple one-component melts is similar to the growth from solutions (Chernov 1961, 1984). When a building unit is incorporated into a site of growth, a heat of crystallization is released and the local temperature becomes higher. Assuming as before that the mean kink spacing δ_0 is small enough, the step will

act as a linear source of heat. The undercooling around the step will decrease just like the supersaturation in the solution in the near vicinity of the steps. Then a temperature, gradient in a semicylindrical space around the steps arises. The mathematical equations which govern the conduction of heat in condensed phases are exactly the same as the diffusion equations (Carslaw and Jaeger 1960), and we have to solve precisely the same mathematical problem as for solution growth (Chernov 1961, 1984). The heat of crystallization can be taken away through the melt or, more typically, through the crystal as the thermal conductivity of the crystals is usually higher than that of the liquids. For instance, the thermal conductivities of the solid and liquid aluminum at the melting point are 0.51 and 0.21 cal $\mathrm{cm}^{-1}\ \mathrm{s}^{-1}\ \mathrm{K}^{-1}$, respectively. In the first case when the heat is taken away through a stirred melt, we have precisely the same solution of the master equation as in growth in stirred solutions and the thickness of the boundary layer have the same physical meaning as before. In the second case, the thickness of the single-crystal wafer can be taken instead. Obviously, the same expressions are obtained as in the previous section in which the supersaturation $\sigma = (C_\infty - C_0)/C_0$ should be replaced by the undercooling $\sigma = (T_m - T_\infty)/T_m$, the diffusion coefficient D by the coefficient of the temperature conductivity $\varkappa_{\mathrm{T}} = k_{\mathrm{T}}/C_p\rho$ ($\mathrm{cm}^2\ \mathrm{s}^{-1}$) ($k_{\mathrm{T}}$ is the coefficient of the thermal conductivity, C_p is the specific heat capacity (cal $\mathrm{g}^{-1}\ \mathrm{K}^{-1}$), and ρ (g cm^{-3}) is the density. Instead of the kinetic coefficient of the crystal face β_{st} in solutions, one has to take the kinetic coefficient of the step for melts

$$\beta_{\mathrm{st}}^{\mathrm{T}} = a\nu \frac{\Delta s_m}{kT} \frac{a}{\delta_0} \exp\Big(-\frac{\Delta s_m}{k}\Big) \exp\Big(-\frac{\Delta U}{kT}\Big), \tag{3.78}$$

multiplied by a characteristic temperature $T_q = \Delta H_m / C_p^{\mathrm{liq}}$ which is given by the ratio of the heat of crystallization (or melting) and the molar heat capacity of the liquid. As C_p^{liq} is the quantity of heat required to increase the temperature of one mol of the melt by 1° and ΔH_m is the quantity of heat per mol that is introduced into the melt as a result of the crystallization process, T_q is the temperature up to which the melt will be heated up if the heat of crystallization is

not taken away from the system. For metal melts, it has the value of several hundreds of degrees (445° for Ag), but is considerably higher for semiconductors (1860° for Si and 1490° for GaAs).

Then the expression for the rate of advance of the step reads

$$v_\infty = \frac{\beta_{\rm st}^{\rm T} T_m \sigma}{1 + (a\beta_{\rm st}^{\rm T} T_q/\pi\varkappa_{\rm T}) \ln[(y_0/a)\sinh(\pi d/y_0)]}. \tag{3.79}$$

This expression is valid for both cases of taking away of the heat of crystallization through the melt and the crystal. One has to bear in mind that, in the first case, the coefficient of the temperature conductivity $\varkappa_{\rm T}$ has the value for the liquid and vice versa. In the case of growth of Si at $\Delta T = T_m - T = 1\,{\rm K}$, $k_{\rm T} = 0.356$ cal/cm s K, $C_p^{\rm sol} = 5.455$ cal/g.atom K $= 0.194$ cal/g K, $C_p^{\rm liq} = 6.5$ cal/g.atom K, $\rho = 2.328$ g cm^{-3}, $\Delta H_m = 12\,082$ cal mol^{-1}, and $\varkappa_{\rm T} = 0.787$ cm^2 s^{-1}, $T_q = 1860$ K. With $\Delta U \cong 5000$ cal mol^{-1}, $\delta_0 = 3.5a$ and $\Delta s_m/k = 3.6$, $\beta_{\rm st}^{\rm T} = 3.7$ cm s^{-1} K and $a\beta_{\rm st}^{\rm T} T_q/\pi\varkappa_{\rm T} \cong 1 \times 10^{-4} \ll 1$, i.e., the growth proceeds in a kinetic regime. For the rate of advance of the step, one obtains $v_\infty = \beta_{\rm st}^{\rm T}\Delta T = 3.7$ cm s^{-1}. The value for GaAs is two orders of magnitude smaller ($v_\infty \cong 0.1$ cm/s, $\varkappa_{\rm T} = 0.267$ cm^2 s^{-1}, $T_q = 1490\,{\rm K}$, $\beta_{\rm st}^{\rm T} \cong 0.1$ cm^{-1} s^{-1} K^{-1}) due to the higher entropy of melting. Comparing the above values with the one valid for growth in solutions, one can see that they are about five orders of magnitude higher. The latter is due to the better supply of growth units in the melts in comparison with the (dilute) solutions, on the one hand, and to the smaller barrier for crystallization, $\Delta U/kT$, in the melts, on the other.

3.2.2 *Spiral growth of F faces*

As discussed in Chapter 1, the screw dislocations offer nonvanishing steps on the crystal surface. A growth hillock is formed (Fig. 3.10) and, in order to calculate the rate R of growth of the crystal face, we have to find an expression for the step density p of the side face of the hillock, or in other words, the distance y_0 between the successive turns of the spiral.

Figure 3.10: Consecutive stages from (a) to (d) of the formation of a growth pyramid around an emergency point of a single-screw dislocation. As, in Fig. 3.2, the side faces of such pyramids represent, in fact, vicinal surfaces. Their slopes are proportional to the supersaturation.

3.2.2.1 *Shape of the growth spiral*

Let us consider first, for simplicity, the formation of a growth hillock around a single screw dislocation (Fig. 3.11). We assume that the spiral is polygonized with a square shape and that the rate of advance v_∞ of the steps in every direction is one and the same. In the initial moment (Fig. 3.11(a)), the dislocation offers a single step with a lower terrace to the right of it. Atoms diffuse towards the step (on the crystal surface or in the bulk of the solution) and join kink sites along it. As a result, the step moves to the right and a new step normal to the first one appears (Fig. 3.11(b)). As long as the second step is shorter than the edge of the critical 2D nucleus and $l_2 = 2\rho_c$ at the given supersaturation, it will not move because a 2D cluster smaller than the critical nucleus is thermodynamically unfavored and has a greater tendency to decay than to grow (the step "does not know" whether it belongs to a 2D nucleus or to a growth spiral). Once the size $2\rho_c$ is reached, the second step begins to grow with a velocity v_∞ and a third step appears which is parallel to the first

Figure 3.11: Consecutive stages from (a) to (e) of the formation of a growth spiral. (a) Shows a single step originating from the emergency point of the dislocation denoted by the black point. The arrow shows the direction of the step advance. During the growth of the initial step, a new step is formed as shown in (b). When the length of this step exceeds $2\rho_c$ the second step begins to grow and a new step is formed as shown in (c). As seen in (e), the distance between the consecutive turns of the growth spiral is proportional to the radius of the critical 2D nucleus. The radius of curvature of the step which comes out from the emergency point is always equal to the radius of the critical 2D nucleus. These are, in fact, the properties of the Archimedean spiral.

one (Fig. 3.11(c)). This third step will begin to grow when its length becomes greater than $2\rho_c$. At that moment, the length of the second step will be equal to $4\rho_c$. Then, a fourth step will appear and so on. Following this procedure further, we arrive at the picture shown in Fig. 3.11(e) and see that the distance between two successive turns of the growth spiral is equal to $8\rho_c$. Obviously, this consideration is oversimplified and gives only an indication of the real processes which take place during growth. It reflects, however, correctly two very important facts: (i) the spacing of the steps originating from a single dislocation is proportional to the size (radius) of the critical 2D nucleus at the given supersaturation and (ii) the length of the step which comes out from the emerging point of the screw dislocation is

always equal to $2\rho_c$. If we assume that the growth is isotropic, the spiral will be rounded. Then, conclusion (ii) means that the radius of the curvature of the step at the emerging point of the screw dislocation is always equal to the radius ρ_c of the critical nucleus.

In order to find a more accurate expression for the shape of the spiral and, in turn, for the interstep distance, we will follow the approach of Burton, Cabrera and Frank (1951).

The radius of the curvature ρ in polar coordinates (the polar angle φ and the radius-vector r) is given by

$$\rho = \frac{(r^2 + r'^2)^{3/2}}{r^2 + 2r'^2 - rr''}, \tag{3.80}$$

where $r' = dr/d\varphi$ and $r'' = d^2r/d\varphi^2$.

We consider further a spiral with a center in the point O as shown in Fig. 3.12. The rate of advance $v(r)$ in the direction of the radius vector r is

$$v(r) = \frac{dr}{dt} = \frac{dr}{d\varphi}\frac{d\varphi}{dt} = \omega r', \tag{3.81}$$

where $\omega = d\varphi/dt$ is the angular velocity of the spiral winding.

Figure 3.12: Schematic view of the growth spiral around the emergency point of a screw dislocation. $v(r)$ and $v(\rho)$ are the rates of step advance in the directions along the radius vector and normal to the step, respectively. γ denotes the angle between them.

The rate of advance in a direction of the radius of curvature $v(r)$ is related to the rate of advance $v(\rho)$ in a direction normal to the step by

$$v(\rho) = v(r)\cos\gamma = \frac{v(r)r}{(r^2 + r'^2)^{1/2}} = \frac{rr'\omega}{(r^2 + r'^2)^{1/2}}. \tag{3.82}$$

Substituting (3.80) and (3.82) into (3.62) gives

$$v_\infty\left(1 - \rho_c\frac{r^2 + 2r'^2 - rr''}{(r^2 + r'^2)^{3/2}}\right) = \frac{\omega rr'}{(r^2 + r'^2)^{1/2}}, \tag{3.83}$$

whose solution $r = r(\varphi)$ will give us the shape of the spiral.

In order to simplify this expression, we consider the case of small r, i.e., around the center of the spiral. We neglect all terms containing r^2 and r and integrate the remaining differential equation $r' = 2\rho_c$. As a result, an equation for the simplest spiral which is well known as an Archimedean spiral is obtained:

$$r = 2\rho_c\varphi. \tag{3.84}$$

Let us consider this equation more carefully. Substituting $r' = 2\rho_c$ and $r'' = 0$ into (3.80), we find that the radius of the curvature of the Archimedean spiral is given by

$$\rho = \rho_c\frac{(1 + x^2)^{3/2}}{1 + (1/2)x^2},$$

where $x = r/2\rho_c$. It is immediately seen that the radius of the curvature is equal to the radius of the 2D nucleus in the center of the spiral ($x = 0$) and goes linearly to infinity far from the spiral center ($x \to \infty$). For comparison, the radius of the curvature $\rho = r(1 + m^2)^{1/2}$ of the logarithmic spiral ($r = a\exp(m\varphi)$) tends to infinity for $r \to \infty$ but is equal to zero at the spiral center.

On the other hand, the multiplier

$$1 - \frac{\rho_c}{\rho} = 1 - \frac{1 + (1/2)x^2}{(1 + x^2)^{3/2}}$$

in the equation for the rate of the step advance, (3.62), is equal to zero at the spiral center and tends asymptotically to unity far from the spiral center. It follows that the rate of the step advance will vary

from zero at the spiral center to the rate of advance of straight steps far from the spiral center. Thus, the first turns of the spiral will move more slowly (slow kinetics) than the more distant ones (fast kinetics).

The distance Λ between two successive turns of the single spiral or two successive steps is

$$\Lambda = r(\varphi + 2\pi) - r(\varphi) = 2\rho_c[(\varphi + 2\pi) - \varphi] = 4\pi\rho_c. \qquad (3.85)$$

A more detailed analysis performed by Cabrera and Levine (1956) based on a better approximation for the spiral shape $r = r(\varphi)$ resulted in the expression

$$\Lambda = 19\rho_c = \frac{19\varkappa a^2}{kT\sigma} \qquad (3.86)$$

which we will use further. It follows that the interstep distance is inversely proportional to the supersaturation and the increase of the latter makes the slope $p = a/\Lambda$ of the cone (or pyramid) of growth steeper and vice versa. Note that $p = \tan\theta$, where θ is the tilt angle with respect to the corresponding singular face, and hence p is equal to the step density.

The existence of only one screw dislocation on a given crystal face is usually less probable than the existence of many dislocations and even groups of dislocations. Two neighboring dislocations can have in general equal or opposite signs. This means that they can turn either both clockwise (or counter-clockwise) or one of them clockwise and the other counter-clockwise. If they have opposite signs and are spaced farther than $2\rho_c$, they will make loops as shown in Fig. 3.13(a) (Frank 1949a). The problem when the dislocations have like signs is more complicated. Two cases are distinguished. In the first one, the dislocation spacing l is smaller than $2\rho_c$, in the second one, l is greater than $2\rho_c$. Imagine now a group of n dislocations ordered in a straight line as along a grain boundary. Let L denotes its length so that the dislocation spacing $l = L/n$. Figures 3.13(b) and 3.13(c) show parts of the dislocation group (the grain boundary) consisting, for clarity, only of two dislocations spaced at a distance AB. The condition $l \gg 2\rho_c$ is equivalent to $L \gg \Lambda$, where Λ is the interstep

Figure 3.13: Shape of growth spirals due to pairs of dislocation. (a) Closed loops due to dislocations with opposite signs when the distance AB between the emergency points is greater than the radius of the critical 2D nucleus. (b) Shape of the spiral due to pair of dislocations of like sign, separated by a distance $l = \mathrm{AB} \gg 2\rho_c$. The step separation is equal to the distance l and does not depend on the supersaturation. (c) Shape of the spiral due to a pair of dislocations of like sign, separated by a distance $l = \mathrm{AB} \ll 2\rho_c$. The step separation is two times smaller than the distance Λ originating from a single dislocation and is inversely proportional to the supersaturation (after Burton, Cabrera and Frank 1951).

distance determined by a single dislocation and is given by Eq. (3.86). The second condition $l \ll 2\rho_c$ is equivalent to $L \ll \Lambda$ (Fig. 3.13(c)). As shown in the figures, the real interstep spacing y_0 is equal either to $l = L/n$ (Fig. 3.13(b)) or to Λ/n (Fig. 3.13(c)), when $L \gg \Lambda$ or $L \ll \Lambda$, respectively. In the general case (Burton, Cabrera and

Frank 1951; Bennema and Gilmer 1973; Chernov 1989),

$$y_0 = \frac{\Lambda}{\mathbf{n}}, \tag{3.87}$$

where

$$\mathbf{n} = n\left(1 + \frac{L}{\Lambda}\right)^{-1}$$

is the so-called strength of the dislocation source. It follows from above that, when $L \gg \Lambda$, the interstep spacing is simply equal to the interdislocation distance $l = L/n$ and does not depend on the supersaturation. In the second limiting case, the interstep spacing depends on the supersaturation but is n times smaller than $19\rho_c$. In the case when the dislocations in the source are not ordered in a straight line but are grouped in a spatial region, L denotes the perimeter of the region (Chernov 1989).

3.2.2.2 *Growth from a vapor phase*

The rate of growth normal to the surface is given by Eq. (3.15) $R = pv_\infty = av_\infty/y_0$, where v_∞/y_0 is the flux of steps with thickness a passing in a direction parallel to the singular crystal face over any point of the latter. We assume first that the crystal face is entirely covered by a growth pyramid formed by a single dislocation (or by a group of dislocations such that $L \ll \Lambda$ and $y_0 = \Lambda/n$). Substituting (3.50), (3.86), and (3.87), into (3.15) (diffusion regime of growth and far from the spiral center) gives

$$R = C\frac{\sigma^2}{\sigma_c}\tanh\left(\frac{\sigma_c}{\sigma}\right), \tag{3.88}$$

where

$$\sigma_c = \frac{19\varkappa a^2}{2nkT\lambda_s} \tag{3.89}$$

is a characteristic supersaturation and

$$C = a\nu\exp\left(-\frac{\varphi_{1/2}}{kT}\right) \tag{3.90}$$

is a rate constant.

Let us study Eq. (3.88) more closely. For typical values of the parameters included in (3.89): $\varkappa \cong 3 \times 10^{-5}$ erg cm^{-1},

$a \cong 3 \times 10^{-8}$ cm, $T = 1000$ K, $n = 1$, and $\lambda_s = 2 \times 10^3 a$, $\sigma_c = 3 \times 10^{-2}$. However, the growth of crystals is observed at supersaturations σ as low as 1×10^{-4}. Obviously, two limiting cases can be distinguished. At small supersaturations such that $\sigma_c/\sigma \gg 1$, $\tanh(\sigma_c/\sigma) \to 1$, and R obeys the famous parabolic law of Burton, Cabrera and Frank (1951)

$$R = C\frac{\sigma^2}{\sigma_c}. \tag{3.91}$$

At supersaturations sufficiently higher than σ_c, $\tanh(x \to 0) = x$, and R obeys a linear law

$$R = C\sigma. \tag{3.92}$$

The dependence of R on σ is shown in Fig. 3.14. As shown, the parabolic law holds up to the characteristic supersaturation σ_c. Beyond it, a linear relationship is gradually established. The condition for the latter is $\sigma \gg \sigma_c$ or $\lambda_s \gg y_0/2$. Physically, this means

Figure 3.14: Plot of the rate of spiral growth vs the supersaturation. For supersaturations smaller than the characteristic one, σ_c, the growth obeys the parabolic law of Burton, Cabrera and Frank (1951). Beyond σ_c, the growth rate is a linear function of the supersaturation (after Burton, Cabrera and Frank 1951).

that the density of rough steps and hence of that of kinks on the surface are so high that every adatom is incorporated into a growth site before succeeding to re-evaporate. Hence, R is directly proportional to σ as in the case of the normal growth of rough F faces. In the other extreme ($\lambda_s \ll y_0/2$), the diffusion fields of the neighboring steps do not overlap and a large fraction of adatoms re-evaporate before joining the growth sites. The proportionality of v_∞ and the step density $1/y_0$ with respect to σ result in the parabolic law (3.91).

Let us consider now the case when $L \gg \Lambda$ ($l \gg 2\rho_c$) and $y_0 = l = L/n$ (Fig. 3.13(b)) do not depend on the supersaturation. A linear law for the rate of growth R results instead of the parabolic one

$$R = C'\sigma, \tag{3.93}$$

where

$$C' = C\frac{2\lambda_s}{l}\tanh\Big(\frac{l}{2\lambda_s}\Big). \tag{3.94}$$

This is the so-called *second linear law* (Bennema and Gilmer 1973). It results from the specific interrelation of the spacing of the dislocations in the source and the radius of the critical 2D nucleus. The interstep distance and, in turn, the slope of the pyramids no longer depend on the supersaturation. Two limiting cases are distinguished: (i) $l \ll 2\lambda_s$, $\tanh(x) \cong x$, and $C' = C$, and (ii) $l \gg 2\lambda_s$, $\tanh(l/2\lambda_s) \cong 1$, and $C' = 2\lambda_s C/l \ll C$. Thus, the linear dependence of the growth rate vs the supersaturation should be observed which is a characteristic for the normal growth of rough faces.

On the other hand, a parabolic dependence of the growth rate vs the supersaturation (*the second parabolic law*) (Bennema and Gilmer 1973) can be observed under the conditions of a kinetic regime of growth. Then, the velocity of the step advance is given by Eq. (3.41′) $v_\infty = 2a^2\beta_{\rm st}n_{se}\sigma$, which when combined with (3.15), (3.86), and (3.87) gives

$$R = C''\sigma^2, \tag{3.95}$$

where

$$C'' = \frac{2nkTa}{19\varkappa}n_{\rm se}\beta_{\rm st}. \tag{3.96}$$

It is interesting to compare the constants C and C'' in order to distinguish the diffusion and kinetic mechanisms. The ratio $C''/(C/\sigma_c)$ is given by

$$\frac{C''}{C/\sigma_c} = \frac{a}{\lambda_s}\frac{a}{\delta_0}\frac{n_{\rm se}}{N_0}\exp\Big(\frac{\varphi_{1/2} - \Delta U}{kT}\Big).$$

Taking into account Eqs. (3.21), (3.18), and (1.75), the above equation turns into

$$\frac{C''}{C/\sigma_c} = \exp\Big(\frac{E_{\rm des} + E_{\rm sd} - 2\Delta U - 2\omega}{2kT}\Big),$$

where ω is the work to produce a kink at the step edge. As seen, the value of the ratio $C''/(C/\sigma_c)$ depends on the interrelation of the activation energies for desorption and crystallization. Obviously, when $E_{\rm des}+E_{\rm sd} > 2\Delta U+2\omega$, $C'' \gg C/\sigma_c$ and vice versa. However, in order to derive Eq. (3.95), we assumed a kinetic regime of growth, i.e., the condition (3.29) which is equivalent to $E_{\rm des} + E_{\rm sd} < 2\Delta U + 2\omega$. Then, $C'' \ll C/\sigma_c$, and the second parabolic law dependence will cross the straight line of the linear BCF law at a characteristic supersaturation

$$\sigma_c'' \cong \sigma_c \exp\Big(-\frac{E_{\rm des} + E_{\rm sd} - 2\Delta U - 2\omega}{2kT}\Big),$$

which is much greater than σ_c. It may happen that the second parabola $R = C''\sigma^2$ would not cross the BCF linear dependence in the experimental interval of the supersaturation.

The Back Stress Effect: It follows from Eq. (3.86) that the higher the supersaturation, the smaller the interstep distance Λ will be. The latter, in turn, leads to the linear law of growth (3.92). Cabrera and Coleman (1963) discussed this question and found that the analysis of Cabrera and Levine (1956) underestimates the interstep distance particularly at the center of the growth spiral. The center of the spiral "will see" a supersaturation smaller than σ because of the diffusion field which is due to the first turn of the spiral. The higher the supersaturation, the smaller should be the radius of the first turn and the stronger should be its influence on the adatom concentration at the center which, in turn, leads to an increase of the radius of the

Figure 3.15: For the evaluation of the "back stress effect." The spiral center is approximated by a circle of radius Λ_0 (after Cabrera and Coleman 1963).

first turn of the spiral. Thus, we should observe a feedback effect which is known in the literature as a "back stress" effect (Cabrera and Coleman 1963). In principle, we should observe the back stress effect not only at the center of the spiral as each step is under the influence of the diffusion fields of the neighboring steps at higher supersaturations.

In order to estimate it, we approximate the first turn of the spiral by a circular step with a radius Λ_0 (Fig. 3.15). The supersaturation at the center can be found easily from Eq. (3.59b). Under the condition $r = 0$, the Bessel function $I_0(0) = 1$ and the supersaturation in the center, σ_{s0} reads

$$\sigma_{s0} = \sigma\Big[1 - I_0^{-1}\Big(\frac{\Lambda_0}{\lambda_s}\Big)\Big]. \tag{3.97}$$

$I_0(x)$ is always greater than unity and the supersaturation at the spiral center σ_{s0} will always be smaller than σ. We multiply both sides of Eq. (3.97) with Λ_0/λ_s and bearing in mind that $\sigma_{s0}\Lambda_0/\lambda_s = \sigma_c$ (Eq. (3.89)) with $n = 1$ (elementary steps), we rewrite (3.97) in the form

$$\frac{\sigma}{\sigma_c} = \frac{1}{(\Lambda_0/2\lambda_s)[1 - I_0^{-1}(\Lambda_0/\lambda_s)]}. \tag{3.98}$$

We then tabulate the left-hand side of (3.98) and construct a plot of Λ_0/λ_s vs σ/σ_c (curve 1 in Fig. 3.16). As seen, the interstep

Figure 3.16: Dependence of step spacing in units of λ_s on the supersaturation σ in units of σ_c when the back stress effect is accounted for (curve 1). The dependence given by Eq. (3.86) is also shown for comparison (curve 2).

distance at the spiral center is always larger than the one predicted by Eq. (3.86) (curve 2, $\Lambda = 19\rho_c$, or $\Lambda/\lambda_s = 2/(\sigma/\sigma_c)$).

In the more interesting region of high supersaturations (small values of Λ_0/λ_s ($\Lambda_0/\lambda_s \to 0$)), the reciprocal of the Bessel function $I_0^{-1}(x)$ can be approximated by the parabola

$$I_0^{-1}(x) \cong 1 - \frac{1}{4}x^2,$$

which results in (Cabrera and Coleman 1963)

$$\frac{\Lambda_0}{\lambda_s} \cong 2\left(\frac{\sigma_c}{\sigma}\right)^{1/3}. \tag{3.99}$$

One can conclude that with increasing supersaturation, the interstep distance decreases much more slowly than required by the simple hyperbolic law $\Lambda \sim 1/\sigma$. The step spacing practically no longer depends on the supersaturation, but on the temperature through the mean free path λ_s. What is more important, however, is that the slopes p of the growth pyramids can never become too

steep and the growing surface will remain macroscopically more or less smooth. As for the $R(\sigma)$ dependence, the back stress effect leads to a more gradual transition from the parabolic to the linear growth law than required by Eq. (3.89).

One can conclude that when the source of the steps on the crystal surface is due to the presence of screw dislocations, one can observe a parabolic as well as a linear dependence of the rate of growth on the supersaturation. In the diffusion regime, one should observe a parabolic dependence at small supersaturations which goes gradually to linear one at high supersaturations. The latter is due to the strong overlapping of the diffusion fields around each step. The back stress effect makes the transition from parabolic to linear dependence more gradual. A linear dependence should be observed also from the beginning when the length or the perimeter of the step source is much smaller than the interstep spacing due to a single dislocation. In this case, the constant of the proportionality should be smaller than that due to the diffusion field overlapping, provided the interdislocation distance is greater than the mean free path of the adatoms and equal to it in the opposite case. In the case of the kinetic regime of growth, a parabolic dependence of the growth rate on the supersaturation should be observed with a rate constant much smaller than that in the diffusion regime.

3.2.2.3 *Growth in solutions*

Combining (3.15), (3.86), and (3.76) gives an expression for the rate of growth in a diffusion regime:

$$R = C\frac{\sigma^2}{\sigma_c}\frac{1}{\ln[(d/\pi a)(\sigma_c/\sigma)\sinh(\sigma/\sigma_c)]}, \tag{3.100}$$

where

$$\sigma_c = \frac{19\varkappa a^2}{\pi nkTd} \tag{3.101}$$

is the characteristic supersaturation and

$$C = \frac{DC_0 v_c}{d} \tag{3.102}$$

is the rate constant.

The condition $\sigma \ll \sigma_c$ ($\sinh(\sigma/\sigma_c) \cong \sigma/\sigma_c$) results in the parabolic dependence

$$R = C\frac{\sigma^2}{\sigma_c}\frac{1}{\ln(d/\pi a)}. \tag{3.103}$$

At $\sigma \gg \sigma_c$, the hyperbolic sine transforms into $\exp(\sigma/\sigma_c)/2$ and, neglecting $\ln(d\sigma_c/2\pi a\sigma)$ with respect to σ/σ_c, one obtains the linear dependence

$$R = C\sigma \tag{3.104}$$

as in the case of growth from a vapor phase.

In the kinetic regime of growth ($a\beta_{\rm st}/\pi D \ll 1$), one obtains the second parabolic law

$$R = C''\sigma^2, \tag{3.105}$$

where

$$C'' = \frac{nkT}{19\varkappa a}\beta_{\rm st}C_0 v_c. \tag{3.106}$$

Bearing in mind (3.101), (3.102), and (3.103), we find that $C''/[C/\sigma_c \ln(d/\pi a)] = (a\beta_{\rm st}/\pi D)\ln(d/\pi a) \ll 1$ ($\ln(d/\pi a) \cong 10$), i.e., the rate constant in the second parabolic law in a kinetic regime of growth is again smaller than that in the diffusion regime.

Finally, when $L \gg \Lambda$, $y_0 = L/n = l$, and $p = an/L$, we obtain the second linear law of growth

$$R = C'\sigma, \tag{3.107}$$

where

$$C' = \frac{a}{l}\frac{\beta_{\rm st}C_0 v_c}{1 + (a\beta_{\rm st}/\pi D)\ln[(l/a)\sinh(\pi d/l)]}. \tag{3.108}$$

We consider again the example of growth of ADP crystals in aqueous solutions at room temperature (Chernov 1989). We can estimate the radius ρ_c of the critical nucleus and, in turn, the interstep spacing from independent measurements of the rate of growth of a perfect crystal face without screw dislocations. As will be shown in the

next chapter, such measurements allow the evaluation of the work of nucleus formation and of all parameters connected with it, as the rate of growth is limited by 2D nucleation. Thus, the interpretation of the experimental results gave for the specific edge energy the value $\varkappa \cong 5.5 \times 10^{-7}$ erg cm^{-1}. Then, at $\sigma = 0.03$, $\rho_c \cong 0.95 \times 10^{-6}$ cm, $y_0 = \Lambda = 18 \times 10^{-6}$ cm ($n = 1$), and $p \cong 2.6 \times 10^{-3}$. With the value $v_\infty = 2.4 \times 10^{-5}$ cm s^{-1} calculated in the previous chapter for $\sigma = 0.03$, one obtains for R the value 6.24×10^{-8} cm s^{-1}. The latter is in good agreement with the experimentally measured value 5.8×10^{-8} cm s^{-1}.

3.2.2.4 *Growth in melts*

The rate of growth in melts obeys the same equations as in solutions. We assume that the interstep distance is again given by (3.86). In Sec. 3.2.1.3, we evaluated the rates of step advance of Si and GaAs to be 3.7 cm s^{-1} and 0.1 cm s^{-1}, respectively, at undercooling $\Delta T = 1$ K. In order to evaluate the slopes p, we need data for the specific edge energies. We can estimate the latter from data of the specific surface energies. However, such data concerning the crystal–melt boundary for semiconductor substances are scarce in the literature. It is believed that they are around some hundreds of ergs per square centimeter (181 erg cm^{-2} (Turnbull 1950) and 251 erg cm^{-2} (Skripov, Koverda and Butorin 1975) for Ge). Adopting the value 200 erg cm^{-2} for both Si and GaAs, we find $y_0(\text{Si}) = 1.52 \times 10^{-4}$ cm, $y_0(\text{GaAs}) = 1.44 \times 10^{-4}$ cm, $p(\text{Si}) = 2 \times 10^{-4}$ and $p(\text{GaAs}) = 2.8 \times 10^{-4}$ at $\Delta T = 1$ K. Then, for the rate of growth $R = pv_\infty$, the values 7.4×10^{-4} cm s^{-1} and 2.8×10^{-5} cm s^{-1} can be obtained for Si and GaAs, respectively. As seen, they are 3–5 orders of magnitude higher than the respective values for growth in solutions.

3.2.3 *Growth by 2D nucleation*

The growth of defectless crystals of Si, Ge, GaAs, CdTe, etc. for the demands of the microelectronics stressed the necessity of developing in more detail the theory of growth through formation and lateral propagation of 2D nuclei. Historically, it was the first theory of crystal growth whose foundations were laid down more than hundred years

ago by Gibbs (1928). He pointed out in his famous footnote (see also (Frank 1958a)) that the continuous growth of a given crystal face is impossible if new molecular layers could not be built. The building of a new layer is particularly *difficult at the beginning or immediately after the beginning of the new layer formation.* The change of the Gibbs free energy necessary for the growth of the crystal face to take place is not, however, one and the same on different crystal faces. It is possible that it is greater for surfaces with smaller surface energies. Thus, without even mentioning the term "nucleus" Gibbs gave the concept of the growth of perfect crystals through the formation and lateral spreading of 2D nuclei. He even gave a hint concerning the effect of the surface structure of the crystal faces with respect to the rate of 2D nucleation.

We will consider first the *layer-by-layer growth*, or, in other words, the growth when the next atomic plane is nucleated after the completion of the previous one. Then, we will consider the case when the nucleation of the next atomic plane takes place before the completion of the previous one. This is the so-called *multilayer growth* when two or more monolayers (MLs) grow simultaneously. We will consider first the simpler case of the constant nucleation rate and the constant rate of propagation of the 2D islands (constant rate of step advance) and then we will allow the nucleation rate and the rate of step advance to depend on time through the size of the underlying 2D islands. In fact, the latter takes place during the growth from a vapor phase or MBE growth. In doing all that, we will follow one and the same approach which will be outlined when considering the simplest case of layer-by-layer growth with constant rates of 2D nucleation and step advance.

3.2.3.1 *Constant rates of nucleation and step advance*

Layer-by-layer Growth: Consider a face of a perfect defectless crystal with size L (Fig. 3.17) (Chernov 1984). At the given supersaturation, 2D nuclei are formed with a rate $J_0 = \text{const}$ ($\text{cm}^{-2}\ \text{s}^{-1}$). We define first the frequency (s^{-1})

$$\tilde{J}_0 = J_0 L^2 \tag{3.109}$$

Figure 3.17: Crystal face of linear size L with growing 2D islands on top of it.

of 2D nucleation on the crystal face with an area L^2.

If the rate of lateral growth or the rate of the step advance is $v =$ const (cm s^{-1}), then the time for the complete coverage of the face by one ML will be

$$T = \frac{L}{v}.$$

The number of nuclei formed during this time interval is a product of the nucleation frequency and the time for complete coverage of the face, or

$$N = \tilde{J}_0 T = J_0 L^2 \frac{L}{v} = J_0 \frac{L^3}{v}. \tag{3.110}$$

One can distinguish two cases. In the first one, $N < 1$ which is equivalent to $L < (v/J_0)^{1/3}$. This means that every succeeding nucleus will be formed after the complete coverage of the crystal face by the ML initiated by the preceding nucleus. As a result, we will observe layer-by-layer growth. Hence, the growth of the crystal face will be a periodic process of successive formation of 2D nuclei and their lateral propagation (see Fig. 3.23). The rate of growth of the crystal face will be determined by the rate of 2D nucleation and will be given by

$$R = \tilde{J}_0 a = J_0 L^2 a, \tag{3.111}$$

where a is the height of the step originated by the nucleus and J_0 is given by Eqs. (2.89), (2.92) or (2.99) in the particular cases of growth from vapors, solutions, or melts, respectively. This case is known in the literature as *mononuclear* monolayer growth.

Figure 3.18: Supersaturation dependence of the rate of 2D growth in the case of layer-by-layer growth (curve 1) and multilayer growth (curve 2).

Having in mind that v depends linearly on the supersaturation while the nucleation rate increases exponentially with it, one can conclude from (3.110) that layer-by-layer growth should be observed at low enough supersaturations. Besides, the smaller the crystal face is, the more pronounced the mononuclear layer-by-layer growth will be. Bearing in mind the estimates of J_0 and v made in the previous chapters (Eqs. (2.92) and (3.76)), we find that the linear size L of the face of a crystal growing in the solution should be smaller than 2×10^{-4} cm at $\sigma = 0.01$, or 2×10^{-6} cm at $\sigma = 0.02$, or 4×10^{-7} cm at $\sigma = 0.03$, etc., in order to grow layer after layer.

The growth rate R vs supersaturation according to Eq. (3.111) is illustrated in Fig. 3.18 (curve 1). As shown, a critical supersaturation

$$\sigma_c = \frac{\pi \varkappa^2 a^2}{(kT)^2 \ln(K_1 L^2 a / R_c)} \tag{3.112}$$

should be overcome for visible growth to take place. In Eq. (3.112), K_1 is the pre-exponential term in Eq. (2.89) (or (2.92)) and R_c is a more or less arbitrary chosen critical value of the growth rate. For example, in the growth of the prismatic face of an ADP crystal in the aqueous solution at room temperature (surface energy 11.8 erg cm^{-2} and $a = 8 \times 10^{-8}$ cm) (Chernov 1989) with $\varkappa \cong 11.8$ erg cm^{-2} $\times 8 \times 10^{-8}$ cm $\cong 1 \times 10^{-6}$ erg cm^{-1}, $K_1 \cong 1 \times 10^{19}$ cm^{-2} s^{-1},

Figure 3.19: Illustration of the multilayer growth of a crystal face with a size L by 2D nucleation.

$R_c \cong 1 \times 10^{-9}$ cm s^{-1}, and $L = 1 \times 10^{-4}$ cm, $\sigma_c = \Delta\mu_c/kT \cong 0.38$, or $C/C_0 \cong 1.5$. Thus, a critical supersaturation as high as 50% is required for the layer-by-layer growth of the prismatic face of the ADP crystal to take place.

Multilayer Growth: In the other extreme $L > (v/J_0)^{1/3}$ $(N > 1)$, new nuclei will form on top of the growing ML before the latter is completed and the situation given in Fig. 3.19 results. Several MLs grow simultaneously. The theoretical analysis of this case is much more complicated (Chernov and Lyubov 1963; Nielsen 1964; Hillig 1966). An approximate treatment will be given here following Chernov (1984).

Consider a crystal face with a ML island growing onto it with a rate v. At a given moment when the size of the island reaches a lateral size l, a 2D nucleus appears on top of it. The frequency of nucleation on top of the island is now $\tilde{J}_0 = J_0 l^2$ and the average time elapsed from the moment of nucleation of the first island to the moment of nucleation of the second island is $l/v \cong 1/\tilde{J}_0$. We then find that the mean size of the lower 2D island when a new 2D nucleus if formed on top is

$$l \cong \frac{v}{\tilde{J}_0}. \tag{3.113}$$

Thus, the critical island size for second-layer nucleation is larger, the larger is the rate of island growth and the smaller is the nucleation frequency. As will be shown later, this quantity plays a significant role in MBE growth and we will treat this question in more detail

when considering the effect of the Ehrlich–Schwoebel (ES) barrier to downstep diffusion on the growth morphology.

Bearing in mind that $\tilde{J}_0 = J_0 l^2$, (3.113) turns into $l = (v/J_0)^{1/3}$. The rate of growth of the crystal face is proportional to $J_0 l^2 a$ or

$$R \cong J_0 l^2 a = a(J_0 v^2)^{1/3}. \tag{3.114}$$

This expression is valid for two cases. The first case is when the 2D nuclei belong to a single layer (SL) which results again to a layer-by-layer growth. This is known in the literature as *polynuclear layer-by-layer* growth. The second case is the multilayer growth or *polynuclear multilayer* growth or the formation of mounds or stacks of 2D islands on top of each other. Both cases differ up to a constant which is slightly greater in the second case (Kashchiev 2000).

Recollecting that the pre-exponential factor in Eqs. (2.89), (2.92), and (2.99), for the rate of 2D nucleation is proportional to the square root of the supersaturation and that the rate of the step advance is a linear function of the latter, we find

$$R = \mathrm{const}(\Delta\mu)^{5/6} \exp\Big(-\frac{\Delta G^*}{3kT}\Big), \tag{3.115}$$

where the constant is equal to $[K_1'(\beta_{\mathrm{st}} C_0 v_c)^2]^{1/3}$ ($K_1' = K_1/\sqrt{\sigma}$) (in the particular case of growth from solutions). The rate of growth does not depend any more on the size of the crystal, but still a critical supersaturation should be overcome in order the growth to take place. Obviously, this critical supersaturation should be smaller than the one calculated on the base of the layer-by-layer growth (Fig. 3.18, curve 2). Taking into account the values of $v = 2.4 \times 10^{-5}$ cm s^{-1}, $K_1 = 1 \times 10^{19}$ cm^{-2} s^{-1}, and $R_c \cong 1 \times 10^{-9}$ cm s^{-1} calculated before, we find a critical supersaturation of about 8.6%, instead of 50%. Comparison with the experiment (Chernov 1989) shows that this value is still an overestimation, but gives the right tendency.

One concludes that initially the perfect crystals grow by the mononuclear layer-by-layer mechanism up to a critical size determined by the condition $N = 1$ or $L = (v/J_0)^{1/3}$. Beyond this size, a gradual transition from mononuclear layer-by-layer to polynuclear layer-by-layer growth and then to multilayer mechanism takes place

Figure 3.20: Illustration of the three modes of growth through 2D nucleation: (a) mononuclear layer-by-layer growth, (b) polynuclear layer-by-layer growth, (c) multilayer growth.

(Fig. 3.20). Large enough crystal faces grow by the multilayer mechanism and the growth front consists of several monomolecular layers which grow simultaneously. This question is closely connected with the RHEED intensity oscillations of the specular beam during MBE growth and will be considered here in some more detail.

We denote the surface coverage of the first ML by Θ_1. The growth rate is $R_1 = ad\Theta_1/dt$ and from Eq. (2.148) we find that the completion with time of the first ML follows the time law

$$R_1 = \pi a J_0 v^2 t^2 \exp\Big(-\frac{\pi}{3} J_0 v^2 t^3\Big), \tag{3.116}$$

which is illustrated in Fig. 3.21 (curve 1). As seen, the rate of deposition of the first ML increases parabolically at short times, then displays a maximum at $t_m = (2/\pi J_0 v^2)^{1/3}$ and after that decreases exponentially at large times up to the completion of the layer.

It is useful to express the growth rate (3.116) in terms of the surface coverage Θ_1. Making use of (2.148) gives

$$R_1 = a(9\pi J_0 v^2)^{1/3}(1-\Theta_1)[-\ln(1-\Theta_1)]^{2/3}. \tag{3.116$'$}$$

The growth rate displays a maximum at $\Theta_m = 1 - \exp(-2/3) = 0.4866$. As seen, the maximum is slightly shifted to the left from $\Theta_1 = 1/2$ when constant growth v and nucleation J_0 rates are assumed.

Figure 3.21: Plot of the rate of 2D growth as a function of time in terms of the characteristic time $\tau = (J_0 v^2)^{-1/3}$. Curve 1 gives the layer-by-layer growth. Curve 2 represents the multilayer growth calculated with the mean field approximation of Borovinski and Tzindergosen (1968). Curve 3 is a result of Monte Carlo simulation by Gilmer (1980).

In fact, Eq. (3.116) describes the behavior with time of the layer-by-layer growth when each layer is initiated by several nuclei growing simultaneously (multinuclei layer-by-layer growth, see Fig. 3.25). Then, the maximum value $R_m = 1.19a(J_0 v^2)^{1/3}$ gives the amplitude of the growth oscillations. The theoretical treatment of the multinuclei multilayer growth is much more complicated and has not been solved analytically up to now. That is why the time evolution of the separate MLs and of the growth front is usually studied numerically by the method of Monte Carlo (Gilmer 1980a, 1980b).

The analysis is based again on the approach of Kolmogorov (1937) and Avrami (1939, 1940, 1941). Recalling (2.147), the surface coverage Θ_1 of the first layer now reads

$$\Theta_1 = 1 - \exp\left[-\pi J_0 c^2 \int_0^t \left(\int_{t'}^t k(\tau - t')d\tau\right)^2 dt'\right].$$

Assuming $k(t) = 1$ results in (2.148) and (3.116). For every succeeding ML, the above expression is not valid any more as the

formation of 2D nuclei of each new layer depends on the surface coverage of the preceding one, or, more precisely, on the probability that there is a crystallized part of the underlying layer just under the 2D nuclei. Instead, one writes the expression

$$\Theta_n = 1 - \exp\left[-\pi J_0 c^2 \int_0^t p_{n-1}(t')\left(\int_{t'}^t k(\tau - t')d\tau\right)^2 dt'\right], \quad (3.117)$$

where $p_{n-1}(t')$ is the probability at the moment t' of the formation of a 2D nucleus of the nth layer the latter to find a crystallized part under itself in the preceding $n-1$st layer. Obviously, $p_{n-1}(t') = 1$ for the first ML $n = 1$.

In the more general case when the nucleation rate is time dependent, the latter enters into the integral and Eq. (3.117) turns into

$$\Theta_n = 1 - \exp\left[-\pi c^2 \int_0^t J(t')p_{n-1}(t')\left(\int_{t'}^t k(\tau - t')d\tau\right)^2 dt'\right]. \quad (3.117')$$

Differentiation of (3.117′) gives an expression which is often used in calculations of the growth rate:

$$\frac{d\Theta_n}{dt} = [1 - \Theta_n(t)]\int_0^t J(t')p_{n-1}(t')2\pi\rho_n(t')v_n(t')dt', \quad (3.117'')$$

where $v_n(t', t) = d\rho_n(t', t)/dt$ is the rate of growth of the 2D island of the nth layer.

In order to find a solution of (3.117), one has to determine the probability $p_{n-1}(t')$ which is the main problem. To solve it, Borovinski and Tzindergosen (1968) used the mean-field approximation assuming that the probability $p_{n-1}(t')$ is equal to the surface coverage of the preceding ML, i.e., $p_{n-1}(t') = \Theta_{n-1}(t')$, and computed the set of recurrent equations for Θ_n. First, the expression for Θ_1 is substituted into Eq. (3.117″) for Θ_2 and the latter is solved numerically, then the result is substituted into the equation for Θ_3, etc. A set of S-shaped curves for Θ_n going from zero to unity and a set of bell-shaped curves $R_n/a = d\Theta_n/dt$ are obtained. The integration is carried out up to the moment in which a steady state is reached such that the shift of each curve with respect to the preceding one

Figure 3.22: Variation with time of the rates of growth of the separate MLs, $R_n = ad\theta_n/dt$, in the case of steady-state multilayer growth. The curves are shifted by a period T. One ML is completed in a time interval T'. The overall rate of growth, $R = \Sigma R_n$, is also shown by the straight line (after Borovinski and Tzindergosen 1968).

remains constant (Fig. 3.22), i.e.,

$$\Theta_{n+1}(t) = \Theta_n(t - T), \tag{3.118}$$

where T is the period or the time of advance of the front of crystallization by one ML. Numerical calculations have shown that $T = 0.63(J_0 v^2)^{-1/3}$. The steady-state rate of growth is then given by

$$R = \frac{a}{T} = 1.59a(J_0 v^2)^{1/3} \tag{3.119}$$

which coincides up to a constant with Eq. (3.114).

A very important question is the number of MLs which grow simultaneously or, in other words, the thickness of the front of crystallization. The numerical calculations have shown that an S-shaped curve giving the time dependence of Θ_n in the steady state varies from 0.001 to 0.999 in a time interval $T' = 2.6(J_0 v^2)^{-1/3}$ (or so does

the width of the bell-shaped curves in Fig. 3.22). The number of the simultaneously growing MLs is then given by $T'/T \cong 4$. Note that the growth front thickness does not depend on the rates of nucleation and step advance in the model under study.

Figure 3.22 shows also the sum of the bell-shaped curves,

$$R = \sum_{n=1}^{\infty} R_n = a \sum_{n=1}^{\infty} d\Theta_n dt, \tag{3.120}$$

which represents the overall rate of growth of the crystal face.

Figure 3.22 gives the steady state, i.e., after enough time is elapsed from the beginning of the growth. In the beginning of the process, the growth rate displays several oscillations (or a series of maxima and minima) which gradually attenuate (Fig. 3.21, curve 2) due to the thickening of the growth front. The value of $R(t)$ at long enough times goes to a time-independent value given by Eq. (3.120).

Numerical simulations performed by using the method of Monte Carlo (Gilmer 1980a, 1980b) (Fig. 3.21, curve 3) have shown that the mean-field approximation used by Borovinski and Tzindergosen (Fig. 3.21, curve 2) overestimates the rate of growth. This is the reason different approximations for the probability $p_{n-1}(t)$ have been used (Armstrong and Harrison 1969) which give the same qualitative behavior but different asymptotic values for the steady-state growth rate (Gilmer 1980).

3.2.3.2 *Time-dependent rates of nucleation and step advance*

The MBE (Chang and Ludeke 1975; Ploog 1986) is a powerful technique for the investigation of the elementary processes of crystal growth in detail which are unaccessible by other methods. Besides, *in situ* measurements with surface analytical tools such as RHEED and LEED are easily performed during growth and detailed information concerning the mechanism of growth is easily gathered. That is why we will consider the MBE growth in more detail. It is worth noting that the MBE growth represents simply a crystal growth via 2D nucleation or step flow at higher temperature. This is the reason we will consider it in this chapter rather than in Chapter 4.

Figure 3.23: RHEED intensity oscillations on Si(0 0 1) taken from ⟨1 1 0⟩ azimuth at 500°C. (T. Sakamoto, N. J. Kawai, T. Nakagawa, K. Ohta, T. Kojima and G. Hasegawa, *Surf. Sci.* **174**, 651 (1986). By permission of Elsevier Science Publishers B.V. and courtesy of T. Sakamoto.)

As was shown above, the basic postulates $J_0 = \text{const}$ and $v = \text{const}$ lead to several, in fact, not more than four or five oscillations of the overall growth rate (Fig. 3.21). The latter is in agreement with experimental observation for electrolytic growth of Ag from aqueous solutions where the above postulates are fulfilled. This is not, however, the case of MBE growth. Strong oscillations of the RHEED intensity have been reported during the growth of a series of materials such as Si, Ge, GaAs (Wood 1981; Harris, Joyce and Dobson 1981; Neave *et al.*, 1983; Van Hove *et al.*, 1983). oscillations of the specular beam during the growth of $Al_xGa_{1-x}As(1\,0\,0)$ face ($x = 0.41$) in the [100] azimuth (Sakamoto *et al.*, 1985b, 1990) and 2200 oscillations of the specular beam during the growth of Si(1 0 0) in the [1 1 0] azimuth (Fig. 3.23) (Sakamoto *et al.*, 1986a, 1987) have been reported.

The decoding of the true nature of the oscillations leads to accumulation of new knowledge about the crystal growth processes. It was proved that one period of the oscillations corresponds exactly to the time T of the growth of one complete ML. We, thus, measure exactly the rate of growth. On the other hand, we could use the oscillations in order to taylor more precisely the epitaxial layers or superlattices. Obviously, if the deposition of one material is interrupted in order to

deposit another material when the RHEED intensity goes through a maximum the possibility of producing a sharp interface is much greater. This is usually known as "phase-locked epitaxy" (Sakamoto *et al.*, 1985b).

Another example of the use of the RHEED intensity oscillations is the measurement of the composition of, say, a ternary alloy and, in turn, the natural misfit between it and the underlying binary (Sakamoto *et al.*, 1985b; Chang *et al.*, 1991). If, for example, a superlattice $Al_xGa_{1-x}As/GaAs(1\,0\,0)$ is grown (Sakamoto *et al.*, 1985b), the opening and closing of the shutter of the Al source lead to the increase and decrease of the growth rate and, in turn, of the oscillations frequency (Fig. 3.24). Measuring the oscillations frequencies $\mathcal{F}(GaAs)$ and $\mathcal{F}(Al_xGa_{1-x}As)$, one can calculate the mol fraction x

Figure 3.24: RHEED intensity oscillations of the specular beam observed in the $\langle 1\,0\,0 \rangle$ GaAs substrate during the continuous growth of GaAs, $Al_xGa_{1-x}As$ and AlAs. (T. Sakamoto, H. Funabashi, K. Ohta, T. Nakagawa, N. G. Kawai, T. Kojima and Y. Bando, *Superlatt. Microstruct.* **1**, 347 (1985). By permission of Academic Press Ltd and courtesy of T. Sakamoto.)

through the relation (Sakamoto *et al.*, 1985b)

$$x = \frac{\mathcal{F}(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}) - \mathcal{F}(\mathrm{GaAs})}{\mathcal{F}(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As})}.$$

Then, the natural misfit f can be easily estimated through the Vegard law (1921). According to the latter, the relative change of the lattice parameter (increase or a decrease) of the host crystal is directly proportional to the concentration of the solute atoms within a certain interval. In other words,

$$f = x\frac{a_0(\mathrm{AlAs}) - a_0(\mathrm{GaAs})}{a_0(\mathrm{GaAs})}.$$

In this section, we will consider the growth of a defectless crystal face via 2D nucleation in the more realistic case when J_0 and v depend on the size of the underlying 2D islands through the adatom concentration on top of it. First, we will consider the multinuclei layer-by-layer growth (Fig. 3.25) and the simultaneous growth of two MLs (Fig. 3.26). Then, we will generalize the model for the arbitrary number of simultaneously growing MLs and study the dependence of the total step density on the thickness of the growth front. The influence of the anisotropy of the growing surface on the mode of growth will be considered on the example of the growth of the (0 0 1) face of Si. At the end of this section, the asymmetry of incorporation of atoms into ascending and descending steps owing to the existence of the ES barrier which inhibits the interlayer transport will be briefly considered. Its consequences on the mechanism of crystal growth and the morphology of the growing surfaces will be discussed.

Polynuclear Layer-by-layer Growth: We make the following assumptions. First, we consider the case of complete condensation or the absence of re-evaporation. This means that all material deposited joins the growing 2D islands. In fact, this is usually the case when films of semiconductors and most of the metals are grown due to the high binding energies. Second, we assume that the nucleation of the first ML takes place in a short (in fact negligible) period of time in the beginning of deposition (this is the so-called *instantaneous nucleation*). In other words, N_s nuclei are formed in the initial moment

Figure 3.25: Different stages of growth of a crystal face by polynuclear layer-by-layer growth. After the deposition of a ML, the face restores its initial state.

$t = 0$ of the growth of each ML (Toschev, Stoyanov and Milchev 1972). After the complete coverage of the crystal face, N_s nuclei are again formed in a short interval of time and so on. In considering this problem, we will follow the treatment given by Stoyanov (1988).

Before going into detail, a certain point should be clarified. As discussed above, any deviation from the layer-by-layer growth (Fig. 3.25), i.e., transition to simultaneous growth of two, three, etc. MLs, leads to a decrease of the amplitude of the RHEED intensity oscillations with time. Two parameters vary periodically with time during growth. First, this is the rate of growth of each

Figure 3.26: Different stages of growth of a crystal face by bilayer growth. In this case, the crystal face never restores its initial state. Instead, states with higher and lower total step densities alternate.

ML $R_n = ad\Theta_n/dt$ (Fig. 3.22) and, second, this is the total step density. The overall growth rate is a sum of the growth rates of the separate MLs (see Eq. (3.120) and Fig. 3.22) and should vary periodically with time also. It will be shown in this section that the rate of growth of each ML is directly proportional to the step density and the proportionality constant is simply the rate of advance v of the separate 2D islands. In the model considered above, the rate of advance v was assumed constant and, hence, both the step density

and the rate of growth of each ML R_n oscillate in a phase. When more than four or five layers grow simultaneously, the growth rate ceases to oscillate visibly. A more elaborate model of growth should account for the surface diffusion of adatoms between the steps originated from 2D islands on different levels and the rate of advance of the steps depends on the island size and, hence, on time. Then, the total step density and the rates of growth of the separate MLs cease to oscillate in a phase. The second important assumption made is that the re-evaporation of adatoms is negligible. This means that at a constant rate of deposition, the overall rate of growth should be constant, i.e., it will not oscillate irrespective of the oscillations of the growth rates of the separate MLs. However, the total step density oscillates and the amplitude of the oscillations is a decreasing function of the growth front thickness. It follows that the oscillations of the RHEED intensity during MBE growth are due solely to the oscillations of the total step density but not to the oscillations of the surface coverages or the rates of growth.

With the assumption for instantaneous nucleation, the surface coverage of the first ML Θ_1 is given by (see Chapter 2)

$$\Theta_1 = 1 - \exp\left[-\pi N_s \left(\int_0^t v(t')dt'\right)^2\right]. \tag{3.121}$$

The growth rate $R_1 = ad\Theta_1/dt$ of the first ML then reads

$$R_1 = 2av(t)\sqrt{\pi N_s}(1-\Theta_1)\sqrt{-\ln(1-\Theta_1)}. \tag{3.122}$$

The total step density is given by (see Fig. 3.27)

$$L = \frac{1}{v(t)}\frac{d\Theta_1}{dt} = \frac{R_1}{av(t)}. \tag{3.123}$$

Equation (3.123) gives the proportionality between the step density and the growth rate discussed above. As seen, if the rate of step advance v is time independent, both L and R_1 should have the same time behavior.

Figure 3.27: For the determination of the step density $L(t)$ through the surface coverage $\Theta(t)$. The change of $\Theta(t)$ with time is represented by the shadowed area.

Substituting (3.122) into (3.123) gives

$$L = 2\sqrt{\pi N_s}(1-\Theta_1)\sqrt{-\ln(1-\Theta_1)}. \qquad (3.123')$$

The step density displays a maximum $L_{\max} = (2\pi N_s/e)^{1/2}$ at a certain value of the surface coverage $\Theta_{\max} = 1 - \exp(-0.5) = 0.393$. The maximum is shifted much more to the left of $\theta = 0.5$ than in the case of constant rates of nucleation and step propagation. As seen, the variation of the step density is reduced to the finding of the number of nuclei N_s.

We consider a system of N_s regularly spaced 2D islands, and, at a moment t, the surface coverage is

$$\Theta_1 = \pi\rho_1^2 N_s = \frac{\Re t}{N_0}, \qquad (3.124)$$

where N_0 (cm^{-2}) is the density of a ML and $\Re$ (cm^{-2} s^{-1}) is the atom arrival rate. Equation (3.124) means that all atoms arriving from the vapor phase join the 2D islands, or in other words, all material deposited until the moment t, $\Re t/N_0$, is equally distributed among the growing 2D islands.

Further, we will follow the same approach as developed by Chernov (1984) and Borovinski and Tzindergosen (1968). Analogously to the frequency of nucleation on a crystal face with a lateral size L, J_0L^2 (see Eq. (3.109)), the frequency of nucleation on the surface of

a growing island with a radius $\rho_1(t)$ is

$$\tilde{J}_0(\rho_1) = \int_0^{\rho_1} J_0(r) 2\pi r dr. \tag{3.125}$$

In Eq. (3.125), $J_0(r) = J_0[n_s(r)]$ is the nucleation rate which is now a function of the time through the size dependence of the adatom concentration $n_s(r)$ on the surface of the latter.

The adatom concentration on the surface of the growing 2D island can be found by solving the diffusion problem in polar coordinates (Eq. (3.58)) which in the case of complete condensation reads

$$\frac{d^2 n_s}{dr^2} + \frac{1}{r}\frac{dn_s}{dr} + \frac{\Re}{D_s} = 0. \tag{3.126}$$

This equation differs from (3.58) only by the absence of the desorption flux n_s/τ_s. The solution reads

$$n_s = A - \frac{\Re}{4D_s} r^2, \tag{3.127}$$

where the constant A should be determined from the boundary condition

$$n_s(r = \rho_1) = n_{\text{se}}, \tag{3.128}$$

which means that the exchange of atoms between the island edges and the adlayer is fast enough, and, near the island edge, the adatom concentration has its equilibrium value n_{se}. In other words, the growth proceeds in a diffusion regime.

The solution of the problem reads

$$n_s(r) = n_{\text{se}} + \frac{\Re}{4D_s}(\rho_1^2 - r^2). \tag{3.129}$$

It is immediately seen that the adatom concentration has its highest value $n_s(r = 0) = n_{\text{s,max}} = n_{\text{se}} + \Re\rho_1^2/4D_s$ at the island center and that the larger the island, the higher this adatom concentration will be. Obviously, the nucleation on the island center is most probable. Besides, the flux of atoms toward the edge of the island $j_s = -2\pi\rho_1 D_s (dn_s/dr)_{r=\rho 1} = \pi\Re\rho_1^2$ also increases with the island size and so does the rate of growth (cf Eq. (3.62)). It follows that the nucleation rate and the rate of the step advance become greater with increasing island size.

At high temperatures, the equilibrium adatom concentration $n_{\rm se}$ increases, whereas the second term in (3.129) decreases (see Eq. (3.20)). Bearing in mind that $\Re \cong 1 \times 10^{13} - 1 \times 10^{14}$ cm^{-2} s^{-1}, $\nu \cong 3 \times 10^{13}$ s^{-1}, and $\rho_1 \cong 1 \times 10^{-6} - 1 \times 10^{-5}$ cm, we find that at high enough temperatures, $n_{\rm se}$ becomes much greater than $\Re\rho_1^2/4D_s$ and $n_{\rm s,max} \to n_{\rm se}$. The latter means that the supersaturation tends to zero at high temperatures. At low temperatures, we can neglect $n_{\rm se}$ in comparison with $\Re\rho_1^2/4D_s$ and $n_s \cong \Re/4D_s(\rho_1^2 - r^2)$. Bearing in mind Eq. (3.18), it follows that for Si ($\varphi_{1/2} - E_{\rm des} \cong 1.8$ eV) $n_{\rm se}$ can be neglected in the whole temperature interval of interest (300–800°C). This is valid also for many other materials.

The nucleation rate as a function of the adatom concentration reads (see Eq. (2.117))

$$J_0 = \alpha^* D_s \frac{n_s^{n^*+1}}{N_0^{n^*-1}} \exp\Big(\frac{E^*}{kT}\Big). \tag{3.130}$$

Substituting (3.129) into (3.130) (neglecting $n_{\rm se}$) and the latter into (3.125) gives upon integration for the nucleation frequency $\tilde{J}_0$:

$$\tilde{J}_0(\rho_1) = A\rho_1^{2(n^*+2)}, \tag{3.131}$$

where A combines all quantities which are independent of the island size:

$$A = \frac{\pi\alpha^*}{n^*+2} D_s N_0^2 \Big(\frac{\Re}{4D_s N_0}\Big)^{n^*+1} \exp\Big(\frac{E^*}{kT}\Big). \tag{3.131$'$}$$

The condition for layer-by-layer growth in complete analogy with the condition (3.110) is

$$N = \int_0^T \tilde{J}_0(\rho_1)dt = 1, \tag{3.132}$$

where the integral gives the number of nuclei which can be formed on top of the growing island for the time of deposition of one ML $T = N_0/\Re$. In other words, this condition states that a nucleus of the second ML will be formed exactly at the moment of completion of the first one.

We then substitute ρ_1^2 from (3.124) into (3.131) and (3.132) and after the integration and rearrangement of the results, one obtains

$$\begin{aligned} N_s &= \frac{1}{4\pi} C^* N_0 \Big(\frac{D}{F}\Big)^{-\chi} \exp\Big(\frac{E^*}{(n^*+2)kT}\Big) \\ &= \frac{1}{4\pi} C^* N_0 \Big(\frac{\nu}{F}\Big)^{-\chi} \exp\Big(\frac{E^* + n^* E_{\mathrm{sd}}}{(n^*+2)kT}\Big), \end{aligned} \tag{3.133}$$

where $D = D_s N_0 = \nu \exp(-E_{\mathrm{sd}}/kT)$ is the hopping frequency, $F = \Re/N_0$ is the atom arrival rate in the number of MLs per unit time, and

$$C^* = \Big(\frac{4\pi\alpha^*}{(n^*+2)(n^*+3)}\Big)^{1/(n^*+2)}$$

is a very weak function of n^* of the order of unity, and $\chi = n^*/(n^*+2)$.

We have just obtained an expression for the density of nuclei which give rise to 2D islands belonging to the first ML. In fact, we obtained Eq. (2.156) with a scaling exponent (2.157) (see Chapter 2, Sec. 2.2.11). This was possible, thanks to the conditions of complete condensation (3.124) and layer-by-layer growth (3.132) of a perfect crystal face. The second condition requires a diffusion regime of growth (fast incorporation of the atoms to the islands) which is the necessary condition for the scaling exponent (2.157).

Let us evaluate N_s. In the case of the growth of Si(0 0 1) at $T = 600$ K (high supersaturation) $n^* = 1$, $E^* = 0$, $E_{\mathrm{sd}} \cong 0.67$ eV, $\Re = 1 \times 10^{13}$ cm^{-2} s^{-1}, $\nu = 1 \times 10^{13}$ s^{-1}, $\alpha^* = 4$, and $N_0 = 6.78 \times 10^{14}$ cm^{-2}. Then, $N_s \cong 7.4 \times 10^{10}$ cm^{-2}. In the case of higher temperature $T = 1200$ K (low supersaturation), $n^* = 3$. We assume that the cluster consisting of four atoms with a shape of square (two parallel dimers) is a stable cluster with greater probability of growing than to decay. The nucleus then represents a cluster consisting of three atoms situated at the apexes of a rectangular triangle — a dimer plus an isolated atom situated in a position to form a second dimer. We note that the bonds between the dimers are second nearest bonds, and we can assume that $\psi_2 \cong E_{\mathrm{bond}}/10$. We take the values $E_{\mathrm{bond}} \approx 1.9$ eV and $E_{\mathrm{dimer}} \approx 1.7$ eV for the usual first neighbor bond and the dimer's bond, respectively (Ratsch and Zangwill 1993). Then,

$E^* = E_{\text{dimer}} + E_{\text{bond}}/10 \approx 1.89$ eV, and $\alpha^* = 8$. Then, $N_s \cong 1.6 \times 10^8$ cm^{-2}. Thus, the decrease of the supersaturation leads to an increase of the size of the critical nucleus which, in turn, leads to a sharp decrease of the saturation nucleus density by approximately three orders of magnitude in the particular case.

The maximum step density reads (the minimum step density is equal to zero)

$$L_{\max} = \frac{1}{\sqrt{2e}} C^* N_0^{1/(n^*+2)} \left(\frac{\Re}{\nu}\right)^{\chi/2} \exp\left(\frac{E^* + n^* E_{\text{sd}}}{2(n^*+2)kT}\right). \tag{3.134}$$

Values of 4×10^5 and 2×10^4 cm^{-1} for the maximum step density on Si (0 0 1) are obtained at high ($n^* = 1$) and low ($n^* = 3$) supersaturations, respectively. It follows that the amplitude of the oscillations of the step density during the periodic process of consecutive 2D nucleation and lateral propagation will decrease with decreasing supersaturation (increasing temperature). Obviously, at too high temperature (too low supersaturation), the RHEED intensity oscillations should disappear because of the inhibition of the 2D nucleation process. The same should be expected at too low temperatures or at high supersaturations but for another reason. The step density becomes very high and the step spacing too small. In other words, the crystal surface will behave as rough one, although the temperature is lower than the critical temperature for thermodynamic roughness (see Chapter 1). As discussed at the end of Chapter 1, this phenomenon is called kinetic roughness. What follows is that the oscillations of the step density and, in turn, the RHEED intensity oscillations will disappear as the steps are practically no more detectable for kinetic reasons.

Multilayer growth — Simultaneous Growth of Two Monolayers: In considering this case (Stoyanov and Michailov 1988), we follow the same procedure as described above. We consider again the case of complete condensation and instantaneous nucleation. The latter now means that, before the complete coverage of the crystal face by 2D islands of the nth ML, 2D nuclei of the $(n+1)$st ML are formed in a short period of time (as if by a pulse) on top of the islands of

Figure 3.28: Bilayer pyramid of growth. ρ_1 and ρ_2 denote the radii of the lower and upper 2D islands, respectively.

the nth ML. Then, the growth of the crystal face is realized by the simultaneous growth of pyramids with two MLs thickness. We assume further that the number of 2D nuclei giving rise to the islands of the nth ML is equal to that of the $(n+1)$st ML, or in other words, the growth proceeds by the simultaneous growth of N_s bilayer pyramids (Fig. 3.28). This pattern is preserved indefinitely and every deviation from it leads to the further increase of the growth front thickness and, in turn, to further damping of the oscillations of the step density.

Making use of (3.123) gives the step density for each ML

$$L_n(t) = \frac{1}{v_n(t)}\frac{d\Theta_n}{dt} = 2\sqrt{\pi N_s}(1-\Theta_n)\sqrt{-\ln(1-\Theta_n(t)}. \quad (3.135)$$

The total step density then is

$$L(t) = 2\sqrt{\pi N_s}\sum_n (1-\Theta_n)\sqrt{-\ln(1-\Theta_n(t)}. \quad (3.136)$$

Note that in this case, the rates of the step advance $v_n(t)$ and the surface coverages $\Theta_n(t)$ $(n = 1, 2)$ are not independent but are interconnected through the diffusion fields. Then, our next task is to solve again the diffusion problem and to find the density of the bilayer pyramids.

The solution for the adatom concentration on top of the upper island $(r < \rho_2)$ (see Eq. (3.129)) is

$$n_s(r) = n_{\rm se} + \frac{\Re}{4D_s}(\rho_2^2 - r^2). \quad (3.137)$$

The adatom concentration on the terrace ($\rho_2 < r < \rho_1$) is given by

$$n_s(r) = A - \frac{\Re}{4D_s} r^2 + B \ln r, \tag{3.138}$$

where A and B are constants which can be determined by the boundary conditions $n_s(\rho_1) = n_s(\rho_2) = n_{\text{se}}$. The solution reads

$$n_s(r) = n_{\text{se}} + \frac{\Re}{4D_s}(\rho_1^2 - r^2) - \frac{\Re}{4D_s}(\rho_1^2 - \rho_2^2)\frac{\ln(r/\rho_1)}{\ln(\rho_2/\rho_1)}. \tag{3.138$'$}$$

The flux of adatoms diffusing to the edges of the lower islands on the surface of the complete $(n-1)$st layer is

$$j_1 = \frac{\Re}{N_s}(1 - \pi\rho_1^2 N_s). \tag{3.139}$$

In Eq. (3.139), it is assumed that the atoms arriving from the vapor phase on the area $1 - \pi\rho_1^2 N_s$ uncovered by growth pyramids are equally distributed among the latter.

Correspondingly, the flux of adatoms diffusing to the same edges but on the terraces is

$$j_2 = -2\pi\rho_1 D_s \Big(\frac{dn_s(r)}{dr}\Big)_{r=\rho_1}.$$

The rate of growth v_1 is then given by

$$v_1 = \frac{d\rho_1}{dt} = \frac{1}{2\pi\rho_1 N_0}(j_1 + j_2)$$

or

$$\frac{d\rho_1}{dt} = \frac{\Re}{2\pi\rho_1 N_0 N_s}\Big(1 - \pi N_s \frac{\rho_1^2 - \rho_2^2}{2\ln(\rho_1/\rho_2)}\Big).$$

By the same way for the upper island, one obtains

$$\frac{d\rho_2}{dt} = \frac{\Re}{2\rho_2 N_0}\frac{\rho_1^2 - \rho_2^2}{2\ln(\rho_1/\rho_2)}.$$

We have to solve now a set of two nonlinear differential equations for the rates of advance of the steps. The latter can be written in

terms of surface coverages:

$$\Theta_n = \pi \rho_n^2 N_s \quad (n = 1, 2) \tag{3.140}$$

as a function of a dimensionless time $\theta = \Re t/N_0$, which is, in fact, the number of MLs deposited, in the form

$$\frac{d\Theta_1}{d\theta} = 1 - \frac{\Theta_1 - \Theta_2}{\ln(\Theta_1/\Theta_2)}, \tag{3.141a}$$

$$\frac{d\Theta_2}{d\theta} = \frac{\Theta_1 - \Theta_2}{\ln(\Theta_1/\Theta_2)}. \tag{3.141b}$$

As seen, the overall rate of growth $R = \sum R_n = a \sum d\Theta_n/dt = \Re a/N_0$ does not vary with the time. This is a direct consequence of the lack or re-evaporation or complete condensation.

An approximate analytical solution of (3.141) can be obtained if the equations are linearized assuming $\ln(\Theta_1/\Theta_2) = \text{const} = 2$. Then, the solution of (3.141) subject to the boundary conditions $\Theta_2(\theta = 0) = 0$ and $\Theta_1(\theta = 1) = 1$ reads (Kamke 1959)

$$\Theta_1 = 1 + \frac{1}{2}\theta - \frac{\mathrm{e}}{2(\mathrm{e}+1)}(1 + e^{-\theta}), \tag{3.142a}$$

$$\Theta_2 = \frac{1}{2}\theta - \frac{\mathrm{e}}{2(\mathrm{e}+1)}(1 - e^{-\theta}), \tag{3.142b}$$

where $e = 2.71828$ is the base of the Napierian logarithms.

As seen, at $\theta = 0$, $\Theta_1 = 1/(e+1) = 0.27$ and $\Theta_2 = 0$, whereas at $\theta = 1$, $\Theta_1 = 1$, and $\Theta_2 = 1/(e+1) = 0.27$. In other words, the solution reflects the periodicity inherent in the front of growth consisting of two MLs.

Substituting (3.142) into (3.136) results in a periodic curve with amplitude $L_{\max} = 0.23(4\pi N_s)^{1/2}$ (Stoyanov and Michailov 1988). So our next task is to find the number N_s of the growth pyramids, and we follow exactly the procedure used in the previous section. The frequency of nucleation on top of the upper islands is obtained by substituting the solution (3.137) (neglecting n_{se}) in expression (3.130) for the nucleation rate and the latter in (3.125). The integration gives an expression completely equivalent to (3.131) with the

only exception being that ρ_1 is replaced by ρ_2:

$$\tilde{J} = A\rho_2^{2(n^*+2)}, \tag{3.143}$$

where A is given by (3.131′).

From (3.140) and (3.142b), we have

$$\rho_2^2 = \frac{1}{2\pi N_s}\Big(\theta - \frac{e}{e+1}(1-e^{-\theta})\Big). \tag{3.144}$$

Substituting (3.144) into (3.143) and the latter into (3.132), and carrying out the integration, gives after the rearrangement of the result

$$N_s = \frac{1}{8\pi}C^* N_0\Big(\frac{\nu}{F}\Big)^{-\chi}\exp\Big(\frac{E^* + n^* E_{\rm sd}}{(n^*+2)kT}\Big), \tag{3.145}$$

where $C^* = [4\pi\alpha^*\mathcal{J}^*/(n^*+2)]^{1/(n^*+2)}$, and the definite integral

$$\mathcal{J}^* = \int_0^1 \Big(\theta - \frac{e}{e+1}(1-e^{-\theta})\Big)^{n^*+2} d\theta$$

is a function only of the number of atoms in the critical nucleus n^* and has values 0.03, 0.0125, 0.0056, and 0.00056 for $n^* = 1, 2, 3$ and 6, respectively.

We can estimate now the decrease of the amplitude of the step density oscillations when the growth front increases from one to two MLs. The latter depends on the height and the density of the corresponding numbers of bilayer pyramids given by (3.145) and ML 2D islands given by (3.133). The ratio of the square root of the islands densities is not much sensitive to the number of atoms in the critical nuclei n^* and is approximately equal to 0.5. In addition, the decrease of the amplitude due to the fact that the surface never reaches a state without steps when two MLs grow simultaneously is also approximately equal to 0.5 so the overall decrease of the amplitude of the total step density is about 0.2–0.25. Obviously, further decrease of the amplitude should be expected when a further increase of the growth front thickness takes place.

Simultaneous Growth of Arbitrary Number of Monolayers: We consider now the problem of the simultaneous growth of $N > 2$ MLs, where N is an integer. This means that the instantaneous nucleation

of 2D islands of the Nth ML coincides exactly with the completion of the zeroth ML. We assume further that the nucleation of the $(N+1)$st ML takes place before a significant coalescence of the 2D islands of the first ML occurs. Then, N_s pyramids of growth each consisting of N 2D islands one on top of the other will be formed as shown in Fig. 3.2. This model is a variation of the "birth-death model" proposed by Cohen *et al.* (1989) (see also (Kariotis and Lagally 1989)).

We solve the same diffusion problem as above. The adatom concentration on top of the islands of the Nth ML is given by (3.137) in which ρ_2 is replaced by ρ_N. The adatom concentration on the terraces is given by (3.138′) where ρ_1 and ρ_2 are replaced by ρ_n and ρ_{n+1}, respectively. Then, instead of (3.141), one obtains

$$\begin{aligned}
\frac{d\Theta_1}{d\theta} &= 1 - \frac{\Theta_1 - \Theta_2}{\ln(\Theta_1/\Theta_2)}, \\
\frac{d\Theta_n}{d\theta} &= \frac{\Theta_{n-1} - \Theta_n}{\ln(\Theta_{n-1}/\Theta_n)} - \frac{\Theta_n - \Theta_{n+1}}{\ln(\Theta_n/\Theta_{n+1})}, \\
\frac{d\Theta_N}{d\theta} &= \frac{\Theta_{N-1} - \Theta_N}{\ln(\Theta_{N-1}/\Theta_N)}.
\end{aligned} \tag{3.146}$$

As above, the overall rate of growth $R = \sum R_n = \Re a/N_0 = \text{const}$.

A remarkable property of the system (3.146) is that the dependence of the surface coverages on the number of the MLs does not involve any other parameter. This means that the solution of the system subject to the steady-state boundary conditions $\Theta_n(\theta = 0) = \Theta_{n+1}(\theta = 1)$ is unique. The solutions of (3.146) for $N = 2$ and $N = 3$ in a reduced form are shown in Fig. 3.29. The solutions for $N = 2$ and $N = 4$ are shown in Fig. 3.30 in an unfolded form. As shown, they represent S-shaped curves with an inflection point between the surface coverages of the second and first MLs. It follows that with increasing growth front thickness N, the rates of growth of the separate monolayes, $R_n = a d\Theta_n/d\theta$, will become more and more asymmetric with a maximum which shifts more and more to the right of $\theta = 0.5$. In other words, the bell-shaped curves obtained by the differentiation of the curves as shown in Fig. 3.30 will have

(a)

(b)

Figure 3.29: Steady-state variation with time in a folded form of the surface coverage of the separate MLs in (a) bilayer and (b) trilayer growth. In (a), curves 1 and 2 correspond to the first and second MLs, respectively, and the straight line 3 gives the layer-by-layer growth. In (b), the surface coverages of the first, second, and third MLs are shown by curves 1, 2, and 3, respectively. The curves are obtained by the numerical solution of the system of Eq. (3.146).

a downward branch after the maximum steeper than their upward branch before the maximum.

The total step density is given by (3.136) and is shown in Fig. 3.31 in terms of $2\sqrt{\pi N_s}$ for N varying from 1 to 6. The curves are obviously asymmetric with a maximum shifted to the left of 0.5.

Figure 3.30: Unfolded view of the steady-state variation with time of the surface coverages of the separate MLs in bilayer ($N = 2$) and tetralayer ($N = 4$) growth. The curves are obtained by the numerical solution of the system of Eq. (3.146).

Making use of the same approach as above (Eqs. (3.125) and (3.132)), we can calculate the number N_s of the growth pyramids at different values of the growth front thickness N and then the amplitudes of the time variations of the total step density. The latter are shown in Fig. 3.32 relative to that of $N = 1$ for N varying from 1 to 6. It is seen that the total step density decreases by an order of magnitude when the number of the simultaneously growing MLs N increases from 1 to 4, and about 20 times when $N = 6$.

The most important conclusions we can draw are the following:

(i) The shape of the oscillations of the total step density depends only on the surface coverages. In that sense it is unique.

(ii) The amplitude of the total step density oscillations is a function of the height and the density of the growth pyramids. In the extreme case of layer-by-layer growth stepped and completely smooth surfaces alternate (Fig. 3.25) and the amplitude has its highest value. The increase of the number of the simultaneously growing crystal planes leads to alternation of states with higher and lower step density (see Fig. 3.26), thus decreasing the overall amplitude. In addition, the density of the growth pyramids is a decreasing function of the thickness of the growth front

Figure 3.31: Variation with time of the total step density in units of $(4\pi N_s)^{1/2}$ at different thicknesses of the growth front denoted by the figure at each curve. As shown, the curves are visibly asymmetric. The amplitude decreases with increasing thickness of the growth front. In the case of layer-by-layer growth ($N = 1$), the step density varies from zero to the maximum density, thus reflecting the fact that the crystal face restores its initial (smooth) state after deposition of one ML. The variation of the step density in the case of multilayer growth never reaches zero. This means that the crystal face never becomes smooth again.

(the density of the higher pyramids must be obviously smaller than that of the lower ones), thus leading to the additional decrease of the amplitude of the step density.

(iii) The decrease of the amplitude due to the decrease of the density of the growth pyramids is a function only of the size n^* of the critical nucleus at the particular temperature.

(iv) The amplitude of the step density oscillations is not very sensitive to the atom arrival rate $\Re$ as the exponent $\chi/2 = n^*/2(n^* + 2)$ is smaller than unity.

Figure 3.32: Dependence on the thickness of the growth front of the amplitude of the total step density $L_{\max}$ relative to the step density in layer-by-layer growth (curve 3), the amplitude of the total step density $L_{\max}$ relative to the step density in layer-by-layer growth in units of $(4\pi N_s/e)^{1/2}$ (curve 2), and the square root of the density of the pyramids of growth $(4\pi N_s/e)^{1/2}$ relative to the layer-by-layer growth (curve 1).

(v) A decrease of the temperature leads to a sharp increase of the number of the growth pyramids N_s and to a kinetic roughness of the crystal face. The latter leads in turn to the disappearance of the oscillations.

(vi) The increase of the temperature leads to the decrease of the supersaturation. The nucleation is suppressed and the density of growth pyramids and, in turn, of the step density can become smaller than the resolution capabilities of the surface analytical tools. The latter leads again to the disappearance of the oscillations. It follows that the oscillations of the step density can be observed in a limited interval of the temperature which is in qualitative agreement with the experimental observations (Neave *et al.*, 1985).

Note that the size of the critical nucleus depends on the temperature but remains constant in comparatively large intervals of the

latter (see Sec. 2.2.9). The lower the temperature, the broader are the intervals of constant nucleus size. This is in agreement with the statement of Neave *et al.* (1983) that the damping of the oscillations is not sensitive to the temperature. It is, however, worth noting that, at high enough temperatures, the condensation can become incomplete. In other words, the significant part of the material deposited can re-evaporate before being incorporated into growth sites.

3.3 Some Particular Cases of Crystal Growth

In the following two chapters, we will consider two particular cases of crystal growth: the growth of nanowires by 2D nucleation and the growth of anisotropic Si(0 0 1) surface by step flow where half of the steps are smooth and propagate by one-dimensional (1D) nucleation and the other half are rough and propagate by direct incorporation of adatoms. The reason for this choice is the importance of these two systems for device fabrication. The nanowires (whiskers, nanorods) are hair-like, 1D nanostructures with diameters in the submicron scale and lengths ranging up to a few centimeters. Materials such as elemental semiconductors (Si, Ge), III–V (GaAs, InAs, GaN), and II–VI (ZnO, ZnSe) binaries and many other compounds can be grown as 1D structures because of their unique properties. The Si(0 0 1) growth is of crucial importance for the fabrication of integrated circuits and it is a billions dollars business.

3.3.1 *Growth of nanowires by vapor–liquid–solid mechanism*

In 1964, Wagner and Ellis (1964, 1965) reported the growth of whiskers catalyzed by small Au droplets. A thin Au layer is deposited on the Si(1 1 1) surface at low temperature and is then annealed at temperatures higher than the melting point of Au. As a result, the layer disintegrates into small droplets which do not wet the Si surface. Si is dissolved into the Au droplet, thus forming a liquid Au-Si alloy (see Fig. 3.33(a)). A mixture of H_2 and $SiCl_4$ is introduced and the alloy becomes supersaturated with respect to Si. The latter is then deposited onto the Si surface under the droplet and a whisker or NW

Figure 3.33: Illustration of the Au-catalyzed growth of Si NW. (R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964). By permission of AIP Publishing.)

begins to grow (Fig. 3.33(b)). The droplet rests on top of the NW and determines its diameter. The Au–Si alloy droplet serves as a catalyst and the process of growth takes place through it, which gives the name vapor–liquid–solid (VLS) mechanism of growth. If the growth temperature is lower than 1000°C, the nucleation on the Si surface between the Au droplets is suppressed and only the whiskers grow. It was found that thicker wires grow faster and the rate of growth becomes equal to zero under some critical wire thickness (Givargizov 1975). The interested reader can find more details in the review papers and monographs (Zhang *et al.*, 2011; Dick 2008; Ross 2010; Givargizov 1987; Dubrovskii 2014, 2015)

As the growth takes place in an alloy medium, it is instructive to consider briefly some points of the thermodynamics of alloys. We consider a simple binary system with eutectic point in coordinates of temperature T and composition X_A at constant pressure (Fig. 3.34). Such kind of phase diagram is obtained when both components of the binary do not make stoichiometric chemical compound and are weakly soluble in each other in bulk. The term eutectic comes from

Figure 3.34: Eutectic phase diagram of the two-component system A–B where both components are slightly soluble in each other in bulk. The phases α and β represent solutions of B in A and A in B, respectively.

the Greek "$\varepsilon\upsilon$" (eu = easy) and "$\tau\eta\xi\eta$" (texe = melting). The eutectic point is characterized by fixed eutectic composition and fixed eutectic temperature which is much lower than the melting points of the separate components. Thus, in the case of the Au–Si system, the melting points of Au and Si are 1064°C and 1410°C, respectively, whereas the eutectic temperature is only 363°C. The lines denoted by L are called "*liquidus*" because the system above them is in a liquid state. In turn, the curves denoted by S are called "*solidus*" because the systems under them are in a solid state. The area under the liquidus line to the left of the eutectic point the system consists of a melt and crystals α representing a solution of B in A. The same is valid to the right of the eutectic composition where the phase β is a solution of A in B. If both components are infinitesimally soluble in each other in bulk, the phase diagram is considerably simplified (Fig. 3.35). Then, the systems between the liquidus and solidus lines consist of the melt plus crystallites of both components A and B, respectively. The latter means that, on the liquidus line, the melt is in equilibrium with the solid phase A to the left of the eutectic

Figure 3.35: Eutectic phase diagram of the two-component system Au–Si where both components are infinitesimally soluble in each other in bulk.

composition and their chemical potentials are equal. The same holds to the right of the eutectic ratio where now the chemical potential of the melt is equal to the chemical potential of the crystallites of B. Below the eutectic temperature, the whole melt is solidified. The solid phase represents a mixture of crystallites of A and B. This mixture may have different structures (Swalin 1991).

As mentioned above, the chemical potentials of the melt and, say, solid B are equal on the liquidus line. This means that the concentration of B in the melt is the equilibrium concentration C_{eq}. If we introduce a mixture of H_2 and $SiCl_4$ ($A \equiv$ Au, $B \equiv$ Si) in the case of the CVD process, the reaction $SiCl_4 + 2H_2 = Si + 4HCl$ will take place on the liquid surface. A part of Si atoms will dissolve in the droplet and a part will re-evaporate. The concentration C_{LS} of Si in the melt will become higher than the equilibrium concentration. In other words, the melt will be supersaturated with respect of Si and, hence, a process of crystallization must begin at the solid–liquid interface. If the rate of re-evaporation is equal to the rate of dissolution of Si atoms in the droplet, the concentration of Si in the droplet will be given by C_{VS}. At this concentration, the vapor phase

is in equilibrium with the alloy which, in turn, is supersaturated with respect to the solid Si. The supersaturation will be given in the usual way $\sigma = \ln(C_{\mathrm{VS}}/C_{\mathrm{eq}})$ as the logarithm of the ratio of the concentration in the vapor phase and the concentration in equilibrium with the solid Si. As discussed in Ch. 1, this is proportional to the difference of the chemical potentials of the vapor phase and the bulk solid Si, or, $\Delta\mu_\infty = RT\sigma$.

The most closed packed singular (1 1 1) surface of Si in the Wagner–Ellis experiment is exposed. If we apply, for simplicity, the Jackson criterion for surface roughness, the Si(1 1 1) surface in contact with the Si melt at the melting temperature should be smooth ($\Delta H_m = 12\,000$ cal mol^{-1} K^{-1}, $T_m = 1685$ K, $\Delta s_m/k = 3.6$, and $\alpha = (\Delta s_m/k)(Z_1/Z) = 2.7, (Z_1/Z = 3/4)$). We could argue that the interface of Si with the nonwetting Au–Si alloy at much lower temperature will be smooth too. Then, the normal growth as defined in the beginning of this chapter could be excluded. Although in the beginning of studies of growth of whiskers it was assumed that screw dislocations could be responsible (Blakely and Jackson 1962), we will exclude this possibility also on the argument that the spiral growth gives rise to pyramids or cones rather than to prisms or cylinders as experimentally observed (Bostanov *et al.*, 1969). Thus 2D nucleation remains as the only possibility (Fig. 3.36). The above is valid in the case when the NWs are perpendicular to the substrate surface and the top surface of the wire is a close packed one. If the whiskers are tilted to another crystallographic direction (e.g., $\langle 2\,1\,1\rangle$), the top surface is stepped and the growth rate is higher (Givargizov 1975; Liu *et al.*, 1999). We consider here, for simplicity, the more common case of smooth liquid–solid interface.

Although we consider the case of small droplet on top of the NW, the above thermodynamic considerations are, in fact, applicable to the case of the planar liquid surface. We have to account for the curvature of the droplet's surface. Decreasing the droplet's radius and, in turn, the NW diameter leads to the increase of the evaporation of Si from the surface of the droplet, on the one hand, and to the increase of the solubility of Si in the alloy, on the other. It is worth noting that the latter takes place when the partial molar volume of Si in the alloy

Figure 3.36: Schematic view of a NW with a droplet on its tip and a 2D nucleus at the liquid–solid interface.

(the change of the volume occupied by Si atoms with the change of their number (Swalin 1991)) is greater than the volume of a Si atom in a bulk Si crystal. This is usually the case due to the Laplace pressure in the small droplet (Kashchiev and van Rosmalen 1995). The former leads to the smaller influx of Si to the droplet, while the latter means an increase of the equilibrium concentration of Si in the melt. Both effects result in a decrease of the supersaturation up to the moment it becomes equal to zero and the growth stops. As a result, there should be a critical minimum size, $r_{\min}$, below which the growth of NWs is impossible. Thus, the supersaturation must account for the droplet's curvature through the Thomson–Gibbs equation. This problem was intensively debated in the literature (Schmidt, Senz and Gösele 2007; Dubrovskii 2013, 2014).

Wagner and Ellis wrote an expression for this radius, $r_{\min}$, in the form (Wagner and Ellis 1965; Wagner 1970)

$$r_{\min} = \frac{2\gamma_{\mathrm{LV}}\Omega_L}{RT\sigma}, \tag{3.147}$$

where γ_{LV} is the specific energy of the liquid–vapor interface, Ω_{L} is the partial molar volume of Si in the liquid alloy (Vehkamäki 2006), and R and T have their usual meanings. This expression obviously follows from

$$\Delta\mu = \Delta\mu_{\infty} - \frac{2\gamma_{\mathrm{LV}}\Omega_{\mathrm{L}}}{r}, \tag{3.148}$$

with $\Delta\mu = 0$ and where $\Delta\mu_{\infty}$ is the supersaturation in an infinitely large alloy ($r \to \infty$).

Later Givargizov and Chernov (Givargizov and Chernov 1973; Givargizov 1975) wrote a similar expression but with different meanings of the parameters involved. They considered a NW with a diameter $D = 2r$ and a liquid alloy droplet on top. They postulated that the supersaturation responsible for the growth of the NW will be given by the difference of the chemical potentials of the vapor, μ_{V}, and the NW, μ_{NW}, so that $\Delta\mu = \mu_{\mathrm{V}} - \mu_{\mathrm{NW}}$. The supersaturation with respect to the bulk crystal with a planar surface will be given by $\Delta\mu_{\infty} = \mu_{\mathrm{V}} - \mu_{\mathrm{bulk}}$. Then, the supersaturation with respect to the NW will be given by

$$\Delta\mu = \Delta\mu_{\infty} - \frac{2\gamma_{\mathrm{CV}}\Omega_{\mathrm{S}}}{r}, \tag{3.149}$$

where Ω_{S} is the molar volume of the solid Si and γ_{CV} is the specific energy of the crystal–vapor interface where the side wall of the NW crystal is assumed.

In Eq. (3.149), the second term on the right-hand side is, in fact, valid for a spherical droplet. If we consider, for simplicity, a cylindrical NW, the chemical potential for a cylindrical surface is written as

$$\mu_{\mathrm{NW}} = \mu_{\infty} + \frac{\gamma_{\mathrm{CV}}\Omega_{\mathrm{S}}}{r} \tag{3.150}$$

and Eq. (3.149) becomes

$$\Delta\mu = \Delta\mu_{\infty} - \frac{\gamma_{\mathrm{CV}}\Omega_{\mathrm{S}}}{r}. \tag{3.151}$$

In turn, the critical minimum radius reads

$$r_{\mathrm{min}} = \frac{\gamma_{\mathrm{CV}}\Omega_{\mathrm{S}}}{RT\sigma}. \tag{3.152}$$

The radius of the critical nucleus with circular shape which is formed in the alloy droplet reads (see Sec. 2.1.4)

$$r^* = \frac{\varkappa_{\mathrm{CL}} s_c}{\Delta\mu} \approx \frac{\gamma_{\mathrm{CL}} \Omega_{\mathrm{S}}}{RT\sigma}, \tag{3.153}$$

where $\varkappa_{\mathrm{CL}}$ is the edge energy of the ML high 2D nucleus in the liquid ambient phase and s_c is the area occupied by an atom. We can write approximately $\varkappa_{\mathrm{CL}} \approx a\gamma_{\mathrm{CL}}$, where a is the height of the step which encloses the nucleus. As $as_c = \Omega_{\mathrm{S}}$, Givargizov and Chernov concluded that $r_{\min}$ is, in fact, the radius of the critical 2D nucleus at the given supersaturation and temperature. Note that, in the above equation, the edge energy of the nucleus, $\varkappa$, and the respective surface energy, γ, will be valid for the solid–liquid interface as long as the nucleus radius is smaller than $r_{\min}$. Only when $r^* = r_{\min}$, the edge energy will equal the value for the solid–vapor interface (γ_{CV}) as then the nucleus edge becomes a part of the side wall of the whisker.

Two reasons are responsible for the catalytic effect of the alloy droplet. First, the 2D nucleation of Si takes place at the solid–liquid interface. The energy of the edge which encloses the ML high 2D nucleus in the liquid environment is about an order of magnitude smaller compared with that in a solid–vapor medium which, in turn, leads to much smaller work for nucleus formation and a higher nucleation rate. Second, the liquid surface has much greater condensation coefficient than the solid surface. The liquid surface could be considered as very rough solid surface and atoms can join it at any place. The latter means that the desorption flux will be very small and the concentration of Si in the alloy droplet will be much higher than the equilibrium concentration.

We have to determine now the rate-limiting process. In general, this is one of the most important problems in crystal growth. In our case of CVD-VLS growth, we have three phases and two interface boundaries, vapor–liquid and liquid–solid. In addition, the building units are supplied by a chemical reaction. There are four processes (we consider the classical case of Wagner and Ellis and neglect the surface diffusion along the whisker's side wall) that can take place during growth: (1) mass transport in the gas phase, (2) chemical

Figure 3.37: The four steps in the growth of NWs by CVD–VLS: (1) mass transport in the gas phase, (2) chemical reaction on the liquid droplet surface, (3) diffusion in the alloy to the liquid–solid interface, (4) 2D nucleation and growth on the solid surface under the liquid droplet (after Givargizov 1975).

reaction on the liquid surface, (3) diffusion in the liquid to the liquid–crystal interface, and (4) formation and growth of 2D nuclei at the liquid–solid interface (Fig. 3.37) (Givargizov 1975).

The mass transport in the gas phase (step 1) is not a slow process in particular in the VLS–MBE case. In VLS–CVD case, the material is supplied by a gas flow with the flow rate and $SiCl_4/H_2$ ratio as parameters. Givargizov and Chernov performed a special experiment to check the effect of the mass transport. They divided the substrate in two regions and grew whiskers with equal thickness but with different densities. Then, they compared the length of the whiskers in the two regions (Givargizov and Chernov 1973). It was assumed that the whiskers which are less dense should have a greater supply of Si precursor and should grow faster. It turned out, however, that the length of the whiskers in the less dense part of the substrate is equal to the length of the whiskers in the more dense part. In addition, the diffusion coefficient in the vapor phase follows as a rule a power

law: $D \propto (T/T_0)^n$, where n varies between 1.5 and 2, whereas the temperature dependence of the kinetic coefficient shows very strong exponential behavior. Thus, the mass transport in the gas phase can be excluded as a rate-limiting step.

The diffusion in the liquid phase (step 3) can be excluded immediately as thicker wires in a CVD process with larger droplets on top of them grow faster than thin ones irrespective of the fact that in larger droplets the atoms should cover a greater distance to the solid–liquid interface. In addition, it was observed that the growth rate of Si NWs on Si(1 1 1) by an Au catalyst does not depend on whisker thickness when Si is supplied by the decomposition of Si_2H_6 rather than by a chloride process ($SiCl_4 + H_2$) (Liu *et al.*, 1999).

Steps (2) and (4) are in series and both are energetically activated and it is difficult to decide which one is rate determining. Initial observations showed that the axial growth rate is proportional to the concentration of the precursor (Bootsma and Gassen 1971). However, this is not convincing evidence as the increase of the growth rate could be due to the increase of the supersaturation. Another argument in favor of step (2) is the observation that the growth of SiC whiskers is affected by the metal used as a catalyst (Tumanov *et al.*, 1974). However, it was observed that the kinetic coefficients of growth with different metals as growth catalysts, Au, Pd, Ni, and Pt, are nearly equal, whereas the rates of growth differ. The latter is due to the different supersaturations owing to the different equilibrium concentrations of Si in them. On the other hand, the NWs which grow tilted with respect to the solid surface grow faster compared with the wires which are perpendicular to the surface. The tilted whiskers grow in a $\langle 2\,1\,1 \rangle$ direction and expose a (2 1 1) surface which is stepped and does not require the formation of 2D nuclei (Givargizov 1975a; Fulk *et al.*, 2006). In addition, the nuclei which are formed on the (1 1 1) surface require the largest barrier for nucleus formation as this is the most closed packed surface. Besides, it was observed that the growth of GaAs NWs on the Ga and As (1 1 1) surfaces considerably differ which is a clear evidence for the role of the process of growth on the solid surface. We conclude that step (4) is the rate-determining process and as considered above it could be

connected with a 2D nucleation. However, in some particular cases depending mostly on the precursor the chemical reaction could be the step determining process (Lew and Redwing 2003; Kikkawa, Ohno and Takeda 2005).

We consider further the rate of axial growth of the NWs assuming the crystallization on the liquid–solid interface is the rate determining step. As discussed above, the growth takes place by the formation and growth of 2D nuclei. Givargizov and Chernov (1973) suggested an approximate expression of the form

$$R = \beta\left(\frac{\Delta\mu}{kT}\right)^2, \tag{3.154}$$

where β is the kinetic coefficient, and $\Delta\mu$ is given by Eq. (3.151).

Then,

$$\sqrt{R} = \frac{\sqrt{\beta}\Delta\mu_\infty}{kT} - \frac{\sqrt{\beta}\gamma_{\mathrm{CV}}\Omega_s}{kTr}. \tag{3.155}$$

The treatment of the experimental data in coordinates $\sqrt{R} - 1/r$ allows us to extract information about the supersaturation $\Delta\mu_\infty$, the critical radius $r_{\min}$, and the kinetic coefficient β once the surface energy is known from another experiment or evaluation. Although the above parabolic dependence is an approximation for the exponential law in narrow interval of the supersaturation, it is still widely used for the interpretation of the experimental data. Experimental data for the growth of GaAs whiskers at four different supersaturations in coordinates $\sqrt{R}$ vs $1/r$ are shown in Fig. 3.38 (Givargizov and Chernov 1973).

The above empirical equation for the growth rate has one more disadvantage. It does not account for the intimate mechanism of the 2D nucleation process. As discussed in Sec. 3.2.3, the growth can proceed by the formation of a single 2D nucleus (mononuclear ML growth) at a small area of the growing surface or by the formation of several nuclei (polynuclear ML growth) or by the formation of second-layer nuclei (polynuclear multilayer growth) at large size of the growing surface. Obviously, sufficiently thin NWs should grow by the mononuclear mechanism, whereas thicker wires should grow by the polynuclear mechanism. At sufficiently thick whiskers,

Figure 3.38: Experimental data for the growth of GaAs NWs at four different supersaturations in coordinates $\sqrt{R} - 1/r$. (E. I. Givargizov, *J. Cryst. Growth* **31**, 20 (1975). By permission of Elsevier.)

the growth rate will no longer depend on the whisker thickness. The latter was observed by Givargizov and Chernov in the case of the Au-assisted growth of Si, Ge and GaAs (1973). To elucidate the problem, Dubrovskii *et al.* (2004a, 2004b) derived a system of equations for numerical fit of the experimental data of the Au-assisted growth of GaAs NWs.

Recently, Kashchiev (2006) suggested an analytic approach to the problem. We consider the case when the nucleation rate is constant with respect to time (time-independent), the nucleation process is progressive in time, and the rate of lateral growth of the supercritical nuclei is given by

$$r_{\text{isl}} = (v_{\text{isl}} t)^n, \tag{3.156}$$

where r_{isl} is the current island radius, v_{isl} is the growth rate constant, t is the time, and n is a constant varying between 1/2 and 1. In the case of diffusion limited growth n more often is equal to 1/2, whereas in the case of direct attachment of atoms to the edge upon striking $n = 1$ and $r_{\text{isl}} = v_{\text{isl}} t$. Then, v_{isl} is simply the rate of the propagation of the step enclosing the island.

When only a single nucleus is formed on the whisker tip (the whisker diameter is sufficiently small so that the formation of the first nucleus and its fast lateral growth do not allow the formation of other nuclei), the growth rate is given by Eq. (3.111) (Volmer and Marder 1931; Stranski and Kaischew 1934d). The growth represents then a process of successive formation and lateral growth of single nuclei. We have the mononuclear layer-by-layer mechanism

$$R = a\pi r^2 J_0. \tag{3.157}$$

When the whisker radius is larger, several nuclei can be formed on the top surface of the whisker. Then, the latter grows by the polynuclear layer-by-layer mode and the growth rate is given by Eq. (3.114) (Hillig 1966)

$$R = a(\frac{\pi}{3} v_{\text{isl}}^2 J_0)^{1/3}. \tag{3.158}$$

Kashchiev suggested a general formula which combines Eqs. (3.157) and (3.158) in a single expression:

$$R = a\frac{\pi r^2 J_0}{1 + (\sqrt{3}\pi J_0/v_{\text{isl}})^{2/3} r^2}. \tag{3.159}$$

Obviously, when the whisker radius, $r \ll (\sqrt{3}\pi J_0/v_{\text{isl}})^{-1/3}$, Eq. (3.159) transforms into (3.157). In this case, the rate of axial growth is independent of the rate, v_{isl}, of lateral growth of the islands. In the opposite case, $r \gg (\sqrt{3}\pi J_0/v_{\text{isl}})^{-1/3}$, Eq. (3.159) gives the other limit (3.158). In this limit, the axial growth rate of the NWs does not depend anymore on the NW thickness. Note that in Eq. (3.159) the dependence of J and v_{isl} on r is neglected as it becomes substantial for very thin NWs in the submicron region. It is, thus, not valid for very thin NWs close to r_{min}.

The comparison of Eq. (3.159) with experimental data of growth of GaAs NWs (Dubrovskii and Sibirev 2004a; Dubrovskii *et al.*, 2004) is shown in Fig. 3.39. As the three models of Kashchiev (2006), Dubrovskii *et al.* (2004), and Givargizov and Chernov (1973) describe well the experimental data. A more detailed analysis Kashchiev (2006), however, shows that the model of Givargizov and Chernov gives for the supersaturation a rather low value of 0.37 kT and for

Figure 3.39: Dependence of the NW growth rate on the NW diameter: circles — experimental data (Dubrovskii and Sibirev 2004a; Dubrovskii *et al.*, 2004b) for GaAs NWS grown by the VLS mechanism at T = 823 K; solid curve — Eq. (3.159) (Kashchiev 2006); dashed curve — numerically obtained $R(r)$ dependence by Dubrovsskii *et al.* (2004a), dotted curve — the model of Givargizov and Chernov (1973). (D. Kashchiev, *Crystal Growth & Design* **6**, 1154 (2006). By permission of the American Chemical Society and courtesy of D. Kashchiev.)

the corresponding number of molecules in the critical nucleus the value of the order of 200. This value is rather high in the case of vapor growth (Dash 1977), but nothing could be said for the case of nucleation in high temperature solution.

VlS growth of NWs can be performed not only by chemical reaction in a CVD reactor but it could take place by a direct supply of the reactant in MBE machine (Schubert *et al.*, 2004), MOCVD, CBE, magnetron sputtering deposition, or any other technique of growth. In some cases of lower temperatures, the supply of precursor can take place through diffusion along the side wall of the whisker (Dubrovskii *et al.*, 2006). The atoms which arrive by diffusion from the substrate surface in addition to the atoms which join directly the alloy droplet first dissolve in the droplet and after that crystallize at the liquid–solid interface, thus giving substantial rise of the axial growth rate. In some cases of growth of binary compounds like GaAs or InAs, the group III metals can play the role of catalysts,

thus avoiding the contamination of the NWs. The 2D nuclei can be formed not only in the middle of the NW tip but also at the triple phase line crystal–droplet–vapor, thus changing the work of formation of the nuclei. The interrelation of the surface energies of the crystal and the liquid is also of crucial importance. For these and more other details, the interested reader is referred to the monograph of Dubrovskii (2014).

3.3.2 *Growth of Si(0 0 1) vicinal surface — influence of surface anisotropy*

A simplification of the model outlined above is obtained by assuming the isotropy of the growing crystal face, which leads to the circular shape of the islands at high enough temperatures (Fig. 3.28), and the correspondingly shape of the diffusion fields around them. This model describes well the case of growth of materials with central forces like metals. This is not the real case, however, when particularly materials with diamond lattice, such as GaAs and Si, are grown. The (0 0 1) surfaces of such crystals show significant anisotropy, which, in turn, affects strongly the parameters which control the growth process, namely, the height and roughness of the consecutive steps and the surface diffusion. The problems discussed in the present section illustrate the difficulties the theory encounters in treating real experimental observations.

We consider as an example the vicinal face of Si which is obtained by a slight tilt with respect to the $\langle 1\,0\,0 \rangle$ direction toward the $[\bar{1}\,1\,0]$ azimuth. Then, the monoatomic steps which accommodate the macroscopic inclination are directed along the $[1\,1\,0]$ azimuth and have a height $a_0/4$ where $a_0 = 5.4307$ Å is the lattice parameter of silicon (Fig. 3.40(a)). The projections of the dangling bonds on the unreconstructed surface on the upper terrace are directed along the same $[\bar{1}\,1\,0]$ direction, and those on the lower terrace along the perpendicular $[1\,1\,0]$ direction. In other words, assuming the crystal surface preserves its bulk structure, the projections of the dangling bonds will rotate by 90° on every next terrace. This means that the consecutive steps will be parallel or normal to the projections of the dangling bonds on the upper terraces.

Figure 3.40: (a) Bulk and (b) reconstructed Si(0 0 1) vicinal surfaces tilted toward the $\langle \bar{1}\,1\,0 \rangle$ direction. A rotation by 90° of the projection of the dangling bonds is clearly seen in (a). The dimers also rotate by 90° on every next terrace. The terraces are separated by SL steps denoted by S_A and S_B according to the notation of Chadi (1987). The structure of the steps also alternates, due to the rotation of the chemical bonds. The step height is $a_0/4 = 1.36$ Å, where $a_0 = 5.4307$ Å is the bulk lattice constant of Si.

This is the case when the (1 0 0) surface is unreconstructed, i.e., it preserves its bulk structure. The latter is characterized by two dangling bonds per atom on the surface, and the surface energy is very high. In order to reduce the surface free energy, the dangling bonds of two neighboring atomic rows interact with each other, thus forming π bonds (Levine 1973). As a result, only one bond per atom remains unsaturated on the surface. The π bonded atoms move closer

Figure 3.41: Side view of a dimer. (a) Shows the bulk structure. (b) Shows a symmetric (nonbuckled) dimer. (c) Shows an asymmetric (buckled) dimer. The buckling causes a partial charge transfer from the "down" to the "up" atom and the dimer's bond is partially ionic.

than required by the lattice geometry (the bulk 1×1 spacing is $a = a_0/\sqrt{2} = 3.84$ Å), thus forming "dimers" (Fig. 3.41), which, in turn, are spaced broader than the normal interatomic spacing a. The dimers form rows which rotate by 90° on every next terrace (Fig. 3.40(b)). The latter leads to the appearance of strong elastic deformations which spread deep under the crystal surface. The so-called 2×1 and 1×2 reconstructed surfaces result. They alternate on every second terrace and it is said that 1×2 and 2×1 domains alternate. Such a surface is often called nonprimitive. It is worth

noting that a π bonded chain model has also been proposed for the Si(1 1 1) surface (Pandey 1981).

3.3.2.1 *Dimer's structure*

Chadi (1979) concluded that when the atoms which constitute the dimer are situated in one plane which is parallel to the surface (the so-called symmetric dimer, Fig. 3.41(b)), the dimer is unstable. The lowest energy state is reached when the dimer's atoms are displaced in a direction normal to the surface in addition to the in-plane displacements toward one another. Thus, one of the atoms is displaced upward and the other downward (Fig. 3.41(c)). Such "buckled" dimer is called asymmetric. Whereas the bonding between the atoms of the symmetric dimers is covalent, the bonding in the asymmetric dimer is partially covalent and partially ionic. The formation of an asymmetric dimer results in a charge transfer from the "down" to the "up" atom of the dimer (Chadi 1979). The same conclusion concerning the dimer's geometry has been drawn by Pauling and Herman (1983) (see also (Lin, Miller and Chiang 1991)).

Both symmetric and asymmetric dimers have been observed to exist simultaneously on Si(1 0 0) by Tromp, Hamers and Demuth (1985) (see also Hamers, Tromp and Demuth 1986) with the help of scanning tunneling microscopy (STM). They found that the (1 0 0) surface of Si has many defects, particularly, vacancies or missing dimers which, in turn, give rise to additional elastic strains. Far from the defects, only symmetric (nonbuckled) dimers were observed, while near the defects asymmetric (buckled) dimers were observed as a rule. It was concluded that the vacancy-type defects stabilize the dimer asymmetry, and often zigzag patterns were observed near large defect sites. These zigzag structures were explained as rows of asymmetric dimers in which the direction of buckling alternates from dimer to dimer along the row. Rows in which the dimers are buckled in one direction only have never been detected. Moreover, the degree of buckling (or asymmetry) is not always the same as predicted by theory. A gradual transition from symmetric to asymmetric dimers has been observed when going from the defectless area to an area consisting of large defects. It is interesting to note that the dimers

which belong to a row at the edge of a step are always strongly buckled. For more details, the reader is referred to the excellent review paper of Griffith and Kochanski (1990).

3.3.2.2 *Structure and energy of steps*

The consecutive steps on a vicinal (1 0 0) surface will be either parallel or normal to the dimers rows. Adopting the notation suggested by Chadi (1987) the monoatomic steps which are parallel to the dimers' rows on the upper terrace (or normal to the dimers bonds) are labeled S_A (single A) steps and those perpendicular to the dimers' rows (parallel to the dimers bonds) on the upper terrace are labeled S_B (single B) steps (Fig. 3.40(b)). The corresponding upper terraces with 2×1 and 1×2 reconstructed surfaces are labeled type A and type B terraces, respectively (Fig. 3.40(b)). We will consider both types of the steps separately.

Two S_A steps can be produced by cleaving imaginary the uppermost lattice plane between two dimers' rows (parallel to the dimers rows) and shifting of one of the half-planes far enough from the other (Fig. 3.42). It is very important to note that strong first neighbor bonds are not broken during this process, which means that extra dangling bonds are not created. It follows that the edge energy of

Figure 3.42: Illustration of an imaginary process of formation of a S_A step. First, we cleave the uppermost atomic plane between two dimer rows and shift (to infinity) the right-hand half-plane to the right as shown in (a). Two S_A steps are formed (the second not shown) as shown in (b). Dimers on the lower B type terrace are formed and are directed perpendicular to the plane of the figure. The atoms which form dimers are shown by solid circles.

Figure 3.43: Illustration of an imaginary process of the formation of S_B step. First, we cleave the uppermost atomic plane perpendicular to the dimer rows shown in (a) and shift (to infinity) the right-hand half-plane to the right. Two S_B steps are formed (the second not shown) as shown in (b) and (c). The atoms of the exposed surface then form dimers. In (b), the bonds belonging to the atoms at the step edge do not take part in dimer formation. Nonbonded S_B step results. In (c), the bonds belonging to the atoms at the step edge take part in dimer formation and rebonded S_B step results.

such steps should be very small. In order to produce two S_B steps, we cleave the uppermost lattice plane in a direction normal to the dimers rows between two neighboring dimers and shift apart the two half-planes. For doing that, we break a first neighbor σ-bond per atom between the atoms of the uppermost and the underlying layers (Fig. 3.43(a)). Then, an extra dangling bond per atom of the underlying layer is created, the specific edge energy of the S_B step should be much greater than that of the S_A steps (Fig. 3.43(b)). Such a step is called a nonbonded S_B step. The dangling bonds at the step edges can interact with the dangling bonds belonging to the atoms of the neighboring parallel row of the lower terrace. As a result, an additional π-bond per atom is created to reduce the step energy. The so-called rebonded S_B step is formed as shown in Fig. 3.43(c) (Chadi 1987). The calculations of Chadi (1987) gave the values $\varkappa_{S_A} = 0.01$ eV$/a = 4.16 \times 10^{-7}$ erg cm^{-1}, and $\varkappa_{S_B} = 0.15\,\text{eV}/a = 6.24 \times 10^{-6}$ erg cm^{-1}

for the specific edge energies of the S_A and the rebonded S_B steps, respectively, in qualitative agreement with the above considerations. Obviously, the edge energy of nonbonded S_B step (Fig. 3.43(b)) should be greater than that of the rebonded one. Note that no rebonding of the S_A steps can take place as no extra dangling bonds are formed.

Monoatomic steps have been studied by Hamers, Tromp and Demuth (1986) with the help of STM. As mentioned above, the dimers row which forms the upper S_A step edge is strongly buckled. An interesting picture is observed in the vicinity of a kink site along the S_A step. Before the kink, the dimers which constitute the row on the upper edge are strongly asymmetric. After the kink, the same row is spaced at a distance $2a = 7.68$ Å from the edge and the dimers are no longer buckled. Besides, simultaneous existence of rebonded and nonbonded S_B steps have been established, although minimum energy considerations (Chadi 1987) showed that the nonbonded steps are energetically unfavored. The experimental observations of Hamers *et al.* (1986) are in good qualitative agreement with theoretical conclusions which follow from calculations of the electronic states of the Si(1 0 0)-stepped surface (Yamaguchi and Fujima 1991).

An immediate consequence of the calculations of the specific edge free energies of the monoatomic steps is that a 2D island with a ML height will be surrounded by two S_A and two S_B steps. As $\varkappa_{S_A} < \varkappa_{S_B}$, the equilibrium shape of the island will be elongated along the dimers' rows according to the Gibbs–Curie–Wulff's theorem (see Chapter 1).

It was found by LEED measurements that in the case of a highly misoriented Si(1 0 0) surfaces ($6° \leq \theta \leq 10°$) the macroscopic inclinations are accommodated in all cases by steps with double height (DH) $a_0/2$ (Henzler and Clabes 1974; Kaplan 1980). It is worth noting that the cleaning procedure included annealing for 2 min at 1100°C and for 30 min at 950°C (Kaplan 1980). Double steps have been observed in the case of smaller inclinations ($2° \leq \theta \leq 4°$) (Sakamoto *et al.*, 1985a) after annealing for 85 min at 1000°C. Even well-oriented surfaces ($\theta < 0.5°$) (Sakamoto and Hashiguchi 1986) showed double

Figure 3.44: Schematic view of (a) D_A (double A) and D_B (double B) steps. The double steps can be thought of as consisting of single steps, one on top of the other. In the case of the D_A step, the S_A is on top of the S_B step and vice versa.

steps after sufficiently prolonged annealing at high temperature. Double height steps D_A and D_B in the notation of Chadi (1987) are shown in Fig. 3.44. As shown, only one type of terrace, either of type A or type B, exists in these cases. The double steps can also be rebonded. We can imagine the D_A step as been formed by an S_A step which has caught up an S_B step. Then, π bonds are formed between the atoms in the lower edge and the neighboring atoms belonging to the lower terrace. In the reverse case, when an S_B step is on top of an S_A step, a D_B step results. The rebonding is between the neighboring atoms of the intermediate lattice plane. The energy of rebonded double steps has been calculated in a series of papers (Aspnes and Ihm 1986; Chadi 1987). The values $\varkappa_{D_A} = 0.54$ eV$/a = 2.25 \times 10^{-5}$ erg cm^{-1} and $\varkappa_{D_B} = 0.05$ eV$/a = 2.08 \times 10^{-6}$ erg cm^{-1} have been estimated (Chadi 1987).

Figure 3.45: (a) and (b) For the determination of the works of formation of kinks ω_A along S_A steps. The atoms of the lower terrace are shown by filled circles. The same in the case of an S_B step is shown in (c) and (d).

In order to find the equilibrium structure of the steps, we should estimate as before the corresponding works for kink formation. To this aim, we follow a procedure analogous to that used above for the estimation of the specific step energies. In doing that, we have to bear in mind that we have to preserve the integrity of the dimers. We consider first a completely smooth S_A step (Figs. 3.45(a) and (b)). We break a bond between two neighboring dimers and shift apart the two half-rows of atoms to form two single kinks. It is immediately seen that we spent a work which is exactly equal to the work to form a step S_B with a length $2a$. Then, the work of formation of a single kink on the S_A step is $\omega_A = 2a\varkappa_{S_B}/2 = a\varkappa_{S_B}$. Applying the same procedure to the S_B step (Figs. 3.45(c) and (d)), we find $\omega_B = a\varkappa_{S_A}$. It follows that the work of kink formation is greater

Figure 3.46: Train of alternating smooth S_A and rough S_B steps.

for the step with lower specific edge energy and vice versa (Van Loenen *et al.*, 1990). This leads, in turn, to the conclusion that the S_A steps will be smooth to much higher temperatures than the S_B steps. Then, smooth, and rough steps will alternate on a nonprimitive Si(0 0 1) surface (Fig. 3.46). Numerous STM investigations confirmed this conclusion (e.g., see Swartzentruber *et al.*, 1990).

In other words, one of the edges of the kinks represents a part of an S_A step and the other edge a part of an S_B step irrespective of whether the kink is on an S_A or an S_B step. It is, thus, obvious that the detachment of a single atom from the kink position is no more a repeatable step. One has to detach four atoms constituting two dimers in order to restore the initial state. It follows that the work spent to evaporate a complex of two dimers from a single kink is one and the same irrespective of the type of the step. Namely, this work (per atom) taken with a negative sign is equal to the chemical potential of the Si crystal at the absolute zero as shown in Chapter 1. Moreover, this leads to the conclusion that every kink should have a length multiple of $2a$ because of the way in which the step must terminate at the lower terrace and the latter has a periodicity of $2a$ normal to the step. The distance between two kinks should be multiple of $2a$ for the same reason. These considerations were confirmed by STM observations of S_A and S_B steps (Swartzentruber

et al., 1990). These authors also showed that the kinks on the S_B step which is very rough even at moderate temperatures have often a length greater than $2a$ (but always multiple of $2a$). This means that a statistics of kinks of amount greater than unity should be applied.

We can now calculate the density of kinks along the S_A and S_B steps as an illustration of the above considerations. To this aim, we follow the ideal gas approximation (noninteracting kinks) of Burton, Cabrera and Frank (1951), although it was shown that there is considerable kink–kink interaction (Zhang, Lu and Metiu 1991c).

In analogy with Eq. (1.72), the sum of all kinks with arbitrary length r is

$$n_0 + \sum_{r=1}^{2L} n_{+r} + \sum_{r=1}^{2L} n_{-r} = n = 1/2a, \tag{3.160}$$

where n_{+r} and n_{-r} are the numbers of positive and negative kinks of length r respectively and n_0 is the number of the smooth parts. The summation now is carried out from $r = 1$ to $r = 2L$, where $2L$ is the mean distance between two steps in units of $2a$ of one and the same type A or B.

Equation (1.74) now becomes

$$\sum_{r=1}^{2L} r n_{+r} - \sum_{r=1}^{2L} r n_{-r} = \varphi/a, \tag{3.161}$$

where φ is the angle between the step direction and the $\langle 1\,1\,0 \rangle$ azimuth.

As before (see Eq. (1.73))

$$\frac{n_+}{n_0}\frac{n_-}{n_0} = \eta^2, \tag{3.162}$$

where $n_\pm \equiv n_{\pm 1}$ and

$$\eta \equiv \eta_{\mathrm{A,B}} = \exp\Big(-\frac{\omega_{\mathrm{A,B}}}{kT}\Big). \tag{3.163}$$

Burton, Cabrera and Frank (1951, Appendix C) showed that the following thermodynamical relation between multikinks of amount r

and single kinks of amount $r = 1$ holds

$$\frac{n_{\pm r}}{n_0} = \left(\frac{n_{\pm}}{n_0}\right)^r. \tag{3.164}$$

The latter is easy to understand having in mind that in order to form a kink of amount r a kink of amount $r - 1$ must be formed before that. In other words, the probability of formation of a kink of amount r, P_r, is a product of the probability of formation of a kink of amount $r - 1$, P_{r-1}, and the probability of formation of a single kink, P_1, i.e., $P_r = P_{r-1}P_1$. Then by induction ($P_{r-2} = P_{r-1}P_1$, etc.) $P_r = P_1^r$.

The average spacing δ_0 between kinks of any amount is given now by (compare with (1.75))

$$\delta_0 = \left(\sum_{r=1}^{2L} n_{+r} + \sum_{r=1}^{2L} n_{-r}\right)^{-1}. \tag{3.165}$$

Solving the systems (3.160)–(3.164) by summing a geometric series with $\varphi = 0$ gives

$$\delta_0(\mathrm{A},\mathrm{B}) \cong a\left(1 + \frac{1}{\eta}\right) = a\left[1 + \exp\left(\frac{\omega_{\mathrm{A,B}}}{kT}\right)\right]. \tag{3.166}$$

which is a good approximation for wide enough terraces ($L > 10a$). Using the values taken by Van Loenen *et al.* (1990) for Monte Carlo simulation of the growth process $\omega_{\mathrm{A}} = 0.5$ eV and $\omega_{\mathrm{B}} = 0.05$ eV for the mean kink spacings at $T = 750$ K we obtain the values $\delta_0(\mathrm{A}) \cong 2.3 \times 10^3 a$ and $\delta_0(\mathrm{B}) \cong 2a$. The values estimated by Chadi (1987) $\omega_{\mathrm{A}} = 0.15$ eV and $\omega_{\mathrm{B}} = 0.01$ eV give smaller value for $\delta_0(\mathrm{A}) \cong 12a$ and the same value for $\delta_0(B) \cong 2a$. In any case $\delta_0(\mathrm{A})$ is always greater than $\delta_0(\mathrm{B})$. It is worth noting, however, that Eq. (3.166) is approximate as the ideal gas model (noninteracting kinks) has been used. More elaborate calculations including kink–kink interaction give more realistic results (Zhang, Lu and Metiu 1991(c)).

Following the same procedure as in Chapter 1 but solving Eqs. (3.160)–(3.164) for the Gibbs free energy of the $\mathrm{S_B}$ steps one

obtains

$$G_{\mathrm{S_B}} = \varkappa_{\mathrm{S_B}} - nkT \ln\left(\frac{1+\eta_{\mathrm{B}} - 2\eta_{\mathrm{B}}^{2L+1}}{1-\eta_{\mathrm{B}}}\right), \tag{3.167}$$

where $\varkappa_{S_B}$ is the energy of the straight step.

The Gibbs free energy of the $\mathrm{S_A}$ step is obtained by replacing the index B by A. In the extreme case of steps far apart ($L \to \infty$) Eq. (3.167) turns into the one derived by Burton, Cabrera and Frank (1951)

$$G_{\mathrm{S_B}} = \varkappa_{\mathrm{S_B}} - nkT \ln\left(\frac{1+\eta_{\mathrm{B}}}{1-\eta_{\mathrm{B}}}\right). \tag{3.167$'$}$$

3.3.2.3 *Ground state of vicinal Si(1 0 0) surfaces*

The question of the lowest energy state of the Si(1 0 0) vicinal surfaces is very important as the latter are used as substrates for growth of epitaxial films of GaAs and other III–V compounds. The latter are of utmost importance for potential device applications (Shaw 1989). Obviously, the surface with single height steps necessarily leads to antiphase boundaries in the III–V epilayers (Kroemer 1986).

As seen, the $\mathrm{S_A}$ steps have the lowest edge energy. However, they unavoidably lead to the existence of $\mathrm{S_B}$ steps and the overall energy is $\varkappa_{\mathrm{S_A}} + \varkappa_{\mathrm{S_B}} = 0.16$ eV$/a = 6.66 \times 10^{-6}$ erg cm^{-1}. This value is three times higher than the energy of a $\mathrm{D_B}$ step but more than three times lower than that a $\mathrm{D_A}$ step. It was concluded that the $\mathrm{D_B}$ steps are thermodynamically favored on a vicinal (0 0 1) surface of Si and a single domain 1×2 reconstruction should dominate always after long enough annealing at high temperatures (Chadi 1987). Such a surface is often called a primitive surface.

As shown in Fig. 3.40(b) terraces with 2×1 and 1×2 reconstruction alternate on the nonprimitive surface. Due to the displacements of the dimers atoms towards one another, such a reconstructed surface is under tensile stress $\sigma_=$ parallel to the dimers bonds and under compressive stress $\sigma_\perp$ in the perpendicular direction. The overall stress $\Delta\sigma = \sigma_= - \sigma_\perp$ is tensile. The stress rotates by 90° on the neighboring terrace and as a result tensile and compressive stresses

alternate on a vicinal Si(1 0 0) surface, the period of alternation being given by the terrace width. It was first pointed out by Marchenko (1981) that on a surface with alternating stress domains (parquet-like surface) the stress relaxation lowers the surface energy. The decrease of the surface energy due to strain relaxation was found to depend logarithmically on the interstep distance (Marchenko 1981; Alerhand *et al.*, 1988). Obviously, in the case of a surface with double height steps (Fig. 3.44) all dimers strain the crystal in one and the same direction, the surface stress does not alter its sign and there is no strain relaxation. Then the difference between the Gibbs free energies of single height (SH) and double height (DH) stepped surfaces will be given by (Alerhand *et al.*, 1990)

$$\Delta G = L^{-1}\left[\frac{1}{2}(G_{\mathrm{S_A}} + G_{\mathrm{S_B}} - G_{\mathrm{D_B}}) - \lambda_\sigma \ln\Big(\frac{L}{\pi a}\Big)\right], \qquad (3.168)$$

where $\lambda_\sigma = \Delta\sigma^2(1-\nu)/2\pi G$ (energy per unit length) originates from the anisotropy of the stresses, $\Delta\sigma$, and depend on the shear modulus G and the Poisson ratio ν of the bulk silicon (Marchenko 1981; Alerhand *et al.*, 1988).

As discussed above, the work for kink formation is high for the $\mathrm{S_A}$ step and low for the $\mathrm{S_B}$ step. The same is valid for the double height steps. The $\mathrm{D_B}$ steps have high energy excitations, i.e., $\omega_{\mathrm{D_B}} = a\varkappa_{\mathrm{D_A}}$, and we can approximate $G_{\mathrm{S_A}}$ and $G_{\mathrm{D_B}}$ by the edge energies of the perfectly straight steps $\varkappa_{\mathrm{S_A}}$ and $\varkappa_{\mathrm{D_B}}$. We have to take the full expression (3.167) only for $G_{\mathrm{S_B}}$.

Then in the ideal gas approximation (neglecting for simplicity the term $2\eta^{2L+1}$ in (3.167)) (3.168) turns into

$$\Delta G \cong L^{-1}\left[\frac{1}{2}(\varkappa_{\mathrm{S_A}} + \varkappa_{\mathrm{S_B}} - \varkappa_{\mathrm{D_B}} - \frac{kT}{2a}\ln\left(\frac{1+\eta_{\mathrm{B}}}{1-\eta_{\mathrm{B}}}\right) - \lambda_\sigma \ln\Big(\frac{L}{\pi a}\Big)\right].$$

The condition $\Delta G = 0$ determines the first-order phase transition from nonprimitive (SH-stepped) to primitive (DH-stepped) surface. A critical terrace width L_c (or a critical tilt angle $\theta_c = \tan^{-1}(h/L_c)$; $h = a_0/4 = 1.36$ Å is the single step height) can be determined showing that the primitive surface will be energetically favored at

Figure 3.47: Phase diagram of a vicinal Si(0 0 1) surface showing regions of stability of double layer (DL) and SL stepped surfaces (after Alerhand *et al.*, 1990).

$L < L_c$ ($\theta > \theta_c$), and the nonprimitive surface at $L > L_c$ ($\theta < \theta_c$). L_c is then given by

$$L_c = \pi a \exp\left[\frac{\varkappa_{\mathrm{S_A}} + \varkappa_{\mathrm{S_B}} - \varkappa_{\mathrm{D_B}}}{2\lambda_\sigma} - \frac{kT}{2a\lambda_\sigma}\ln\left(\frac{1+\eta_{\mathrm{B}}}{1-\eta_{\mathrm{B}}}\right)\right]. \qquad (3.169)$$

θ_c vs temperature is plotted in Fig. 3.47 with $\varkappa_{\mathrm{S_A}} + \varkappa_{\mathrm{S_B}} - \varkappa_{\mathrm{D_B}} = 110$ meV/a, $\lambda_\sigma = 11.5$ meV/a, and $\omega_{\mathrm{B}} = 10$ meV. As seen at low temperatures the entropy term in the right-hand side of (3.169) goes to zero and $L_c \to L_{\mathrm{c0}} = 1440$ Å or $\theta_c \to \theta_{\mathrm{c0}} \cong 0.05°$. In general the primitive surface is the ground state at high tilt angles, and vice versa, the SH stepped surface being energetically favored at low tilt angles. Equation (3.169) overestimates the result obtained by Alerhand *et al.* (1990). More elaborate studies take into account the influence of the strain relaxation onto the step roughness (Alerhand *et al.*, 1990), the corner energy of the kinks (Poon *et al.*, 1990), etc. In particular, more elaborate evaluation of the specific edge energies (Poon *et al.*, 1990) give for θ_{c0} a much higher value of about 1°.

Pehlke and Tersoff (1991a) found that at the ground state the B type terraces are narrower than the A type terraces. The reader, interested in the problem of the equilibrium structure of the vicinal Si(100) surfaces, is referred to the original papers (De Miguel *et al.*, 1991; Barbier and Lapujoulade 1991; Barbier *et al.*, 1991; Pehlke and Tersoff 1991b).

3.3.2.4 *Anisotropy of surface diffusion coefficient*

The anisotropy of the surface diffusion follows directly from the anisotropy of the crystal surface itself (Stoyanov 1989). The first questions which arise are connected with the location of the adsorption sites on the reconstructed surface, what happens to the dimers when adatoms appear on top of them or in their vicinity, etc. Then an energy surface should be constructed and the lowest energy path for surface diffusion should be determined. Brocks, Kelly and Car (1991a, 1991b) found that the deepest minima for an adsorbed atom are located along the dimers rows between two neighboring dimers belonging to the same row (point M in Fig. 3.48). This site is favored by the fact that the bonds between the adatom and the nearest dimers atoms have the same lengths $a_0\sqrt{3}/4 = 2.35$ Å as the nearest neighbor spacing in the bulk silicon. The site B, which connects two dimers in adjacent rows, although looks very favorable, requires too long bonds of 2.49 Å and the dimer's bond should be stretched also. Thus the energy of an adatom in site B is 1.0 eV higher than that in the deepest minimum M. The energy of the site H which is located between two adjacent dimers of one row is 0.25 eV higher than that of the site M, whereas the energy of the site D which is just on top of the dimer is 0.6 eV higher than the energy of the absolute minimum M. It was thus found that the lowest energy path of an adatom in a direction parallel to the dimers rows is D–H–M and the activation energy for surface diffusion is 0.6 eV. The activation energy for surface diffusion in a direction perpendicular to the dimers rows is greater than 1.0 eV. It was thus concluded that the direction of fast diffusion is parallel to the dimers rows. Miyazaki, Hiramoto and Okazaki (1991) found that an atom adsorbed on top of the dimer (site D) causes a little distortion of the dimer whereas adsorbed in

Figure 3.48: Illustration of the direction of fast and slow surface diffusion of Si atoms on Si(0 0 1). Top view of the three topmost layers of a (2×1) reconstructed Si(0 0 1) surface is shown. The large filled circles represent the uppermost atoms, the medium-sized open circles represent the second layer atoms and the small filled circles represent the third layer atoms. The points denoted by B, D, M, and H are explained in the text (after Brocks, Kelly and Car 1991).

site B causes the dimer to break. They reached the same conclusion concerning the direction of fast diffusion as Brocks, Kelly and Car (1991a, 1991b). The activation energy along the path D–H–D parallel to the dimers rows was found to be 0.6 eV whereas in the perpendicular direction D–B–D the latter is somewhat larger (1.7 eV). Using a Stillinger–Weber interatomic potential (Stillinger and Weber 1987) Zhang, Lu and Metiu (1991a, 1991b) (see also (Lu, Zhang and Metiu 1991)) found even smaller activation energies for surface diffusion of about 0.3 eV along the dimers rows when the adatoms diffuse on top of the dimers, 0.7 eV when the adatoms diffuse by the side of the dimers string and 0.9 eV when the adatoms diffuse along the valley between the dimers rows. At the same time the latter authors found an activation energy higher than 1.0 eV in a direction perpendicular to the dimers rows. It follows that an adatom adsorbed on a dimer string can quickly move to the end of the string and increase its length (Zhang, Lu and Metiu 1991b). They found also that diffusion of dimers as entities is highly improbable. Ashu, Matthai and Shen

(1991) found the values 0.2 eV and 2.8 eV for the activation energies for surface diffusion in directions parallel and perpendicular to the dimers rows, respectively. Based on STM measurements of the saturation island density Mo *et al.* (1991) extracted the values 0.67 ± 0.08 eV and 1×10^{-3} cm^2 s^{-1} for the activation energy for fast diffusion and the pre-exponential factor. Excellent agreement with the above values was found by Roland and Gilmer (1991, 1992a), the latter authors having used the Stillinger–Weber potential for their study. In addition they found that exchange between substrate atoms and adatoms takes place even at low temperatures. This phenomenon gives additional contribution to the surface diffusion.

The general conclusion is that irrespective of the quantitative differences due to the different methods of calculations, the surface diffusion on the reconstructed Si(1 0 0) 2×1 surface is highly anisotropic and the direction of fast diffusion is parallel to the dimers rows. The values for the activation energy, although varying from 0.2 to nearly 0.7 eV in different studies suggest that considerable surface diffusion takes place even at room temperature. What is much more important is that a critical temperature should exist below which surface diffusion in one direction only takes place and above which the diffusion in a direction normal to the dimers rows could become significant.

3.3.2.5 *Theory of 1D nucleation*

It follows from above that rough (S_B) and smooth (S_A) steps alternate on a vicinal double domain Si (0 0 1) surface. The S_B steps advance by direct incorporation of growth units to the kink sites in complete analogy with the normal growth of rough crystal faces. The growth of the S_A steps is more complicated. It requires the precursory formation of kinks. As thermally activated formation of kinks with sufficiently great density is inhibited another mechanism should obviously be involved. In analogy with the formation of 2D nuclei on a smooth defectless crystal surface one can think of the formation of 1D nuclei which represent finite atomic rows. Every row will thus give rise to two kinks. The theory of 1D nucleation has been treated by many authors (Voronkov 1970; Frank 1974; Zhang and Nancollas 1990).

Figure 3.49: Schematic view of 1D nucleus at the edge of a single step on the surface of a Kossel crystal.

Let us try to treat thermodynamically the problem of formation of 1D nuclei just as we did that in the case of three-dimensional (3D) and 2D nuclei. To this aim we will use the atomistic approach suggested by Stranski and Kaischew (1934).

We consider first the formation of a 3D nucleus of a Kossel crystal with a cubic equilibrium shape. The nucleus consists of $N = n^3$ atoms, where n is the number of atoms in the nucleus edge. The work for nucleus formation is given by Eq. (2.22), $\Delta G_3^* = N\bar{\varphi}_3 - U_N$, where $\bar{\varphi}_3 = 3\psi - 2\psi/n$ is the mean separation work (Eq. (1.60)). The equilibrium vapor pressure of the nucleus is defined by Eq. (1.61), $\Delta\mu = \varphi_{1/2} - \bar{\varphi}_3 = 2\psi/n$. Substituting $\bar{\varphi}_3$ in Eq. (2.22) and bearing in mind that $U_N = 3n^3\psi - 3n^2\psi$ for the Gibbs free energy one obtains $\Delta G_3^* = n^2\psi$. Substituting for n by the Eq. (1.62′) of Thomson–Gibbs and for ψ by the definition (1.67) of the edge energy $\varkappa$ we obtain the expression for ΔG_3^* in its familiar form (2.11).

Applying the same procedure to a 2D nucleus with a square shape one correspondingly obtains $\Delta\mu = \psi/n$ and $\Delta G_2^* = n\psi$ where n now is the number of atoms in the edge of the square nucleus. Using again the definition of the edge energy and the equation of Thomson–Gibbs for the 2D case we obtain the familiar Eq. (2.38).

We consider now a row of n_1 atoms in a step edge (Fig. 3.49). The mean separation work is calculated now by detachment of the end atoms and is exactly equal to the separation work from a kink position, i.e., $\bar{\varphi}_1 = 3\psi = \varphi_{1/2}$. Then $\Delta\mu = \varphi_{1/2} - \bar{\varphi}_1 = 0$, i.e., the atomic row has the same chemical potential as the bulk crystal irrespective of its length. The potential energy is $U_N = 3n_1\psi - \psi$

Table 3.1: Gibbs free energies of formation and supersaturations for 3D, 2D, and 1D nuclei of a Kossel crystal. n denotes the number of atoms in the edges of the 3D nucleus with a cubic shape, 2D nucleus with a square shape and a 1D row of atoms. ψ denotes the work required to break the bond between the first neighbors.

Dimensionality of the nucleus	ΔG^*	$\Delta\mu$
3D	$n^2\psi$	$2\frac{\psi}{n}$
2D	$n\psi$	$\frac{\psi}{n}$
1D	ψ	0

and for the Gibbs free energy one obtains $\Delta G_1^* = \psi$. The results of the above calculations are summarized in Table 3.1. As seen the Gibbs free energy does not depend on the nucleus size and hence *one cannot define thermodynamically a critical size of the row of atoms*. However, as shown by the authors mentioned above a critical 1D nucleus can be well defined kinetically. In what follows we will consider the problem of the step advance by 1D nucleation following the approach of Voronkov (1970).

We consider the growth and dissolution of the row of atoms shown in Fig. 3.49 assuming atoms attach to the row ends directly from the terraces. We rule out diffusion of atoms along the step edge. The diffusion of atoms to the kinks is fast enough and the step advances in a kinetic regime. Then a constant adatom concentration $n_{\rm st}$ or a constant supersaturation $\sigma = n_{\rm st}/n_{\rm se} - 1$ exists in the near vicinity of the step. We denote by $\omega^+ dt$ and $\omega^- dt$ the probabilities for attachment and detachment of adatoms to and from a kink position in a time interval dt. The corresponding frequencies ω^+ and ω^- are given by

$$\omega^- = \nu \exp\left(\frac{\Delta W + \Delta U}{kT}\right), \tag{3.170}$$

$$\omega^+ = \nu \frac{n_{\rm st}}{N_0} \exp\left(-\frac{\Delta U}{kT}\right), \tag{3.171}$$

where $\Delta W = \varphi_{1/2} - E_{\mathrm{des}}$ is the work to transfer an atom from a kink position on the surface of the nearby terrace (Eq. (3.18)).

Bearing in mind that $\sigma = n_{\mathrm{st}}/n_{\mathrm{se}} - 1$ and $n_{\mathrm{se}}/N_0 = \exp(-\Delta W/kT)$ (Eq. (3.18)) Eq. (3.171) can be rewritten in the form

$$\omega^+ = \omega^-(1+\sigma). \tag{3.172}$$

As seen, at equilibrium ($\sigma = 0$) $\omega^+ = \omega^-$ and $n_{\mathrm{st}} = n_{\mathrm{se}}$.

The kink performs random walk back and forth with a diffusion coefficient

$$D = a^2\omega^- \tag{3.173}$$

around a given constant position.

When not in equilibrium ($\sigma \neq 0$) $\omega^+ > \omega^-$ and the rate of advance of the kink is given by

$$v_{\mathrm{k}} = a(\omega^+ - \omega^-) = a\omega^-\sigma. \tag{3.174}$$

At small supersaturations the probabilities of attachment and detachment of atoms are close. The kink can perform simultaneously random walk backward (dissolution of the row) and steady advance forward with a rate v_{k}. The direction of the random walk is opposite to the direction of advance. Then during a time t, n_{b} atoms will detach from the kink and n_{f} atoms will join the kink. The kink will shift backward at a distance

$$l = a(n_{\mathrm{b}} - n_{\mathrm{f}}) \cong 2\sqrt{Dt} - v_{\mathrm{k}}t.$$

As seen the shift of the kink backward displays a maximum at some time $t_{\max} = D/v_{\mathrm{k}}^2$. The maximum or the most probable shift of the kink backward is then

$$l_{\max} = \frac{D}{v_{\mathrm{k}}} = \frac{a}{\sigma}. \tag{3.175}$$

Let the mean kink spacing be

$$\delta_0 = a\Big(1 + \frac{1}{2}\exp(\omega/kT)\Big)$$

as given by Eq. (1.75) (Burton, Cabrera and Frank 1951). If $a/\sigma \gg \delta_0$, the probability for the kink to encounter a neighboring kink with an opposite sign and to annihilate with it is very large. If this happens the atomic row will disappear. In other words, the atomic rows

smaller than a/σ will have greater tendency to decay than to grow further.

If, however, the system is sufficiently far from equilibrium so that the supersaturation is large enough $a/\sigma \ll \delta_0$ or

$$\sigma \gg a\rho_0, \tag{3.176}$$

where $\rho_0 = 1/\delta_0$ is the equilibrium kink density, the steady growth will prevail over the random walk. An atomic row longer than a/σ most probably will not disappear but will grow with a steady state rate v_{k}. Thus, it is namely the quantity a/σ which plays the role of the critical size of the 1D nucleus. The latter is defined solely on the base of kinetic considerations.

It follows that when the inequality (3.176) is fulfilled the advance of the step will take place by formation and growth of 1D nuclei. Thus this inequality gives the lower limit of validity of the 1D nucleation mechanism of growth. Obviously, an upper limit should exist. In complete analogy with the growth of atomically smooth and defectless crystal face the upper limit will be defined by the condition of the kinetic roughness of the step. In the particular case of step advance the kinetic roughness is determined by the condition every atom adsorbed at the step edge to remain there for a sufficiently long time. Then each adsorbed atom will give rise to two kinks.

We denote the frequencies of adsorption and desorption of atoms by ω_{a}^{+} and ω_{a}^{-}. The adsorption frequency ω_{a}^{+} should be nearly equal to the frequency ω^{+} of attachment to kink sites. The desorption frequency ω_{a}^{-} should be much greater then ω^{-} as the adsorbed atoms are more loosely bound to the steps than the atoms in the kink positions. If the supersaturation is not large an atom adsorbed at the step will desorb with greater probability then attach new atoms on either side of it. In other words, when the frequency of desorption is comparable with the double frequency of attachment of atoms to kink positions, $\omega_{\mathrm{a}}^{-} \cong 2\omega^{+}$, the step will by kinetically rough and the 1D nucleation mechanism will be no longer valid. The reverse condition, or the condition that the step is still smooth, obviously is $\omega_{\mathrm{A}}^{-} \gg 2\omega^{+}$, or

$$\frac{2\omega^{+}}{\omega_{\mathrm{a}}^{-}} \ll 1. \tag{3.177}$$

The inequality (3.177) can be expressed through the equilibrium kink density and the supersaturation by using the condition for adsorption-desorption equilibrium. We denote by $\rho_{\mathrm{a},0}$ the equilibrium density of atoms adsorbed at the step. The condition of detailed balance reads $\omega^+_{\mathrm{a},0}/a = \omega^-_{\mathrm{a}}\rho_{\mathrm{a},0}$, or

$$\frac{\omega^+_{\mathrm{a},0}}{\omega^-_{\mathrm{a}}} = a\rho_{\mathrm{a},0}.$$

Each adsorbed atom creates two kinks, one positive and one negative. Then the probability to find an adsorbed atom, $a\rho_{\mathrm{a},0}$, will be equal to the probability to find simultaneously one positive, $a\rho^+_0$, and one negative, $a\rho^-_0$, kink. Neglecting the possible energetic interaction between the kinks, the above results in $a\rho_{\mathrm{a},0} = (a\rho^+_0)(a\rho^-_0)$. Bearing in mind that $\rho_0 = \rho^+_0 + \rho^-_0$ and $\rho^+_0 = \rho^-_0$, one obtains $\rho_{\mathrm{a},0} = a(\rho_0/2)^2$. Then

$$\frac{\omega^+_{\mathrm{a},0}}{\omega^-_{\mathrm{a}}} = \left(\frac{a\rho_0}{2}\right)^2. \tag{3.178}$$

Excluding ω^-_{a} from (3.177) and (3.178) and bearing in mind that $\omega^+ \cong \omega^+_{\mathrm{a}} = \omega^+_{\mathrm{a},0}(1+\sigma)$, Eq. (3.177) turns into

$$\sigma \ll \frac{1}{(a\rho_0)^2}. \tag{3.179}$$

Thus the conditions (3.176) and (3.179) give the lower and upper limits of validity of the 1D nucleation mechanism of advance of single steps. Obviously, if $a\rho_0 \ll 1$ as in the case under study this mechanism of growth will be valid in a very wide interval of supersaturations. In the particular case of $\mathrm{S_A}$ steps on the vicinal surface of Si(0 0 1) at $T = 600$ K, $\delta_{\mathrm{A}} = 870a$. Then $a\rho_0 = 1.15 \times 10^{-3}$ and the advance of the steps through 1D nucleation will take place from supersaturations as low as 1.15×10^{-3} up to supersaturations as high as 7.6×10^5.

We can calculate now the steady state rate of formation of 1D nuclei by using the classical approach of Becker and Döring (1935)

described in Chapter 2. The system of consecutive bimolecular reactions in this particular case will look like

$$J_0 = \omega_{\mathrm{a}}^{+}\frac{1}{\mathrm{a}} - \omega_{\mathrm{a}}^{-}\rho_{\mathrm{a}}, \tag{3.180a}$$

$$J_0 = 2\omega^{+}\rho_{\mathrm{a}} - 2\omega^{-}\rho_2, \tag{3.180b}$$

$$\vdots$$

$$J_0 = 2\omega^{+}\rho_{n-1} - 2\omega^{-}\rho_n. \tag{3.180c}$$

The first equation differs from all the others. That is why we will solve the system beginning from the second Eq. (3.180b). Thus we will determine the density of the adsorbed atoms, ρ_{a}, and will substitute it into the first Eq. (3.180a) to obtain an expression for J_0.

The expression (2.53) now reads (from Eq. (3.180b) onwards)

$$J_0 = 2\omega^{+}\rho_{\mathrm{a}}\left[1 + \sum_{k=1}^{n}\left(\frac{\omega^{-}}{\omega^{+}}\right)^{k}\right]^{-1}.$$

The sum in the denominator represents that of a geometric series and can be easily found. The upper limit should be greater than the number of atoms in the critical nucleus $1/\sigma$. The ratio $\omega^{-}/\omega^{+} = 1/(1+\sigma)$ (Eq. (3.172)) is always smaller than unity as $\sigma > 0$. At large supersaturations the critical size $1/\sigma$ is small and the upper limit n should be a small number, and vice versa. At the same time, at large supersaturations the terms in the sum vanish faster than at small ones so that we will not make a large error if we extend the upper limit to infinity in both cases of large and small supersaturations. Then the sum in the denominator is equal to $1/\sigma$ and $J_0 = 2\omega^{+}\rho_{\mathrm{a}}\sigma/(1+\sigma) = 2\omega^{-}\sigma\rho_{\mathrm{a}} = 2(\omega^{+} - \omega^{-})\rho_{\mathrm{a}}$, or

$$\rho_{\mathrm{a}} = \frac{J_0}{2(\omega^{+} - \omega^{-})}.$$

This result can be immediately obtained from Eq. (3.180c) assuming $\rho_n = \rho_{n-1} = \rho_{\mathrm{a}} = \mathrm{const}$ (Voronkov 1970), i.e., the densities of the clusters do not depend on the cluster size as follows from the thermodynamic considerations given in the beginning of this section.

Substituting ρ_{a} in (3.180a) gives for J_0 (Voronkov 1970)

$$J_0 = \frac{\omega_{\mathrm{a}}^{+}}{a} \frac{2(\omega^{+} - \omega^{-})}{\omega_{\mathrm{a}}^{-} + 2(\omega^{+} - \omega^{-})}. \tag{3.181}$$

This expression can be easily simplified taking into account that $\omega_{\mathrm{a}}^{-} \gg 2\omega^{+}$ (Eq. (3.177)) and hence $\omega_{\mathrm{a}}^{-} \gg 2(\omega^{+} - \omega^{-})$. Substituting $\omega_{\mathrm{a}}^{+} = \omega_{\mathrm{a},0}^{+}(1+\sigma)$, $\omega_{\mathrm{a},0}^{+} = \omega_{\mathrm{a}}^{-}(a\rho_0/2)^2$ from Eq. (3.178) and $\omega^{+} - \omega^{-} = \omega^{-}\sigma$ from Eq. (3.174) in Eq. (3.181) gives

$$J_0 = \frac{1}{2} a\omega^{-} \rho_0^2 \sigma(1+\sigma). \tag{3.182}$$

Finally, making use of Eq. (3.170) and $\rho_0 = 1/\delta_0$ gives

$$J_0 = 2\frac{\nu}{a}\sigma(1+\sigma)\exp\left(-\frac{\varphi_{1/2} - E_{\mathrm{des}} + 2\omega + \Delta U}{kT}\right). \tag{3.183}$$

As seen the steady state rate of 1D nucleation is a linear function of the supersaturation when the latter is much smaller than unity, but increases parabolically with it when $\sigma \gg 1$. Then at low temperatures, e.g., $T = 600$ K, with $\nu = 3 \times 10^{13}$ s^{-1}, $a = 3.84 \times 10^{-8}$ cm, $\sigma \cong 1 \times 10^3$, $\varphi_{1/2} = 4.33$ eV, $E_{\mathrm{des}} = 2.99$ eV (Roland and Gilmer 1991, 1992a), $\omega_{\mathrm{A}} = 0.5$ eV and $\Delta U = 0.2$ eV, the steady state 1D nucleation rate is of order of 7×10^5 cm^{-1} s^{-1}. At $T = 1000$ K, $\sigma \cong 1 \times 10^{-3}$, and $J_0 \cong 2 \times 10^5$ cm^{-1} s^{-1}.

3.3.2.6 *Rate of step advance by 1D nucleation*

As in the case of growth of a smooth and defectless crystal face by the formation and lateral spreading of 2D nuclei we will consider separately the advance of infinitely long step and a step of a finite length. In doing that we will follow exactly the same approach.

In the case of infinitely long step we assume that a row with length l is formed. Then the frequency of 1D nucleation of a new row of atoms next to the first one is $\tilde{J}_0 = J_0 l$. The time elapsed from the nucleation of the first row to the nucleation of the second row is l/v_{k}. The latter is approximately inversely proportional to the nucleation frequency, or $l/v_{\mathrm{k}} \cong 1/J_0 l$. Then $l = (v_{\mathrm{k}}/J_0)^{1/2}$. The rate of step

advance is given by $v = J_0 la$, or (Voronkov 1970; Frank 1974)

$$v = a(J_0 v_{\mathrm{k}})^{1/2}. \tag{3.184}$$

Making use of the expressions for J_0 and v_{k}, (3.182) and (3.174), gives for v

$$v = a^2 \rho_0 \omega^- \sigma (1+\sigma)^{1/2} \tag{3.185}$$

or

$$v = 2a\nu\sigma\sqrt{1+\sigma}\exp\left(-\frac{\varphi_{1/2} - E_{\mathrm{des}} + \omega + \Delta U}{kT}\right). \tag{3.186}$$

On the other hand, $v = a\rho v_{\mathrm{k}} = a^2 \rho \omega^- \sigma$ where ρ is the real kink density under conditions far from equilibrium. Comparing this expression with Eq. (3.185) gives for the kink density

$$\rho = \rho_0 \sqrt{1+\sigma}. \tag{3.187}$$

It follows that at high temperatures (small supersaturations) when the equilibrium density of thermally activated kinks is large, the kink density is close to the equilibrium one, i.e., the contribution of the 1D nucleation to the kink formation is negligible. The contribution of the 1D nucleation to the kink formation is significant at low temperatures.

The propagation of steps with a finite length is completely analogous to the layer-by-layer growth of finite crystal faces. The advance of a step with a finite length l in the *row-by-row mode* will be given by

$$v = J_0 la. \tag{3.188}$$

Equation (3.188) is particularly important when the growth of a Si(0 0 1) surface through formation of 2D islands is considered. As mentioned above the latter are surrounded by two smooth S_A edges and two rough S_B edges of finite length.

3.3.2.7 *Growth of Si(0 0 1) vicinal by step flow*

As follows from the above, the growth of a double domain vicinal Si(0 0 1) 2×1 surface is characterized by two fundamental properties: first, this is the nonequivalency of the steps, and second, the anisotropy of the surface diffusion. As a consequence of the first

property the alternating steps will propagate in general with different velocities and catch up with each other to form higher steps. The second factor leads to the conclusion that on B type terraces the atoms will diffuse predominantly in a direction perpendicular to the steps, whereas on the A type terraces the adatoms will diffuse in a direction parallel to the steps. It follows that the steps will in fact propagate only at the expense of the atoms diffusing to them on the B type terraces. The atoms on the A type terraces will not take part in the growth process at high enough temperatures. If the temperature is low enough the adatoms on the A type terraces will give rise to 2D nucleation and growth. Thus, the S_A steps will propagate at the expense of the atoms diffusing to them on the lower terraces whereas the S_B steps will advance at the expense of the atoms diffusing on their upper terraces. In addition Roland and Gilmer (1991) found that the attachment of adatoms to the S_A steps from the above A type terrace is less probable than from the lower B type terrace. The reverse is valid for rebonded S_B steps. Note that at lower temperatures 2D nucleation will take place on the terraces and the growth will proceed by 2D nucleation mechanism. A critical temperature for transition from step flow growth to 2D nucleation growth should exist (Myers-Beaghton and Vvedensky 1990). The problem of the growth of Si(0 0 1) vicinal surfaces has been studied in detail by many authors (Vvedensky *et al.*, 1990a, 1990b; Wilby *et al.*, 1989) and the interested reader is referred to them. A Monte Carlo simulation with video animation to visualize the results was performed by Wilby *et al.* (1991). We will consider in this section the growth of Si(0 0 1) at high temperature to avoid 2D nucleation on A type terraces following the analysis given by Stoyanov (1990).

We consider a double domain (nonprimitive) vicinal Si(1 0 0) surface on which S_A and S_B alternate (see Fig. 3.46). The initial interstep spacing is denoted by λ. The beginning of the co-ordinate system is at the middle point of a B type terrace so that the S_A and the S_B steps are located at $x = -\lambda/2$ and $x = \lambda/2$, respectively.

The S_B steps are rough and propagate with a rate

$$v_B = a^2 \beta_B n_{se} \sigma_B. \tag{3.189a}$$

The S_a steps are smooth and propagate through 1D nucleation with a rate

$$v_A = a^2\beta_A\sigma_A\sqrt{1+\sigma_A} \cong a^2\beta_A\sigma_A. \tag{3.189b}$$

In the above equations $\beta_{A,B}$ and $\sigma_{A,B} = n_{A,B}/n_{se} - 1$ are the corresponding kinetic coefficients and supersaturations in the vicinities of the steps. $n_{A,B}$ are the corresponding adatom concentrations.

In the case of complete condensation (the re-evaporation is strongly inhibited), the diffusion on the B type terraces is governed by the diffusion equation

$$\frac{d^2 n_s(x)}{dx^2} + \frac{\Re}{D_s} = 0. \tag{3.190}$$

The solution of the equation subject to boundary conditions $x = -\lambda/2$, $n_s = n_A$, and $x = \lambda/2$, $n_s = n_B$ reads

$$n_s(x) = \frac{\Re}{2D_s}\left(\frac{\lambda^2}{4} - x^2\right) + \frac{x}{\lambda}(n_B - n_A) + \frac{1}{2}(n_B + n_A). \tag{3.191}$$

Bearing in mind that $v_{A,B} = a^2 D_s (dn_s/dx)_{x=\pm\lambda/2}$ for the rates of growth one obtains

$$v_A = \frac{\Re\lambda}{2N_0} - \frac{D_s n_{se}}{\lambda N_0}(\sigma_A - \sigma_B), \tag{3.192a}$$

$$v_B = \frac{\Re\lambda}{2N_0} + \frac{D_s n_{se}}{\lambda N_0}(\sigma_A - \sigma_B). \tag{3.192b}$$

Comparing (3.189a) with (3.192a) and (3.189b) with (3.192b) we find σ_A and σ_B and in turn for v_A and v_B we obtain

$$v_A = \frac{\Re\lambda}{2N_0}\frac{M_A(2+M_B)}{M}, \tag{3.193a}$$

$$v_B = \frac{\Re\lambda}{2N_0}\frac{M_B(2+M_A)}{M}, \tag{3.193b}$$

where $M_{A,B} = \beta_{A,B}\lambda/D_s$ and $M = M_A + M_B + M_A M_B$.

The ratio of the step velocities reads

$$\frac{v_A}{v_B} = \left(\frac{\rho_{A,0}}{\rho_{B,0}} + \frac{\beta_A\lambda}{2D_s}\right)\left(1 + \frac{\beta_A\lambda}{2D_s}\right)^{-1}. \tag{3.194}$$

It follows that the rates ratio depend on the ratio of the crystallization rate β_A and the rate of diffusion D_s/λ. When $\beta_A \gg D_s/\lambda$

both steps will propagate in a diffusion regime with equal rates. The supersaturations σ_A and σ_B will be equal and $v_A = v_B = \Re\lambda/2N_0$. As a result the Si(0 0 1) vicinal will grow with SH steps. In the reverse case, $\beta_A \ll D_s/\lambda$, the propagation rates relate as the corresponding equilibrium densities of the thermally activated kinks $\rho_{A,0}/\rho_{B,0} \ll 1$. The rate of growth of the S_B steps is much greater than the rate of growth of the S_A steps. Then the former will catch up with the latter and D_B steps will be formed. Roland and Gilmer (1992b) treated the growth of Si(0 0 1) vicinal by step flow in detail using Eq. (3.184) and found that the S_B steps always propagate with higher velocity than S_A steps.

Let us now try to define the conditions of growth with single and DH steps. The ratio $\beta_A\lambda/2D_s$ reads

$$\frac{\beta_A\lambda}{2D_s} = \frac{\lambda}{a}\exp\left(\frac{E_{sd} - \omega_A - \Delta U}{kT}\right), \tag{3.195}$$

where $\lambda/a = \sqrt{2}/4\tan\theta \gg 1$, θ being the tilt angle.

The condition for diffusion regime of growth, $\beta_A\lambda/2D_s \gg 1$, and hence of SH steps will be always fulfilled when $E_{sd} - \omega_A - \Delta U > 0$ because $\lambda \gg a$. Only in the reverse case when $E_{sd} - \omega_A - \Delta U < 0$ should a transition from SH steps to DH steps be observed.

A critical temperature for transition from single to double steps can be defined from the condition $\beta_A\lambda/2D_s = 1$

$$T_{tr} = -\frac{E_{sd} - \omega_A - \Delta U}{k\ln(4\tan\theta/\sqrt{2})}. \tag{3.196}$$

As discussed above the activation energy for surface diffusion in a direction parallel to the dimers rows was calculated to vary in the interval 0.3–0.65 eV. The value 0.15 eV was estimated for ω_A (Chadi 1987) but a higher value of 0.5 eV has been taken by van Loenen *et al.* (1990). The kinetic barrier ΔU should be connected with the attachment of a single atom to the kink site, bearing in mind that the repeatable step consists of attachment and detachment of building units containing four atoms. A value of the order 0.2–0.4 eV seems reasonable. Thus the difference $E_{sd} - \omega_A - \Delta U$ could vary

Figure 3.50: Diagram of a vicinal Si(0 0 1) surface $\theta - T$ showing regions of formation of DL and SL stepped surfaces during growth. The S_A steps grow by 1D nucleation mechanism.

between -0.6 and $+0.3$ eV. A value of -0.1 eV seems reasonable. The critical temperature T_{tr} is plotted against the tilt angle θ in Fig. 3.50. As seen single steps should be observed at high temperatures. At low temperatures double steps should be observed as a result of the kinetic regime of growth of the S_A steps. Note that this result which is based on a kinetic treatment should obviously be considered as complementary to the equilibrium considerations of Alerhand *et al.* (1990) (Fig. 3.47). Following the same approach but using Eq. (3.188) for the rate of advance of the S_A steps one can study the dynamical evolution of the step density on Si(0 0 1) as this was done in the previous section (Markov 1992).

3.4 Ehrlich–Schwoebel Barrier and its Consequences

When considering the propagation of ML steps we accepted that the probability of attachment of atoms to the step from the upper and lower terraces is one and the same. In other words, we accepted that the barrier (if any) which inhibits the attachment of atoms to the

Figure 3.51: Schematic snapshots of (a) a simple hopping diffusion, and (b) concerted substitutional or site-exchange diffusion. In the second case, the adatom performs a diagonal or "checkerboard" hop in ⟨1 0 0⟩ direction (after Feibelman 1993).

step and thus leads to a kinetic regime of growth is one and the same from both sides of the step. A passing glance at Fig. 3.4 shows that this should not be correct even from geometric point of view. The reason becomes clear if we compare the diffusion across the step with the diffusion on a terrace far from a step.

An atom can diffuse on the terrace following in general two mechanisms (see Fig. 3.51). First, this is the familiar hopping mechanism in which the atom passes through a saddle point between two neighboring atoms. Approaching the saddle point the atom stretches one or two bonds (depending on the surface symmetry) with the atoms he leaves behind (atoms 1 and 2 in Fig. 3.51(a)). Beyond the saddle point the atom is attracted by the atoms 3 and 4 in front of it. Thus, the maximum of the barrier is when the atom is precisely on the saddle. At the final stage the bonds with atoms 1 and 2 are broken but new bonds with atoms 3 and 4 are created. Bassett and Webber (1978) have found that in addition to this traditional view of surface diffusion the adatoms on the fcc(1 1 0) perform a cross channel diffusion rather than a diffusion along the channels. (The fcc(1 1 0) surface

Figure 3.52: Schematic representation of different pathways of atoms to join a step: an atom denoted by A diffusing to an ascending step, an atom denoted by B making a jump over a descending step, and an atom denoted by C which "pushes out" the atom D in order to occupy its place.

consists of parallel rows of atoms. The atoms in a row are first neighbors whereas the spacing between neighboring rows is equal to the lattice parameter which is $\sqrt{2}$ larger than the first neighbor distance. Thus channels in the $\langle 1\bar{1}0 \rangle$ direction are formed between neighboring rows). On the fcc(1 0 0) surface the atom can perform diagonal or "checkerboard" movement in $\langle 100 \rangle$ direction (Kellog and Feibelman 1990; Chen and Tsong 1990) as shown in Fig. 3.51(b)). The adsorbed atom exchanges its place with an atom embedded into the uppermost atomic plane. Moving in this way the atoms "respect a fundamental rule of chemistry — minimizing the breaking of bonds" (Feibelman 1993).

Let us consider now the case when an atom on a fcc(1 0 0) surface approaches an ascending step by a hopping mechanism (the atom denoted by A in Fig. 3.52). Beyond the saddle point the atom will be attracted not only by the front atoms 3 and 4 of the lower atomic plane as in the case of terrace diffusion, but also by the atoms belonging to the upper atomic plane which make the step, mostly by the nearest atom denoted by 5. It follows that an atom which joins a step from the lower terrace should surmount a smaller barrier as compared with that for terrace diffusion owing to the enhanced coordination at

the ascending step. On the contrary, the atom B which approaches the step from the upper terrace will not be attracted from atoms beyond the saddle point. Thus, the atom B should surmount a larger barrier as compared with the one for terrace diffusion owing to the reduced coordination at the descending step. It follows that ascending steps should attract adatoms whereas atoms which descend by rolling down should be repulsed by the step.

Ehrlich and Hudda (1966) were the first who discovered the reflective properties of the descending steps by using the technique of the field-ion microscopy (FIM), a powerful tool for studies of surfaces invented by Erwin Müller (1951) in the early fifties (see also Müller 1965; Tsong 1990, 1993; Ehrlich 1995; and Kellogg 1994). The method is based on the "lightning rod effect". The microscope system consists of a needle of the metal to be studied (usually a refractory metal like W, Mo, Ir) with a sharp single crystal tip pointed to a fluorescent screen in a vacuum tube. After evacuating the tube the latter is filled with a noble gas. A high voltage is applied between the tip and the screen. As a result the noble gas is positively ionized, preferentially at the protruding parts of the tip (the edges of the single crystal planes and the adsorbed on them single atoms) where the field is highest. The ions are accelerated by the field in a straight line to the screen where an atomic resolution picture of the tip is thus obtained. After making a photograph of the screen the field is lowered and the noble gas is pumped out. The temperature is increased for a short period of time in order to allow the atoms to diffuse. The temperature is then decreased again, the tube is filled with the gas and the whole procedure is repeated.

Schwoebel immediately grasped the significance of the discovery of Ehrlich and Hudda, and in the same year published a paper in which showed that the asymmetrical attachment–detachment kinetics at steps should lead to a different morphology of the growing surfaces and the appearance of bunches of steps divided by wider terraces (Schwoebel and Shipsey 1966; Schwoebel 1969). In their first paper Schwoebel and Shipsey went even further to envisage other mechanisms of incorporation of atoms to descending steps with different energetic characteristics. Thus they assumed that an atom on

the upper terrace can push out an atom embedded into the step in order to occupy its place in complete analogy with the site-exchange diffusion on terraces. This event requires the correlated motion of at least two atoms (denoted by C and D in Fig. 3.52).

Thus, an atom approaching the step should sample a potential as shown in Fig. 3.53(a). The additional barrier, E_{ES}, at the descending step is well known in the literature as Ehrlich-Schwoebel (ES) barrier. Detailed measurements in the case of Re, Ir, and W on W(1 1 0) gave values for E_{ES} varying from 0.15 to 0.2 eV (Wang and Tsong 1982). The short-range attractive behavior of the ascending steps was experimentally established much later (Wang and Ehrlich 1993a, 1993b). The push-out mechanism (Fig. 3.52) has been recently observed in the case of Ir(1 1 1) by Wang and Ehrlich (1991). It turned out that the atoms in the last potential trough before the step edge are trapped there for a longer time and do not return back upon increasing the temperature but join the descending step. The atoms thus sample the potential shown in Fig. 3.53(b). Later studies of Pt(1 1 1) by using the same technique showed that the potential has even more complicated shape than the one shown in Fig. 3.53 (Gölzhäuser and Ehrlich 1996). The possible shapes of the potential an atom samples when incorporating a descending step and their effect on crystal growth are considered in detail by Kyuno and Ehrlich (1997). We will restrict ourselves with the simplest shape of the potential shown in Fig. 3.53(a).

The ES barrier has a crucial effect on the morphology of growth in both cases of step-flow growth and growth by 2D nucleation. In the first case the ES barrier changes both the structure of the surface (the interstep spacing) and that of the steps themselves. The latter is known as Bales–Zangwill instability (Bales and Zangwill 1990). In the second case the ES barrier changes drastically the nucleation on top of the first layer islands and thus influences the transition from layer-by-layer to multilayer growth, or in other words leads to the formation of mounds or towers of 2D islands formed one on top of the other, a phenomenon which was first predicted by Villain (1991). Thus the ES barrier stabilizes the growing vicinal surface against the formation of step bunches from the pre-existing steps but destabilizes

Figure 3.53: Schematic potential diagram for atoms moving toward ascending and descending steps. (a) Traditional view of the ES barrier for atoms joining a descending step and attractive behavior of the ascending steps, (b) view of the potential sampled by an atom incorporating into a descending step by a push-out mechanism according to the observations of Wang and Ehrlich (1991, 1993).

the growing singular surface against the formation of mounds. This is the reason so many papers were devoted to the determination of the ES barrier from experimental data (Meyer *et al.*, 1995; Šmilauer and Haris 1995; Bromann *et al.*, 1995; Markov 1996; Krug, Politi

and Michely 2000; Gerlach *et al.*, 2001) and in numerous theoretical studies of different materials like Al(1 1 1) (Stumpf and Scheffler 1994), Cu(1 0 0) (Tian and Rahman 1993), Pt(1 1 1) and Ag(1 1 1) (Li and DePristo 1994), Pt(1 1 1) (Jakobsen *et al.*, 1995; Villarba and Jónsson 1994; Liu and Metiu 1996), Si(1 1 1) (Kodiyalam, Khor and Das Sarma 1996), etc. In analogy with the ES barrier to interlayer transport one could anticipate island corner barriers (Jakobsen *et al.*, 1995; Ramana Murty and Cooper 1999; Zhong *et al.*, 2001) which determine the 2D island morphology in submonolayer homoepitaxy. We will not consider this question here. The interested readers are referred to the original papers.

We would like to remind the readers that all the theoretical problems connected with the effect of the ES barrier on different aspects of crystal growth are still under intensive study. That is why most of the material included in this chapter should be considered more as the state of the art rather than well established and proven facts.

3.4.1 *Ehrlich–Schwoebel effect on step-flow*

3.4.1.1 *Bunching and debunching of steps*

We study first briefly the effect of the ES barrier in the case of growth by propagation of pre-existing steps — the step-flow growth. It is well established that the ES barrier leads to stability or instability of the equidistant train of steps in the sense of formation of bunches of steps coupled with much wider terraces than are expected from the miscut angle (Schwoebel and Shipsey 1966; Bennema and Gilmer 1973). During growth the ES barrier stabilizes the step train making the steps equidistant. On the contrary, during evaporation the ES barrier leads to the formation of bunches of more closely spaced steps separated by wider terraces and thus destabilizes the surface (Bennema and Gilmer 1973). This behavior could be expected from qualitative reasoning.

If a growing step is lagging for some reason behind its normal (equidistant) position (see the upper profile in Fig. 3.54(a)) the length of the catchment area in front of it increases, and that behind

Figure 3.54: Evolution of terraces during (a) growth and (b) evaporation. The arrows show the direction of step movement. If during growth the step lags owing to some reason, the front terrace will become wider (the upper profile). The wider terrace contributes more to the total flux of atoms and overcompensates the loss of material from the rear terrace. Thus, after some time both terraces will become equally wide (the lower profile). If during evaporation (b) the step lags, it is the upper terrace that becomes wider. The step emits atoms much easier onto the lower narrow terrace. The flux to the upper terrace cannot compensate the total flux and the step lags still more. A bunch consisting of two steps behind the wide terrace results (after Bennema and Gilmer 1973).

it decreases (the arrow shows the direction of the step advance). The front wider terrace contributes more to the total flux of atoms and overcompensates the loss of atoms from the upper terrace (recall that atoms from the lower terrace join the step upon striking). As a result the step increases its velocity until both front and rear terraces become equally wide (the lower profile in Fig. 3.54(a)).

The opposite situation takes place during evaporation (Fig. 3.54(b)). It is now the upper terrace which is in front of the step which now moves to the left. If the step lags the upper terrace becomes wider and the rear lower terrace becomes narrower. The step emits

atoms easier onto the lower narrow terrace and the total evaporation flux is reduced. The latter cannot be compensated by emitting on the upper terrace because of the additional barrier to interlayer transport, the step decreases further its velocity and lags still more. This continues up to the moment when the rear terrace become, so narrow that a significant repulsion of the two neighboring steps compensate the effect of the ES barrier. As a result, after a sufficiently long annealing, a steady state will be reached such that the surface is resolved into bunches of steps similar to kinematic waves (Sato and Uwaha 1995) (see Sec. 3.5). In other words, wide terraces and step bunches (regions of much narrower terraces) will alternate.

All the above plays a crucial role when surfaces are experimentally studied. As discussed in Sec. 1.4.4, the terrace width depends first of all on the miscut angle. However, the pretreatment of the crystal surface prior to deposition can change the situation drastically even in the absence of impurity atoms. The pretreatment usually includes repeated cycles of ion (Ar^+, Ne^+) sputtering and annealing followed by a prolonged annealing at temperatures close to the melting point. All these lead to intensive evaporation of material from the crystal surface. Thus, 2 μm have been evaporated from the surface of Ag(1 1 1) during the pretreatment of the crystal prior to deposition (Elliott *et al.*, 1996). It follows that, after the pretreatment, wide (between the bunches) and narrow (within the step bunches) terraces will coexist. The more narrow the terrace, the lower temperature is required in order 2D nuclei to be formed on it. We thus could anticipate that at higher temperatures, 2D nucleation will take place on the wide terraces but not on the narrow ones. Nucleation should occur on the narrow terraces at much lower temperatures. Thus, a mixture of step flow growth and 2D nucleation is expected to occur into some intermediate temperature interval. In order to avoid this effect and to work with well-defined surface with equally wide terraces, a sufficiently thick buffer layer should be deposited after the pretreatment.

3.4.1.2 *Bales–Zangwill instability*

As shown in the theory of Burton, Cabrera, and Frank (Sec. 3.2.1), the steps are always rough at any temperature higher than the absolute zero. It is also assumed that the kinks are randomly distributed along the steps. Thus, the steps preserve on average a constant shape in the sense that they are considered as straight irrespective of the degree of roughness. And this is really the case if we accept that the probabilities of attachment of atoms to the steps from both sides are equal. Bales and Zangwill (1990) paid attention to the experimental observation that, in some cases, the step roughness has a nonrandom nature in the sense that the steps reveal a characteristic waviness (Sunagawa and Bennema 1982). In order to explain the latter, Bales and Zangwill developed a model which includes the asymmetric attachment kinetics at steps. We will present here only the qualitative reasoning given by the authors. The readers interested in the quantitative results are referred to the original paper quoted above (see also Bales and Zangwill 1993) as well as to the book of Pimpinelli and Villain (1998) in which this question has been extensively reviewed.

As we know, the rate of propagation of a step is proportional to the net sum of the fluxes of atoms that join the step from the upper and lower terraces

$$v = v_{\mathrm{up}} + v_{\mathrm{down}},$$

where the partial rates v_{up} and v_{down} are proportional to the corresponding gradients of the adatom concentration from both sides of the step (see Eq. (3.33))

$$v_{\mathrm{up,down}} \propto \mp D_s \left(\frac{dn_s}{dy}\right)_{\mathrm{down,up}}.$$

(In Eq. (3.25), we assumed both rates being equal which resulted in a factor of 2).

Assume now that for some reason some protuberances alternating with concavities are formed on a step that is generally straight. The result will be a wavy step. We can represent such a step as a sinusoid with a small amplitude as shown in Fig. 3.55 by the thick lines. We

Figure 3.55: Top-view representation of a wavy step denoted by the thick lines. The thin lines represent the isoconcentration profiles. The arrows give the fluxes of atoms proportional to the gradient of the adatom concentration, grad n_s, to the protuberances (denoted by A) and to the concavities (denoted by B). The length of the arrows reflects the flux intensity. In (a), the probabilities of attachment of adatoms from the upper and lower terraces are equal and the total velocity is one and the same for both the protuberances and the concavities. In (b), the flux from the upper terrace is smaller owing to the ES barrier to interlayer transport. As a result, the total rate of advance of the protuberances is greater than that of the concavities (after Bales and Zangwill 1990).

look for the conditions the amplitude of the protuberances (denoted by A) to grow larger or to become equal to zero. We consider first the case of complete symmetry of attachment of atoms to the step from both sides (absence of ES barrier) (Fig. 3.55(a)). We solve the master equation ((3.38)) assuming fast exchange of atoms between the step and the adlayer (diffusion regime of growth). The result will be given by the isoconcentration lines shown by the thin lines. They have the same sinusoidal shape but with a decreasing amplitude going to zero at a sufficiently long distance from the step. The lines are more dense

Figure 3.56: A protuberance at a straight step. The arrows show the direction of the adatom motion. A fraction of the atoms which should join a straight part of the step in absence of the protuberance are now directed to the latter.

in front of the protuberances and behind the concavities (denoted by B). Correspondingly, they are less dense in front of concavities and behind protuberances. Physically, this means that the flux of atoms on the lower terrace ($\propto$ gradn_s) to the protuberances is greater than that to the concavities as shown in Fig. 3.56. Note that the protuberance from the side of the lower terrace is, in fact, a concavity when seen from the upper terrace. Then, the flux of atoms to the protuberance from the upper terrace will be smaller than that from the lower terrace.

It follows that the partial velocity v_{down} of the protuberances will be larger than that of the concavities and vice versa for v_{up}. Thus, the smaller flux towards concave parts B from the lower terrace will be fully compensated by the larger flux on the upper terrace and vice versa (Fig. 3.55(a)). As a result, the total rate will be constant and the step shape will remain unchanged or, at least, the amplitude of the protuberances will not grow.

Assume now that the kinetic coefficient of the partial rate v_{up} from the upper terrace is smaller compared with that of v_{down} owing to the existence of an ES barrier to the descending step (Fig. 3.55(b)).

The flux from the upper terrace will not compensate the smaller flux in front of the concavity B. As a result, the protuberances will speed up forward and the concave parts will lag still more. The straight step will, thus, become unstable against small perturbations.

As noted by the authors, the protuberances cannot grow indefinitely as the perturbations increase the length and, in turn, the total energy of the step. A smoothing effect of thermodynamic origin will take place. Bearing in mind that the steps are curved, the smoothing will be naturally based on the Thomson–Gibbs effect. Assuming fast attachment–detachment kinetics at the ascending step (diffusion regime), the adatom concentration at the near vicinity of the step will be given by Eq. (3.54)

$$n_{\mathrm{se}}(\rho) = n_{\mathrm{se}} \exp\left(\frac{\varkappa a^2 \kappa}{kT}\right),$$

where $\kappa = 1/\rho$ is the curvature of the perturbation.

The adatom concentration will be largest in front of the protuberances and smallest in front of the concavities. A diffusion of atoms parallel to the step to regions in front of the concave parts will begin and their advance will be accelerated. Simultaneously, the concentration in front of the protuberances will be reduced and their growth will be delayed. A smoothing of the perturbations will result. In the absence of an ES barrier, the protuberances should disappear.

3.4.2 *Ehrlich–Schwoebel effect on 2D nucleation*

3.4.2.1 *Second-layer nucleation*

We consider the case when the crystal surface consists of sufficiently wide terraces and the temperature is sufficiently low so that the diffusivity of the adatoms is so small that they do not reach the preexisting steps. Then, they collide with each other and give rise to 2D nuclei. As long as they are small, they grow by incorporation of atoms which diffuse preferentially on the surface between them. With the increase of the island size, more and more atoms from the vapor phase begin to fall on the island surface. As on the terraces the atoms on the island surface can reach the island edges and attach to them, or meet each other to give rise of second layer nucleus. Thus, two

Figure 3.57: Typical STM image of mounds appearing on the surface after the deposition of 37 MLs of Pt on Pt(1 1 1). (J. Krug, P. Politi and T. Michely, *Phys. Rev. B* **61**, 14037 (2000). Copyright 2002 by the American Physical Society and courtesy of Thomas Michely.)

parallel processes — growth of the first ML islands and nucleation on top of them — lead to the existence of a critical island's size Λ for second-layer nucleation. If the surface coverage $\pi\Lambda^2 N_s \geq 1$, the first ML islands will coalesce and cover completely the growing surface before second layer nucleation to occur. A layer-by-layer growth and oscillations of the specular beam intensity as shown in Fig. 3.23 will result. In the opposite case $\pi\Lambda^2 N_s < 1$, the growing surface will resolve into multilayer pyramids of growth (mounds, "wedding cakes") (see Fig. 3.57) and the specular beam intensity decreases monotonously to zero without any oscillations. Such behavior has been observed in series of cases of growth of fcc(1 1 1) surfaces like Cu(1 1 1) (Wulfhekel *et al.*, 1996; van der Vegt *et al.*, 1995; Camarero *et al.*, 1998), Ag(1 1 1) (van der Vegt *et al.*, 1993).

The concept of the critical island size for second-layer nucleation has been initially introduced by Chernov (1977) and later used by Stoyanov and Markov (1982) to explain the 2D–3D transition in heteroepitaxial growth in a diffusion regime of growth. We define Λ by the same way as in Sec. 3.2.3.1 but writing Eq. (3.113) in an integral

form

$$\int_0^{\Lambda} \frac{\tilde{J}_0(\rho)}{v(\rho)} d\rho = 1, \tag{3.197}$$

where

$$v(\rho) = \frac{d\rho}{dt} = \frac{\Re}{2\pi\rho N_s N_0} \tag{3.198}$$

is the rate of growth of the first ML islands in the case of complete condensation before nucleation on their upper surfaces takes place. Equation (3.198) is obtained by differentiation of Eq. (3.124).

$\tilde{J}_0$ is the nucleation frequency on the upper surface of the island defined as before (see Eq. (3.125))

$$\tilde{J}_0(\rho) = 2\pi \int_0^{\rho} J_0(r, \rho) r dr, \tag{3.199}$$

where $J_0(r, \rho)$ is the nucleation rate as given by the atomistic theory (Eq. (2.117)) which depends on the island's radius ρ through the adatom concentration n_s. The latter is given by Eq. (3.127) in which the integration constant A should be determined by the boundary condition

$$j = -D_s \Big(\frac{dn_s(r)}{dr} \Big)_{r=\rho}, \tag{3.200}$$

where $j = j_+ - j_-$ is the net flux of atoms to the descending step which encloses the island, j_+ and j_- being the attachment and detachment fluxes, respectively.

Bearing in mind Fig. 3.53, the flux of atoms from the upper surface of the island to the descending step reads (Schwoebel 1969)

$$j_+ = a\nu n_{\mathrm{st}} \exp\Big(-\frac{E_{\mathrm{sd}} + E_{\mathrm{ES}}}{kT} \Big),$$

where $n_{\mathrm{st}} = n_s(r = \rho)$ is the adatom concentration in the proximity of the descending step as before, and ν is the attempt frequency.

The opposite flux of atoms from the kink sites along the steps to the island's surface is

$$j_- = a\nu n_{\mathrm{k}} \exp\Big(-\frac{\Delta W + E_{\mathrm{sd}} + E_{\mathrm{ES}}}{kT} \Big),$$

where n_{k} is the concentration of atoms detachable from the step (presumably, atoms in kink positions), and $\Delta W = \varphi_{1/2} - E_{\mathrm{des}}$ is the energy required to transfer an atom from a kink position to the flat surface (see Eq. (3.18)).

The total flux j then reads

$$j = a\nu(n_{\mathrm{st}} - n_{\mathrm{se}}) \exp\Big(-\frac{E_{\mathrm{sd}}}{kT}\Big)\frac{1}{S}, \tag{3.201}$$

where $n_{\mathrm{se}} = n_{\mathrm{k}} \exp(-\Delta W/kT)$ is the equilibrium adatom concentration (see Eq. (3.18)) and $S = \exp(E_{\mathrm{ES}}/kT)$.

Combining (3.200) and (3.201) and bearing in mind that $n_{\mathrm{st}} = A - \Re\rho^2/4D_s$ yields (Tersoff *et al.*, 1994)

$$n_s = n_{\mathrm{se}} + \frac{\Re}{4D_s}\big(\rho^2 + 2\rho aS - r^2\big). \tag{3.202}$$

As follows from the above, in the case of a negligible ES barrier ($2aS/\rho \ll 1$), (3.202) turns into (3.129). The adatom concentration on top of the island surface has a profile of a dome with a maximum above the island's center ($r = 0$) and reaches its equilibrium value n_{se} near the island's edge ($r = \rho$). It follows that second-layer nucleation is favored around the middle of the island.

In the other extreme $2aS/\rho \gg 1$, we neglect the difference $\rho^2 - r^2$ and

$$n_s \approx \frac{\Re}{2D_s}\rho aS.$$

This means that the adatom population on top of an island with repelling boundaries is uniformly distributed all over the surface of the island and a nucleation event can occur with equal probability at any point of it.

We substitute (3.202) into (2.117) and the latter into (3.199) to obtain, after integration (Tersoff *et al.*, 1994),

$$\tilde{J}_0 = A\big[\big(\rho^2 + 2\rho aS\big)^{n^*+2} - \big(2\rho aS\big)^{n^*+2}\big], \tag{3.203}$$

where (see (3.131′))

$$A = \frac{\pi\alpha^*}{(n^*+2)} D_s N_0^2 \exp\Big(\frac{E^*}{kT}\Big)\left(\frac{\Re}{4D_s N_0}\right)^{n^*+1}.$$

As seen, a negligible ES barrier, $2aS \ll \rho$, turns Eq. (3.203) into (3.131) as expected. The number of the growth pyramids will be given by (3.133) or, what is the same, by (2.156) with the familiar scaling exponent $\chi = n^*/(n^* + 2)$ (see Eq. (2.157)).

In the other extreme, $2aS \gg \rho$, we take the last two terms of the expansion of the sum

$$(\rho^2 + 2\rho aS)^{n^*+2} \approx (2\rho aS)^{n^*+2} + (n^* + 2)\rho^2(2\rho aS)^{n^*+1}$$

in (3.203) and the latter turns into

$$\tilde{J}_0 = B\rho^{n^*+3}, \tag{3.204}$$

where

$$B = \pi\alpha^* D_s N_0^2 \exp\Big(\frac{E^*}{kT}\Big)\Big(\frac{\Re aS}{2D_s N_0}\Big)^{n^*+1}.$$

It is of interest to calculate the density of islands and to compare the result with (3.133) obtained in the absence of the ES barrier. For this purpose, we follow the same procedure as in Sec. 3.2.3.2. We make use of Eq. (3.124) and substitute ρ for the time t in (3.204), and the result into (3.132). After integration and rearrangement, one obtains

$$\begin{aligned} N_s &= \frac{1}{\pi}C^* N_0\Big(\frac{D}{F}\Big)^{-\chi}\exp\Big(\frac{2[E^* + (n^*+1)E_{\mathrm{ES}}]}{(n^*+3)kT}\Big) \\ &= \frac{1}{\pi}C^* N_0\Big(\frac{\nu}{F}\Big)^{-\chi}\exp\Big(\frac{2[E^* + n^*E_{\mathrm{sd}} + (n^*+1)E_{\mathrm{ES}}]}{(n^*+3)kT}\Big), \end{aligned} \tag{3.205}$$

where

$$C^* = \Big(\frac{\pi\alpha^*}{2^{n^*}(n^*+5)}\Big)^{2/(n^*+3)} \tag{3.206}$$

is again a constant of the order of unity and $\chi = 2n^*/(n^* + 3)$. This is, in fact, Eq. (2.156) with the scaling exponent (2.158) obtained by Kandel (1997) and Markov (1997).

We can now calculate the critical radii of the islands for second-layer nucleation in both cases of low (subscript "0") and high (subscript "ES") ES barrier. Substituting (3.131), (3.204), and (3.198)

in, (3.197) gives after integration (Tersoff *et al.*, 1994)

$$\Lambda_0 = aC_0\left(\frac{D}{F}\right)^{n^*/2(n^*+3)} \tag{3.207}$$

with

$$C_0 = \left(\frac{4^{n^*}(n^*+2)(n^*+3)N_0 e^{-E^*/kT}}{\pi^2\alpha^* N_s}\right)^{1/2(n^*+3)} \tag{3.208}$$

for the case of a negligible ES barrier, and

$$\Lambda_{\mathrm{ES}} = aC_{\mathrm{ES}}\left(\frac{D}{F}\right)^{n^*/(n^*+5)} S^{-(n^*+1)/(n^*+5)} \tag{3.209}$$

with

$$C_{\mathrm{ES}} = \left(\frac{2^{n^*}(n^*+5)N_0 e^{-E^*/kT}}{\pi^2\alpha^* N_s}\right)^{1/(n^*+5)} \tag{3.210}$$

for the other limiting case of a significant ES barrier.

Let us compare N_s and Λ in both cases. For this purpose, we take typical values for the quantities involved $N_0 = 1 \times 10^{15}$ cm^{-2}, $\Re = 1 \times 10^{13}$ cm^{-2}s^{-1}, $F = \Re/N_0 = 1 \times 10^{-2}$ s^{-1}, $E_{\mathrm{sd}} = 0.4$ eV, $E_{\mathrm{ES}} = 0.2$ eV, $T = 400$ K, $n^* = 1$, and $E^* = 0$. Then, in the case of $E_{\mathrm{ES}} = 0$, $N_s \approx 6 \times 10^{10}$ cm^{-2}, and $\Lambda_0 \approx 180$ Å. In the other extreme, $N_s \approx 1 \times 10^{12}$ cm^{-2} and $\Lambda_{\mathrm{ES}} \approx 50$ Å is 3 times smaller.

As seen, both expressions (3.207) and (3.209) contain the corresponding number, N_s, of first ML 2D nuclei. If we substitute (3.133) in (3.208) and the latter in, (3.207) as well as (3.205) in (3.210) and (3.209), respectively, we will find that in both cases, $\Lambda = 1/\sqrt{\pi N_s}$. This is not surprising bearing in mind that in order to calculate N_s and Λ, we made use of the condition (3.132) for layer-by-layer growth. This is more or less correct in the case of the absence of the ES barrier where layer-by-layer growth is observed, but is obviously incorrect in the other extreme. In other words, the condition $\pi\Lambda^2 N_s \ll 1$ is valid in this case. In order to solve the problem, we should replace the condition for layer-by-layer growth by a condition for multilayer growth. For this purpose, we accept that a definite number, n, of MLs grow simultaneously and the condition for that is that *the $n+1$st layer nucleates when the first ML reaches completion.* Then, we make the

simplifying assumption that the surface roughness remains constant during growth, or in other words, the surface replicates itself. The result of this oversimplified treatment is that expression (3.205) is multiplied by a factor smaller than unity (Markov 1997).

In order to check the above theory, we calculate the number n of atoms on the surface of the base island when its radius has just reached the critical value Λ. For this purpose, we integrate the adatom concentration on the island's surface

$$n = 2\pi \int_0^{\Lambda} n_s(r, \Lambda) r dr,$$

where $n_s(r, \Lambda)$ is given by Eq. (3.202). We find

$$n = \frac{\pi F}{8D} N_0^2 \Lambda^4 \Big(1 + \frac{4aS}{\Lambda}\Big).$$

We will consider as examples two surfaces of fcc crystals — (1 0 0) and (1 1 1). The reason is that the (1 0 0) surfaces are characterized with a large terrace diffusion barrier and a small step-edge barrier. This is the reason why during growth the (1 0 0) surfaces demonstrate as a rule oscillations of the intensity of the specular beam. On the contrary, the smoother (1 1 1) surfaces are characterized with small intralayer diffusion barriers and large interlayer barriers. The result is a monotonous decrease of the intensity of the specular beam (Markov 1997).

We consider first the case of Cu(0 0 1) (Gerlach *et al.*, 2001). The authors have measured the step kinetics of a pyramid consisting of 2D islands, one on top of the other, and determined the critical radius $\Lambda \approx 3 \times 10^{-5}$ cm of the uppermost island at which the next layer nucleus is formed ($T = 400\,\mathrm{K}$, $F = 0.0075\ \mathrm{s}^{-1}$, $E_{\mathrm{sd}} = 0.4$ eV (for a compilation of data concerning E_{sd} see Markov (1996a)), $a = 2.55 \times 10^{-8}$ cm, $N_0 = 1.53 \times 10^{15}\ \mathrm{cm}^{-2}$). The authors measured the radii $\rho_i(t)$ ($i = 1, 2, 3, ...$) of the growing successive islands belonging to one and the same pyramid as a function of time, t, and fitted the data with a system of equations of step propagation similar to (3.146) but accounting for the existence of an ES barrier as a fitting parameter (see Eqs. (3.214) and (3.215)). The value $E_{\mathrm{ES}} = 0.125$ eV has been found. Then, by using the above formula, we find for the number

of atoms which give rise to the new ML nucleus the value $n = 70$. Note that $aS/\Lambda \approx 0.03$, which confirms the above statement that the kinetics at fcc(0 0 1) surfaces is not dominated by the interlayer diffusion and the profile of the adatom concentration looks like a dome.

We consider next the most studied and most controversial case of Pt(1 1 1). Bott, Hohage and Comsa (1992) observed by STM the appearance of second-layer nuclei at surface coverages of 0.3 (425 K, $N_s = 3.37 \times 10^{10}$ cm^{-2}) and 0.8 (628 K, $N_s = 3.5 \times 10^9$ cm^{-2}) ($\Re = 5 \times 10^{12}$ cm^{-2}s^{-1}). The activation energy for terrace diffusion is well known to be 0.25–0.26 eV from FIM (Feibelmann, Nelson and Kellogg 1994) and nucleation (Bott *et al.*, 1996) measurements. Values for E_{ES} varying from 0.12 eV (Krug *et al.*, 2000) to 0.44 eV (Markov 1996) have been estimated. The average number of atoms on the island's surface as computed with the help of the above equation (and as also noted by Krug, Politi and Michely 2000) turned out to be of the order of 1×10^{-2}, i.e., much less than unity which is unphysical. In fact, n becomes greater than unity when $E_{\mathrm{ES}} > 0.5$ eV, which means that the atoms at the island's periphery must overcome a total barrier of about 0.75 eV, which is too large to be believed. In contrast to the previous case, however, $aS/\Lambda \gg 1$, which means that it is the interlayer diffusion that dominates the kinetics, and the adatom population on top of the island is spatially uniform.

Whereas the Cu(0 0 1) case is physically reasonable, the (1 1 1) case looks puzzling. In order to solve the problem of the high ES barrier, Krug, Politi and Michely (2000) accounted for the probabilistic nature of the main processes involved. We will give a brief outline of their approach. For more details, the interested reader is referred to the original paper. The authors take into account the fact that the atoms arrive randomly on the island's surface $\pi\rho^2$ but not at equal intervals $\Delta t = 1/\pi\rho^2\Re$ as is implicitly assumed in the model described above. Second, the time, τ, the atoms reside on the island before rolling over and join the descending edge is also a random quantity. The latter is directly proportional to the island's periphery $2\pi\rho$ and inversely proportional to the rate of step-edge diffusion $\omega = a\nu \exp[-(E_{\mathrm{sd}}+E_{\mathrm{ES}})/kT]$, i.e., $\tau \approx 2\pi\rho/\omega = 2\pi\rho aS/D_s$.

We introduce further the time $\tau_{\rm tr} = \pi\rho^2/D_s$ required for an atom to visit all sites of the island. The condition $\tau/\tau_{\rm tr} \gg 1$ is equivalent to $2aS/\rho \gg 1$ which is, in fact, the condition for a nucleation kinetics dominant by the step-edge diffusion (see Eq. (3.204)). Assuming $n^* = 1$ (the dimers are stable and immobile), it is concluded that as soon as two atoms are present simultaneously on the island's surface, their encounter is inevitable. Thus, the necessary and sufficient condition for the atoms to meet each other and give rise to a stable cluster is $\tau_{\rm tr} \ll \tau$. Then, the probability of nucleation, $p_{\rm nuc}$, is equal to the probability, p_2, of two adatoms to be present simultaneously on the island. p_2 is determined by the condition the time of arrival, t_2, of the second atom to be shorter than the time, t_1, of departure of the first atom. Assuming t_1 and t_2 are randomly distributed around the average values τ and Δt, respectively, one obtains, after integration,

$$p_{\rm nuc} = \frac{1}{\tau\Delta t}\int_0^\infty dt_1 e^{-t_1/\tau}\int_0^{t_1} dt_2 e^{-t_2/\Delta t} = \frac{\tau}{\tau+\Delta t}.$$

Two limiting cases are possible. The case $\tau \gg \Delta t$ and $p_{\rm nuc} \approx 1$ is trivial. It means that the ES barrier is infinitely high and there always be at least one atom on top of the island. The physically interesting case is when $\Delta t \gg \tau$ and $p_{\rm nuc} = \tau/\Delta t$. Then, the nucleation frequency $\bar{J}_0 = \pi\rho^2\Re p_{\rm nuc}$ reads

$$\bar{J}_0 \propto \frac{a\Re^2\rho^5 S}{D_s}. \tag{3.211}$$

This equation should be compared with (3.204). With $n^* = 1$, the latter gives

$$\bar{J}_0 \propto \frac{a^2\Re^2\rho^4 S^2}{D_s}. \tag{3.212}$$

Comparing both formulae shows that the mean-field expression (3.212) is $aS/\rho \gg 1$ times larger than the probabilistic one (3.211). The explanation is simple. Equation (3.212) is based on the implicit

assumption that, on top of the island, there is all the time, although smaller than unity but constant, time average number of atoms. As shown above, this is indicative for a large ES barrier whose mathematical expression is just $aS/\rho \gg 1$. In fact, the island's surface is empty most of the time, and sometimes it is populated by a single atom, and very rarely it happens that during this time a second atom arrives. Once two atoms are simultaneously present on the island, a nucleus is formed with a probability close to unity. That is why the authors coined for this model the term "the lonely adatom model". The problem of the second-layer nucleation is still intensively studied (Rottler and Maass 1999; Heinrichs, Rottler and Maass 2000). These authors found that the mean-field approach is applicable for critical nuclei consisting of more than three atoms. If this is not the case ($n^* = 1, 2$), the random character of the processes involved becomes significant.

3.4.2.2 *Step kinetics*

We finish the chapter of the effect of the ES step-edge barrier with considering the kinetics of step propagation of islands constituting a pyramid of growth as shown in Fig. 3.28 similar to the system of equations (3.146).

We solve the simpler case of the traditional ES barrier omitting the attractive behavior of the ascending step. We calculate as before the adatom concentration on the terrace between two circular islands (Fig. 3.28). For this purpose, we have to find the integration constants A and B of the solution (3.138) of the diffusion Eq. (3.126). The boundary conditions are the same as in the previous sections (see (3.200))

$$j_i = \pm D_s \left(\frac{dn_s(r)}{dr} \right)_{r=\rho_i}, \qquad (i = 1, 2), \tag{3.213}$$

where j_1 is given by Eq. (3.201) and $j_2 = a\nu(n_2 - n_{\mathrm{se}}) \exp(-E_{\mathrm{sd}}/kT)$.

The exact expressions for A and B, and in turn for the n_s, are very cumbersome, so we do not use them; instead, we proceed further and calculate the rates of growth of the separate 2D islands in terms of the respective surface coverages $\Theta_n = \pi\rho_n^2 N_s$. We obtain again a

system of N equations

$$\frac{d\Theta_n}{d\theta} = F(\Theta_{n-1}, \Theta_n) - F(\Theta_n, \Theta_{n+1}), \tag{3.214}$$

where $\theta = \Re t/N_0$, $F(\Theta_0, \Theta_1) = 1$, $F(\Theta_N, \Theta_{N+1}) = 0$, with (Gerlach *et al.*, 2001)

$$F(\Theta_n, \Theta_{n+1}) = \frac{\Theta_n - \Theta_{n+1} + qS\sqrt{\Theta_n}}{\ln(\Theta_n/\Theta_{n+1}) + qS/\sqrt{\Theta_n}}, \tag{3.215}$$

where $q = \sqrt{\pi a^2 N_s}$.

Equation (3.214) becomes more clear if we write F in terms of islands' radii

$$F(\rho_n, \rho_{n+1}) = \pi N_s \frac{\rho_n^2 - \rho_{n+1}^2 + aS\rho_n}{\ln(\rho_n^2/\rho_{n+1}^2) + aS/\rho_n}. \tag{3.216}$$

It is immediately seen that Eq. (3.214) turns into (3.146) when $aS \ll \rho_n$ (aS/ρ_n is also much smaller than the logarithm which is of the order of unity). In this case, the material deposited on the terrace is approximately equally distributed between both islands (a little bit more of the half of the material joins the lower island because of its longer periphery).

In the other extreme, $F(\Theta_n, \Theta_{n+1}) = \Theta_n$ and, thus, does not depend anymore on the ES effect (the ES barrier is infinitely high). The system can be solved analytically. Thus, for the bilayer pyramid, shown in Fig. 3.28, $F(\Theta_1, \Theta_2) = \Theta_1$ and

$$\Theta_1 = 1 - (1 - \Theta_1^0)e^{-\theta}, \tag{3.217}$$

$$\Theta_2 = \Theta_2^0 + \theta - (1 - \Theta_1^0)(1 - e^{-\theta}), \tag{3.218}$$

where Θ_1^0 and Θ_2^0 are some initial values at $\theta = 0$. The above equations clearly show that all the material deposited on the surface of the lower island feeds only the upper island. The latter thus grows faster

than the lower island (upto the moment of third layer nucleation) which in turn grows only at the expense of the material deposited on the bare substrate between the pyramids.

The ES factor S increases exponentially with decreasing temperature. At sufficiently high temperature, one can expect that $aS/\rho_n \ll 1$ and $F = (\Theta_n - \Theta_{n+1})/\ln(\Theta_n/\Theta_{n+1})$ (Eq. (3.146)). At low temperature, $aS/\rho_n \gg 1$ and $F = \Theta_n$. It follows that the ES factor has an effect on the step kinetics in an intermediate temperature interval. In the case of Cu(0 0 1) discussed above (Gerlach *et al.*, 2001), this interval varies approximately from 120 to 480 K. This means that at $T > 480$ K, the ES barrier is practically equal to zero, while at $T < 120$ K, E_{ES} can be considered as infinitely high.

It follows first that the critical radius Λ for second-layer nucleation will depend on the ES barrier in a limited interval of temperature. Second, at low temperatures, the system (3.214) is reduced to the system of differential equations given by Cohen *et al.* (1989):

$$\frac{d\Theta_n}{d\theta} = \Theta_{n-1} - \Theta_n,$$

which have to be solved subject to the initial conditions $\Theta_n = 0$ at some initial moments (coverages) θ_n. Assuming $\theta_n \ll 1$, which means that the surface roughens very fast from the very beginning of deposition, $\pi\Lambda^2 N_s \ll 1$, the solution of the above system reads (Cohen *et al.*, 1989)

$$\begin{aligned}
\Theta_1 &= 1 - e^{-\theta}, \\
\Theta_2 &= 1 - (1+\theta)e^{-\theta}, \\
\Theta_3 &= 1 - \left(1 + \theta + \frac{1}{2}\theta^2\right) e^{-\theta}, \\
&\ldots,
\end{aligned}$$

or, in a general form

$$\Theta_n = 1 - e^{-\theta} \sum_{i=0}^{n-1} \frac{\theta^i}{i!}. \tag{3.219}$$

The solution of Eq. (3.219) is shown in Fig. 3.58. As seen, a great number of layers grow uncovered and the growth front is very

Figure 3.58: Surface coverages vs time in multilayer growth according to Eq. (3.219) (after Cohen *et al.*, 1989).

thick. As has been shown by Cohen *et al.* (1989), this mode of growth leads to an exponential decay of the intensity of the reflected beam ($I/I_0 = e^{-4\theta}$). Thus, the above equations describe the ideal 3D growth, or growth of mounds predicted by Villain (1991).

3.5 Kinematic Theory of Crystal Growth

The layer growth is often realized as a lateral propagation of monomolecular (monoatomic) steps which is not always the case. Just the opposite, the propagation of thicker steps is frequently observed. As discussed briefly in Sec. 3.2, the rate of advance of such steps should be lower than that of monomolecular or elementary steps. This is easy to understand, but nevertheless we will illustrate it with the help of a simple example.

The example consists in the comparison of the rates of advance of two elementary steps due to 2D nuclei formed one over the other (Fig. 3.28) and the double step which is formed when the upper step catches up with the lower step. In other words, we consider a pyramid of growth as shown in Fig. 3.28.

The solution of the diffusion problem (3.58) now reads

$$\Psi(r) = \Psi(\rho_2)\frac{I_0(r/\lambda_s)}{I_0(\rho_2/\lambda_s)}, \qquad \text{for} \quad r < \rho_2,$$

$$\Psi(r) = AI_0(r/\lambda_s) + BK_0\left(\frac{r}{\lambda_s}\right), \qquad \text{for} \quad \rho_2 < r < \rho_1,$$

$$\Psi(r) = \Psi(\rho_1)\frac{K_0(r/\lambda_s)}{K_0(\rho_1/\lambda_s)}, \qquad \text{for} \quad r > \rho_1,$$

where

$$A = \frac{\Psi(\rho_1)K_0(\rho_2/\lambda_s) - \Psi(\rho_2)K_0(\rho_1/\lambda_s)}{I_0(\rho_1/\lambda_s)K_0(\rho_2/\lambda_s) - I_0(\rho_2/\lambda_s)K_0(\rho_1/\lambda_s)},$$

$$B = -\frac{\Psi(\rho_1)I_0(\rho_2/\lambda_s) - \Psi(\rho_2)I_0(\rho_1/\lambda_s)}{I_0(\rho_1/\lambda_s)K_0(\rho_2/\lambda_s) - I_0(\rho_2/\lambda_s)K_0(\rho_1/\lambda_s)}.$$

Following Burton, Cabrera and Frank (1951) and making use of the relation $I_1(z)K_0(z) + I_0(z)K_1(z) = 1/z$ and the approximations valid for $\rho_{1,2} > \lambda_s$, $I_0(z) = (\pi z/2)^{1/2}\exp(z)$, and $K_0(z) = (\pi/2z)^{1/2}\exp(-z)$, we find

$$v(\rho_1) = v_\infty\left(1 - \frac{\rho_c}{\rho_1}\right)\frac{1 - (\Psi(\rho_2)/\Psi(\rho_1))\sqrt{(\rho_2/\rho_1)}\exp(-\lambda/\lambda_s)}{1 - \exp(-2(\lambda/\lambda_s))},$$

$$v(\rho_2) = v_\infty\left(1 - \frac{\rho_c}{\rho_2}\right)\frac{1 - (\Psi(\rho_1)/\Psi(\rho_2))\sqrt{(\rho_1/\rho_2)}\exp(-\lambda/\lambda_s)}{1 - \exp(-2(\lambda\lambda_s))},$$

where now $\lambda = \rho_1 - \rho_2$ is the step spacing. $\Psi(\rho_2) > \Psi(\rho_1)$, $\rho_1 > \rho_2$, and the rate of propagation of the upper island is smaller than that of the lower one. This holds up for small enough radii ρ_1 and ρ_2. At large enough sizes of ρ_2 and ρ_1 when $(\rho_1/\rho_2)^{1/2} \cong 1$, $\Psi(\rho_1)/\Psi(\rho_2) \cong 1$ and $v(\rho_1) \cong v(\rho_2)$. Expanding the exponents in power series to the linear term at $\lambda \to 0$ we find that the rate of advance of a double

step is exactly twice smaller than that of a single elementary step (Eq. (3.62)).

When considering the propagation of a step with arbitrary thickness $h > a$ in the case of growth from vapors, one has to take into account the direct incorporation of atoms from the vapor phase to the step in addition to the surface diffusion (Chernov 1984). The surface diffusion flux per unit length of the step is (the diffusion gradient is approximated by $(n_s - n_{\mathrm{se}})/\lambda_s$, see Eq. (3.33))

$$j_s \cong 2\frac{D_s}{\lambda_s}(n_s - n_{\mathrm{se}}) = 2\lambda_s \frac{P - P_0}{\sqrt{2\pi mkT}}.$$

The flux from the vapor phase directly onto the step per unit length of the step is

$$j_v = h\frac{P - P_0}{\sqrt{2\pi mkT}}.$$

Bearing in mind that the total number of atoms required to shift the step by one atomic spacing a is $a^2 h/v_c = h/a$, the step velocity is equal to

$$v_\infty = \frac{j_s + j_v}{hN_0}a = \left(1 + \frac{2\lambda_s}{h}\right)v_c \frac{P - P_0}{\sqrt{2\pi mkT}}.$$

In other words, the factor $1+2\lambda_s/h$ should be added in the expressions for the rate of step advance in vapors to account for the step height. Obviously, when $h \gg \lambda_s$, the step should be considered as a separate crystal face and its growth does not depend on the step height. In the opposite case $h \ll \lambda_s$, the rate of the step advance is inversely proportional to the step height.

In growth from solutions (and melts), the boundary condition (3.65a) should read $C(r = h/\pi) = C_{\mathrm{st}}$ and the height a of the elementary step should be replaced by h everywhere. Then, v_∞ becomes dependent on the step thickness. Figure 3.59 illustrates the decrease of the rate of step advance with increasing step height for the particular case of solution growth (Eq. (3.77)).

Once a double step is formed, it can be caught up with other elementary steps and grow thicker becoming a bunch of steps or a macrostep. On the other hand, elementary steps can leave the

Figure 3.59: Dependence of the rate of advance $v(h)$ of a step of height h relative to the rate of advance of a SH step, $v(a)$, on the step height in units of a. The curve represents the case of solution growth after Eq. (3.77) in which the step height a is replaced by h.

bunch of elementary steps and the macrostep can dissipate. Thus, macrosteps and elementary steps usually coexist, making the detailed description of the processes of growth very complex. As has been discussed in Chapter 1, vicinal surfaces can break up into close packed facets under the influence of impurity atoms adsorbed on them. The facets should grow through the formation of 2D nuclei if they are larger than the size of the 2D nucleus (Chernov 1961). In order to overcome the difficulties connected with the complicated relief of the crystal surfaces, Frank (1958b), Cabrera and Vermilyea (1958) developed the so-called kinematic theory of crystal growth (see also (Bennema and Gilmer 1973)).

In order to illustrate the essence and the consequences of the kinematic theory, we will use an example whose mathematical treatment served as a basis of the Frank considerations. This is the model of the road traffic developed by Lighthill and Whitham (1955).

We consider a road and cars moving along it. The cars cannot outstrip each other but can catch up with each other. In fact, the same is the behavior of the single elementary steps on a vicinal 2D crystal surface (prismatic or cylindrical). The speed of the cars depends

on their proximity just like the rate of advance of steps in a train depends on their spacing (see Eq. (3.50)). In other words, we assume that the speed of the cars depends on their local density only. When the cars (steps) are equidistant, all cars move with one and the same speed v. We denote by ρ the density of the cars (cars per mile) which is just equal to the reciprocal of the distance between them. Obviously, the local car density is analogous to the slope of the vicinal hillock p. As the system is discrete, the local car density cannot be determined at a point. That is why we take the average of large distance neglecting the small fluctuations of speed and density. Imagine now, an arbitrary car drops accidentally its speed and is caught up with the car behind. The pair of cars (a double step) moves together and its speed is lower than the speed of a single car (the cars cannot overtake each other). Then, more and more cars catch up with them, thus forming a pack or a "wave" of cars which moves with a speed of its own denoted by c. Assuming now, the flux of the cars along the road is constant (the number of the cars per unit time entering the road is equal to the number of cars per unit time leaving the road) waves and nearly empty spacings will alternate. Plotting the local car density along the road we find a wavy line. That is why the speed c of the wave has been called by Lighthill and Whitham a "kinematic wave velocity." The same result would be obtained if by some reason an arbitrary car increases its speed and catches up with the car in front. Thus, the kinematic wave velocity can be, in general, larger or smaller than the speed v of the single cars. If $v > c$, the front cars of the wave break off and leave the wave, whereas cars from behind catch up with the wave. When $v < c$, the wave catches up with the front cars, but the back cars drop behind and leave the wave. Thus, the wave does not consist of one and the same cars but continuously exchange them. A particular car will join a kinematic wave, then leave it and join the next one, and so on. In between the waves, its speed will be higher than that of the waves. In some cases, the shape of the wave could display a discontinuity in the sense of a sharp edge which can be either behind or in front of the wave. The edge divides the wave into two regions with different density. Such a wave is called a "kinematic shock wave" or simply a shock wave, and

it will move with a speed determined by the difference of the density of cars on either side of the edge and their respective speeds.

Precisely, the same can occur on vicinal crystal surfaces or on the sides of growth hillocks due to screw dislocations. Besides, external factors like the hydrodynamic conditions in solutions (the direction of solution flow above the crystal face with respect to the direction of step advance) can affect the formation or dissipation of the kinematic waves, thus smoothing or roughening the crystal face (Chernov and Nishinaga 1987; Chernov 1989).

The growing crystal face is represented by the surface

$$z = z(x, y, t), \tag{3.220}$$

where the axis z is normal to the crystal surface and which is on average parallel to the growing singular crystal plane.

The rate of growth of the crystal face is

$$R = \frac{\partial z}{\partial t}. \tag{3.221}$$

The real profile $z(x, y, t)$ deviates locally from $z = 0$ and the slopes p and q at particular points x and y of the crystal surface are

$$p = -\frac{\partial z}{\partial x} \qquad \text{and} \qquad q = -\frac{\partial z}{\partial y}. \tag{3.222}$$

Assuming $z(x, y, t)$ is an analytic function, i.e., neglecting the discrete character of the system,

$$\frac{\partial^2 z}{\partial x \partial t} = \frac{\partial^2 z}{\partial t \partial x}, \qquad \frac{\partial^2 z}{\partial y \partial t} = \frac{\partial^2 z}{\partial t \partial y} \quad \text{and} \quad \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x},$$

then

$$\frac{\partial p}{\partial t} + \frac{\partial R}{\partial x} = 0, \quad \frac{\partial q}{\partial t} + \frac{\partial R}{\partial y} = 0 \quad \text{and} \quad \frac{\partial p}{\partial y} + \frac{\partial q}{\partial x} = 0. \tag{3.223}$$

In fact, the set of Eq. (3.223) represent the law of conservation of the elementary steps. If $p = h/\lambda$, where h is the step height and λ is the step spacing, the local density of the steps is $\rho_{\text{st}} = 1/\lambda = p/h$. From Eq. (3.15), it follows that $J_{\text{st}} = v/\lambda = R/h$ is the flux of steps which pass over a point of the crystal surface. Then,

$$\frac{1}{h}\frac{\partial p}{\partial t} + \frac{1}{h}\frac{\partial R}{\partial x} = \frac{\partial (p/h)}{\partial t} + \frac{\partial (R/h)}{\partial x} = \frac{\partial \rho_{\text{st}}}{\partial t} + \frac{\partial J_{\text{st}}}{\partial x} = 0.$$

The basic Eq. (3.223) are unusable if some simplifying assumptions were not made. We assume that the growth rate depends on x and y only through the local average slopes p and q, i.e., $R(x, y) = R(p, q)$. Second, when determining the slopes p or q, we take the average of a region sufficiently wider than the step spacing, i.e., in this respect the theory neglects the microscopic changes in the surface relief. Nevertheless, some very valuable consequences can be drawn at the expense of the approximation used. In the analysis to follow, we will consider for simplicity the 2D case accepting $q = 0$.

With the above approximation, (3.223) becomes

$$\frac{\partial p}{\partial t} + \frac{\partial R}{\partial x} = \frac{\partial p}{\partial t} + \frac{\partial R}{\partial p}\frac{\partial p}{\partial x} = 0. \tag{3.224}$$

We then denote $\partial R/\partial p = c(p)$ and

$$\frac{\partial p}{\partial t} + c(p)\frac{\partial p}{\partial x} = 0 \tag{3.224$'$}$$

or

$$\frac{dx}{dt} = -c(p). \tag{3.224$''$}$$

It follows that $c(p)$ is the x component of the velocity of a point of the surface relief with a slope p. In other words, we have regions with a constant slope which are called *kinematic waves.* In fact, the kinematic waves represent bunches of elementary steps divided by regions with wider terraces (Fig. 3.60(b)), and $c(p)$, which is a function of the slope only, represents the velocity of the bunches as a whole. As $c(p)$ is a function of p only, x is a linear function of time.

Let us follow the change of the relief of the growing crystal surface with time (Fig. 3.61) and find the trajectories of the waves or the lines which connect points with one and the same slope p or step density $1/\lambda = p/h$. The slope dz/dx at $p = \text{const}$ (z and x are coordinates of points on the crystal surface) is given by ($R = pv$, Eq. (3.15))

$$\left(\frac{dz}{dx}\right)_p = \frac{\partial z}{\partial t}\left(\frac{dt}{dx}\right)_p + \frac{\partial z}{\partial x} = \frac{R}{c} - p = \frac{pv}{c} - p = p\frac{v-c}{c}. \tag{3.225}$$

Thus, the slope of the wave trajectory is proportional to the relative difference of the velocities of the elementary steps and the kinematic wave. When $v > c$, the slope $(dz/dx)_p > 0$ (Fig. 3.61(a)) and

Figure 3.60: Schematic view of a kinematic wave (b) as compared with a train of equidistant steps (a).

vice versa (Fig. 3.61(b)). As seen in the latter case, when the wave moves faster than the train of more distant steps, the wave tends to leave the vicinal and to disappear from the crystal face.

Figure 3.62 illustrates the same phenomenon in the space of the growth rate R (or the flux $J_{\rm st} = R/h$) vs the step density p. Figure 3.62(a) gives the dependence of R on p in the diffusion regime of growth under clean conditions (no impurities adsorbed). The growth is proportional to p, but with increasing step density, the step velocity decreases according to Eq. (3.48) and R deviates from the straight line. Hence, the second derivative d^2R/dp^2 is negative everywhere. In the case of the kinetic regime of growth under clean conditions, the step velocity does not depend on the step density up to a very high value of the latter ($\cong 1$); R is a linear function of p as shown in Fig. 3.62(b) and $d^2R/dp^2 = 0$. In the intermediate case (kinetic regime at small p but overlap of the diffusion fields at large p), R increases initially linearly with p and then gradually deviates from the straight line. Then, $d^2R/dp^2 = 0$ for small p and $d^2R/dp^2 < 0$ for larger p. Figure 3.62(c) illustrates the case when impurity atoms are adsorbed on the terraces between the steps (Frank 1958). At small p (wide terraces), there is time enough for an adsorption equilibrium to be established and there the concentration of the impurity atoms is high. The latter inhibits strongly the propagation of the steps. At large p (narrow terraces), there is not enough time for considerable adsorption to take place and the propagation of the steps is faster,

Figure 3.61: Time behavior of kinematic waves: (a) $v > c$ and (b) $v < c$, where v and c are the velocities of the single steps far from the wave and the wave, respectively. The latter are shown by arrows denoted by v and c. The straight lines connect points of the same densities of steps.

although they are nearer to each other. Then, the $R(p)$ dependence has a positive curvature ($d^2R/dp^2 > 0$) at small p but negative one ($d^2R/dp^2 < 0$) at large p. When $d^2R/dp^2 < 0$ (Fig. 3.62(a), purely a diffusion regime of growth) on the whole crystal surface, the rate of advance of single steps $v = R/p$ is always greater than the rate of advance of the step bunch, $c = dR/dp$, the slope of the trajectory $(dz/dx)_p$ is always positive, and the kinematic waves will be present on the crystal surface. Under conditions of a kinetic regime of growth

Figure 3.62: Three possible variations of the rate of growth vs the step density. (a) The growth occurs in a diffusion regime in an absence of impurities. The growth rate $R = pv$ is determined by the overlapping of the diffusion fields (the hyperbolic tangent in the BCF theory) and deviates downward from the straight line at large p. The curvature of the $R(p)$ dependence is everywhere negative ($d^2R/dp^2 < 0$). The rate of advance of the shock wave, $c_{\rm sh}$, with slopes $p = p_{\rm a}$ and $p \approx 0$ on both sides of the edge is given by the slope of the chord represented by the dashed line. It lies between the slopes of the tangents at $p = 0$ and $p = p_{\rm A}$ (the latter being given by the tangent t at the point A). (b) The growth takes place in a kinetic regime in an absence of impurities. The rate of step advance v is independent of the step density and R is a linear function of p. The curvature of the $R(p)$ dependence is equal to zero. The single steps and the shock waves propagate with equal rates, i.e., $v = c$. (c) The growth takes place in a diffusion regime in the presence of impurities. The concentration of impurity atoms is large at small p, i.e., on wide terraces, and vice versa. Then the curvature of the $R(p)$ dependence is positive at small p and negative at large p. The rate of propagation of the shock wave $c < v$ at smaller p, but $c > v$ at larger p. The slopes of the dashed lines OA and OB give the rates of propagation of the shock waves, c, whereas the slopes of the tangents denoted by $t_{\rm A}$ and $t_{\rm B}$ give the rates of propagation of the single steps, v.

(Fig. 3.62(b)), $c = v$ all over the crystal surface and the slope of the trajectory $(dz/dx)_p = 0$. If there are regions where $d^2R/dp^2 > 0$, as shown in Fig. 3.62(c), $v < c$, $(dz/dx)_p < 0$ and the kinematic waves tend to leave the vicinals.

We consider now the formation of shock waves or waves with sharp edges. Figure 3.63 shows the step density or $p/h = -(1/h)dz/dx$ in

Figure 3.63: The transformation in time ($t_2 > t_1$) of a kinematic wave into a shock wave.

a kinematic wave as a function of x at different times. At some initial moment t_1, the step density represents a symmetric bell-shaped curve. Trajectories far from the wave are parallel. Near the wave, the trajectories are no longer parallel because their slopes are directly proportional to the step density according to Eq. (3.225). Therefore, the trajectories become more and more steep from the rear end; they are steepest at the maximum, and after passing the latter, they again tend to take the initial slope. As a result, the trajectories in the rear part of the wave will intersect each other after some time. The step density will have the shape shown by the curve denoted by t_2. Going back to the representation in coordinates (z, x), a discontinuity or a sharp edge will appear on the crystal surface as shown in Figs. 3.64(b) and (c). This is, namely, the shock wave to distinguish it from the usual kinematic wave (Fig. 3.64(a)).

The rate of advance c_{sh} of the shock wave is easy to find. It follows from Eq. (3.225)

$$p_1(v_1 - c_{\text{sh}}) = p_2(v_2 - c_{\text{sh}})$$

or

$$c_{\text{sh}} = \frac{p_2 v_2 - p_1 v_1}{p_2 - p_1} = \frac{R_2 - R_1}{p_2 - p_1}. \tag{3.226}$$

Figure 3.64: Kinematic shock waves with the sharp edge (b) in front of the wave and (c) behind the wave. A usual kinematic wave is given for comparison in (a). p_1 and p_2 denote the slopes on both sides of the edge.

Thus, the rate of advance of the shock wave is determined by the differences of the growth rates and the slopes of the crystal surface on the two sides of the edge. In fact, the shock wave represents a boundary between two regions with different step densities or, in other words, between two kinematic waves.

Figure 3.64 shows the geometrical construction illustrating the interrelation between the velocities of the kinematic waves constituting the shock wave and of the shock wave itself in the case of a diffusion regime of growth (see Fig. 3.62(a)). The velocities of the two kinematic waves are given by the slopes of the tangents $(dR/dp)_{p=p_1}$ and $(dR/dp)_{p=p_2}$. The velocity of the shock wave $c_{\mathrm{sh}} = (R_2 - R_1)/(p_2 - p_1)$ is given by the chord connecting the points $R_1(p_1)$ and $R_2(p_2)$. Its slope is obviously in between the slopes $(dR/dp)_{p=p_1}$ and $(dR/dp)_{p=p_2}$. Then, the velocity of the shock wave has a value in between the velocities of the kinematic waves that constitute it. It is evident that, in the kinetic regime of growth (linear dependence of R on p, Fig. 3.62(b)), the velocities of the kinematic waves as well as that of the shock wave do not depend on the step density and are equal to each other.

As mentioned above, the retardation (or acceleration) of elementary steps which leads to the bunching or formation of kinematic waves is due primarily to impurities (Frank 1958) or accidental local changes (fluctuations) of the supersaturation. In the first case, the bunches are usually stabilized by the impurities and should move faster than the isolated steps (van der Eerden and Müller-Krumbhaar 1986). As discussed above, this is due to the fact that on the wide terraces between the isolated steps, an adsorption–desorption equilibrium of the impurities is established and the concentration of the impurities there is higher compared with that on the narrow terraces which divide the steps constituting the bunch. Under clean conditions where the rate of advance of the elementary steps depends on the overlap of the diffusion fields, the rate of advance of the bunch should be smaller than that of the isolated steps.

3.6 A Classical Experiment in Crystal Growth

The predictions of the crystal growth theories have been an object of numerous experimental verifications in different media (vapors, solutions, and melts). Many accurate experiments have been carried out and, as shown above, most of the theoretical conclusions have been confirmed. In this chapter, we describe one of the most elegant and precise experiments in crystal growth — the electrocrystallization of silver in aqueous solutions. In doing this, we do not mean to underestimate the fine experimental work of many other investigators (Chernov 1989; Neave, Joice and Dobson 1984; Neave *et al.*, 1985; Wolf *et al.*, 1985; Keshishev, Parshin and Babkin 1981; Avron *et al.*, 1980, etc.).

In the case of electrocrystallization of metals, the rate of growth is given by the electric current flowing through the electrolytic cell, the amount of material deposited is given by the amount of the electricity, and the supersaturation is given by the overpotential. The electrical quantities and then the parameters characterizing the process of growth can be measured with great accuracy. A particular advantage of the experiments of this kind is that a single-crystal face with a definite crystallographic orientation can be produced and put

into contact with the electrolyte solution. As will be shown below the screw-dislocation-free crystal faces can be prepared as well as faces with definite number of dislocations. Thus, the spiral growth of a single-crystal face as well as the 2D nucleation growth both layer-by-layer and multilayer can be studied in one and the same system under well-defined conditions.

The electrolytic cell for the preparation of single-crystal faces both dislocation-free and with one or more dislocations is shown in Fig. 3.65 (Kaischew, Bliznakow and Scheludko 1950; Budewski and Bostanov 1964; Budewski *et al.*, 1966; see also Kaischew and Budewski 1967). The cathode represents a glass tube containing the seed crystal which ends with a capillary with inner diameter of approximately 200 μm. In some cases, a capillary with rectangular cross-section (100 μm$\times$400 μm) has been used for measuring the rate of advance of a single monoatomic step or a train of steps (see Fig. 3.74). The bottom of the cell is a plane–parallel glass window which permits the microscopic observation of the front face of the growing crystal. The cell is filled with the $6N$ aqueous solution of $AgNO_3$ acidified with HNO_3. Special measures have been usually taken in the process of preparation of as pure as possible solutions. After switching on the electric current, the seed crystal begins to grow and fills in the capillary. A single-crystal filament is formed which has the same crystallographic orientation as the seed crystal. Thus, single-crystal faces with (1 0 0) and (1 1 1) orientations are obtained (Budewski *et al.*, 1966). When alternating current is superimposed onto the direct current of growth, the silver filament begins to grow thicker and fills in the whole cross-section of the capillary and the area of the front face becomes equal to the opening of the capillary.

The filament inherits defects (screw dislocations) from the seed crystal which can be detected easily by the following procedure. The crystal face is initially smoothed by applying a low current. Then, a high current pulse is applied which results in the appearance of distinct pyramids of growth in the places of the emergency points of the screw dislocations. Figure 3.66 shows a (1 0 0) face with several square-based growth pyramids revealed by this method (Budewski *et al.*, 1966). Triangular pyramids of growth (not shown) are the

Figure 3.65: Electrolytic cell for the investigation of the growth of Ag single-crystal faces: (a) Ag seed crystal, (b) capillary, (c) silver anode, (d) brass block. The inset shows an enlargement of the end of the capillary. (E. Budewski and V. Bostanov, *Electrochim. Acta* **9**, 477 (1964). By permission of Pergamon Press Ltd. and courtesy of V. Bostanov.)

result in the case of (1 1 1) single-crystal faces. Burger's vectors of the screw dislocations are usually inclined with respect to the growing crystal face (in most cases $\frac{1}{2}\langle 1\,1\,0\rangle$ dislocations are detected). When the filament is carefully grown, the emergency points of the screw dislocations inherited from the seed crystal leave the front face and appear on the side faces of the filament. Defectless single-crystal faces are thus prepared.

Figure 3.66: Pyramids of growth obtained by applying a short overpotential pulse, showing the emergency points of screw dislocations on Ag(0 0 1). (E. Budewski, V. Bostanov, T. Vitanov, Z. Stoynov, A. Kotzeva and R. Kaischew, *Electrochim. Acta* **11**, 1697 (1966). By permission of Pergamon Press Ltd. and courtesy of V. Bostanov.)

First convincing evidence of the growth through 2D nucleation has been obtained on perfect faces prepared by the above method. A constant current density $i = 0.5$ mA cm^{-2} has been applied and the overpotential has been measured. It has been found that the latter oscillates from zero to a maximum value of about 10 mV (Fig. 3.67) (Budewski *et al.*, 1966). Increasing the current density has led to a decrease of the period of oscillations, but the product of the current density and the period of oscillations remained constant. The latter is exactly equal to the amount of electricity required for the completion of a ML, $itS = 3.83 \times 10^{-8}$ C, where i is the constant current density, $S = 2 \times 10^{-4}$ cm^2 is the area of the opening of the capillary, and t is the period of the oscillations. The amount of electricity required for completion of a ML of 1 cm^2 is $zeN_0 \cong 1.92 \times 10^{-4}$ C cm^{-2}, where $N_0 = 1.2 \times 10^{15}$ cm^{-2} [for Ag(1 0 0)] is the atom density of the corresponding crystal face, $e = 1.6 \times 10^{-19}$ C is the elementary charge of an electron and $z = 1$ is the valency of the neutralizing ions. Then, $itS = zeN_0S$. This behavior of the overpotential, which is a measure of the difficulties accompanying the electrodeposition

Figure 3.67: Oscillations of the overpotential when a constant current is applied on the cell. The product of the current and the period of oscillations gives the amount of electricity to complete one ML. (E. Budewski, V. Bostanov, T. Vitanov, Z. Stoynov, A. Kotzeva and R. Kaischew, *Electrochim. Acta* **11**, 1697 (1966). By permission of Pergamon Press Ltd. and courtesy of V. Bostanov.)

process, can be easily explained if one assumed that each oscillation is due to the formation and lateral propagation of one 2D nucleus. In the initial moment, the crystal face does not offer growth sites and the overpotential increases up to a critical value of about 10 mV necessary for 2D nucleation to take place. Once a 2D nucleus is formed, it begins to grow, offering more and more kink sites along its periphery, crystallization becomes easier, and the overpotential rapidly drops to zero when the edges surrounding the growing ML island reach the walls of the capillary. Then, the formation of a new 2D nucleus is required for further growth and the process is repeated. Therefore, the amplitude of the oscillations should be equal to the critical supersaturation for 2D nucleation and the value 36% has been estimated for it ($\sigma_c = ze\eta_c/kT$, where $\eta_c = 10$ mV is the critical overpotential) in good agreement with the prediction of the theory of layer-by-layer growth in solutions.

When the overpotential is fixed slightly above the critical, spontaneous oscillations of the current are observed (Fig. 3.68) (Bostanov *et al.*, 1981). The oscillations appear through irregular intervals of

Figure 3.68: Oscillations of the current at a constant overpotential slightly higher than the critical overpotential for 2D nucleation. The variation of the time elapsed between consecutive peaks reflects the random character of the nucleation process. (V. Bostanov, W. Obretenov, G. Staikov, D. K. Roe and E. Budewski, *J. Crystal Growth* **52**, 761 (1981). By permission of Elsevier Science Publishers B.V. and courtesy of V. Bostanov.)

time, thus reflecting the random character of the nucleation process (Toschev, Stoyanov and Milchev 1972; Toschev 1973). However, the mean value of number of oscillations, averaged over a longer period of time, remains one and the same. Ascribing the formation of a 2D nucleus to each oscillation, it becomes obvious that the mean value of the number of the oscillations per unit time gives the steady-state nucleation rate.

In another experiment, a constant overpotential lower than the critical one has been applied on the electrolytic cell. No current has been detected, except for a very low capacitive current. The cell under these conditions was cut off. Then, short potentiostatic pulses higher than the critical overpotential ($\cong$ 9–10 mV) have been superimposed on the constant overpotential and a current has been detected to flow through the cell. The latter increased with the time, displayed a maximum, and dropped again to zero. No current was detected until a new pulse was applied (Fig. 3.69) (Budewski *et al.*, 1966). The current–time curves have different shape, but the integral of the current or the amount of electricity remained constant and equal again to that required for completion of a ML. The difference of the shape of the current–time curves is easily explained by the different

Figure 3.69: Oscillations of the current obtained by the superposition of high short potentiostatic pulses over a constant overpotential lower than the critical one for 2D nucleation. The shape of the curves reflects the site on the electrode surface on which the 2D nucleus is formed (e.g., the narrow high peak in the middle is originated by a nucleus formed at nearly the center of the electrode). The areas under the curves are equal to each other and to the amount of electricity to complete one ML. (E. Budewski, V. Bostanov, T. Vitanov, Z. Stoynov, A. Kotzeva and R. Kaischew, *Electrochim. Acta* **11**, 1697 (1966). By permission of Pergamon Press Ltd. and courtesy of V. Bostanov.)

location of the nucleation event. Obviously, the potentiostatic pulse provokes the formation of a 2D nucleus which then grows to cover completely the crystal face. The current is proportional to the length of the steps surrounding the growing island and goes to zero when the latter reaches the walls of the capillary.

The experimentally observed current transients have been compared with the time variation of the edge length of a ML island calculated numerically under the assumption of a different location of the nucleation event on the crystal face. This led to the conclusion that in most cases only one 2D nucleus has been formed or, in other words, an artificial layer-by-layer growth has taken place. Then, the expression for the layer-by-layer growth rate (3.111) can be compared with the experimental observations. To this aim, the height and the duration of the nucleation pulse have been adjusted in such a way

that nucleation took place only in 50% of the pulses applied. Then, the pulse duration τ can be treated as the time necessary for the formation of one nucleus. Neglecting the nonsteady state effects, one can accept that the reciprocal of τ is just equal to the rate of 2D nucleation $J_0(2\mathrm{D})$.

In the particular case of electrolytic nucleation, the flux of atoms to the critical nucleus is given by

$$\omega^* = 4l^* \frac{i_{\mathrm{st}}}{ze} = \frac{8\varkappa a^2}{ze\eta} \frac{i_{0,\mathrm{st}}}{ze} \exp\left(\frac{(1-\alpha)ze\eta}{kT}\right),$$

where $i_{\mathrm{st}} = i_{0,\mathrm{st}} \exp[(1-\alpha)ze\eta/kT]$ is the cathodic part of the current per unit length of the step (A cm^{-1}), $i_{0,\mathrm{st}}$ is the exchange current density per unit step length ($i_s = i_{\mathrm{st}}/a$ is the current density per unit area in A cm^{-2}), and $\alpha \cong 0.5$ is the so-called charge transfer coefficient.

The factor of Zeldovich reads

$$\Gamma = \frac{(ze\eta)^{3/2}}{8\varkappa a (kT)^{1/2}}.$$

Then, for the nucleation rate of square-shaped nuclei, one obtains

$$J_0(2\mathrm{D}) = A\sqrt{\eta} \exp\left(\frac{(1-\alpha)ze\eta}{kT}\right) \exp\left(-\frac{4\varkappa^2 a^2}{kTze\eta}\right),$$

where A (cm^{-2} s^{-1} V$^{-1/2}$) is a constant given by

$$A = aN_0 \frac{i_{0,\mathrm{st}}}{ze} \left(\frac{ze}{kT}\right)^{1/2}.$$

With $N_0 = 1.2 \times 10^{15}$ cm^{-2}, $i_{0,\mathrm{st}} = 5.5 \times 10^{-6}$ A cm^{-1}, $T = 318$ K, $A = 7.1 \times 10^{21}$ cm^{-2} s^{-1}V$^{-1/2}$, and with $\eta = 0.01$ V, for the pre-exponential, one obtains $K_1 = 7.1 \times 10^{20}$ cm^{-2} s^{-1}.

Figure 3.70 shows the plot $\ln \tau$ vs $1/\eta$ (Budewski *et al.*, 1966). As seen a straight line is obtained as required from the theory. The value 1.9×10^{-13} J cm^{-1} has been found for the specific edge energy $\varkappa$ from the slope and $A = 1 \times 10^{19}$ cm^{-2} s^{-1} V$^{-1/2}$ from the cross-section of the line with the ordinate. Approximately, the same value ($\varkappa = 2 \times 10^{-13}$ J cm^{-1}) has been found for the specific edge energy in the case of nucleation on the (1 1 1) face. Using the relations

Figure 3.70: Logarithmic plots of the time of appearance of one 2D nucleus vs the reciprocal of the overpotential. The open and filled circles are from two series of measurements under slightly different conditions. The plots are, in fact, equivalent to the plots of the steady-state nucleation rate vs the reciprocal of the overpotential if one neglects the time lag for transient nucleation. The straight lines show the validity of the classical theory of nucleation. (E. Budewski, V. Bostanov, T. Vitanov, Z. Stoynov, A. Kotzeva and R. Kaischew, *Electrochim. Acta* **11**, 1697 (1966). By permission of Pergamon Press Ltd. and courtesy of V. Bostanov.)

$\sigma_{1\,0\,0} = 4\varkappa_{10}/d_{1\,0\,0}$ and $\sigma_{1\,1\,1} = 2\varkappa_{11}/d_{1\,1\,1}$ following the first neighbor model ($d_{1\,0\,0}$ and $d_{1\,1\,1}$ are the interplanar spacings of the (1 0 0) and (1 1 1) planes, respectively) for the fcc lattice (Markov and Kaischew 1976), we find $\sigma_{1\,0\,0} = 372$ erg cm^{-2} and $\sigma_{1\,1\,1} = 170$ erg cm^{-2} for the Ag/$AgNO_3$ (aq. 6N) boundary.

The rate of the step advance has been measured directly as a function of the supersaturation by using the rectangular capillary mentioned above (see Fig. 3.74) (Bostanov, Staikov and Roe 1975). Figure 3.71 shows the current–time curves which follow the application of a short potentiostatic pulse. As seen, the shape of the

Figure 3.71: The current of growth of SH steps vs time in rectangular capillary (see Fig. 3.74). The inset below each curve shows the site of the nucleation event: (a) at the very end of the capillary, (b) at approximately one third from the end of the capillary, (c) at the middle of the capillary. (V. Bostanov, G. Staikov and D. K. Roe, *J. Electrochem. Soc.* **122**, 1301 (1975). By permission of Electrochemical Society Inc. and courtesy of V. Bostanov.)

transients depends again on the location of the nucleation event. It displays a plateau with single or double height when the nucleus was formed at the very end or in the middle of the capillary, respectively. It follows first that the current is directly proportional to the total step length L. Second, a linear dependence of the plateau current on the overpotential is established as shown in Fig. 3.72 (Bostanov, Staikov and Roe 1975). Besides, the current is proportional to the

Figure 3.72: The current of growth of SH steps vs the overpotential in a rectangular capillary (see Fig. 3.74). Curves a and b are for nuclei oriented along $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,0 \rangle$ directions as shown in the inset. (V. Bostanov, G. Staikov and D. K. Roe, *J. Electrochem. Soc.* **122**, 1301 (1975). By permission of Electrochemical Society Inc. and courtesy of V. Bostanov.)

length of the advancing step. The latter depends on the orientation of the seed crystal and, in turn, of the 2D nucleus with respect to the capillary edge. Thus, in the case of the $\langle 1\,0\,0 \rangle$ direction of the step advance, the current is greater by $\sqrt{2}$ than the current which flows when the direction of the step advance is $\langle 1\,1\,0 \rangle$.

In order to shift the step with a length L by one atomic spacing, we have to add L/a atoms or zeL/a coulombs of electricity. The time elapsed will be $t = zeL/ia$, where $i(A)$ is the current of growth. Then, the rate of step advance will be $v_\infty = a/t$ or $v_\infty = i/qL$, where $q = zeN_0$ is the amount of electricity required for the completion of a ML. The current i is given by the well-known expression (the Butler–Volmer equation) in the electrochemistry

$$i = i_0 \left[\exp\left(\frac{\alpha z e \eta}{kT} \right) - \exp\left(-\frac{(1-\alpha) z e \eta}{kT} \right) \right],$$

which gives, in fact, the net flux of atoms $j_+ - j_-$ to the propagating step. At small values of the overpotential ($\eta \ll kT/ze$), the latter turns into $i = k\eta$, where $k = i_0 ze/kT$ and i_0 is the exchange current. Then, $v_\infty = k\eta/qL$, where obviously the ratio $\beta_{\rm st} = k/qL$ is just the kinetic coefficient of the step in the case of electrocrystallization. In other words,

$$v_\infty = \beta_{\rm st}\eta,$$

where

$$\beta_{\rm st} = \frac{k}{qL} = \frac{ze}{kTqL} i_0.$$

k is simply the slope of the current–overpotential curves, and from Fig. 3.72 one finds $k = 2 \times 10^{-6}$ ohm^{-1}. Bearing in mind that $q = 1.92 \times 10^{-4}$ C cm^{-2} and $L = 1 \times 10^{-2}$ cm, we find $\beta_{\rm st} = 1$ cm s^{-1} V^{-1}. Step advance rates are then of the order of 1×10^{-3} cm s^{-1}. The exchange current is equal to $i_0 = 5.5 \times 10^{-8}$ A, or $i_{0,\rm st} = 5.5 \times 10^{-8}/1 \times 10^{-2} = 5.5 \times 10^{-6}$ A cm^{-1} per unit length of the step.

One can express the kinetic coefficient in the usual form (Eq. (3.26))

$$\beta_{\rm st} = a\nu \frac{a}{\delta_0} \frac{ze}{kT} \exp\left(-\frac{\Delta U}{kT}\right),$$

and to estimate the energy barrier for crystallization. In the particular case of electrocrystallization, it includes the energy of desolvation as well as the transition of Ag^+ ions through the electric double layer.

First, one has to evaluate the roughness factor a/δ_0 through Eq. (1.75). In order to do that, one has to find the energy to break a first neighbor bond, ψ. To account for the situation in electrolytic solutions, it is better if one uses the value of the specific edge energy found from the experiment. Assuming for simplicity the existence of monoatomic kinks only, Eq. (1.80) gives

$$\varkappa = G_{\rm st} = -nkT \ln\eta - nkT \ln(1 + 2\eta) \cong \frac{\psi}{2a} - \frac{2kT}{a}\eta,$$

from where

$$\frac{\varkappa a}{kT} = \frac{\psi}{2kT} - 2\exp\left(-\frac{\psi}{2kT}\right).$$

The same result is obtained if we come out from Eq. (1.81) valid for polyatomic kinks having in mind the simplification $(1+\eta)/(1-\eta) \cong 1+2\eta$ valid for small η.

Solving numerically the above equation with $\varkappa = 1.9 \times 10^{-13}$ J cm^{-1}, $a = 2.889 \times 10^{-8}$ cm, and $T = 318$ K, we find $\psi/2kT = 1.64$ and $\delta_0 \cong 4a$ (Budewski 1983). Bearing in mind that $\beta_{\rm st} = 1$ cm s^{-1}V^{-1} for ΔU, one obtains the value 9 kcal mol^{-1} which is typical for aqueous solutions.

At this point, it is interesting to compare the possible contribution of the surface diffusion processes in the lateral spreading of the steps. Dividing the exchange current $i_{0,\rm st}$ per unit step length by the atomic spacing $a = 2.889 \times 10^{-8}$ cm, we find the value $i_{0,\rm s} = 190$ A cm^{-2} for the exchange current per unit area (Vitanov, Popov and Budevski 1974). Vitanov *et al.* (1969) (see also Vitanov, Popov and Budevski 1974) carried out impedance measurements on dislocation-free (1 0 0) Ag crystal faces at $T = 318$ K in $6N$ $AgNO_3$ and found that the exchange current density due to adsorbed atoms is $i_{0,\rm ad} = 0.06$ A cm^{-2}. Comparison with the above value $i_{0,\rm s} = 190$ A cm^{-2} shows that the surface diffusion contribution to the step advance does not exceed 0.03%. Estimations of the rate of step advance assuming surface diffusion supply of growth units show that the latter should be 60 times smaller than that found experimentally (Bostanov, Staikov and Roe 1975; Bostanov 1977; see also Budewski 1983).

The rate of step advance has been measured independently by using quite a different method. A small number of screw dislocations have been left on the crystal surface. The monoatomic steps are invisible, while growth pyramids with apparently smooth sides are observed during growth. The step spacing is a function of the overpotential applied, and increasing the latter leads to the increase of the slope of the pyramids. Assume now that we grow the crystal face at a low value of the overpotential. Comparatively flat pyramids of growth are observed. When a short overpotential pulse of higher amplitude is superimposed on the lower one, a stripe with higher slope will result. The latter is visible under the microscope. In fact, this stripe is an artificially produced kinematic wave. If now high overpotential pulses are applied regularly at equal intervals, a train

Figure 3.73: Pyramids of growth on Ag(1 1 1). The darker stripes are obtained by the periodical superposition of higher overpotential pulses and represent trains of steps with larger densities (larger slopes), or in other words, artificially produced kinematic waves. (E. Budewski, T. Vitanov and V. Bostanov, *Physica Status Solidi* **8**, 369 (1965). By permission of Akademie Verlag GmbH and courtesy of V. Bostanov.)

of kinematic waves will be formed (Fig. 3.73) (Budewski, Vitanov and Bostanov 1965). As shown in the previous section, the velocity c of the kinematic waves is equal to the rate of advance v of the elementary steps in a kinetic regime of growth (Fig. 3.62(b)). Then, measuring the velocity of the kinematic waves, we find, in fact, the rate of advance of the elementary steps. The velocity of the kinematic waves is easily estimated from the distance between the stripes and the frequency of the high overpotential pulses. The value $\beta_{\mathrm{st}} \cong 1$ cm s^{-1} V^{-1} has been found confirming once again that the electrolytic growth of silver in aqueous solutions takes place under conditions of a kinetic regime and the surface diffusion plays a negligible role (Bostanov, Russinova and Budewski 1969; see also Budewski 1983).

If higher pulses are superimposed on the overpotential of growth, a macrostep instead of an elementary step is produced. With the help of Nomarski differential contrast technique steps thicker than, say, 10–15 atomic diameters can be observed directly in the rectangular capillary mentioned above (Fig. 3.74) (Bostanov, Staikov and Roe 1975). Thus, the rate of propagation of such steps can be measured directly, and knowing the current, the thickness can be estimated. It

Figure 3.74: Micrograph of the opening of the rectangular capillary with a macrostep photographed at different times to measure its rate of advance. (V. Bostanov, G. Staikov and D. K. Roe, *J. Electrochem. Soc.* **122**, 1301 (1975). By permission of Electrochemical Society Inc. and courtesy of V. Bostanov.)

was found, quite unexpectedly, that the velocity of the macrostep, $v = 4.8$ cm s^{-1}, was the same as that of the elementary step up to thicknesses of the order of 100 Å. The slope of the macrostep has been estimated by analyzing the decay of the current–time curve when the step reached the end of the capillary (Bostanov, Staikov and Roe 1975). In a particular case, the height of a macrostep, $h = 61\,\mathring{A} \approx 30$ elementary steps, was measured. The current decreased to zero for about 40 ms. The value of $p = \tan\theta = 3.2 \times 10^{-3}$ for the slope has been found. The macrosteps can, thus, be considered as kinematic waves and, as before, their velocity should be equal to that of the elementary steps when the crystal grows in a kinetic regime.

We now have all the information we need to make predictions concerning the mechanism of growth through 2D nucleation. The lateral size of the crystal plane ($L = 2 \times 10^{-2}$ cm) becomes smaller than $(v_\infty/J_o)^{1/3}$ at $\eta \geq 7$ mV. Then layer-by-layer growth should be observed at overpotentials smaller than 7 mV. At higher overpotentials, multilayer growth should take place. Indeed, increasing the overpotential beyond 8 mV leads to current transients of the kind shown in Fig. 3.75 (Bostanov *et al.*, 1981). As shown, the curve reproduces fairly well what has been theoretically predicted by Borovinski and Tzindergosen (1968) and by Gilmer (1980).

The steady-state current density at large times is given in this case by

$$i_{\mathrm{st}} = qb(J_0 v_\infty^2)^{1/3},$$

where b is a constant of the order of unity.

Figure 3.75: The current of growth vs time at an overpotential considerably higher than the critical overpotential. Several oscillations are clearly visible. At a longer time, the current reaches a constant value which corresponds to steady-state growth. This is the first experimental recording of the oscillations of the rate of multilayer growth. (V. Bostanov, W. Obretenov, G. Staikov, D. K. Roe and E. Budewski, *J. Crystal Growth* **52**, 761 (1981). By permission of Elsevier Science Publishers B.V. and courtesy of V. Bostanov.)

The interpretation of the experimental results in coordinates $\log\{i_{\rm st}\eta^{-5/6}\exp[-(1-\alpha)ze\eta/kT]\}$ vs $1/\eta$ (see Eq. (3.115)) gives a straight line (Fig. 3.76) in good qualitative agreement with the theory (Bostanov *et al.*, 1981). From the slope and the intercept of the straight line, the values $\varkappa = 2.0 \times 10^{-13}$ J cm^{-1} and $A = 2 \times 10^{18}$ cm^{-2} s^{-1} V$^{-1/2}$ have been estimated for the specific edge energy and the pre-exponential constant, respectively, in good agreement with the results from the study of the layer-by-layer growth.

In the case when the crystal face is not defectless but contains several screw dislocations, polygonized pyramids of growth are usually visible (Fig. 3.77) (Bostanov, Russinova and Budewski 1969; see also Budewski 1983), which represent hillocks due to growth spirals. No critical supersaturation should be overcome in order for the growth to take place and the current density is a parabolic function of the overpotential (Fig. 3.78) as required by the theory of Burton, Cabrera and Frank (1951) (Bostanov, Russinova and Budewski 1969).

Figure 3.76: Plot of the logarithm of the steady-state current of growth vs the reciprocal of the overpotential according to Eq. (3.115). (V. Bostanov, W. Obreetenov, G. Staikov, D. K. Roe and E. Budewski, *J. Crystal Growth* **52**, 761 (1981). By permission of Elsevier Science Publishers B. V. and Courtesy of V. Bostanov.)

(a) (b)

Figure 3.77: Pyramids of growth around the emergency points of screw dislocations on (a) Ag(1 1 1) and (b) Ag(0 0 1). As shown the pyramids are well polygonized. (V. Bostanov, R. Russinova and E. Budewski, *Comm. Dept. Chem.* (*Bulg. Acad. Sci.*) **2**, 885 (1969). Courtesy of V. Bostanov.)

Assuming, the growth rate is given by (3.15) and the slope of the growth pyramid is given by

$$p = \frac{a}{19\rho_c},$$

one obtains for the growth rate

$$R = \frac{aq\beta_{\mathrm{st}}}{19\varkappa}\eta^2.$$

The rate of growth is given by $R = d/t$, where d is the thickness of a ML and $t = q/i$ is the time to deposit a ML. Then, the current density should be proportional to the square of the supersaturation:

$$i = \frac{aq^2\beta_{\mathrm{st}}}{19\varkappa d}\eta^2.$$

Obviously, one can calculate the value of the specific edge energy $\varkappa$ from the slope of the straight line i vs η^2 (Fig. 3.78). Bostanov, Staikov and Roe (1975) estimated the value $\varkappa = 2.4\times10^{-13}$ J cm^{-1} in good agreement with the value found from a study of 2D nucleation.

Figure 3.78: Plot of the growth current vs the square of the overpotential of a Ag(0 0 1) crystal face with screw dislocations. The straight line confirms the validity of the theory of Burton, Cabrera, and Frank (1951) for small supersaturations. (V. Bostanov, R. Russinova and E. Budewski, *Comm. Dept. Chem.* (*Bulg. Acad. Sci.*) **2**, 885 (1969). Courtesy of V. Bostanov.)

The latter shows that the expression found by Cabrera and Levine for the step spacing is valid for the case of electrolytic growth. At sufficiently high supersaturations, the step spacing should become so small that the diffusion fields around the step should overlap and the parabolic dependence of the growth rate on the supersaturation should change gradually to a linear one. It is then interesting to calculate the step spacing $\lambda = 19\varkappa a^2/ze\eta = 19\varkappa/q\eta$ at the highest overpotential used, at which a parabolic dependence is still observed. The value 793 Å is obtained at the highest overpotential $\eta = 3$ mV applied. The latter is equal to 275 interatomic spacings. Investigations (Bostanov, Staikov and Roe 1975) on the rate of advance in the rectangular capillary of macrosteps which represent, in fact, trains of monoatomic steps, have shown that the rate of advance of a such a step train is just the same as that of a monoatomic step when the overall thickness of the macrostep does not exceed 80 Å. Moreover, it has been found that the interstep spacing is 160 Å. We conclude that the parabolic law of growth should be observed approximately at least up to $\eta = 15$ mV.

Thus, all aspects of the growth of crystals, the growth through 2D nucleation, the mononuclear and polynuclear layer-by-layer growth, the polynuclear multilayer growth, the spiral growth around screw dislocations, the propagation of single monoatomic steps, and kinematic waves were studied. The only exception was understandably the normal growth of rough crystal faces. The theories of Stranski and Kaischew, Burton, Cabrera and Frank, Borovinski and Tzindergosen, Cabrera and Vermiliya, etc. were successfully verified and confirmed in a single model, the electrocrystallization of silver in aqueous solutions, under different conditions.

Chapter 4

Epitaxial Growth

4.1 Basic Concepts and Definitions

The oriented growth of one crystalline material on the single-crystal surface of a different material is called epitaxy (or "ordered on" from the Greek words $\varepsilon\pi\iota$ — on and $\tau\alpha\xi\iota\sigma$ — in order). The term has been coined by Royer (1928) more than half a century ago. A typical example of epitaxial overgrowth is shown in Fig. 4.1 in the case of deposition of copper on the (1 1 1) surface of silver (Markov, Stoycheva and Dobrev 1978). As seen the truncated triangular copper crystallites are lying with their (1 1 1) faces on the (1 1 1) Ag surface. What is not immediately evident from the micrograph is that the $\langle 1\,1\,0\rangle$ direction of the copper crystallites is parallel to the $\langle 1\,1\,0\rangle$ direction of the silver substrate. This parallelism of directions which we call *epitaxial orientation* is usually described in terms of the Miller indices of crystal planes and directions. In our particular case, it is $(1\,1\,1)\langle 1\,1\,0\rangle_{\text{Cu}} \parallel (1\,1\,1)\langle 1\,1\,0\rangle_{\text{Ag}}$ and we say that the copper deposit is in *parallel* epitaxial orientation with the silver substrate. Although the parallel epitaxial orientation is frequently observed particularly in the very important cases of deposition of semiconductor compounds one on top of the other, this is not always the case. For example, when PbS or PbTe are deposited onto the (1 0 0) surface of MgO the epitaxial orientation is $(1\,0\,0)_d\ \langle 1\,1\,0\rangle_d \parallel (1\,0\,0)_s\langle 1\,0\,0\rangle_s$. This means that the crystal planes in contact with each other are (1 0 0) for both the substrate and the deposit but the $\langle 1\,1\,0\rangle$ direction of the deposit

Figure 4.1: Electron micrograph of 3D copper crystallites electrodeposited at constant overpotential on Ag(1 1 1) surface. The crystallites are in a parallel epitaxial orientation $(1\,1\,1)\langle 1\,1\,0\rangle_{\mathrm{Cu}} \parallel (1\,1\,1)\langle 110\rangle_{\mathrm{Ag}}$ with the substrate. The Ag(1 1 1) substrate is prepared by evaporation of Ag on mica in conventional vacuum. (I. Markov, E. Stoycheva and D. Dobrev, *Commun. Dept. Chem.* [*Bulg. Acad. Sci.*] **3**, 377 (1978)).

coincides with the $\langle 1\,0\,0\rangle$ direction of the substrate (Honjo and Yagi 1969, 1980).

In general, the epitaxial orientation depends on the temperature. Massies and Linh (1982a, 1982b, 1982c) deposited Ag on the As side $(0\,0\,\bar{1})$ of GaAs and established that at temperatures lower than 200°C the Ag plane in contact with GaAs$(0\,0\,\bar{1})$ is $(1\,1\,0)$, i.e., the Ag $\langle 1\,1\,1\rangle$ direction is parallel to the direction $\langle \bar{1}\,1\,0\rangle$ of the As dangling bonds. The epitaxial orientation is $(0\,1\,1)\langle 1\,1\,1\rangle_{\mathrm{Ag}} \parallel (0\,0\,\bar{1})\langle \bar{1}\,1\,0\rangle_{\mathrm{GaAs}}$. The $(0\,1\,1)$ plane of fcc metals consists of parallel rows of atoms whose spacing is equal to the lattice parameter (4.086 Å of Ag). Along the rows, the atom spacing is equal to the first neighbor distance 2.889 Å for Ag. The lattice parameter of GaAs is $a_0 = 5.6531$ Å and the atom spacing in the $(1\,0\,0)$ plane is $a_0/\sqrt{2} = 3.9973$ Å. So across the rows, the lattice misfit is compressive and is equal to +2.22%. The lattice misfit is defined as the relative difference of the unit atom spacings, $f = (b - a)/a$, where b and a are the atom

spacings of the deposit and the substrate, respectively. Along the rows, the relative difference of the unit atom spacings is very large in absolute value -27.7% but with the opposite sign. However, it is easy to realize that four atom spacings of the silver nearly coincide with three atom spacings of the GaAs. Then, the lattice misfit can be expressed as the relative difference of the multiple atom spacings $f = (4b - 3a)/3a = -3.63\%$ (Matthews 1975b). In other words, along the rows, the silver bonds are stretched out, whereas across the rows, they are compressed. At temperatures higher than 200°C, the silver deposit is in parallel epitaxial orientation with $(0\,0\,\bar{1})$ GaAs, i.e., the epitaxial orientation is $(0\,0\,1)\langle 0\,1\,0\rangle_{\mathrm{Ag}} \parallel (0\,0\,\bar{1})\langle 0\,1\,0\rangle_{\mathrm{GaAs}}$ and the lattice misfit in both orthogonal directions is equal to -3.63%, i.e., the silver bonds are stretched out in both directions. As will be shown below, such an orientation is connected with the lower energy due to the anharmonism of the interatomic bonding.

Another interesting example of epitaxial orientation is established in the case of deposition of Cu on Ag(0 0 1) by Bruce and Jaeger (1977, 1978a, 1978b). Both bulk metals have one and the same fcc lattice, but the thin Cu films have a bcc lattice, the epitaxial orientation being $(0\,0\,1)\langle 1\,\bar{1}\,0\rangle_{\mathrm{bcc,Cu}} \parallel (0\,0\,1)\langle 0\,1\,0\rangle_{\mathrm{fcc,Ag}}$. No evidence for the existence of bcc Cu in nature has been found.

The two last examples show that the epitaxial orientation is determined by the condition of minimum of the free energy of the system. We know, however, that the bcc lattice of the copper has higher energy than the natural fcc one. It follows that the energy of the epitaxial interface between bcc Cu and fcc Ag overcompensates the energy difference between the bcc and fcc lattices of Cu. It is clear that this situation holds up to some critical thickness of the Cu film. The reason is that the energy difference between the fcc and bcc lattices of Cu increases linearly with thickness, whereas the energy of the epitaxial interface between bcc Cu and fcc Ag remains constant. As will be shown below in more detail, the same is the reason of existence of a critical thickness for pseudomorphous growth. We can conclude that the structure and hence the energy of the epitaxial interface play a significant role in determining the epitaxial orientation.

The parallelism of the contact planes is often called a *fiber* or *texture orientation*, whereas the parallelism of the crystallographic directions at the contact plane is called *azimuthal orientation.* Thus, epitaxy means a simultaneous realization of texture and azimuthal orientations (Gebhardt 1973). Very often only texture orientation takes place the deposit being azimuthally misoriented. Here, we will not discuss this case.

In general, epitaxy does not require the parallelism of low-index crystallographic directions. A nonzero angle between these directions is possible provided that it is the same for all islands (both 2D or 3D) of the deposit. This is the case, for example, with the Pb deposit on the (1 1 1)Ag surface which rotated about $+4°$ and $-4°$ from the parallel orientation around the $\langle 1\,1\,1 \rangle$ surface normal (Takayanagi 1981; Rawlings, Gibson and Dobson 1978). In such cases, which while appearing more exotic are not that rare, we have to look for a parallelism of higher index crystallographic directions. For more details the reader is referred to Stoyanov (1986).

There exist terms in the specialized literature homoepitaxy, autoepitaxy, heteroepitaxy, etc. They are used sometimes quite arbitrarily. Thus, homoepitaxy and autoepitaxy are often confused. This is the reason we will define them here more rigorously in terms of the chemical potentials of the substrate and deposit materials.

One way to understand the epitaxial growth, may be the best one, is to compare it with the crystal growth, or in other words, with the growth of a single-crystal film on the surface of the same material (Stranski 1929; Stranski and Kuleliev 1929; Stranski and Krastanov 1938). What differ the epitaxial growth from the crystal growth are the nature and strength of the chemical bonds of both substrate and deposit crystals, on the one hand, and the crystal lattices and/or the lattice parameters, on the other. In other words, both crystals differ *energetically* (*or chemically*) *and geometrically.* If both crystals do not differ simultaneously, energetically, and geometrically which means that they are identical we have the usual crystal growth. Strictly speaking, this means that the chemical potentials of the substrate μ_s and the deposit μ_d are precisely equal. Obviously, terms like autoepitaxy or homoepitaxy for the description of this case

are irrelevant. Epitaxial growth takes place only when the chemical potentials of the deposit and the substrate crystals differ.

Let us consider, for example, the case of the deposition of Si on the Si single crystal, the latter being doped with B (Sugita, Tamura and Sugawara 1969). The nature and strength of the chemical bonds in both substrate and deposit crystals are one and the same and we can neglect the effect of the dopant on the strength of the chemical bonds. However, due to the presence of the dopant in the substrate crystal, its lattice parameter is different (smaller) from that of the pure silicon and the deposit film should be compressed to match the substrate. Then, the chemical potential of the strained deposit differs from that of the large deposit crystal. The difference of the chemical potentials is just given by the strain energy per atom. Thus, we have a case in which both crystals have different chemical potentials ($\mu_s \neq \mu_d$) and the difference is due solely to the difference of the lattice parameters, the nature and the strength of the chemical bonds remaining practically the same. We will call this case *homoepitaxy.*

There are cases, such as the deposition of $In_xGa_{1-x}As$ on (1 0 0)InP with $x = 0.47$, when the lattice parameters coincide exactly and the lattice misfit is equal to zero. The difference of the chemical potentials is due in this case to the difference in strength of the chemical bonds (different bonds strength means different works of separation from half-crystal positions and different equilibrium vapor pressures). In the general case, however, the two materials differ geometrically as well. Then, the strain energy per atom due to the lattice misfit is added to the difference in bonds' strength in both materials. This case is known as *heteroepitaxy.*

Summarizing we distinguish in general two cases:

1. Homoepitaxy. When the difference of the chemical potentials of the substrate and deposit crystals is mainly due to the lattice misfit rather than to the difference in chemistry.
2. Heteroepitaxy. When the difference of the chemical potentials of the substrate and deposit crystals is due mainly to the difference in strength of the chemical bonds irrespective of the value of the lattice misfit.

When both substrate and deposit crystals do not differ in any way and their chemical potentials are exactly equal, we have a crystal growth which we have just considered in the previous chapter. Some investigators call this case *autoepitaxy*, but we will restrain ourselves of using this term. In the last decade, the term homoepitaxy has been widely used to define the usual crystal growth. This means that the crystal growth is considered as a limiting case of the epitaxial growth. This is a matter of convention and is not essential in our case. We note only that in this chapter we deal with homoepitaxy and heteroepitaxy in the sense defined above. In other words, we confine ourselves to the case in which $\mu_s \neq \mu_d$ for some reason.

Note that if $\mu_s \neq \mu_d$, the bonding in the film will differ from that in the bulk deposit crystal owing to the chemical and geometrical influence of the substrate. Then, as shown below, the above inequality leads to $\mu(n) \neq \mu_\infty$ where $\mu(n)$ and μ_∞, are the chemical potentials of the epilayer (as a function of the thickness n) and the bulk deposit crystal. It is namely this inequality which determines the occurrence of one or another mode of growth.

The influence of the bonding across the interface and the lattice misfit on the occurrence of epitaxy was noted for the first time in the famous rules of Royer (1928). On the basis of experimental observations of epitaxial growth of ionic crystals, one on top of the other, he formulated the following rules:

(i) The crystal planes in contact must have one and the same symmetry and close lattice parameters, the difference of the latter being not greater than approximately 15%. The lattice misfit should be considered in a more generalized sense — one has to compare not only the unit but also the multiple lattice parameters;
(ii) Both crystals must have one and the same nature of the chemical bonds.
(iii) When ionic crystals grow one upon the other, the alteration of ions with opposite signs across the interface should be preserved.

Although Royer mentioned the importance of the bonding in both materials, he emphasized more on the effect of the difference of the

lattice parameters. The importance of the lattice misfit was noted even earlier by Barker (1906, 1907, 1908) who concluded that the oriented growth of alkali halide crystals one upon the other was more likely to occur when their molecular volumes are approximately equal. More details concerning the early works on epitaxy the interested reader can find in the excellent historical review of Pashley (1975).

When dealing with epitaxial problems, one has to have in mind the following. The epitaxial orientation of the deposit depends on the structure of the crystal planes in contact and the nature of the bonding across the epitaxial interface. In other words, it does not depend on the process of growth. Indeed, as stated at the beginning of this chapter, the phenomenon epitaxy by definition does not refer to growth at all. On the other hand, the kinetics of growth is just the same as outlined in Chapter 3 of this book. Thus, in the case of vapor deposition, it includes the same processes of adsorption and desorption, surface diffusion of adatoms, and incorporation into kink sites. In deposition from solutions, the bulk diffusion of the growth species should be accounted for, etc. It follows that when considering epitaxy, we treat the problems of the equilibrium structure of the epitaxial interface, which is intimately connected with the epitaxial orientation, separately from the problems of the growth kinetics of the epitaxial films and the problems connected with it.

Since the time Royer (1928) formulated his rules, the epitaxial growth of thin films has been developed to the basis for the fabrication of numerous modern devices. Thus, microelectronic devices are fabricated by the epitaxial deposition of materials varying from such "simple" ones as elementary semiconductors (Si, Ge) to binary compounds (GaAs, CdTe), and even to ternary and quaternary alloys such as $In_xGa_{1-x}As$ and $In_xGa_{1-x}As_yP_{1-y}$. Bubble memory devices are prepared by the epitaxial deposition of ferromagnetic garnets such as $Y_xGd_{3-x}Ga_yFe_{5-y}O_{12}$ on the surface of nonmagnetic garnets, e.g., $Gd_3Ga_5O_{12}$, in high temperature solutions. Varying the values of x and y, one can change smoothly the crystallographic parameters (e.g., the lattice parameter) and the physical properties (e.g., the width of the forbidden energy gap in semiconductors).

Research in epitaxial growth is unseparable from the surface analytical methods that are employed and the development of the corresponding tools. At about the same time as vacuum techniques were developed, the electron diffraction methods, RHEED and LEED (i.e., "Reflection High Energy Electron Diffraction" and "Low Energy Electron Diffraction") arose from the work of Thomson and Reid (1927) and Davisson and Germer (1927). In addition, X-ray diffraction (XRD), X-ray topography (XRT), replica electron microscopy (REM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Auger electron spectroscopy (AES), and so on, allowed quite an accurate characterization of the epitaxial films. REM and SEM investigations give information concerning the surface morphology of the growing deposit. TEM micrographs of cross-sections of the substrate–deposit system reveal the structure of the epitaxial interface (Gowers 1987). The *in situ* measurement of the variation of the RHEED intensity of the specular beam as a function of time gives the possibility the growth and to determine the thickness of the growth front, the concentration of the dopant, etc. (Neave *et al.*, 1983, Neave, Joice and Dobson 1984; Sakamoto *et al.*, 1987). In particular, the combination of LEED and AES has made it possible to obtain information on the initial stages of the epitaxial deposition. AES allows very small fractions of a monolayer (ML) of the deposited material to be detected on the substrate surface. It is, in addition, a powerful analytical method for detecting any impurities on the surface of the substrate prior to deposition. On the other hand, LEED gives a very accurate picture of the geometric disposition of the substrate atoms and of the adsorbed atoms of the deposit as well. Combining further AES and LEED with other methods like work function measurements, thermal desorption spectroscopy (TDS), the mechanism of growth of epitaxial films can be followed from the very beginning (fraction of a ML) to the formation of a continuous film (Bauer *et al.*, 1974, 1977). A new powerful method, the scanning tunneling microscopy (STM), has been recently invented, which allows the surface of the growing deposit to be visualized to the resolution of single atoms (Binnig *et al.*, 1982a, 1982b; Binnig and Rohrer 1983). The structure of the growing

surface, monoatomic steps, 2D islands and their edges can, thus, be observed and analyzed (Hamers, Tromp and Demuth 1986; Swartzentruber *et al.*, 1990; Frenken, Hoogeman and Kuipers 1996/1997).

A great variety of methods for the epitaxial deposition of different materials have been invented so far. Chemical vapor deposition (CVD), liquid phase epitaxy (LPE), atomic layer epitaxy (ALE), molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), and such combinations as low pressure metal organic chemical vapor deposition (LP-MOCVD), and metal organic molecular beam epitaxy (MOMBE), are among the most widely used at present (Farrow *et al.*, 1987). That is why the list of the epitaxial systems studied up to 1975 contains approximately 6000 entries (Grünbaum 1975). Review papers and monographs (Pashley 1956, 1965, 1970; Kern, LeLay and Metois 1979; Honjo and Yagi 1980; Vook 1982; van der Merwe 1979; Markov and Stoyanov 1987; Matthews 1975; Brune 1998; Zinke-Allmang 1999; Voigtländer 2001), etc., and whole volumes of journals such as *Surface Science* and the *Journal of Crystal Growth* are devoted to different aspects of epitaxial growth and the characterization of epitaxial films.

4.2 Structure and Energy of Epitaxial Interfaces

4.2.1 *Boundary region*

The interface represents the region between two bulk phases. The surface of a crystal in contact with its vapor or melt is considered also as an interface. The epitaxial interface is the boundary between two single crystals — the overgrowth crystal and the substrate crystal, the former being in epitaxial orientation with the latter.

In principle, the boundary between two single crystals which are characterized by their bulk properties can have the different structure depending on the nature of the chemical bonds, the crystal lattices and lattice parameters, the chemical properties of both materials, etc. Mayer (1971) classified the boundaries in five groups:

(i) Layers of ordered adatoms or adions. For example, the layer between the bulk K deposit and W(1 0 0) substrate consists of

one ML of negatively charged W ions, one ML of positively charged K ions and two MLs of K dipoles (Mayer 1971).

(ii) Layers in which the difference between the lattice parameters is accommodated by periodic strains due to misfit dislocations (Fig. 4.5(d)). The latter were predicted theoretically by Frank and van der Merwe (1949) and found experimentally in a multitude of systems (Matthews 1961, 1963).

(iii) Pseudomorphic layers in which the deposit is homogeneously strained to fit exactly the periodicity of the substrate (Fig. 4.5(c)). Such layers have been detected in many epitaxial systems, e.g., Ni on Cu(1 1 1) (Gradmann 1964, 1966), Ge on GaAs(1 0 0) (Matthews and Crawford 1970), etc. (for a review see Pashley 1970; Matthews 1975). The concept of pseudomorphism (or forced isomorphism) was introduced by Finch and Quarrell (1933, 1934) to explain the experimental observations of epitaxial growth of ZnO on Zn. Frank and van der Merwe (1949) found theoretically that a critical misfit exists under which the overgrowth should be pseudomorphous with the substrate. Beyond this misfit, the interface should be resolved in a sequence of misfit dislocations. The value 14% was estimated for the critical misfit, in tempting agreement with the experimental finding of Royer (1928).

(iv) Layers due to interdiffusion or consisting of alloys, solid solutions, metastable phases, etc. Thus, an intermetallic compound Au_2Pb is formed upon the deposition of Pb on Au(100) (Green, Prigge and Bauer 1978).

(v) Layers consisting of chemical compounds between the substrate and deposit crystals. A typical example is the formation of $NiSi_2$ on Si(1 1 1) (Jentzsch, Froitzheime and Theile 1989). Stoichiometric metal silicides are, in fact, often observed in the deposition of metals on Si(1 1 1) and Si(0 0 1) (for a review see Chen and Tu 1991).

The considerations in this chapter will be confined to the accommodation of the lattice misfit by homogeneous strain (HS) (pseudomorphism) or by periodic strain (misfit dislocations), all

other phenomena like interdiffusion, alloying, or chemical reactions between both partners being ruled out. We then consider the epitaxial interface as a geometric plane dividing two crystals which, in general, differ energetically and geometrically. We assume further that the structure of the interface is such that it minimizes the energy of the system.

4.2.2 *Models of epitaxial interfaces*

Various models have been invented for the theoretical description of the equilibrium (minimum energy) structure of the epitaxial interfaces.

The *coincidence lattice model* developed by Bollmann (1967, 1972) considers the two lattices of the substrate and deposit crystals as rigid. The interatomic forces are assumed to have spherical symmetry and the model is valid for materials with metallic or van der Waals bonds. Two lattice points, one from each crystal, are brought into coincidence and the density of lattice points which are in perfect or near coincidence serves as a measure of registry of the two lattices (Fig. 4.2). The azimuthal orientation with a maximum coincident points is considered as the minimum energy (the ground state) orientation.

The *ball-and-wire model* (Hornstra 1958) was developed initially to describe the dislocations in diamond. It assumes anisotropic chemical bonds such as the directional covalent bonds and is applicable to semiconductor materials. Holt (1966) extended it further to describe the structure of the semiconductor heterojunctions and found that dangling (unsaturated) bonds should exist at the interface originating from the material with lesser lattice parameter (Fig. 4.3). Depending on the surface polarity of the adjacent crystal planes, the dangling bonds can act as acceptors or donors (Holt 1966). Oldham and Milnes (1964) showed that the dangling bonds are expected to constitute deep energy levels in the forbidden energy gap and, thus, to play a role of recombination centers. When the density of the dangling bonds is too high, they can create a conducting band in the forbidden energy gap and alter significantly the properties of the heterojunction (Holt 1966; Sharma and Purohit 1974).

Figure 4.2: Illustration of the coincidence lattice model of epitaxial interfaces. The atoms of the two planes in contact are denoted by the open and filled circles.

Figure 4.3: Illustration of the ball-and-wire model of epitaxial interfaces between two crystals with the diamond lattice. The misfit dislocations represent unsaturated dangling bonds spaced at an average distance p (after Holt 1966).

In the *variational approach* developed by Fletcher (1964, 1967), Adamson (Fletcher and Adamson 1966), and Lodge (Fletcher and Lodge 1975), the positions of the atoms of the adjacent crystal planes have been varied to find the minimum of the energy. A pairwise interatomic potential has been used for this purpose. The calculations were carried out in the reciprocal space. It has been found

that the energy has a minimum value when as many as possible lattice points of either side of the interface coincide as in the coincidence lattice model. If elastic displacements of the atoms are allowed (restricted for simplicity to the crystal planes in contact with each other), the resulting structure of the interface is very much alike the one in the misfit dislocation model developed by Frank and van der Merwe (1949).

The *Volterra dislocation model* was developed on the base of the dislocation theory of low-angle grain boundaries (Brooks 1952; Matthews 1975). The concept of edge-type dislocations for the accommodation of the lattice misfit was introduced explicitly in the model, both substrate and deposit crystals having been considered as elastic continua. The most general definition of edge dislocations given by Volterra (1907) in the beginning of the century (see also Hirth and Lothe (1968)) has been used. The energy of the interface is represented as a sum of the energy of the dislocations and the energy of the residual homogenous strain (HS). Minimization of the energy with respect to the HS allows the calculation of the equilibrium strain and the critical thickness for pseudomorphous growth. The advantage of the model is its mathematical simplicity. An arbitrariness in the choice of the quantities determining the energy of the cores of the dislocations is, however, a shortcoming of the model. More details will be given below.

The *misfit dislocation model* of Frank–van der Merwe (1949a, 1949b) (for a review see van der Merwe (1974)) deals with a linear chain of atoms connected with elastic springs subject to an external periodic potential exerted by a rigid substrate (Fig. 4.4). The misfit dislocations appear naturally as a result of the mathematical analysis of the model.

In the present chapter, the dislocation models of Frank and van der Merwe (1949) and van der Merwe (1950) will be described in more detail as they are the most well known and most exploited. Besides, the Volterra approach of Matthews will also be described in more detail. The reader interested in the other models mentioned above is referred to the original papers and the review papers of van der Merwe (1974) and Woltersdorf (1981).

Figure 4.4: Illustration of the one-dimensional misfit dislocations model of Frank and van der Merwe (1949a). The deposit is simulated by a chain of atoms connected by elastic springs of length b and force constant γ. The rigid substrate exerts a periodic potential with period a and amplitude W. The figure shows the atomic chain before and after being put in contact with the substrate. In the latter case, 11 atoms of the chain are distributed over 12 potential troughs of the substrate, thus forming a misfit dislocations.

4.2.3 *Misfit dislocations*

We will confine our considerations in this chapter only to the case when the deposit crystal possesses a crystal face with the same symmetry as that of the substrate surface.

In general, when two geometrically dissimilar crystals (A and B) join each other in such a way that two particular crystal planes come into contact at the interface, the only physical reality is that the atoms in the adjoining crystal halves in the near vicinity of the boundary between them are displaced from their ideal positions, which they should occupy, if the foreign crystal was replaced by the same crystal. Two lateral forces act on each atom. The first is the force exerted by the neighboring atoms of the same crystal which tends to preserve its natural crystal lattice and to keep the interatomic distances equal to their natural bond lengths. The second is the force exerted by the atoms of the adjoining crystal which tends to force the atoms to occupy the lattice sites of the foreign crystal. One can distinguish several limiting cases. First, when the interfacial bonding ψ_{AB} is very weak compared with the bonds strengths, ψ_{AA} and ψ_{BB}, both crystals tend to preserve their natural lattices. In such a case, the difference of the periodicities of the two adjoining crystal

Figure 4.5: Four possible modes of misfit accommodation: (a) vernier of misfit, (b) coincidence lattices, (c) HS, (d) misfit dislocations (MDs) (after van der Merwe, Woltersdorf and Jesser 1986).

lattices degenerates into a vernier of misfit (Fig. 4.5(a)). A special case is when the lattice parameters a and b are multiples of each other, i.e., $ma = nb$, where m and n are small integers such that $m = n + 1$ (Fig. 4.5(b)). Then, every mth atom of A coincides with every nth atom of B, and we arrive at the coincidence lattice model outlined above. In the other limiting case in which ($\psi_{\mathrm{AB}} \gg \psi_{\mathrm{BB}}$ and $\psi_{\mathrm{AB}} \cong \psi_{\mathrm{AA}}$), the crystal B is forced to adopt the lattice of A, or in other words, the crystal B is homogeneously strained to fit the crystal A. We say then that B is pseudomorphous with A (Fig. 4.5(c)). However, the elastic strains and, in turn, the energy of B increase linearly with the thickness. That is why beyond some critical thickness, the pseudomorphous growth becomes energetically unfavored and the homogenous stain (HS) should be replaced by a periodical strain which can attenuate with increasing film thickness. Thus, misfit dislocations (MDs) with a lower energy are introduced at the

interface to accommodate the lattice misfit. Obviously, the smaller the natural misfit, the greater will be the critical thickness for pseudomorphous growth. In the intermediate case ($\psi_{AB} \cong \psi_{AA} \cong \psi_{BB}$), the interfacial forces are not strong enough to produce a pseudomorphous layer with considerable thickness and the lattice misfit will be accommodated by MDs, or in other words, by periodical strain (Fig. 4.5(d)), from the beginning of the growth process.

Misfit dislocations are a convenient concept for the description of the lattice distortions in the vicinity of the epitaxial interface. They represent atomic planes in excess in the material with the smaller atomic spacing (Fig. 4.5(d)). Their fundamental feature is the local strain with the opposite sign in the cores of the dislocations. If the atomic spacing of the overgrowth is smaller than that of the substrate, the chemical bonds in-between the MDs will be stretched out but the bonds in the cores of the dislocations will be compressed, and vice versa. Thus, an interface resolved in a sequence of MDs is characterized by a periodical elastic strain with a period equal to the dislocation spacing. That is why the concept of the MDs is applicable only when the bonding across the interface is strong enough to ensure the appearance of local strains. It follows that the periodic distortions of both lattices (substrate and deposit) lead to an almost perfect match of the crystal planes in contact in some areas of the epitaxial interface. These areas are separated by stripes in which the two lattices are out of registry. Figure 4.6 is an illustration of an epitaxial interface between PbS and PbSe resolved in a sequence of MDs (Böttner, Schießl and Tacke 1990). The situation is similar, in a topological sense, to that existing in a single-crystal containing edge dislocations, from where the term "dislocation" was borrowed. Unlike edge dislocations, however, the MDs are not linear defects of the crystal lattices themselves and their equilibrium density does not tend to zero with decreasing temperature.

There are two separate, though similar, MD models which are solved exactly: the model of overgrowth with ML thickness, which is, in fact, the famous one-dimensional model of Frank and van der Merwe (1949) and the model of fairly thick deposit developed later by van der Merwe (1950, 1963a, 1963b). We consider first the ML

Figure 4.6: High-resolution TEM micrograph of a PbS/PbSe interface. The MDs are shown by arrows (H. Böttner, U. Schießl and M. Tacke, *Superlattices and Microstructures* **7**, 97 (1990). By permission of Academic Press Ltd. and courtesy of H. Böttner.)

model in more detail, although it can be taken only as a first approximation to a growing epitaxial film. However, it is very illustrative and helpful for a deeper understanding of the more realistic models of the epitaxial interfaces. Then, the model of thick overgrowth will be briefly outlined. The MD models have been comprehensively reviewed in a series of papers by van der Merwe (1973, 1975, 1979) and others (Matthews 1975b).

4.2.4 *Frank–van der Merwe model of thin overlayer*

The Frank and van der Merwe model (1949) recently gained prominence not only in the field of epitaxy but also in various fields, a common feature of which is the competing periodicities. Thus, it provided the grounds of the theory of commensurate–incommensurate phase transitions in physisorbed layers (Villain 1980) and in layer compounds (McMillan 1976), the alignments of cholesteric liquid crystals in a magnetic field (de Gennes 1968), etc. (for a review, see Bak 1982). The treatment is based on an earlier model of Frenkel and Kontorova (1939) who considered the "worm-like motion" of edge dislocations

in crystals to explain the plastic flow of the latter. That is why the 1D model is also known as a model of Frenkel and Kontorova.

In this chapter, the original 1D model of Frank and van der Merwe (1949) will be considered first. Then, it will be generalized for a 2D ML overgrowth, and after that, it will be applied to the case of thickening overgrowth, although it is inadequate for quantitatively describing this situation (van der Merwe, Woltersdorf and Jesser 1986). The influence of the anharmonicity of the more realistic interatomic potentials will be discussed at the end of the chapter.

4.2.4.1 *Interatomic potentials*

Pairwise interatomic potentials with a simple analytical form are often used in direct lattice calculations in solid state physics. The potentials of Morse and Lennard-Jones (the 6–12 Mie potential) are the common choices (Kaplan 1986).

The potential of Morse (1929)

$$V(r) = V_0 \left\{ \left[1 - \exp\left(-\omega \frac{r - r_0}{r_0} \right) \right]^2 - 1 \right\}, \tag{4.1}$$

where V_0 is the energy of dissociation, r_0 is the equilibrium atom spacing, and ω is a constant which governs the range of action of the interatomic forces, was originally suggested for the evaluation of the vibrational energy levels in diatomic molecules. By varying ω, we shift both the repulsive and the attractive branches of the potential in opposite directions so that the degree of anharmonicity remains practically the same. Girifalco and Weiser (1959) adjusted the constants of the Morse potential to fit the lattice parameters, the cohesive energies, and the elastic properties of a series of metals and found a value for ω varying around 4.

The potential of Morse does not behave well at small and large atom spacings. At $r = 0$, the potential does not go to infinity but has a finite value. The exponential dependence is not believed to describe well the atom attraction at $r > r_0$. In this respect, the inverse power

Mie potential

$$V(r) = V_0 \left[\frac{n}{m-n} \left(\frac{r_0}{r} \right)^m - \frac{m}{m-n} \left(\frac{r_0}{r} \right)^n \right] \tag{4.2}$$

is much more flexible than the Morse potential. The repulsive and the attractive branches are governed by two independent parameters, m and n ($m > n$). The Mie potential with $m = 12$ and $n = 6$ which is known as the Lennard-Jones potential (Lennard-Jones 1924) describes satisfactorily the properties of the noble gases.

A generalized Morse potential

$$V(r) = V_0 \Big(\frac{\nu}{\mu - \nu} e^{-\mu(r-r_0)} - \frac{\mu}{\mu - \nu} e^{-\nu(r-r_0)} \Big) \tag{4.3}$$

has been recently suggested (Markov and Trayanov 1988; Markov 1993). It has all the shortcomings of the Morse potential except that the repulsive and the attractive branches are governed by two independent parameters μ and ν ($\mu > \nu$). An advantage of both Morse potentials particularly for solving interface problems is that they are expressed in terms of strains $r - r_0$ which makes the mathematical formulation of the problems and the calculation of the strains, stresses, and strain energy easier. If we put $\mu = 2\omega/r_0$ and $\nu = \omega/r_0$ into (4.3), it turns into the Morse potential. It is worth noting that the 6–12 Lennard-Jones potential is practically undistinguishable from the one expressed by (4.3) with $\mu = 18$ and $\nu = 4$. The generalized Morse potential with $\mu = 4$ and $\nu = 3$ is plotted in Fig. 4.7.

The pairwise potentials counted above have two fundamental properties. First they are anharmonic in the sense that the repulsive branch is steeper than the attractive one, and second, they have an inflection point r_i beyond which they become nonconvex. In order to distinguish the influence of the anharmonicity from that of the nonconvex character, one can use the well-known potential of Toda (Toda 1967)

$$V(r) = V_0 \Big(\frac{\alpha}{\beta} e^{-\beta(r-r_0)} + \alpha(r - r_0) - \frac{\alpha}{\beta} - 1 \Big) \tag{4.4}$$

which is shown in Fig. 4.7 with $\alpha = 2$ and $\beta = 6$. By varying α and β but keeping their product constant, we can go smoothly from the

Figure 4.7: The generalized Morse potential (Eq. (4.3)) (shown as real) with $\mu = 4$ and $\nu = 3$ and the Toda potential (Eq. (4.4)) with $\alpha = 2$ and $\beta = 6$. The parameters α, β, μ, and ν are chosen in such a way that the repulsive branches of both potentials coincide up to the third digit and have one and the same harmonic approximation given by the dashed line. For misfits smaller than $f_i = (r_0 - r_i)/a$, where r_i denotes the inflection point of the real potential, the atoms of the chain are equidistant as shown below to the left. For misfits larger than f_i, the distorted state shown below to the right is the ground state. The latter consists of alternating short, strong and long, weak bonds. (I. Markov and A. Trayanov, *J. Phys.: Condens. Matter* **2**, 6965 (1990). By permission of IOP Publishing Ltd.)

harmonic approximation ($\alpha \to \infty$, $\beta \to 0$, $\alpha\beta = \text{const}$) to the hard sphere limit ($\alpha \to 0$, $\beta \to \infty$, $\alpha\beta = \text{const}$). It has no inflection point (or has an inflection point at infinity) and can be used to study the effect of anharmonicity in its pure form on the equilibrium structure of the epitaxial interfaces (Milchev and Markov 1984; Markov and Milchev 1984a, 1984b, 1985). It is immediately seen that expanding the second exponential term of the generalized Morse potential (4.3) in Taylor series to the linear term results in the Toda potential with $\alpha = \mu\nu/(\mu - \nu)$ and $\beta = \mu$.

Expanding any of the above potentials in Taylor series to the parabolic term gives the harmonic approximation (the dashed line in

Fig. 4.7), which for the generalized Morse potential (4.3) reads

$$V(r) = \frac{1}{2}\mu\nu V_0 (r - r_0)^2 - V_0, \tag{4.5}$$

where the product $\gamma = \mu\nu V_0$ gives the elastic modulus. The force between the neighboring atoms $F(r) = \gamma(r - r_0)$ satisfies Hooke's law exactly. Obviously, the harmonic approximation can be used for small deviations from the equilibrium atom separation, i.e., for small strains $r - r_0$. This is equivalent to small misfits in interface problems. The force constant γ is a measure of the bonding between the overgrowth atoms.

Let us analyze more closely the above pairwise potentials. Figure 4.8(a) demonstrates the variation with the atom spacing of the first derivative, or the force exerted on one atom by its neighbor. As seen, the force goes linearly to infinity in the harmonic case. This means

Figure 4.8: (a) First and (b) second derivatives of the harmonic, Toda, and real potentials. The force acting between the atoms (the first derivative) goes to infinity for the harmonic potential but is finite for the other potentials. The maximal force is, in fact, the theoretical tensile strength of the material. The second derivative which determines the sign of the curvature is positive for both the harmonic and Toda potentials but becomes negative beyond the inflection point in the case of the real pairwise potentials.

that increasing the atom spacing leads to an increase of the force which tends to keep the atoms together. The Toda force, however, goes to a constant value at large atom separations. This means that applying a force greater than the maximum one, the corresponding bond can break up and both atoms can be separated from each other. The same is valid for the potentials (4.1)–(4.3) (henceforth to be referred to as real potentials). The force displays a maximum — the theoretical tensile strength of the material.

Figure 4.8(b) demonstrates the variation of the second derivative of the pairwise potentials which, in fact, determines the sign of the curvature. In the harmonic case, the second derivative is constant and positive. In the Toda case, it is a decreasing function of the atom separation and goes asymptotically to zero but remains always positive. Only in the case of the real potentials, the curvature changes its sign from positive to negative at the inflection point $r = r_{\mathrm{i}}$. In other words, the real potentials become nonconvex at $r > r_{\mathrm{i}}$. As shown by Haas (1978, 1979), the nonconvex character of the real potential results in distortion (or polymerization) of the chemical bonds in expanded chain (or epilayers). The latter means that long, weak and short, strong bonds alternate (Fig. 4.7). The driving force of such a distortion is the energy difference between the distorted and undistorted structures. It is easy to show that the mean energy of the distorted (dimerized) structure $[V(r+u)+V(r-u)]/2 < V(r)$ for a curve with a negative curvature, $[V(r+u)+V(r-u)]/2 = V(r)$ for a straight line (zero curvature), and $[V(r+u)+V(r-u)]/2 > V(r)$ for a curve with a positive curvature. It follows that when applying the harmonic potential or the real potential at misfits smaller than that corresponding to the inflection point, the ground state will be the undistorted structure. The distorted structure will be the ground state in epilayers expanded beyond the inflection misfit when a real potential is adopted.

A 2D distortion of the chemical bonds (clustering of four and eight atoms) has been theoretically predicted with the help of the embedded atom method in a Ni ML grown on Ag(0 0 1) by Bolding and Carter (1992). The absolute value of the negative misfit is very large $f = -13.9\%$. The growth of the second ML causes a relaxation

of the distortion of the first ML bonds, i.e., the atoms of the first ML tend to occupy the bottoms of the potential troughs of the silver substrate. The bonds in the second ML become distorted, but their distortion is weaker. After deposition of four MLs, the distortion of the bonds between the atoms of the first ML practically vanishes. Thus, the Ni atoms closest to the substrate are under the largest uniform expansive strain and the strain diminishes away from the contact plane.

4.2.4.2 *Interfacial interactions*

A single atom moving on a single-crystal surface should feel a 2D periodic potential relief. It is convenient to represent it in the form (Frank and van der Merwe 1949b)

$$V(x,y) = \frac{1}{2}W_x\left(1 - \cos 2\pi\frac{x}{a_x}\right) + \frac{1}{2}W_y\left(1 - \cos 2\pi\frac{y}{a_y}\right), \quad (4.6)$$

where a_x and a_y are the atom spacings (or more correctly the spacings between the neighboring potential troughs) and W_x and W_y are the overall amplitudes (the depths of the potential troughs) in both directions x and y. A potential relief of this kind should be exerted, for example, by the (1 1 0) face of an fcc crystal.

In the case of a face with quadratic symmetry $a_x = a_y = a$ and $W_x = W_y = W$, the relief (4.6) simplifies to

$$V = \frac{1}{2}W\left(1 - \cos 2\pi\frac{x}{a}\right) + \frac{1}{2}W\left(1 - \cos 2\pi\frac{y}{a}\right). \quad (4.7)$$

If one assumes a corrugation in one direction only, (4.6) simplifies further to the potential field (Fig. 4.4)

$$V(x) = \frac{1}{2}W\left(1 - \cos 2\pi\frac{x}{a}\right) \quad (4.8)$$

introduced initially by Frenkel and Kontorova (1939).

It is generally believed that the interfacial potential has a flatter crest than is represented by a single sinusoide. That is why Frank

and van der Merwe (1949c) suggested a refined potential of the form

$$V = \frac{1}{2}W\Big(1 - \cos 2\pi\frac{x}{a}\Big) + \frac{1}{2}\omega\Big(1 - \cos 4\pi\frac{x}{a}\Big),$$

where the maximum flattening is achieved when $\omega/W = 1/4$.

The amplitude W is related to the substrate–deposit bond strength by

$$W = g\varphi_d, \tag{4.9}$$

where φ_d is the desorption energy of an overlayer atom from the substrate surface and g is a constant of proportionality varying from 1/30 for long-range van der Waals forces to approximately 1/3 for short-range covalent bonds (van der Merwe 1979). In fact, W is the activation energy for surface diffusion and g gives the relation between the activation energies for surface diffusion and desorption.

In some cases, the rather unrealistic parabolic model has been employed which replaces the smooth sinusoide (4.8) by a sequence of parabolic arcs

$$V(x) = \text{const } x^2 \qquad (\mid x \mid \leq a/2)$$

with sharp crests between them (van der Merwe 1963a; Stoop and van der Merwe 1973). The parabolic model permits the linearization of the mathematical problem and gives the possibility to obtain exact analytical solutions (Markov and Karaivanov 1979) in order to illustrate some properties of the system.

A smooth potential known as the biparabolic potential consists of parabolic segments

$$V(x) = \frac{1}{2}\lambda x^2, \qquad |x| \leq \frac{1}{4}a,$$

$$V(x) = -\frac{1}{2}\lambda\Big(x - \frac{1}{2}a\Big)^2 + \frac{1}{16}\lambda a^2, \qquad \frac{1}{4}a \leq x \leq \frac{1}{2}a,$$

$$V(x) = -\frac{1}{2}\lambda\Big(x + \frac{1}{2}a\Big)^2 + \frac{1}{16}\lambda a^2, \qquad -\frac{1}{2}a \leq x \leq -\frac{1}{4}a,$$

was constructed by Stoop and van der Merwe (1973) and in a more general form by Kratochvil and Indenbom (1963). The different interfacial potentials are shown in Fig. 4.9.

Figure 4.9: Comparison of several interfacial potentials: curve 1 — the sinusoidal potential (Eq. (4.8)), curve 2 — the refined sinusoidal potential, curve 3 — the parabolic potential.

4.2.4.3 *1D model of epitaxial interface*

Description of the Model: The overgrowth is simulated by a chain of atoms connected by purely elastic (Hookean) springs (Eq. (4.5)) as a substitute of the real interatomic forces (Fig. 4.4). The springs are characterized by their natural length b ($\equiv r_0$) and force constant γ. The chain is subject to an external periodic potential field (4.8) exerted by a rigid substrate. The assumption of the substrate rigidity could be considered to reflect the real situation in the case of sufficiently thin overgrowth (not more than a few MLs). In the case of thick deposit, this assumption is not valid anymore and elastic strains in both substrate and deposit should be allowed (van der Merwe 1950).

As b is not equal to a, the atoms will not sit at the bottoms of the potential troughs but will be displaced. In fact, our task is to find the atom displacements. Then, the energy can be calculated and, in turn, the ground state of the system can be easily found. To do this, we have to analyze the forces acting upon every atom. As mentioned above, two forces act on each atom: first, a force exerted by the neighboring atoms, and second, a force exerted by the substrate. The first force tends to preserve the natural atom spacing b between the atoms, whereas the second one tends to place all the atoms at the bottoms of the corresponding potential troughs of the substrate, i.e., to place the atoms at distance a. As a result of the competition between the two forces, the atoms will be spaced in general at some compromise distance $\bar{b}$ in between b and a. In the case $\bar{b} = a$, the natural misfit will be accommodated by HS and the overgrowth will be pseudomorphous with the substrate. At the other extreme, $\bar{b} = b$, the deposit preserves on average its own atom spacing and the natural misfit is accommodated entirely by MDs. It follows that in the intermediate case, $a < \bar{b} < b$, part of the natural misfit defined as

$$f = \frac{b - a}{a} \tag{4.10}$$

will be accommodated by MDs

$$f_d = \frac{\bar{b} - a}{a} \tag{4.11}$$

and the remaining part

$$f_e = \frac{\bar{b} - b}{b} = \frac{a}{b}(f_d - f) \tag{4.12}$$

by HS. In other words, the natural misfit appears in the general case as a sum of the HS and the periodical strain due to the MDs, i.e.,

$$f \cong f_d + |f_e|. \tag{4.13}$$

In order to find the forces acting on the atoms and, in turn, the atom displacements, we have to write an expression for the potential energy of the system. The force exerted by the neighboring atoms

Figure 4.10: For the determination of the atom displacements X_n and x_n and the atomic spacing $\Delta X_n = X_{n+1} - X_n$ in the 1D model of Frank and van der Merwe (1949a).

depends on the distance between them. To find it, we choose the origin of the coordinate system at an arbitrary point to the left of the atoms under consideration (Fig. 4.10). Without a loss of generality, we can place the origin at the bottom of an arbitrary potential trough. Then, the distances from the origin to the $(n+1)$st and nth atoms will be $X_{n+1} = (n+1)a + x_{n+1}$ and $X_n = na + x_n$, respectively, where x_n and x_{n+1} are the displacements of the atoms from the bottoms of the potential troughs with the same numbers. Then, the distance $\Delta X_n = X_{n+1} - X_n$ between the $(n+1)$st and the nth atoms is

$$\Delta X_n = x_{n+1} - x_n + a = a(\xi_{n+1} - \xi_n + 1),$$

where $\xi_n = x_n/a$ is the relative displacement of the nth atom from the bottom of the nth potential trough. The strain of the bond between the atoms will be

$$\varepsilon(n) = \Delta X_n - b = a(\xi_{n+1} - \xi_n - f). \tag{4.14}$$

Bearing in mind (4.8) the potential energy of a chain consisting of N atoms reads

$$E = \frac{1}{2}\gamma a^2 \sum_{n=0}^{N-2} (\xi_{n+1} - \xi_n - f)^2 + \frac{1}{2} W \sum_{n=0}^{N-1} (1 - \cos 2\pi\xi_n), \tag{4.15}$$

where the first sum gives the strain energy of the system, while the second sum accounts for the interaction across the interface.

We assume for definiteness that $b > a$ and $f > 0$ (compression of the chain). The analysis is valid for the opposite case $b < a$ and $f < 0$ (expansion of the chain), which follows from the symmetric (Hookean) shape of the interatomic potential. The only difference consists in the fact that at positive misfits the atom (corresponding to atomic plane in the 3D case) in excess is in the substrate. In the 1D case, this is equivalent to an empty potential trough as shown in Fig. 4.11(a). At negative misfits, the atom (plane) in excess is in the overgrowth which is equivalent to a pair of atoms in one trough (Fig. 4.11(b)). In the harmonic approximation adopted, both configurations are symmetric and have one and the same energy. As shown below, this is not the case when a more realistic interatomic potential is adopted.

The derivative of the potential energy E with respect to the displacement ξ_n gives the overall force acting on the nth atom. At equilibrium, this force is equal to zero and $dE/d\xi_n = 0$ appears as the condition for equilibrium. Minimizing (4.15) with respect to ξ_n leads to the following of set of recurrent equations:

$$\begin{aligned} \xi_1 - \xi_0 - f &= \frac{\pi}{2l_0^2} \sin 2\pi\xi_0, \\ \xi_{n+1} - 2\xi_n + \xi_{n-1} &= \frac{\pi}{2l_0^2} \sin 2\pi\xi_n \\ \xi_{N-1} - \xi_{N-2} - f &= -\frac{\pi}{2l_0^2} \sin 2\pi\xi_{N-1}, \end{aligned} \tag{4.16}$$

where

$$l_0 = \left(\frac{\gamma a^2}{2W}\right)^{1/2} \tag{4.17}$$

is a parameter which accounts for the ratio of the forces between the overgrowth atoms and across the interface. Equation (4.16) can be solved numerically and the atom displacements can, thus, be found. However, another procedure can be used to find an analytical solution for ξ_n.

Assuming that the displacements vary slowly with the atom number, we can approximate the discrete quantities ξ_n by continuous

(a)

(b)

Figure 4.11: Structure of MDs in the chain model of Frank and van der Merwe at (a) positive ($b > a$) and (b) negative ($b < a$) misfits. In (a), the MD represents an empty potential trough (light wall) which corresponds to an excess atomic plane in the substrate. In (b), the dislocation represents two atoms in one trough (or three atoms in two troughs, heavy wall) which corresponds to an excess atomic plane in the overgrowth.

variables $\xi(n)$ and replace the differences $\xi_{n+1} - \xi_n$ by the derivative $d\xi(n)/dn$. Expanding it in a Taylor series and neglecting higher order differentials result in a differential equation of second order (Frank and van der Merwe 1949):

$$\frac{d^2\xi(n)}{dn^2} = \frac{\pi}{2l_0^2} \sin 2\pi\xi(n). \tag{4.18}$$

This is the continuum approximation of the problem. It replaces the real discrete chain of atoms by an elastic continuum (a rubber cord). Although some details are usually lost in this procedure, it has the merit of giving rise to an analytical solution. In fact, Eq. (4.18) is the pendulum equation but in this particular case it is known as the static sine-Gordon equation or simply the sine-Gordon equation (Barone *et al.*, 1971; Scott, Chu and McLaughlin 1973; Villain 1980).

The integration of the sine-Gordon equation can be carried out in two stages. First, we find the first integral by using the following simple procedure. We multiply both sides of (4.18) by $d\xi$ and reorganize the left-hand side to obtain

$$d\xi \frac{d^2\xi(n)}{dn^2} = d\xi \frac{d}{dn}\left(\frac{d\xi}{dn}\right) = \frac{d\xi}{dn} d\left(\frac{d\xi}{dn}\right) = \frac{\pi}{2l_0^2} \sin 2\pi\xi(n) d\xi.$$

The integration then gives

$$\left(\frac{d\xi}{dn}\right)^2 = -\frac{\cos 2\pi\xi(n)}{2l_0^2} + C,$$

where C is the integration constant. To find it, we assume that, in general, the solution $\xi(n)$ crosses the zero at some angle so that $d\xi/dn = \omega$ at $\xi = 0$. Then, $C = (1 + 2\omega^2 l_0^2)/2l_0^2$ and

$$\left(\frac{d\xi}{dn}\right)^2 = -\frac{\cos 2\pi\xi(n)}{2l_0^2} + \frac{1 + 2\omega^2 l_0^2}{2l_0^2}.$$

Making use of the relations $\cos 2\pi\xi = 2\cos^2 \pi\xi - 1$ and $\omega^2 l_0^2 = 1/k^2 - 1$, one finally obtains

$$\frac{d\xi}{dn} = \frac{\sqrt{1 - k^2 \cos^2 \pi\xi(n)}}{kl_0}. \tag{4.19}$$

Single Dislocations: We consider first for illustration the limiting case of a single dislocation assuming $\omega = 0$ and $k = 1$. Then, the integration of the resulting equation

$$\frac{d\xi(n)}{dn} = \frac{\sin \pi\xi(n)}{l_0}$$

subject to the boundary condition $n = 0$, $\xi(n) = 1/2$ gives

$$\xi(n) = \frac{2}{\pi} \arctan\left[\exp\left(\frac{\pi n}{l_0}\right)\right]. \tag{4.20}$$

The atomic displacements as a function of the atom number according to Eq. (4.20) are plotted in Fig. 4.12 (curve 1). As seen, the solution has the form of a single wave. On the left-hand side ($n \to -\infty$), the displacements approach zero, which means that the atoms lie in the bottoms of their respective troughs. On the right-hand side ($n \to +\infty$), the displacements approach unity, i.e., the atoms lie in the bottoms of the neighboring potential troughs. In other words, N atoms are distributed over $N + 1$ (or $N - 1$ at negative misfit) potential troughs. This is equivalent to one missing atomic plane (or a plane in excess) in the overgrowth with respect to the substrate if we imagine the 1D model under consideration as a cross section of two crystal halves. (Note that the overgrowth crystal has as many atomic planes as its own structure demands.) It is known in the literature as a *misfit* or *interface dislocation* (Frank and van der Merwe 1949a) or a *soliton* (Scott, Chu and McLaughlin 1973; Villain 1980). As will be shown below, this is the shape the dislocations possess when they are far apart and do not interact with each other.

As shown in Fig. 4.12, atoms which are in marked disregistry with the substrate potential troughs (or atoms) occupy a region with a width l_0 measured in the number of atoms. The atoms to the left and to the right of this region are in a good fit, and those far enough from it are in a perfect fit, with the substrate potential. Thus, l_0 gives the width of single isolated MDs which do not interact with each other. Within the framework of the harmonic approximation under consideration, the dislocation width does not depend on the natural misfit, but on the energetic parameters γ and W only. It becomes a steep

Figure 4.12: Dependence of the atom displacements on the atom number. Curve 1 represents a single-MD (single soliton) given by Eq. (4.20). Curve 2 represents a MD in a sequence of interacting dislocations given by Eq. (4.23). As shown, the latter crosses zero and unity under an angle ω which determines the boundary condition for finding the first integral and the value of the modulus k of the elliptic integrals $K(k)$ and $E(k)$. The greater the dislocation density, the greater the angle ω and the smaller than unity the modulus k. Thus, the latter is a measure of the dislocation density. In the case of a single dislocation or dislocations far apart, $\omega = 0$ and $k = 1$. l_0 denotes the width of a single dislocation. The width of a dislocation in a sequence of dislocations is given by $l = kl_0 < l_0$. The reciprocal of the length L gives the density of the MDs according to Eq. (4.25).

function of the misfit in the more realistic model with anharmonic interactions (Markov and Trayanov 1988).

It is of interest to consider the elastic strains of the consecutive springs. The latter can be written in the continuum approximation in the form

$$\varepsilon(n) = a(\xi_{n+1} - \xi_n - f) \cong a\Big(\frac{d\xi}{dn} - f) = a\Big(\frac{1}{l_0 \cosh(\pi n/l_0)} - f\Big). \tag{4.21}$$

Figure 4.13: Plot of the consecutive strains ε_n of the chemical bonds vs the atom displacements $\xi(n)$ in a chain containing dislocations far apart from each other (curve 1, Eq. (4.21)) and a sequence of interacting dislocations (curve 2, Eq. (4.27)). In the first case, the strains in between the dislocations reach the value $-af = -(b-a)$, i.e., the dislocations divide the interface into regions of perfect fit with the substrate. The sequence of dislocations leads to an appearance of periodical strains which change their sign.

The variation of $\varepsilon(n)$ with n is plotted in Fig. 4.13 (curve 1). As seen, far from the dislocation, $(n \to \pm\infty)$, the first term in the brackets goes to zero and the strains are equal to $\varepsilon(n) = -af = -(b-a)$. In other words, the bonds between the overgrowth atoms are strained to fit exactly with spacings of the potential troughs of the substrate, and the strains are precisely equal to the natural misfit taken with a negative sign. In the core of the dislocation $(n = 0)$, the strain

$$\varepsilon_c = a\Big(\frac{1}{l_0} - f\Big)$$

is positive as long as $1/l_0 > f$. As will be shown below, it becomes equal to zero only when the misfit reaches the so-called *limit of metastability* of the pseudomorphous state defined as $f_{\rm ms} = 1/l_0$.

Sequence of Dislocations: Making use of the substitution

$$\phi = \pi\Big(\xi - \frac{1}{2}\Big)$$

and after integration of (4.19) subject to the boundary condition $\xi(n = 0) = 1/2$ and $\phi = 0$, we obtain the general solution of (4.18):

$$\frac{\pi n}{kl_0} = \int_0^{\phi} \frac{d\varphi}{\sqrt{1 - k^2 \sin^2 \varphi}} = F(\phi, k), \tag{4.22}$$

where $F(\phi, k)$ is the incomplete elliptic integral of the first kind (Janke, Emde and Lösch 1960) or by inversion

$$\xi(n) = \frac{1}{2} + \frac{1}{\pi}\mathrm{am}\Big(\frac{\pi n}{kl_0}\Big), \tag{4.23}$$

where $\mathrm{am}(F(\phi, k), k)$ denotes the elliptic amplitude and $k < 1$ is the modulus of the elliptic integrals. At $k = 1$ (4.23) turns into (4.20).

A graphical representation of (4.23) is given in Fig. 4.12 (curve 2). When the dislocations are far apart, $\omega \to 0$ and $k \to 1$. The nearer the dislocations, the greater ω is and the smaller than unity k becomes. Thus, the modulus of the elliptic integrals determines the spacing between the dislocations, or in other words, the mean dislocation density, on the one hand, and the dislocation width, on the other. The latter is now smaller than that of a single dislocation and is equal to $l = kl_0$.

The dislocation spacing measured in the number of atoms can be easily calculated from (4.22) and reads

$$L = \frac{1}{\pi} 2kl_0 K(k), \tag{4.24}$$

where $K(k) = K(\pi/2, k)$ is the complete elliptic integral of the first kind. The reciprocal of the dislocation spacing gives the mean dislocation density in the ground state

$$f_d = \frac{\pi}{2kl_0 K(k)}. \tag{4.25}$$

For values of k near the unity, the elliptic integral $K(k)$ can be approximated by $K(k) \cong \ln[4/(1 - k^2)^{1/2}]$ and the mean dislocation

density reads

$$f_d = \frac{\pi}{2kl_0 \ln[4/(1-k^2)^{1/2}]}. \tag{4.26}$$

It is immediately seen that at $k = 1$, the dislocation spacing tends to infinity and the mean dislocation density to zero. The overlayer is strained to fit exactly the periodicity of the substrate, its atomic spacing being equal to that of the latter.

In fact, the mean dislocation density f_d is just the part of the natural misfit given by Eq. (4.11) which is accommodated by MDs. The mean atomic spacing $\bar{b}$ is equal to

$$\bar{b} = \frac{a}{N-1} \sum_{-N/2}^{N/2} (\xi_{n+1} - \xi_n + 1) \cong \frac{a}{L} \int_{-L/2}^{L/2} \Big(\frac{d\xi}{dn} + 1 \Big) dn = a + \frac{a}{L},$$

from where (4.11) follows.

Strains: The elastic strain of the consecutive springs now is

$$\varepsilon(n) = a\Big(\frac{d\xi(n)}{dn} - f \Big) = a\left(\frac{\sqrt{1 - k^2 \cos^2 \pi\xi(n)}}{kl_0} - f \right), \tag{4.27}$$

which reduces to (4.21) at $k = 1$. The strain varies periodically with the spring number, compression, and expansion alternating with a period equal to the dislocation spacing (Fig. 4.13, curve 2). In the cores of the dislocations, the strain $\varepsilon_c = a(1/kl_0 - f)$ is now greater than that in the core of a single dislocation. In between the dislocations, $\xi = 0, 1$, the strain

$$\varepsilon = a\left(\frac{\sqrt{1-k^2}}{kl_0} - f \right)$$

no longer reaches the maximum strain $\varepsilon = -af$ as shown in Fig. 4.13 (curve 2). With increasing dislocation density (decreasing k), the strain in the dislocation cores increases and the one in between the dislocations decreases in absolute value, i.e., the strain varies more and more symmetrically around the zero. When the sum of the positive strains becomes equal to that of the negative strains, or in other words, when the areas under the $\varepsilon(n)$ curve from either side of the

zero become equal, the mean atomic spacing $\bar{b} = b$. When the latter takes place, the natural misfit is completely accommodated by MDs, or in other words, by the periodical strain connected to them. When the positive and the negative areas under the $\varepsilon(n)$ curve are not equal, their difference gives the part of the natural misfit which is accommodated by HS.

Energy: We can now find the energy of the system. For this purpose, we have to substitute the solution (4.22) in the continuum approximation of (4.15):

$$E = \frac{1}{2}\gamma a^2 \int_{-L/2}^{L/2} \left[\left(\frac{d\xi}{dn}\right) - f\right]^2 dn + \frac{1}{2}W \int_{-L/2}^{L/2} (1 - \cos 2\pi\xi) dn. \tag{4.28}$$

Substituting (4.23) into the second integral of the right-hand side of (4.28) gives

$$\frac{1}{2}W \int_{-L/2}^{L/2} (1 - \cos 2\pi\xi) dn = Wl^2 \int_{-L/2}^{L/2} \left[\left(\frac{d\xi}{dn}\right)^2 - \frac{1-k^2}{k^2 l_0^2}\right] dn$$

and (4.28) turns into

$$E = Wl^2 \int_{-L/2}^{L/2} \left[2\left(\frac{d\xi}{dn}\right)^2 - 2f\frac{d\xi}{dn} + f^2 - \frac{1-k^2}{k^2 l_0^2}\right] dn.$$

Substituting (4.19) into the above expression and carrying out the integration give the energy per atom (Fig. 4.18):

$$\mathcal{E} = \frac{E}{L} = W\left(\frac{4E(k)}{\pi k} l_0 f_d - \frac{1-k^2}{k^2} + l_0^2 f^2 - 2l_0^2 f f_d\right), \tag{4.29}$$

where f_d is given by (4.25) and

$$E(k) = \int_0^{\pi/2} \sqrt{1 - k^2 \sin^2 \varphi} d\varphi$$

is the complete elliptic integral of the second kind.

Minimization of the energy per atom with respect to the mean dislocation density f_d gives

$$\frac{d\mathcal{E}}{df_d} = 2Wl_0\Big(\frac{2E(k)}{\pi k} - l_0 f\Big), \tag{4.30}$$

the relationships $d[E(k)/k]/dk = -K(k)/k^2$ and $d[kK(k)]/dk =$-$E(k)/(1-k^2)$ having been used.

The condition for the lowest energy state then reads

$$f = f_s = \frac{2}{\pi l_0}\frac{E(k)}{k}. \tag{4.31}$$

Substituting $E(k)/k$ from (4.31) (4.29) gives the energy of the ground state

$$\mathcal{E}_0 = Wl_0^2 f^2 - W\frac{1-k^2}{k^2} = \frac{1}{2}\gamma a^2 f^2 - W\frac{1-k^2}{k^2}. \tag{4.32}$$

This means that as long as $k = 1$, $\mathcal{E}_0 = 0.5\gamma a^2 f^2$, and the pseudomorphous state is always the ground state.

Beyond the limit of stability, the system in the ground state contains MDs whose density is determined by Eq. (4.25). Excluding k from (4.25) and (4.31), we find the mean dislocation density in the ground state as a function of the natural misfit. The dependence is plotted in Fig. 4.14 (curve 1). As shown, the dislocation density is equal to zero up to the stability limit and then sharply increases and goes asymptotically to the value of the natural misfit. In fact, this is a plot of the mean atom spacing $\bar{b}$ relative to a as function of the natural spacing b.

Let us analyze Eq. (4.29) in more detail. At $k = 1$ (dislocations far apart), it turns into

$$\mathcal{E} = \frac{4}{\pi}Wl_0 f_d + Wl_0^2(f^2 - 2ff_d) = \frac{4}{\pi}Wl_0 f_d\left(1 - \frac{f}{f_s}\right) + \mathcal{E}(0), \tag{4.33}$$

where $\mathcal{E}(0) = Wl_0^2 f^2$ is the energy of the pseudomorphous state and f_s is the limit of the stability of the pseudomorphous state (see Eq. (4.37)).

Figure 4.14: Plot of the mean dislocation density $f_d = (\bar{b} - a)/a$ vs natural misfit $f = (b - a)/a$ in the 1D model (curve 1) and the 2D model (curve 2). The plot represents, in fact, the dependence of the average atomic spacing $\bar{b}$ on the bulk spacing b. At large enough values of the misfit, $\bar{b} \to b$, and the misfit is accommodated completely by MDs. At misfits smaller than the stability limit f_s, $\bar{b} = a$ and the misfit is accommodated completely by HS. The overgrowth is pseudomorphous with the substrate. The straight line gives the case $\bar{b} = b$ (after van der Merwe 1975).

The term

$$\mathcal{E}_d = \frac{4}{\pi} W l_0 f_d$$

represents the energy of a single MDs or a single soliton

$$\mathcal{E}_1 = \frac{4}{\pi} W l_0 \tag{4.34}$$

multiplied by the density of the dislocations f_d. In other words, $\mathcal{E}_d$ is the energy of the MDs.

The second term

$$\mathcal{E}_{\text{hs}} = W l_0^2 (f^2 - 2 f f_d) = \frac{1}{2} \gamma a^2 (f^2 - 2 f f_d) \cong \frac{1}{2} \gamma a^2 f_e^2$$

is, in fact, the energy of the HS. It turns out that in the case of noninteracting MDs ($k = 1$), the energy is a sum of the energy of the HS and the energy of the MDs, i.e., $\mathcal{E} = \mathcal{E}_d + \mathcal{E}_{\text{hs}}$.

Energy of Interaction of MDs: The difference of the energies at $k = 1$ and $k < 1$ represents obviously the energy of interaction of the MDs. The latter is implicitly accounted for in the k-containing terms. The energy of interaction of a pair of dislocations has been calculated to give (Villain 1980; Theodorou and Rice 1978) the following asymptotic expression.

$$\mathcal{E}_{\text{int}} = \varkappa \mathcal{E}_d \exp\Big(-\frac{\pi}{f_d l_0}\Big), \tag{4.35}$$

which is valid for dislocations far apart and $\varkappa$ is a constant of the order of unity (Bak and Emery 1976; Theodorou and Rice 1978). The exponential behavior of the interaction energy obviously reflects the dependence of k on the mean dislocation density (4.26).

The energy of the incommensurate state then becomes

$$\mathcal{E} = \mathcal{E}_1 f_d \Big[1 - \frac{f}{f_s} + \varkappa \exp\Big(-\frac{\pi}{f_d l_0}\Big)\Big] + \mathcal{E}(0). \tag{4.36}$$

Limit of Stability of the Pseudomorphous State: As shown above, the pseudomorphous state is always the ground state as long as $k = 1$. When $k < 1$, the state with dislocations becomes the ground state, their density being determined by the value of k. Then, from (4.31) with $k = 1$, one obtains

$$f = f_s = \frac{2}{\pi l_0} \tag{4.37}$$

which appears as a *limit of stability of the pseudomorphous state*. The limit of stability of a state with a particular density of dislocations is given by Eq. (4.31). Frank and van der Merwe calculated the value of l_0 under the condition that the energies ψ_{AA}, ψ_{BB}, and ψ_{AB} are equal and found $l_0 = 7.35$. Hence, $f_s \cong 9\%$ in this particular case.

Equilibrium of Chain with Finite Length: As the strains (and the stresses) change their signs periodically (Fig. 4.13), there are obviously springs which are unstrained. If we cut such springs, the parts of the chain to the left and to the right of the cut will remain in equilibrium with their free ends. This means that when a chain with a finite length is in equilibrium, its hypothetical end springs with numbers $n = -1$ and $n = N$ are unstrained. In such a case, the

end atoms will have a specific displacements ξ_0. They can be found assuming the periodic variation of the strain $\varepsilon(n)$ given by (4.27) crosses zero

$$\cos \pi\xi_0 = \left(\frac{1}{k^2} - l_0^2 f^2\right)^{1/2}.$$

As seen, ξ_0 depends on the value of the misfit. When the misfit increases, the end atom climbs the slope of its respective potential trough. Obviously, there exists a critical value of the misfit at which the end atom is just on top of the hill between its respective and the neighboring potential troughs, i.e., $\xi_0 = \pm 1/2$. If the misfit is infinitesimally increased, the end atom will go down in the neighboring trough. The situation is equivalent to a generation of a new MD at the chain end. Mathematically, this means that $l_0^2 f^2 > 1/k^2$, and the quantity under the square root becomes negative. On the other hand, the misfit cannot be too small as this means that the quantity under the square root will become larger than unity and the equation will have no solution. Physically, this means that under some critical value of the misfit, an existing dislocation should leave the chain at its free end. The above considerations are illustrated in Fig. 4.15 where the chains are shown in a folded form (Dubnova and Indenbom 1966). We have to imagine that each atom occupies the same position but in a separate potential trough. Figure 4.15(a) demonstrates a chain which does not contain MDs. All displacements lie between $-1/2$ and $1/2$. If the natural misfit is equal to zero, all atoms will lie in the bottom of the potential troughs, i.e., $\xi(n) = 0$ (Fig. 4.15(b)). Increasing the misfit leads to a situation when the end atoms reach the tops of the respective hills, i.e., $\xi(0) = -1/2$ and $\xi(N-1) = 1/2$ (Fig. 4.15(c)). The difference of the overall lengths of the chains shown in Fig. 4.15(b) and c is precisely equal to a. This means that in Fig. 4.15(b) N atoms are distributed over N potential troughs, whereas in Fig. 4.15(c) N atoms are distributed over $N+1$ troughs. The analogous situation for a chain containing one dislocation is shown in Figs. 4.15(d) and 4.15(e). In Fig. 4.15(d), N atoms are distributed over $N+1$ troughs, whereas in Fig. 4.15(e), over $N+2$ troughs.

Figure 4.15: Illustration in a folded form of chains at different values of the misfit and containing different numbers of dislocations. Imagine that each atom has the same displacement as shown in the figure but is positioned in the next potential trough. (a) A chain without a dislocation at a misfit smaller than the metastability limit f_{ms}. (b) A chain without a dislocation at $f = 0$. All the atoms are situated exactly at the bottoms of the corresponding potential troughs. (c) A chain without a dislocation at $f = f_{\mathrm{ms}}$. The end atoms are exactly on top of the crests between their respective troughs and the next ones. (d) A chain containing one dislocation at $f = 0$. (e) A chain containing one dislocation at $f = f_{\mathrm{ms}}$.

Limit of Metastability: The necessary and sufficient condition a finite chain in a certain state (dislocated or not, depending on the value of k) to exist in equilibrium with its free ends is the upper bound $\varepsilon(\xi_0 = 1/2)$ of the periodic variation of the strain $\varepsilon(n)$ (Eq. (4.27)) be positive and the lower bound $\varepsilon(\xi_0 = 0)$ be negative. This leads to

$$\frac{1}{k^2} - l_0^2 f^2 \leq 1 \qquad \text{or} \qquad \frac{1}{k^2} - 1 \leq l_0^2 f^2,$$

$$\frac{1}{k^2} - l_0^2 f^2 \geq 0 \qquad \text{or} \qquad l_0^2 f^2 \leq \frac{1}{k^2},$$

or, in other words, to

$$\left(\frac{1}{k^2} - 1\right)^{1/2} \leq l_0 f \leq \frac{1}{k}. \tag{4.38a}$$

The inequalities (4.38a) determine the interval of misfit in which there exist solutions of the sine-Gordon equation for a finite chain. Outside of this interval, there are no solutions and the corresponding configurations do not exist. For a chain which is pseudomorphous with the substrate ($k = 1$), this interval is

$$0 \leq f \leq \frac{1}{l_0}. \tag{4.38b}$$

This means that the pseudomorphous state will be stable up to $f \leq f_s$ and will exist but not as a ground state at misfits larger than f_s but smaller than the *limit of metastability*

$$f_{\mathrm{ms}} = \frac{1}{l_0}. \tag{4.39}$$

Summarizing, we conclude that chains containing MDs will be stable beyond a misfit determined by Eq. (4.31). The value of the stability limit depends in this case on the density of the dislocations, or in other words, on the value of k. The region of metastability of dislocated chains is now shifted to larger limits according to (4.38a) determined again by the value of k. It follows that the misfit dependence of the energy of a finite chain of atoms will consists of intersecting parabolic segments (Eq. (4.29)) each segment corresponding to a particular number of MDs increasing by 1 (Fig. 4.16). The intersections define the corresponding stability limits the first one being given by Eq. (4.37). Each segment is confined in a misfit interval determined by (4.38a). The envelope of the parabolic segments gives the ground state of the energy of infinitely long chain.

4.2.4.4 *2D model of Frank and van der Merwe*

In considering this problem, we follow the analysis of van der Merwe (1970, 1973). We consider an overlayer with rectangular symmetry and natural atom spacings b_x along the x axis and b_y along the y axis. The substrate periodic potential is given by Eq. (4.6).

Figure 4.16: Misfit dependence of the potential energy per atom of a finite chain. The plot consists of a sequence of parabolic segments corresponding to states with increasing number of dislocations denoted by the figures at each segment. The segments intersect each other at the corresponding stability limits given by Eq. (4.31). f_s and $f_{\rm ms}$ denote, respectively, the limits of stability (Eq. (4.37)) and metastability (Eq. (4.39)) of the pseudomorphous state. The solid line gives the ground state, whereas the dashed lines represent the corresponding metastable states.

We enumerate the overlayer atoms and the substrate potential troughs by n in the x direction and by m in the y direction. Then, the Cartesian coordinates of an atom (n, m) from an arbitrarily placed origin of the coordinate system are

$$X_{nm} = a_x(n + \xi_{nm}), \qquad Y_{nm} = a_y(m + \eta_{nm}). \tag{4.40}$$

As shown in Fig. 4.17, the linear and shear strains in the film are

$$\varepsilon_x = \frac{1}{b_x}(X_{n+1,m} - X_{nm} - b_x),$$

$$\varepsilon_y = \frac{1}{b_y}(Y_{n,m+1} - Y_{nm} - b_y),$$

$$\varepsilon_{xy} = \frac{1}{b_y}(X_{n,m+1} - X_{nm}) + \frac{1}{b_x}(Y_{n+1,m} - Y_{nm}).$$

Figure 4.17: Deformation of a rectangular unit atomic mesh of the overgrowth (open circles) from which the strains can be derived. The substrate atomic mesh is given by the filled circles (after van der Merwe 1975).

Making use of (4.40) gives

$$\varepsilon_x = \frac{a_x}{b_x}(\xi_{n+1,m} - \xi_{nm} - f_x), \tag{4.41a}$$

$$\varepsilon_y = \frac{a_y}{b_y}(\eta_{n,m+1} - \eta_{nm} - f_y), \tag{4.41b}$$

$$\varepsilon_{xy} = \frac{a_x}{b_y}(\xi_{n,m+1} - \xi_{nm}) + \frac{a_y}{b_x}(\eta_{n+1,m} - \eta_{nm}), \tag{4.41c}$$

where

$$f_x = \frac{b_x - a_x}{a_x} \qquad \text{and} \qquad f_y = \frac{b_y - a_y}{a_y} \tag{4.42}$$

are the natural misfits in both orthogonal directions.

According to the theory of elasticity (Timoshenko 1934; van der Merwe 1973), the stresses and the energy of isotropic elastic 2D continuum (rubber sheet) are given by

$$\begin{aligned} T_x &= \frac{2Gt}{1-\nu}(\varepsilon_x + \nu\varepsilon_y), \\ T_y &= \frac{2Gt}{1-\nu}(\varepsilon_y + \nu\varepsilon_x), \\ T_{xy} &= Gt\varepsilon_{xy}, \\ E &= Gtb_xb_y\left(\frac{\varepsilon_x^2 + \varepsilon_y^2 + 2\nu\varepsilon_x\varepsilon_y}{1-\nu} + \frac{1}{2}\varepsilon_{xy}^2\right), \end{aligned} \tag{4.43}$$

where G is the shear modulus and ν is the Poisson ratio of the film material, and t is the thickness of the film which is equal to b_z in our particular case of monoatomic overlayer, z being the direction normal to the interface. Then, $\Omega = b_xb_yb_z$ is the volume of an overlayer molecule.

Having in mind (4.6), the potential energy of the overlayer is

$$\begin{aligned} E = \sum_{n,m}\Bigg\{ & \frac{G\Omega}{1-\nu} \\ & \times \Bigg[\left(\frac{a_x}{b_x}\right)^2(\xi_{n+1,m} - \xi_{nm} - f_x)^2 + \left(\frac{a_y}{b_y}\right)^2(\eta_{n,m+1} - \eta_{nm} - f_y)^2 \\ & + 2\nu\frac{a_xa_y}{b_xb_y}(\xi_{n+1,m} - \xi_{nm} - f_x)(\eta_{n,m+1} - \eta_{nm} - f_y)\Bigg] \\ & + \frac{1}{2}G\Omega\Big(\frac{a_x}{b_y}(\xi_{n,m+1} - \xi_{nm}) + \frac{a_y}{b_x}(\eta_{n+1,m} - \eta_{nm})\Big)^2\Bigg\} \\ & + \frac{1}{2}\sum_{n,m}[W_x(1-\cos 2\pi\xi_{nm}) + W_y(1-\cos 2\pi\eta_{nm})]. \end{aligned} \tag{4.44}$$

The conditions of equilibrium of the nmth atom now read

$$\frac{\partial E}{\partial \xi_{nm}} = \frac{\partial E}{\partial \eta_{nm}} = 0.$$

Applying the first condition gives

$$(\xi_{n+1,m} - 2\xi_{nm} + \xi_{n-1,m}) + \frac{1}{2}(1-\nu)\Big(\frac{b_x}{b_y}\Big)^2(\xi_{n,m+1} - 2\xi_{nm} + \xi_{n,m-1})$$
$$+ \nu\frac{a_y b_x}{a_x b_y}(\eta_{n,m+1} - \eta_{nm} - \eta_{n-1,m+1} + \eta_{n-1,m})$$
$$+ \frac{1}{2}(1-\nu)\frac{a_y b_x}{a_x b_y}(\eta_{n,m-1} - \eta_{nm} - \eta_{n+1,m-1} + \eta_{n+1,m})$$
$$= \frac{\pi}{2l_x^2}\sin 2\pi\xi_{nm}. \tag{4.45}$$

In the continuum limit,

$$\xi_{n+1,m} - 2\xi_{nm} + \xi_{n-1,m} \cong \frac{\partial^2\xi}{\partial n^2},$$
$$\times\, \eta_{n,m+1} - \eta_{nm} - \eta_{n-1,m+1} + \eta_{n-1,m}$$
$$= \eta_{n,m-1} - \eta_{nm} - \eta_{n+1,m-1} + \eta_{n+1,m} \cong \frac{\partial^2\eta}{\partial n\partial m}$$

and (4.45) turns into

$$\frac{\partial^2\xi}{\partial n^2} + \frac{1}{2}(1+\nu)\frac{a_y b_x}{a_x b_y}\frac{\partial^2\eta}{\partial n\partial m} + \frac{1}{2}(1-\nu)\Big(\frac{b_x}{b_y}\Big)^2\frac{\partial^2\xi}{\partial m^2} = \frac{\pi}{2l_x^2}\sin 2\pi\xi_{nm}. \tag{4.46a}$$

The second equilibrium condition gives the corresponding equation for η_{nm}.

$$\frac{\partial^2\eta}{\partial m^2} + \frac{1}{2}(1+\nu)\frac{a_x b_y}{a_y b_x}\frac{\partial^2\xi}{\partial n\partial m} + \frac{1}{2}(1-\nu)\Big(\frac{b_y}{b_x}\Big)^2\frac{\partial^2\eta}{\partial n^2} = \frac{\pi}{2l_y^2}\sin 2\pi\eta_{nm}. \tag{4.46b}$$

where

$$l_x = \left(\frac{G\Omega a_x^2}{W_x(1-\nu)b_x^2}\right)^{1/2}, \qquad l_y = \left(\frac{G\Omega a_y^2}{W_y(1-\nu)b_y^2}\right)^{1/2}. \tag{4.47}$$

In the case of quadratic symmetry of the contact planes, the above set of equations simplifies to (Frank and van der Merwe 1949b)

$$\frac{\partial^2\xi}{\partial n^2}+\frac{1}{2}(1+\nu)\frac{\partial^2\eta}{\partial n\partial m}+\frac{1}{2}(1-\nu)\frac{\partial^2\xi}{\partial m^2}=\frac{\pi}{2l^2}\sin 2\pi\xi_{nm}, \tag{4.48a}$$

$$\frac{\partial^2\eta}{\partial m^2}+\frac{1}{2}(1+\nu)\frac{\partial^2\xi}{\partial n\partial m}+\frac{1}{2}(1-\nu)\frac{\partial^2\eta}{\partial n^2}=\frac{\pi}{2l^2}\sin 2\pi\eta_{nm}, \tag{4.48b}$$

where

$$l=\left(\frac{G\Omega a^2}{W(1-\nu)b^2}\right)^{1/2}. \tag{4.49}$$

If we are looking for solutions with edge-type dislocations, the mixed derivatives $\partial^2\xi/\partial m^2$, $\partial^2\eta/\partial n^2$, $\partial^2\xi/\partial n\partial m$, and $\partial^2\eta/\partial n\partial m$ vanish (in fact, we neglect the shear strains $\varepsilon_{xy}=0$) and the set of equations (4.46) turns into a set of two independent sine-Gordon equations.

$$\frac{\partial^2\xi}{\partial n^2}=\frac{\pi}{2l_x^2}\sin 2\pi\xi_{nm}, \tag{4.50a}$$

$$\frac{\partial^2\eta}{\partial m^2}=\frac{\pi}{2l_y^2}\sin 2\pi\eta_{nm}. \tag{4.50b}$$

One could consider the following limiting cases:

(i) $f_y\cong 0$, $\xi=\xi(n)$ and $\eta=\text{const}$ (corrugation of the substrate surface in one direction only). The system (4.50) reduces to

$$\frac{\partial^2\xi}{\partial n^2}=\frac{\pi}{2l_x^2}\sin 2\pi\xi, \qquad \frac{\pi}{2l_y^2}\sin 2\pi\eta=0. \tag{4.51}$$

The solution of the first equation is given in the previous chapter. The solution of the second one is $\eta=0$. The result is a sequence of edge-type MDs lines parallel to the y-axis and a HS $\varepsilon_y=-f_ya_y/b_y$ in the y direction. Such a situation is observed in the case of, epitaxial growth of tetragonal $MoSi_2$ on Si(1 0 0) (Chen, Cheng and Lin 1986). The epitaxial orientations and the natural misfits in the two orthogonal directions are $(1\,0\,0)\langle 0\,0\,4\rangle_d \parallel (1\,0\,0)\langle 2\,2\,0\rangle_s$, $f_x=2.34\%$ and $f_y=0.1\%$, and $(1\,1\,1)\langle 1\,1\,\bar{2}\rangle_d \parallel (1\,0\,0)\langle 2\bar{2}0\rangle_s$, $f_x=2.21\%$ and $f_y=0.1\%$.

(ii) $f_x \neq f_y \neq 0$, $\xi = \xi(n)$, and $\eta = \eta(m)$. This is the general case leading to a cross grid of MDs. Particular cases are $f_x = f_y$ (quadratic symmetry of the contact planes) and $f_x \approx -f_y$. The latter is observed in some rare cases such as for instance in the epitaxial growth of tetragonal $MoSi_2$ on Si(1 0 0) (Chen, Cheng, and Lin 1986) where the epitaxial orientation is $(1\,1\,0)\langle 0\,0\,4\rangle_d \parallel (0\,0\,1)\langle 2\,2\,0\rangle_s$. The natural misfits in both orthogonal directions are $f_x = 2.34\%$ and $f_y = -1.69\%$. We will not treat this case here because the considerations of the model with a more realistic anharmonic potential show a considerable influence of the sign of the natural misfit on the properties of the model.

Following the same procedure as before, we find the solutions for $\xi(n)$ and $\eta(m)$ which have the same form as Eq. (4.22) with the only exception that l_0 is replaced by l_x and l_y. The first and the second integrals now read

$$\frac{d\xi}{dn} = \frac{\sqrt{1 - k_x^2 \cos^2 \pi\xi}}{k_x l_x}, \tag{4.52}$$

$$\frac{\pi n}{k_x l_x} = \boldsymbol{F}\Big[k_x, \pi\Big(\xi - \frac{1}{2}\Big)\Big], \tag{4.53}$$

and the corresponding solutions for $\eta(m)$ have the same form.

Substituting the solutions into the continuum approximation of (4.44) (with $\varepsilon_{xy} = 0$)

$$\begin{aligned} E = \int_{-L_x/2}^{L_x/2} dn \int_{-L_y/2}^{L_y/2} dm \Bigg\{ & W_x l_x^2 \left[2\Big(\frac{d\xi}{dn}\Big)^2 - 2 f_x \frac{d\xi}{dn} + f_x^2 - \frac{1 - k_x^2}{k_x^2 l_x^2} \right] \\ & + W_y l_y^2 \left[2\Big(\frac{d\eta}{dm}\Big)^2 - 2 f_y \frac{d\eta}{dm} + f_y^2 - \frac{1 - k_y^2}{k_y^2 l_y^2} \right] \\ & + 2\nu \sqrt{W_x W_y} l_x l_y \Big(\frac{d\xi}{dn} - f_x\Big)\Big(\frac{d\eta}{dm} - f_y\Big) \Bigg\} \end{aligned} \tag{4.54}$$

gives for the energy per overlayer atom the expression

$$\mathcal{E} = \frac{E}{L_x L_y} = W_x \left(\frac{4E(k_x)}{\pi k_x} l_x f_d(x) - \frac{1 - k_x^2}{k_x^2} + l_x^2 f_x^2 - 2 l_x^2 f_x f_d(x) \right)$$

$$+ W_y \left(\frac{4E(k_y)}{\pi k_y} l_y f_d(y) - \frac{1 - k_y^2}{k_y^2} + l_y^2 f_y^2 - 2 l_y^2 f_y f_d(y) \right)$$

$$+ 2\nu \sqrt{W_x W_y} l_x l_y [f_d(x) - f_x][f_d(y) - f_y], \tag{4.55}$$

where $f_d(x)$ and $f_d(y)$ are the mean dislocation densities, and k_x and k_y are the corresponding moduli of the elliptic integrals in both orthogonal directions x and y, respectively.

In the case of quadratic symmetry ($f_x = f_y = f$, $f_d(x) = f_d(y) = f_d$, $k_x = k_y = k$, $W_x = W_y = W$),

$$\mathcal{E} = 2W \left(\frac{4E(k)}{\pi k} l f_d - \frac{1 - k^2}{k^2} + l^2 f^2 - 2 l^2 f f_d \right) + 2\nu W l^2 (f_d - f)^2. \tag{4.56}$$

As seen, the first term in the square brackets (which is multiplied by 2 to account for the grid of MDs) in (4.56) is identical by form to Eq. (4.29). Both expressions differ only in the second term that includes explicitly the Poisson ratio. The last term in (4.55) and (4.56) contains the difference $f_d - f = f_e$, which is, in fact, the residual HS and should vanish at large misfits when $f_d = f$ in the ground state.

Minimization of the energy with respect to $f_d(x)$ (or $f_d(y)$) yields the condition for the ground state.

$$f_x = \frac{2E(k_x)}{\pi k_x l_x} + \nu \left(\frac{W_y l_y^2}{W_x l_x^2} \right)^{1/2} [f_d(y) - f_y]. \tag{4.57}$$

The corresponding expression for f_y can easily be obtained.

Bearing in mind (4.47), the latter simplifies to

$$f_x = \frac{2E(k_x)}{\pi k_x l_x} + \nu \frac{a_y b_x}{b_y a_x} [f_d(y) - f_y]. \tag{4.58}$$

The condition $k_x = 1$ gives the limit of stability of the pseudomorphous state

$$f_s(x) = \frac{2}{\pi l_x} - \nu \frac{a_y b_x}{b_y a_x} f_y, \tag{4.59}$$

which for quadratic symmetry reduces to

$$f_s(\mathrm{2D}) = \frac{2}{\pi l (1 + \nu)}. \tag{4.60}$$

Note that in the 2D case, the stability limit $f_s(x)$ in one of the directions depends on the misfit in the other orthogonal direction. The latter reflects the increased dimensionality of the system.

Substituting the elliptic integrals $E(k_x)$ and $E(k_y)$ from (4.58) and the respective expression for f_y into (4.55) gives the energy of the ground state.

$$\mathcal{E}_{\min} = W_x l_x^2 f_x^2 + W_y l_y^2 f_y^2 - W_x \frac{1-k_x^2}{k_x^2} - W_y \frac{1-k_y^2}{k_y^2}$$
$$+ 2\nu\sqrt{W_x W_y} l_x l_y [f_x f_y - f_d(x) f_d(y)]. \tag{4.61}$$

In the case of quadratic symmetry, (4.61) reduces to

$$\mathcal{E}_{\min} = 2W\left(l^2 f^2 (1+\nu) - \frac{1-k^2}{k^2} - \nu l^2 f_d^2\right),$$

which for $k = 1$ gives the energy of the commensurate state

$$\mathcal{E}_{\min} = 2W l^2 f^2 (1+\nu), \tag{4.62}$$

in which the term $1+\nu$ containing the Poisson ratio accounts for the dimensionality of the system.

4.2.4.5 *Comparison of 2D and 1D models*

In order to compare numerically the 1D and 2D models, we have first to find a relation between the shear modulus G and the force constant γ. For a quadratic symmetry of the contact planes, this relation reads (van der Merwe 1973)

$$\gamma b = \mathbf{E} b^2,$$

where $\mathbf{E}$ is the Young modulus. The theory of elasticity (Hirth and Lothe 1968) gives the relationship between the Young and the shear moduli

$$\mathbf{E} = 2G(1+\nu).$$

Upon substitution, we find

$$\gamma = 2G(1+\nu)b. \tag{4.63}$$

Then, from (4.17) and (4.49) follows

$$l = \frac{l_0}{\sqrt{1-\nu^2}}. \tag{4.64}$$

From (4.37), (4.60), and (4.64), we find

$$f_s(2\mathrm{D}) = f_s(1\mathrm{D})\left(\frac{1-\nu}{1+\nu}\right)^{1/2}. \tag{4.65}$$

With a reasonable value for $\nu = 1/3$, $[(1-\nu)/(1+\nu)]^{1/2} = 1/\sqrt{2}$, or $f_s(2\mathrm{D}) = f_s(1\mathrm{D})/\sqrt{2}$. Recalling that $f_s(1\mathrm{D}) \cong 9\%$ with $l_0 = 7$, $f_s(2\mathrm{D}) \cong 6\%$, or in other words, the Poisson effect in 2D systems leads to the considerable decrease of the stability limit.

The dependence of the mean dislocation densities f_d on the natural misfit in the case of quadratic symmetry of the contact planes has the same behavior as shown in Fig. 4.14 (curve 2). The only exception is that it does not increase as steeply as the mean dislocation density $f_d(1\mathrm{D})$ in the 1D case.

Figure 4.18 demonstrates the dependence of the energy per atom in both the 1D and 2D models. The difference is more pronounced

Figure 4.18: Plots of the misfit energy per atom vs misfit in 1D model (curves 2 and 2′) and 2D model with quadratic symmetry (curves 1 and 1′). Curves 1 and 2 represent the ground-state energies. Curves 1′ and 2′ represent the energies when the misfit is completely accommodated by MDs ($\bar{b} = b$) and the HS is equal to zero (after van der Merwe 1975).

in the lowest energy state (curves 1 and 2). The difference of the energies when they are not in the ground state (curves 1′ and 2′) is due to the last term in Eq. (4.56) which vanishes at large misfits.

4.2.4.6 *Application of 1D model to thickening overlayer*

Obviously, the 1D Frenkel–Kontorova model is inadequate to describe the case of thickening overlayers as three very important factors are not taken into account. First, this is the rigidity of the substrate, which is believed to be valid for very thin deposits not exceeding a couple of MLs. The second is the strain gradient normal to the interface when the latter is resolved in a sequence of MDs. As long as the underlying ML is homogeneously strained to fit the substrate, the upper one is strained to the same degree. After breaking up of the commensurability, the amplitude of the periodic strain in every next ML is smaller than that of the previous one. The mathematical treatment of the problem is formidable (Stoop and van der Merwe 1973). Third, this is the Poisson effect in a direction normal to the interface. Obviously, if for example $b > a$ and at least part of the natural misfit is accommodated by HS, the overgrowth will be compressed in a direction parallel to the interface. At the same time, the overgrowth will be expanded in a direction normal to the interface.

Assuming as a first approximation that (i) the substrate is rigid, (ii) no strain gradient normal to the interface exists, and (iii) the normal strain due to the Poisson effect is negligible, one can obtain qualitative results which give a good enough impression concerning the properties of a "thick" overlayer (van der Merwe, Woltersdorf and Jesser 1986).

We simulate the thick overgrowth by 1D chains of atoms "piled up" one on top of the other. The film will, in general, be pseudomorphous with the substrate up to some critical thickness which is a function of the natural misfit. This follows from the fact that HS accumulates linearly with increasing film thickness and at some value of the latter the strain energy becomes greater than the energy of the MDs. Then, the commensurability breaks down and MDs are introduced at the interface. The HS is replaced by a periodic strain and the overgrowth lattice is relaxed in average. Obviously, if the misfit

is small, the critical thickness will be large and vice versa. The aim of this oversimplified model is to give some impression about the misfit dependence of the equilibrium critical thickness.

The thickness t of the film is then given by

$$t = t_n = nb, \tag{4.66}$$

where n denotes the number of atom chains "piled" up one on top of the other.

Another oversimplified assumption is concerned with the force constant or "rigidity" of the overlayer

$$\gamma_n = n\gamma. \tag{4.67}$$

Then,

$$l_n = \left(\frac{\gamma_n a^2}{2W}\right)^{1/2} = \left(\frac{n\gamma a^2}{2W}\right)^{1/2} = l_0\sqrt{n}. \tag{4.68}$$

Replacing l_0 by l_n in the 1D model gives the solution of the model of thick overlayer. Thus, the limit of stability becomes

$$f_s(n) = \frac{2}{\pi l_n} = \frac{2}{\pi l_0\sqrt{n}} = \frac{f_s}{\sqrt{n}}. \tag{4.69}$$

The commensurability breaks down when $k = 1$ and this happens at some critical thickness

$$n = n_c = \frac{t_c}{b} \tag{4.70}$$

at a misfit

$$f = f_s(n_c) = \frac{f_s}{\sqrt{n_c}}. \tag{4.71}$$

It follows from (4.70) and (4.71) that the equilibrium critical thickness beyond which the film will be no longer pseudomorphous with the substrate is

$$t_c = b\left(\frac{f_s}{f}\right)^2. \tag{4.72}$$

As follows from this oversimplified model, the critical thickness for pseudomorphous growth decreases steeply with increasing lattice misfit and goes to infinity when the misfit vanishes. This behavior

agrees qualitatively with the experimental evidence and, as will be shown below, appears as a better approximation for large misfits. Obviously, Eq. (4.72) cannot be compared quantitatively with experimental data but has one important advantage. It can be used to predict qualitatively the influence of the anharmonicity of the interatomic forces on the critical thickness of expanded and compressed epitaxial films as will be shown in Sec. 4.2.5.

4.2.5 *1D model with non-Hookean interatomic forces*

One of the basic restrictions of the model adopted originally by Frank and van der Merwe (1949) which makes it applicable for small lattice misfits only is the purely elastic interaction between neighboring atoms as a substitute of the real interatomic forces (see Fig. 4.7). This restriction can be relaxed by replacing the harmonic approximation with one of the more realistic pairwise potentials (4.1)–(4.3). Besides, one can use a combination of a Toda potential and a real potential such that the respective repulsive branches coincide. Then, they will differ only for values of r larger than r_0, and by comparison of the results, one can distinguish the purely anharmonic effects from those due to the nonconvexity of the real potentials. This is shown in Fig. 4.7 where the Toda potential is plotted with $\alpha = 2$ and $\beta = 6$ together with the generalized Morse potential (4.3) with $\mu = 4$, $\nu = 3$, and $V_0 = -1$. The repulsive branches are indistinguishable and the two potentials differ perceptibly only at $r > 1.2r_0$. Moreover, the harmonic approximations of both potentials coincide (the broken curve) so that we can refer our results to those obtained with the harmonic potential.

Making use of the Toda potential (4.4) and the substrate periodic potential (4.8), the potential energy of the chain reads (Milchev and Markov 1984; Markov and Milchev 1984a)

$$E = \sum_{n=0}^{N-2} \Big(\frac{\alpha}{\beta} \exp[-\beta a(\xi_{n+1} - \xi_n - f)] + \alpha a(\xi_{n+1} - \xi_n - f) - \frac{\alpha}{\beta} \Big) + \frac{W}{2} \sum_{n=0}^{N-1} (1 - \cos 2\pi\xi_n). \tag{4.73}$$

The equilibrium condition $\partial E/\partial \xi_n = 0$ leads to the set of equations

$$
\begin{aligned}
e^{-\beta a(\xi_1-\xi_0-f)} - 1 &= -\frac{\pi W}{\alpha a}\sin 2\pi\xi_0, \\
e^{-\beta a(\xi_{n+1}-\xi_n-f)} - e^{-\beta a(\xi_n-\xi_{n-1}-f)} &= \frac{\pi W}{\alpha a}\sin 2\pi\xi_n \qquad (4.74) \\
e^{-\beta a(\xi_{N-1}-\xi_{N-2}-f)} - 1 &= \frac{\pi W}{\alpha a}\sin 2\pi\xi_{N-1},
\end{aligned}
$$

which turns into the harmonic set (4.16) when expanding the exponents in the Taylor series up to the linear term at $\beta \to 0$.

In the continuous limit, the system (4.74) turns into an anharmonic analog of the sine-Gordon equation (Milchev and Markov 1984) and analytical solution can be found (Milchev 1986). On the other hand, the discrete system (4.74) can be easily solved numerically and the properties of the model studied.

The disparity in the structural properties of the overgrowth with respect to the sign of the misfit is clearly demonstrated in Fig. 4.19 (Markov and Milchev 1985) where the variation of the strains of the consecutive springs $\varepsilon_n = \xi_{n+1} - \xi_n - f$ is shown. As seen, the expanded dislocationless chain ($f = -10\%$) is in a much better fit with the substrate periodicity than is the compressed one ($f = 10\%$). Neglecting the deviations near the chain ends, the strains of the springs in the expanded chain are exactly equal to the absolute value of the lattice misfit. In compressed chains, however, the strains approach the lattice misfit but do not become equal to it. The latter means that an expanded overgrowth adheres more strongly to the substrate than the compressed one.

One of the most significant results of the anharmonic model is the split of the limits of stability f_s and metastability f_{ms} with respect to the misfit sign. As shown in Fig. 4.20 (Markov and Milchev 1984b), increasing the degree of anharmonicity β results in a reduction in the values of f_s and f_{ms} for compressed chains ($b > a$) and an increase in the absolute values of f_s and f_{ms} for expanded chains ($b < a$). The respective values for the harmonic model are given by the dashed lines. Thus, the harmonic limit of stability $f_s^{\mathrm{h}} = \pm 8.6\%$ splits into 6.7% and -12.2%, whereas the limit of metastability $f_{\mathrm{ms}}^{\mathrm{h}} = \pm 13.6\%$

Figure 4.19: Plot of the strains of the consecutive springs in compressed ($f = 10\%$) and expanded ($f = -10\%$) anharmonic Toda chain. (I. Markov and A. Milchev, *Surf. Sci.* **145**, 313 (1984). By permission of Elsevier Science Publishers B.V.)

splits into 10.2% and −23.2% at some average degree of anharmonicity $\beta = 6$. Therefore, a pseudomorphous overlayer can be in a state of stable (below f_s) or metastable (below f_{ms}) equilibrium up to quite different stability limits at positive and negative incompatibilities with the substrate.

Another very important conclusion which follows from the split of the critical misfits with respect to the misfit sign is connected with the critical thickness for pseudomorphous growth. As discussed above (Eq. (4.72)), the latter is qualitatively proportional to the square of the limit of stability f_s. It should be expected that the critical thickness for pseudomorphous growth will be 3–4 times greater when the

Figure 4.20: The characteristic split of the limits of stability f_s and metastability $f_{\rm ms}$ of the pseudomorphous state with the sign of the natural misfit when anharmonic (Toda) interactions between the overgrowth atoms are adopted. The critical misfits are plotted vs the degree of anharmonicity β of the Toda potential. The dashed lines give the critical misfits $f_s^{\rm h}$ and $f_{\rm ms}^{\rm h}$ in the harmonic approximation. (I. Markov and A. Milchev, *Surf. Sci.* **145**, 313 (1984). By permission of Elsevier Science Publishers B.V.)

natural misfit is negative rather than positive, if all other parameters remain unchanged. This prediction of the model seems particularly important for the epitaxial growth of semiconductor films and strained layer superlattices where the dangling bonds associated with the MDs have a deleterious effect on the properties of the corresponding heterojunctions. LPE grown $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}_y\mathrm{P}_{1-y}$ on InP(1 0 0) shows clear asymmetric behavior of the critical thickness for pseudomorphous growth with the sign of the misfit (Krasil'nikov *et al.*, 1988). The critical thickness of the expanded epilayers is always greater than that of the compressed epilayers (Fig. 4.21). The

Figure 4.21: Plot of the critical thickness for pseudomorphous growth vs the natural misfit of LPE grown $In_xGa_{1-x}As_yP_{1-y}$ on InP(1 0 0). The misfit is varied by changing the alloy composition. The asymmetrical behavior around a zero misfit has clearly been shown. (V. Krasil'nikov, T. Yugova, V. Bublik, Y. Drozdov, N. Malkova, G. Shepenina, K. Hansen and A. Rezvov, *Sov. Phys. Crystallogr.* **33**, 874 (1988)).

same is observed in MBE grown $In_xGa_{1-x}As$ on InP(1 0 0) (Franzosi *et al.*, 1986).

It follows that an epitaxial film with a given thickness and different values of the misfit in different crystallographic directions x and y can be pseudomorphous with the substrate when the absolute values of the negative misfit are even larger than the values of the positive misfit at a different epitaxial orientation. An excellent example is the deposition of tetragonal and hexagonal $MoSi_2$ (t-$MoSi_2$ and h-$MoSi_2$) on the (1 1 1) and (1 0 0) faces of Si, respectively (Chen, Cheng and Lin 1986; Lin and Chen 1986). In the first case, the epitaxial orientation is $(1\,1\,0)\langle 0\,0\,4\rangle_d \parallel (1\,1\,1)\langle 2\,0\,\bar{2}\rangle_s$, the values of the natural misfit are 2.34% and 2.21%, respectively, and the epitaxial interface is resolved in a hexagonal grid of MDs. In the latter case, the epitaxial orientation is $(\bar{2}\,4\,\bar{2}\,3)\langle 2\,\bar{1}\,\bar{1}\,2\rangle_d \parallel (0\,0\,1)\langle 2\,\bar{2}\,0\rangle_s$, $f_x = -2.89\%$, $f_y = -1.84\%$ and the film is pseudomorphous with the substrate.

Figure 4.22: Plot of the mean density of MDs of the ground state in the anharmonic Toda chain vs positive (dashed line) and negative (solid line) natural misfit. The curves are shown in one and the same quadrant for easier comparison. f_s^+ and f_s^- denote the corresponding limits of stability. The dotted line gives for comparison the mean dislocation density in the continuous harmonic model of Frank and van der Merwe (1949a). (I. Markov and A. Milchev, *Surf. Sci.* **145**, 313 (1984). By permission of Elsevier Science Publishers B.V.)

Even more illustrative is the case when the epitaxial orientation is $(1\,1\,1)\langle 1\,1\,\bar{2}\rangle_d \parallel (1\,1\,1)\langle 2\,0\,\bar{2}\rangle_s$ and the values of the misfit are 2.21% and −2.68%. Instead of a hexagonal grid of dislocations, which is expected on the base of the harmonic model, a set of parallel dislocation lines is observed. The film is partially pseudomorphous even though the absolute value of the negative misfit is larger than the value of the positive one.

Figure 4.22 shows the characteristic split of the misfit dependence of the mean dislocation density f_d with respect the misfit sign (Markov and Milchev 1984b). The stepwise behavior is due to the finite length of the chains used for the computation. It must not be confused with the "devil staircase" (Aubry 1983). As shown, f_d^- is always smaller than f_d^+, although the difference gradually decreases

at large natural misfits. It can also be seen that the harmonic approximation is much closer to the positive misfit curve. What is more important, however, is that the curves, although shifted from the harmonic one, preserve their continuous character. In other words, the transition from the pseudomorphous ($f_d = 0$) to the completely dislocated ($f_d = f$) state is gradual and there is a misfit interval in which HS and MDs coexist.

The misfit dependence of the ground state energy per atom is shown in Fig. 4.23 (Markov and Milchev 1984b) for both positive (the dashed line) and negative (the solid line) misfits. The curves consist of a series of curvilinear segments as in the harmonic case (see Fig. 4.16). The segments again correspond to the different number of MDs increasing from 0 by 1. It is seen that, in the case of compressed chain and particularly at small misfits, the energy is considerably higher. At larger misfits, the energy curves go closer and merge eventually. At low misfits, both positive and negative, the first sum in Eq. (4.73) (the strain energy) is dominant. At a positive misfit, the steeper repulsive branch of the interatomic potential is mainly involved and accordingly the energy is higher than in the case of a negative misfit, where the strain energy is determined by the weaker attractive part of the interaction. At larger misfits, both positive and negative, the second sum in (4.73) predominates and the energy difference between the two cases gradually vanishes. It is worth noting that the harmonic curve (not shown) is again much closer to the positive misfit curve. The above result is in agreement with the finding of Murthy and Rice (1990) that the interface energy of the low positive misfit couple Cu/Ni(0 0 1) ($f = 2.56\%$) is considerably greater than that of the negative misfit couple Ni/Cu(0 0 1) ($f = -2.49\%$).

It can be concluded that the negative misfit appears to be more favorable than the positive misfit for the epitaxial growth of thin films. If several epitaxial orientations are possible for a given overgrowth material on the same substrate plane, the orientation connected with the negative misfit should be favored as it is connected with lower energy. An example for that is the

Figure 4.23: Plot of the energy of the ground state per atom of the anharmonic Toda chain vs positive (dashed line) and negative (solid line) natural misfits. The separate curvilinear segments represent states with the different number of MDs denoted by the figure at each segment ($N = 30$, $\alpha = 2$, $\beta = 6$). (I. Markov and A. Milchev, *Surf. Sci.* **145**, 313 (1984). By permission of Elsevier Science Publishers B.V.)

orientation of Ag on GaAs(0 0 1) mentioned above (Massies and Linh 1982a,1982b,1982c). At temperatures lower than 200°C, the epitaxial orientation is $(1\,1\,0)\langle 1\,1\,1\rangle_{\mathrm{Ag}} \parallel (0\,0\,\bar{1})\langle \bar{1}\,1\,0\rangle_{\mathrm{GaAs}}$ with $f_x = 2.23\%$ and $f_y = -3.62\%$. At higher temperatures, the overgrowth is in parallel orientation $(0\,0\,1)\langle 0\,1\,0\rangle_{\mathrm{Ag}} \parallel (0\,0\,\bar{1})\langle 0\,1\,0\rangle_{\mathrm{GaAs}}$ and the lattice misfit in both orthogonal directions is negative $f_x = f_y = -3.62\%$.

Figure 4.24: Model of epitaxial interface between two semi-infinite crystals resolved in a sequence of MDs spaced at an average distance p. The dashed lines located at a distance $p/2$ from the contact plane show the boundary beyond which the periodic strains originating from the dislocations practically vanish (after van der Merwe 1950).

4.2.6 *van der Merwe model of thick overgrowth*

The case of thick overgrowth is considered in a more or less similar way. By "thick" we mean mathematically infinite. In this case (Fig. 4.24), the two crystal halves A and B with the quadratic symmetry of the contact planes and atomic spacings a and b, respectively, are considered as elastic continua with shear moduli G_{a} and G_b and Poisson ratios ν_{a} and ν_b, respectively (van der Merwe 1963a). An important feature of the system consisting of two semi-infinite crystals is that the HS is equal to zero and the natural misfit is accommodated entirely by MDs. As shown in Sec. 4.2.4.4, the energy of a cross grid of MDs of an edge type to the first approximation represents a sum of two arrays of dislocations parallel to the two orthogonal directions. In other words, the energies of the two arrays are additive and we can consider them independently assuming a misfit in one direction only.

Here, we allow both crystals to be elastically strained. In order to describe the displacements at either side of the interface, we introduce a reference lattice C with a parameter c (van der Merwe 1950,

1973) along the x axis.

$$Pb = (P+1)a = \left(P + \frac{1}{2}\right)c,$$

where $P = a/(b-a)$ is an integer.

Assuming for definiteness that $b > a$, we can imagine that the two lattices A and B are generated from C by the contraction of A and expansion of B. Then, the reference lattice spacing reads

$$\frac{2}{c} = \frac{1}{a} + \frac{1}{b}$$

or

$$c = \frac{ab}{(1/2)(a+b)}. \tag{4.75}$$

The vernier of misfit or the dislocation spacing p is given by

$$p = \left(P + \frac{1}{2}\right)c = \frac{ab}{(b-a)}. \tag{4.76}$$

Bearing in mind that both lattices A and B are strained, it is reasonable to define the misfit as

$$f = \frac{c}{p} = \frac{b-a}{(1/2)(a+b)} \tag{4.77}$$

rather than as $f = 1/P = (b-a)/a$ as in the rigid substrate model.

Assume now that the atoms of A and B are located at points of the reference lattice and there is an atom of B exactly opposite to an atom of A. Then, we allow the atoms of A and B to occupy their natural positions in their respective lattices. The atoms of A and B will be displaced with respect to the respective positions of the reference lattice C. The displacement between the atoms with respect to each other will be

$$U = \frac{c}{2} + \frac{c}{p}x,$$

where the first term $c/2$ locates the origin of the x-axis at a dislocation line, while the second term cx/p accounts for the linear increase of the atom spacing due to the vernier of misfit. If we now allow elastic displacements $u_{\mathrm{a}}(x)$ and $u_b(x)$ of the corresponding atoms of

the A and B lattices, then the displacement of a B atom with respect to the corresponding A atom will be

$$U = \frac{1}{2}c + \frac{c}{p}x + u_b(x) - u_\mathrm{a}(x). \tag{4.78}$$

As in the previous case (Eq. (4.8)), each crystal half exerts a periodic potential on the atoms of the other half in the form

$$V = \frac{G_\mathrm{i}c^2}{4\pi^2 d}\left[1 - \cos\left(2\pi\frac{U}{c}\right)\right], \tag{4.79}$$

where G_i is the shear modulus at the interface and $d \cong c$ is the separation of the atoms of the adjoining crystal planes.

The mathematical treatment of the problem, although connected with much greater difficulties, leads to the expressions for U similar to (4.20) and (4.23). Thus, for dislocations far apart ($b \to a$, $p \to \infty$) and, assuming for simplicity $\nu_\mathrm{a} = \nu_b = \nu$ and $G_\mathrm{a} = G_b = G_\mathrm{i} = G$, the solution reads

$$\frac{U}{c} = \frac{1}{2} + \frac{1}{\pi}\arctan\left(\frac{x}{x_0}\right), \tag{4.80}$$

where $x_0 = c/2(1-\nu)$.

The general solution reads (van der Merwe 1975)

$$\frac{U}{c} = \frac{1}{2} + \frac{1}{\pi}\arctan\left[\left(\sqrt{1+\lambda^{-2}} + \lambda^{-1}\right)\tan\left(\pi\frac{x}{p}\right)\right], \tag{4.81}$$

where

$$\lambda = 2\pi\frac{G'}{G_\mathrm{i}}\frac{c}{p} \tag{4.82}$$

and

$$\frac{1}{G'} = \frac{1-\nu_\mathrm{a}}{G_\mathrm{a}} + \frac{1-\nu_b}{G_b}. \tag{4.83}$$

It is immediately seen that (4.80) can be easily obtained in the limit $p \to \infty$ with $G_\mathrm{a} = G_b = G_\mathrm{i}$. Equations (4.80) and (4.81) show a behavior similar to that plotted in Fig. 4.12, curves 1 and 2, respectively. In other words, as in the case of a ML overgrowth, the interface is resolved in a sequence of MDs.

The energy of the MDs (the HS is absent) is naturally divided into two parts. The first is the energy of interaction between the atoms of the two crystal halves:

$$E_{\mathrm{i}} = \frac{1}{p}\int_{-p/2}^{p/2} \frac{G_{\mathrm{i}}c^2}{4\pi^2 d}\left[1-\cos\left(2\pi\frac{U}{c}\right)\right]dx$$
$$= \frac{G_{\mathrm{i}}c^2}{4\pi^2 d}\left(1+\lambda-\sqrt{1+\lambda^2}\right), \tag{4.84}$$

which is obtained by the substitution of (4.81) in the integral of (4.84) and carrying out the integration.

The second is the energy of the periodic elastic strain which is distributed in the two crystal halves A and B. For the average strain energy per atom stored in that part of the crystal B which extends from the interface to a distance h from the latter, one obtains

$$E_e^b(h) = -\frac{(1-\nu_b)c^2G'G_{\mathrm{i}}}{4\pi^2 G_b d}$$
$$\times\lambda\left[\ln\left(\frac{1-A^2}{1-A^2e^{-2\mathrm{H}}}\right)+\frac{HA^2e^{-2H}(H-1+A^2e^{-2\mathrm{H}})}{(1-\nu_b)(1-A^2e^{-2\mathrm{H}})^2}\right], \tag{4.85}$$

where

$$H = 2\pi\frac{h}{p}$$

and

$$A = \sqrt{1+\lambda^2}-\lambda.$$

The limit $H\to\infty$ gives the total strain energy per atom in the crystal B:

$$E_e^b = -\frac{(1-\nu_b)c^2G'G_{\mathrm{i}}}{4\pi^2 G_b d}\ln(1-A^2)$$
$$= -\frac{(1-\nu_b)c^2G'G_{\mathrm{i}}}{4\pi^2 G_b d}\lambda\ln\left(2\lambda\sqrt{1+\lambda^2}-2\lambda^2\right). \tag{4.86}$$

The analogous expression can be written down for the strain energy per atom stored in the crystal A. The ratio of the strain

energies gives the distribution of the strain in the two crystal halves:

$$\frac{E_e^b}{E_e^{\mathrm{a}}} = \frac{(1-\nu_b)G_{\mathrm{a}}}{(1-\nu_{\mathrm{a}})G_b}.$$

As seen, the "stiffer" the crystal, the less strained it is and vice versa.

Bearing in mind (4.83), the total strain energy per atom in the bicrystal connected with the MDs is

$$E_e = E_e^b + E_e^{\mathrm{a}} = -\frac{G_{\mathrm{i}}c^2}{4\pi^2 d}\lambda \ln\Big(2\lambda\sqrt{1+\lambda^2} - 2\lambda^2\Big). \tag{4.87}$$

Summing up (4.84) and (4.87) gives the total energy per atom of the MDs

$$E_d = \frac{G_{\mathrm{i}}c^2}{4\pi^2 d}\Big[1+\lambda-\sqrt{1+\lambda^2} - \lambda\ln\Big(2\lambda - \sqrt{1+\lambda^2} - 2\lambda^2\Big)\Big]. \tag{4.88}$$

The energies E_e, E_{i}, and E_d are plotted as a function of the misfit c/p in Fig. 4.25. As can be seen, the strain energy E_e is greater than the energy of interaction E_{i} for small misfits. At larger misfits, E_e gradually diminishes and the total energy approaches a constant value

$$E_d^{\infty} = \frac{G_{\mathrm{i}}c^2}{4\pi^2 d}, \tag{4.89}$$

which can be taken as a measure of the interfacial bonding, analogous to W in the ML model. This should be the energy if the two lattices A and B were assumed rigid. Then, the relative displacements of the atoms with respect to each other would be given by $U/c = 1/2 + x/p$.

One of the most important results of this analysis, which is closely connected with the mechanism of growth of thin films, is concerned with the distribution of strain energy with the distance from the interface. Making use of (4.85) and (4.86) gives for the fraction of average strain energy per atom stored beyond a distance h from the

Figure 4.25: Misfit dependence of the strain energy E_e, the interaction energy E_i, and the total dislocation energy $E_d = E_e + E_i$, in units of $G_i c^2/4\pi^2 d$. The upper axis shows the variation of the parameter λ (after van der Merwe 1950).

interface

$$\Delta E_e^b(h) = \frac{E_e^b - E_e^b(h)}{E_e^b}$$
$$= \left(\ln(1 - A^2 e^{-2\mathrm{H}}) - \frac{HA^2 e^{-2\mathrm{H}}(H - 1 + A^2 e^{-2\mathrm{H}})}{(1 - \nu_b)(1 - A^2 e^{-2\mathrm{H}})^2}\right)$$
$$\times [\ln(1 - A^2)]^{-1}. \tag{4.90}$$

The latter is plotted in Fig. 4.26. As shown, it decreases rapidly with the distance from the interface and practically vanishes at a distance equal to $p/2$. It follows that, first, we can qualify a deposit as thick when it is thicker than half of the dislocation spacing, and second, beyond this thickness the atoms of the deposit will not "feel" the presence of the foreign substrate.

Figure 4.26: Plots of the fraction $\Delta E_e^b(h)$ of the strain energy stored in the crystal B beyond a distance h from the contact plane as a function of h/p. Curves 1 and 2 correspond to misfits $c/p = 2\%$ and 20%, respectively ($G_a = G_b = G_i$, $\nu_a = \nu_b = \nu = 0.3$) (after van der Merwe 1975).

The gradual decrease of the fraction of the elastic energy $\Delta E_e^b(h)$ which is stored in the deposit crystal beyond a distance h from the interface is illustrated schematically in Fig. 4.27. The amplitude of the periodic variation of the bond strains is greatest for the first ML. Expansion and compression alternate periodically with a period equal to the dislocation spacing. The amplitude gradually decreases in every next ML. Beyond a thickness $h \cong p/2$, the amplitude becomes practically equal to zero and the atoms become equidistant. However, if the deposited film is thinner than $p/2$, a periodic variation of the bond lengths on the surface of the film should be detected. Such a variation is really observed on the surface of the overlayers of Fe(1 1 0) on W(1 1 0) (Gradmann and Waller 1982) and of Cu on Pd(1 0 0) (Asonen *et al.*, 1985). In the former case, the thickness of the film samples varied between 2 and 9 MLs and $p/2 = 7d_{110}$ ($a_{Fe} = 2.866$ Å, $a_W = 3.165$ Å).

Let us illustrate the formulae we have just derived. In a system of low misfit, e.g., Ag on Au(0 0 1), $a_{Ag} = 2.8894$ Å and $a_{Au} = 2.8841$ Å, $c/p = 0.00184$, $c = d = 2.8867$ Å, $G_{Ag} = 3.38 \times 10^{11}$ dyne

Figure 4.27: Schematic plot of the strains of consecutive bonds against the atom displacements as shown in Fig. 4.13 (curve 2) demonstrating the gradual decrease of the amplitude of the periodic strain with the distance from the contact plane. The figure at each curve denotes the number of the corresponding ML counted from the contact plane.

cm^{-2} and $G_{\mathrm{Au}} = 3.1 \times 10^{11}$ dyne cm^{-2}, $\nu_{\mathrm{Ag}} = 0.354$, and $\nu_{\mathrm{Au}} = 0.412$ (Huntington 1958; see also Hirth and Lothe, 1968, Appendix), $G' = 2.63 \times 10^{11}$ dyne cm^{-2} and $G_{\mathrm{i}} \cong (G_{\mathrm{Ag}} G_{\mathrm{Au}})^{1/2} = 3.24 \times 10^{11}$ dyne cm^{-2}. Then, $G_{\mathrm{i}} c^2/4\pi^2 d = 237$ erg cm^{-2}, $\lambda = 0.0094$, and $E_d \cong 11$ erg cm^{-2}. In a system with a larger misfit, e.g., Ag on Cu(0 0 1), with $G_{\mathrm{Cu}} = 5.46 \times 10^{11}$ dyne cm^{-2}, $\nu_{\mathrm{Cu}} = 0.324$, and $a = 2.556$ Å, $c/p = 0.1223$, $\lambda = 0.568$, $G_{\mathrm{i}} c^2/4\pi^2 d = 294$ erg cm^{-2}, and $E_d = 192$ erg cm^{-2}.

It is doubtful whether the above theory can be used in the case of semiconductor materials with covalent bonds which are rather brittle and unflexible. Nevertheless, for the case of a Ge deposit on Si(0 0 1), with $G_{\mathrm{Ge}} = 5.64 \times 10^{11}$ dyne cm^{-2}, $G_{\mathrm{Si}} = 6.42 \times 10^{11}$ dyne cm^{-2}, $\nu_{\mathrm{Ge}} = 0.2$, $\nu_{\mathrm{Si}} = 0.215$, $a_{0,\mathrm{Ge}} = 5.6575$ Å, and $a_{0,\mathrm{Si}} = 5.4307$ Å, $c/p = 0.041$, $G_{\mathrm{i}} \cong 6 \times 10^{11}$ dyne cm^{-2}, $G' = 3.78 \times 10^{11}$ dyne cm^{-2}, and $E_d \cong 300$ erg cm^{-2}. Comparing these results with the

values of the specific surface energies which are usually of the order of 1×10^3 erg cm^{-2}, we can conclude that the theory of van der Merwe predicts reasonable values for the energy of the MDs at the interface between semi-infinite crystals.

It is worth noting, however, that a comparison of the energy of the MDs with surface energies is in principle incorrect. The energy of the MDs is often erroneously identified with the energy of the interface. As will be shown below, the energy of the MDs is only a part of the energy of the interface which is due to the lattice misfit. The interfacial energy is composed of two parts. The first one is due to the difference in nature and strength of the chemical bonds in the absence of misfit. The second part, which we have just derived, is due to the lattice misfit. A good example is the energy of the interface between $In_xGa_{1-x}As$ and InP(0 0 1). When $x = 0.47$, the lattice misfit and the misfit energy are equal to zero. At the same time, the interfacial energy is not equal to zero owing to the difference of the strength of the chemical bonds in both materials.

4.2.7 *Thickening overgrowth*

As shown above, a thin film consisting of one to several MLs can be either commensurate or incommensurate with the substrate. In other words, the natural misfit can be accommodated either by HS or by MDs or by both in the general case. In contrast, the natural misfit between an infinitely thick deposit and the substrate is accommodated entirely by MDs. Thus, in overgrowth with finite thickness, the HS can eliminate partially or entirely the MDs. The purpose of this chapter is to study what will be the equilibrium (lowest energy) structure of the interface during the process of thickening of the deposit.

As mentioned above, owing to the interaction across the interface, the lattice parameter b of the overgrowth tends to take the value of the substrate lattice parameter a. On the other hand, owing to the cohesive forces between the overgrown atoms, they tend to keep their natural spacing b. As a result, the atoms will be spaced at some average spacing $\bar{b}$ such that $a < \bar{b} < b$.

We can define now the natural misfit as (Matthews 1975)

$$f = \frac{a-b}{b}, \tag{4.91}$$

and it will be accommodated partly by HS

$$f_e = \frac{\bar{b}-b}{b} \tag{4.92}$$

and partly by MDs

$$f_d = \frac{a-\bar{b}}{b} \tag{4.93}$$

so that for small misfits

$$f_e + f_d \cong \frac{\bar{b}-b}{b} + \frac{a-\bar{b}}{b}\frac{\bar{b}}{b} = f. \tag{4.94}$$

The MDs will be spaced in the general case at a distance

$$\bar{p} = \frac{a}{f_d} = \frac{a\bar{b}}{a-\bar{b}} \tag{4.95}$$

and will have a Burger's vector

$$\bar{c} = \frac{a\bar{b}}{(1/2)(a+\bar{b})}. \tag{4.96}$$

Minimum energy considerations of epitaxial bicrystal systems (van der Merwe 1963b; Jesser and Kuhlmann-Wilsdorf 1967) have shown that initially the deposit grows pseudomorphically with the substrate up to a critical thickness t_c (see Eq. (4.72)). The natural misfit will be entirely accommodated by a HS so that the average atomic spacing $\bar{b} = a$. Then, $f_e = f$ and $f_d = 0$. The interface is not resolved into a sequence of MDs as their spacing $\bar{p}$ tends to infinity. In the case of square atomic meshes of the adjoining crystal planes, the energy of the interface due to the lattice misfit will be equal to the energy of the HS E_{hs} given by

$$E_{\text{hs}} = 2G_b t f^2 \frac{1+\nu_b}{1-\nu_b}. \tag{4.97}$$

Beyond the critical thickness, MDs are introduced at the interface so that initially HS and MDs coexist. The MDs energy is then given by Eq. (4.88) but with p and c replaced by $\bar{p}$ and $\bar{c}$. With the

Figure 4.28: Plot of the dislocation energy E_d and the energy of the HS $E_{\rm hs}$ vs misfit of overlayers with different thicknesses shown by the figures which denote the number of MLs. The points of intersection determine the critical misfits f_n ($n = 1, 2,...$) which decrease with increasing film thickness given in number n of MLs. (I. Markov and S. Stoyanov, *Contemp. Phys.* **28**, 267 (1987). By permission of Taylor & Francis Ltd.)

thickening of the film, the HS gradually vanishes, and in sufficiently thick film ($t > p/2$), the natural misfit is totally accommodated by MDs. Then, $\bar{b} = b$, $f_e = 0$, $f_d = f$ and the dislocations are separated by a distance p. In other words, the other extreme case is reached.

In order to illustrate the minimum energy considerations, we plot the HS energy $E_{\rm hs}$ for films of various thickness and the MDs energy E_d against the misfit as has been done in Fig. 4.28. As we see, the HS energy curves intersect the MDs energy curve at some critical values of the misfit f_n varying with film thickness $n = t/b$ measured in the number of MLs. It follows that if $f > f_1$, $E_{\rm hs}$ is greater than E_d even for a ML film, and it will resolve into a sequence of MDs rather than be homogeneously strained. If $f_2 < f < f_1$, the first ML will be pseudomorphous with the substrate, but when a second ML is deposited on top of the first one, MDs will be introduced at the interface to relieve the HS if the necessary thermal activation exists. The smaller the natural misfit, the thicker the film can grow under HS. When

the misfit is very small, the film can grow under HS to a considerable thickness as in the growth of Ge on GaAs (Matthews, Mader and Light 1970). For this reason, superlattices such as $Al_xGa_{1-x}As/GaAs$ can be grown without MDs at the interface. If the temperature is low enough so that MDs are not introduced during the growth, then when the film thickness exceeds the critical value, the bicrystal system will be in a metastable state and any pumping of energy will lead to the nucleation of dislocations and, hence, to the deterioration of the performance of any device made in this way.

Equating the energy $2E_d$ of a square grid of two perpendicular and noninteracting arrays of MDs from (4.88) and the energy $E_{\rm hs}$ of the HS from (4.97) gives ($\nu_{\rm a} = \nu_b = \nu$)

$$\frac{t_c}{c} = \frac{G_{\rm i}}{8\pi^2 G_b}\frac{1-\nu}{1+\nu}\frac{f(\lambda)}{f^2}, \tag{4.98}$$

where

$$f(\lambda) = 1 + \lambda - \sqrt{1+\lambda^2} - \lambda \ln\Big(2\lambda\sqrt{1+\lambda^2} - 2\lambda^2\Big). \tag{4.99}$$

For small misfits where second-order terms can be neglected ($\lambda^2 \ll 1$), (4.99), reduces to

$$f(\lambda) = \lambda(1 - \ln 2\lambda) = \lambda(\ln e - \ln 2\lambda) = \lambda \ln\Big(\frac{e}{2\lambda}\Big),$$

which appears as a very good approximation (Kasper and Herzog 1977).

Accounting for (4.82) and (4.83), Eq. (4.98) turns into (van der Merwe 1973)

$$\frac{t_c}{c} = \frac{1}{4\pi(1+\nu)(1+G_b/G_{\rm a})}\frac{\mathcal{Q} - \ln f}{f}, \tag{4.100}$$

where

$$\mathcal{Q} = \ln\Big(\frac{(1-\nu)(1+G_b/G_{\rm a})G_{\rm i}e}{4\pi G_b}\Big). \tag{4.101}$$

Figure 4.29: Misfit dependence of the equilibrium critical thickness for pseudomorphous growth in units of the Burger vector c according to the theory of van der Merwe (1973) (curve 1) (Eq. (4.100) with $G_a = G_b = G_i$, $\nu_a = \nu_b = \nu = 0.3$) and the Volterra approach of Matthews (Matthews and Blakeslee 1974) (curve 2) (Eq. (4.108) with $G_s = G_d$, $\nu = 0.3$).

Equation (4.100) is plotted in Fig. 4.29 (curve 1) with $G_a = G_b = G_i$. As shown, the critical thickness goes to infinity with the vanishing misfit. Moreover, it decreases with increasing ratio G_b/G_a. In other words, the "stiffer" the deposit and the "softer" the substrate crystals, the lower the critical thickness will be, and vice versa. A similar analysis for finding t_c for crystals with the diamond lattice has been performed by Kasper and Herzog (1977).

Let us evaluate the critical thickness for some real systems. In the case of deposition of Ag on Au with the material constants given in Eq. (4.98) predicts $t_c/c = 168$ or $t_c \cong 485$ Å. In the case of deposition of Ag on Cu, $t_c/c = 0.7$ or dislocations will be introduced after the deposition of the first ML. The theory predicts the value $t_c/c = 5.7$ for the system Ge/Si. This means that a film consisting of five MLs should be pseudomorphous with the substrate, but after the deposition of the sixth ML, the interface should resolve in a cross grid of MDs.

An example of interest is the deposition of alloys where one could change the value of the natural misfit by varying the alloy composition. One of the most studied systems is Ge_xSi_{1-x}/Si (Kasper and Herzog 1977; Kohama, Fukuda and Seki 1988; Bean *et al.*, 1984; Bean 1985). The natural misfit as a function of composition x is given by $f = 0.041x$. Thus, at $x = 0.5$, $f = 0.021$ and the experimentally found critical thickness is 100 Å or about 25 MLs (Bean 1985). The calculations based on Eq. (4.98) give the value $t_c/c = 9$, i.e., approximately three times smaller than the experimentally found value.

The above disagreement can be explained bearing in mind that Eq. (4.98) gives the equilibrium critical thickness for pseudomorphous growth. In other words, this is the thickness beyond which the MDs become energetically favored. However, in real experiments, an energetic barrier for the nucleation of dislocations should be overcome. It follows that the real critical thickness should be greater than that given above. The nucleation of the MDs has been taken into account in a series of papers (Marée *et al.*, 1987; Van de Leur *et al.*, 1988; Fukuda, Kohama and Ohmachi 1990; Kamat and Hirth 1990) and the interested reader is referred to them.

Recalling (4.65), we conclude that the approximate expression for $t_c(f)$ given by Eq. (4.72) is, in fact, determined by the intersection of the HS energy (Eq. (4.97)) with the maximum energy of the MDs E_d^∞ given by Eq. (4.89). Obviously, it overestimates the critical thickness.

(a) (b) (c)

Figure 4.30: Volterra models of (b) screw and (c) edge dislocations based on the consideration of a hollow cylinder (a) with outer diameter R and inner diameter r_0 cut parallel to the cylinder axis (after Hirth and Lothe 1968).

4.2.8 *The Volterra approach*

At the beginning of 20th century, the Italian mathematician Vito Volterra (1907) considered the elastic properties of a hollow cylinder with inner and outer diameters r_0 and R, respectively, cut parallel to the cylinder axis (Fig. 4.30(a)). When a force parallel to the cylinder axis is applied along the cut, a screw dislocation is formed (Fig. 4.30(b)). When the force applied is normal to the cylinder axis and the one edge of the cut is displaced normally with respect to the other, an edge dislocation results (Fig. 4.30(c)). The displacement along the cut of the one-half of the cylinder with respect to the other is just equal to the Burger vector of the dislocation.

The strain energy of the edge dislocation per unit length is given by (Hirth and Lothe 1968)

$$E_s = \frac{Gb^2}{4\pi(1-\nu)} \ln\left(\frac{R}{r_0}\right),$$

where G is the shear modulus of the crystal, ν is the Poisson ratio, and b is the magnitude of the Burger vector. The total energy is obtained by the addition of the core energy. The latter represents a fraction of Gb^2 and its contribution is formally accounted for by assuming $r_0 = b/\alpha$, where α is a constant varying from 1 to 2 for metals and to 4 for nonmetals. Then, the total energy of an edge

dislocation reads

$$E_d = \frac{Gb^2}{4\pi(1-\nu)}\left(\ln\frac{R}{b} + \ln\alpha\right). \tag{4.102}$$

For the energy of the MDs between two misfitting crystals with shear moduli G_s and G_d and a Poisson ratio ν, Matthews (1975) used a similar expression

$$E_d = \frac{G_s G_d c^2}{2\pi(G_s+G_d)(1-\nu)}\left[\left(\ln\frac{R}{c}\right)+1\right], \tag{4.103}$$

which turns into (4.102) with $G_d = G_s = G$ and $\alpha = e$. R denotes the distance to the outermost boundary of the strain field of the dislocation, and c, which is given by Eq. (4.75), is the magnitude of the Burger vector.

If the film thickness t is smaller than the dislocation spacing $p/2$, R can be approximated by the film thickness t (Fig. 4.31(a)) and the energy reads

$$E_d = \frac{G_s G_d c^2}{2\pi(G_s+G_d)(1-\nu)}\left[\left(\ln\frac{t}{c}\right)+1\right]. \tag{4.104}$$

In the other extreme $t > p/2$, R is approximated by $p/2$ (Fig. 4.31(b)). This choice of R becomes immediately understandable

Figure 4.31: For the determination of the outermost boundary R of the strain field created by the dislocation. (a) $t < p/2$, $R = t$; (b) $t > p/2$, $R = p/2$ (t: film thickness, p: dislocation spacing).

if one recollects the fact that the strain field of the dislocations practically vanishes beyond $p/2$ (see Fig. 4.26). Then, the energy reads

$$E_d = \frac{G_s G_d c^2}{2\pi(G_s + G_d)(1-\nu)}\left[\ln\left(\frac{p}{2c}\right) + 1\right]. \tag{4.105}$$

In the case of quadratic interfacial symmetry ($f_x = f_y = f$) and assuming the natural misfit is accommodated partly by MDs and partly by HS, the energy E_m due to the lattice misfit is a sum of the energy of two noninteracting arrays of MDs each one with a density $f_d = f - f_e$ and the energy of the HS E_{hs} given by Eq. (4.97). Neglecting the energy of interaction between neighboring dislocations in the array, one writes

$$E_m = 2(f - f_e)\frac{G_s G_d \bar{c}}{2\pi(G_s + G_d)(1-\nu)}\left[\ln\left(\frac{\bar{R}}{\bar{c}}\right) + 1\right] + 2G_d t f_e^2 \frac{1+\nu}{1-\nu},$$

where $\bar{R} = t$ or $\bar{p}/2$ when t is smaller or greater than $\bar{p}/2$.

The condition $\mathrm{d}E_m/df_e = 0$ yields the HS f_e^* which minimizes the energy. In the first case ($t < \bar{p}/2$ and $\bar{R} = t$) for f_e^*, one obtains

$$f_e^* = \frac{G_s \bar{c}}{4\pi(G_s + G_d)(1+\nu)t}\left[\ln\left(\frac{t}{\bar{c}}\right) + 1\right]. \tag{4.106}$$

In the second limiting case ($\bar{R} = \bar{p}/2$ and $\bar{c}/\bar{p} = f_d = f - f_e$), the minimization gives

$$f_e^* = -\frac{G_s \bar{c}}{4\pi(G_s + G_d)(1+\nu)t}\ln[2(f - f_e^*)]. \tag{4.107}$$

The critical thickness t_c is determined by the condition $f_e = f$. Making use of Eq. (4.106) (the equilibrium thickness is usually smaller than $p/2$) gives

$$\frac{t_c}{\bar{c}} = \frac{G_s}{4\pi(G_s + G_d)(1+\nu)f}\left[\ln\left(\frac{t_c}{\bar{c}}\right) + 1\right]. \tag{4.108}$$

Equation (4.108) gives values for the critical thickness very close to that predicted by the theory of van der Merwe (see Fig. 4.29,

curve 2). One should, however, note the uncertainty in the determination of the core energy of the dislocations.

Thus, the main advantage of the Volterra approach consists in the simplicity of the expression for the dislocation energy which allows the easy treatment of more difficult problems such as the equilibrium structure of the interface between tile-shaped 3D islands and the substrate (Matthews, Jackson and Chambers 1975c), in multilayers (Matthews and Blakeslee 1974), imperfect dislocations with Burger's vectors inclined with respect to the interface, generation of MDs, etc. (Matthews 1975a, 1975b). The interested reader is referred to the review paper of Matthews (1975b) and the references therein.

As mentioned in the previous section, a considerable discrepancy is established when experimental data are compared with the theoretical expressions for the critical thickness for pseudomorphous growth. On the other hand, the problem of the critical thickness for pseudomorphous growth turned out to be very important from technological point of view. The reasons are well described in the review paper of Hu (1991). First, the MDs deteriorate the performance of the heterostructure devices due to the increased leakage current. On the other hand, the MDs are often generated by dislocations which are inherited from the substrate and end at the film surface (threading dislocations). The diffusion of the dopant is usually enhanced along the threading dislocation line and the latter forms the so-called "transistor pipe" connecting the emitter and the collector. Second, in uniformly strained epilayers, the interatomic spacing differs from that in unstrained (relaxed) ones, thus changing the width of the forbidden energy zone (Land *et al.*, 1985). It is, thus, obvious that the HS can serve, in addition to the alloy composition, as a parameter for further tailoring of the heterostructure properties.

What both approaches of van der Merwe (1963b) and Matthews (1975b) to the problem of the critical thickness have in common is that the latter is inversely proportional to the lattice misfit. Recently, People and Bean (1985, 1986) derived an expression for the critical thickness comparing the energies of the HS and the areal energy of a single-screw dislocation. They found that the critical thickness is inversely proportional to the square of the lattice misfit and has an

absolute value which is of one order of magnitude greater than that predicted by van der Merwe and Matthews. As their result is still under discussion (see Hu 1991), we will not reproduce it here. The reader who is interested in the present day state of the problem of the critical thickness for pseudomorphous growth is referred to the excellent review paper of Hu (1991).

4.3 Mechanism of Growth of Epitaxial Films

4.3.1 *Classification of the growth modes*

As mentioned in the introduction of this chapter, the difference between the crystal growth and the epitaxial growth is of purely thermodynamic nature. The chemical potential of the film differs from that of the infinitely large deposit crystal owing to the difference of bonding across the interface (see Eq. (1.59)), on the one hand, and to the difference of lattices and/or lattice parameters, on the other. The atoms of the deposit can be bound more loosely or more tightly to the substrate atoms than to the atoms of the same crystal. As a result, the chemical potential (or what is the same, the equilibrium vapor pressure) of the first layers of the deposit will be higher or lower than the chemical potential (the equilibrium vapor pressure) of the infinitely large deposit crystal. In other words, the chemical potential of the overlayer $\mu(n)$ will vary with the film thickness due to the interaction with the substrate.

In addition, the overgrowth can be pseudomorphous with the substrate or the interface can be resolved in a grid of MDs. Then, the film can be homogeneously or periodically strained and the strain energy per atom should change the chemical potential of the film. The HS does not change from ML to ML of the overgrowth, whereas the periodic strain due to the MDs attenuate with the distance from the interface (see Figs. 4.26 and 4.27). Hence, the chemical potential again varies with film thickness owing to the elastic strains in addition to the bonding with the substrate (Venables 1979; Kern, LeLay and Metois 1979; Stoyanov 1986; Markov and Stoyanov 1987; Grabow and Gilmer 1988). It is namely this interplay of misfit and interfacial bonding which constitutes the main difference of the epitaxial

Figure 4.32: Schematic representation of the three possible mechanisms of growth of thin epitaxial films according to the classification of Bauer (1958): (a) Volmer–Weber mechanism or island growth, (b) Frank–van der Merwe mechanism ot layer-by-layer growth, and (c) Stranski–Krastanov mechanism or layer-by-layer growth followed by 3D islands. (I. Markov and S. Stoyanov, *Contemp. Phys.* **28**, 267 (1987). By permission of Taylor & Francis Ltd.)

growth from the usual crystal growth and which leads to the appearance of the three well-known mechanisms of epitaxial growth that are known in the literature: (i) *Volmer–Weber* (VW) mechanism or island growth (Fig. 4.32(a)), (ii) *Frank–van der Merwe* (FM) mechanism or layer-by-layer growth (Fig. 4.32(b)), and (iii) *Stranski–Krastanov* (SK) mechanism or layer-by-layer growth followed by the formation of isolated 3D islands (Fig. 4.32(c)).

This classification has been given for the first time by Bauer (1958) on the basis of a detailed thermodynamic analysis of the wetting of the substrate by the deposit material. A simple criterion in terms of surface energies was derived which, in fact, follows from Eq. (1.70) for the equilibrium shape of the deposit crystal. The change of the surface energy $\Delta\sigma = \sigma + \sigma_i - \sigma_s$, which accompanies the film deposition, is, in fact, a measure of the wetting. In the case of incomplete wetting

$$\sigma_s < \sigma + \sigma_i, \tag{4.109}$$

the film grows as 3D islands (VW mode). On the contrary, the complete wetting

$$\sigma_s > \sigma + \sigma_i \tag{4.110}$$

favors the layer-by-layer (FM) growth if the misfit is negligible, or the Stranski–Krastanov mode at the perceptible misfit.

The historical reason the island growth was named after Volmer and Weber was that Volmer was the first to develop the theory of the rate of 3D nucleation on a foreign substrate and together with Weber (Volmer and Weber 1926) interpreted the experimental data of Frankenheim (1836), which were the first laboratory experiments on epitaxial growth, in the light of his theory.

Frank and van der Merwe simulated the overgrowth by an infinite chain of atoms, thus assuming implicitly that the overgrowth covers completely the substrate. In other words, they assumed that the overgrowth follows the layer-by-layer pattern of growth and they did not specify at that time that different values of the energetic parameter l_0 should lead, in fact, to different modes of growth. This was the reason Bauer named the layer-by-layer growth after their names.

The first paper devoted solely to the problem of the mode of epitaxial growth of thin films was written by Stranski (Stranski 1929; Stranski and Kuleliev 1929). The considerations, which were naturally based upon the concept of the work of separation of a building unit from a half-crystal position, were further developed by Stranski and Krastanov (1938). We will outline their model in more detail as it lies in the base of our further considerations of the mode of growth.

Stranski and Kuleliev studied the stability of the first, second, third, etc., MLs of a monovalent ionic crystal K^+A^- with a sodium chloride lattice on the surface of a bivalent ionic crystal $K^{2+}A^{2-}$ with the same lattice, assuming that both crystals have equal lattice parameters (Fig. 4.33). As a measure of stability, they accepted the equilibrium vapor pressure of each ML. According to Eq. (1.58), it is a function of the corresponding work of separation from the half-crystal position. As can be judged from Fig. 4.33, the ions of the first layer of K^+A^- are attracted by the underlying doubly charged ions more strongly than by the surface of their own monovalent crystal; the lateral interactions remain the same. Hence, the work of separation from the half-crystal position $\varphi_{1/2}^{(1)}$ of the first ML is larger than that of the bulk K^+A^- crystal $\varphi_{1/2}^{(0)}$ and, correspondingly, the equilibrium vapor pressure P_1 will be lower than that of the bulk K^+A^-

Figure 4.33: Illustration of the model of Stranski and Kuleliev (1929) for the growth of monovalent ionic crystal K^+A^- on the surface of an isomorphous bivalent ionic crystal $K^{2+}A^{2-}$ (left), compared with the growth of the same monovalent ionic crystal K^+A^- (right). The symbols on the front face of the left-hand crystal represent doubly charged positive and negative ions. The stability of the consecutive MLs is determined by the work of separation of the ions from the corresponding half-crystal positions denoted by the bold cubes. (I. Markov and S. Stoyanov, *Contemp. Phys.* **28**, 267 (1987). By permission of Taylor & Francis Ltd.)

crystal P_∞. It follows that one ML of K^+A^- can be adsorbed on the surface of $K^{2+}A^{2-}$ at any vapor pressure higher than P_1 and lower than P_∞, in other words, at undersaturation with respect to the bulk K^+A^- crystal. The ions of the second layer are attracted by the ions of the first layer as on the same crystal K^+A^- but are repulsed by the doubly charged ions of $K^{2+}A^{2-}$ more strongly than if the substrate were monovalent. Thus, $\varphi_{1/2}^{(2)} < \varphi_{1/2}^{(0)}$ and $P_2 > P_\infty$. Hence, a supersaturation is required in the system in order to deposit the second ML. Stranski and Kuleliev concluded that every odd or even overlayer will have an equilibrium vapor pressure that is, respectively, less than or greater than P_∞, or in other words the equilibrium vapor pressures of the consecutive MLs should oscillate around the equilibrium vapor pressure P_∞. The dependence of the chemical potential of the consecutive MLs according to the considerations of Stranski and Kuleliev is shown in Fig. 4.34. As can be seen, after a few layers of

K^+A^-, the energetic influence of the substrate vanishes ($P_n \cong P_\infty$) and the film will continue to grow as if on the same crystal.

Ten years later, Stranski and Krastanov (1938) extended the considerations of the same model by calculating the Gibbs free energies of formation of 2D nuclei of the first, second, third, etc., MLs, as well as two and four-ML thick 2D nuclei. It turned out that, after the complete coverage of the substrate crystal $K^{2+}A^{2-}$ by an adlayer of K^+A^- at undersaturation (for reasons given above), the work of formation of 2D nuclei of the second ML is significantly greater than that of 2D nuclei that are two-ML thick. The reason is that the chemical potential of a bilayer deposited on the first ML is lower than that of a single ML (see Fig. 4.34). Simple considerations show that the work of separation of a whole K^+A^- molecule from a doubly high half-crystal position (Fig. 4.35) is equal to the arithmetic average of the works of separation of single ions from the kink positions of

Figure 4.34: Dependence of the chemical potential μ_i or the equilibrium vapor pressures P_i of the consecutive uppermost MLs on their number as follows from the model of Stranski and Kuleliev (1929) of the growth of monovalent ionic crystal K^+A^- on the surface of a bivalent ionic crystal $K^{2+}A^{2-}$ with the same lattice parameter (open circles). As shown, the chemical potential oscillates around the chemical potential of the bulk crystal K^+A^-. The filled circle gives the chemical potential of a bilayer formed on top of the completely built first ML (after Stranski and Krastanov 1938). It is exactly equal to the arithmetic average of the chemical potentials of the separate second and third MLs. (I. Markov and S. Stoyanov, *Contemp. Phys.* **28**, 267 (1987). By permission of Taylor & Francis Ltd.)

Figure 4.35: Half-crystal position with a bilayer height (after Stranski and Krastanov 1938).

the second and third MLs, i.e., $\varphi_{1/2}(\mathrm{K}^+\mathrm{A}^-) = \frac{1}{2}(\varphi^{(2)}_{1/2} + \varphi^{(3)}_{1/2})$. Then, the chemical potential of the bilayer will be precisely equal to the arithmetic average of the chemical potentials of the second and third MLs, i.e., $\mu(2+3) = \frac{1}{2}(\mu_2 + \mu_3)$. Note that when writing the chemical potential of the bilayer, we do not account for the chemical potential of the first ML. The reason is that, it is more strongly bound to the substrate and is completely built up. On this account, it does not take part in the process of exchange of atoms with the vapor phase.

Thus, Stranski and Krastanov predicted the possibility — admittedly in a very particular system — of the formation of nuclei with many layer thickness on the first stable adlayer (or adlayers) of the overgrowth, a mechanism of growth well known today and bearing their names. As will be shown below, the physical reason for such a mode of growth is the lattice misfit. Owing to the latter, too much strain energy accumulates into the film during the initial planar growth, and the strong adhesion exerted by the substrate (which is the reason for the planar growth) disappears beyond several atomic diameters. A *wetting layer* consisting of several equally strained MLs is, thus, formed. The growth continues further by the formation of 3D crystallites, in which the additional surface energy is overcompensated by the strain relaxation owing to the introduction of MDs at

the interface (Matthews, Jackson and Chambers 1975c). Later studies showed that 3D islands of nanometer scale can be formed on the wetting layer in highly mismatched epitaxy without the accommodation of the misfit by dislocations. The elastic relaxation takes place at the free lateral surfaces of the 3D islands in exactly the same way as near the free edges of the chains in Fig. 4.19. Eaglesham and Cerullo (1990) who discovered this kind of growth in the case of deposition of Ge on Si(0 0 1) coined for it the term "coherent" Stranski–Krastanov growth. In other words, the higher free energy phase representing a homogeneously strained planar film is replaced beyond some critical thickness by a lower free energy phase of (completely or partially) relaxed 3D crystallites.

The coherent Stranski–Krastanov growth immediately became a subject of intense research owing to possible optoelectronic applications as quantum dots for lasers and light-emitting diodes (Reed 1993; Petroff, Lorke and Imamoglu 2001). Elemental semiconductors Ge/Si (Mo *et al.*, 1990; Voigtländer and Zinner 1993a; Voigtländer 2001) and binary compounds like InAs/GaAs (Moison *et al.*, 1994), InAs/InP (Rudra *et al.*, 1994; Houdré *et al.*, 1993), CdSe/ZnSe (Schikora *et al.*, 2000; Strassburg *et al.*, 2000), PbSe/PbTe (Pinczolits *et al.*, 1998) were studied.

In order to establish the factors affecting the mode of growth, we will consider briefly some experimental examples, dividing them into several groups according to the different nature of the chemical bonds: metals on insulators, metals on metals, metals on semiconductors, and semiconductors on semiconductors (Markov and Stoyanov 1987). Recently, a new growth mode has been discovered when a stiff metal like Cu is deposited on a very soft metal like Pb (Nagl *et al.*, 1995). The formation of 3D crystallites under the surface of the substrate is then preferred. We will not consider here such cases.

4.3.2 *Experimental evidence*

4.3.2.1 *Metals on insulators*

A typical example of island growth is the deposition of metals on MgO, mica, molybdenite (MoS_2), and on alkali halide crystals such

as NaCl, KCl, KBr, etc., (for a review, see Pashley 1956, 1965, 1970; Grünbaum 1974; Kern, Lelay and Metois 1979). Metals, such as Ag, Au, Cu, Fe, Pd, Ni, Co, etc., on these insulators comprise systems which are characterized by adhesion forces between the metal atoms and the insulator substrates that are considerably weaker than the cohesion forces within the metals themselves. An exception is the deposition of Ag on MgO(0 0 1) at extremely low temperatures. Lord and Prutton (1974) established with the help of LEED and AES that at −200°C, Ag grows layer-by-layer on the MgO(0 0 1) surface cleaved in the vacuum chamber. At room temperature, however, Ag grows on MgO as separate islands.

4.3.2.2 *Metals on metals*

In the case of deposition of metals on metals, there is the greatest variety of modes of growth owing to the broad range of the ratio of adhesion to cohesion forces and of the lattice misfit as well (for review see Vook 1982, 1984; Bauer 1982). An interesting example is the deposition of Cu on the (1 1 1) plane of Ag (Horng and Vook 1974). When less than one-third of a ML of Cu is deposited on the (1 1 1) plane of Ag at 210°C, the RHEED pattern consists of diffraction streaks originated from the Ag substrate plus bright spots belonging to the Cu deposit. At room temperature, the RHEED pattern of the Ag substrate plus one-third of a Cu ML exhibits intense Ag streaks with fainter streaks for Cu overgrowth, which is indicative for a very smooth surface. It follows that at high substrate temperature, Cu begins to grow in isolated particles or islands from the very beginning of the process, while at low temperature, the Cu streaks originate from a deposit with a layer structure. When more than two Cu MLs are deposited at room temperature, the material in excess of two MLs form 3D islands. Thus Volmer–Weber growth mode is established at high temperatures and, Stranski–Krastanov mechanism takes place at low temperatures. Besides, the thinner the overgrowth, the larger is its average lattice parameter. For thicker deposits, it has its bulk value. In other words, thin Cu overlayers are at least partly homogeneously strained. It should be noted that the enthalpy of evaporation of Cu (80 500 cal/g.atom)

is greater than that of Ag (67 900 cal/g.atom) which means that the cohesion forces are expected to be stronger than the adhesion forces. Besides, the misfit is quite large in the absolute value, $f = (b - a)/a = -11.5\%$.

Face-centered cubic metals grow on the most densely packed planes (1 1 0) and (1 0 0) faces of body-centered cubic metals W and Mo, usually following the layer-by-layer mechanism at low temperatures and, Stranski–Krastanov mechanism at high temperatures (Bauer 1982). It should be noted that the enthalpies of evaporation of Mo and W (142 000 and 191 000 cal/g.atom, respectively) are much greater than these of the fcc metals deposited which vary from 61 000 for Ag to 94 000 cal/g.atom for Pd (Hultgren *et al.*, 1973; Emsley 1991). Hence, adhesion forces much stronger than the cohesion forces should be expected.

A typical example is the case of deposition of Cu on (1 1 0) and (1 0 0) W (Bauer *et al.*, 1974). LEED and AES measurements have shown that at room temperature, the growth follows the layer-by-layer pattern. When the substrate plane is (1 1 0), the first Cu ML has 1.41×10^{15} atoms cm^{-2}, which is exactly the surface density of the W atoms in the adjoining W(1 1 0) plane. Hence, the first Cu ML is pseudomorphous with the substrate. The second ML is expanded in the $\langle 1\,0\,0 \rangle$ direction and not strained in the $\langle 1\,1\,1 \rangle$ direction, thus having 1.6×10^{15} atoms cm^{-2}, which is somewhere between the surface densities of the W(1 1 0) and Cu(1 1 1) planes. If a film thicker than two MLs is annealed at higher temperature, all material in excess of two MLs agglomerates into isolated 3D islands, which means that the first two MLs are stable. In the case of the (1 0 0) substrate plane, the first two MLs have 1×10^{15} atoms cm^{-2} each, i.e., they have the same density as the W(1 0 0) plane, and hence, they are pseudomorphous with the substrate. Even at room temperature, the slope of the AES signal vs film thickness plot is very small after the second break point, which is an indication that 3D islands are formed on top of the second ML. This is unlike the (1 1 0) plane where 3D islands are formed on top of the second ML at temperatures higher than 700 K. Thus, layer-by-layer growth is observed at low temperatures and Stranski–Krastanov growth at higher temperatures. The critical

temperature for transition from one to the other mechanism is considerably higher in the case of the more densely packed (1 1 0) than for the (1 0 0) substrate plane. Similar results are also obtained in the case of deposition of Ag and Au on both low-index planes of W (Bauer *et al.*, 1977).

When evaporating Fe on Cu(1 1 1) in the temperature range 20–400°C Gradmann, Kümmerle and Tillmanns (1976, 1977) (see also Gradmann and Tillmanns 1977) established that the LEED patterns of the Fe films cannot be distinguished from the pattern of the pure Cu substrate. Note that, at temperatures below 912°C, the thermodynamically stable phase of iron is α-Fe with a bcc lattice; above this temperature, it is γ-Fe with an fcc lattice. Hence, the thinnest Fe films (< 20 Å) consist of the thermodynamically unstable γ-Fe, and grow pseudomorphous with the Cu substrate. Moreover, AES measurements showed that at low temperature and/or high enough atom arrival rates, the films grow in the layer-by-layer mode, while and high temperature and/or at low atom arrival rates, island growth is observed from the very beginning of the deposition. Thus, the mode of growth depends on the supersaturation $\Delta\mu$, independent of whether the latter was changed by the temperature or by the atom arrival rate. Note that the enthalpy of evaporation of γ-Fe (96 000 cal/g.atom) is higher than that of Cu (72 800 cal/g.atom). The atom spacings of the α-Fe and γ-Fe are 2.4823 and 2.578 Å, respectively, and the corresponding values of the misfit with the copper substrate are 2.88% and 0.85%, respectively.

4.3.2.3 *Metals on semiconductors*

The deposition of metals on semiconductors followed more or less the same pattern as that of metals on metals systems. Stranski–Krastanov or Volmer–Weber growth at high temperatures and layer-by-layer growth at low temperatures are usually observed. The interpretation of the observations is much more complicated in view of the different nature of the chemical bonds in the substrate and deposit crystals.

In the case of deposition of Ag on the As$(0\,0\,\bar{1})$ face of GaAs described above (Massies and Linh 1982a–1982c), AES measurements have shown that above 100°C, 3D islands are formed on the GaAs substrate (Volmer–Weber mode), while at lower temperature, the growth is very close to the layer-by-layer pattern.

Gold and silver films on Si(1 1 1) and Si(1 0 0) are the most often studied systems ((Hanbücken and Neddermeyer 1982; Hanbücken, Futamoto and Venables 1984a,1984b; Hanbücken and Lelay 1986); for a review, see Lelay 1983). A characteristic feature of the Au/Si system is the alloying which takes place even at room temperature. Silver has a much weaker tendency to make alloys with Si, and Ag adlayers on Si(1 1 1) are believed to form sharp interfaces with the Si substrate. It has been found that at room temperature, the Ag films grow either via the Stranski–Krastanov mode with very flat islands (Venables, Derien and Janssen 1980) or via the layer-by-layer mode (LeLay *et al.*, 1981; Bolmont *et al.*, 1981).

In a comparative study of Ag on (1 1 1) and (1 0 0) planes of Si by AES and SEM, Hanbücken, Futamoto and Venables (1984b) found that at high temperatures (400–500°C), the 3D Ag islands are flatter on Si(1 1 1) (relative height 0.01–0.04) compared to those on Si(1 0 0) (relative height 0.3–0.6). An increase of the relative height of the 3D islands with the temperature has been observed during the deposition of Bi on Si(1 0 0) where a transition from layer-by-layer to Stranski–Krastanov growth at a critical temperature of about 280 K has been found (Fan, Ignatiev and Wu 1990).

4.3.2.4 *Semiconductors on semiconductors*

The epitaxial growth of one semiconductor material on the single-crystal surface of another material is closely connected with device fabrication. Here, both the substrate and the deposit materials are characterized by their directional covalent bonds. The growth of elementary semiconductors Si and Ge on top of each other as well as of Ge_xSi_{1-x} alloys on (1 0 0) and (1 1 1) faces of Si is most often studied (Voigtländer 2001).

Considering the covalent bonds as "brittle" and "inflexible," the lattice misfit between Ge and Si, (4.1%) can be accepted as very

large. Narusawa, Gibson and Hiraki (1981b, 1982) interpreted their data of Rutherford backscattering spectroscopy (RBS) that Ge films deposited at 350°C grow pseudomorphically with the substrate up to three MLs, after which 3D islands are formed on top. Alloying does not occur and the interface is abrupt irrespective of the tendency of both elements to make ideal solutions in bulk (Swalin 1991; Hultgren *et al.*, 1973a). These conclusions were later confirmed by LEED and AES experiments of Shoji *et al.* (1983) and by Asai, Ueba, and Tatsuyama (1985) for both (1 1 1) and (1 0 0) faces of Si. These authors reported that, at room temperature, layer-by-layer growth takes place until six MLs are formed, further deposition giving rise to amorphous Ge. Above 350°C, the growth mode follows the Stranski–Krastanov pattern in which 3D islands are formed on top of three MLs of Ge. Marée *et al.* (1987) found with the help of RBS and RHEED that 3D Ge islands were formed on four MLs (two bilayers) which remained stable on the Si(1 1 1) substrate at temperatures up to 800°C. The results obtained by deposition at room temperature with further annealing at higher temperature were practically the same as the ones obtained by deposition at elevated temperatures. The room temperature deposited films were continuous and smooth. The high-temperature overlayers showed drastic changes that were attributed to island formation. The SEM micrograph of a Ge film 50-MLs-thick deposited at room temperature and annealed at 500°C for 3 min showed the presence of 3D islands with a density of approximately 1×10^9 cm^{-2}. Thus, layer-by-layer growth has been established up to 500°C and Stranski–Krastanov growth beyond this temperature. Similar investigations of the deposition of Si on Ge(1 1 1) Marée *et al.* (1987) showed that the layer-by-layer growth takes place at temperatures up to 600°C, which was then replaced by the growth of isolated islands with approximate density 4×10^7 cm^{-2} directly on the Ge substrate (Volmer–Weber growth).

A marked dependence of the mechanism of growth on the value of the natural misfit has been observed in the case of deposition of Ge_xSi_{1-x} alloys on Si(1 0 0). Kasper, Herzog and Kibbel (1975) established that when the Ge content x in the alloy exceeded 0.2 so that the lattice mismatch is larger than 0.85%, the growth proceeds

by the formation of 3D islands. Two dimensional growth takes place when the Ge content is less than 0.2. The lower the Ge content, the thicker can the Ge film be grown by successive MLs pseudomorphous with the substrate. These findings were later confirmed by Bean *et al.* (1984), who found, however, that a pseudomorphous 2D growth can take place for alloys with the Ge content up to 0.5 and thicknesses as great as 0.25 μm.

Xie *et al.* (1994) studied the deposition of $Si_{0.5}Ge_{0.5}$ films on relaxed buffer layers of Si_xGe_{1-x} starting from $x = 0$ (pure Ge) to $x = 1$ (pure Si), thus covering the whole range from 2% tensile to 2% compressive misfit. They found that coherent (dislocation-free) 3D islands are formed only under the compressive misfit larger than 1.4%. Films under tensile misfit were, thus, stable against 3D islanding. Pinczolits *et al.* (1998) have found that the deposition of $PbSe_{1-x}Te_x$ on PbTe(1 1 1) remains purely 2D when the misfit is less than 1.6% in absolute value (Se content $< 30\%$). Leonard *et al.* (1993) have successfully grown quantum dots (coherent 3D islands) of $In_xGa_{1-x}As$ on GaAs(0 0 1) with $x = 0.5$, or $f \approx 3.6\%$, but 60 Å thick 2D quantum wells (smooth planar films) at $x = 0.17$ ($f \approx 1.2\%$). Walther *et al.* (2001) found that the critical In content is approximately $x = 0.25$, or, in other words, a critical misfit of about 1.8% has to be reached in order 3D islands to nucleate and grow on top of the wetting layer in Stranski–Krastanov mode. Below this critical misfit, the latter is accommodated by MDs when the corresponding thickness is reached.

Effect of Surfactants: Grünbaum and Matthews (1965) long ago found that, very often the epitaxial films show better quality when the vacuum is poor. The unavoidable conclusion was that the presence of contaminations improves somehow the epitaxy. Steigerwald, Jacob and Egelhoff, Jr (1988) found that at 200–300 K, Fe films grow on Cu(0 0 1) as 3D clusters, but intentionally adsorbed oxygen on Cu before the deposition of Fe suppresses agglomeration and interdiffusion. The oxygen itself "floated" above the film surface without being incorporated into the latter. Much later, Kalff, Comsa and

Michely (1998) established that coverages of carbon monoxide as low as 1×10^{-3} MLs, an amount that is often present in the ultra high vacuum systems, were found to affect strongly the shape of the 2D islands, the island density, the step-edge barriers, and, as a result, the surface morphology during the growth of Pt(1 1 1). Copel *et al.* (1989) were the first who studied the effect of pre-adsorption of a third element on the epitaxy of semiconductor materials one on top of the other. They found that As alters drastically the mode of growth of Ge on Si(0 0 1) and of Si on Ge/Si(0 0 1). Instead the Stranski-Krastanov and Volmer-Weber mechanisms characteristic of the growth of Ge on Si(0 0 1) and Si on Ge(0 0 1), respectively, a planar, layer-by-layer-like growth has been established in both cases. The authors explained their results with a change of the surface energies of both materials by the adsorption of the third element, or in other words, by a change of the sign of the inequality (4.109). That is why, in order to emphasize the thermodynamic nature of the effect of the third element, they called it a "surfactant." As will be shown below, the third element changes not only the thermodynamics but also the kinetics of the epitaxial growth. In any case, we will preserve the term surfactant as it is already widely accepted in the literature. These observations of Copel *et al.* gave rise to numerous investigations of both hetero- and homoepitaxial systems (for a review, see Kandel and Kaxiras 2000).

The examples given above do not exhaust all the cases described in the literature. Deposition of noble gases is another interesting example. For instance, in the case of deposition of Xe on Si(1 1 1) at 25 K (Bartha and Henzler 1985), layer-like growth has been established, the film being pseudomorphous with the substrate. At elevated temperatures (36 K), clear island growth has been observed. The same tendency has been found in a quite different system, namely the growth of tungsten oxide on tungsten (Lepage, Mezin, and Palmier 1984). In the low-temperature regime ($<600°$C), the oxide seems to grow layer-by-layer, while at high temperatures ($>700°$C), the deposit is formed by discontinuous islands.

4.3.3 *General tendencies*

We can summarize the main tendencies in the mode of growth which are more or less applicable to systems involving any kind of chemical bonds as follows (Markov and Stoyanov 1987):

1. When the interfacial bonding is weaker than the bonding in the deposit itself, the formation and growth of isolated 3D islands rather than MLs are favored.
2. High substrate temperature favors the growth of 3D islands either directly on the substrate (Volmer–Weber mechanism) or on one or several stable adlayers of the deposit (Stranski–Krastanov mechanism). In addition, the higher the temperature, the greater is the relative height of the 3D crystallites.
3. Higher deposition rates favor layerlike growth. The higher the deposition rate, the more layerlike is the growth pattern, and vice versa.
4. The lattice misfit plays a prominent role in determining the mode of growth. The larger the misfit, the greater is the tendency to island-like growth and vice versa. The formation of 3D islands in coherent SK growth requires a misfit larger than some critical value.
5. The crystallographic orientation of the substrate also affects the mechanism of growth. The more densely packed the substrate plane, the greater the tendency to layerlike growth in comparison with less densely packed planes. In particular, this tendency is expressed by the fact that the more densely packed are the substrate planes, the flatter grow the 3D crystallites.
6. The presence of surface-active species (surfactants) favors the deposition of planar films rather than clustering.

4.3.4 *Thermodynamics of epitaxy*

The growth of thin epitaxial films in particular by MBE usually takes place far from equilibrium. Nevertheless, thermodynamic considerations are a necessary step for the understanding of the phenomena. Thermodynamics tells us what is possible and what is not.

We derive first the thermodynamic condition for the occurrence of planar growth and clustering from general principles. In other words, we study the stability of uniformly thick films, or what is the same, the instability of the uniformly thick films against clustering, following the approach of Peierls (1978). In doing that, we pretend that we have never heard before about the relation of Young or the criterion of Bauer. After that, we derive the relation of Dupré for misfitting crystals and the thickness dependence of the chemical potential accounting for the real structure of the epitaxial interface.

4.3.4.1 *Wetting and clustering*

We consider the Gibbs free energy $G(n)$ per unit area of a uniform adsorbed layer on a substrate. In general, $G(n)$ should be a monotonically decreasing function of the amount n of atoms per unit area as the chemical potential

$$\mu = \frac{dG}{dn}$$

must be negative.

The intercept with the G axis ($n = 0$) is the free energy of the bare substrate, or in other words, the free surface energy, σ_{s0}, of the interface substrate–vacuum. At large n, the thickness of the adsorbate is large and its properties are the same as the properties of the bulk adsorbate. This means that $G(n)$ should tend asymptotically to the free energy of the bulk adsorbate (see Fig. 4.36). The equation of the asymptote reads

$$G_{\text{asym}} = n\mu_\infty + \alpha_\infty, \tag{4.111}$$

where α_∞ is the intercept of the asymptote with the G axis.

As G is a free energy per unit area and α_∞ is a constant, it follows that the latter has the meaning of surface free energy. At large n, the system represents a substrate plus a thick adsorbate (we do not account for the free energies of the semi-infinite substrate and vapor phase which are constant). This means that there are two interface boundaries: substrate–adsorbate and adsorbate–vapor. Going along the asymptote back to $n = 0$, we make the adsorbate thinner leaving the energies of the phase boundaries. Therefore, α_∞ is the sum of the

Figure 4.36: The schematic representation of the Gibbs free energy of a uniform film per unit area vs coverage n. The dashed line gives the asymptote to large n, the dotted line is the tangent at an arbitrary n (after Peierls 1978).

surface free energies of both interfaces, $\sigma_{\rm i}$ of substrate–adsorbate, and σ of adsorbate–vapor, or

$$\alpha_\infty = \sigma + \sigma_i. \tag{4.112}$$

We consider first the case when the free energy tends to the asymptote from above (Fig. 4.36). For any value of n, we can draw a tangent which has an intercept with the G axis

$$\alpha(n) = G(n) - n\frac{dG}{dn}.$$

We differentiate the above equation and obtain

$$\frac{d\alpha(n)}{dn} = -n\frac{d^2G}{dn^2} = -n\frac{d\mu}{dn}$$

or

$$d\alpha(n) = -nd\mu. \tag{4.113}$$

We compare this equation with the Gibbs adsorption isotherm (Moelwyn-Hughes 1961)

$$d\sigma_s(n) = -nd\mu, \tag{4.114}$$

which gives the change, $d\sigma_s(n)$, of the surface energy of the substrate upon the adsorption of an amount n per unit area of an adsorbate with a chemical potential μ. The change of the surface

energy is usually expressed in terms of the so-called *spreading pressure* $\phi = -d\sigma_s(n)$ (Mutaftschiev 2001). The reason is that the interfacial tension between the solid and the vapor is affected by adsorption, which reduces σ_s by an amount equal to the spreading pressure ϕ of the film. The latter can be defined also as $\phi = \sigma_{\mathrm{s0}} - \sigma_s(n)$ (Dash 1977).

Comparing (4.113) and (4.114) gives a simple differential equation for $\alpha(n)$

$$d\alpha(n) = -\phi.$$

The integration gives

$$\alpha(n) = -\phi + C.$$

We find the value of the integration constant C from the initial condition $n = 0$, $\phi = 0$, and $\alpha(n) = \sigma_{\mathrm{s0}}$. Then, $C = \sigma_{\mathrm{s0}}$ and

$$\alpha(n) = -\phi + \sigma_{\mathrm{s0}} = \sigma_s. \tag{4.115}$$

Subtracting (4.115) from (4.112) gives

$$\alpha_\infty - \alpha(n) = \sigma + \sigma_{\mathrm{i}} - \sigma_s, \tag{4.116}$$

where $\alpha_\infty - \alpha(n) < 0$ for all n as follows from the shape of the curve in Fig. 4.36. This means that the condition for complete wetting $\Delta\sigma = \sigma + \sigma_{\mathrm{i}} - \sigma_s < 0$ is satisfied for all n for the shape of $G(n)$, shown in Fig. 4.36.

Looking at Fig. 4.36, we notice something else. In order the free energy to tend to the asymptote from above, the curve should have a positive curvature. This means that the second derivative $d^2G/dn^2 > 0$, or what is the same $d\mu/dn > 0$ for all n (see also Dash 1977; Landau and Lifshitz 1958). In other words, the condition for complete wetting $\Delta\sigma < 0$ is equivalent to $d\mu/dn > 0$. We conclude that the planar adsorbate is stable as long as $d\mu/dn > 0$. As $\mu = \mu_0 + kT \ln P$ and $\mu < \mu_\infty$, the equilibrium vapor pressure of the planar adsorbate will be always lower than the equilibrium vapor pressure P_∞ of the bulk adsorbate. It follows that a stable planar film is always in equilibrium with an undersaturated vapor phase (Stranski and Krastanov 1938; Kern, LeLay and Metois 1979; Mutaftschiev 2001).

Figure 4.37: The schematic representation of the Gibbs free energy of a uniform film vs coverage n with an inflection point. The dashed line is the asymptote at large n, the dotted line is the tangent with the same slope μ_∞ as the asymptote at $n = n_c$ (after Peierls 1978).

We consider now the case when G approaches the asymptote from below, i.e., $\alpha_\infty > \alpha(n)$. To this aim, the curve should have an inflection point, i.e., to become a negative curvature $d^2G/dn^2 < 0$ beyond some point n (Fig. 4.37), or to have a negative curvature all the way (Fig. 4.38).

We consider first the curve with the inflection point. There is a coverage n_c such that the tangent to $G(n)$ is parallel to the asymptote, i.e., the slope of the tangent has the value of the bulk chemical potential. At $n = n_c$, $\mu = \mu_\infty$ and $P = P_\infty$. The amount of material $n = n_c$ which completely wets the substrate is known in the literature as the "wetting layer." Beyond the coverage n_c, the asymptote represents a planar film of amount n_c plus clusters with bulk properties of the total amount $n - n_c$. The uniformly thick adsorbate is stable for $0 < n < n_c$ but becomes unstable at $n > n_c$ because the free energy $G(n)$ is above the tangent.

Finally, when the $G(n)$ curve has a negative curvature from the very beginning (Fig. 4.38), no planar film can form. We can draw a straight line beginning from the starting point σ_{s0} and being parallel to the asymptote. This line $G = \sigma_{s0} + n\mu_\infty$ represents the free energy of a bulk adsorbate in the shape, for example, of a single drop on top of the substrate. The fact that the $G(n)$ lies above this line means

Figure 4.38: The schematic representation of the Gibbs free energy of a uniform film vs coverage n with a negative curvature from the very beginning of adsorption (after Peierls 1978).

that a bulk liquid rather than a planar film is thermodynamically favored from the very beginning of adsorption.

We conclude that as long as $d\mu/dn > 0$, the uniformly thick adsorbate is stable. The uniform adsorbate becomes unstable against clustering when $d\mu/dn < 0$. The latter can take place from the very beginning of adsorption $n = 0$, or beyond some critical coverage $n = n_c$. If we differentiate the three curves in Figs. 4.36–4.38, we will obtain the three curves $\mu(n)$, shown in Fig. 4.41. Thus, as defined by Dash (1977), three general classes of behavior: (i) uniform deposits at all thicknesses, (ii) clustering after a thin uniform adsorbate, and (iii) clustering with no preadsorption, corresponding to the Frank–van der Merwe, Stranski–Krastanov, and Volmer–Weber mechanisms of growth.

4.3.4.2 *Relation of Dupré for misfitting crystals*

As discussed above, the substrate and deposit crystals differ not only in their lattices and lattice parameters but also in the nature and strength of the chemical bonds. In the case of a zero misfit, the quantity which gives properly the catalytic potency of the substrate, or in other words, the energetic influence of the substrate on the film growth is the specific adhesion energy which is determined by

Eq. (1.28). To account for the lattice misfit, we perform the same imaginary process as described in Chapter 1 (Fig. 1.9).

We assume that the two infinitely large crystals A and B have different lattice parameters a and b (van der Merwe 1979). We again cleave both crystals reversibly and isothermally and produce two surfaces of A and two surfaces of B. We then uniformly strain the halves of one crystal, say B, to match exactly the lattice parameter of the other (A), and put the halves of A and B in contact as before. Assuming that the lateral HS does not affect the bonding across the interface, we gain energy, $-2U_{\mathrm{AB}}$. After that we allow the bicrystal system to relax completely so that MDs, are introduced at the interface. The energy of HS is regained completely, but energy E_d of a cross-grid of MDs is introduced. The energy balance now reads

$$2U_i = U_{\mathrm{AA}} + U_{\mathrm{BB}} - 2U_{\mathrm{AB}} + 2E_d.$$

Then

$$\sigma_i^* = \sigma_{\mathrm{A}} + \sigma_{\mathrm{B}} - \beta + \mathcal{E}_d = \sigma_i + \mathcal{E}_d \tag{4.117}$$

or

$$\sigma_i^* = \sigma_{\mathrm{A}} + \sigma_{\mathrm{B}} - \beta^*, \tag{4.118}$$

where $\mathcal{E}_d = E_d/\Sigma$ is the MD energy per unit area and the asterisks indicate that the quantities refer to misfitting crystals. The specific adhesion energy is now given by the difference

$$\beta^* = \beta - \mathcal{E}_d. \tag{4.119}$$

As we see, the dislocation energy appears as a decrement to the binding between both crystals. This is not surprising if we recollect that when $E_d = 0$, the atoms are not displaced from their positions in the bottoms of the potential troughs provided by the other crystal.

On the other hand, the dislocation energy appears as an increment to the specific interfacial energy which is due to the lattice misfit. The remaining part σ_{i} is due to the different nature and strength of the chemical bonds and does not depend on the misfit. Thus, the interfacial energy $\sigma_i^* = \sigma_i + \mathcal{E}_d$ consists of two parts: chemical part σ_{i} and misfit part $\mathcal{E}_d$.

Figure 4.39: For the derivation of the relation of Dupré in the case of thin films on a semi-infinite substrate.

We can repeat this process assuming now that the crystal B is not infinitely thick, but thinner than the double critical thickness $2t_c$ for pseudomorphous growth (Fig. 4.39). We again cleave both crystals reversibly and isothermally, strain uniformly the halves of B to match exactly the lattice parameter of A, and put the halves of A and B in contact as before. Carrying out this operation, we strain the free surfaces of B and change the specific surface energy. Drechsler and Nicholas (1967) found that the change of the specific surface energy does not exceed several percent of the absolute value. We assume that this change is much smaller than the work done to strain the crystals and neglect it. Then, we allow the bicrystal systems to relax. MDs will not be introduced at the interface as the half-thickness of B is smaller than the equilibrium critical thickness for pseudomorphous growth and the pseudomorphous film is stable. The energy balance will read

$$\sigma_i^* = \sigma_{\mathrm{A}} + \sigma_{\mathrm{B}} - \beta + \mathcal{E}_e(f) = \sigma_i + \mathcal{E}_e(f), \tag{4.120}$$

where $\mathcal{E}_e$ is the strain energy per unit area of the interface stored in crystal B. The latter is a parabolic function of the lattice misfit f.

Finally, in the general case (the crystal B is again thin but is thicker than the double critical thickness $2t_c$ for pseudomorphous growth), part of the HS is regained and MDs are introduced at the interface, but their density is partially reduced owing to the residual strain. Then (Markov 1988),

$$\begin{aligned}\sigma_i^* &= \sigma_{\mathrm{A}} + \sigma_{\mathrm{B}} - \beta + \mathcal{E}_e(f_e) + \mathcal{E}_d(f - f_e) \\ &= \sigma_i + \mathcal{E}_e(f_e) + \mathcal{E}_d(f - f_e) \end{aligned} \tag{4.121}$$

and

$$\beta^* = \beta - \mathcal{E}_e(f_e) - \mathcal{E}_d(f - f_e), \tag{4.122}$$

where the strain energy $\mathcal{E}_e(f_e)$ and the dislocation energy $\mathcal{E}_d(f - f_e)$ depend on the HS f_e and the mean dislocation density $f_d = f - f_e$, respectively.

4.3.4.3 *Thickness variation of chemical potential*

As discussed in Chapter 1, the chemical potentials of the first deposited layers differ from the chemical potential of the bulk deposit crystal, μ_∞. First, the interaction with the substrate differs from that with the same crystal, and second, the lattice misfit leads to the appearance of HS and/or MDs. We know that elastically strained crystals have higher chemical potentials and, hence, the HS energy and the average value of the periodical strain energy due to the MDs contribute to the chemical potential of the film. On the other hand, the atom displacements affect the interaction across the interface and lead to a reduction of the wetting of the substrate by the overlayer.

The chemical potential and, hence, the equilibrium vapor pressure of a semi-infinite ML on a foreign substrate is a function of the separation work from half-crystal position $\varphi'_{1/2}$, where the prime reflects the influence of the foreign substrate. An atom in a half-crystal position is again connected with half-atomic row, half-crystal, plane, and the underlying half-crystal block, but now the latter is of different material and the corresponding energy of desorption φ'_{a} differs from the energy for desorption φ_{a} from the surface of the same crystal. Thus, we can write the following general expression for the chemical

potentials of the atoms in the first, second, third, etc., MLs:

$$\mu(n) = \mu_\infty + a^2(\sigma + \sigma_i^* - \sigma_s), \tag{4.123}$$

where $\Delta\sigma = \sigma + \sigma_\mathrm{i}^* - \sigma_s$ is the change of the surface energy connected with the deposition. It is exactly equal to the difference of bonding between like and unlike substrates (see Chapter 1) and accounts for the wetting of the substrate by the overlayer (see Eq. (4.116)). The chemical potential of each ML is just equal to the chemical potential of the bulk crystal plus the difference of the bondings per atom with the like and unlike crystals. In fact, Eq. (4.123) is equivalent to Eq. (1.59) with the exception that it accounts for the lattice misfit. In this respect, it appears as a generalization of Eq. (1.59).

Substituting σ_i^* from (4.121) into (4.123) and replacing σ and β by φ_a and φ_a', respectively, gives (Markov 1988)

$$\mu(n) = \mu_\infty + [\varphi_\mathrm{a} - \varphi_\mathrm{a}'(n) + \varepsilon_d(n) + \varepsilon_e(n)], \tag{4.124}$$

where $\varepsilon_d(n) = a^2\mathcal{E}_d(n)$ and $\varepsilon_e(n) = a^2\mathcal{E}_e(n)$ are now the energies per atom of the MDs and the HS.

The term in the square brackets accounts for the strength of the interfacial bonding related to the strength of bonding with the same crystal. It includes the energy per atom, ε_d, of a cross-grid of MDs as shown in the previous section. The last term in the brackets is the contribution of the HS energy per atom, ε_e, to the chemical potential.

Let us neglect for the moment the contributions of the lattice misfit. Then, Eq. (4.124) simplifies to

$$\mu(n) = \mu_\infty + \varphi_\mathrm{a} - \varphi_\mathrm{a}'(n). \tag{4.125}$$

φ_a' can be either greater or smaller than φ_a and, hence, their difference can be either positive or negative and $\mu(n)$ can be either greater or smaller than μ_∞. In order to follow the $\mu(n)$ dependence, we should consider the thickness dependence of $\varphi_\mathrm{a}'(n)$. The latter accounts only for the atomic interaction across the interface, in the absence of a misfit. For short-range interactions, it changes rapidly

Figure 4.40: Dependence of the energy of desorption of an atom from unlike substrate on the distance from the interface measured in the number of MLs. $\varphi'_a > \varphi_a$ corresponds to complete wetting and vice versa.

with film thickness, going to φ_a from above or from below (Fig. 4.40). Assuming a pairwise interaction of the 6–12 Lennard–Jones type (4.2) between the atoms of the adsorbate and the substrate leads to a n^{-3} power law (Dash 1977; Mutaftschiev 2001)

$$\varphi'_a(n) = \varphi_a - \frac{\varphi_a - \varphi'_a(1)}{n^3}, \tag{4.126}$$

where the distance from the substrate is measured in number n of MLs, and $\varphi'_a(1)$ is the energy of desorption of an atom belonging to the first ML from the unlike substrate at a coverage tending to zero. It follows that the energetic influence of the substrate on atoms of the second ML will be nearly 10 times weaker compared with that of the first ML, and atoms of the fifth ML will not "feel" the energetic presence of the unlike substrate at all. It is worth noting that the above formula has been derived by making use of the Lennard–Jones potential which describes satisfactorily the properties of the noble gases. That is why Eq. (4.126) is in good agreement with experimental data of multilayer adsorption of krypton on exfoliated graphite (a powder of very thin graphite flakes about 500 Å in size) which show a stepwise behavior (Thomy, Duval and Regnier 1981).

Figure 4.41: Schematic representation of the dependence of the chemical potential on the film thickness in the number of MLs for the three modes of growth denoted at each curve: VW–Volmer-Weber growth, SK–Stranski–Krastanov growth, and FM–Frank–van der Merwe growth. The curve denoted by WL represents the chemical potential of a hypothetical thicker wetting layer. The height of the plateau gives the strain energy per atom in the homogeneously strained wetting layer. (J. E. Prieto and I. Markov, *Phys. Rev. B* **66**, 073408 (2002). Copyright 2002 by the American Physical Society.)

Substituting (4.126) into (4.125) gives

$$\mu(n) = \mu_\infty + \frac{\varphi_\mathrm{a} - \varphi'_\mathrm{a}(1)}{n^3}. \tag{4.127}$$

Equation (4.127) is plotted in Fig. 4.41 (the curve denoted by FM). As shown, it describes qualitatively quite well the mechanism of Frank–van der Merwe, the condition for which is the complete wetting $\varphi_\mathrm{a} < \varphi'_\mathrm{a}(n)$ for all n. We see that the description of the Frank–van der Merwe mode does not require the existence of any misfit. Just the opposite, a lattice misfit, could change dramatically the growth mode (Kern, LeLay and Metois 1979; Grabow and Gilmer 1988).

Equation (4.127), however, does not describe the opposite case of incomplete wetting, $\varphi_\mathrm{a} > \varphi'_\mathrm{a}(n)$. The reason is the following. As the wetting is incomplete, 3D crystallites will nucleate and grow from the very beginning of deposition. Every crystallite has side faces which also take part in the exchange of atoms with the vapor phase (not only the uppermost layer as in the layer-by-layer growth). Then,

the equilibrium with the vapor phase will be realized through a half-crystal position of a multilayer height (Fig. 4.35). The chemical potential of 3D islands of n-layer thickness will be given by the average value of the chemical potentials of the constituent MLs:

$$\mu(n) = \frac{1}{n}\sum_{k=1}^{n}\mu(k). \tag{4.128}$$

We can easily derive a qualitative expression for the chemical potential of 3D islands by making use of the atomistic approach of Stranski and Kaischew (1935) as in Sec. 1.5. We can imagine that, instead of numerous small 3D crystallites, all the amount of deposited material is spent to build one large crystal with even lower energy as the total surface area is smaller. We then apply macroscopic considerations to it. Assuming that only atoms of the first atomic plane "feel" the energetic influence of the substrate, $\mu(1) = \mu_\infty + \varphi_\mathrm{a} - \varphi'_\mathrm{a}(1)$ and $\mu(k) = \mu_\infty$ for $2 \le k \le n$. The summation of (4.128) gives

$$\mu(n) = \mu_\infty + \frac{\varphi_\mathrm{a} - \varphi'_\mathrm{a}(1)}{n}, \tag{4.129}$$

which is plotted in Fig. 4.41 and denoted by VW. Note that n is the average height of the 3D crystallite rather than the average thickness of the film. As both parameters are connected with each other through the island density, the above equation gives the general behavior. The real curve should be shifted by a constant. Note that the energetic effect of the substrate extends to much thicker deposits compared with the layer-by-layer growth.

Note that Eq. (4.129) reminds too much of the Thomson–Gibbs equation. We can see that if we exclude the lateral size n from Eqs. (1.68) and (1.69). We emphasize, however, that Eq. (4.129) has nothing to do with the Thomson–Gibbs effect. The positive supersaturation $\Delta\mu$ is due to the incomplete wetting. If the deposit is dispersed into small islands, the Thomson–Gibbs effect should be added to Eq. (4.129).

We particularly note that the variable n has a different meaning in Eqs. (4.127) and (4.129). In Eq. (4.127), n denotes the number of the uppermost incomplete ML, whereas in Eq. (4.129), n gives the total number of atomic planes which constitute the 3D island. In fact, the meaning of n reflects the layer-by-layer growth and the simultaneous growth of several MLs which are described by both equations.

As shown above, we have successfully treated in a more or less qualitative way the Frank–van der Merwe and the Volmer–Weber growth modes without the necessity to include the lattice misfit into consideration. This is not, however, the case with the Stranski–Krastanov mode that takes place when $\varphi'_{\mathrm{a}}(n) > \varphi_{\mathrm{a}}$ (complete wetting) and the lattice misfit is nonzero. In general, the presence of lateral strains owing to the lattice misfit in our particular case leads to different phenomena connected with the different ways of accommodation of the misfit. As was shown in the previous sections, one of these ways is the introduction of MDs beyond some critical thickness. Another way is the specific roughening of the surface. In some cases, the lateral stress gives rise to undulations which are known as Asaro–Tiller–Grinfeld instability (Asaro and Tiller 1972; Grinfeld 1986). The relaxation of the strain, or the gain of strain energy at the side walls and the summits, is the physical reason for this instability. Rounded cones with 12° side walls have been observed during the growth of 8 ML of Ge on Si(0 0 1) at about 1000 K in the presence of a ML of Sb to prevent the formation of isolated well-polygonized truncated pyramids (Fig. 4.42 (Horn-von Hoegen *et al.*, 1994)). In the absence of Sb, isolated well-polygonized full pyramids ("hut clusters") (Mo *et al.*, 1990) are formed on top of a wetting layer consisting of three MLs (Fig. 4.43). We will not consider here the Asaro–Tiller–Grinfeld instability as it is enlightened in numerous review papers and books (Nozières 1991; Pimpinelli and Vilain 1998; Politi *et al.*, 2000). We are interested in the formation of isolated, well-separated, and polygonized crystallites on top of the wetting layer. In other words, we are interested in the true Stranski–Krastanov mechanism of growth.

Before going into details, it is worth noting that the mechanism of misfit accommodation can be different on different crystal surfaces

Figure 4.42: A perspective STM image (1000 × 700 Å) of the surface of 8 MLs-thick Ge film deposited on Sb precovered Si(0 0 1). The height scale is exaggerated by a factor of 2. (M. Horn-von Hoegen, A. Al Falou, B. H. Müller, U. Köhler, L. Andersohn, B. Dahlheimer and M. Henzler, *Phys. Rev. B* **49**, 2637 (1994). Copyright 2002 by the American Physical Society and courtesy of Michael Horn-von Hoegen.)

Figure 4.43: Perspective STM image of "hut" clusters of Ge on Si(0 0 1). (B. Voigtländer, *Surf. Sci. Rep.* **43**, 127 (2001). By permission of the Elsevier Science B.V. and courtesy of Bert Voigtländer.)

in one and the same epitaxial system. Joyce *et al.* (1997) reported recently that the mismatch of 7.2% between InAs and GaAs is accommodated by MDs on (1 1 1)A and (1 1 0) surfaces of GaAs after the first InAs ML, whereas 3D InAs islands are formed on top of the first InAs ML on GaAs(0 0 1) (for more details and comments, see Joyce and Vvedensky 2002). This result clearly shows that the mode of misfit accommodation depends on the interrelation of the energetic barriers for the nucleation of 3D islands and MDs on the particular crystal face.

Bearing in mind Fig. 4.5(c), we could expect that under the conditions $\varphi'_{\mathrm{a}}(n) > \varphi_{\mathrm{a}}$ and $f \neq 0$, the film will grow initially pseudomorphous with the substrate and

$$\mu(n) = \mu_\infty + \varphi_{\mathrm{a}} - \varphi'_{\mathrm{a}}(n) + \varepsilon_e(f), \tag{4.130}$$

where (see Eq. (4.97))

$$\varepsilon_e(f) = 2G_b a^2 h f^2 \frac{1+\nu_b}{1-\nu_b} \tag{4.131}$$

is the energy of the HS energy per atom stored in each separate ML (h is the thickness of a ML).

As long as $\varphi'_{\mathrm{a}}(n) - \varphi_{\mathrm{a}} > \varepsilon_e(f)$ $\mu(n)$ will be smaller than μ_∞ and the overlayer will grow in a uniform way as the condition for the stability of the latter, $\sigma + \sigma_i^* - \sigma_s < 0$ is not violated. Thus, as a result of the interplay between the bonding $\varphi_{\mathrm{a}} - \varphi'_{\mathrm{a}}(n)$ and strain energy $\varepsilon_e(f)$, a wetting layer composed of an integer number of MLs will be formed. Its thickness is determined by the condition $\mu(n) = \mu_\infty$, or $\varphi_{\mathrm{a}} - \varphi'_{\mathrm{a}}(n) = -\varepsilon_e(f)$. The latter means that the thickness of the wetting layer decreases with increasing lattice misfit and vice versa but should always be of the order of the range of the interatomic forces.

As follows from the thermodynamic analysis (Sec. 4.3.4.1), the wetting condition $\sigma + \sigma_i^* - \sigma_s < 0$ should be violated beyond the wetting layer. Two factors can be responsible. The first is the introduction of MDs at the interface between the wetting layer and the 3D island. If the island is completely relaxed (the classical Stranski–Krastanov growth (Matthews, Jackson and Chambers 1975c)), the

interfacial energy should be given by (see Eq. (4.121))

$$\sigma_i^* = \mathcal{E}_d(f) \tag{4.132}$$

as $\sigma_{\mathrm{A}} = \sigma_{\mathrm{B}}$, $\beta = 2\sigma_{\mathrm{A}}$ (the Stranski–Krastanov growth is a growth of A on strained A), and $f_e = 0$ (complete relaxation). Hence, $\Delta\mu = a^2(\sigma + \sigma_i^* - \sigma_s) = \varepsilon_d(f) > 0$.

It is tempting to explain the coherent Stranski–Krastanov growth in a similar way: $\sigma_i^* = \mathcal{E}_e(f)$ and $\Delta\sigma = \sigma + \sigma_i^* - \sigma_s = \mathcal{E}_e(f) > 0$. As shown in Fig. 4.39, Eq. (4.121) has been derived under the assumption of the infinitely wide interface. It can be applied to the case of misfit accommodated by dislocations as above, if the island's size is sufficiently larger than the periodicity of the dislocations but cannot be applied to coherently strained small islands. As shown in Fig. 4.19, the strain energy is concentrated in the middle of the chain (island), whereas the edges are relaxed. Figure 4.44 is an illustration of the difference (and resemblance) between the classical and the coherent SK mode. It shows the vertical displacements of the atoms belonging to the base atomic plane of 3 MLs-thick islands (Prieto and Markov 2002). The 3D islands are represented by linear chains of atoms stacked one upon the other in 1+1 dimensions (substrate + height) (Stoop and van der Merwe 1973; Ratsch and Zangwill 1993). One of the islands contains two MDs and the other is coherent (dislocation free). As shown, in both cases, the 3D islands lose contact with the wetting layer. The vertical displacements are largest at the chain's ends in the coherent SK mode and around the dislocation cores in the classical case, but the physics is essentially the same. Thus, it is the edge effect that decreases the average wetting of small islands to the wetting layer and makes $\Delta\sigma$ positive beyond the wetting layer.

It is important to emphasize that in the layer-by-layer growth $\mu(n)$ goes asymptotically to μ_∞ with increasing n from below as required by the macroscopic considerations, and never become greater than the latter when the wetting is complete for any thickness. This means that every ML can be in equilibrium only with an *undersaturated vapor phase*, i.e., $P_n < P_\infty$. Contrary to the layer-by-layer growth, the chemical potential of the 3D islands is always greater than μ_∞. This means that 3D islands in Volmer–Weber

Figure 4.44: Vertical displacements of the atoms of the base chain of a coherent (•) and a dislocated (○), three MLs-thick island, given in units of the lattice parameter of the wetting layer and measured from the bottoms of the potential troughs provided by the homogeneously strained wetting layer. The misfit amounts to 7% and the islands contain 30 and 34 atoms in their base chains, respectively. (J. E. Prieto and I. Markov, *Phys. Rev. B* **66**, 073408 (2002). Copyright 2002 of the American Physical Society.)

growth mode can be in equilibrium only with a *supersaturated vapor phase* owing to the weaker attraction to the unlike substrate.

Applying the above considerations to the Stranski–Krastanov growth leads unavoidably to the conclusion that the 3D islands and the wetting layer represent necessarily different phases in the definition of Gibbs (1928) (homogeneous parts of a heterogeneous system) and, thus, have different chemical potentials. The reason is that the two phases are in equilibrium with the mother phase (the vapor) under different conditions which never overlap. The wetting layer can be in equilibrium only with an undersaturated vapor phase, while small 3D islands can be in equilibrium only with a supersaturated vapor phase. The dividing line is, thus, $\Delta\mu = kT\ln(P/P_0) = 0$ at which the wetting layer cannot grow thicker and the 3D islands cannot nucleate and grow. Hence, the wetting layer and the 3D islands can never be in equilibrium with each other.

4.3.4.4 *Thermodynamic criterion of the growth mode*

It follows that, depending on the interrelation between the adhesive and cohesive forces, on the one hand, and on the value of the misfit, resulting in an interplay between the energies of the MDs and HS, on the other, three different types of thickness dependences of the chemical potential can be distinguished:

1. $d\mu/dn < 0$, when $\varphi'_{\mathrm{a}} < \varphi_a$ (incomplete wetting) at any value of the misfit.
2. $d\mu/dn > 0$, when $\varphi'_{\mathrm{a}} > \varphi_a$ (complete wetting) at small misfits.
3. $d\mu/dn \lesseqgtr 0$, when $\varphi'_{\mathrm{a}} > \varphi_a$ at large misfits (transition from complete to incomplete wetting at some critical thickness).

Obviously, when $d\mu/dn$ is positive (every next ML has a higher chemical potential, Fig. 4.41), the completion of the first ML before the start of the second one, of the second before the start of the third, etc., is thermodynamically favored — layer-by-layer growth is expected. In the opposite case, the formation of a second ML before the completion of the first one is thermodynamically favored and the formation of 3D islands should take place. It follows that the above inequalities define the *thermodynamic criterion* for the mechanism of growth of thin epitaxial films (Stoyanov 1986; Grabow and Gilmer 1988):

1. Volmer–Weber growth, when $d\mu/dn < 0$.
2. Frank–van der Merwe growth, when $d\mu/dn > 0$.
3. Stranski–Krastanov growth, when $d\mu/dn \lesseqgtr 0$.

We remind the reader that the sign of the derivative $d\mu/dn$ gives simply the sign of the curvature of the free energy $d^2G(n)/dn^2$ of the system. In the case of growth by isolated 3D islands without preadsorption, $G(n)$ goes asymptotically to the bulk free energy from below being with a negative curvature from the very beginning of deposition. In the other extreme of layer-by-layer growth, $G(n)$ goes to the asymptote from above with a positive curvature all the way. In the intermediate case of Stranski–Krastanov growth, $G(n)$ goes to the asymptote from below but changes the sign of the curvature at

some thickness. As shown above, the sign of the curvature is directly connected with the wetting. Thus, this thermodynamic criterion is equivalent to that given by Bauer (1958) in terms of the specific surface energies. The latter becomes clear if one looks at Eq. (4.123).

Once the chemical potential acquires its bulk value μ_∞, the epilayer will grow further by the simultaneous growth of several MLs (Borovinski and Tzindergozen 1968; Gilmer 1980a; Chernov 1984).

Although the above criterion looks very scientific, it is, in fact, useless for predicting the mode of growth. The reason is that nobody knows the sign of the curvature of the free energy of the uniform adsorbate. The same criterion given in terms of surface energies is also difficult to use. The reason is that the values of these quantities which can be found in the literature are very unreliable. That is why the criterion (4.125) written in terms of desorption energies φ_a and φ'_{a} can be used first and then an attempt to account for the effect of the lattice misfit can be made. However, the desorption energies φ_a and in particular φ'_{a} are also scarce in the literature. That is why the enthalpies of evaporation ΔH_{ev} can be compared instead. If the crystals A and B have one and the same crystal lattice, which is often the case, $\varphi_a = k\Delta H_{\mathrm{ev}}$, where the proportionality constant k is one and the same for both materials. For example, $k = 1/2$ for fcc(1 1 1) or $k = 2/3$ for fcc(0 0 1) surfaces. φ'_{a} can be evaluated by making use of the approximation $\varphi'_{\mathrm{a}} \approx (\varphi_{\mathrm{A}}\varphi_{\mathrm{B}})^{1/2}$ [London 1930) which is valid when both materials have similar chemistry.

Let us consider, for example, the cases of Si/Ge(0 0 1) and Ge/Si(0 0 1). The enthalpies of evaporation are 4.72 and 3.88 eV for Si and Ge, respectively (Hultgren *et al.*, 1973). With $k = 2/3$, we find $\varphi_{\mathrm{Si}} = 3.15$ eV, $\varphi_{\mathrm{Ge}} = 2.59$ eV, and $\varphi'_{\mathrm{a}} = 2.86$ eV. Then, $\varphi_{\mathrm{Si}} - \varphi'_{\mathrm{a}} = 0.29$ eV. Volmer–Weber growth has to be expected irrespective of the value of the misfit. In the reverse, case $\psi_{\mathrm{Ge}} - \psi'_{\mathrm{a}}(1) = -0.42$ eV, and we have to estimate the HS energy per atom. With $G = 5.64 \times 10^{11}$ dyne cm^{-2}, $\nu = 0.2$, $a = 3.84$ Å, $h = 1.4$ Å, and $f = 0.041$, we obtain by using (4.131), the value $\varepsilon_e = 0.036$ eV atom^{-1}. The difference $-0.42/n^3 + 0.036 = 0$ and $n = 2.26$ is of the order of the error. The latter means that we have to expect Stranski–Krastanov mode

of growth with a wetting layer consisting of two MLs. We, thus, predicted correctly the mode of growth and made only a quantitative mistake. In reality, the wetting layer consists of three MLs.

4.3.5 *Kinetics of growth of thin epitaxial films*

We are now in a position to study the growth of thin epitaxial films bearing in mind the above thickness dependence of the chemical potential. The latter predicts the equilibrium morphology of the deposit whereas the deposition, process is usually carried out under conditions far from equilibrium. So we have to study the question how the substrate temperature and the rate of deposition affect the mechanism of growth. We consider the case of formation of 3D islands. The case of layer-by-layer growth does not differ significantly from the growth by 2D nucleation which we considered in Chapter 3. First of all, we have to study the mechanism of the formation of 3D islands.

4.3.5.1 *Mechanism of 2D–3D transformation*

We study first the stability of islands which consist of a different number of ML as a function of their volume. To this aim, we follow the binding energy U_N of the islands as a function of the number N of atoms in them. The binding energy, as defined by Eq. (2.23), is thus equal to the surface energy Φ upto a constant $N\varphi_{1/2}$ (Stoyanov and Markov 1982).

We consider, for simplicity, Kossel crystals with simple cubic lattice in the Volmer–Weber morphology ($\varphi_{\mathrm{a}} > \varphi'_{\mathrm{a}}$). We calculate first the binding energy of a ML island with a square shape with n atoms in the edge, thus consisting of $N = n^2$ atoms. Restricting ourselves to first neighbor interactions ψ and ψ', and assuming that the energy is given by the number of bonds, the binding energy reads

$$\frac{U_1}{N\psi} = -\Big(3 - \phi - \frac{2}{\sqrt{N}}\Big), \tag{4.133}$$

where $\phi = 1 - \psi/\psi'$ is the wetting parameter discussed above.

Figure 4.45: Binding energy per atom of ML, bilayer, and trilayer islands with simple cubic lattice as a function of the number of atoms in them. The wetting parameter $\phi = 1 - \psi'/\psi = 0.1$.

We consider next a bilayer island with n atoms in the edge, thus consisting of $N = 2n^2$ atoms. The binding energy reads

$$\frac{U_2}{N\psi} = -\Big(3 - \frac{\phi}{2} - \frac{2\sqrt{2}}{\sqrt{N}}\Big). \tag{4.134}$$

Correspondingly, for U_3 ($N = 3n^2$), one obtains

$$\frac{U_3}{N\psi} = -\Big(3 - \frac{\phi}{3} - \frac{2\sqrt{3}}{\sqrt{N}}\Big). \tag{4.135}$$

The binding energy is plotted in Fig. 4.45 with $\phi = 0.2$. As shown the curves intersect each other at consecutive numbers of atoms N_{12}, N_{23}, etc., which define the intervals of stability of the corresponding islands as a function of their volume. In other words, initially, an island grows as a ML and becomes unstable against the bilayer configuration beyond the critical number N_{12}. Equating U_1 and U_2

gives for the latter $N_{12} = 16(\sqrt{2}-1)^2/\phi^2$. When the island's size N become greater than N_{12} the ML island should transform into the bilayer island. In turn, the latter will transform into trilayer islands at $N > N_{23}$, etc. Thus, we reached the extremely important conclusion that the ML islands appear as necessary precursors for the 3D islands. Priester and Lannoo (1995) reached the same conclusion by making use of a different approach.

We can further study the mechanism of the transformation of a ML to the bilayer island (Stoyanov and Markov 1982). We can imagine this process as follows. Atoms detach from the edges of the ML island and diffuse on top of it, meet each other, and give rise to second-layer nucleus. The latter grows at the expense of atoms detached from the lower island. The process continues up to the moment the upper island size becomes equal to that of the lower island (Fig. 4.46). Assume that we have a square ML island with n_0 atoms in the edge. At some stage of the transformation process, its size shrinks to n and a second-layer island consisting of $n'^2 = n_0^2 - n^2$ atoms is formed on top. The energy change accompanying

Figure 4.46: For the evaluation of the activation energy for ML–bilayer transformation. The initial state is a square ML island with n_0 atoms in the edge. The intermediate state is a ML island with n atoms in the edge and a second island on top with n' in the edge so that $n_0^2 = n^2 + n'^2$. The final state is a bilayer island with equal sizes of both layers.

the transformation process is given by the difference between the energy of the initial ML island with n_0 in the edge, and that of the incomplete bilayer island having n atoms in the edge of the first ML island and n' atoms in the edge of the second-ML island, respectively:

$$\frac{\Delta U_{12}(n')}{\psi} = -n'^2\phi - \frac{n'^2}{n_0} + 2n', \tag{4.136}$$

where the approximation $n_0 + n \cong 2n_0$ in the beginning of the transformation had been used.

Equation (4.136) is plotted in Fig. 4.47. As shown, it displays a maximum at some critical size $n'^* = n_0/(1 + n_0\phi)$. The height of the maximum is given by $\Delta U_{12}^* = n_0\psi/(1 + n_0\phi) = n'^*\psi$ as should be expected by a classical consideration of a nucleation process (see Table 3.1 in Sec. 3.2.4.5).

We note that the same conclusion concerning the ML high islands as necessary precursors for 3D islanding in coherent Stranski–Krastanov growth has been made by a series of authors (Priester and Lannoo 1995; Chen and Washburn 1996; Duport, Priester and Villain 1998). Curves similar to these shown in Fig. 4.45 have also

Figure 4.47: The energy change accompanying the ML–bilayer transformation.

been obtained for this case (Korutcheva *et al.*, 2000; Markov and Prieto 2002). As shown in the figure, in Volmer–Weber growth, the critical size of the 2D island is reciprocal to the square of the wetting parameter. In coherent Stranski–Krastanov growth, the latter is a function of the misfit. Plotting N_{12} as a function of misfit in coherent Stranski–Krastanov growth revealed the existence of a critical misfit beyond which coherent 3D islands can be formed, and below which the misfit should be accommodated by MDs when the corresponding thickness is reached. Coexistence of stable one, two, three, four, etc., MLs-thick islands of InAs on InP(0 0 1) (Rudra *et al.*, 1994; Houdré *et al.*, 1993) and GaAs(001) (Colocci *et al.*, 1997) were experimentally observed. Chang *et al.* (2002) reported the gradual transformation of five-layer-thick Pb island into six-layer-thick island on a double-layer wetting the Si(1 1 1) surface without deposition of Pb.

Figure 4.48 shows the energies per atom of the ML and bilayer islands as a function of the number of atoms at a value of the misfit of 4% (Prieto and Markov 2005). The calculations are performed by

Figure 4.48: Binding energy per atom of ML and bilayer islands with fcc lattice as a function of the number of atoms in them. The curves cross each other at a critical size beyond which the ML island becomes unstable against the bilayer island. (J. E. Prieto and I. Markov, *Phys. Rev. B* **72**, 205412 (2005)).

Figure 4.49: The energy of transformation of a ML island with a fcc (001) surface into bilayer island as a function of the number of atoms in the second layer. The curve shows clearly a nucleation behavior with a critical nucleus consisting of 3 atoms. The discrete atomistics of the transfer process is responsible for the nonmonotonic behavior of the curve. (J. E. Prieto and I. Markov, *Phys. Rev. B* **72**, 205412 (2005)).

making use of an fcc crystal lattice with (1 0 0) orientation. The figure clearly demonstrates the instability of the ML island against the bilayer (3D) island beyond a critical size. The energy of ML–bilayer transformation as shown in Fig. 4.49 is an illustration of the nucleation behavior of the transformation with a critical nucleus consisting of three atoms. Both figures support the idea of the minimum-energy pathway in the stress-driven 2D–3D transformation in the Stranski–Krastanov mode of growth as a nucleation process.

4.3.5.2 *Kinetics of 2D–3D transformation*

We consider the case of complete condensation when all atoms arriving at the crystal surface join sites of growth before re-evaporation. As in the case of growth of a defectless atomically smooth crystal face, the atoms from the vapor phase strike the substrate and, after a period of thermal accommodation, randomly walk to give rise to

2D nuclei. The 2D nuclei grow further by the attachment of adatoms diffusing to their edges on the substrate surface and on their exposed surface as well. An adatom population is formed on top of them (Fig. 4.50(a)) whose concentration $n_s(r)$ can be found upon solving the master equation (3.126) subject to the boundary conditions $n_s(r=\rho) = n_{s1}^e$ and $(dn_s/dr)_{r=0} = 0$. The solution reads (see Eqs. (3.129) and (3.137))

$$n_s(r) = n_{s1}^e + \frac{\Re}{4D_s}(\rho^2 - r^2), \tag{4.137}$$

where $\Re = P(2\pi mkT)^{-1/2}$ (cm^{-2} s^{-1}) is the atom arrival rate. The quantity n_{s1}^e is the concentration of adatoms in equilibrium with the island edges given by

$$n_{s1}^e = n_{se} \exp\left(\frac{\mu(1) - \mu_\infty}{kT}\right), \tag{4.138}$$

where n_{se} is the adatom concentration on the surface of the same bulk deposit crystal given by Eq.(3.18).

Equation (4.137) shows a parabolic dependence of the adatom concentration on the distance from the island center (Fig. 4.51(a)) which displays a maximum

$$n_{s,\max} = n_{s1}^e + \frac{\Re}{4D_s}\rho^2$$

just over the island center. The increase in ρ leads to values of $n_{s,\max}$ high enough to give rise to nuclei on top of the islands (Fig. 4.50(b)). Thus, nuclei of the second ML appear before the completion of the first one. Once such nuclei are formed, they grow initially at the expense of the atoms diffusing to their edges on the terrace between the edges of the upper and lower islands. The adatom concentration on the terrace (Fig. 4.51(b)) is given by Eq. (3.138) subject to the boundary conditions $n_s(\rho_1) = n_{s1}^e$ and $n_s(\rho_2) = n_{s2}^e$, where

$$n_{s2}^e = n_{se} \exp\left(\frac{\mu(2) - \mu_\infty}{kT}\right) \tag{4.139}$$

is the adatom concentration that is in equilibrium with the edges of the second-ML islands (Markov and Stoyanov 1987).

Figure 4.50: Subsequent stages of film growth and atom exchange between the kinks and the dilute adlayer. (a) The concentration of atoms adsorbed on top of the first ML island increases with island size, which leads to nucleation of 2D islands of the second ML. (b) Surface transport from the edges $A_1B_1C_1D_1$ to the edges $A_2B_2C_2D_2$ takes place when $\mu(2) < \mu(1)$. (c) Surface transport transforms the layer configuration into a crystal of two MLs height, which grows further by nucleation of islands of the third ML. (I. Markov and S. Stoyanov, *Contemp. Phys.* **28**, 267 (1987). By permission of Taylor & Francis Ltd.)

The solution reads (cf Eq. (3.138′))

$$n_s(r) = n_{s1}^e + \frac{\Re}{4D_s}(\rho_1^2 - r^2) - \left(\Delta n_s + \frac{\Re}{4D_s}(\rho_1^2 - \rho_2^2)\right)\frac{\ln(r/\rho_1)}{\ln(\rho_2/\rho_1)}, \qquad (4.140)$$

where $\Delta n_s = n_{s1}^e - n_{s2}^e$.

Suppose now that $\mu(1) > \mu(2)$, i.e., $d\mu/dn < 0$. The adatom population on top of the first-ML islands is supersaturated with respect to the bulk deposit crystal. This favors the nucleation on top of the first-ML islands and the thermodynamic driving force for nucleation to occur should be greater than $\Delta\mu = \mu(1) - \mu_\infty$. On the other hand, $n_{s1}^e > n_{s2}^e$ and *surface transport* from the edges of the lower island to the edges of the upper island will take place whose driving force is given by $\Delta n_s/\lambda = (n_{s1}^e - n_{s2}^e)/\lambda$, where λ is the distance between the edges (Fig. 4.51(b)). Thus, the upper islands will grow at the expense of the lower islands and after some time will catch up with the lower islands to produce islands with double height (Fig. 4.50(c)). Hence, at high enough temperatures to facilitate the surface transport island growth will be observed. However, if the temperature is low, the surface transport from edge to edge will be hindered so that the first-ML islands will grow laterally to coalesce and cover completely the substrate before a significant growth on top of them to take place. Layerlike growth will occur for kinetic reasons. However, such films grown at low temperature are metastable. Upon heating, they will break up and agglomerate into 3D islands. Note that the growth will not follow the true layer-by-layer mechanism (complete coverage of the substrate by one ML before the next one to nucleate) as the thermodynamics favor island growth.

In the opposite case, $\mu(1) < \mu(2)$, $(d\mu/dn > 0)$ (Fig. 4.51(b)), the islands of the second ML will have a chemical potential higher than that of lower islands and the surface transport of atoms will occur from the edges of the upper islands to the edges of the lower islands. As a result, the upper islands will decay. Thus, layer-by-layer growth will be observed irrespective of the temperature.

Figure 4.51: Profile of the adatom concentration on (a) the surface of a ML island and (b) the terrace formed between the edges of the lower and upper ML islands with radii ρ_1 and ρ_2, respectively. n^e_{s1} and n^e_{s2} are the adatom concentrations in equilibrium with the corresponding island edges.

Finally, when $d\mu/dn$ changes its sign with film thickness, the first MLs will grow layer-by-layer for reasons cited above. Once a particular thickness is reached (the so-called Stranski–Krastanov thickness) such that the corresponding chemical potential is higher than μ_∞ 3D islands will form and grow at high temperatures. Surface transport from the edges of more strained ML islands to the edges of less strained or not strained at all will take place. As a result,

Stranski–Krastanov mechanism will be observed. At low temperatures, the growth will proceed further by the successive formation of MLs. Again, if such low temperature films are annealed at higher temperatures, the material in excess of the first stable MLs (for which $d\mu(n)/dn > 0$) will break up and agglomerate into 3D islands.

It is important to note once more that a true layer-by-layer growth takes place only when the chemical potential is an increasing function of the film thickness, i.e., $d\mu/dn > 0$. At low temperatures and $d\mu/dn < 0$, the film growth will proceed by the simultaneous growth of several MLs as described in Chapter 3.

Thus, we have to expect a change of the mechanism of growth from layerlike to either Volmer–Weber or Stranski–Krastanov with increasing temperature. The necessary condition for a transition to occur is $d\mu/dn < 0$. In other words, the thermodynamics should favor island growth either on the substrate surface or on several stable MLs of the deposit. Our next task is to find the critical temperature for transition to occur.

We consider the case when $\mu_1 > \mu_2 > \mu_3 \cdots$ so that Volmer–Weber or island growth is expected under near-to-equilibrium conditions. The same is valid in the case of Stranski–Krastanov growth after the completion of the stable wetting layer. As discussed above, 2D nuclei of the second, third, etc., MLs are formed on top of the first-ML islands which results in the formation of flat pyramids of growth as shown in Fig. 3.28. A very nice picture of such pyramids of growth of Cu on Ru(0 0 0 1) can be seen in the paper of Pötschke *et al.* (1991). As the chemical potential is a decreasing function of the ML number n, the surface transport will be directed from the lower to the upper steps. We make use of the solutions of the diffusion Eq. (3.126) subject to boundary conditions $n_s(\rho_1) = n^e_{s1}$, $n_s(\rho_2) = n^e_{s2}$, $n_s(\rho_3) = n^e_{s3}$, etc. assuming the rapid exchange of atoms between the steps and the dilute adlayers on the terraces (diffusion regime). We obtain then solutions for $n_s(r)$ on every terrace (Eq. (4.140)) and, following the same procedure as in Chapter 3, we calculate the rates of advance of the circular steps $v_n = d\rho_n/dt$ (Stoyanov and Markov 1982).

Thus, for the first ML island, we have

$$\frac{d\rho_1}{dt} = \frac{\Re}{2\pi N_0 N_s \rho_1}\left(1 - \frac{\pi\rho_1^2 N_s(1-\rho_2^2/\rho_1^2)}{\ln(\rho_1^2/\rho_2^2)}\right) - \frac{2\Delta n_s^e D_s}{N_0\rho_1 \ln(\rho_1^2/\rho_2^2)},$$

where N_s is the density of the growth pyramids formed by successive nucleation per unit area of the substrate.

In this expression, the first term on the right-hand side which contains $\Re$ is always positive as the surface coverage $\pi\rho_1^2 N_s$ is smaller than the unity before the coalescence and $\rho_1 > \rho_2$. The second term which contains the equilibrium concentration difference Δn_s^e is also positive as $n_{s1}^e > n_{s2}^e$. It follows that v_1 can be either positive or negative, depending on the values of the deposition rate $\Re$ and the difference Δn_s^e which is a steep function of the temperature. In the extreme case of absence of deposition (annealing at $\Re = 0$), the first term in the right-hand side is equal to zero and $v_1 < 0$, thus, reflecting the process of detachment and transport of atoms from the lower ML island edge to the edge of the upper island. The same process takes place during deposition, but at higher temperature, when the negative term overcompensates the positive one. If this occurs before the coalescence of the first ML islands, say, at surface coverage $\Theta_1 = \pi\rho_1^2 N_s < 0.5$, the island growth has to be expected. On decreasing the temperature, Δn_s^e decreases, and under a given temperature the term containing Δn_s^e has a negligible contribution to v_1. The rate v_1 is then just the same as in the case of deposition on an own substrate, i.e., in the case of a growth of a bulk crystal when $\mu(n) = \mu_\infty$.

We have to solve now a set of differential equations for the rates of advance of the steps. The latter can be written in terms of surface coverages $\Theta_n = \pi\rho_n^2 N_s (n = 1, 2, 3\ldots)$ as a function of a dimensionless time $\theta = \Re t/N_0$, which is in fact the number of MLs deposited, in the form

$$\frac{d\Theta_1}{d\theta} = 1 - \frac{M_1 + \Theta_1 - \Theta_2}{\ln(\Theta_1/\Theta_2)},$$

$$\frac{d\Theta_n}{d\theta} = \frac{M_{n-1} + \Theta_{n-1} - \Theta_n}{\ln(\Theta_{n-1}/\Theta_n)} - \frac{M_n + \Theta_n - \Theta_{n+1}}{\ln(\Theta_n/\Theta_{n+1})}, \quad (4.141)$$

$$\frac{d\Theta_N}{d\theta} = \frac{M_{N-1} + \Theta_{N-1} - \Theta_N}{\ln(\Theta_{N-1}/\Theta_N)},$$

where the subscript N denotes the uppermost ML and the parameters

$$M_n = \frac{4\pi D_s N_s (n^e_{s,n} - n^e_{\mathrm{s,n+1}})}{\Re} \quad (4.142)$$

include all the materials quantities and the differences of the adatom concentrations, or, in other words, the differences of the chemical potentials (see Eqs. (4.138) and (4.139)).

4.3.5.3 *Critical temperature for 2D–3D transition*

The numerical analysis of (4.141) shows that the solutions for Θ_n and, hence, the time evolution of the shape of the growth pyramids are very sensitive to the values of M_n. The latter are strongly increasing functions of the temperature and are inversely proportional to the atom arrival rate $\Re$. When the chemical potentials are independent of the layer number, or in other words, $n^e_{\mathrm{sn}} = n_{\mathrm{se}}$, $M_{\mathrm{n}} = 0$. In this case, there is no directed surface transport between the steps and the growth pyramids preserve their shape. This means that the epitaxial film will grow as the bulk crystal face following the 2D nucleation mechanism with simultaneous growth of several layers. It is immediately seen that the system (4.141) turns into (3.146) for a pyramid of growth consisting of 2D islands with $M_n = 0$.

Let us consider the simplest case of the bilayer pyramid shown in Fig. 4.50 or Fig. 4.51(b), assuming in addition that $n^e_{\mathrm{s2}} = n_{\mathrm{se}}$, i.e., $\mu(2) = \mu_\infty$. This is a sufficient condition for the island growth to take place as bilayer islands will be formed as a result of it. As discussed in Chapter 3, the bilayer steps propagate more slowly than single steps and the double step will be caught up with by the upper step. Trilayer island will be formed, etc. The numerical solution of the system (4.141) in the case of a bilayer pyramid is shown in Fig. 4.52. At $M_1 = 0.25$, Θ_1 increases initially, displays a maximum $\Theta_1 = 0.5$ and decreases. The latter means that at some stage of growth, the

Figure 4.52: Dependence of the surface coverages of the first (curves 1 and 1′) and second (curves 2 and 2′) MLs on the number of MLs deposited. Curves 1 and 2: $M_1 = 0.25$ ($\mu(2) < \mu(1)$); curves 1′ and 2′: $M_1 = -1.5$ ($\mu(2) > \mu(1)$).

rate of advance of the first ML island, $d\rho_1/dt$, becomes negative, or, in other words, the first island decays and the atoms feed the second island. Then the edges of the latter catch up with the edges of the former and an island with double height is produced (Fig. 4.50(c)). The double step advances more slowly than the single step, and after some time the third step catches up the double one, thus, producing an island with triple height. As a result, island growth takes place, the *kinetic criterion* for it being

$$\frac{4\pi D_s N_s (n_{\mathrm{s1}}^e - n_{\mathrm{se}})}{\Re} \geq 0.25. \tag{4.143}$$

The physical meaning of this criterion becomes transparent if we write it in the form

$$\frac{4\pi D_s(n_{\mathrm{s1}}^e - n_{\mathrm{se}})}{\Re/N_s} \geq 0.25.$$

The numerator represents the total diffusion flux from the edge of the lower island to that of the upper island resulting from the difference of the equilibrium adatom concentrations. The denominator is equal to the number of atoms joining one pyramid per unit time. Therefore, the criterion simply states that in order island growth to take place, the diffusion flux from edge to edge should be equal to or larger than 25% of the total number of atoms joining the pyramid. The increase of the deposition rate $\Re$ leads to an increase of the overall growth rate of the pyramid without affecting the diffusion flux, which is responsible for the transformation of the pyramid to a 3D island. The result is a transition to layer-by-layer growth. An increase of the temperature has the opposite effect: it results in a faster surface transport which in turn facilitates the 2D to 3D transformation.

It is interesting to see what will happen when M_1 has a negative value, i.e., when $\mu(1) < \mu_\infty$. As shown in Fig. 4.52, the surface coverage of the second ML, Θ_2, decreases, thus, reflecting the fact that the surface transport is directed from the upper to the lower islands edges. The lower islands grow at the expense of the upper ones and cover completely the substrate. True layer-by-layer growth results.

Making use of Eqs. (4.138), (3.18), and (3.20) for the transition temperature T_t from (4.140), one obtains

$$T_t = \frac{(\varphi_{1/2} - \varphi_{\mathrm{a}}) - [\mu(1) - \mu_\infty] + E_{\mathrm{sd}}}{k\ln(16\pi\nu N_s/\Re)}. \tag{4.144}$$

Substituting the difference of the chemical potentials from Eq. (4.124) into (4.144) for the transition from layerlike growth to island growth one obtains

$$T_t = \frac{[(\varphi_{1/2} - \varphi_{\mathrm{a}}) - (\varphi_{\mathrm{a}} - \varphi'_{\mathrm{a}})] - \varepsilon_d + E_{\mathrm{sd}}}{k\ln(16\pi\nu N_s/\Re)}. \tag{4.145}$$

Bearing in mind that the lateral bonds of an atom in a kink position remain practically unchanged $\varphi_{1/2} - \varphi_{\mathrm{a}} \cong \varphi'_{1/2} - \varphi'_{\mathrm{a}}$, and the energy difference in the square brackets is just equal to the energy $\varphi'_{1/2} - \varphi_{\mathrm{a}}$ for transfer of an atom from a kink position in the step of the first ML island to the dilute adlayer on top of it.

Equation (4.145) is valid for transition from layer-by-layer to island growth where the contribution of the interatomic forces across the interface to the chemical potential is greatest. In the case of transition from layer-by-layer to Stranski–Krastanov growth, $\varphi_{\mathrm{a}} - \varphi'_{\mathrm{a}}$ can be neglected. Assuming that the 3D islands are completely relaxed, i.e., they are incoherent or dislocated, Eq. (4.144) simplifies to

$$T_t = \frac{(\varphi_{1/2} - \varphi_{\mathrm{a}}) - \varepsilon_d + E_{\mathrm{sd}}}{k \ln(16\pi\nu N_s/\Re)}. \tag{4.146}$$

Then, the surface transport will occur from edges of more elastically strained ML islands to the edges of less strained, or unstrained at all, ML islands.

It should be noted that, whereas $\varphi_{1/2}$ is characteristic for the bulk material, φ_{a} and φ'_{a} depend on the crystallographic orientation of the substrate. It follows that the critical temperatures will be higher for (1 1 1) face of an fcc crystal ($\varphi_{\mathrm{a}} = 3\psi$, $\varphi'_{\mathrm{a}} = 3\psi'$) than for the (1 0 0) face ($\varphi_a = 4\psi$, $\varphi'_{\mathrm{a}} = 4\psi'$). This is, indeed, what is observed in a series of experiments (for a review, see Markov and Stoyanov 1987; Markov 1983).

The temperature for transition from layer-by-layer growth to Stranski–Krastanov growth (Eq. (4.146)) is plotted against the natural misfit in Fig. 4.53. The MD energy per atom $\mathcal{E}_d$ is calculated as a function of the misfit by using the theory of van der Merwe (Eq. (4.88)) with an average shear modulus $G = 5 \times 10^{11}$ dyne cm^{-2} and Poisson ratio $\nu = 0.3$. An average enthalpy of evaporation, $\Delta H_{\mathrm{ev}} \equiv \varphi_{1/2} = 70$ kcal mol^{-1}, has been taken. As the temperature decreases by no more than 140–150 degrees when the misfit increases from zero to 0.20, and a transition from planar to Stranski–Krastanov growth can be expected with increasing temperature or misfit. Besides, the transition temperature for more closed packed surface is more than 200° higher in comparison with the

Figure 4.53: Plot of the temperature (in K) for transition from a planar (layer-like) growth to Stranski–Krastanov growth as a function of the natural misfit at two different orientations (111) and (001) of fcc substrate crystal. An average enthalpy of evaporation, $\Delta H_{\rm ev} \equiv \varphi_{1/2} = 70$ kcal mol^{-1}, has been taken. The MD energy $\mathcal{E}_d$ is computed using the theory of van der Merwe (Eq. (4.88)) with an average shear modulus $G = 5 \times 10^{11}$ dyne cm^{-2} and Poisson's ratio $\nu = 0.3$.

less closed packed surface. A transition from planar to Stranski–Krastanov growth can be expected even at room temperature for the latter. As will be shown below, this result is in fairly good agreement with experimental observations.

Thus, the morphology of the growing epitaxial film is a result of the kinetics of deposition and can be quite different from the morphology required by the thermodynamic criterion. As shown, the criterion (4.144) accounts for both the kinetics and the thermodynamics of the growth of thin epilayers.

Let us go back to some of the experimental data mentioned in the beginning of this chapter. We consider first the transition from layer-by-layer to Stranski–Krastanov growth in the case of deposition of Cu on W(1 1 0) and W(1 0 0) (Bauer *et al.*, 1974). The upper stable adlayer has 1.6×10^{15} atoms cm^{-2} and assuming an approximate (1 1 1) structure of the adlayer the average atom spacing is 2.686 Å. Bearing in mind that the first neighbor distance of Cu is 2.556 Å, the natural misfit between the Cu crystallites and the underlying

strained copper adlayer is $f \cong 0.05$. $G_\mathrm{a} = G_b = G_\mathrm{i} = G = 5.46 \times 10^{11}$ dyne cm^{-2}, $\nu_\mathrm{a} = \nu_b = \nu = 0.324$, $G' = G/2(1-\nu)$, and $\lambda = \pi f/(1-\nu) = 0.23$. Using the theory of van der Merwe (Eq. (4.88)), we find $\mathcal{E}_d = 310$ erg cm^{-2}. Then $\varepsilon_d = a^2\mathcal{E}_d \cong 2 \times 10^{-20}$ J atom^{-1} = 0.126 eV/atom. The enthalpy of evaporation of Cu is $\Delta H_e = 72\,800$ cal mol^{-1} and $\varphi_{1/2} - \varphi_\mathrm{a} = 36\,400$ cal mol^{-1} = 1.58 eV atom^{-1}. With $\nu \cong 3 \times 10^{13}$ s^{-1}, $N_s \cong 1 \times 10^{10}$ cm^{-2}, $\Re = 5.9 \times 10^{12}$ cm^{-2} s^{-1}, and neglecting E_sd, we find $T_t = 600$ K in good agreement with the experimentally found value 700 K. The same calculations performed for the case of deposition of Cu on W(1 0 0) give $f = 0.21$, $\lambda = 0.976$, $\mathcal{E}_d = 600$ erg cm^{-2} and $\varepsilon_d = 0.245$ eV atom^{-1}. Bearing in mind that $\varphi_\mathrm{a} = 4\psi$, $\varphi_{1/2} - \varphi_\mathrm{a} = 26\,830$ cal mol^{-1} = 1.053 eV atom^{-1}, $T_t = 330$ K. As mentioned above, 3D islands have been experimentally observed to form on the stable adlayers even at room temperature.

As shown, Eq. (4.146) predicts quantitatively the transition from layer to Stranski–Krastanov mode of growth and gives correctly the dependence of the transition temperature on the crystallographic orientation of the substrate. As for transition from layer to island growth, we need reliable values for the adhesion energy φ'_a. It follows that Eq. (4.145), will operate satisfactorily when the enthalpies of evaporation and the bonds strengths of both materials do not differ too much provided the nature of the chemical bonds is one and the same. We can assume then that the adhesion energy lies between the cohesion energies of both materials. We will consider as an example the deposition of Ge on Si(1 1 1) and Si on Ge(1 1 1) (Marée, Barbour and van der Veen 1987).

A transition from layer to Stranski–Krastanov growth is observed when Ge is deposited on Si(1 1 1), the transition temperature being 500°C. Making use of Eq. (4.146) and following the procedure outlined above, we find $\mathcal{E}_d = 400$ erg cm^{-2}, $\varepsilon_d = 0.4$ eV/atom, $\varphi_{1/2} - \varphi_\mathrm{a} = 44\,750$ cal mol^{-1} = 1.94 eV/atom. With $N_s = 1 \times 10^9$ cm^{-2} and $\Re = 0.1$ ML s^{-1} = 7.2×10^{13} cm^{-2} s^{-1}, $T_\mathrm{t} = 480$°C in excellent agreement with the experimental observation.

The transition from layer-by-layer to island growth in the deposition of Si on Ge(1 1 1) is more difficult to handle. We assume first that

the shear modulus at the interface G_{i} has a value in between the shear moduli of Si and Ge, 6.41×10^{11} and 5.46×10^{11} dyne cm^{-2}, respectively. We accept the average value $G_{\mathrm{i}} = (G_{\mathrm{Ge}} G_{\mathrm{Si}})^{1/2} = 5.9 \times 10^{11}$ dyne cm^{-2}. Then $\mathcal{E}_d = 600$ erg cm^{-2} and $\varepsilon_d = 0.6$ eV/atom. The same assumption is made for evaluating φ'_{a}. From $\varphi_{\mathrm{a}}(\mathrm{Si}) = \Delta H_e(\mathrm{Si})/2 = 54\,450$ cal mol^{-1} and $\varphi_{\mathrm{a}}(\mathrm{Ge}) = \Delta H_e(\mathrm{Ge})/2 = 44\,750$ cal mol^{-1}, we find $\varphi'_{\mathrm{a}} \cong [\varphi_{\mathrm{a}}(\mathrm{Si})\varphi_{\mathrm{a}}(\mathrm{Ge})]^{1/2} = 49\,360$ cal mol^{-1}. Then, $\varphi_{1/2} - \varphi_{\mathrm{a}} = 54\,450$ cal mol^{-1} $= 2.362$ eV/atom, $\varphi_{\mathrm{a}} - \varphi'_{\mathrm{a}} = 5090$ cal mol^{-1} $= 0.221$ eV/atom. With $\Re = 7.2 \times 10^{13}$ cm^{-2} s^{-1} and $N_s = 4 \times 10^7$ cm^{-2}, and neglecting again φ_{sd}, for the transition temperature, one finds $T_{\mathrm{t}} = 590°$C. It is worth noting that the approximation concerning φ'_{a} is quite reasonable. If we approximate φ'_{a} by either $\varphi_{\mathrm{a}}(\mathrm{Si})$ or $\varphi_{\mathrm{a}}(\mathrm{Ge})$, then $T_{\mathrm{t}} = 720°$C and $480°$C. We can conclude that the real value of φ'_{a} lies, indeed, between $\varphi_{\mathrm{a}}(\mathrm{Si})$ and $\varphi_{\mathrm{a}}(\mathrm{Ge})$.

We have to bear in mind, however, that the theoretically predicted values of T_{t} are underestimated as the activation energies for surface diffusion have been neglected. In the case of diffusion of Si atoms on Si(1 1 1) the value 1.3 eV has been reported (Farrow 1974; Kasper 1982). In addition, Sakamoto, Miki and Sakamoto (1990) found that the surface diffusion on a vicinal Si(1 1 1) surface is anisotropic. Another uncertainty in calculating the transition temperatures comes from the application of the theory of van der Merwe (1973) for the calculation of the MD energy in the case of materials with covalent bonds which are considered as brittle and inflexible. Additional uncertainty comes from using the nearest-neighbor model for the calculation of the desorption energies. It is, thus, surprising that irrespective of all the approximations made in the quantities involved in Eqs (4.145) and (4.146), the latter are in good semiquantitative agreement with the experimental data.

Equations (4.145) and (4.146) explain readily the transition from layer-by-layer to Stranski–Krastanov or island growth with increasing misfit. As an example, we will consider the deposition of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ on Si (Kasper, Herzog and Kibbel 1975). When the composition x varies from 0.15 to 0.25, the natural misfit varies from 0.006 to 0.01, the parameter λ varies from 0.024 to 0.04, and ε_d varies from 0.12 to 0.175 eV. The critical temperature for 2D–3D transition decreases

with about 30° which is sufficient to change the mode of growth when the deposition is carried out at a constant temperature.

4.3.6 *Surfactants in epitaxial growth*

The interest of the influence of adsorbates on the properties of the surfaces dates back a long time (Moelwin-Hughes 1961). The presence of surface active species (surfactants) on the surface of growing crystals changes dramatically the equilibrium shape (Eaglesham, Unterwald and Jacobson 1993), mode of growth (Copel *et al.*, 1989; Horn-von Hoegen *et al.*, 1994), the rate of nucleation (Rosenfeld *et al.*, 1993; van der Vegt *et al.*, 1998), the transient character of nucleation (Hwang, Chang and Tsong 1998), the transition from step flow to 2D nucleation (Iwanari and Takayanagi 1992; Iwanari, Kimura and Takayanagi 1992), the structure of steps (Voigtländer and Zinner 1993; Hernán *et al.*, 1998), the surface diffusivity (Massies and Grandjean 1993; Voigtländer *et al.*, 1995), the mechanism of surface diffusion (Camarero *et al.*, 1998; Ferron *et al.*, 2000), the strain relaxation (LeGoues, Copel and Tromp 1989; Thornton *et al.*, 1992; Meyer, Voigtländer and Amer 1992), surface alloying (Katayama *et al.*, 1996), the concentration of defects (Camarero *et al.*, 1994; van der Vegt *et al.*, 1995), physical properties of the resulting films (Prieto *et al.*, 2000), etc. The major effect is the suppression of the 3D islanding so that smooth films suitable for the fabrication of microelectronic devices could be produced. We will consider briefly both the thermodynamic and the kinetic aspects of the effect of surfactants on the thin film-growth mode. We will do that in the most general way without accounting for the particular properties of the materials.

The surfactants influence both the crystal growth (homoepitaxy) and the epitaxial growth (heteroepitaxy). In this section, we pay more attention to the heteroepitaxial growth and in particular to the change of the mode of growth. The effect on homoepitaxy is mainly of kinetic nature. A classical example is the effect of a submonolayer amount of Sb on the growth of Ag(1 1 1) (van der Vegt *et al.*, 1992; Vrijmoeth *et al.*, 1994) where the monotonic fall of the X-ray reflection beam intensity is replaced by oscillations. The latter is a

clear indication of a change of the multilayer growth to layer-by-layer growth.

4.3.6.1 *Thermodynamic considerations*

If we want to change the direction of a process, e.g., to deposit a smooth film instead of 3D islands, we have to change the sign of the thermodynamic force that drives it. If we want to prevent a particular process to take place, we have to suppress the corresponding thermodynamic driving force making it as close to zero as possible. In other words, we have to check whether the presence of the surfactant on the surface of the growing epitaxial film can reverse the sign of the difference of the chemical potentials $\mu(n) - \mu_\infty$ derived in Sec. 4.3.4.3 or make the latter equal to zero. For this purpose we have to find if the presence of adsorbed atoms or molecules can change the chemical potential of the film. We compare the effect of surfactants on bulk crystals and thin overlayers.

We would like to remind the reader that although the first attempt to explain the effect of the surfactants was based on thermodynamic grounds (Coppel *et al.*, 1989) the problem is far from being solved. Thus this section contains the most fundamental concepts in the field, and is rather an illustration of the problems the researchers face.

Chemical Potential of a Bulk Crystal: One very important fact that was established long ago (Bliznakov 1953; Pangarov 1983) is that the chemical potential of an infinitely large crystal does not depend on the adsorption of impurities on its surface. We will confirm that by using the method of Stranski (1928, 1929) calculating the work of separation of an atom from a half-crystal position on the surface of a Kossel crystal in absence and presence of a complete ML of a surfactant. As was shown in Chapter 1 the work of separation of an atom from a half-crystal position taken with a negative sign is precisely equal to the chemical potential of the crystal at the absolute zero, $\mu = -\varphi_{1/2}$ (Eq. (1.58)). We consider for simplicity the 2D case (the left panel in Fig. 4.54). The 3D case is easy to reproduce having a look in Fig. 1.19 and imagining that its surface is covered by a ML of a surfactant. We assume further additivity of the energy and

Figure 4.54: To the determination of the chemical potential of a bulk crystal (the left panel) and a ML thick film (the right panel) covered by a complete ML of a surfactant.

absence of misfit between the atoms of crystal A and the surfactant S. We consider only interactions in the first coordination sphere.

We evaporate the atom in the kink position. In the case shown in Fig. 4.54 without of a surfactant $\varphi^0_{1/2} = 2\psi_{\rm AA}$. We detach first the surfactant atom which is on top of the kink atom. We break one SA and one SS bond spending thus energy $\psi_{\rm SA} + \psi_{\rm SS}$. We evaporate then the atom in the kink position breaking two AA and one SA bonds. We spend energy $2\psi_{\rm AA} + \psi_{\rm SA}$. Finally, we put back the surfactant atom gaining energy $-2\psi_{\rm SA} - \psi_{\rm SS}$. The sum is $2\psi_{\rm AA}$, i.e., $\varphi_{1/2} = \varphi^0_{1/2}$ or $\mu_{{\rm S},\infty} = \mu_{0,\infty}$. What follows is that *the chemical potential of the infinitely large crystal does not depend on whether there are impurities adsorbed on its surface or not.* This is a very important conclusion because the chemical potential of the infinitely

large crystal is our energetic reference point when studying the mode of growth.

It is worth noting that the above analysis was in fact unnecessary. The reason is that the chemical potential of a crystal is a characteristic of the bulk material and is not connected in any way with the effect of the surfactant which is a characteristic of the crystal surface.

Chemical Potential of a Thin Film: We calculate the separation work from a half-crystal position using the same approach. The only difference is that the half-crystal block of A is replaced by a block of a different material B (the right panel in Fig. 4.54). The lattice misfit is assumed equal to zero. The atoms of the surfactant are as large as the atoms of A and B.

In absence of a surfactant the separation work from a kink position is $\varphi^0_{1/2} = \psi_{\mathrm{AA}} + \psi_{\mathrm{AB}} = 2\psi_{\mathrm{AA}} - (\psi_{\mathrm{AA}} - \psi_{\mathrm{AB}})$. Then

$$\mu(n) = \mu_{0,\infty} + (\psi_{\mathrm{AA}} - \psi_{\mathrm{AB}})$$

For the 3D case and an arbitrary crystal lattice we will obtain Eq. (4.125)

$$\mu(n) = \mu_\infty + E_{\mathrm{AA}} - E_{\mathrm{AB}}(n), \tag{4.147}$$

where E_{AA} and $E_{\mathrm{AB}}(n)$ are the energies per atom to disjoin a half-crystal A from a like half-crystal A and from an unlike half-crystal B, respectively.

In presence of a surfactant we first detach a S atom and spend a work $\psi_{\mathrm{SA}} + \psi_{\mathrm{SS}}$. Then we detach an A atom and spend a work $\psi_{\mathrm{AA}} + \psi_{\mathrm{AB}} + \psi_{\mathrm{SA}} = 2\psi_{\mathrm{AA}} - (\psi_{\mathrm{AA}} - \psi_{\mathrm{AB}}) + \psi_{\mathrm{SA}}$. Finally, we put back the S atom and gain an energy $-(\psi_{\mathrm{SA}} + \psi_{\mathrm{SB}} + \psi_{\mathrm{SS}})$. As a result we obtain

$$\mu_s(n) = \mu_{0,\infty} + (\psi_{\mathrm{AA}} - \psi_{\mathrm{AB}}) - (\psi_{\mathrm{SA}} - \psi_{\mathrm{SB}}),$$

which in the 3D case reads (Paunov 1998)

$$\mu_s(n) = \mu_\infty + (E_{\mathrm{AA}} - E_{\mathrm{AB}}) - (E_{\mathrm{SA}} - E_{\mathrm{SB}}). \tag{4.148}$$

Note that not only E_{AB} but also E_{SB} is a function of the film thickness or rather of the distance from the substrate B. The same

result can be easily obtained if we consider a block of B, covered by a ML of A and a ML of S. We evaporate first the whole ML of S, then the ML of A, and finally condense back the ML of S.

Using the definition of the specific surface energy ($\sigma = E_{\mathrm{AA}}/2a^2$) and the relation of Dupré we can write the above equation in terms of surface energies

$$\mu_s(n) = \mu_\infty + a^2(\sigma_{\mathrm{SA}} + \sigma_{\mathrm{AB}} - \sigma_{\mathrm{SB}}),$$

which was derived more than a century ago by Gibbs (1878). If we remove the letter S from the subscripts we see that it appears as a generalization of the 3-σ criterion of Bauer.

Thermodynamic Effect of Surfactants: Bearing in mind Eqs. (4.147) and (4.148) we can make some conclusions concerning the effect of the surfactants on the wetting of the substrate by the overlayer.

We assume first that the misfit is nil and the wetting is incomplete in the absence of a surfactant, i.e., $E_{\mathrm{AA}} > E_{\mathrm{AB}}(n)$. Then according to Eq. (4.147) we have to expect clustering directly on the substrate from the very beginning of deposition (Volmer–Weber growth). Let us assume now that the surfactant adsorbs stronger to the overlayer rather than to the substrate, $E_{\mathrm{SA}} > E_{\mathrm{SB}}$, so that the third term in (4.148) overcompensates the second, i.e., $(E_{\mathrm{SA}} - E_{\mathrm{SB}}) > (E_{\mathrm{AA}} - E_{\mathrm{AB}})$. Then $\Delta\mu < 0$ and layer-by-layer growth has to be expected. Beyond some thickness $E_{\mathrm{SA}} = E_{\mathrm{SB}}$, but also $E_{\mathrm{AB}} \to E_{\mathrm{AA}}$. Then $\Delta\mu = 0$ and, as the strain is zero, there is not a driving force to change the mode of growth. As $E_{\mathrm{SA}} < E_{\mathrm{AA}}$ the surfactant will "float" on the surface of the overlayer A. The surfactant thus successfully reversed the sign of the thermodynamic driving force. The reason is that Eqs. (4.147) and (4.148) have been derived to describe precisely this case.

Let us now assume that the lattice parameters of A and B differ which is usually the case. The wetting is again incomplete in the "clean" case but the surfactant overcompensates the difference in bonding $E_{\mathrm{AA}} - E_{\mathrm{AB}}$ as before. The growth begins by deposition of successive MLs. After several MLs of A, the energetic contact between the surfactant and the substrate B is completely lost

– $E_{\mathrm{SB}} \rightarrow E_{\mathrm{SA}}$. Similarly, $E_{\mathrm{AB}} \rightarrow E_{\mathrm{AA}}$. However, if the misfit is nonzero, 3D islands will form on top of the first MLs as $\Delta\mu = \varepsilon_d > 0$ as discussed above (see Eq. (4.132)). The result will be a Stranski–Krastanov growth rather than Frank - van der Merwe growth. For the same reason Eq. (4.148) cannot explain the action of the surfactant in systems that obey Stranski–Krastanov growth in "clean" conditions. Beyond the wetting layer, A is deposited on strained A, and $E_{\mathrm{SA}} \approx E_{\mathrm{SB}}$.

The reason for this discrepancy is that the criterion (4.148) is oversimplified. It takes into account only the energetics in its simplest form which is obviously insufficient. The bond energies are not additive, and more distant neighbors should be accounted for. In addition, the lattice misfit and, in particular, the surface reconstruction should be taken into account. Jenkins and Srivastava (1998) carried out first principle calculations of the chemical potential of 1, 2, 3, and 4 MLs thick Ge films on clean and Sb precovered Si(001) relative to the chemical potential of the bulk Ge. Such kind of calculations account for all the factors mentioned above. The authors found that the ground state without Sb is (2×1) reconstruction with buckled Ge dimers (Fig. 3.41)(c)). The floating Sb makes nonbuckled dimers (Fig. 3.41)(b)) exactly where the Ge dimers should be. They compared the free surface energies of the supercells consisting of 12 Si MLs plus n (= 1,2,3,4) Ge MLs plus zero or one ML of Sb. Eq. (2.23) has been used for the calculation of the free surface energy. As seen the latter is a linear function of the chemical potentials of the constituent species, $\varphi_{i,1/2} = -\mu_i$ (i = Si, Ge, Sb). In absence of Sb, they established that the first four MLs follow exactly the curve denoted by SK in Fig. 4.41. On Sb precovered surface the second ML already acquired the value of the bulk chemical potential following qualitatively the curve denoted by FM in Fig. 4.41. The authors interprete the results in terms of saturation of the dangling bonds of the Ge overlayer or by the better wetting.

Similar results were obtained by González-Méndez and Takeuchi (1999) for the reverse case of Si on Ge(001). These authors established that Si prefers to grow on Ge(001) layer-by-layer rather than by clustering if the substrate is precovered by a ML of As. The Si

atoms occupy almost bulk-like positions and the wetting is nearly complete. In addition, the alloying is strongly suppressed.

As discussed above vanishing of the thermodynamic driving force for 3D islanding on top of the wetting layer in the Stranski–Krastanov mode for a considerable film thickness is equivalent to complete wetting, $\Delta\mu = 0$. The latter can be achieved by not allowing large atomic displacements (Markov 2001). As mentioned above in the SK mode the atoms which are in contact with the wetting layer should be considerably displaced from their "bulk-like" positions either to introduce MDs or near the islands' edges (Fig. 4.44). These displacements make the wetting incomplete. As found in a series of papers the surfactant group-V atoms form dimers on Si(Ge)(001) which reside exactly where the Si(Ge) dimers should be located (Boshart, Bailes III and Seiberling 1996; Nogami, Baski and Quate 1991; Cao *et al.*, 1992; Yu and Oshiyama 1994). After the surfactant and overlayer dimers exchange places the latter occupy the epitaxial sites that are provided by the outgoing surfactant. The surfactant dimers on top do not permit large displacements of the overlayer atoms underneath, and in turn incomplete wetting. In other words, the surfactant atoms press the overlayer atoms into bulk-like positions and do not allow the formation of MDs. Thus, the surfactants suppress the thermodynamic driving force for 3D islanding by "locking" the crystal atoms into bulk-like positions.

We finish this section with the remark that a surfactant is thermodynamically effective when it adsorbs more strongly to the film rather than to the substrate, i.e., $E_{\mathrm{SA}} > E_{\mathrm{SB}}$. However, conclusions that "the surfactant decreases the surface energies of both crystals and thus leads to layer-by-layer growth" appear quite often in the literature. Such notions appear even in the case of homoepitaxy, like say Si on As-precovered Si(111), where $E_{\mathrm{SA}} \equiv E_{\mathrm{SB}}$. Obviously, generalizations of this kind are irrelevant.

4.3.6.2 *Kinetics*

In absence of a surfactant the atoms arriving at the crystal surface diffuse on it, join pre-existing steps or islands, or give rise to new islands. At sufficiently high temperatures the diffusivity of the atoms

on the terraces is high and they reach the pre-existing steps before meeting with each other. This results in a step-flow growth. At low temperatures and in turn low diffusivity the atoms meet with each other before reaching the steps and give rise to 2D nuclei on the terraces. In presence of a complete ML of S atoms two new phenomena take place. First, the surfactant changes the energetics of incorporation of atoms into ascending and descending steps even it is present in a very small amount just necessary to decorate the steps. Second, the overlayer atoms have to exchange places with the S atoms on the terraces or at the steps in order to join the crystal lattice. Both phenomena lead to a change of the diffusivity of the adatoms across the steps and on terraces, and in turn exert an effect on the direction of transport (upward or downward) of atoms. Moreover, the change of diffusivity on terraces affects strongly the kinetics of nucleation and growth of the islands thus stimulating either the step flow or 2D nucleation. We consider in more detail the effect of the surfactant on the kinetics of attachment and detachment of atoms to and from the steps, and the exchange–de-exchange kinetics on terraces. But before doing that we will consider briefly the "classical" question of the effect of surfactants on the kinetics of 2D nucleation.

Effect of Surfactant on 2D Nucleation: We explore this question in the simpler case of homoepitaxy. Accounting for the unlike substrate (unlike half-crystal block B) requires only adding of a term of the kind $l^2(\sigma + \sigma_{\mathrm{i}} - \sigma_s)$ to the work for nucleus formation.

In order to grasp easier the essential physics we treat first the classical theory of nucleation. The Gibbs free energy of formation of square nucleus with edge length l and consisting of $n = l^2/a^2$ atoms can be easily evaluated by using the following imaginable process (Fig. 4.55). The initial state is a surface covered by one ML of surfactant atoms. First we evaporate all surfactant atoms reversibly and isothermally. Then on the clean surface we produce a cluster consisting of n atoms. The work of its formation is (Eq. (2.33))

$$\Delta G_0 = -n\Delta\mu + 4l\varkappa_c, \tag{4.149}$$

where $\varkappa_c$ is the energy per unit length of the step surrounding the cluster.

Figure 4.55: The calculation of the Gibbs free energy for nucleus formation on surfactant precovered surface. (a) The initial surface covered with surfactant atoms denoted by filled circles; (b) the surfactant atoms are evaporated and a cluster consisting of n atoms is created; (c) the surfactant atoms are condensed back and a cluster consisting of n surfactant atoms is formed on top. (I. Markov, *Phys. Rev. B* **53**, 4148 (1996). Copyright 2002 by the American Physical Society.)

Finally, we condense back all the surfactant atoms. In doing this we gain energy $-4ls\varkappa_c$ when saturate the dangling bonds along the steps with S atoms, and spend energy $4l\varkappa_s$ to create a new step surrounding the cluster consisting of S atoms. Then the work for nucleus formation reads (Markov 1996, 1999)

$$\Delta G_s = \Delta G_0 - 4ls\varkappa_c + 4l\varkappa_s, \tag{4.150}$$

where $\varkappa_s$ is the energy per unit length of the step surrounding the cluster consisting of S atoms. The parameter

$$s = 1 - \frac{\omega}{\omega_0} \tag{4.151}$$

accounts for the saturation of the dangling bonds by S atoms and appears as a measure of the surfactant efficiency, where

$$\omega = \frac{1}{2}(\psi_{\mathrm{cc}} + \psi_{\mathrm{ss}}) - \psi_{\mathrm{sc}} \tag{4.152}$$

and

$$\omega_0 = \frac{1}{2}\psi_{\mathrm{cc}} \tag{4.153}$$

is the energy of a dangling bond or, what is the same, the energy required to form a kink (see Sec. 1.6.2).

Looking at Eq. (4.152) it becomes immediately clear that it in fact represents the relation of Dupré where ω is the energy per bond of the boundary between two infinitely large half-blocks of the surfactant S and the crystal C. This can be easily verified if we divide Eq. (4.152) by the area a^2 occupied by an atom. In other words, ω is the interfacial energy per atom. Note also that ω is the energetic parameter that determines the enthalpy of mixing the two species C and S (Swalin 1991). It must be positive in order to allow the segregation of the surfactant. In the absence of a surfactant $\psi_{\mathrm{ss}} = \psi_{\mathrm{sc}} = 0$, $\omega_0 = \psi_{\mathrm{cc}}/2$, and $s = 0$. At the other extreme, $\psi_{\mathrm{ss}} + \psi_{\mathrm{cc}} = 2\psi_{\mathrm{sc}}$ and $s = 1$. Thus, the parameter s varies from 0 at complete inefficiency to 1 at complete efficiency. (In general, the parameter s can be greater than unity which means $\omega < 0$. However, this means an alloying of the surfactant with the growing crystal which will have a deleterious consequences for the quality of the overlayer and should be avoided.)

In addition, comparing Eqs. (4.152) and (1.71) allows us to conclude that ω is also the work to create a kink in a presence of a surfactant that decorates the steps. Then, the kink density as given by the reciprocal of Eq. (1.75)

$$\rho = \frac{1}{\delta_0} = \frac{2}{a}e^{-\omega/kT},$$

which should be larger than the density $\rho_0 = (2/a)\exp(-\omega_0/kT)$ in absence of a surfactant. We conclude that the steps are rougher in the presence of a surfactant. The latter has been experimentally observed by Voigtländer *et al.* (1995) in the case of homoepitaxy of

Si(111). Kandel and Kaxiras (2000) reached the same conclusion by kinetic Monte Carlo calculations.

It follows from Eq. (4.150) that in the case of surfactant mediated growth the Gibbs free energy for nucleus formation contains two more terms that have opposite signs and thus compete with each other. The s-containing term accounts for the decrease of the edge energy of the cluster owing to the saturation of the dangling bonds by the surfactant atoms. The energy, $4l\varkappa_s$, of the dangling bonds of the periphery of the cluster, consisting of surfactant atoms, which is unavoidably formed on top of the 2D nucleus due to the segregation of the mediate, increases the work of cluster formation.

Finding a solution for small number of atoms in the critical nucleus in the atomistic extreme is straightforward. We simply have to make use of Eq. (2.23)

$$\Phi = n\varphi_{1/2} - U_n,$$

for the edge energy of both clusters instead of using the capillary term for the edge energy $\varkappa$.

The binding energy U_n can be divided into lateral energy E_n and desorption energy E_{des} (assuming additivity of the bonding energy)

$$U_n = E_n + nE_{\text{des}} \tag{4.154}$$

and for Φ one obtains

$$\Phi = n\Delta W - E_n, \tag{4.155}$$

where $\Delta W = \varphi_{1/2} - E_{\text{des}}$ is the energy to transfer an atom from a kink position onto the terrace.

We then substitute Φ for $4l\varkappa_c$ in (4.150) to obtain

$$\Delta G_s(n) = -n\Delta\mu + n(1-s)\Delta W - (1-s)E_n + \Phi_s, \tag{4.156}$$

where Φ_s has the meaning of the edge energy $4l\varkappa_s$ of the surfactant cluster.

Figure 4.56 shows the dependence of $\Delta G_s(n)$ relative to the crystal bond strength, ψ_{cc}, on cluster size n for the (111) surface of fcc metals ($\varphi_{1/2} = 6\psi_c$, $E_{\text{des}} = 3\psi_c$ and $\Delta W = 3\psi_c$), with $\psi_{\text{ss}}/\psi_{\text{cc}} = 0.2$, a constant supersaturation $\Delta\mu = 1.1\psi_{\text{cc}}$, and different values of s

Figure 4.56: The change of the Gibbs free energy for cluster formation relative to the work needed to disjoin two crystal atoms, $\Delta G_s(n)/\psi_{\rm cc}$, vs the number of atoms on the (111) surface of a fcc crystal. The values of the surfactant efficiency s are denoted by figures at each curve. The structure of the nucleus is given by the filled circles. The empty circles denote the atoms that turn the critical nuclei into stable clusters. The supersaturation $\Delta\mu = 1.1\psi_{\rm cc}$ for all curves. As it could be seen the increase of efficiency of the surfactant leads to a decrease of the of the critical nucleus size and the work needed for its formation. The only exception is at small values of s at which the edge energy of the surfactant cluster, Φ_s, overcompensates for the decrease of the edge energy of the crystalline cluster. In this case n^* and $\Delta G_s(n^*)$ are larger than in the clean case. (I. Markov, *Phys. Rev. B* **53**, 4148 (1996). Copyright 2002 by the American Physical Society.)

denoted by figures at each curve. As it could be seen $\Delta G_s(n)$ represents a broken line (as it should be expected for a small number of atoms, c.f. Fig. 2.18) displaying a maximum at $n = n^*$. Under clean conditions ($s = 0$) the critical nucleus consists of 2 atoms. When s is very small ($= 0.05$) (the surfactant is almost inefficient), the number of atoms in the critical nucleus equals 6 due to the contribution of the edge energy of the of the surfactant cluster, $4l\varkappa_s$. The work of formation of the critical nucleus also increases. Increasing s to 0.3 (decrease of the edge energy of the cluster) leads to a decrease of the nucleation work and n^* again becomes equal to 2. At some greater value of s ($= 0.7$) $n^* = 1$ and the nucleation work decreases drastically.

We see that the critical nucleus size can differ under one and the same conditions (temperature, rate of deposition) in absence and presence of a surfactant. In general, we should expect a decrease of the nucleus work and, in turn, a steep increase of the nucleation rate. The calculation of the latter requires to know the particular processes that take part during condensation, which will be considered in the next paragraphs. We mention here only that increasing the nucleation rate leads to larger density of smaller 2D islands. The latter can coalesce and cover completely the surface before reaching the critical island's size for second layer nucleation (see paragraph 3.4.2.1). Thus the surfactants can induce layer-by-layer growth by enhancing nucleation (Rosenfeld *et al.*, 1993; van der Vegt *et al.*, 1998).

The rate of nucleation reads (see Chapter 2)

$$J_s = \omega^* \Gamma N_0 \exp\Big(-\frac{\Delta G_s(n^*)}{kT}\Big), \tag{4.157}$$

where ω^* is the flux of atoms to the critical nucleus, and $\Gamma \cong 1$ is the Zeldovich factor. $\Delta G_s(n^*)$ is given by Eq. (4.156) with $n = n^*$.

Bearing in mind that $\Delta\mu = kT \ln(n_s/n_{\rm se})$, we can write

$$\Delta\mu = kT \ln\Big(\frac{n_s}{N_0}\Big) - kT \ln\Big(\frac{n_{\rm se}}{N_0}\Big), \tag{4.158}$$

where (see Eq. (3.18))

$$\frac{n_{\rm se}}{N_0} = \exp\Big(-\frac{\Delta W}{kT}\Big). \tag{4.159}$$

Combining Eqs. (4.156)–(4.159) gives

$$J_s = \omega^* \Gamma N_0 \Big(\frac{n_s}{N_0}\Big)^{n^*} \exp\Big(\frac{n^* s \Delta W + (1-s)E^* - \Phi_s}{kT}\Big). \tag{4.160}$$

In the absence of a surfactant, $s = 0$ and we obtain the familiar expression

$$J_0 = \omega^* \Gamma N_0 \Big(\frac{n_s}{N_0}\Big)^{n^*} \exp\Big(\frac{E^*}{kT}\Big). \tag{4.161}$$

Note that the presence of the surfactant is not accounted for only by the s-containing terms in the exponential. It is the flux ω^* which depends on the mechanism of transport of building units to

the critical nucleus, and in turn on the presence of absence of a ML of a third species. And do not forget that n^* and E^* can have different values in Eqs. (4.160) and (4.161).

Attachment–Detachment Kinetics: As discussed in Chapter 3, whereas an atom approaching an ascending step joins it upon striking, an atom approaching a descending step has to overcome an additional Ehrlich-Schwoebel (ES) barrier (Ehrlich and Hudda 1966; Schwoebel and Shipsey 1966). If the ES barrier is low the overlayer grows more or less in a layer-by-layer mode. Otherwise, instabilities of different kind appear (Politi *et al.*, 2000). The ES barrier can be reduced and become even negative if the roll-over mechanism is replaced by the push-out mechanism (see Fig. 3.53(b)) (Wang and Ehrlich 1991).

Zhang and Lagally (1994) suggested that the ES barrier will be further reduced if the step is decorated by surfactant atoms and the relation $\psi_{\rm cc} > \psi_{\rm sc} \gg \psi_{\rm ss}$ holds. When overlayer atoms exchange sites with S atoms that decorate the steps an energy $n(\psi_{\rm cc} - \psi_{\rm sc})$ is expected to be gained where n is the coordination number of an atom in the kink position. In such a way the last barrier before descending is shifted further downwards below the level of the surface diffusion barrier as shown in Fig. 4.57. The latter is in good agreement with first principle molecular dynamics calculations of displacement of Sb dimer at the step edge by a Si dimer through a push-out mechanism (Oh, Kim and Lee 1996).

On the other hand, an atom approaching the step from the lower terrace should displace the surfactant atom in addition to overcoming of the diffusion barrier. Thus it should overcome an extra energetic barrier, $E_{\rm A}$ (Fig. 4.57, compared with that in absence of a surfactant (Markov 1994). We already discussed this in the beginning of Chapter 3 (see Fig. 3.1). As a result, the potential sampled by the atoms will be just the opposite to that shown in Fig. 3.53(a). Thus the surfactant can reverse the attachment-detachment kinetics at the steps. These effects which are of purely kinetic origin can suppress the thermodynamic driving force for 3D islanding in heteroepitaxial growth.

Figure 4.57: Schematic potential diagram for atoms moving to ascending and descending steps that are decorated by surfactant atoms. Atoms joining descending steps can sample a negative Ehrlich–Schwoebel barrier due to the push-out mechanism, on the one hand, and the weaker SC bonding compared with the CC bonding, on the other. On the contrary, atoms joining an ascending step have to overcome an extra barrier owing to the necessity to displace the surfactant atom which has been already there.

When thermodynamics predict 3D islanding, ($\Delta\mu > 0$) the atoms are more strongly bound to the upper layers rather than to the lower layers. In other words the upper layers have lower chemical potentials (Fig. 4.41). This results in a gradient of the chemical potential that drives the atoms upwards and is the driving force for the 2D–3D transformation. The appearance of an additional barrier at the ascending steps, and the reduction of the ES barrier at the descending steps owing to the decoration of the steps by S atoms, reverse the asymmetry of the attachment–detachment kinetics and thus lead to a suppression of the thermodynamic driving force for 2D–3D transition. A reverse gradient of adatoms of a *kinetic origin* appears that drives the atoms downwards. The latter results in a planar rather than a 3D growth (Markov 1994).

In order to show this, we solve the same problem as in Sec. 4.3.4. We obtain the same system of differential equations as (4.141)

$$\frac{d\Theta_n}{d\theta} = F(\Theta_{n-1}, \Theta_n) - F(\Theta_n, \Theta_{n+1}),$$

where $F(\Theta_0, \Theta_1) = 1$, $F(\Theta_N, \Theta_{N+1}) = 0$, and $F(\Theta_n, \Theta_{n+1})$ contains a parameter $A = \exp(E_{\mathrm{A}}/kT)$ which accounts for the additional barrier, E_{A}, for attachment of atoms at the ascending steps. As discussed above the latter is due to the necessity of displacement of the surfactant atom which has occupied the kink site before the arrival of the crystal atom. The result is (Markov 1994)

$$F(\Theta_n, \Theta_{n+1}) = \frac{M_n + \Theta_n - \Theta_{n+1} + qA\sqrt{\Theta_{n+1}}}{\ln(\Theta_n/\Theta_{n+1}) + qA/\sqrt{\Theta_{n+1}}}, \qquad (4.162)$$

where $q = \sqrt{\pi a^2 N_s}$ as before, Θ_n in the last terms in the numerator and denominator is replaced by Θ_{n+1} (to reflect the fact that the barrier is on the other side of the step), and M_n is given by (4.142)

$$M_n = \frac{4\pi D_s N_s (n^e_{s,n} - n^e_{\mathrm{s,n+1}})}{\Re}.$$

The discussed above parameter M_n contains the difference $n^e_{s,n} - n^e_{\mathrm{s,n+1}}$ which is the thermodynamic driving force for 2D-3D transformation. The latter is an increasing function of the temperature, whereas N_s and in turn q as well as A decrease steeply with increasing temperature. That is why at high temperatures $qA \ll 1$ the A-containing terms in (4.162) can be neglected and we obtain the result shown by curves 1 and 2 in Fig. 4.52. At lower temperatures $qA \gg 1$ and $F(\Theta_n, \Theta_{n+1}) = \Theta_{n+1}$. Then for the bilayer pyramid shown in Fig. 3.28 (or 4.51) the surface coverages read (c.f. Eq. (3.217))

$$\begin{aligned} \Theta_1 &= \Theta_1^0 + \theta - \Theta_2^0(e^\theta - 1), \\ \Theta_2 &= \Theta_2^0 e^\theta. \end{aligned} \qquad (4.163)$$

As seen, contrary to Eq. (3.217), the above equations reflect the fact that the upper island grows only at the expense of the atoms arriving on its surface. All the atoms which arrive on the uncovered

Figure 4.58: Dependence of the surface coverages of the first (curves 1 and 1′) and second (curves 2 and 2′) MLs on the amount of the material deposited measured in a number of MLs. Curves 1′ and 2′: growth in the absence of a surfactant or at sufficiently high temperature ($F(\Theta_1, \Theta_2$ is given by Eq. (4.141), $M_1 = 0.25$); curves 1 and 2: surfactant mediated growth with $F(\Theta_1, \Theta_2) = \Theta_2$ (Eq. (4.163)). The insets show schematically the morphology of the overlayer – a bilayer (3D) island and a nearly complete first ML with a small fraction of the second ML on top. (I. Markov, *Phys. Rev. B* **50**, 11271 (1994). Copyright 2002 by the American Physical Society.)

substrate and on the terrace between the two edges feed the lower islands. That is why they grow fast and coalesce before a significant fraction of the upper ML to be grown. Equations (4.163) are plotted in Fig. 4.58 together with curves 1 and 2 of Fig. 4.52 for comparison. As seen Θ_1 reaches unity while Θ_2 is still negligible. The 2D islands should coalesce and cover completely the surface before 2D–3D transformation to occur. Layer-by-layer growth will be observed rather than 3D islanding because the thermodynamic driving force for clustering is totally suppressed by the kinetic barrier at the ascending step. The surface transport is directed downwards. This is due to the diffusion gradient of *kinetic origin* which appears on the terrace and drives the atoms towards the lower steps. Thus, this prevents the transformation of the pyramid into a 3D island. The upper islands

remain small and the nucleation on top of them is also suppressed. As a result the growth follows a mode that is nearly layer-by-layer owing to the reversed attachment — detachment kinetics at steps.

Thus the attachment — detachment kinetics suppress the thermodynamic driving force for 3D islanding. At high temperature the thermodynamics prevail and SK growth takes place irrespective of the presence of the surfactant. Surfactant induced FM growth occurs at lower temperatures.

The attachment–detachment kinetics has been recently discussed by Kandel and Kaxiras (2000) in the case of semiconductor epitaxy from another point of view. These authors suggested that it is the passivation of the island's edges that plays crucial role in determining whether a particular surfactant will suppress 3D islanding or not. Whereas the group-V elements (As and Sb) successfully passivate the edges of the tetravalent Si and Ge islands, the tetravalent Sn and Pb fail to do that. Formation of 3D islands has been observed as a result of a Kinetic Monte Carlo simulation at an amount of deposited material less than one ML, only in the case of passivated edges. The suppression of 3D islanding by group-V elements can be clarified in the framework of the model developed in Sec. 4.3.5. The 2D–3D transformation shown in Fig. 4.50 requires an easy detachment of atoms from the lower island's edges. Once this detachment is inhibited the transformation of the 2D precursor into a 3D island will be in turn arrested.

Exchange–De-exchange Kinetics: In the presence of a complete ML of the surfactant, a new kinetic effect takes place owing to the necessity of the overlayer atoms to join the crystal lattice and of the S atoms to float over the surface. These are the phenomena of exchange and de-exchange of overlayer and S atoms. Zhang and Lagally (1994) first assumed that an exchange process between overlayer and S atoms on the terraces should take place on the S precovered surfaces (Fig. 4.59). Kandel and Kaxiras (1995) assumed later that a de-exchange process (Fig. 4.59) is also possible and can play a significant role in epitaxial growth. They calculated the values of the activation energies 0.5 eV for surface diffusion of Ge on top of the Sb-passivated

Figure 4.59: Schematic view of the exchange (a→b→c) and de-exchange (c→b→a) processes. The crystal and the surfactant atoms are denoted by the filled and empty circles, respectively. (I. Markov, *Surf. Sci.* **429**, 102 (1999). By permission of Elsevier Science B.V.).

surface, and 0.8 eV and 1.6 eV, for the exchange and de-exchange processes, E_{ex} and E_{dex}, respectively. Schroeder *et al.* (1998) studied the effect of As on the homoepitaxial growth of Si(111). They found a very complicated exchange path, which avoids to a large extent the breaking of chemical bonds, and computed nearly equal values of 0.25 and 0.27 eV for E_{sd} and E_{ex}, respectively, and 1.1 eV for E_{dex}. Ko, Chang and Yi (1999) computed through first-principles pseudopotential total energy calculations the values of the barriers for surface diffusion, exchange and de-exchange for Ge on Ga, As and

Sb precovered Si(111) surface. They found that in the cases of As and Sb the barriers for exchange are even smaller than the respective barriers for surface diffusion (0.35, 0.2 and 0.55 eV for As, and 0.7, 0.3 and 0.75 eV for Sb, for $E_{\rm sd}$, $E_{\rm ex}$ and $E_{\rm dex}$, respectively).

Kandel and Kaxiras (2000) noted that the de-exchange process affects the diffusivity and in turn the kinetics of nucleation. They suggested that the atoms diffuse on top of the compact surfactant layer between de-exchange and exchange events. Thus, a generalized diffusion coefficient should account for the times the atoms spent to perform an exchange, $\tau_{\rm ex} = \nu^{-1}\exp(E_{\rm ex}/kT)$, and a de-exchange, $\tau_{\rm dex} = \nu^{-1}\exp(E_{\rm dex}/kT)$, event. The effective diffusion coefficient $D_{\rm eff}$ is given by $D_{\rm eff} = a^2 n/\tau_{\rm eff}$, where a is the distance of a single diffusion hop, n is the number of hops the atoms performs between a de-exchange and exchange events, and $\tau_{\rm eff} = \tau_{\rm ex} + \tau_{\rm dex}$. n is given by the ratio of the time for an exchange event and the time for a diffusion hop, or $n = \exp[(E_{\rm ex} - E_{\rm sd})/kT]$. Then

$$D_{\rm eff} = D_s^0 \frac{\exp[(E_{\rm sd}^0 - E_{\rm sd})/kT]}{1 + \exp[(E_{\rm dex} - E_{\rm ex})/kT]}, \tag{4.164}$$

where $E_{\rm sd}^0$ and D_s^0 are the barrier and the coefficient for diffusion on the clean surface.

As $E_{\rm dex}$ is always greater than $E_{\rm ex}$ we can neglect the unity in the denominator and compare the two exponentials. Obviously, when $E_{\rm dex} - E_{\rm ex} > E_{\rm sd}^0 - E_{\rm sd}$, $D_{\rm eff} < D_s^0$, and the island density will be $\exp\{\chi[(E_{\rm dex} - E_{\rm ex}) - (E_{\rm sd}^0 - E_{\rm sd})]/kT\}$ times greater on the surface passivated by the surfactant, where χ is the corresponding scaling exponent $n^*/(n^*+2)$ or $2n^*/(n^*+3)$. On clean Si(111) surface $E_{\rm sd,0} =$ 0.75 eV (Voigtländer and Zinner 1993). Then, according to Kandel and Kaxiras $E_{\rm dex} - E_{\rm ex} = 0.8$ eV, and $E_{\rm sd}^0 - E_{\rm sd} = 0.25$ eV for Sb mediated growth of Si(111). For the same surface but with As as a surfactant (Schroeder *et al.*, 1998), $E_{\rm dex} - E_{\rm ex} = 0.8$ eV, and $E_{\rm sd}^0 - E_{\rm sd} = 0.5$ eV. Thus, in both cases we have to expect an increase of the island density by one or two orders of magnitude.

This is a very important conclusion which should be considered in more detail. We introduce as above two time constants which characterize the exchange and the de-exchange processes both being

normalized to the time, $t_1 = 1/F$, necessary for deposition of a complete ML, $F = \Re/N_0$ being the the atom arrival frequency. First, this is the mean residence time of the atoms on top of the S layer before exchange $\tau_{\rm ex} = (F/\nu)\exp(E_{\rm ex}/kT)$ where ν is the attempt frequency. Second, this is the mean residence time before de-exchange of an atom embedded in (or under) the S layer $\tau_{\rm dex} = (F/\nu)\exp(E_{\rm dex}/kT)$ (Markov 1999a, 1999b). Obviously, if a particular time constant is greater than unity the corresponding process will not occur.

As $\tau_{\rm dex} \gg \tau_{\rm ex}$ three possibilities exist. The first is $\tau_{\rm dex} \ll 1$. This extreme describes the *reversible exchange* as the adatoms have sufficient time to go back on top of the S layer through a de-exchange process. A dynamic *exchange–de-exchange equilibrium* is established. With the value of $E_{\rm dex} = 1.6$ eV calculated by Kandel and Kaxiras we find, at 600 K, $\tau_{\rm dex} \approx 0.002$. Then the exchange–de-exchange equilibrium is established in the very beginning of the deposition process. The nucleation process takes place in a more or less disordered (because of the different size of the atoms involved) 2D phase — a ML consisting of mixed S and overlayer atoms. A considerable fraction of the incoming atoms remains on top of the S layer and diffuse fast to the pre-existing steps. The formation, growth and decay of nuclei take place through exchange and de-exchange processes. The second extreme is $\tau_{\rm ex} \ll 1 < \tau_{\rm dex}$. This is the case of *irreversible exchange*. The incoming atoms rapidly exchange places with S atoms and remain buried under the S layer. All processes of diffusion, nucleation and incorporation into islands and steps occur under (or between) the S atoms. The case $1 < \tau_{\rm ex} \ll \tau_{\rm dex}$ should be excluded as it means that the S atoms will remain buried under the arriving overlayer atoms. Note that the two cases of reversible and irreversible exchange can take place in one and the same system substrate–adsorbate but at different temperatures. It is obvious that we could expect a transition to irreversible exchange at lower temperatures.

Let us consider in more detail the case of the reversible exchange. (The case of irreversible exchange is more or less trivial. The atoms undergo an exchange event after several diffusion hops (Markov 1999a). All the processes of diffusion, nucleation and incorporation

to islands and steps occur in a mixed layer of crystal and surfactant atoms with displaced surfactant atoms on top. The strongly inhibited surface diffusion leads to larger nucleus density.) A dynamic equilibrium between atoms undergoing exchange and de-exchange events (exchange–de-exchange equilibrium (Markov 1999a)) $n_1/\tau_{\rm ex} = n_s/\tau_{\rm dex}$ takes place. Then

$$n_s = n_1 \exp[(E_{\rm dex} - E_{\rm ex})/kT], \tag{4.165}$$

where n_s is the concentration of the atoms embedded into (or under) the surfactant layer, and n_1 is the concentration of atoms on top of the surfactant layer.

We assume that the process of nucleation takes place by attachment of atoms that are on top of the surfactant layer to atoms or clusters embedded into the latter through exchange events. Then, the flux of atoms to the critical nucleus is

$$\omega^* = \alpha^* \nu n_1 \exp[-(E_{\rm sd} + E_{\rm ex}^{(n)})/kT], \tag{4.166}$$

where α^* is the number of the possible exchange events by which an atoms can join the critical nucleus to produce a stable cluster, and $E_{\rm ex}^{(n)}$ is the barrier of an exchange process that takes place in the proximity of a cluster of size n.

Finally, following the same procedure as in Secs. 3.2.3.2 and 3.4.2, we obtain an expression for $N_{\rm S}$ which can be written in the form

$$N_{\rm S} = N_{\rm s,0} \exp\left(-\frac{\chi}{n^*} E_{\rm S}/kT\right), \tag{4.167}$$

where $E_{\rm S}$ combines all energy contributions which depend on the presence of the surfactant (Markov 1999a, 1999b) and

$$N_{\rm s,0} = N_0 \left(\frac{\nu}{F}\right)^{-\chi} \exp\left(\frac{\chi}{n^*} E_0/kT\right) \tag{4.168}$$

is the nucleus density in absence of a surfactant ($E_{\rm S} = 0$). The above equation coincides either with (3.133) if the step edge barrier (or any barrier inhibiting the incorporation of atoms into the nucleus) is negligible ($\chi = n^*/(n^* + 2)$), or with (3.205) if a significant step edge barrier exists ($\chi = 2n^*/(n^* + 3)$). In both cases of diffusion and

a kinetic regime, E_{S} is given by

$$E_{\mathrm{S}} = sE^* - n^* s\Delta W + \Phi_s + E_{\mathrm{ex}}^{(n^*)} - n^*[(E_{\mathrm{dex}} - E_{\mathrm{ex}}) - (E_{\mathrm{sd}}^0 - E_{\mathrm{sd}})]. \quad (4.169)$$

In order to become physically more clear we write the above expression in the capillary terms of edge energies

$$E_{\mathrm{S}} = -4lsx_c + 4lx_s + E_{\mathrm{ex}}^{(n^*)} - n^*[(E_{\mathrm{dex}} - E_{\mathrm{ex}}) - (E_{\mathrm{sd}}^0 - E_{\mathrm{sd}})]. \quad (4.170)$$

As seen, the exponential multiplying $N_{\mathrm{s},0}$ in Eq. (4.167) can be smaller or greater than unity depending on the interplay of the energies involved in E_{S}. The latter must be negative in order to stimulate the nucleus formation ($N_{\mathrm{S}} \gg N_{\mathrm{s},0}$). A greater density of smaller islands will be formed, and the film will grow by 2D nucleation rather than by step-flow. What is more important is that the greater density of smaller nuclei leads to layer-by-layer growth rather than to the mound formation. As discussed in Chapter 3 the latter requires the critical size for second layer nucleation to be reached. In the opposite case the surfactant will inhibit the nucleation and will promote either step-flow growth (this is the case of homoepitaxy of Si(111) mediated by the tetravalent Sn (see Iwanari and Takayanagi 1992 and the analysis of the experimental data by Markov 1999b) or mound formation if the nucleus density is not too large.

There are two negative terms in E_{S} and two positive. As follows from above $(E_{\mathrm{dex}} - E_{\mathrm{ex}}) - (E_{\mathrm{sd}}^0 - E_{\mathrm{sd}})$ is of the order of 0.3–0.5 eV (Kandel and Kaxiras 2000; Schroeder *et al.*, 1998). We recall that the second negative term ΔW is of order of one half of the enthalpy of evaporation, and it is multiplied by $n^* \geq 1$ and by $s < 1$. That is why it is of interest to evaluate the surfactant efficiency s.

Making use of Eqs. (4.151)–(4.153), and the approximation $\psi_{\mathrm{sc}} \cong \sqrt{\psi_{\mathrm{cc}}\psi_{\mathrm{ss}}}$ (London 1930), we obtain

$$s = 2\sqrt{x} - x, \quad (4.171)$$

where $x = \psi_{\mathrm{ss}}/\psi_{\mathrm{cc}}$. The latter can be evaluated from data of the surface energy σ and the atomic volume v

$$\frac{\psi_{\mathrm{ss}}}{\psi_{\mathrm{cc}}} \cong \frac{(\sigma v^{2/3})_s}{(\sigma v^{2/3})_c}, \quad (4.172)$$

We consider now one of the most studied cases of Sb-mediated growth of Si(111) (Voigtländer *et al.*, 1995; Voigtländer and Zinner 1993, 1994; Horn-von Hoegen *et al.*, 1995). Fortunately we have data for the surface energy of both materials, $\sigma(\mathrm{Sb}) = 395$ erg cm^{-2} and $\sigma(\mathrm{Si}) = 1240$ erg cm^{-2} (Swalin 1991). Then $\psi_{\mathrm{ss}}/\psi_{\mathrm{cc}} = 0.4$ and $s = 0.86$, and with $\Delta H_{\mathrm{ev}} = 4.72$ eV (Hultgren *et al.*, 1973) we obtain $s\Delta W \approx 2$ eV. Bearing in mind that $s\Delta W$ is always larger than E^* (at $n^* = 1$, $s\Delta W = 2$ eV, and $E_1 = 0$, at $n^* = 2$, $s\Delta W = 4$ eV and the work, E_2, needed to break a Si-Si bond is of the order of 1.7–2.3 eV (Nakahara and Ichikawa 1993; Honig and Kramer 1969), etc.) this means that the decrement of the edge energy of the nucleus $n^* s\Delta W - E^* \equiv 4ls\varkappa_c$ is expected to play greater role than the purely kinetic factor $n^*[(E_{\mathrm{dex}} - E_{\mathrm{ex}}) - (E^0_{\mathrm{sd}} - E_{\mathrm{sd}})]$.

It is then of interest to evaluate the contribution of the positive terms. For Φ_s, in order to avoid the effect of the shape we evaluate the ratio of the edge energies $\varkappa_s/\varkappa_c \cong (\sigma v^{1/3})_s/(\sigma v^{1/3})_c$. Then for the nucleation of Si on Sb-precovered Si one obtains $\varkappa_s/\varkappa_c \cong 0.36$. Dividing both edge energies in Eq. (4.170) gives the fraction $\Phi_s/\Phi_c = \varkappa_s/s\varkappa_c \cong 0.42$. Finally, we can assume that the exchange process in the proximity of a cluster requires a smaller barrier than far away of clusters of any size, E_{ex}, or $E_{\mathrm{ex}}^{(n^*)} < 0.8$ eV (Markov 1999b).

We thus could argue that in Sb-mediated growth of Si(111) the greatest term in Eq. (4.169) is negative and is of thermodynamic origin. The kinetics in the sense of inhibited surface diffusion plays a secondary role. Note that when a surfactant affects the work for nucleus formation changing the edge energy $\varkappa_c$, it affects in fact the rate of 2D nucleation. In other words, it affects the kinetics of nucleation which is one of the steps of the overall growth process, rather than the thermodynamics in the sense of wetting, as discussed in Sec. 4.3.6.1.

We conclude that the effect of the surfactants on the wetting of the substrate by the overlayer in heteroepitaxy, in the classical sense of reducing the surface energy of the overlayer and in turn increasing the wetting, should be a rare event, as it requires zero misfit. The wetting could be increased artificially by suppressing the thermodynamic driving force for 3D islanding by "locking" the crystal

atoms into bulk-like positions. This is most probably the case of Stranski-Krastanov growth of Ge on Sb-precovered Si(001) surface. If this is not the case the surfactant changes the mode of growth kinetically, either by suppressing the detachment of atoms from the islands' edges, or by inhibiting the surface diffusion, or increasing the rate of nucleation. Neither of the three factors should be overlooked.

Chapter 5

The Shoulders on Which We Stand

The processes of nucleation, crystal growth, and epitaxy lay in the foundation of the fabrication of modern materials, low-dimensional structures, microelectronic devices, and in fact of many "old" technologies beginning from the production of salt from sea water to the casting of church bells and cannons. Crystallization processes also occur in the nature: snowflakes in the atmosphere, ores, minerals, and gem stones in the earth's crust, are formed by nucleation and growth in vapors, solutions, and melts. The understanding of these processes is of crucial importance for the manipulation of the processes in the atmosphere, geology, and the mining. The fundamental concepts like half-crystal (kink) position, three- and two-dimensional (3D and 2D) nuclei, equilibrium crystal shape, wetting, surface diffusion, surface roughness, crystal defects, spiral growth, misfit dislocations, etc., seem natural, a priori understandable, to the present day researchers. However, they have been discovered and debated for more than a century. Everybody who works in nucleation and growth knows what is the Gibbs free energy, Wulff construction, Wulff-Kaischew theorem, Volmer-Weber, Frank-van der Merwe and Stranski-Krastanov mechanisms of growth, Frenkel-Kontorova model, Zeldovich factor, and Burton, Cabrera and Frank theory. The people who introduced these fundamental ideas in science, Gibbs, Wulff, Volmer, Frenkel, Stranski, Kaischew, Krastanov, Frank, Cabrera, Zeldovich, and van

der Merwe, are known to all scientists of the crystal growth community from textbooks and review papers but often as nothing more than names. That is why, it is the goal of this chapter to describe briefly the life and achievements of the above mentioned scientists in the historical background and the scientific atmosphere in which they lived and created, and to show as far as possible their personalities. All of them lived in the turbulent 20th century with the only exception of Gibbs who lived uneventfully in the bell époque. This is the reason to describe in some detail the historical background, if we want to understand their behavior and the decisions they had to make in their lives. They were all devoted to science but they all had the courage to oppose any injustice in real life according to their moral convictions. That is why I would like to express our respect and give tribute to them as our teachers. The stories are put in the order of their birth dates. It turned out that this order matches well with the development of the ideas in the field. The title of this chapter is taken from a website of the Technical University of Berlin, where Volmer and Stranski were teachers.

5.1 J. W. Gibbs

Josiah Willard Gibbs (1839–1903). American mathematical physicist whose work in thermodynamics, statistical mechanics, and mathematics laid the basis for the development of physical chemistry as a science (Fig. 5.1). Albert Einstein called him "the greatest mind in American history." Gibbs was born in New Haven, Connecticut. He graduated from Yale College in 1858 and continued his studies at Yale. Gibbs was a 7th generation of academics. One of his grandfathers, Samuel Willard, was a president of Harvard College (1701–1707), another of his ancestors, Jonathan Dickinson, was the first president of College of New Jersey (later Princeton University). His father Josiah Gibbs was a linguist and theologian who served as a professor of sacred literature at Yale. In 1858, he received his bachelor's degree with distinction in Latin and in Mathematics. In 1863, Gibbs received the first Doctorate of Philosophy in engineering granted in the United States, for a thesis entitled "On the Form

Figure 5.1: Josia Willard Gibbs.

of the Teeth of Wheels in Spur Gearing", and in 1866, he patented a design for a railway brake. This was the time when North America has been covered by railways. After graduating from Yale, he accepted an appointment as a tutor in Yale College. There he taught Latin and Natural Philosophy for three years. Realizing that his education in Yale was insufficient for theoretical research, Gibbs went to Europe for three years with the money he inherited from his father. There, he attended the lectures of famous mathematicians like Jean-Marie Duhamel, Joseph Liouville, and Michel Chasles in Sorbonne and Collége de France, Karl Weierstrass and Leopold Kronecker in Berlin, Georg Kantor in Halle, of the physicists Gustav Kirchhoff and Hermann von Helmholtz, and the chemist Robert Bunsen in Heidelberg. In 1871, he was appointed Professor of Mathematical Physics at Yale, the first such professorship in the world, half a year before such a department was to be established at Cambridge for James Clerk Maxwell, the most influential physicist of the 19th century. At that time, Gibbs had not published any scientific paper, and when he noted this fact to his colleagues, they answered that they were sure he would write papers in the future.

In 1875 and 1878, he published in two parts his famous monograph (total of 300 pages) entitled "On the Equilibrium of Heterogeneous Substances" in Transactions of Connecticut Academy of Arts and Sciences. The presentation of the ideas in these papers was so rigorous and difficult to read that a joke later circulated in New Haven that "only one man lived who could understand Gibbs's papers. That was Maxwell, and now he is dead". (Maxwell died in 1879 at the age of 48). The works of Gibbs became very popular in Europe when his monograph "On the Equilibrium of Heterogeneous Substances" was translated into German (the then leading language in chemistry) by Wilhelm Ostwald in 1892 under the title "Thermodynamische Studien", and into French by Henri Louis Le Châtelier in 1899 under the title "Équilibre des Systémes Chimiques".

In fact, it was Gibbs who laid the foundation of the theory of crystal growth by 2D nucleation more than a hundred years ago. He pointed out in a footnote in "On the Equilibrium of Heterogeneous Substances" that the continuous growth of a given crystal face is impossible, if new molecular layers could not be built. The building of a new layer is particularly *difficult at the beginning or immediately after the beginning of the new layer formation.* The change of the Gibbs free energy necessary for the growth of the crystal face to take place is not, however, one and the same on different crystal faces. It is possible that it is greater for surfaces with smaller surface energies. Thus, without even mentioning the term "nucleus", Gibbs gave the concept of growth of perfect crystal surfaces through the formation and lateral spreading of 2D nuclei. He even gave a hint concerning the effect of the surface structure of the crystal faces with respect to the formation of 2D nuclei.

This paper, which is considered as his most important contribution, overshadowed in some extent some other works of no less significance. In 1873, he published two papers entitled "Graphical methods in the thermodynamics of fluids" and "A method of geometrical representation of the thermodynamic properties of substances by means of surfaces". In the second paper, the graphical methods in thermodynamics developed in the first papers were extended to

Figure 5.2: The clay plaster construction of the Gibbs' thermodynamic surface made by James Clerk Maxwell which is now kept in Yale University.

diagrams in three-dimensions. He constructed a diagram in coordinates volume, energy, and entropy. If the general relation between these quantities of any substance is known, the relation between the pressure, temperature, and volume can be immediately found by simple differentiation. The exceptional importance and beauty of this work by a hitherto unknown researcher was immediately recognized by Maxwell, who, in the last years of his life, spent considerable time in carefully constructing, with his own hands, a clay plastic 3D model of the thermodynamic surface suggested by Gibbs in coordinates of volume, -entropy, and -energy, a cast of which he sent to Gibbs (Fig. 5.2). The cast is now on display at the Physics Department of Yale University.

Another very important work of Gibbs is the creation (independently and simultaneously with the British electrical engineer, mathematician, and physicist Oliver Heaviside) and introduction in physics of the vector algebra to replace the so-called quaternions introduced by the Irish mathematician William Rowan Hamilton. Gibbs printed, in 1881 and 1884, a very detailed description of the vector calculus for the use of his students. He did not publish this work, instead one of his students, Dr E. B. Wilson published in 1901 a textbook "Vector analysis" based on the lecture notes of Gibbs.

The contributions of Gibbs are numerous, we will list just a few of them: statistical mechanics, statistical ensemble, phase space, Gibbs free energy, chemical potential, Thomson–Gibbs equation, Gibbs phase rule, Gibbs–Helmholtz equation, Gibbs–Duhem relation, Gibbs isotherm, Gibbs paradox, and Gibbs–Donnan effect.

The scientific achievements of Gibbs were recognized by many learned societies and universities both in the United States and abroad, the London Mathematical Society, the Royal Academy of Amsterdam, the Royal Society of London, the Royal Prussian Academy of Berlin, the Royal Society of Sciences, Göttingen, the French Institute, and the Physical Society of London being among them. In 1881, he received the Rumford Medal from the American Academy of Boston, and in 1901, the Copley Medal from the Royal Society of London.

Gibbs' personality is also very interesting. He was a very modest and delicate man. He never married and lived with the family of his sister. He always prepared the salad for the Sunday lunches because as he noted, he was an expert in heterogeneous systems. An interesting story about Gibbs circulates. When he had to give an exam in physics for entering the University, a friend of his father, the dean of the Department of Physics, Professor Thatcher, visited his father, and asked the young Gibbs whether he would apply for the examination. Gibbs answered that he felt he was not well prepared and would not apply. Professor Thatcher asked him to talk on the most difficult problem for him. After the presentation, Professor Thatcher said: "You are right, young man, no need to apply for examination.

You are already a student". In the first years in Yale, Gibbs lectured without a salary. At that time, this was a practice in European universities as well. In 1880, the newly established Johns Hopkins University in Baltimore offered him a professorship with a salary of US$ 3000 per year. Yale made a counter offer of US$ 2000. Gibbs stayed in Yale. The modesty and the sense of humor of Gibbs is well illustrated by a remark that he once made to a close friend of his concerning his abilities as a mathematician. He said "If I have had any success in mathematical physics, it is, I think, because I have been able to dodge mathematical difficulties."

A bronze bas-relief is installed in the Sloane Physics Laboratory in Yale University with the inscription "Josiah Willard Gibbs, Professor of mathematical physics in Yale College from 1871 to 1903. Discoverer and interpreter of the laws of chemical equilibrium" (Fig. 5.3).

Figure 5.3: The bas-relief of Gibbs installed on the wall of the Sloane Physics Lab in Yale.

5.2 G. Wulff

Georgii Viktorovich Wulff (1863–1925). He was a Russian crystallographer and mineralogist, born in Nezhin (provincial capital of the Chernigov Governorate in Ukraine). He graduated in physics from the University of Warsaw (Fig. 5.4). He was still a student when he published two papers on the morphology (1883) and physical properties of crystals (1884); and he was awarded a gold medal by the university for his research on the physical properties of quartz. It is worth noting that at that time Poland was partitioned by Austria–Hungary, the German, and the Russian Empires. Warsaw was under Russian rule. In 1895, he published in the Proceedings of the Warsaw University his famous paper on the growth of crystals and the Wulff construction. Wulff submitted the results in this paper for a PhD thesis in the Warsaw University, but it was rejected on the ground of the argument that the results are not sufficient in volume for a doctoral thesis. The thesis was defended the next year in the Novorossiisk University in Odessa. Several decades should pass in order the importance of the results in this paper to be highly

Figure 5.4: Georgii Viktorovich Wulff.

estimated only after publishing it in German language in 1901 in Zeitschrift für Kristallographie. Today, whole books are devoted to the problem of the Wulff construction (e.g., Dobrushin, Kotecky and Shlosman 1993). After defending his thesis, he lectured in the Imperial University of Kazan, in the Warsaw University, and in Moscow State University. In 1909, Wulff proposed a stereographic projection of a sphere with its meridians and parallels, called Wulff net, which is still widely used in optical and X-ray crystallography.

In 1911, the Russian minister of education L. A. Kasso issued an order with which the meetings and societies of the university students were forbidden. The university administration should see to the execution of the order, thus executing function of the police. In protest, Wulff, together with more than a hundred university professors, resigned. Wulff joined the private Moscow People's University which was built on the funds of a Russian army general of Polish origin, Alfons Leonovich Shanyavskii. He transferred his laboratory there and supported it on the means of his own.

It is instructive to describe the situation in the European universities at the second half of the 19th century. W. Paszkowicz (2006) wrote: "Since 1905 the Imperial Warsaw University had to exclude non-Russian professors and it was boycotted by Polish students. At the Imperial University (the only university in Warsaw, existing until 1915 in Warsaw and later, until 1917 in Rostov in south Russia), women were not admitted. Due to this restriction, Maria Sklodowska (later Mme Curie) had to get education in France, as numerous other Polish and Russian ladies. It is noteworthy that French universities were closed until at least late 1880s inaccessible to French girl students but to foreign ones they started to be open a decade earlier." Women were not allowed to attend public institutions of higher education in Vienna up to 1900. Thus, Lise Meitner was able to achieve education in physics as a private student.

In 1913, Wulff published a paper in Physikalische Zeitschrift on the diffraction of X-rays from crystal surfaces independently and simultaneously with the paper by William Lawrence Bragg in Proceedings of Cambridge Philosophical Society. Today, the fundamental equation in crystallography $2d \sin\theta = n\lambda$, where d is the interplanar

spacing in the crystal, θ is the incident angle, n is an integer, and λ is the wavelength of the incident wave, is known as Bragg–Wulff law for which Bragg received (together with his father William Henry Bragg) a Nobel prize in 1915. These papers put the foundation of a new field of knowledge — the X-ray crystallography.

At the end of his autobiography, Wulff wrote: "Georgii Viktorovich is now deprived of any means and a pension, which would give him the possibility to continue with his previous activity, and shares the fate of the ordinary Russian scientist — a concern about elementary conditions of living".

5.3 M. Volmer

Max Volmer (1885–1965): He was a renowned German physical chemist (Fig. 5.5) and was born in Hilden, Rheinland. In 1908, he graduated in chemistry from the University of Marburg and was awarded a doctorate in 1910, based on his work on photochemical reactions in high vacuum in the University of Leipzig. After a couple

Figure 5.5: Max Volmer as a President of the Academy of Sciences of the German Democratic Republic, 1958.

of years at the University of Hamburg in 1922, he was appointed ordinarius professor and director of the Institute of Physical Chemistry and Electrochemistry of the Technische Hochschule Berlin (Berlin–Charlottenburg), the position which was previously held by Walther Nernst.

In 1926, in co-authorship with A. Weber, he derived an expression for the rate of formation of 3D nuclei by making use of a thermodynamic approach and found that the rate should be inversely proportional to the exponential of the work for nucleus formation. This was the reason one of the mechanisms of heteroepitaxial growth to be named by Ernst Bauer (1958) after their names — Volmer–Weber growth.

In 1921, together with J. Estermann, he studied the growth of mercury crystals from vapor as a function of the supersaturation. The authors eliminated several other possibilities and concluded that the basal plane of the crystals should grow by formation and lateral spreading of the 2D nuclei. This idea was quantitatively developed six years later by H. Brandes, who calculated the work of formation of the 2D nuclei as one half of the edge energy. A detailed experiment was performed 10 years later together with W. Schultze in the case of growth of iodine from vapor as a function of the supersaturation. It was found that the rate of surface growth increases sharply with the supersaturation as required by a Boltzmann dependence of the rate on the work for nucleus formation. Simultaneously, Volmer and M. Marder studied the crystallization of glycerol. In order to interpret the results, the authors suggested that a consideration similar to that applied in the case of 3D nucleation by Volmer and Weber five years earlier should be applied to calculate the rate of 2D nucleation and in turn to the rate of surface growth. Thus Volmer introduced the concept of the 2D nucleus and enforced it in the theory of crystal growth. Years later, F. C. Frank in the University of Bristol would find a quantitative discrepancy of the data of iodine crystallization with the theory of 2D nucleation and would suggest the concept of spiral growth around the emergency points of screw dislocations.

In 1919 together with Otto Stern, he published a paper on the mechanism of the fluorescence which resulted in the well-known Stern–Volmer equation. In 1930, he published a paper in which he

derived the fundamental equation in electrochemistry which connects the current density and the overpotential of an electrochemical reaction, known as Butler–Volmer equation. In 1939, Volmer published the first monograph on the processes of nucleation and crystallization "Kinetik der Phasenbildung" (Kinetics of Phase Formation).

In 1943, Volmer was elected as a full member of the Prussian Academy of Sciences. The appointment, however, was prevented by the Nazi regime although Otto Hahn supported his nomination. The Minister of Science, Art, and Education of the Third Reich, Bernhard Rust motivated the rejection by the words: "The Representation of the National-Socialist state regards that the political convictions of Volmer are not clear enough." He was accused of having helped a Jewish employee to escape the deportation. The procedure initiated against him was suspended. Volmer's importance for research for military purposes have played a crucial role, but his salary was reduced by one-fifth.

At the end of the war, Peter Adolf Thiessen, director of the Kaiser-Wilhelm Institute for Physical Chemistry and Electrochemistry, baron Manfred von Ardenne, director of his private laboratory Forschungslaboratoriums für Elektronenphysik (Research Laboratory for Electron Physics), Gustav Hertz, Nobel Laureate and director of the Siemens Research Laboratory II, and Max Volmer, the then ordinarius professor and director of the Institute of Physical Chemistry at the Berlin Technische Hochschule, had made a pact. The pact was a pledge that whoever first made contact with the Russians would speak for the rest. The objectives of their pact were threefold: (1) prevent plunder of their institutes, (2) continue their work with minimal interruption, and (3) protect themselves from prosecution for any political acts of the past (Thiessen had been a member of the Nazi party since 1925). On April 27, 1945, Thiessen arrived at von Ardenne's institute in an armored vehicle with a major of the Red Army, who was also a leading Soviet chemist. All four were taken to the Soviet Union together with about 3000 scientists, engineers, and skilled workers to work on the Soviet uranium project. However, not all of them were kindly invited. Werner Hartmann, a German physicist who later introduced the microelectronics into

East Germany, then 33 years of age, remembers: "Du. Dokument. Ich. Revolver". In the Soviet Union, Volmer's group designed a heavy water production process and the corresponding facility (Augustine 2007).

In 1955, Volmer returned to East Germany where he became an ordinarius professor at the Humboldt University of Berlin. From December 1955 to 1959, he became president of the German Academy of Sciences, after which he was vice-president until 1961. Volmer died in Berlin in 1965.

5.4 Ya. I. Frenkel

Yakov Ilich Frenkel (1894–1952) was renowned Russian theoretical physicist, "one of the fathers of the modern solid state physics", according to Sir Nevill Mott (Mott 1975). He was born in a Jewish family in Rostov-on-Don. His interests towards the natural sciences (in addition to painting and music) were manifested early. As a student in the high school, he wrote a 100 pages paper in which he

Figure 5.6: Yakov Ilich Frenkel.

developed the calculus of finite differences without knowing that it already existed. This work fell into the hands of the St. Petersburg University Professor J. V. Uspensky, a student of the famous mathematician Andrey Andreyevich Markov. Uspensky strongly encouraged the young man and gave him a list of textbooks. In 1913, Frenkel graduated from the high school with a gold medal and in the same year, he left to the United States to look for a University where to study physics. The reason was that there were quotas for Jewish students in the universities of the Russian Empire and Frenkel was not sure he would be admitted. However, while in USA, he was informed that he was admitted and returned to St. Petersburg. He graduated in 1916 from the St. Petersburg University taking the whole course in three years. As a student in the University, he wrote a paper of about 300 pages in which he developed a theory on the origin of the Earth's magnetic field. In 1921, he joined the newly established Tavria University in Yalta, Crimea, where he spent three years. The "father" of the Russian atomic bomb Igor Kurchatov was a student of his there, and the future Nobel Prize winner for 1958 for the Cherenkov radiation, Igor Tamm, was his assistant. Frenkel returned to St. Petersburg in 1923. In 1925, he was awarded a scholarship of the Rockfeller Foundation to visit universities in Western Europe. He was recommended by Paul Ehrenfest who warned him to come to Leiden University without his family because "a physicist can do in his lifetime as much as his wife permits him". Frenkel spent a year in 1930 as a visiting professor in University of Minnesota, again recommended by Ehrenfest. It was during his stay in USA that he developed the idea of the excitons. During the Second World War, Frenkel together with his family was evacuated in Kazan, where he wrote his famous monograph "Kinetic Theory of Liquids". He used the laundry room of his landlady as a study and for the lack of a table he wrote on a board of plywood on his knees. After the war, Frenkel was awarded with a Stalin Prize for this book.

For nearly 30 years of active life in physics, he published about 300 scientific papers and 30 books. The latter covered practically all fields of physics beginning with electrodynamics, quantum physics, statistical physics, theory of relativity, semiconductor physics, theory

of metals, vector and tensor analysis, etc. The most well-known of them are perhaps the following: "Structure of matter" (in 3 volumes) — 1922/1924; "The theory of relativity" — 1923; "Electrical theory of solids" — 1924; "Electricity and matter" — 1925; "Vector and Tensor Analysis" — 1925; "Electrodynamics" (in 2 volumes in German) — 1926/28; "Wave Mechanics" (in 2 volumes) — 1932/34 (Oxford University Press, German version — 1929); "Statistical physics" — 1934; "Theory of solids and liquids" — 1934; "Analytical mechanics" — 1935; "Theory of metals" — 1939; "Theoretical mechanics based on vector and tensor analysis" — 1940; "Kinetic theory of liquids" — 1943. In fact, most of the students of physics all over Europe in between the two world wars studied physics from his books. Even Arnold Sommerfeld recommended to his students Frenkel's book on electrodynamics rather than his own.

It is difficult to count all the contributions Frenkel made in physics, chemistry, geophysics, materials science, biophysics, for most of which he was the pioneer: the classical theory of nucleation (it was later used by H. Reiss to develop the nucleation theory of alloys), roughening of crystal surfaces (alas, without accounting for the cooperative phenomena), physical theory of adsorption, surface diffusion of atoms and molecules, 2D phase transition in adsorbate layers, vacancies in crystals, Frenkel defects, quantum theory of metals, light absorption in solids — the exciton, definition of temperature for a single molecule, Frenkel-Kontorova model of plastic flow (which was used 10 years later by Frederick Charles Frank and J. H. van der Merwe to develop the theory of the interfacial boundary between misfitting crystals), quantum theory of electric conductivity of metals, theory of magnetic domains, tunnel effect, the theory of liquids, theoretical stiffness of crystals, theory of the magnetic field of Earth (the Earth's dynamo), critical mass of stars (if a star has a mass slightly larger than that of our Sun, it can become unstable and collapse into a neutron star), the liquid drop model of the atomic nucleus, theory of seismic waves, theory of muscle contraction, even a thermodynamic theory of life (unpublished). (For more details, see (Frenkel 1996)).

Figure 5.7: Frenkel teaching.

After the war, he returned to Leningrad and resumed the teaching and research (Fig. 5.7). However, the atmosphere in Russia, particularly the attitude towards the scientists of Jewish origin, gradually changed. Frenkel was accused that publishing papers in western journals and books first in German and English languages before being available in Russian was "to help the Americans use the achievements of the Soviet science in the interest of the monopolistic capitalism" He was even accused by some colleagues of his that the use of terms like "forced collectivization of electrons" and "collectivization under pressure" is a mockery of the collectivization of the private farms after the October revolution in 1917 (Lopatnikov and Cheng 2005). As a result of the persecutions, his health deteriorated and he died on January 23, 1952, at the age of 58.

5.5 I. N. Stranski

Iwan Nikolow (Nicolá) Stranski (1897–1979) was a prominent Bulgarian and German physical chemist (Fig. 5.8). He is a descendant of a highly respected Bulgarian family which had given to its country several outstanding personalities, fighters against Turkish oppression, scientists and politicians. One of them, his uncle Georgi Stranski, is well known from the history of Bulgarian Reunion (1885).

Figure 5.8: Iwan Nikolow (Nicolá) Stranski.

(In the Berlin Congress of 1878, the newly liberated Bulgaria as a result of the Russo-Turkish War of 1877–78 was partitioned into Principality of Bulgaria to the North of the Balkan mountain and Eastern Rumelia under Turkish sovereignty to the South. In 1885, after a mutiny in Rumelia both parts reunited in violation of the clauses of the Berlin Treaty. Georgi Stranski took part in the organization of the uprising and became a chairman of the Eastern Rumelia provisional government).

Iwan Stranski was born in Sofia, Bulgaria, in the family of the royal court pharmacist Nikola Stranski and his wife of Baltic-German origin Maria Krohn. He graduated in chemistry from the University of Sofia in 1922 and then went to Berlin in the Friedrich-Wilhelms-Universität (now Humboldt University) to do a PhD thesis on X-ray structural analysis under the supervision of Professor Paul Günter. In Berlin, he attended the famous seminars of Walter Nernst and Fritz Haber and returned to Sofia in 1925 as a well-educated physical chemist. In 1925, he was elected as an extraordinarius professor in the

Department of Chemistry of Sofia University, and organized the first Chair of Theoretical Chemistry (now Physical Chemistry) in Bulgaria. In the same year, he began reading lectures of physical chemistry. As the University, at this time, lacked qualified teachers, Stranski gave in addition lectures on colloid chemistry, electrochemistry, structure of molecules, catalysis and adsorption, and even differential and integral calculus. Simultaneously, he organized a seminar similar to that of Nernst in which all new discoveries in physics and chemistry were considered and analyzed in detail. In 1936, he was invited to organize a Department of Physical Chemistry in the Ural Institute of Physics and Mechanics in Sverdlovsk in the Soviet Union. He became an ordinarius professor in Sofia University in 1937. In 1941, he was invited as a visiting professor in the University of Breslau (now Wroclaw in Poland) (Fig. 5.9). In 1944, he became a scientific fellow in Kaiser–Wilhelm–Institut für physikalische Chemie und Elektrochemie (now Fritz-Haber-Institut der Max–Planck–Gesellschaft) in Berlin–Dahlem.

Figure 5.9: Iwan Stranski teaching in the University of Breslau, 1941.

In the history of Fritz-Haber-Institut der Max-Planck-Gesellschaft, in the chapter "National Socialism and the Second World War" we read:

"Towards the end of the war some of the experimental and workshop equipment as well as the contents of the library had to be evacuated. The latter provided the basis for the Otto-Hahn Library in Göttingen, which is now located in the Max–Planck Institute for Biophysical Chemistry. The buildings of the institute, however, escaped extensive damage. Only the striking pointed roof of the main building fell victim to the bombing. After the occupation of Berlin by the Soviet army the equipment remaining in the institute was confiscated and transferred to the Soviet Union. This occurred before the American army had set up its Berlin sector in which the institute was located. Of all scientists, only Iwan N. Stranski, Kurt Moliére, and Kurt Ueberreiter remained in Berlin. Their courageous protection of the institute during this chaotic time deserves much praise. P. A. Thiessen went to the Soviet Union. He returned to the German Democratic Republic (Deutsche Demokratische Republik, DDR) in the mid 50s as a Fellow of the Academy of Sciences and became President of the DDR Research Council".

What is the true story? The daughter of Institute's director, Professor Peter Adolf Thiessen, who was in the basement of the Institute together with other scientists, remembers:

"The day is April 24, 1945. The Soviet army enters the Dahlem section of Berlin, where the Kaiser Wilhelm Institutes are situated. A small group of scientists from the Institute of Physical Chemistry and Electrochemistry has been barricaded in the basement of the building. Dorothea Thiessen is also there. The rest of the scientists, like most of the residents of Berlin, in their fear, have already left the city. Through a small window of the basement they are horrified to see how several Soviet soldiers armed with machine guns enter the yard of the institute and start carefully to survey the visibly empty building. The expectations of the barricaded scientists are that if the soldiers start to search in the building they will be found and all will be executed. In that dramatic moment the horrorstruck people in the basement see their colleague and friend Iwan Stranski,

absolutely calmly, come out alone from the institute, set out directly for the Soviet soldiers, and start in pure Russian language to speak with their commander. It is not clear what exactly he has said to him. Maybe he has said that he is a Bulgarian professor that he used to work for about a year in Sverdlovsk in the Soviet Union, etc. It is, however, sure that, one way or another, he succeeds to convince them that the research in the institute is purely scientific and by no means related to development of military weapons of any kind and he guarantees his words with his name and authority as a scientist. Thus, satisfied, the Russian soldiers leave the yard of the institute and the group of scientists barricaded in the basement takes a deep breath. Of course, this is an emotional episode, because the Russian army had not executed German scientists. But how could the small group of scientists, scared, but ready somehow to defend their institute, have known in advance what exactly would happen in that moment of a complete chaos in Berlin". (Sretenova 2007)

Most probably, the Soviet soldiers had come to confiscate the Institute's library as they did in other scientific institutions. It seems that Stranski succeeded to convince them that the books are very old and useless but the equipment (which could be easily built again) is much more valuable. Thus, Stranski saved the Institute's library.

There is evidence that the Russians twice invited Stranski to work in the Soviet Union just like Thiessen and many others German scientists, the second time through his friends Volmer and Thiessen. In 2005, after declassification of American military archives, it turned out that there was a file on Stranski containing biographical data and a list of his most important scientific contributions. It could be suggested that the Americans also invited Stranski to work for them (Sretenova 2007). However, Stranski decisively refused to go abroad and remained loyal to the country which gave shelter to him in difficult times.

After the war, Stranski remained in Kaiser–Wilhelm Institute (renamed Fritz-Haber Institute). In the same history of the Institute we read:

"Apart from the department of the institute director there was a large department headed by Iwan N. Stranski who held also a position

as Professor of Physical Chemistry at the Technical University of Berlin. His department focused on investigations concerning crystal structure, nucleation and crystal growth processes. At a later stage, also studies on properties of zeolites and of catalytic processes in such microporous solids were performed. In 1954, I. N. Stranski became Deputy Director of the institute. Erwin W. Müller, the inventor of the field electron microscope, had been working as an assistant in Stranski's department since 1947. During this period he developed the field ion microscope which could achieve extremely high resolution of atomic structures. In 1950 E. W. Müller was given his own department in the institute but in 1952 he took up an appointment in the USA. He remained connected with the institute as an External Scientific Fellow until his death in 1977".

Stranski was highly esteemed by his colleagues. The notorious American physical chemist Howard Reiss remembers (Reiss 2001):

"In 1951, I met Ivan Stranski at a meeting on nucleation and surface phenomena in Boston. Stranski took a liking to me and, in 1952, invited me to the first post war meeting of the Bunsengesellschaft attended by foreigners. It was to be held in Berlin. At the time, my accomplishments did not really merit an invitation and I assume that it was Stranski's friendship that included me in the invited group of fourteen American Scientists. I was only thirty years old and, as a Jew, I debated whether to accept the invitation. In the end I decided to go. We were flown to Frankfurt by the Military Transport and from Frankfurt to Berlin, over the Russian zone, by the American "Courier" plane. Frankfurt had been leveled by Allied bombers and only the I. G. Farben plant had been surgically spared. In Berlin, it was just after the "airlift" and all the trees in the Tiergarten had been cut and used as firewood. At the meeting, Germans only spoke reluctantly about the concentration camps and the associated atrocities, and most claimed ignorance of what had transpired (although this was hard to believe). Some French scientists had agreed to attend the conference, but several refused to present papers. Nevertheless, the conference was a marked success. We had dinner with Ernst Reuter (beret and all) the liberal Burgermeister of Berlin. Indeed he was a wonderful influence. Ten years later, in 1962, Stranski was Rektor of

the Berlin Technische Hochshule in Charlottenburg. He invited me to present some lectures on thermodynamics. He had twice been Rektor of the University, a signal honor, and had also succeeded Max von Laue (whom I had met on my earlier visit) as Director of the Kaiser Wilhelm Institute. His colleagues addressed him with deference."

After the Second World War, the communist authorities in Bulgaria declared Stranski a fascist, political émigré, and a nonreturnee and discharged him from the University. Thanks to the efforts of his former students in Bulgaria, Lubomir Krastanov and Rostislaw Kaischew (at that time they were President and vice-President of the Bulgarian Academy of Sciences, respectively), he was elected, in 1966, a Foreign Member of the Bulgarian Academy of Sciences. He visited his home country for the first time after the World War II WW2 in 1969 on the occasion of the 100th anniversary of the Bulgarian Academy of Sciences.

After Max Volmer went to Soviet Union in 1945, the Technical University (TU) of Berlin made Stranski a successor of him as Professor of Physical Chemistry. He became a rector of TU Berlin for two consecutive tenures 1952–1953. He also taught at the Free University of Berlin as an honorary Professor. Stranski died on June 19, 1979, in Sofia.

In 1927, he published his first paper in the field of crystal growth in Annuaire de l'Université de Sofia. After reading the paper of W. Kossel on the same subject and published in the same year in Nachrichren der Gesellschaft der Wissenschaften Göttingen (Proceedings of the Göttingen Scientific Society), he published his paper in German in Zeitschrift für physikalische Chemie in 1928. Thus, both scientists introduced simultaneously and independently of each other the Kossel-Stranski model of crystals and the concept of the half-crystal position (Halbkristallage) in the theory of crystal growth. (Fig. 5.10) The work of detachment of an atom from this position is precisely equal to the chemical potential of an infinitely large crystal at zero absolute temperature taken with negative sign. Making use of this concept, Stranski and Kuleliev studied the stability of consecutive monolayers of a monovalent crystal on the surface of isomorphous bivalent crystal. Thus, the first theoretical paper on epitaxial growth

Figure 5.10: Iwan Stranski and Walther Kossel at a conference of the Bunsen Society, 1931.

appeared in 1929. In 1933, together with D. Totomanow, Stranski published a paper in which he explained theoretically, by making use of the theory of nucleation developed by Max Volmer, the well-known Ostwald's rule of stages. In 1934, Stranski and Kaischew published a series of five papers on the equilibrium of crystals with a finite size and introduced the concept of the "mean separation work" which determines the equilibrium of a small crystal with the ambient phase. (Fig. 5.13) The difference of the work of detachment of an atom from half-crystal position and the mean separation work gives the famous Thomson–Gibbs equation. Thus, they derived this purely thermodynamic relation from a kinetic point of view. Later, in 1939, Stranski and Krastanov further extended the results of Stranski and Kuleliev and discovered what is known today as the Stranski-Krastanov mechanism of growth in heteroepitaxy. For more details, see (Tassev and Bliss 2008).

In Germany, he again formed a group of very skillful and bright scientists. Together with Rudolf Suhrmann, he studied the emission of electrons from metal surfaces and found a connection of the electron emission and the surface morphology. In collaboration with Ottmar Knacke, Günter Wolff, Kurt Moliére, and B. Hirschwald,

Stranski studied the processes of evaporation and condensation of white phosphorus and arsenic trioxide and advanced a new mechanism of evaporation of covalent-bonded crystals where the surface diffusion is inhibited. With Rolf Lacmann, he studied the effect of the adsorption of impurities on the shapes of equilibrium and the growth of crystals. The collaboration with Ludwig von Bogdandy on some fundamental problems of the metallurgy of iron like deoxidation of molten iron and the reduction of iron oxides saved millions of Deutsche marks for the postwar reviving German economy. Later, von Bogdandy founded an Institute of Metallurgy in Oberhausen (Rheineland, Germany) which he named after his teacher. In 1947, Stranski invited Erwin Müller in his laboratory. In 1951, Müller published his famous paper in which he described the principle of the field ion microscopy. Obviously, Stranski possessed the talent to discover talents.

On March 24, 2007, at a conference of the German Physical Society, Professor D. Linke had given a talk entitled "Iwan N. Stranski (1897–1979), der bulgarisch-deutsche "Grossmeister des Kristallwachstums", und sein Wirken im Spannungsfeld von Wissenschaft und Politik." (Ivan Stranski, the Bulgarian-German "grandmaster of crystal growth" and his influence on science and politics).

5.6 R. Kaischew

Rostislaw Kaischew (1908–2002). A Bulgarian physical chemist renowned for his studies on crystal growth together with Iwan Stranski, and founder of the Bulgarian school of Physical Chemistry (Fig. 5.11). He was born in Saint Petersburg where his father, an officer of the Bulgarian Army, studied in the Imperial Military Staff Academy. He graduated in chemistry from Sofia University in 1930. At that time, the course of physical chemistry was taught by Iwan Stranski and the textbook of Arnold Eucken (in German) was used. In 1930, he went to Germany with Humboldt scholarship in Berlin to work on his PhD thesis under the supervision of Professor Franz (later Sir Francis) Simon, FRS. Half a year later, Franz Simon

Figure 5.11: Rostislaw Kaischew.

was offered a professorship in the Technical University of Breslau (now Wroclaw, Poland) and the whole group of Simon moved there. In 1932, Kaischew defended his PhD thesis with distinction (*summa cum laude*) on the thermal properties of the liquid and solid helium (Fig. 5.12).

In the middle of the same year, Stranski offered him a position of an assistant in the chair of Physical Chemistry in Sofia University without payment. He became an ordinarius assistant professor half a year later. In 1935, he was invited in the Ukrainian Physico-Technical Institute in Kharkov for three months in order to organize a laboratory of low temperatures. He was offered a renewal of the contract but, according to his own words, he refused because of the persecutions and purges following the assassination of Sergey Kirov (first secretary of the Leningrad (Saint Petersburg) communist party organization) in December of the previous year. As he learned later, many of his colleagues disappeared in the concentration camps. In 1937, he spent his sabbatical in the Institute of Physical Chemistry of Munich University headed by Professor Klaus Clusius, where he tried to verify the Third Law of thermodynamics defined by Walther Nernst in the case of crystalline carbon oxide.

Figure 5.12: Rostislaw Kaischew in the laboratory of low temperatures in the University of Breslau, 1932.

After the Second World War, he had problems with the communist authorities in Bulgaria because of his relations with Stranski, who was declared a "fascist", and more specifically because his father was a general of the "tsarist" army. He succeeded to avoid a discharge but several distinguished professors of the Chemical Department of the University were released from their positions. The remaining, including Kaischew, were sent to a small village nearby Sofia to attend courses on "Marxist-Leninist philosophy". In 1944 (in fact, already in 1941), he stood at the head of the Chair of Physical Chemistry until 1962. He became a full-time professor and a corresponding member of the Bulgarian Academy of Sciences in 1947, and a deputy chairman of the Bulgarian Academy of Sciences in the period 1961–1968. In 1958, he founded the Institute of Physical Chemistry of

the Bulgarian Academy of Sciences and was its Director until his retirement at the end of 1988. Two specialized laboratories, the Central Laboratory of Electrochemical Power Sources (now Institute of Electrochemistry) and the Central Laboratory of Photographic Processes in Solids, split from the Institute of Physical Chemistry. He was a honorary member of many Academies and Universities; in the period from 1975 to 1981, he was elected as a Vice-President of the International Union of Pure and Applied Physics (YUPAP).

Rostislav Kaischew entered the "big" science when he was still a student in his third year in the University. Professor Iwan Stranski noticed the bright young man and offered him to work together. They published their first joint paper on the equilibrium shape of homopolar crystals in 1931, when both were in Germany. Kaischew was then 23 years old. Thus, for about 10 years, they published in collaboration about 20 papers which put the foundations of the quantitative theory of crystal growth. In 1934, Kaischew and Stranski published a series of five papers in which they defined the so-called "mean separation work" which determines the equilibrium of finite size crystals with the ambient phase. This quantity represents the energy per atom to evaporate a whole atomic plane of a 3D crystal or a whole row of atoms from the edge of a 2D island. The idea was that in equilibrium with the vapor phase the probabilities of formation and dissolution of whole crystal planes or edge atomic rows must be equal. The difference of the work of detachment from half-crystal position on the surface of an infinitely large crystal and the mean separation work represents the famous equation of Thomson–Gibbs, which was, thus, derived on the base of a kinetic approach. All these works laid the foundation of the molecular-kinetic theory of crystal growth. The latter, in fact, introduced the energetics of the basic processes which take place on the crystal surfaces during growth and dissolution (Fig. 5.13).

After the war, Kaischew continued to work in the field of crystal growth. It was in this period that he derived the formula for the equilibrium shape of crystals on the surface of an unlike crystal which is known today as the Wulff–Kaischew theorem. He concluded that at complete wetting of the substrate by the film material, the work

Figure 5.13: Iwan Stranski and Rostislaw Kaischew in the study of Stranski after the publication of their papers on the mean separation works, 1934.

of formation of 3D nucleus will be equal to zero, but still a barrier for further growth should be overcome which is connected with the formation of a 2D nucleus.

Young bright disciples gathered around him. Gradually, the research branched out in other fields like electrochemical power sources, solids state chemistry, colloid chemistry, physics of thin liquid films, and catalysis. Thus, Kaischew put the beginning of the Bulgarian school of Physical Chemistry. However, this was not so easy a task as is described here. He wanted to appoint promising young men who rarely were members of the communist party. On the other hand, the party organization in the Academy of Sciences wanted him to appoint party members. Kaischew solved the problem in his own way. He traded off a nonparty member for a party member, but of his own choice.

During the period after the Second World War, Bulgaria was isolated from the Western Europe. The Iron Curtain prevented in practice all scientific contacts with the world. This, however, did not stop Kaischew to gather around him in Bulgaria all well known specialists

in crystal growth of the communist countries. Every second year, he organized in Bulgaria International Summer Schools on Crystal Growth. Eminent scientists like A. A. Chernov, E. I. Givargizov, H. Bethge, J. Heydenreich, H. S. Bagdasarov, V. V. Osiko, and D. Temkin, lectured regularly in the Summer Schools. Joint workshops with the Institute of Solid State Physics and Electron Microscopy in Halle (on Saale) in East Germany, directed by Professor Heinz Bethge, were regularly conducted. Thus, he succeeded in avoiding the isolation to some degree and even in making Bulgaria a center of the fundamental research in the field of crystal growth on the East side of the Iron Curtain. He made friendship with many renowned scientists all over the world, particularly researchers in the field of crystal growth. Aleksander Aleksandrovich Chernov from the Institute of Crystallography of the Soviet Academy of Sciences and (Fig. 5.14) Heinz Bethge from the Institute of Solid State Physics and Electron Microscopy in German Academy of Sciences in Halle (on Saale) in German Democratic Republic, were among the best friends of his. His Institute was frequently visited by renowned scientists from all over the world, Professor Heinz Gerischer from Fritz-Haber Institute of Max-Planck Society, Professor Nikolai Bassov, Nobel Laureate for invention of the lasers, the famous Russian electrochemist Alexander

Figure 5.14: R. Kaischew and A. A. Chernov during a Conference on Crystal Growth in a ski resort in Rodopi mountains, Bulgaria,1995.

Naumovich Frumkin, Frederick Charles Frank from Bristol University, Yakov Borisovich Zeldovich, and many others. Professor Heinz Bethge related a story: "After the war the whole library of the Martin Luther University of Halle–Wittenberg was confiscated by the Russians. Then I decided to go around the second-hand bookshops to look for old books and journals. In one of them I found old issues of Zeitschrift für physikalische Chemie, in which I found the papers of Stranski and Kaischew. After reading them I decided to begin with studies of the processes taking place on the crystal surfaces during growth and dissolution. After some time I met Kaischew, we became close friends and our Institutes began actively to collaborate".

Kaischew never forced his views to the research fellows of his Institute. Kaischew never put his name under a paper of his coworkers for which he did not made a substantial contribution. Every fellow of the Institute could work on an idea of his own. His nickname in the Institute was "the Chief", even the foreign researchers visiting the Institute or the Summer Schools called him that way. The following story shows why so many people liked and respected him. One Sunday, two of the fellows of the Institute were skiing in the nearby mountain, Vitosha, where they met "the Chief". The next morning, he entered the lab and asked them whether they enjoyed the skiing. "Yes, answered they, it was very nice, the only problem was that there were very long queues at the ski lifts". "But why do you go for skiing on Sunday?" he asked them with great surprise. "But in the other days we should be working in the lab" answered the fellows with even greater surprise. "I am not interested when you work and when you go for skiing. I am only interested to show me results at the end of the year". In 1981, he was invited to visit Japan and to give several lectures on crystal growth. The fee was more than generous. With the fee which belonged personally to him, Kaischew bought for the Institute an Apple computer of the first generation. That was "the Chief".

5.7 L. Krastanov

Lubomir Krastanov (1908–1977) (see Fig. 5.15). A Bulgarian physical chemist and geophysicist. He was born in the North-Bulgarian city of Pleven in the family of a postal employee and a school teacher.

Figure 5.15: Lubomir Krastanov as a President of Bulgarian Academy of Sciences, 1967.

Figure 5.16: Lubomir Krastanov as a reservist in the winter of 1939 after the defense of his PhD thesis.

He graduated in physics from the University of Sofia in 1931 and joined the Central Meteorological Institute, where he later became a head of the Department of Physics of the Atmosphere. He began his scientific activity when he was still a student under the guidance of Professor Iwan Stranski with whom in 1932, he published his first paper on the equilibrium shape of homopolar crystals. In 1938, he defended his PhD thesis under the supervision of Iwan Stranski on the deposition of monovalent crystal on the surface of a bivalent crystal both with equal lattice parameters (Fig. 5.16). This work was based on an earlier paper by Stranski and Kuleliev of 1929. The result was the famous Stranski–Krastanov mechanism of growth in which 3D crystallites are formed on a thin planar wetting layer formed at undersaturation with respect to the bulk monovalent crystal. This is one of the most cited papers in the field of epitaxial growth. Quantum dots of Ge on Si and In As on Ga As are formed through this mode of growth. As many researchers erroneously think that Iwan Stranski is of German ethnic origin, many of them often cite Krastanov as "L. von Krastanow".

He devoted his further research to the physics of the atmosphere and made use of his profound knowledge of the crystallization processes acquired in the group of Professor Stranski in order to study the processes of formation and growth of liquid droplets and ice crystallites in the atmosphere. Krastanov found that the supersaturation of water vapor in undercooled humid air is insufficient for the formation of homogeneous nuclei of the liquid phase. Instead, the nuclei are formed heterogeneously on foreign particles which act as "condensation seeds". The latter require much smaller work of formation as a result of the wetting of the foreign particles by the water. Another problem solved by Krastanov is the formation of ice crystallites in an undercooled humid air. The explanation is based on the empirical "rule of stages" or a "step rule" found by Wilhelm Ostwald, which was theoretically explained by Stranski and Totomanow in 1933. The interpretation is based on the expressions for the nucleation rate derived by Max Volmer in 1926. If under the triple point two phases exist, say, stable ice and metastable water, the metastable phase — the water — will nucleate first. The reason is that the energy

of the liquid–vapor interface is much smaller than the energy of the crystal-vapor one and the rate of nucleation of the liquid water will be higher. Then, at the second stage, the liquid droplets will solidify into the thermodynamically stable ice.

Simultaneously with the research, Krastanov performed large-scale organizational work. He founded the Institute of Geophysics at the Bulgarian Academy of Sciences which unified all laboratories of atmospheric studies, seismology, Earth magnetism, and physics of the ionosphere. Later, the Institute of Space Studies split off with the Institute of Geophysics.

In 1961, Krastanov was elected as a member of the Bulgarian Academy of Sciences and became its President until 1968, Rostislaw Kaischew was then Deputy-President. Krastanov replaced, at this position, the Marxist philosopher Todor Pavlov and thus, the political direction of the Academy was replaced by a scientific one. Krastanov opened the Academy to the world. He established contacts with the biggest scientific centers in Europe and many perspective young scientists had a chance to improve their qualifications. However, it was not an easy task to manage a big scientific institution in a communist country at that time. The quantum mechanics, modern biology, and the cybernetics, were considered by the communist party functionaries as "bourgeois fabrications". In particular, this was a crucial time for the biological sciences in Bulgaria. They were under the political influence of the Soviet anti-scientific conceptions of Trofim Denisovich Lisenko. The names of Gregor Mendel and Thomas Morgan were taboo in the Department of Biology in Sofia University. Although being a member of the communist party, himself Krastanov was in the first place a scientist. He succeeded to evade the rules, sent young people to universities and institutions in Western Europe, and found financial support for development of modern biology in the Bulgarian Academy of Sciences.

Immediately after the invasion of Bulgaria by the Soviet army in 1944, the Bulgarian Academy of Sciences was "reorganized" by the communist authorities, following the model of the Soviet Academy of Sciences. Many renowned members of the Academy and lecturers in Sofia University were dismissed and replaced by young members

of the communist party (Zhivkova 2008). In particular, the purges affected most of the historians, the biologists, and the linguists. One striking and strange exception was the life sentence of the former mayor of Sofia and member of the Academy of Sciences, the hydro-engineer Ivan Ivanov. He was accused of being a "fascist" because he had graduated from a German University before the Second World War. He was released several years later, when a Soviet hydroengineer was invited to help for the water supply of Sofia. "Why do you invite me, asked the Russian engineer, you have the best". In 1968, Krastanov decided to reorganize the Academy according to the model of similar institutions of the West European countries. He was immediately dismissed from his position.

On March 4, 1977, an earthquake of magnitude 7.4 with an epicenter in Vrancea in Eastern Karpathian mountain in Romania took place. The earthquake was felt in the whole of Bulgaria but mostly in the towns along the river Danube. Many buildings were demolished and hundreds of people died under the ruins. Krastanov was summoned to the Central Committee of the Communist Party to give explanations as to why he did not warn for the earthquake. He died of stroke two months later.

5.8 F. C. Frank

Frederick Charles Frank (1911–1998). He was a British theoretical physicist and he was born in Durban, South Africa, of English parents. His parents returned to England a couple of months after his birth. He was educated at Thetford Grammar School and Ipswich School, the first recorded mention of which is of 1416. After that, he went on to study chemistry at Lincoln College, Oxford. From 1936 to 1938, Frank worked at the Kaiser–Wilhelm Institut für Physik in Berlin under Peter Debye. There he became fluent in German and learned the way of thinking of the German scientists. This was to prove of great value to him in the coming world war (Fig. 5.17).

In 1940, Frank's lifelong colleague and friend, Dr Reginald Victor Jones, invited him to join the Air Ministry Intelligence (Science). There Frank successfully used his remarkable attention to details.

Figure 5.17: Frederick Charles Frank.

In one case he noticed in two consecutive aerial photographs that the shadow of "something" differs in length. The difference was just a tenth of a millimeter on the print. Frank concluded that the "something" which rotated could be a radar station. Later, photographs showed that it was the radar Freya called after the goddess Freyja of love, war, and death of the Norse mythology, and used by the Germans to navigate their bombers on the darkened island. In another case, Frank noticed a tiny speck on an aerial photograph on the grounds of a villa on the French coast near Saint-Jouin-Bruneval. There were also tracks which made a loop round the speck. New low-level photographs revealed that the speck was, in fact, a paraboloid antenna of a radar. The size of the antenna led Frank to conclude that this could be the Würzburg radar with 53 cm wavelength. British commandos raided the place on February 27/28 1942 (operation "Biting" or Bruneval raid) and captured the device. For more details, the interested reader can refer to (Jones 1978). For his achievements during the war, Frank was made Officer of the British Empire (OBE) of which he was particularly proud.

Another story connected with WW2 but taking place much later is the transcription of the records of the conversations of top 10 German physicists. Walther Gerlach, Otto Hahn, Werner Heisenberg, Max von Laue and Carl Friedrich von Weizsäcker, amongst

them, were detained in the Farm Hall near Cambridge as a result of Operation "Epsilon". The primary goal of Operation "Epsilon" was to determine how close Nazi Germany had been to constructing an atomic bomb. The house was bugged with microphones.

Excerpt from transcript: July 6, 1945 at Farm Hall: Kurt Diebner, German nuclear physicist: "I wonder whether there are microphones installed here?" Werner Heisenberg, German theoretical physicist: "Microphones installed? (laughing) Oh no, they're not as cute as all that. I don't think they know the real Gestapo methods; they're a bit old fashioned in that respect."

In February 1992, the records were declassified and published. It was Frank who was assigned the task to organize the translation and the editorial work of the records. He ordered the translation to British who were soldiers fluent in German but ignorant in physics. Then, he corrected the translations by making use of his deep knowledge in physics and fluent German. Thus the remark of Heisenberg "the neutrons are scattered into small corners" became "the neutrons are scattered through small angles". The original records were then destroyed.

After the war, Frank joined the Department of physics of the University of Bristol headed then by Nevill (later Sir Nevill) Mott. In 1948, he was appointed a research fellow in theoretical physics, a reader in 1951 and a full professor of physics in 1954, until his retirement in 1976. In Bristol, he began working on dislocations in crystals. Whereas, most physicists concentrated on edge dislocations which are easy to visualize, Frank, who had unusual ability for 3D thinking, concentrated on screw dislocations, which at that were much easier to be mathematically analyzed. In addition to the 1D model developed by Frank in collaboration with J. H. van der Merwe, we will mention the discovery of the partial dislocations (Frank partials) and the Frank-Read mechanism of dislocation multiplication (Frank-Read source).

In the field of crystal growth, the achievements of Frank are remarkable. They range from crystallization of polymers to growth of diamonds, and to the effect of the screw dislocations. It is very interesting to hear Frank's own words about the dramatic history

of the rise and development of the idea of spiral growth. A beautiful presentation of the development of the physical ideas is given by Woodruff (2015).

Karl Wirtz with whom Frank worked in Kaiser-Wilhelm Institut für Physik in Berlin before the war (and "guest" in Farm Hall after the war) sent him the monograph of Volmer "Kinetik der Phasenbildung". In his Award Address, when awarded by the American Association for Crystal Growth [J. Cryst. Growth 46, 593–594 (1979)] Frank said:

"Mott, knowing that I had that book, and could read it, asked me to give three or four seminars on nucleation theory. I did that, fairly slavishly following Volmer. In my fourth seminar I presented Volmer's theory of the rate of crystal growth, calculated as the rate of nucleation of new layers on a perfect crystal surface: and I presented Volmer's comparison of his algebraic expression for the dependence of growth rate on supersaturation — very low for low supersaturation, then taking off with a rapid increase — with the experimental results for growth of iodine crystals from the vapour. These were qualitatively similar, but Keith Burton was in a position to make some reasonably reliable estimates so as to put numbers into Volmer's algebra. And when that was done we found that at one percent supersaturation the experimental growth rate was about 10^{1000} times higher than the theory said: we remarked that that was the largest factor of discrepancy we had ever seen called agreement. Oddly, I needed the shock of that big number to make me take seriously an idea which I had previously produced only as a mental squib, namely that we knew crystals were full of dislocations, that a dislocated crystal was not a stack of layers of atoms but one layer complicatedly overlapping itself, so it need never start a new layer — and that the Volmer calculation of the rate of starting new layers could be irrelevant to the actual growth rate, and in this case clearly was. With taking the idea seriously came calculations of crystal growth rate which were not manifestly absurd, but on the route to that realization that growth steps on a crystal surface would wind themselves into spirals and then the discovery that these were observable, and had indeed already been observed" (Fig. 5.18).

Figure 5.18: Frederick Charles Frank during his talk on the effect of the screw dislocations on crystal growth at the Conference of Crystal Growth at the University of Bristol, 1949.

Frank was a versatile genius. In 1964–1965, during his sabbatical stay at La Jolla University in California, Frank determined the curvature of the islands arcs where two neighboring tectonic plates overlap each other. A typical example is the arc of the Ryukyu islands, where the Eurasian plate overrides the Philippine Sea plate. In 1974, he proposed the model of propagation of a single step by 1D nucleation. He made remarkable contributions in the physics of liquid crystals. More details about the scientific interests and achievements of Frank can be found in the paper of Nabarro and Nye (2000).

For his scientific achievements, Frank was elected a Fellow of Royal Society (1954), was knighted (1977), and was awarded with the Copley medal (1994), the highest award of the Royal Society. On this occasion Jacques Friedel remarked "*S'il y a un prix Nobel de perdu c'est bien lui*" (If there is a lost Nobel Prize, it is his).

Figure 5.19: Nicolás Cabrera in his study in the Universidad Autónoma de Madrid (UAM).

5.9 N. Cabrera

Nicolás Cabrera (1913–1989): A Spanish physicist (Fig. 5.19). He was the son of another famous Spanish physicist, Blas Cabrera y Felipe, who is considered the father of the modern Spanish physics. The family originated from Lanzarote, one of the Canary Islands. His father moved to Madrid where he graduated in physics from the Central University of Madrid (today, Complutense University). He founded the Laboratory for Investigations in Physics and became its director. Nicolás and his brothers grew up in a unique cultural environment for Spain at that time. The home was often visited by musicians, painters, and men of letters. Much later, Cabrera recalled that one day, when he was nine years old, his father invited Albert Einstein at his home, who had visited the Madrid University at that time. In the same evening, his guest was by chance the famous guitarist Andrés Segovia, who played some compositions of his own in honor

of the distinguished guest. Einstein asked for a violin and, in his turn, played for his host.

Nicolás Cabrera graduated in physics from Complutense University in 1935. He began his research in experimental physics at the Institute of Physics and Chemistry, a prestigious international center that had been created and directed by his father. His first project was to extend the measurements of the magnetic susceptibility of rare earth compounds that had been recently obtained by another remarkable Spanish scientist of that time, Salvador Velayos, down to the temperature of liquid helium. These measurements were very important in order to test the theoretical calculations of J. H. van Vleck from Harvard University. As a result of these experiments, he published his first paper in 1935, co-authored by his father and Velayos. However, the Spanish Civil War broke next year and put an end to the project. The family of Cabrera, like many other educated Spaniards, faced the dilemma to emigrate or to stay in Spain, or, in other words, to make science or not. In February of 1939, Blas Cabrera and other 15 professors were stripped of their chairs by the self-proclaimed "national government" of Francisco Franco. Blas Cabrera, along with his family, left Spain to set up in Paris.

In Paris, Nicolás Cabrera found a job in the International Bureau of Weights and Measures. His stay in Paris, which lasted until 1952, was to be decisive in his life. He married Carmen Navarro, also of an exiled family, and completed his PhD in Physics. Despite his ability in experimental physics, he directed his research into theory. His doctoral thesis was a theoretical study of the thermodynamics of phase transitions and was carried out under the supervision of two renowned physicists, Louis de Broglie and Leon Brillouin. Meanwhile, he became interested in the effect of the oxidation of metals in the metrology. This led him to do experiments to understand the process of oxidation of aluminum. In a short period of time, he published 12 papers on the subject. By then, the already renowned physicist Neville Mott in Bristol University had proposed a theory of the oxidation of metals in which this process was driven by the passage of the free electrons from the metal to the conduction band of the oxide. The works of Cabrera attracted the attention of Mott, who invited

him to work with him in the H. H. Wills Physics laboratory at the University of Bristol. Cabrera considered the three years spent there as the most fruitful of his scientific career. He published two famous papers, the first one on the growth of crystals and the equilibrium structure of their surfaces in collaboration with William Keith Burton and Frederick Charles Frank, and the second, the first quantum theory of the oxidation of metals, with Neville Mott. These works made a good name to him and in 1952 he accepted an invitation to become a lecturer in the Physics Department of the University of Virginia at Charlottesville where he remained till 1968, first as a full time professor from 1954, and then as a dean of the department from 1962. He was happy to work in a university where he could combine the research and the teaching. He considered the two activities inseparable. On the other hand, he proved to have a great organizational talent. When he joined the University the Physics Department consisted of five lecturers. 16 years later, the number of teachers reached 30, the graduate students were more than hundred, and the fields of activity practically covered all branches of physics, in particular nuclear physics and low temperature physics. He personally remained faithful to his first love, the physics of surfaces. In addition, his contacts with colleagues, both Hispano-American and Spanish, had been permanent and from his position in Virginia he strove to boost scientific activity in Latin-American countries such as Mexico and Venezuela. He never forgot the generous reception that the National Autonomous University of Mexico gave his father in 1941, who died in exile in 1945.

During all years of Franco's dictatorship, Cabrera longed to go back to his native Spain. Alexander Chernov remembered that when he visited, in the 60s, the Department of Physics in Charlottesville, Cabrera invited him for a dinner. At the end of the evening, some of the guests began singing Spanish songs under the accompaniment of guitars. Cabrera maintained permanent contacts with other renowned Spanish scientists like the physicist Salvador Velayos, the Nobel laureate for medicine and physiology Severo Ochoa, the physician and researcher Francisco Grande Covián, well known for his studies of cardiovascular disease and diabetes. In 1968, the newly

nominated Spanish minister of education Villar Palasi was genuinely concerned with the university education in Spain. He envisaged the creation of autonomous universities as an alternative to the long-standing Spanish universities, too much bureaucratized and thoroughly dependent on the central administration. In these universities, the teachers were civil servants with chairs obtained through examinations where the political adherences sometimes counted more than the academic merits. By contrast, the professorship of the new autonomous universities should be selected, specially in natural sciences, between researchers who already held positions in universities abroad. Villar Palasi contacted Cabrera and invited him to create the Department of Physics in the newly founded Autonomous University of Madrid. Cabrera asked his friends for their advice. All of them encouraged him to go to Spain and to use his organizational experience. However, Francisco Grande warned Cabrera about the difficulties he saw: "The two most serious in my opinion — wrote Grande — are the inertia of the university organization and the reaction from many of our colleagues, who, although they say otherwise, they are perfectly satisfied with the status quo". Severo Ochoa wrote: "the first steps should be directed to create scientific and academic staff which is almost nonexistent".

For readers who occasionally do not know what dictatorship is, it would be instructive to tell briefly the story of Francisco Grande without comments. He made his PhD under the supervision of Dr Juan Negrin, professor of physiology at the Complutense University of Madrid, who later entered politics and became President of the Republic in the last year of the Spanish Civil War (1036–1939). When the Republic fell and Francisco Franco established dictatorship, Grande's involvement with Juan Negrín marked him as persona non grata. For the summer following the war, Grande had to hide in a friend's country estate in Andalucía. Even after officials lost interest in detaining "collaborators" such as him, Grande was banned from seeking a position at any Spanish university for 10 years. It is worth noting that the Franco's dictatorship was "soft" compared with the practices in the East European countries beyond the Iron Curtain.

In his first days in Madrid in 1969, Cabrera had a very active collaborator, Javier Solana, the future Secretary General of NATO, who came from Virginia, where he obtained PhD in condensed matter physics. Solana helped Cabrera to understand various aspects of intricacies of the Spanish society of the time. The first thing Cabrera did was to organize a seminar in the new department. One or two seminars, every week, were virtually obligatory. Cabrera sat in the front row and was easily detectable by the respect, sometimes reverential, which originated from the speaker. He visited the laboratories at any time of the day, Saturdays and sometimes Sundays included. He liked having lunch with young people in the Department "bars" in the campus, and later in the restaurants and cafeterias of the surrounding area of the university. Table tennis championships were organized, in which he participated with great enthusiasm. This simplicity in his behavior was not very common in Professor's stereotypes of the time.

Unfortunately, the autonomy hardly lasted a few months. As Grande correctly presumed, some sections of the established academic community looked with more suspicion than complacency. The campaign against Cabrera and other professors appointed from abroad quickly started. The statutes of the university were overridden and the central government appointed as second governor Julio Rodríguez, an obscure professor of crystallography, without relevant academic merits but a furious right-winger. Quickly, Rodriguez purged several departments of the university. Particularly, the purge on the philosophy faculty triggered critics by many European universities. Also, in the departments of the natural sciences, disciplinary measures were taken against some teachers because of their consent and concurrency in nonauthorized meetings of students. (Later, Rodriguez became Minister of Education and became famous by his whims, like to change suddenly the scholar calendar to adapt it to natural year). In this situation, some prominent members of the faculty decided to go back to their former positions in foreign universities. Despite these difficulties, Nicolás Cabrera remained and along with many others soon placed the UAM on the frontline of scientific

research in Spain. His tenacity and fighting spirit which he had inherited from his father helped him to withstand. Within the Department of Physics, Cabrera founded the group of surface physics, whose main lines of research were the scattering, both elastic and inelastic, of neutral atoms on solid surfaces as tools to explore the structural and vibrational properties of surfaces. Cabrera himself had advanced the theory in several papers (N. Cabrera, V. Celli, R. Manson, Phys. Rev. Letters 22, 346 (1969) for the inelastic scattering, and N. Cabrera, V. Celli, F. O. Goodman, and R. Manson, Surf. Sci. 19, 67 (1970) for the elastic one). Some years later, researchers of the group made contact with Binnig and Rohrer and imported into Spain the technologies of scanning tunneling and atomic force microscopes to directly explore the surfaces.

A special issue of the journal *Philosophical Magazine A* was dedicated to him when he turned 70, a number of original articles being contributed by some eminent physicists. The Institute of Materials Science founded in the Autonomous University of Madrid bears his name. Nicolás Cabrera died in Madrid in 1989. On his tomb it is written: "Nicolás Cabrera Sánchez, physicist, scientist of great humanity".

5.10 Ya. B. Zeldovich

Yakov Borisovich Zeldovich (1914–1987). Russian theoretical physicist.

"Before I meet you here I had thought, that you are a collective of authors, as Burbaki" (Stephen W. Hawking).

"Not a single physicist except Fermi does possess such an abundance of new ideas like Zeldovich" (Lev Davidovich Landau, famous Russian theoretical physicist and Nobel Laureate for physics).

"Yashka is just a genius" (Igor Kurchatov, "father" of the Soviet atomic bomb).

"A man of universal scientific interests" (Andrei Dmitrievich Sakharov, "father" of the Soviet hydrogen bomb and Nobel Laureate for peace).

Zeldovich was born in Minsk (today capital of Belarus) but with the beginning of the First World War, the family moved to Saint Petersburg. Zeldovich began his scientific career at 17 years of age, after graduating from the grammar school, as a laboratory assistant in the Institute of Processing of Minerals. During a visit in the Institute of Chemical Physics (ICP) in Leningrad (Saint Petersburg), he asked a couple of questions which showed that the young technician was well acquainted with thermodynamics, molecular physics, and chemistry. The director of ICP suggested him to join his Institute. There is a legend that the director of the Institute of Processing of Minerals asked in exchange a fore-vacuum oil pump which was a rarity at that time. Thus, Zeldovich was traded off for an oil pump. In his autobiography, Zeldovich wrote that he was not sure about the pump affair but it was possible. A couple of years later in 1936 he presented to the director of ICP several sheets of paper covered with formulae and explained that this is a theory of adsorption and catalysis on heterogeneous solid surfaces. After listening to the explanations, the director advised him to write a candidate (PhD) thesis on the subject. Three years later, in 1939, at the age of 26, he defended his doctor's dissertation on the processes of combustion and detonation. A year later, he was assigned with the task to stabilize the combustion of the solid fuel in the rockets for the famous Soviet rocket launchers "Katyusha" and received his first Stalin Prize (Fig. 5.20).

He tried to study physics and mathematics in the Leningrad University but after several months he gave up and began attending the respective courses in the Leningrad Polytechnic Institute. He was soon again bored and, thus, the future member of the Academy of Sciences of the Soviet Union remained without a University diploma. Later on, already a full member of the Academy of Sciences and triple Hero of Socialist Labor of the Soviet Union and many other decorations for his scientific achievements, he would say, "God bless the times when the Supreme Testimonial Committee permitted people without University education to obtain scientific degrees".

After the discovery of the nuclear fission of uranium in 1938 by Otto Hahn and Fritz Strassmann, Zeldovich, together with Yulii Khariton, developed in 1939 the theory of the nuclear chain reaction.

Figure 5.20: Yakov Borisovich Zeldovich during his stay in Arzamas-16, 1960.

During the war, ICP was evacuated to Kazan. In 1942, with a decision of the Soviet authorities, a special group was created (CB-11, CB for Construction Bureau) for development of the atomic bomb, headed by Igor Kurchatov, a student of Yakov Ilich Frenkel in the Tavria University in Crimea. The document, signed personally by Stalin, stated that the theoretical group of ICP must be commissioned and "comrade Zel'dovich" in particular. Two groups were organized with provisional names "Israel" and "Egypt" under the personal supervision of Lavrentiy Beria, chairman of NKVD (later KGB). Zeldovich joined "Israel" together with Yulii Khariton, Lev D. Landau, Andrei Sakharov, E. Ginzburg, and L. Altshuller. The group "Egypt" worked near Sukhumi in today Abkhazia. Several thousands of German scientists, engineers and skilled workers worked for this group after the war, Max Volmer, Manfred von Ardenne, Peter Adolf Thiessen, and Gustav Hertz being the most renowned. A successful detonation of the first Soviet atomic bomb, called by the Americans Joe-1 (after Josef Stalin) was carried out in 1949.

ICP returned to Moscow (not in Leningrad) in 1943. In 1947/48 persecutions of the intellectuals including scientists of Jewish origin began. The anti-Semitism was implicitly inspired by Stalin himself. In ICP, Zeldovich was accused in "cosmopolitism" and that he tried to publish a paper on the combustion which should be secret in an open journal. Outraged, Zeldovich left ICP and joined the group in the top secret city of Arzamas-16, in order to take part in developing a thermonuclear (hydrogen) bomb. Arzamas-16 was the Soviet version of Los Alamos, where the Soviet H-bombs were constructed. The scientists often called it as a joke Los Arzamas. Again, two groups were organized in Arzamas-16, one under Andrei Sakharov, and the other headed by Zeldovich. The first detonation was accomplished in 1953 (Joe-4) near Semipalatinsk in Kazakhstan in Central Asia. Zeldovich worked there until 1963. It is interesting to note that the idea to ignite the hydrogen bomb by an atomic bomb was suggested by Yakov I. Frenkel, who in fact was not permitted to take part in the project because of his Jewish origin.

He was allowed for the first time to go abroad in 1967 (Fig. 5.21). His first visit to "the West" was in Bulgaria. He gave a talk in the

Figure 5.21: Zeldovich in a discussion with R. Kaischew when visiting the Institute of Physical Chemistry of the Bulgarian Academy of Sciences during his first trip to the "West" in 1967.

Academy of Sciences on the structure of the Universe. He said that the peculiar distribution of clusters of galaxies and huge empty spaces could be understood if one knows the mass of the neutrino, which is closely connected with the dark matter in cosmology. He finished his talk with the words: "I am an old man and could soon present myself to my creator. I do hope he knows the mass of the neutrino and will tell me the value". He was then just 53 years old.

After leaving Arzamas-16, he became a head of division at the Institute of the Applied Mathematics of the Academy of Sciences of the Soviet Union from 1965 until January 1983. Since 1965, he was also a professor at the Department of Physics of the Moscow State University, and a head of the division of Relativistic Astrophysics at the "Sternberg" Astronomical Institute. Zeldovich worked on the theory of the evolution of the hot universe, the properties of the microwave background (relic) radiation with A. G. Doroshkevich and Rashid Syunyaev (the Syunyaev-Zeldovich effect), the large-scale structure of the universe (together with I. D. Novikov), the origin of the Universe, and the theory of black holes. The transition from the theory of detonation to the Big Bang was logical.

One day, after looking at the textbook of math of his son Boris, he was appalled and wrote for him "Calculus for beginners" in which the rigorous proof of the theorems was replaced by intuitive considerations. The textbook was reprinted many times. Years later, together with A. D. Myshkis, he wrote the brilliant "Elements of Applied Mathematics" and "Elements of Mathematical Physics". All in all, Zeldovich published nearly 500 scientific papers and 30 monographs, the most well-known being "Relativistic Astrophysics, Vol. 1: Stars and Relativity, and Vol. 2: The Structure and Evolution of the Universe", written in collaboration with I. D. Novikov. In fact, there is not a field of physics in which Zeldovich did not make a substantial contribution. In the classical theory of nucleation, he introduced the so-called "Zeldovich factor" which accounts for the cluster size fluctuations around the critical size and, in particular, the probability for a stable nucleus to redissolve; he formulated and advanced the first theory of the nonsteady state nucleation. The interested reader can find a detailed review of the scientific achievements of Zeldovich in the preface to the English edition of his "Selected works" (1992).

Figure 5.22: Ya. B. Zeldovich in 1984. The photograph was selected by Zeldovich himself in his "Autobiographical afterwords" at the end of his "Selected Works" published by the Soviet Academy of Sciences on the occasion of his 70th birthday.

For his scientific activity and achievements, he was awarded with more than a dozen of the highest Soviet decorations (Lenin prize, four State prizes and three Gold Stars), the Gold Medal of the Royal Astronomical Society, and was elected a Foreign Fellow of the Royal Society and many scientific institutions and universities. In 2001, the Russian Academy of Sciences gave the name of Zeldovich to a small planet No 11438 for his achievements in nuclear physics, the physics of combustion and detonation, astrophysics, and cosmology. A bronze monument of him was constructed in Minsk in front of the National Academy of Sciences of Belarus. Rudolf Mössbauer recommended him for a Nobel Prize. He hesitated between chemistry and physics but the heart attack caught up with Zeldovich in 1987 before the initiation of the procedure (Fig. 5.22).

Zeldovich was a charismatic person. Everybody liked him but in his own turn he was always concerned with the problems of his coworkers and in general of the people around him. He had a special jacket on which he hanged all his medals and decorations. This jacket played a great role in the lives of his collaborators and friends.

When somebody had a problem with residence permit, accommodation or Soviet authorities, he put on the jacket and visited the respective Soviet employee. Andrei Sakharov remembers: "One night in the small hours somebody knocked at my door. When I opened it I saw Yakov Borisovich. To my question of the strange midnight visit he asked me to give him as a loan 2000 rubles. At that time this was a huge amount of money. We, in Arzamas-16, had received big salaries but which we hadn't where to spend. To my question why he needs the money and in the night, he answered that he should bribe the NKVD officer who was responsible for the prisoners who worked in the secret city in order to send in the morning a young woman, doctor of biological sciences, to a concentration camp, where she would have a chance to survive".

For Zeldovich science was above all. In this respect, he strongly opposed any manifestation of pseudoscience. One day, in a meeting of the members of the Academy of Sciences of the Soviet Union, the biologist Trofim Denisovich Lisenko was giving a talk in which he developed his ideas of inheritance. He stated that if the tails of the mice are cut off immediately after birth, after many generations they would be born without tails. Zeldovich asked a question: "Dear Trofim Denisovich, how could you explain the fact that in millennia the women's hymens have been broken but they are still born with intact hymens".

In 1986, Pope John Paul II invited in the Vatican all the participants of the Conference of the International Academy of Astronautics, taking place in Padua. When Zeldovich approached the Pope, he presented him his "Selected works" and said "Your Holiness, when I was younger I thought that science and cosmology can explain the origin of the Universe. Now I am not so sure" (Fig. 5.23).

5.11 J. H. van der Merwe

Johannes (Jan) Hendrik van der Merwe (1922–): South African physicist (Fig. 5.24). He was born in Humpata (South-West of Angola) where his grandparents had a cattle farm. He was a descendant of an Afrikaner family who did not like the treatment of the Portuguese

Figure 5.23: Ya. B. Zeldovich with Pope John Paul II, 1986.

colonial authorities of foreigners like them. In 1929, when Jan was 7 years old, his parents decided to move South with the cattle and belongings in an ox wagon to the border with German South-West Africa, now Namibia. Jan and his elder brother herded the cattle on horseback to Otjiwarongo. Here, for the first time, Jan attended a school, first in tents and then in a building. He then continued his education in a school in the capital Windhoek. The student's hostel was an abandoned German fort. He was 18 when, in 1940, he qualified for the Department of Engineering of Stellenbosch University in the southern part of South Africa, which was the cultural center of the Afrikaner people. He obtained his bachelor's degree in engineering after three years, then turned to mathematics, and in 1945 obtained with distinction a masters degree in applied mathematics. For his grades, he was awarded a Queen Victoria Scholarship for a year. The South African Council for Scientific and Industrial Research gave him a grant for one more year and Jan left for United Kingdom.

A very strong international group was formed around Nevill Mott, the future Nobel Laureate, in Bristol University. John Douglas

Figure 5.24: Johannes Hendrik van der Merwe in the physics lab in University of Pretoria.

Eshelby, Frederick Charles Frank, Nicolás Cabrera, Doris Kuhlmann-Willsdorf, Jacques Friedel, Frank Reginald Nunes Nabarro, and Alfred Seeger, were among the most active members of the group. Nabarro narrated (Nabarro 2002):

"In Mott's international group, the official language, as Hans Heitler put it, was Broken English. Jan records how in the evenings the speakers of that language would get together and talk about their home countries. Nicolas Cabrera described a bullfight where the toreador pierced the bull between the corns with the spade, while Jan explained that in riding rather wild horses on the farm, horses that would from time to time grip the bit of the bridle in a runaway attempt, the only mechanism by which the horse could be held back was to use the reins in pulling the beak of the horse from side to side in order to subject him to command".

Most of the members of the group of Mott at that time were engaged with defects in solids mostly with dislocations. Mott suggested to van der Merwe to consider the equilibrium structure of epitaxial interfaces between two unlike crystals and proposed to use as an approach, the 1D model of Frenkel and Kontorova published 10 years earlier. Frederick Charles Frank became interested in the problem and joined van der Merwe as his supervisor. The collaboration resulted in the famous series of four papers published in 1949. The critical misfit which appeared as a natural consequence of the mathematical analysis nicely corresponded to the empirical finding of Royer of 1928, although later, the things turned out to be more complicated. Later van der Merwe extended the problem to 2D system, semi-infinite crystals, alloying crystals, thin films. The calculated by him critical thickness for pseudomorphic growth as a function of the lattice misfit coincided with that found by J. W. Matthews who formulated it on the base of considerations of the Italian mathematician Vito Volterra in the beginning of 20th century. It turned out, however, that the experimental values are much higher than the theoretically computed. One possible reason was that the theoretical values were valid for equilibrium, whereas in the real situation, the introduction of misfit dislocations could require considerable energy barriers.

After two years in Bristol, Jan van der Merwe returned to South Africa and taught physics in the University of Pretoria, then headed for three years the Department of Applied Mathematics in the newly founded University of Port Elisabeth, and then returned again to the University of Pretoria as a professor of physics. He retired in 1978 but continued the research and lecturing to graduate students. These years were difficult and crucial for the state, the business, and the scientific institutions as well. Apartheid became increasingly controversial, and some Western nations and institutions began to boycott the business with South Africa because of its racial policies and suppression of civil rights. Some scientists from Europe and the United States also boycotted their colleagues in South Africa erroneously thinking they were fighting the racial segregation. Despite all difficulties Professor van der Merwe contributed considerably for the

development of education and research in physics and mathematics in South Africa so that the universities in the latter can become comparable with those in North America and Western Europe. For his services for the development of science in South Africa, he was awarded with all possible scientific and public prizes in the country, and the Erwin Müller Award of the University of Wisconsin at Milwaukee. The name of professor van der Merwe will remain always connected with the theory of epitaxy as the man who solved one of its main problems.

He never broke the bonds with his old friends from the years in Bristol, in particular with F. C. Frank, F. R. N. Nabarro, and Doris Kuhlmann-Willsdorf. He was often invited as a visiting professor in the University of Virginia where he collaborated with Professor Doris Kuhlmann-Willsdorf and her colleague William Jesser. He spent a sabbatical in the Technical University in Clausthal-Zellerfeld where he successfully collaborated with Ernst Bauer. He is now a honorable professor in the University of Pretoria.

Units, Conversion Factors and Constants

Table A.1: Elemental units in SI system.

Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	degree Kelvin	K

Table A.2: Derived units in SI system.

Quantity	Unit	Symbol
Area	meter^2	m^2
Volume	meter^3	m^3
Density	kilogram·meter^{-3}	kg·m^{-3}
Force	newton	N(kg·m · s^{-2})
Pressure	newton·meter^{-2}	N·m^{-2}
Energy, work	joule	J(N·m)
Power	watt	W
Frequency	Hertz	Hz (s^{-1})
Acceleration	meter/second^2	m·s^{-2}
Voltage	volt	V(W/A)
Electric charge	coulomb	C (A·s)
Electrical resistance	ohm	Ω

Table A.3: Conversion factors.

Convert from	to	Conversion factor
atmosphere	newton/meter^2	1.01×10^5
bar	newton/meter^2	1.0×10^5
millimeter of Hg (0°C)	newton/meter^2	1.333×10^2
torr (0°C)	newton/meter^2	1.333×10^2
dyne	newton	1×10^{-5}
calorie (15°C)	joule	4.185
erg	joule	1×10^{-7}
electron volt	joule	1.602×10^{-19}
electron volt	erg	1.602×10^{-12}

Table A.4: Basic physical constants.

Constant	Symbol	Value in SI	Value in CGS
Avogadro number	N_{A}	6.023×10^{23}/mol	6.023×10^{23}/mol
Planck constant	h	$6.626 \times 10^{-34}\mathrm{J} \cdot \mathrm{s}$	$6.626 \times 10^{-27}\mathrm{erg} \cdot \mathrm{s}$
		$6.626 \times 10^{-34}\ \mathrm{m}^2 \cdot \mathrm{kg/s}$	$4.136 \times 10^{-15}\mathrm{eV} \cdot \mathrm{s}$
Gas constant	R	$8.314 \times 10^0\mathrm{J/K} \cdot \mathrm{mol}$	$1.9866\mathrm{cal/K} \cdot \mathrm{mol}$
			$8.314 \times 10^7\mathrm{erg/K} \cdot \mathrm{mol}$
Boltzmann constant	k	$1.38 \times 10^{-23}\mathrm{m}^2 \cdot \mathrm{kgK}^{-1} \cdot \mathrm{s}^{-2}$	$1.38 \times 10^{-23}\mathrm{J/K}$
			$8.614 \times 10^{-5}\mathrm{eV/K}$
Faraday constant	F	$9.649 \times 10^4\mathrm{C/mol}$	$9.649 \times 10^3\mathrm{cm}^{1/2} \cdot \mathrm{g}^{1/2}/\mathrm{mol}$
Elementary charge	e	$1.602 \times 10^{-19}\mathrm{C}$	$1.602 \times 10^{-20}\mathrm{cm}^{1/2} \cdot \mathrm{g}^{1/2}$
Speed of light	c	$2.998 \times 10^8\mathrm{m/s}$	$2.998 \times 10^{10}\mathrm{cm/s}$

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