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Rate Equation Approaches to Thin Film Nucleation Kinetics

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ABSTRACT

The nucleation and growth of crystals on a substrate are discussed in terms of rate equations for the atom cluster concentrations as a function of time. Simple approximations allow this general set of equations to be reduced to three coupled equations. Many physical processes can be incorporated into these rate equations, including coalescence of clusters, and cluster mobility. The problem of increasing correlation between single atoms and stable clusters as growth proceeds is studied. It is shown that the problem can be solved self-consistently using an auxiliary diffusion equation and that approximations may be obtained which give upper and lower bounds for the cluster growth rates. These diffusion equations also give expressions which enable the cluster-cluster correlations and cluster size distributions to be discussed. With these approximations, expressions are derived for observable quantities and the expressions are compared with one experimental example. In this case, that of gold on alkali halides, it is shown that cluster mobility must be included to obtain agreement with experiment, and that the material parameters required to describe the nucleation behaviour are physically reasonable.

§ 1. INTRODUCTION

In the last few years very considerable progress has been made in both the theoretical and the experimental understanding of the nucleation and early stages of growth of thin films on substrates. This has happened because :

- (a) atomistic nucleation theory (where the critical nucleus contain a few atoms at most) has been developed seriously (Zinsmeister 1966, 1968, 1969, 1970, 1971, Logan 1969, Lewis 1970, Halpern 1969, Stowell 1970, 1972 a, b, Routledge and Stowell 1970, Stowell and Hutchinson 1971 a, b, Sigsbee 1971, Frankl and Venables 1970, and Dettman 1972) ; and
- (b) nucleation experiments have been carried out under clean conditions, by cleaving and cleaning substrates and depositing the films in a U.H.V. environment (e.g. Walton, Rhodin and Rollins 1963, Poppa 1965, 1967, Schmeisser and Harsdorff 1970, Masson, Métois and Kern 1971, Robinson and Robins 1970, Wagner and Voorhoeve 1971, Venables and Ball 1971).

The theories have been developing rapidly at the same time as the experiments, but it is clear that many of the theoretical conclusions are dependent on the details of the model employed. Consequently, many experimenters have had considerable difficulty in deciding which theoretical expressions to use. Also many of these models are not sufficiently general, in that other processes which are not considered could well be influencing the experimental results. This paper is an attempt to include all the processes which are thought to be important, and to develop a simple physical argument which gives approximations for measurable quantities in various regimes of condensation. The paper uses and extends the rate equation formulation (Zinsmeister 1966, Logan 1969, Frankl and Venables 1970), but it also attempts to bridge the gap which separates these papers from the 'diffusion zone' treatment given by Stowell and his co-workers and others. One of the main purposes of this paper is to show that Stowell's treatment is equivalent to the rate equation approach, but that it corresponds to using a particular approximation for the cluster growth rate, which can be shown to be an upper bound. Another expression, which is a lower bound, is also derived and the predictions of these two approximations are compared.

Section 2 describes the mechanisms which are important in nucleation and growth on a defect-free substrate, while § 3 incorporates these processes into suitable rate equations. Section 4 deals with the problem of capture numbers and cluster growth rates. In § 5, solutions to the rate equations are given and expressions for some experimentally measurable quantities are given. In the final section, these expressions are compared with a single experimental example, the work of Robinson and Robins (1970) on the Au/alkali halide systems.

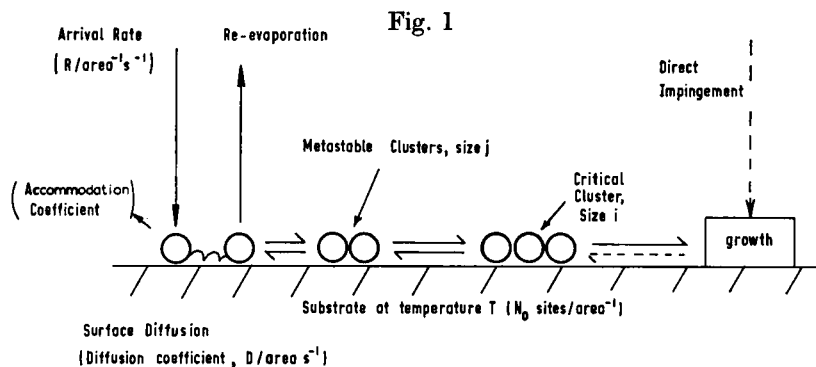
§ 2. MECHANISMS OF NUCLEATION AND GROWTH

The main processes responsible for nucleation and growth (within the first adlayer on the substrate) can be seen with reference to fig. 1. Atoms arrive from the vapour at a rate R ($\text{cm}^{-2} \text{sec}^{-1}$) and are accommodated; the accommodation coefficient is usually considered to be unity. The population of single atoms builds up to the value n_1 (cm^{-2}) and diffuses over the substrate (N_0 adsorption sites cm^{-2}) with diffusion coefficient D at a temperature T . Re-evaporation may occur if the mean stay time τ_a is sufficiently short. The chain reaction of growth starts by the formation of small populations n_j of metastable clusters, with binding energy E_j , which also decay; after $j=i$, growth becomes much more important than decay, i is referred to as the critical nucleus size, and all larger clusters are said to be 'stable'. Thereafter several processes contribute to growth; single atoms can diffuse across the substrate; they can arrive directly from the vapour; moreover it is possible that small (and even large) clusters can diffuse which would also cause growth.

Several processes also contribute to a fall in the number of stable clusters with time. The most obvious is that two clusters which grow

into each other will coalesce into one; if the clusters are mobile the same effect can occur at an earlier stage of growth. It is also conceivable that clusters could evaporate from the substrate directly, though this possibility seems unlikely.

All such nucleation processes can be short-circuited if the substrate contains defect sites to which the adatoms and clusters are strongly bound. Defects can influence both the diffusion coefficient D , and the binding energies E_j , and are certainly important in many practical cases. They will, however, not be discussed in this paper.



Processes in the nucleation of crystals on a substrate.

Following the approach given by Frankl and Venables (1970) it is possible to incorporate all these possibilities approximately into a set of three equations, which can then be used to examine the various regimes of condensation which arise. This is pursued in the next section.

§ 3. SIMPLIFIED RATE EQUATIONS

3.1. Incorporation of Physical Processes into the Rate Equations

General rate equations to describe nucleation and growth have been written down many times before (e.g. Zinsmeister 1966, Frankl and Venables 1970). In the case where single atoms only are mobile and can evaporate, where all stable clusters (size $j > i$) are considered as a group, the number of equations reduces from infinity to $(i + 1)$, as explained by Frankl and Venables (1970). In this case

$$dn_1/dt = R - n_1/\tau_a - 2U_1 - \sum_{j>1}^i U_j - U_x, \quad \dots \quad (1)$$

$$dn_j/dt = U_{j-1} - U_j, \quad (1 < j \leq i), \quad \dots \quad (2)$$

$$dn_x/dt = U_j \quad (\text{for } j = i) \equiv U_i, \quad \dots \quad (3)$$

where n_x is the density of stable clusters, and U_1 , U_j and U_x are the net rates at which single atoms form pairs, form $(j + 1)$ clusters and join stable clusters, respectively. A further simplification can be made if local equilibrium holds for $1 < j \leq i$, for then eqns. (2) are zero. Frankl

and Venables (1970) have shown that this is usually approximately the case. The two remaining equations, (1) and (3), allow one to calculate, with suitable expressions for U_i , U_x (U_1 and $\sum U_j$ in eqn. (1) are rarely important) the evolution of the stable cluster density with time in the early stages of nucleation. This pair of equations, however, will never cause the number of stable clusters to saturate or decrease and for this reason other terms must be included.

One major reason for a decrease in the number of stable clusters is that the clusters grow into each other and coalesce. This gives a negative contribution to eqn. (3), which one might anticipate will be proportional to n_x^2 ; for the present we will call it U_c . Mobile clusters cause somewhat more difficulty. In principle mobile clusters of size j should be included in eqns. (2) in a variety of ways, such as loss to stable clusters (—ve), formation of size j clusters from $(j-k)$ clusters by diffusion of k -sized clusters, etc. However, provided that the diffusion coefficients, D_k , of these clusters are substantially smaller than the single atom diffusion coefficient D , these terms will be much smaller than U_{j-1} and U_j ; hence the local equilibrium will be only weakly perturbed, and eqns. (2) can still be equated to zero approximately. The contribution to eqn. (3) has two main causes; the nucleation rate is promoted by subcritical clusters diffusing to other subcritical clusters to form stable clusters; and the stable cluster density is decreased by stable clusters diffusing to each other and coalescing. The second effect is likely to be more important; in any case both can be included in eqn. (3), the first as part of U_i and the second as a mobile cluster term U_m .

We now need explicit expressions for the various rates U_x , U_i , U_c and U_m in eqns. (1) and (3). The term U_x is the loss of single atoms to stable clusters. These clusters are of various sizes, k , with corresponding 'radii', r_k ; the area of the substrate covered by each cluster is a_k . The rate of removal of single atoms by direct impingement is therefore $Ra_k n_k$. The rate of removal of single atoms by diffusion may be written as $\sigma_k D n_1 n_k$, where σ_k is referred to as a capture number, which will be discussed in more detail in § 4. Thus U_x is given by

$$U_x = \sum_k (\sigma_k D n_1 n_k + R a_k n_k). \quad \dots \dots \dots (4 a)$$

Defining σ_x and a_x as suitable averages of σ_k and a_k , respectively, allows one to write

$$U_x = \sigma_x D n_1 n_x + R a_x n_x. \quad \dots \dots \dots (4 b)$$

The term U_i , the nucleation rate, can be expressed as

$$U_i = \sigma_i D n_1 n_i + \sum_k \sum_l \sigma_{kl} n_k n_l (D_k + D_l),$$

where, in the summations, k and l lie between 1 and i and $(l+k)$ is greater than i . The normal expression is the first term and the second term is expected to be small provided $D_k \ll D$. Again σ_i and σ_{kl} are capture numbers.

On a substrate devoid of stable clusters, the density of critical clusters n_i can be calculated by the equilibrium relation (Walton 1962)

$$(n_i/N_0) = C_i(n_1/N_0)^i \exp(\beta E_i), \quad . \quad . \quad . \quad (5)$$

where $\beta = 1/kT$ and C_i is a statistical weighting factor. The values of C_i were overestimated by Frankl and Venables (1970) and better values are given in Appendix A. To take account of the departure from equilibrium in the chain of eqns. (2) the Zeldovich factor should be incorporated into U_i . We incorporate it into the σ_i and note that it lies between 1 and i^{-1} (Walton 1962, Frankl and Venables 1970). Thus with these approximations

$$U_i = \sigma_i C_i N_0^{(1-i)} D n_1^{i+1} \exp(\beta E_i) = \gamma_i D n_1^{i+1}, \quad . \quad . \quad . \quad (6)$$

where $\gamma_i = \sigma_i C_i N_0^{1-i} \exp(\beta E_i)$. It should be noted that in this expression, as in the other equations, the density n_1 is defined as the number of atoms per unit area over a *macroscopic* area, which is much larger than the area occupied, for example, by a single cluster. In several recent papers (e.g. Lewis 1970, Stowell and Hutchinson 1971 a) the density n_1 has been used in a local sense, and an attempt has been made to correct eqn. (6) for the presence of stable clusters, which cover a fraction, Z , of the substrate. If one simply says that the 'density' on the uncovered area of the substrate is $n_1/(1-Z)$ and nucleation can only take place on this uncovered area, then the nucleation rate is just eqn. (6) divided by $(1-Z)^i$. This is equivalent to the expressions used by the authors quoted and it will be used here. However this correction factor is rather uncertain. The use of eqn. (5) has not been justified when stable clusters are also present; a justification using the rate equations would involve the detailed balance arguments derived from setting the U_j equal to zero in the eqns. (2). But this would involve us in arguments about how the spatial correlations develop between the various sized clusters, and, although this is explored in § 4 and by Dettman (1972), the general case has not been solved. Because of this uncertainty, any further corrections required might just as well be incorporated into the (also uncertain) Zeldovich factor mentioned previously; this point will not be pursued further here.

The two terms which cause the stable cluster density to decrease, U_c and U_m , can be estimated as follows. The coalescence rate is estimated first, for circular clusters where $a_k = \pi r_k^2$. A circular k -sized cluster will coalesce with an l -cluster when the distance between their centres becomes equal to $(r_k + r_l)$. By considering all possible sets of coalescences, one can show, for low substrate coverages, that the rate of removal of randomly positioned stable clusters by coalescence is given by

$$U_c = \frac{1}{2} \sum_k \sum_l n_k n_l \frac{d}{dt} (\pi(r_k + r_l)^2). \quad . \quad . \quad . \quad (7a)$$

If we make the oversimplification that

$$\pi(r_k + r_l)^2 = 4\pi r_x^2 = 4a_x,$$

then U_c can be expressed simply as

$$U_c = n_x^2 \frac{d}{dt} (2a_x). \quad (7b)$$

Vincent (1971), in a more sophisticated analysis of coalescence (but which does not include nucleation), concluded that the n_x was reduced by a factor $[1 - \exp(-4Z)]/4Z$, from its original value at a coverage Z , where $Z = n_x a_x$. Vincent's expression reduces to

$$U_c = 2n_x \cdot dZ/dt \quad (7c)$$

for small Z ; eqn. (7c) is the same as (7b) for $(dn_x/dt) = 0$. Care must be taken in correcting eqn. (7c) for the effect of finite Z using Vincent's formula. The correction to order Z is $(1 - 2Z/3)$ —(Stowell and Hutchinson (1971a) obtained $(1 + 2Z/3)$)—but terms of order Z^2 compensate this correction almost completely in the region of coverage ($Z \sim 0.1$ – 0.2) which is of most interest. We will therefore use eqn. (7c) in its simple form in this paper.

The more regular the nucleation pattern and the more uniform the growth rate, the lower the coalescence term should be. For example, in the extreme case of uniform circular growth at points of a square lattice coalescence would not occur until a coverage of $(\pi/4)$, i.e. 78%, and then n_x would be reduced instantly to a very small value. Thus, although eqn. (7) is the only estimate available at present, non-random nucleation may render it an overestimate in the stages of growth ($\lesssim 5$ – 15% coverage) in which coalescence starts to be important.

The term U_m can be written formally as

$$U_m = \frac{1}{2} \sum_k \sum_l \sigma_{kl} n_k n_l (D_k + D_l), \quad (8a)$$

where the summations run over all values of $k, l > i$, since this describes the diffusive encounters of all stable clusters. Clearly, not much is known about diffusion coefficients of clusters as a function of size; but if all clusters have a similar diffusion coefficient, D_x , this term can be written

$$U_m = \sigma_{xx} D_x n_x^2. \quad (8b)$$

If, on the other hand, only small stable clusters, density n_m , are mobile with diffusion coefficient D_m and $n_m \ll n_x$, then

$$U_m = \sum_m \sigma_{mx} D_m n_m n_x. \quad (8c)$$

Lewis (1970) has computed the effects of mobile clusters by assuming a specific dependence of cluster mobility on size. This case is intermediate between eqns. (8b) and (8c) and will be discussed further in § 5.4.

Inserting expressions (4b), (6), (7c) and (8) into eqns. (1) and (3) (and neglecting the terms $2U_1$ and $\sum U_j$ in eqn. (1)) gives the required simplified rate equations:

$$dn_1/dt = R - n_1/\tau_a - (\sigma_x D n_1 + R a_x) n_x, \quad (9)$$

$$dn_x/dt = (1 - Z)^{-i} \gamma_i D n_1^{i+1} - 2n_x dZ/dt - U_m. \quad . . . (10)$$

These equations cannot yet be solved because we have not given ways of calculating σ_x and a_x . In order to calculate a_x , we evaluate the way in which the total number of atoms in stable clusters changes with time. If the mean number of atoms in a stable cluster is ω_x , the total number in such clusters is $(n_x \omega_x)$ and $d(n_x \omega_x)/dt$ is given by the last term of eqn. (9); i.e. atoms arrive either by diffusion or by direct impingement, if the very small numbers of atoms in the nucleation event itself, $(i+1)U_i$, and the diffusion of subcritical clusters are neglected. This can be written

$$d(n_x \omega_x)/dt = (\sigma_x D n_1 + R a_x) n_x. \quad (11)$$

The relationship between the quantities ω_x , a_x and r_x used in the above equations clearly depends on the mode of growth of the stable clusters, and only simple (and constant) shapes of clusters can be treated analytically. The most important distinction is between growth such that the shape of the cluster is constant (i.e. $\omega_x \sim r_x^3$, $a_x \sim r_x^2$) and growth when the thickness is constant, when $\omega_x \sim a_x \sim r_x^2$. These cases produce different equations which correspond to growth of three-dimensional clusters and two-dimensional monolayer discs, respectively. For three-dimensional growth as a hemisphere $\omega_x \simeq 2\pi r_x^3/(3\Omega)$, $a_x = \pi r_x^2$, where Ω is the atomic volume of the atoms in the cluster†. For the monolayer disc case, $a_x = \pi r_x^2 = \omega_x \Omega^{2/3}$. Equation (11) can be cast in a more convenient form by using the coverage $Z = n_x a_x$ as a variable. Using Z , the left-hand side of (11) can be expressed as $(2/3\sqrt{\pi\Omega}) \cdot d(Z^{3/2}/n_x^{1/2})/dt$ or $\Omega^{-2/3} dZ/dt$ for the three- and two-dimensional cases, respectively. Thus eqn. (11) can be considered as a rate equation for the coverage, when written in the form

$$\frac{dZ}{dt} \left(1 - \frac{1}{3} \frac{d(\ln n_x)}{d(\ln Z)} \right) = \Omega \left(\frac{\pi n_x}{Z} \right)^{1/2} \{ \sigma_x D n_1 n_x + R Z \}, \quad (12 a)$$

suitable for three-dimensional growth, or

$$\frac{dZ}{dt} = \Omega^{2/3} \{ \sigma_x D n_1 n_x + R Z \}, \quad (12 b)$$

in the two-dimensional case.

The three required equations are therefore (9), (10) and (12), and with these three equations it is possible to follow the evolution of n_1 , n_x and Z as a function of time for a given rate of arrival R and inverse temperature β . The temperature strongly influences the material parameters τ_a , D , γ_i and D_m which enter these equations. For the purpose of comparison with experiment in § 6 we shall need explicit expressions for these material parameters. Following convention we write

$$\tau_a^{-1} = \nu \exp(-\beta E_a), \quad (13 a)$$

† The \simeq sign is necessary because ω_x is defined as $\sum n_k \omega_k / n_x$ and a_x as $\sum n_k a_k / n_x$. Thus if r_x is defined by $a_x = \pi r_x^2$, it cannot also be defined in terms of ω_x exactly. The factor required depends on the size distribution, but is always near unity.

where E_a is the adsorption energy and ν an atomic vibration frequency ;

$$D = \alpha \nu N_0^{-1} \exp(-\beta E_d), \quad . \quad . \quad . \quad (13\ b)$$

where E_d is the diffusion energy and α is a constant $\simeq 0.25$; and we may write D_m as

$$D_m = \delta_m \alpha \nu N_0^{-1} \exp(-\beta E_m), \quad . \quad . \quad . \quad (13\ c)$$

where E_m is a cluster motion energy and δ_m is a constant.

The remaining unknowns in these equations, σ_x and σ_i (contained in γ_i) are discussed in the next section.

§ 4. CAPTURE NUMBERS AND CORRELATION EFFECTS

In several recent papers the form of the capture numbers, in particular σ_x , have been discussed (Halpern 1969, Logan 1969, Frankl and Venables 1970, Lewis 1970 a, Sigsbee 1971, Zinsmeister 1971, Dettman 1972, Stowell 1972 a). Various functional forms for σ_x have been suggested which vary between a constant and the number of peripheral sites around the cluster ; depending on whether the cluster growth is in two or three dimensions, the latter assumption gives $\sigma_x \sim \omega_x^{1/2}$ or $\omega_x^{1/3}$. Very few of these expressions are exact, and it is the purpose of this section to evaluate the various formulae which have been derived and to show that, in the cases where exact expressions are not available, useful approximations can be obtained which are upper and lower bounds.

Let us first define what we mean by the capture number, σ_k , of a k -sized cluster. In the rate eqns. (9), (10), (12) loss of single atoms by diffusion to a k -cluster (in an 'average' environment) is given by $\sigma_k n_1 D$: the 'average' of all σ_k 's is σ_x . Viewed from a diffusion standpoint, the density of single atoms must vary locally around each stable cluster, i.e. it is $n_1(\mathbf{r}, t)$ for a cluster at the origin, and this diffusive loss is just $2\pi r_k D(\partial n_1(\mathbf{r}, t)/\partial r)_{r_k}$. Thus, in order to evaluate the capture number σ_k , we need a model for how $n_1(\mathbf{r}, t)$ varies in the neighbourhood of a stable k -sized cluster, and the definition† which follows from the equivalence of these two viewpoints :

$$\sigma_k = (2\pi r_k / n_1) \cdot (\partial n_1(\mathbf{r}, t)/\partial r)_{r_k}. \quad . \quad . \quad . \quad (14)$$

In eqn. (14), n_1 is the single atom density defined over a macroscopic area as used in the rate equations. Also, σ_k will be the capture number required for the whole set of n_k k -clusters unless the model of $n_1(\mathbf{r}, t)$ is sufficiently detailed to take into account the specific environment of a given k -cluster. In what follows, this degree of detail will not be attempted, which means that the growth rates of individual clusters cannot, in general, be calculated. Also, in the remainder of the section, capture numbers will be evaluated under steady state diffusion conditions, since

† An extra factor α (see eqn. 13 (b)) has slipped into the definition given by Stowell (1972 a), since he followed an imprecise definition in Frankl and Venables (1970).

it can be shown (Stowell 1972 a, Dettman 1972, Sigsbee 1971 and § 5.1) that this is a very good approximation except for very small times.

There seems to be only one case in which the capture number of a stable cluster has been rigorously evaluated to date. This is the case of incomplete condensation when the correlations between single atoms and stable clusters do not extend to the next cluster, and the concentration of stable, and of subcritical, clusters is very small. In this case the value of σ_k can be found by solving a diffusion equation for the *local* density $n_1(\mathbf{r}, t)$ around a stable cluster of size k of the form :

$$D \nabla^2 n_1(\mathbf{r}, t) - n_1(\mathbf{r}, t)/\tau_a + R = \partial n_1(\mathbf{r}, t)/\partial t \quad . \quad . \quad (15)$$

with the boundary conditions, $n_1(\mathbf{r}, t) = 0$ for $t > 0$ at the periphery of the cluster and $n_1(\mathbf{r}, t) = R\tau_a$ at large distances away. This leads to transients for $t < \tau_a$, but for $t > \tau_a$ the steady-state solution is

$$n_1(\mathbf{r}) = R\tau_a \left[1 - K_0 \left\{ \sqrt{\left(\frac{r^2}{D\tau_a} \right)} \right\} / K_0 \left\{ \sqrt{\left(\frac{r_k^2}{D\tau_a} \right)} \right\} \right], \quad (16)$$

and the corresponding expression for σ_k is obtained by differentiating to find the diffusive flux into the cluster ; the result is

$$\sigma_k = [2\pi r_k / \sqrt{(D\tau_a)}] \cdot K_1 \left[\sqrt{\left(\frac{r_k^2}{D\tau_a} \right)} \right] / K_0 \left[\sqrt{\left(\frac{r_k^2}{D\tau_a} \right)} \right]. \quad (17)$$

There are two interesting limits of the Bessel functions K_1 and K_0 . For very high temperatures (small τ_a) and large clusters, the arguments are large and $K_1 = K_0$. In this case the diffusive contribution to growth of k -clusters, $\sigma_k D n_1$, is just $2\pi r_k R \sqrt{(D\tau_a)}$. The clusters therefore grow as if absorbing all the atoms which fall on an area $[a_k + 2\pi r_k \sqrt{(D\tau_a)}]$. Since $a_k = \pi r_k^2$, the fine details of the diffusive contribution are not of great significance when $r_k \gg \sqrt{(D\tau_a)}$, since direct impingement is then the most important mechanism for growth of these clusters.

At lower temperatures and for smaller clusters, still within the incomplete condensation regime, the situation can be reversed. The σ_k term becomes dominant and the argument of the Bessel functions is small. In this case, the asymptotic behaviour of K_1 and K_0 gives

$$\sigma_k = 2\pi / \ln [\sqrt{(D\tau_a/r_k^2)}]. \quad . \quad . \quad . \quad (18)$$

In this case the loss term clearly varies more slowly, though it still increases with cluster size ; for the largest clusters the full eqn. (17) will still be required. Solutions equivalent to eqns. (17) and (18) have been obtained by Halpern (1969), Sigsbee (1971), Markov (1971) and Stowell (1972 a), and have been used by Lewis (1970).

In order to use eqn. (17) in the simplified rate equations an average of σ_k over all values of k has to be performed. However, since σ_k is a slowly varying function of k , it will usually be sufficient to evaluate σ_k by using

eqn. (17) for the average cluster radius r_x . Correction terms may be required if the size distribution is very pronounced.

For the nucleation theory to be useful generally, we need expressions for σ_i , σ_k (and hence σ_x) in the general case, when n_1 is not necessarily equal to $R\tau_a$. Although no exact solutions have been obtained, two approaches have been developed which can be shown to bracket the true situation.

Lewis (1970) has developed a computational scheme, in which the clusters are randomly distributed, which takes into account the capture processes which compete with re-evaporation. Dettman (1972) has obtained a similar solution. A simple derivation of these results is given here; we call this approximation the 'uniform depletion approximation'. Stowell and Hutchinson (1971 a), Stowell (1972 a) and Sigsbee (1971) have evaluated cluster growth rates by placing all the clusters on a lattice. Stowell (1972 a) has thereby obtained values for σ_x : in this section, this is extended to obtain σ_k and σ_i using the same approximation, which we call the 'lattice approximation'.

The real problem consists of evaluating the loss of single atoms to clusters by solving a diffusion equation, similar to (15), where the local density $n_1(\mathbf{r}, t)$ is zero on the boundary of every stable cluster; this is clearly an impossible problem to solve, since we do not know where the clusters are or how large they are. The 'uniform depletion approximation' consists of singling out an average k -sized cluster and taking account of the loss to all stable clusters as in eqn. (9). The value of $n_1(\mathbf{r}, t)$ around this cluster at $\mathbf{r}=0$ is then given by the solution of

$$D \nabla^2 n_1(\mathbf{r}, t) - n_1(\mathbf{r}, t)(\tau_a^{-1} + \sigma_x D n_x) + R(1 - Z) = \partial n_1(\mathbf{r}, t) / \partial t. \quad (19)$$

The boundary conditions are $n_1(\mathbf{r}, t) = 0$ at $r = r_k^\dagger$ and $\nabla^2 n_1(\mathbf{r}, t) = 0$ as $r \rightarrow \infty$; i.e. for large \mathbf{r} , $n_1(\mathbf{r}, t)$ equals n_1 given by the rate eqn. (9).

Equation (19) has exactly the same form as eqn. (15), if we define τ and R_1 such that

$$\tau^{-1} = \tau_a^{-1} + \sigma_x D n_x, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20 a)$$

and

$$R_1 = R(1 - Z). \quad . \quad . \quad . \quad . \quad . \quad . \quad (20 b)$$

Consequently, this equation has similar solutions: for $t > \tau$, the solution (far away from the cluster) is $n_1 = R_1 \tau$, with τ and R_1 given by eqn. (20). The corresponding expression for $n_1(\mathbf{r}, t)$ around the cluster is the same as eqn. (16) with τ replacing τ_a and R_1 replacing R : hence

$$\sigma_k = 2\pi X_k K_1(X_k) / K_0(X_k), \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

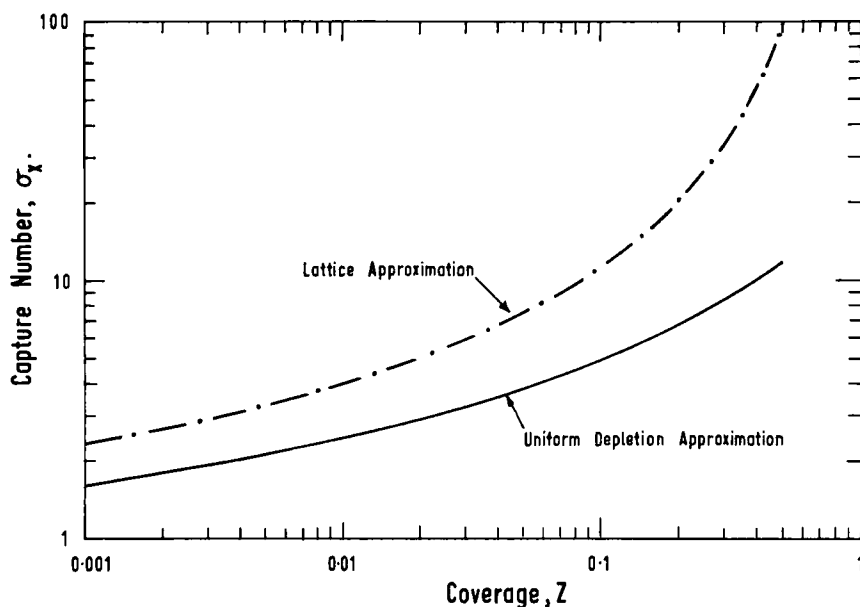
with

$$X_k = \sqrt{(r_k^2 / D\tau)}^\ddagger.$$

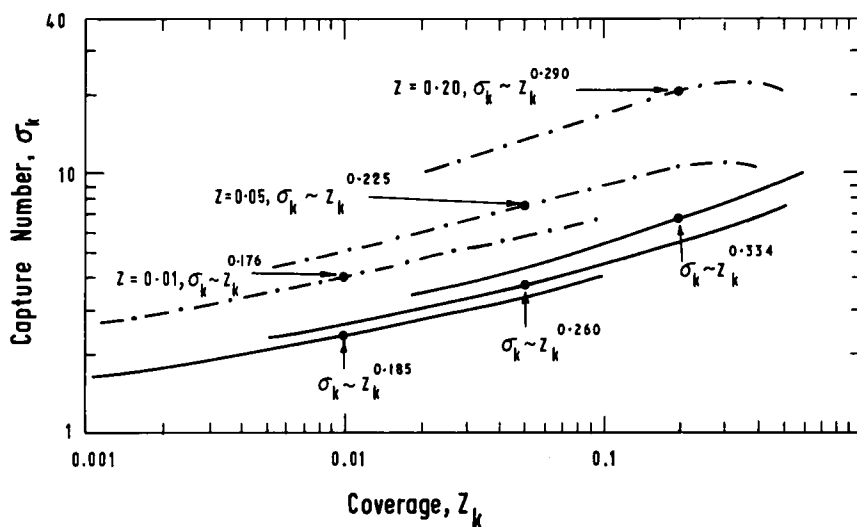
[†] Strictly $n_1(r_k, t)$ should be the single density in equilibrium with the cluster (Sigsbee 1971) but this aspect is not considered here.

[‡] Lewis (1970) has obtained a very similar result and his b_q is equivalent to $\sigma_k/4$. This is because his work is formulated in terms of the single atom velocity, which differs from the diffusion coefficient used here by a factor of $\alpha \simeq 1/4$.

Fig. 2



(a)



(b)

Capture numbers σ_x and σ_k , in the complete condensation case, for both the uniform depletion approximation (full line, eqn. (21)) and the lattice approximation (dot-dashed line, eqns. (22) and (26).) (a) $\sigma_x(Z)$; (b) $\sigma_k(Z_k)$ for $Z=0.01, 0.05$ and 0.20 .

This result has also been obtained by Dettman (1972) for the case $i = 1$. Dettmann has attempted to solve the problem rigorously by solving diffusion equations for various correlation functions, and hence deducing rate equations which automatically contain the correct σ 's. The mathematical difficulties in such an approach are, however, severe, and the present approach obtains the same answer for a general value of the critical nucleus size i , from a simpler physical argument. The approximations implicit in his approach must, therefore, be the same as given here.

The approximations used before, namely $\sigma_x = \sigma_k$ for $r_k = r_x$, enables one to calculate σ_x self-consistently using eqn. (21). Once σ_x has been calculated and hence τ via eqn. (20 a), the individual σ_k 's can be calculated using (21).

In the complete condensation case, $\tau^{-1} = \sigma_x D n_x$, and therefore the argument of the Bessel function, X , in eqn. (21) for σ_x , is given by

$$X^2 = r_x^2 / D\tau = \sigma_x n_x r_x^2 = \sigma_x Z / \pi,$$

since the coverage, Z , equals $\pi n_x r_x^2$. Thus σ_x is a function of Z only in this case.

Stowell (1972 a) has calculated σ_x by using the 'lattice approximation'. For the complete condensation case σ_x is also only a function of Z , and in the present notation is given by

$$\sigma_x = 4\pi(1-Z) / \{\ln(1/Z) - (3-Z)(1-Z)/2\}. \quad (22)$$

A comparison of expressions (21) and (22) is shown in fig. 2 (a). Note that the lattice approximation gives somewhat higher values for σ_x , increasing so with increasing Z .

The form of σ_x in general in the lattice approximation is rather more daunting, but is given in detail by Stowell (1972 a). In converting his expressions to the present notation, it must be realized that his \bar{n}_1 is defined over the uncovered area of the substrate and hence requires multiplication by $(1-Z)$ to be equivalent to the n_1 used here; the factor α in his expressions should also be dropped, as mentioned earlier. The following argument also enables his expressions to be used to calculate σ_k .

In the lattice approximation n_1 can be written (Stowell 1972 a) as

$$n_1 = R\tau_a \{(1-Z) - 2Z \cdot P(X, Y)/X\}, \quad (23)$$

where

$$P(X, Y) = \frac{I_1(Y)K_1(X) - K_1(Y)I_1(X)}{I_1(Y)K_0(X) + K_1(Y)I_0(X)}, \quad (24)$$

with $X = \sqrt{(r_x^2/D\tau_a)}$ and $Y = \sqrt{(L^2/D\tau_a)}$, where $\pi L^2 n_x = 1$; K_j and I_j are modified Bessel functions of order j . If, at one of the lattice points a k -cluster is substituted for an average sized cluster, and the radius, L_k , of the zone around the cluster is chosen so that $n_1(L_k) = n_1(L)$ in the neighbouring zones containing average-sized clusters, the diffusive flux into this k -cluster is $2\pi r_k D(\partial n_1/\partial r)$ and is equal to $2\pi D \cdot R\tau_a \cdot X_k \cdot P(X_k, Y_k)$,

where $X_k = \sqrt{(r_k^2/D\tau_a)}$ and $Y_k = \sqrt{(L_k^2/D\tau_a)}$. Thus, using eqn. (14), the expression σ_k in the lattice approximation can be written

$$\sigma_k = \frac{2\pi X_k \cdot P(X_k \cdot Y_k)}{\{(1-Z) - 2Z \cdot P(X, Y)/X\}} \quad (25)$$

The expression for σ_x is obtained by putting $X_k = X$, and $Y_k = Y$ in this equation. At very high temperatures, where $Y \gg 1$, and $P(X, Y)/X \ll 1$ expression (25) and (21) differ only by the rather unimportant factor $(1-Z)$, present in (25) but not in (21).

Equations (21) and (25) allow one to calculate σ_k , for all sizes of stable clusters, as well as σ_x . As will be seen in § 5.6, σ_k is needed to evaluate the size distribution of stable clusters, even though only σ_x and σ_i are needed to solve the three rate equations (9), (10) and (12) in §§ 5.1 to 5.4.

The lattice approximation expression for σ_k in the complete condensation limit can be expressed in a form similar to eqn. (22), namely

$$\sigma_k = 4\pi(1-Z_k)(L_k^2/L^2)/\{\ln(1/Z) - (3-Z)(1-Z)/2\}, \quad (26)$$

where L_k is determined implicitly (see Routledge and Stowell 1970, eqn. (6)) by

$$(L_k/L)^2\{\ln(L_k/r_k)^2 - (1 - (r_k/L_k)^2)\} = \ln(1/Z) - (1-Z). \quad (27)$$

From eqn. (27), (L_k/L) , and hence σ_k , can be determined as a function of Z and $Z_k = \pi n_x r_k^2$. In the uniform depletion approximation, eqn. (21), σ_k is also a function of these same variables in the complete condensation limit. It is the Z_k dependence of σ_k which is of interest for determining the size distribution; curves of $\sigma_k(Z_k)$ for three values of Z are given in fig. 2 (b) for these two approximations.

If one can determine σ_k , then one can give an upper limit for σ_i as follows. If an $(i+1)$ cluster is completely stable then σ_i should be given by σ_k for $k=i$. This case should apply when $i=1$ and a pair is very stable, as in the examples considered in § 6. If the $(i+1)$ is not completely stable, σ_i can only be less than the result of such a calculation. However it must not be too much less or $(i+1)$ will be the critical size. Calculations reported in the next section using this upper limit for σ_i show that σ_i is a slowly varying function of Z (except in the lattice approximation in the complete condensation regime at high Z) but that it is dependent on temperature through the parameter $(D\tau_a)$; it can increase from below 2 at low temperatures to above 6 at high temperatures. Certainly, the commonly used assumption that σ_i is constant ($\sim 4-6$) given by a geometrical argument related to the number of peripheral sites of an i -cluster (e.g. Frankl and Venables 1970) is only a crude first approximation.

The relationship between the lattice and uniform depletion approximations is interesting. In the lattice approximation the clusters are positioned so that they grow at the maximum possible rate. This approximation therefore represents an upper bound for σ_x and σ_k . The uniform

depletion approximation represents a lower bound for σ_x and σ_k , as can be seen from the following argument. In eqn. (19) the loss term $\sigma_x D n_1 n_x$ was taken to be independent of \mathbf{r} , and n_x includes the cluster under consideration at $\mathbf{r}=0$. But the loss to the cluster at $\mathbf{r}=0$ is taken account of by the $D \nabla^2 n_1$ term in (19), which leads to the depletion of n_1 in the neighbourhood of the origin. However, because of the single atom population is depressed for small \mathbf{r} , the nucleation rate will also be, and hence n_x will be smaller there too. Thus this solution for $n_1(\mathbf{r}, t)$ and σ_x should be thought of as a first approximation in the process of calculating $n_1(\mathbf{r}, t)$, $n_x(\mathbf{r}, t)$ and σ_x self-consistently. This process would undoubtedly raise σ_x and σ_k to values intermediate between the 'lattice' and 'uniform depletion' approximations. A discussion of cluster-cluster correlations (i.e. $n_x(\mathbf{r}, t)$) is given in § 5.5.

It is worth noting that the expression $\sigma_x \sim r_x$ which has been used previously many times (Zinsmeister 1966, 1971, Frankl and Venables 1970) can only be used for stable clusters at very short times $t \lesssim \tau$. It is only apparently correct at very high temperatures (where $K_1 = K_0$ in eqn. (17)), as in this case the σ_x term is better represented as a direct impingement term. The dependence $\sigma_x \sim r_x$ not only overestimates the value of σ_x , it also leads to incorrect dependences of observable quantities on material parameters. If a very simple approximation is required it is better to use $\sigma_i = \text{constant} \simeq 2-4$ and $\sigma_x = \text{constant} \simeq 5-10$, as these approximations are correct to order of magnitude in many circumstances and do lead to the correct dependence on material parameters. However, since a correlation of experimental data with the theory will undoubtedly require some computing, it is an easy matter to construct subroutines to compute one of the more accurate expressions for σ_x and σ_i given in this section, using the expansions for Bessel functions given by Abramowitz and Stegun (1970). The 'uniform depletion approximation' is given by eqn. (21) and the 'lattice approximation' by eqn. (25) in general; the lattice approximation reduces to eqn. (22) in the limit of complete condensation. The influence of these approximations on the solutions of the rate equations is examined in the next section.

§ 5. PARAMETER DEPENDENCES OF OBSERVABLE QUANTITIES

With the relevant approximations for σ_x and σ_i worked out in the last section, the three eqns. (9), (10) and (12) can be solved to give expressions for experimentally observable quantities. The most easily observed quantities are the stable cluster density and the coverage as a function of time. From such observations various data can be extracted, including the maximum or saturation cluster density, and the coverage and the time at the maximum. It is also possible to measure the total amount of material condensed as a function of time. Expressions for all these quantities can be obtained from the solutions to the three coupled rate equations (9), (10) and (12). For all of them, it is instructive to know

their dependence on experimental variables, in particular on the rate of arrival R and the inverse temperature, β . It is also helpful to see if the uncertainties about the exact form of σ_x and σ_i influence the predictions.

In §§ 5.1, 5.2 and 5.3 the mobility of clusters is taken to be unimportant and the maximum in the cluster density is caused by coalescence. These sections deal with 'transient' nucleation, 'steady-state' nucleation and analytic expressions for the maximum cluster density, respectively. Section 5.4 deals with the effects of mobile clusters. It is also possible to measure the size distribution of stable clusters. Although such effects have not been considered in arriving at the three simplified rate equations, it is possible to use the same approach to make predictions about spatial distributions and size distributions. This is attempted in §§ 5.5 and 5.6.

It should be emphasized that this analysis, although seemingly general, is conceived primarily in terms of explaining experimental results like the gold/alkali halide case described in § 6, where the adsorption energy is relatively low and small clusters are stable. In these cases all the processes which are important occur on the bare substrate. A major area of uncertainty exists as to whether the same analysis really applies to systems in which the adsorption energy is high and/or small clusters are very unstable. Although the analysis should apply to the first monolayer, it is possible, though not necessary, that the important processes in nucleation take place on top of, or within, adsorbed multi-layers on the substrate (Wagner and Voorhoeve 1971, Venables and Ball 1971).

5.1. Transient Nucleation

In the very initial stages of nucleation, the single population n_1 builds up as $n_1 = Rt$, all other terms in eqn. (9) being negligible. This regime persists until the remaining terms in (9) limit n_1 . The nucleation which occurs during this period has been termed 'transient' nucleation by Stowell and Hutchinson (1971 *b*). The time at the end of this transient period is just the τ introduced in the last section (eqn. (20 *a*)) and hence it is easy to show, from eqn. (10), that

$$n_x(\tau) \simeq \gamma_i D R^{i+1} \tau^{i+2} / (i+2). \quad (28)$$

Thus, using eqn. (20 *a*), $n_x(\tau)$ is given by

$$n_x(1 + \sigma_x D \tau_a n_x)^{i+2} \simeq \gamma_i D \tau_a (R \tau_a)^{i+1} / (i+2). \quad . . . (29)$$

For 'initially incomplete condensation', when τ_a is small, the term $\sigma_x D \tau_a n_x \ll 1$. But then $n_x(\tau)$ is always negligibly small. For 'initially complete condensation' when $\sigma_x D \tau_a n_x \gg 1$, n_x at time τ may be significant. It is given by

$$n_x(\tau) \simeq \left\{ \frac{\gamma_i}{(i+2)} \cdot \frac{(R/D)^{i+1}}{\sigma_x^{i+2}} \right\}^{1/(i+3)} (30)$$

The value for σ_x is that appropriate to the coverage at time τ ; Stowell (1972 *b*) has suggested that this coverage is approximately that given by

assuming that each stable cluster contains $(i+1)$ atoms. The computations given in Frankl and Venables (1970)—see their fig. 7—indeed show that very little growth has occurred at this stage and that this approximation is therefore reasonable.

This formula for n_x was originally obtained by Stowell (1970), and was derived in a similar way to that given here by Frankl and Venables (1970) and Stowell and Hutchinson (1971 b). The stable cluster density saturates at this stage if σ_x increases as $(\omega_x)^{1/3}$ for $i \geq 2$, as shown by Frankl and Venables (1970). However, for the more accurate forms of σ_x discussed in § 4, which are functions of Z rather than ω_x , n_x continues to increase, though more slowly, until limited by coalescence or cluster mobility.

The treatment of coalescence has been pioneered by Stowell and Hutchinson (1971 a). In the next section their results are rederived from the three rate equations (9), (10) and (12). This is done in order to see how their approach is related to the rate equation approach, and to compare predictions using the different forms of σ_x and σ_i given in § 4.

5.2. Nucleation Limited by Coalescence

5.2.1. General Rate Equations for 'Steady-State' Nucleation

In terms of the variable τ , eqn. (9) for n_1 can be written

$$dn_1/dt = R(1-Z) - n_1/\tau. \quad (31)$$

Thus, for times $t \gtrsim \tau$, n_1 is given by

$$n_1 = R\tau(1-Z), \quad (32)$$

and dn_1/dt is effectively zero. Since τ can only decrease as nucleation proceeds, this means that the single density, n_1 , is always in this 'steady-state' for $t > \tau$. Inserting (32) into the remaining rate equations (10) and (12 a) gives, for three-dimensional hemispherical growth,

$$dn_x/dt = (1-Z)\gamma_i D(R\tau)^{i+1} - 2n_x dZ/dt - U_m, \quad (33)$$

and

$$dZ/dt = \sqrt{\pi} \Omega R (n_x/Z)^{1/2} \{ \sigma_x D n_x \tau (1-Z) + Z \} / (1-m/3), \quad (34)$$

where m has been written for $d(\ln n_x)/d(\ln Z)$; i.e. $n_x \sim Z^m$. The two-dimensional growth case follows entirely analogously using eqn. (12 b) and will not be discussed further here.

Several points can be made very simply from eqns. (33) and (34). At high temperatures, when $\tau = \tau_a$, the nucleation rate, dn_x/dt , will initially be constant and proportional to R^{i+1} : the value of i can be most easily identified by measuring the initial nucleation rate as a function of R in this regime; the temperature dependence of the nucleation rate will determine $(E_i + (i+1)E_a - E_d)$. However, even in this high temperature regime, the behaviour of dZ/dt is not simple. Initially the first term in the curly brackets in eqn. (34) must dominate: atoms arrive at clusters by diffusion. For very small values of $D\tau_a$, the second term then becomes

more important and most growth occurs by direct impingement. In the low temperature regime (complete condensation) the equation for n_x is not particularly simple. The time τ is inversely proportional to both σ_x and n_x and hence the nucleation rate is slower for larger i and for forms of σ_x which increase more rapidly with Z . But in this low temperature limit the term in curly brackets in eqn. (34) is just equal to unity.

Stowell and Hutchinson (1971 a) and Stowell (1972 b) have shown that n_x can be most usefully expressed in terms of the coverage Z . In the first paper this was done using a 'transformation' between Z and t which was different for the various low and high temperature regimes. In the second paper an equation analogous to (34) was used. In the present treatment expressing n_x as a function of Z involves combining eqns. (33) and (34) by writing $dn_x/dZ = (dn_x/dt)/(dZ/dt)$. It is also extremely convenient to use the variables $\mathcal{N} = n_x/N_0$ and $\mathcal{F} = Rt/N_0$, and to use the lumped material parameters $A = D\tau_a N_0$ and $B_i = C_i \exp \beta E_i (R/N_0^2 D)^i$. With these parameters general equations for $d\mathcal{N}/dZ$ and $d\mathcal{F}/dZ$ can be easily obtained from (33) and (34), and written as

$$d\mathcal{N}/dZ = \left\{ (1-Z)\sigma_i B_i \left(\frac{A}{1+\sigma_x A \mathcal{N}} \right)^{i+1} - \frac{U_m}{R} \right\} \cdot (d\mathcal{F}/dZ) - 2\mathcal{N}, \quad (35)$$

and

$$d\mathcal{F}/dZ = \frac{(1-m/3)}{(\pi\Omega^2 N_0^3)^{1/2}} \left(\frac{Z}{\mathcal{N}} \right)^{1/2} \left\{ \frac{1+\sigma A \mathcal{N}}{Z+\sigma_x A \mathcal{N}} \right\} \quad (36)$$

An expression for the total amount of material condensed, \mathcal{F}_c , expressed in the same (monolayer) units at \mathcal{F} can be simply obtained by noting that the rate of re-evaporation of atoms from the substrate is just n_1/τ_a . After some simple manipulation one obtains

$$d\mathcal{F}_c/dZ = d\mathcal{F}/dZ \{ 1 - (1-Z)/(1+\sigma_x A \mathcal{N}) \}. \quad (37)$$

Other 'average' quantities, such as the mean radius of the clusters $(\sqrt{Z/\pi\mathcal{N}})$, can be easily derived by solving the coupled eqns. (35) and (36).

These equations are entirely analogous to those derived by Stowell and Hutchinson (1971 a) and Stowell (1972 b) and differ only in the following (rather trivial) respects. First, the term $(1-m/3)$ which appears in (35) and (36) arises from taking the nucleation rate into account properly in arriving at the expression for the growth rate in eqn. (12). Second, the different size of the lattice of the substrate and of the condensate is taken into account by the parameter $(\Omega N_0^{3/2})$, which need not be equal to one. Similarly, clusters of any fixed three-dimensional shape (not necessarily hemispherical) can be described by varying this parameter only. Third, the use of the capture numbers σ_i, σ_x allows one to evaluate various different models of the diffusion and capture process on an equal footing. However, the fact that the models considered in § 4 all lead to σ_i and σ_x which are functions of Z , A and \mathcal{N} only, means that the qualitative

conclusions of Stowell's work are unchanged; in particular, the dependencies of all quantities on material parameters are necessarily reproduced, and only numerical differences appear.

For any given set of material parameters i , B_i and A , the coupled eqns. (35) and (36) can be integrated, using specific models for σ_i and σ_x . The physical regimes of condensation which arise can, however, be seen more simply as described below.

5.2.2. Regimes of Condensation

For a given value of i and B_i the behaviour of eqns. (35) and (36) depends only on the one parameter $\sigma_x A \mathcal{N} (= \sigma_x D \tau_a n_x)$. For $\sigma_x A \mathcal{N} \gg 1$ we have complete condensation; for $\sigma_x A \mathcal{N} \ll Z$ we have the regime Stowell and Hutchinson (1971 a) have termed 'extreme incomplete condensation'; in this regime all growth is caused by direct impingement of atoms onto the cluster. For $1 > \sigma_x A \mathcal{N} > Z$ we have an intermediate regime, which arises initially under virtually all conditions; in this regime condensation is incomplete, but cluster growth occurs mainly by diffusion of atoms over the substrate.

For the extreme incomplete condensation regime eqns. (35) and (36) simplify, when $U_m = 0$, to

$$d\mathcal{N}/dZ = \frac{(1-Z)(1-m/3)}{(\pi\Omega^2 N_0^3)^{1/2}} \cdot \frac{\sigma_i B_i}{(Z\mathcal{N})^{1/2}} \cdot A^{i+1} - 2\mathcal{N}, \quad \dots \quad (38)$$

and

$$d\mathcal{F}/dZ = \frac{(1-m/3)}{(\pi\Omega^2 N_0^3)^{1/2}} \cdot \left(\frac{1}{Z\mathcal{N}}\right)^{1/2} \cdot \dots \quad (39)$$

Following Stowell and Hutchinson (1971 a), one can write

$$\begin{aligned} \mathcal{N}(Z) &= \eta(Z) \{ \sigma_i B_i A^{i+1} / (\Omega N_0^{3/2}) \}^{2/3} \\ &= \eta(Z) \left(\frac{\sigma_i \alpha C_i}{\Omega N_0^{3/2}} \right)^{2/3} \left(\frac{R}{N_0 \nu} \right)^{2i/3} \exp \left\{ \frac{2\beta}{3} (E_i + (i+1)E_a - E_d) \right\}, \end{aligned} \quad (40)$$

and

$$\mathcal{F}(Z) = \kappa(Z) \{ \sigma_i B_i A^{i+1} \}^{-1/3}, \quad \dots \quad (41)$$

where $\eta(Z)$ and $\kappa(Z)$ are pure numbers which are solutions of the differential equations

$$d\eta/dZ = (1-m/3)(1-Z)(\pi Z\eta)^{-1/2} - 2\eta, \quad \dots \quad (42)$$

and

$$d\kappa/dZ = (1-m/3)(\pi Z\eta)^{-1/2}. \quad \dots \quad (43)$$

The σ_i can be incorporated into eqns. (40) and (41) because the σ_i are not functions of Z in this regime. These equations only have simple solutions when $Z \ll 1$ and the coalescence term 2η in eqn. (42) is unimportant. Under these conditions $m(d \ln \eta / d \ln Z) = 1/3$ and $\eta = \kappa = (8/3\sqrt{\pi})^{2/3} Z^{1/3}$. Under these same conditions the amount of material condensed, \mathcal{F}_c , (from eqn. (37) with $\sigma_x A \mathcal{N} \ll Z$) equals $Z \cdot \mathcal{F}(Z)/4$.

At a later stage the coalescence term 2η in eqn. (42) produces a maximum in $\eta(Z)$. Stowell and Hutchinson (1971 a) showed that this maximum occurs at $Z = Z_0 = 0.21$. By reintegrating this equation, including the $(1 - m/3)$ term, Z_0 is raised to the value 0.23, and $\eta(Z_0) = 0.59$. In the neighbourhood of this maximum, eqn. (43) shows that $\kappa \sim Z^{1/2}$, and $\kappa(Z_0) = 0.88$. In this regime, the form of σ_x is unimportant. Even at lower temperatures, where σ_x is important, the two approximations for σ_x (and σ_i) are essentially the same. So there is very little uncertainty as to the expected behaviour for the incomplete condensation regime.

In the complete condensation regime, $\sigma_x A \mathcal{N} \gg 1$. In an exactly similar way one can derive from eqns. (35) and (36) that

$$\begin{aligned} \mathcal{N}(Z) &= \eta(Z) \{ \sigma_i B_i / (\Omega N_0^{3/2}) \}^{2/(2i+5)} \\ &= \eta(Z) \left(\frac{\sigma_i C_i}{\Omega N_0^{3/2}} \right)^{2/(2i+5)} \\ &\quad \times (R/N_0 \alpha \nu)^{2i/(2i+5)} \exp \{ 2\beta(iE_d + E_i)/(2i+5) \}, \end{aligned} \quad (44)$$

and

$$\mathcal{F}(Z) = \kappa(Z) \{ \sigma_i B_i \}^{-1/(2i+5)}, \quad (45)$$

if we make the approximation that σ_i is independent of \mathcal{N} and Z . This is not quite true, as the forms given in § 4 imply that σ_i is a function of Z and \mathcal{N} in this regime; in particular it is a worse approximation if the lattice approximation expression is used than if the uniform depletion expression is used. However the extremely weak dependence on σ_i implied in eqns. (44) and (45) make the approximation $\sigma_i = \text{constant}$ not very restrictive. With this approximation, η and κ are solutions of the equations

$$d\eta/dZ = (1 - Z)(1 - m/3)(Z/\pi\eta)^{1/2}(\sigma_x\eta)^{-(i+1)} - 2\eta, \quad . . . (46)$$

and

$$d\kappa/dZ = (1 - m/3)(Z/\pi\eta)^{1/2}. \quad (47)$$

Even without the coalescence correction (-2η) there is no simple approximation to these equations, as σ_x is a complicated function of Z . To get an idea of the behaviour, one can suppose $\sigma_x \sim Z^n$ in the region of interest. Then it follows that $\eta \sim Z^p$, where $p = (3 - 2(i+1)n)/(2i+5)$ and that $\kappa \sim Z^q$, where $q = (3i + 6 + (i+1)n)/(2i+5)$. By referring to fig. 2 (a) one can see that n increases with Z and is usually in the range $0.2 \lesssim n \lesssim 0.7$, rising to ~ 1 if the lattice approximation is used at high values of Z . Thus for $i=1$, p is in the range below 0.3 and $1.3 \lesssim q \lesssim 1.6$.

Again the coalescence term causes a broad maximum in the cluster density. The value of the coverage at this maximum depends quite critically on the form of σ_x . As Stowell and Hutchinson (1971 a) have shown for their lattice approximation, the maximum occurs at $Z = Z_0$ with $Z_0 = 0.11$ for $i=1$, 0.064 for $i=2$ and 0.040 for $i=3$. Inclusion of the $(1 - m/3)$ term raises this to 0.125 for $i=1$, but has a negligible effect for

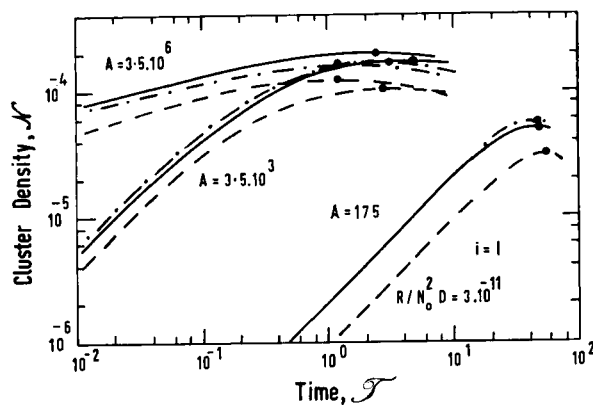
$i=2$ and 3. At this maximum the values of $\eta(Z_0)$ for $i=1$ to 3 are 0.118, 0.134 and 0.152; these values are almost identical to those given by Stowell and Hutchinson (1971 a). The values of $\kappa(Z_0)$ are 0.056, 0.019 and 0.0088, respectively, for $i=1$ to 3. Use of the uniform depletion approximation (eqn. (21)) gives values of $Z_0=0.20$ for $i=1$, 0.11 for $i=2$ and 0.065 for $i=3$; $\eta(Z)=0.179$, 0.199 and 0.222, and $\kappa(Z_0)=0.092$, 0.037 and 0.015, respectively. Thus, given that the uniform depletion and lattice approximations bracket the real behaviour of σ_x , the theoretical uncertainty is less than a factor of 2 in Z_0 , <1.5 in $\eta(Z_0)$ and <1.7 in $\kappa(Z_0)$. In practice, Z_0 may be even lower than calculated by any of these approximations. This is because the assumption that the clusters grow in a constant three-dimensional shape *even after coalescence* is a severe one. Unless the cluster surface diffusion coefficient is extremely rapid, coalescence will lead to a flattening of the clusters and a reduction of Z_0 towards the value calculated for two-dimensional growth. This value, as Stowell and Hutchinson (1971 a) have shown, is about a factor of two lower than for the three-dimensional case.

If one wants to follow the evolution of \mathcal{N} and Z with time in general, there is no alternative but to integrate the coupled eqns. (35) and (36) directly, starting with the solutions at the end of the 'transient' nucleation stage. This integration can easily be performed using a small computer, and examples have been given by Stowell (1972 b). To get reliable numbers, care must be taken with the 'constants' appearing in the equations: for example, in the Au/KCl discussed in § 6, $\Omega N_0^{3/2}=0.193$, if there are two sites for an Au atom on a (100) KCl face; if there are four, $\Omega N_0^{3/2}=0.545$; both values are substantially different from unity. Probably σ_i is the most uncertain parameter. This is because σ_i will be given by the diffusion solutions (eqns. (21) or (25)) only if an $(i+1)$ cluster is completely stable; if it is not, σ_i will be smaller. As an example of the spread of values obtained for a particular case, eqns. (35) and (36) have been integrated using several assumptions for σ_i and σ_x and the results compared with the values obtained by Stowell (1972 b). These curves of $\mathcal{N}(T)$ and $\mathcal{F}(Z)$ are shown in fig. 3. If the only uncertainty were in σ_x , then the curves for the uniform depletion and lattice approximations would bracket the correct solution. However, one can see from the curves that the uncertainty in σ_i is probably more important, and that the two approximations, when used self-consistently for both σ_x and σ_i give values which are very similar.

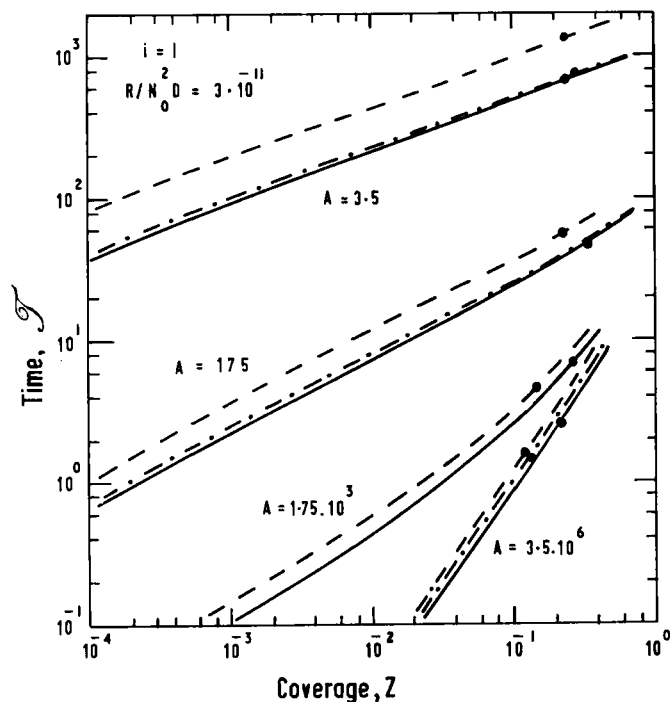
5.3. General Equation for the Maximum Cluster Density

The maximum in the cluster density as a function of coverage or time is one of the most easily measurable quantities. It can be measured, for example, even in the complete condensation case, when the initial nucleation rate is much too large to be measured. A general expression for $\mathcal{N}(Z_0)$ can be written simply by equating the first two terms on the

Fig. 3



(a)



(b)

Cluster density, \mathcal{N} versus time \mathcal{T} and time, \mathcal{T} , versus coverage, Z , for $i=1$, $R/N_0^2 \bar{D} = 3 \times 10^{-11}$, $\Omega N_0^{3/2} = 1$ and the values of A indicated. The black circles indicate the points corresponding to the maxima in the $\mathcal{N}(\mathcal{T})$ curve. (i) Full lines—uniform depletion approximation for σ_i and σ_x ; (ii) dot-dash line—lattice approximation for σ_i and σ_x ; (iii) dashed line—lattice approximation for σ_x and $\sigma_i=1$ (Stowell 1972 b). [For $A = 1.75 \times 10^3$, curves (i) and (ii) effectively coincide.]

right-hand side of eqn. (35). At the maximum, $d(\ln \mathcal{N})/d(\ln Z) = m = 0$ and thus

$$\frac{(1 - Z_0)Z_0^{1/2}}{2} \frac{\sigma_i B_i A^{i+1}}{(\pi \Omega^2 N_0^3)^{1/2}} = \mathcal{N}^{3/2} (1 + \sigma_x A \mathcal{N})^i (Z_0 + \sigma_x A \mathcal{N}). \quad (48)$$

An equation of this form was first derived by Stowell (1972 b). However, as can be seen from the present derivation, this equation contains no approximations, other than the 'steady-state' approximation for n_1 , which is certainly well satisfied. To use eqn. (48) it is easier to use the expressions given in § 4 for σ_i and σ_x than to go through the detailed numerical comparison with computations used by Stowell (1972 b) and a restriction to $\sigma_x = \text{constant}$ is unnecessary; as the present derivation shows, this equation does not depend on a comparison with the computation or on σ_x being constant. All that is needed to supplement eqn. (48) is the value of Z_0 at the maximum in \mathcal{N} : this can be obtained as in the last section. However, $\mathcal{N}(Z_0)$ depends very weakly on the assumed value of Z_0 . Thus, even though Z_0 may vary between 0.06 and 0.30 for different extreme models of σ_x and σ_i , use of a mean value (say $\simeq 0.20$) will change the predicted values of $\mathcal{N}(Z_0)$ by a small amount only. Thus eqn. (48) is a very convenient way of analysing experimental data.

5.4. Mobile Clusters

It is clear that including cluster mobility must introduce considerable complexity and uncertainty into the description of the nucleation process. Nonetheless, recent experiments (Masson, Métois and Kern 1971) have shown that even large clusters of gold on alkali halides are mobile, and we believe that the Au/alkali halide nucleation experiments analysed in § 6 and other experiments cannot be understood without including the effects of mobile clusters. So how do we proceed?

First, it is clear that mobile clusters will only be noticeable if they are sufficiently mobile to limit the number of clusters before coalescence sets in. Thus cluster mobility will make itself obvious by a maximum (or saturation) of the cluster density at very small coverages and times. Second, the two limiting cases considered in eqns. (8 b) and (c) will produce curves of $n_x(t)$ which are quite different. If all clusters are mobile (eqn. (8 a)), then the $n_x(t)$ curve will have a maximum at a reduced coverage Z_1 , but will otherwise be similar to the coalescence case, since $U_m \sim n_x^2$. On the other hand, if only small clusters are mobile (eqn. (8 c)), $n_x(t)$ will become constant after a short time and remain so until limited (much later) by coalescence, because $U_m \sim n_x$ in this case.

Unless we know something about the diffusion coefficients of different sizes of clusters it is difficult to say more; however even much more detailed models of cluster diffusion may well fall into one of these extreme cases. For example, in the model used by Lewis (1970 b) in which the velocity of a k -cluster was taken to be $\sim k^{-5/3}$ only the small clusters are

'effectively' mobile, and a saturation rather than a maximum in $n_x(t)$ was predicted. Masson, Métois and Kern (1971), however, measured much larger diffusion constants for large clusters than predicted by a model such as Lewis's, and in their case it seems likely that all stable clusters are 'effectively' mobile, at least initially. This means that we may obtain a feel for the problem by working through the implications of these two extreme cases.

If all clusters are mobile, the expression for U_m (eqn. (8 b)) can easily be incorporated in the eqn. (35) for $\mathcal{N}(Z)$. In this case, mobile clusters can be characterized by the single parameter $(N_0^2 D_x/R)$ and the mobile cluster term in (35) is $-\sigma_{xx}(N_0^2 D_x/R) \cdot \mathcal{N}^2$. The capture number σ_{xx} must be very similar to σ_x in the limit of complete condensation; this is discussed further in the next section.

In the case where only small clusters are mobile the situation is a little more complex, since we do not know how many such clusters there are. A simple steady-state argument (Appendix B) indicates that in this case $U_m \simeq \sigma_{mx} \cdot D_{(i+1)} n_i n_x$, where n_i is the number of critical clusters and $D_{(i+1)}$ is the diffusion coefficient of the first supercritical cluster. The modification of the nucleation rate $U_i = \sigma_i D n_1 n_i$ due to small mobile clusters can then be written as $U_i(1 - U_m/U_i)$ where

$$U_m/U_i \simeq \sigma_{mx} \cdot D_{(i+1)} \cdot n_x / (\sigma_i D n_1).$$

Inserting the steady state expression for n_1 leads to the simple formula

$$U_m/U_i \simeq (N_0^2 D_m/R) \cdot \sigma_{mx} \mathcal{N} (1 + \sigma_x A \mathcal{N}) / (\sigma_i A). \quad (49)$$

Thus this form of U_m can also be incorporated into the nucleation eqn. (35) using only the same new parameter $(N_0^2 D_m/R)$, where $D_m = D_{(i+1)}$. Again σ_{mx} must be very similar to the complete condensation limit for σ_x , and is discussed further in § 5.5.

An expression for the maximum (or saturation) cluster density can be obtained by extending the argument leading to eqn. (48). Since, with cluster mobility, the nucleation rate $U_i \rightarrow U_i(1 - U_m/U_i)$, the corresponding expression for $\mathcal{N}(Z_1)$ has the form

$$A_1(Z_1) \cdot (1 - U_m/U_i) = A_2(Z_1), \quad (50)$$

where $A_1(Z_1)$ and $A_2(Z_1)$ are the left and right hand sides of eqn. (48) evaluated for the reduced coverage, Z_1 . The problem is, what is the value of Z_1 ? Although we have been unable to give an analytical form for Z_1 , the approximate argument given in Appendix C and many direct integrations of eqn. (35) containing a mobile cluster term have shown that, to a good approximation

$$Z_1/Z_0 \simeq (1 - U_m/U_i) / (1 - C U_m/U_i), \quad (51)$$

where the constant C is in the range $1/3$ to $\frac{1}{2}$. With this approximation, eqn. (50) can be conveniently used to analyse maximum cluster density data even with mobile cluster effects present.

When clusters are highly mobile, $(Z_1/Z_0) \rightarrow 0$ and the maximum in the cluster density is simply given by $(1 - U_m/U_i) = 0$. If all clusters are mobile, this can be expressed as

$$\sigma_i B_i A^{i+1} (R/N_0^2 D_x) \simeq \sigma_{xx} \mathcal{N}^2 (1 + \sigma_x A \mathcal{N})^{i+1}. \quad (52)$$

Thus, for incomplete condensation,

$$\mathcal{N}(Z_1) \simeq (\sigma_i C_i / \sigma_{xx} \delta_x)^{1/2} (R/N_0 \nu)^{(i+1)/2} \exp \left\{ \frac{\beta}{2} ((i+1)E_a + E_i + E_x - E_d) \right\}, \quad (53 a)$$

where D_x has been expressed in the form of eqn. (13 c). In the complete condensation case

$$\begin{aligned} \mathcal{N}(Z_1) &\simeq (\sigma_i C_i / (\sigma_x^{i+1} \sigma_{xx} \delta_x))^{1/(i+3)} (R/N_0 \alpha \nu i)^{(i+1)/(i+3)} \\ &\times \exp \{ \beta (E_i + E_x + i E_d) / (i+3) \}. \end{aligned} \quad (53 b)$$

When only small clusters are mobile the corresponding expressions for $\mathcal{N}(Z_1)$ is

$$\sigma_i A (R/N_0^2 D_m) \simeq \sigma_{mx} \mathcal{N} (1 + \sigma_x A \mathcal{N}); \quad (54)$$

hence for incomplete condensation

$$\mathcal{N}(Z_1) \simeq (\sigma_i / \sigma_{mx} \alpha \delta_m) (R/N_0 \nu) \exp \{ \beta (E_a + E_m - E_d) \}, \quad (55 a)$$

and for complete condensation,

$$\mathcal{N}(Z_1) \simeq (\sigma_i / \sigma_x \sigma_{mx} \delta_m)^{1/2} (R/N_0 \alpha \nu)^{1/2} \exp \{ \beta E_m / 2 \}. \quad (55 b)$$

Two points stand out from the above equations. The first is, by comparison with form of $\mathcal{N}(Z_0)$ given by eqn. (40), that mobile cluster effects may finally dominate at the highest temperatures and lowest arrival rates for $i = 1$, but not for $i \geq 2$. This result means that, for $i \geq 2$, the nucleation rate is eventually so slow relative to the growth rate of stable clusters, that clusters cannot move the large distances to the nearest stable clusters to be 'effectively' mobile. However, this transition from mobile clusters back to coalescence occurs at very high temperatures and low densities. The second point is that, for $i = 1$, the form of the two eqs. (53) and (55) is essentially the same. Writing E_x and δ_x for the large cluster parameters, and inserting $E_x = 2E_m - E_d$, and $\sigma_{xx} \delta_x = (\alpha \sigma_{mx} \delta_m)^2 / \sigma_i$, in eqns. (53) reproduces eqn. (55), since $C_1 = 1$. Thus unless one knows the values of E_x or E_m *a priori*, analysis of maximum cluster density data alone cannot distinguish between these two possibilities; the meaning of the parameters extracted from the data will, of course, depend on which possibility has been assumed. As mentioned earlier, the form of $n_x(t)$ is quite different for the two different extreme cases and this can be used to distinguish whether all clusters, or only small clusters, are mobile.

5.5. Cluster-Cluster Correlations

In § 4 it was shown that the diffusion of single atoms to stable clusters leads to a diffusion zone which depleted the single atom concentration $n_1(\mathbf{r}, t)$ in the neighbourhood of a cluster. Consequently, we would expect the local nucleation rate to be reduced correspondingly, i.e.

$$\dot{n}_x(\mathbf{r}, t)/\dot{n}_x(\text{average}) = [n_1(\mathbf{r}, t)/n_1(\text{average})]^{i+1}. \quad (56)$$

Since both the average values of n_1 and \dot{n}_x are given by the rate equations, (56) can be written

$$n_x(\mathbf{r}, t)/n_x(\text{av}) = g(\mathbf{r}, t) = (n_x(t))^{-1} \int_0^t \{f(\mathbf{r}, t')\}^{i+1} \dot{n}_x(t') dt', \quad (57)$$

where $g(\mathbf{r}, t)$ is the cluster-cluster correlation function and $f(\mathbf{r}, t')$ is the single-cluster correlation function equal, according to the uniform depletion approximation, to $\{1 - K_0[(\sqrt{r^2}/D\tau)]/K_0[(\sqrt{r_x^2}/D\tau)]\}$. The function $g(\mathbf{r}, t)$ is, therefore, a weighted average of the $(i+1)$ th power of the function $f(\mathbf{r}, t')$. For example, if $\dot{n}_x(t')$ is constant, as it is in the incomplete condensation case, and if $f(\mathbf{r}, t')$ were also time independent, then g would be f^{i+1} identically. This means, since f is small within $\sim \sqrt{(D\tau_a)}$ outside r_x , that nucleation is effectively suppressed within this zone, but is otherwise random (see fig. 4 (a) for details).

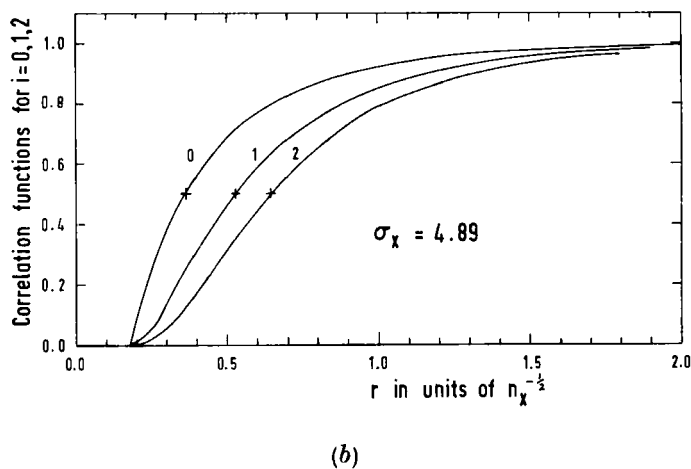
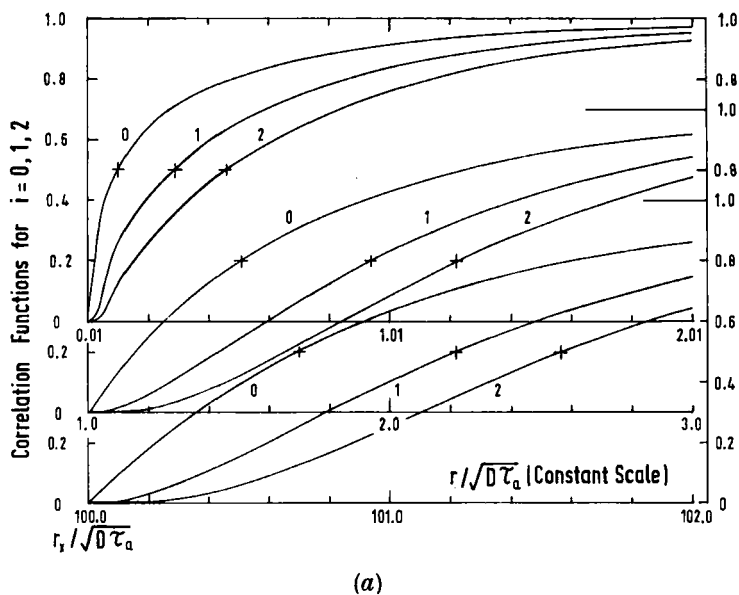
For complete condensation, where \dot{n}_x decreases with increasing time, the average contained in g will be more weighted towards the beginning of nucleation. Certainly, a calculation estimated on the basis of the final values of the nucleation rate and $f(\mathbf{r}, t')$ will underestimate the correlation. Let us, however, ignore this and, therefore, estimate $g(\mathbf{r}, t) \simeq f(\mathbf{r}, t)^{i+1}$. Then, since $\tau^{-1} = \sigma_x D n_x$

$$f(\mathbf{r}, t) = \{1 - K_c[(\sqrt{\sigma_x n_x r^2})]/K_0[(\sqrt{\sigma_x n_x r_x^2})]\}.$$

It is natural to express r^2 in units of n_x^{-1} , since then $r=1$ is of the order of the distance to the nearest cluster. Also $Z = \pi n_x r_x^2$ and, therefore, $\sigma_x n_x r_x^2$ can be given an explicit value at a given coverage. A comparison of the cluster-cluster correlation functions is shown in fig. 4 for both incomplete and complete condensation. In the complete condensation case the extent of the diffusion zone is underestimated, and if sufficiently good experimental data were available, it would be worth improving on this estimate by integrating eqn. (57) using the known function $\dot{n}_x(t')$ and the known time dependence of r_x contained in $f(\mathbf{r}, t')$.

The correlation function $f(\mathbf{r}, t')$, shown in fig. 4, has been calculated for the uniform depletion approximation. A similar function will exist for the lattice approximation but will depend somewhat on how the lattice is arranged. In general, however, this approximation to the correlation function will rise faster at small \mathbf{r} than shown in fig. 4 (b) and will dip below the curves shown at distances between clusters in the lattice. Given sufficient patience $f(\mathbf{r}, t')$, σ_x and $g(\mathbf{r}, t)$ could be calculated self-consistently from either approximation as a starting point. The result

Fig. 4



Correlation functions $\{f(\mathbf{r}, t)\}^{i+1}$ for $i=0, 1$ and 2 , in the uniform depletion approximation. (a) *Incomplete condensation*—the horizontal scale is the same in all cases, r in units of $\sqrt{(D\tau_a)}$. The vertical scale is displaced to show three cases; for $r_x/\sqrt{(D\tau_a)}=0.01, 1$ and 100 . Note that the value of $(r-r_x)$ for which $f=0.5$ is very weakly dependent on r_x , being $0.1, 0.5$ and 0.7 for the three cases shown; (b) *complete condensation*—the horizontal scale r is in units of $n_x^{-1/2}$, and σ_x was calculated self consistently using eqn. (21) with τ given by eqn. (20 a).

for all these quantities would, however, necessarily fall between that calculated using the uniform depletion and lattice approximations described in § 4.

If clusters are mobile, similar effects will be observed. As cluster mobility will only be identifiable when the diffusion zone due to cluster mobility is larger than the diffusion zone of single atoms, we can safely assume the single population to be uniform. The equivalent equation to (19), for small clusters mobile, is then

$$D_m \nabla^2 n_m - n_m (\sigma_{mx} D_m n_x) + G = \partial n_m / \partial t, \quad . \quad . \quad . \quad (58)$$

where G is the nucleation rate of stable, but mobile clusters; thus $G \equiv R_1$ and $\sigma_{mx} D_m n_x \equiv \tau^{-1}$ and the uniform depletion approximation solution is, by analogy with (21),

$$n_m(\mathbf{r}, t) = \frac{G}{\sigma_{mx} D_m n_x} (1 - K_0[(\sqrt{\sigma_{mx} n_x} r^2)] / K_0[(\sqrt{\sigma_{mx} n_x} (r_x + r_m)^2)]), \quad (59)$$

if the concentration of mobile clusters is taken to be zero at $r = (r_x + r_m)^\dagger$. If all clusters are mobile the equation will be the same as (58) and $n_x(\mathbf{r}, t)$ will be zero at $r = 2r_x$. From these equations, expressions analogous to (21) can be worked out for σ_{mx} and σ_{xx} , and these can be used in conjunction with the formulae derived in the last section. Equation (58) shows that σ_{mx} and σ_{xx} will be very similar to the complete condensation limit for σ_x , as implied in the last section. Because of the finite size of the moving clusters we will have $\sigma_{xx} > \sigma_{mx} > \sigma_x$, and the small numerical differences between these three quantities can be taken into account by replacing r_x by $(r_x + r_m)$ or $2r_x$ in eqn. (59).

The main point of this section is not to give final and undisputed values for these correlation functions which will not require any revision. We merely wish to show that, given the diffusion equation which determines the capture numbers, the same equation enables the spatial distribution of clusters to be deduced. Moreover this correlation function can be measured experimentally in a very straightforward manner, simply by determining the coordinates of the centres of observed clusters and asking a computer to determine the radial distribution function $g(\mathbf{r}, t)$. This function contains, via eqn. (57) and its approximate solutions, extra information about the nucleation process. For example, reference to fig. 4 shows that careful measurements ought to make an independent determination of the value of i possible.

A second point of this section is to note that coalescence terms in the rate equation should depend on the function $g(\mathbf{r}, t)$. Because of the diffusion zone, there should be fewer coalescences initially than estimated on the basis of random nucleation. However, the only case where this

[†] This depends on the clusters coalescing when they meet. Some recent observations (Métois, Gauch, Masson and Kern 1972) suggest that this is not always the case.

should be important is in the complete condensation case, and, although the value of Z_0 may be underestimated, the corresponding value of n_x is hardly affected, since this varies as $\{Z_0(1-Z_0)^2\}^{1/(2i+5)}$. Hence it does not seem worth while at present to incorporate this iteratively in the formulation.

5.6. Cluster Size Distributions

So far in this paper we have described the nucleation and early stages of growth in terms of the quantities n_1 , n_x and Z , and little mention has been made of the numbers, n_k , of k -sized clusters which go to make up n_x . To get reliable expressions for n_k , and hence the size distribution, is, in fact, much more difficult, especially if coalescence and cluster mobility are considered. Nevertheless, one can formulate the problem using the expressions for σ_k derived in § 4, as explored in this section.

First, let us exclude coalescence and cluster mobility. Then the rate equation for k -sized clusters in $\dot{n}_k = U_{k-1} - U_k$, where U_k describes the conversion of k 's into $(k+1)$'s, and is equal to n_k multiplied by a growth rate term. Since the clusters are large the U_k must also include direct impingement. The growth rate term, ω_k , is similar to eqn. (11), namely

$$\omega_k = \sigma_k D n_1 + R a_k. \quad . \quad . \quad . \quad . \quad . \quad (60)$$

Now, if we sum up the rate equations for the stable clusters up to and including size k , the U_{k-1} 's cancel out in pairs. Since the nucleation rate \dot{n}_x is equal to the first term U_i , this sum can be written

$$\sum_{j=i+1}^k \dot{n}_j = \dot{n}_x - U_k = \dot{n}_x - n_k \cdot \omega_k. \quad . \quad . \quad . \quad . \quad (61)$$

The form of eqn. (61) is such that, except for the equations describing the largest clusters there will be almost steady-state conditions, where the two terms on the right-hand side of (61) are nearly balanced and the left-hand side is zero, or at worst a small perturbation. This is essentially the same condition as applies to n_1 for $t > \tau$ (eqn. (31)). Thus within the steady-state approximation $n_k = \dot{n}_x / \omega_k$.

The use of n_k as a size distribution is, however, not very convenient for comparison with experimental results. Let us define a general measure of size, s , and the size distribution function $\rho(s, t)$ such that $\rho(s, t) ds$ is the density of clusters in the size range ds at s after time t . Then by entirely analogous argument to that given above

$$\int_{s(i+1)}^s \frac{\partial \rho}{\partial t}(s', t) ds' = \dot{n}_x - \rho(s, t) \cdot \frac{ds}{dt}, \quad . \quad . \quad . \quad . \quad (62)$$

where $s(i+1)$ is the size of an $(i+1)$ cluster and where again, the first term is a perturbation. As an example, we use eqn. (62) to estimate the distribution of cluster areas, a_k , in terms of the coverage $Z_k = n_x a_k$. From eqn. (62), $\rho(a_k, t) \simeq \dot{n}_x / \dot{a}_k$, and by using $\omega_k = (2/3\sqrt{\pi}\Omega) a_k^{3/2}$ in eqn. (60), one obtains

$$\rho(a_k, t) \simeq \sqrt{\pi}\Omega \dot{n}_x / \{\sigma_k D n_1 / a_k^{1/2} + R a_k^{1/2}\}.$$

By using the first term of eqn. (33) for \dot{n}_x , and the steady-state eqn. (32) for n_1 , this distribution can be written as $\rho(Z_k, Z)$, given by

$$\frac{1}{n_x^2} \cdot \rho(Z_k, Z) d(Z_k/Z) = \frac{m}{(1-m/3)} \cdot \frac{(1+a) \cdot d(Z_k/Z)}{\{(\sigma_k/\sigma_x)/(Z_k/Z)^{1/2} + a(Z_k/Z)^{1/2}\}}, \quad (63)$$

where $m = d(\ln n_x)/d(\ln Z)$ and the single material parameter, a , is

$$a = \frac{Z}{(1-Z)} \cdot \frac{(1 + \sigma_x D \tau_a n_x)}{\sigma_x D \tau_a n_x}. \quad (64)$$

Equation (63) can be used to estimate the size distribution in the early stages of nucleation in conjunction with an integration of eqns. (35) and (36), using the expressions for σ_k discussed in § 4. Within the steady-state approximation the maximum size of cluster has $Z_k = Z_{\max}$, where

$$\int_0^{Z_{\max}/Z} \rho(Z_k, Z) d(Z_k/Z) = n_x^2/Z.$$

However, in an accurate calculation, while this integral must be the same, the high Z_k end of the distribution cannot be infinitely sharp. This feature of a realistic calculation is exhibited by the computations of Robertson and Pound (1972) but not by the calculations of Zinsmeister (1971). In neither case have particularly accurate values for the capture numbers σ_k been used.

The qualitative behaviour of eqn. (63) can be easily seen. In the complete condensation regime the parameter $a = Z/(1-Z)$, and therefore at low coverage the first term in curly brackets is dominant. Using either approximation for σ_k , $(\sigma_k/\sigma_x) = (Z_k/Z)^n$ with n in the range 0.17–0.34, increasing slowly with Z , as shown in fig. 2(b). Thus $\rho(Z_k, Z) \sim (Z_k/Z)^{1/2-n}$, i.e. between the 1/3rd and 1/6th power of Z_k . This means that although larger clusters are favoured, the distribution of cluster areas is rather flat, much flatter than if σ_k were constant.

At higher temperatures, in the intermediate regime where

$$Z < \sigma_x D \tau_a n_x < 1,$$

the parameter, a , is still small but the Z_k dependence of σ_k increases slowly: so the area distribution becomes even flatter at higher temperatures. At the highest temperatures, where $Z > \sigma_x D \tau_a n_x$, the parameter a is large and the second term in curly brackets in (63) is dominant; (σ_k/σ_x) is equal to $(Z_k/Z)^{1/2}$ in this limit (see the discussion following eqn. (17)) so the first term is just one. In this case, $\rho(Z_k, Z) \sim (1+a \cdot (Z_k/Z)^{1/2})^{-1}$, and the cluster area distribution is broad with the smallest area most probable, though weakly so.

These distributions can, of course, be expressed in terms of the cluster radii, r_k . The low temperature distribution is then $\rho(r_k, Z) \sim (r_k/r_x)^{2-2n}$, i.e. a power dependence between 1.66 and 1.32; in the high temperature limit all radii are equally likely.

If coalescence and cluster mobility are included then the problem is, of course, much more complex, though Vincent (1971) and Robertson and Pound (1972) have hinted that there may be general asymptotic size distributions derivable from quasi-hydrodynamic arguments. Within the present framework, some progress could be made by incorporating terms derived from eqns. (7 *a*) and (8 *a*) into the rate equation for k -clusters. For both types of effect, n_k increases due to l and $(k-l)$ clusters meeting, and decreases by k -clusters meeting any other stable cluster. The term which increases n_k is, for low substrate coverages, and if the clusters are randomly arranged,

$$U_+ = \sum_i n_{k-i} \left\{ \frac{d}{dt} (\pi(r_k + r_{k-i})^2) + \sigma_{k, k-i} (D_k + D_{k-i}) \right\},$$

where $i < l < k-i$, and the term which decreases n_k is

$$U_- = \sum_l n_k \left\{ \frac{d}{dt} (\pi(r_k + r_l)^2) + \sigma_{kl} (D_k + D_l) \right\},$$

where $l > i$ and where the term in U_- corresponding to $l=k$ is multiplied by two. If the clusters are not randomly distributed, the correlation functions, g , should be incorporated into the coalescence terms, which also require corrections at large coverage.

Thus the rate equation for n_k is

$$\dot{n}_k = U_{k-1} - U_k + U_+ - U_-.$$

This set of equations is, of course, rather intractable except numerically. Even numerical treatments would certainly need clusters to be lumped into rather broad size categories, as has been done by Robertson and Pound (1972). Qualitatively, it may not be so difficult to see what happens. In the coalescence case the clusters which coalesce will tend to be somewhat above average in size. Thus sizes above average will become depleted, and a peak at roughly twice this size will grow. The distribution will therefore probably be bi-modal, since the small size peak will be fed by new nucleation. Since Vincent's (1971) calculations did not include new nucleation, his distribution is uni-modal. If mobile cluster effects predominate, the distribution will almost certainly be uni-modal. This will be especially so if small clusters move faster than large ones, for then new nucleation is completely suppressed. The width of the distribution obtained will depend on the size dependence of the σ_{kl} and on the parameter α . If σ_{kl} is approximately constant and α is small, the size distribution will be narrow, and vice versa.

Unfortunately, it is difficult to be much more precise using this formulation without detailed numerical computation. In particular, the steady-state approximation is useless with coalescence or mobile clusters included, because \dot{n}_x can easily be zero or negative, and because the terms U_+ and U_- , when incorporated into eqn. (61) do not lead to any real simplifications.

§ 6. AN EXPERIMENTAL EXAMPLE—THE GOLD/ALKALI HALIDE SYSTEMS

Recently, Robinson and Robins (1970) have studied the Au/KCl and Au/NaF systems, and Schmeisser and Harsdorff (1970) have studied the Au/NaCl system in considerable detail, under U.H.V. conditions. Even more recently Donohoe and Robins (1972) have studied the Au/NaCl, Ag/KCl, Ag/KBr and Ag/NaCl systems, but these results will not be discussed in detail.

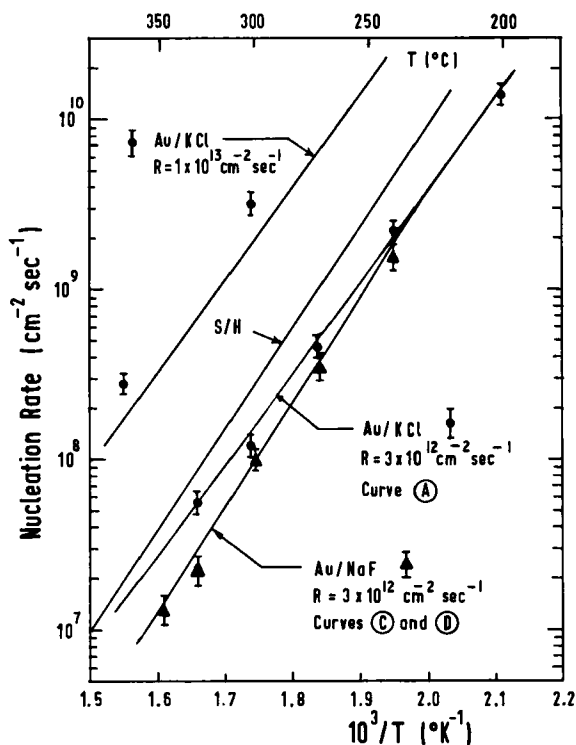
All sets of authors measured the nucleation rate as a function of the arrival rate, R , and substrate temperature, T . In all cases where the nucleation rate was small enough to be measurable they found it to be proportional to R^2 . This is unequivocal evidence that $i=1$, up to the highest temperatures. Robinson and Robins (1970) also measured the maximum cluster density as a function of temperature T , for a fixed value of R and as a function of R for a few values of T . Donohoe and Robins (1972) have also determined the full $n_x(t)$ curve in many cases, and have thereby extracted the time to the maximum as a function of temperature. These authors and Schmeisser and Harsdorff (1972), have also started to study size distributions and spatial correlations of clusters.

In this section an analysis of the nucleation rate and maximum density data of Robinson and Robins (1970) is given using the equations and approximations developed in the previous sections. This was done, firstly, to extract parameter values from Robinson and Robins' data and, secondly, to compare the parameters and curves obtained by using different approximations in the theory.

To perform the analysis two programmes were written for a small computer (PDP8/E). The first solved eqn. (50) for the maximum cluster density using the approximation (51) for Z_1/Z_0 , assuming a value of Z_0 . This programme contained a subroutine for calculating σ_x , σ_1 and σ_{xx} (or σ_{mx}) in either the lattice or the uniform depletion approximations. Alternatively the σ 's could be made constant. The clusters could be mobile or immobile, in which case eqn. (50) reduced to eqn. (48). The programme also contained a routine to evaluate the best material parameters to fit a given set of data. Two nucleation rate data points and two maximum density data points were used to determine the four unknown parameters E_a , E_d , ν and α . These nucleation rate points were chosen to be in the incomplete condensation regime and the maximum density points in the complete condensation regime. As the values of σ_x and σ_i were computed selfconsistently by the programme, this procedure produced values of E_a , E_d , ν and α which gave an arbitrarily good fit to the nucleation rate and to the low temperature region of the maximum cluster density at a given value of R . The main routine of the programme could then be used to calculate the R and T dependence of the nucleation rate and the maximum cluster density, n_x , for immobile clusters; by feeding in values of E_x and δ_x (or E_m and δ_m for only small clusters mobile) the effects of cluster mobility on the values of n_x and Z_1 could be explored.

The second programme simply integrated the coupled eqns. (35) and (36), calculating σ_i , σ_x and σ_{xx} selfconsistently as it proceeded, using the lumped material parameters A , B_i , $\Omega N_0^{3/2}$ and $(N_0^2 D_x/R)$. Although this programme took somewhat longer than the first to run, it was useful to check the approximations involved in the first programme. It was also used to evaluate the full curves of $n_x(t)$ and $t(Z)$, as shown in the example of fig. 3.

Fig. 5

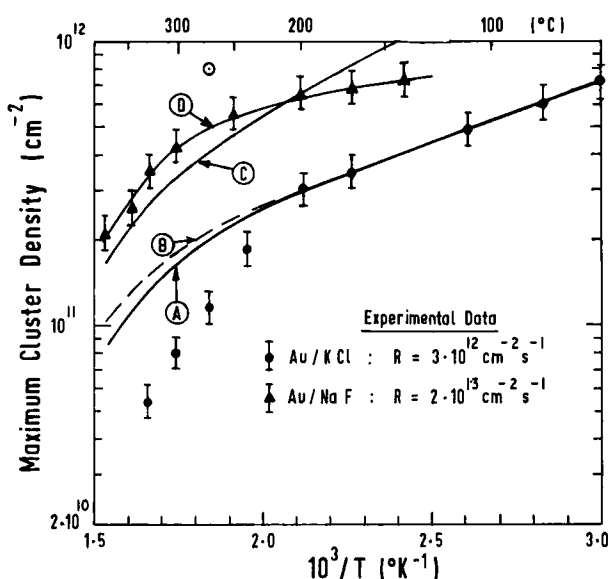


Nucleation rate for Au/KCl and Au/NaF. Data points from Robinson and Robins (1970): line marked S/H from Schmeisser and Harsdorff (1970) for Au/NaCl, $R = 1.3 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. Curves (A), (C) and (D): see caption to fig. 6 for parameter values. Note that the curves are not quite straight lines because of the slight temperature dependence of σ_i .

The results of these computations are compared with Robinson and Robins' data in figs. 5 to 8. Figure 5 shows the nucleation rate versus $1/T$ for Au/KCl and Au/NaF and fig. 6 shows the maximum cluster density versus $1/T$ assuming clusters to be immobile. The Au/KCl data were fitted for $R = 3 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$, and, using the uniform depletion approximation for σ_i , σ_x with $Z_0 = 0.21$, yielded values of $E_a = 0.689 \text{ eV}$, $E_d = 0.279 \text{ eV}$, $\nu = 1.2 \times 10^{11} \text{ Hz}$ and $\alpha = 0.15$. Using the same data

points, with the lattice approximation and $Z_0=0.11$, gave $E_a=0.681$ eV, $E_d=0.297$ eV, $\nu=0.96 \times 10^{11}$ Hz and $\alpha=0.19$. When Z_0 was changed to 0.21 E_a and E_d changed by only 10^{-3} eV and ν and α were reduced by 25% each. Use of the simplest possible approximation, $\sigma_i=1.9$, $\sigma_x=6.8$ and $Z_0=0.21$, gave values $E_a=0.681$ eV, $E_d=0.294$ eV, $\nu=1.3 \times 10^{11}$ Hz and $\alpha=0.26$. Thus, using given data points, the uncertainties in the theory give rise to uncertainties in E_a and E_d of less than 0.02 eV and determine ν and α to within a factor of two†. The curves in fig. 6 differ slightly in the high temperature regime: curve *A* is for the uniform depletion approximation and curve *B* is for σ_x and σ_i constant. The curve for the lattice approximation fell almost on top of curve *B* for both values of Z_0 assumed.

Fig. 6



Maximum cluster density versus $(1/T)$ for Au/KCl and Au/NaF. Curve (*A*)— $E_a=0.689$ eV, $E_d=0.279$ eV, $\alpha=0.15$, $\nu=1.2 \times 10^{11}$ Hz, σ_i and σ_x given by the uniform depletion approximation for $Z_0=0.21$. Curve (*B*)— $E_a=0.681$ eV, $E_d=0.294$ eV, $\alpha=0.26$, $\nu=1.3 \times 10^{11}$ Hz, $\sigma_i=1.9$, $\sigma_x=6.8$, $Z_0=0.21$. Curve (*C*)— $E_a=0.811$ eV, $E_d=0.385$ eV, $\alpha=0.15$, $\nu=1.6 \times 10^{12}$ Hz. Uniform depletion approximation, $Z_0=0.21$. Curve (*D*)— $E_a=0.698$ eV, $E_d=0.120$ eV, $\alpha=0.004$, $\nu=1.2 \times 10^{11}$ Hz. Uniform depletion approximation, $Z_0=0.21$.

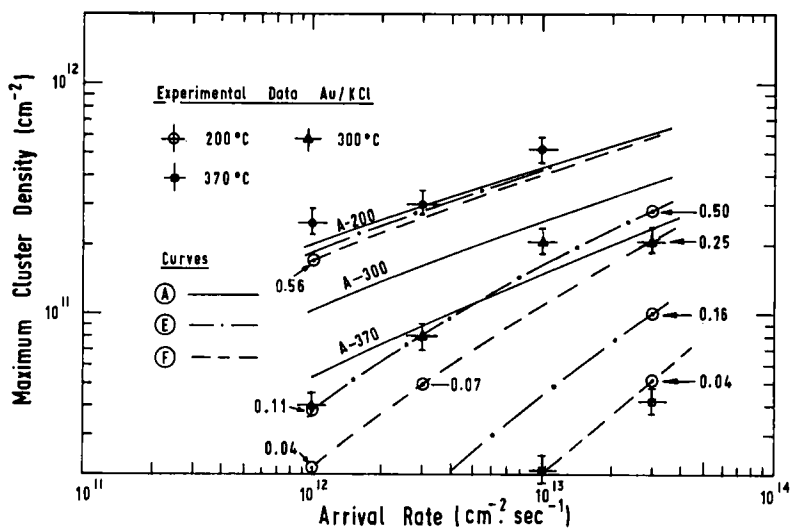
† All these calculations used $\Omega N_0^{3/2}=0.193$ which assumes that there are two adsorption sites per unit cell of (100) KCl for the diffusing Au atoms. These atoms could occupy four such sites on the grounds of atomic size and must do so when incorporated into epitaxial crystals. In this case $\Omega N_0^{3/2}=0.545$; the value of α is then doubled, while leaving the form of the curves and the values of E_a , E_d and ν unchanged.

Perhaps not surprisingly, the parameter values obtained by using data points at the limits given by experimental error in fig. 6 have a larger spread: for example, using the same points for the nucleation rate and maximum and minimum permissible slopes for the cluster density versus $1/T$ at low temperatures gives $0.65 < E_a < 0.74$ eV, $0.23 < E_d < 0.42$ eV, $0.6 \times 10^{11} < \nu < 10^{12}$ Hz and $0.11 < \alpha < 2.0$ for the Au/KCl data. This means that E_a is fairly well determined by the data, E_d less so, and that ν and α may vary considerably because the expression for the maximum cluster density contains these variables raised to a low power. The inter-relations are such that high values of all the parameters go together. It is interesting to note that a gold atom sitting in a sinusoidal well of amplitude E_d on a perfect (100) KCl surface would vibrate 'classically' at a frequency of 6×10^{11} Hz, and that the range of α spans the expected value of 0.25; thus, given that these parameters are not very well determined, the agreement is satisfactory. The above examples also show that either approximation for σ_i and σ_x , and any 'reasonable' value of Z_0 can be used to analyse even such (extremely good) data, as the spread of parameter values introduced by uncertainties in the approximations is much less than the spread introduced by uncertainties in the data.

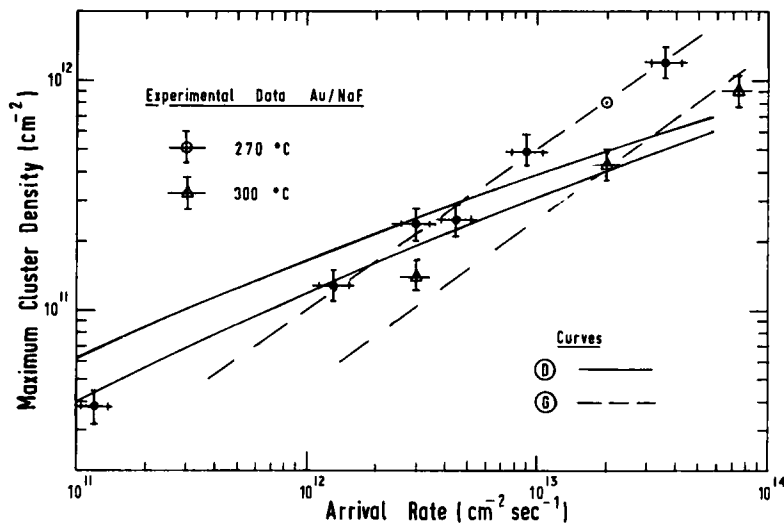
Figure 6 also shows two attempts to fit the Au/NaF data using the same approach, but the result is not quite so satisfying. If the low-temperature maximum cluster density points are assumed to be correct (curve *D*), unrealistically low values of α are obtained (≈ 0.004). If we allow the curve to be steeper at low temperatures (curve *C*) the parameters are more reasonable: in this case, $E_a = 0.81$ eV, $E_d = 0.385$ eV, $\nu = 1.6 \times 10^{12}$ Hz and $\alpha = 0.152$, using the uniform depletion approximation. However, some doubt must be felt about this procedure. In particular, attention is drawn to the circled point for 270°C, which was obtained by interpolating the rate dependence data of fig. 7 (*b*). This point rather suggests that the data at lower temperatures are rather doubtful, and that the points should be much higher, which is conceivable since densities of $\gtrsim 10^{12}$ cm $^{-2}$ are extremely difficult to measure. Alternatively the interpolation could be carried out by transferring curve (*D*) in fig. 6 onto fig. 7 (*b*). This might be a more reasonable procedure, but the difficulty with the low value of α remains.

Despite the good agreement that can be obtained for the Au/KCl data at low temperatures with this simple picture, the agreement at high temperatures is not so satisfying. First, it is apparent from the published micrographs that the coverage at which the maximum density occurs is considerably less than that needed for substantial coalescence to occur ($Z_0 \approx 0.1-0.2$). Second, the experimental transition in this maximum cluster at $490 \pm 10^\circ\text{K}$ for KCl is much sharper than the complete-incomplete transition. Third, as is shown in fig. 7, it is not possible to explain the measured rate dependences of the maximum cluster density at the higher temperatures on this model, as the experiments again have a sharper transition than given by eqn. (48).

Fig. 7



(a)



(b)

Maximum cluster density versus rate of arrival R , for (a) Au/KCl and (b) Au/NaF. Curves (A) and (D)—as for fig. 6, clusters immobile. Curves (E) and (F)—as for curve (A) but with all clusters mobile. The numbers adjoining the circled points give the value of Z_1/Z_0 . (E)— $E_x = 12\,000^\circ\text{K}$ (i.e. 1.03 eV), $\delta_x = 0.05$. (F)— $E_x = 14\,000^\circ\text{K}$ (i.e. 1.21 eV), $\delta_x = 10$. Curves (G) have a similar rate dependence as (E) and (F), and the circled point on (b) has also been plotted on fig. 6.

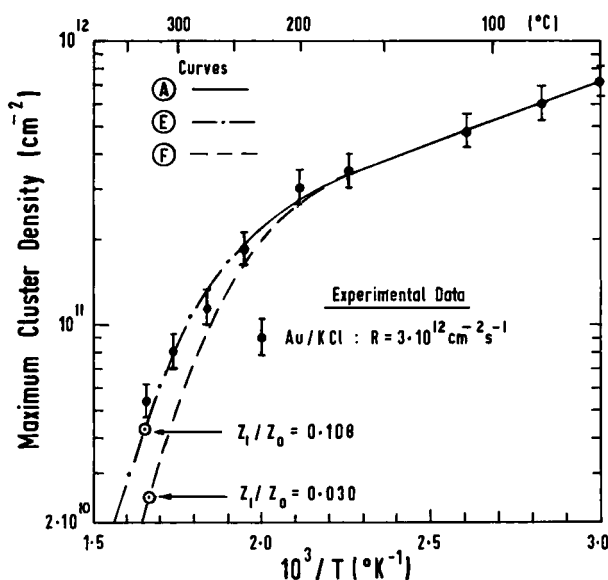
These discrepancies have led us to consider mobile clusters as the cause. This explanation has been substantiated in Donohoe and Robins' recent work because they observed that the time to reach the maximum cluster density *decreased* with increasing temperature rather than increased, as would be expected for the immobile cluster case (see fig. 3 (a) and eqn. (41)). The fact that they also observed a maximum cluster density rather than a saturation implies (§ 5.4) that effectively all clusters are mobile rather than just the small ones. Robinson and Robins' data has therefore been analysed assuming all clusters to be mobile. As can be seen from figs. 7 and 8 the dependence of the maximum cluster density on R and T can be fitted reasonably well by pairs of parameters E_x , δ_x which are in the range 1–1.2 eV and 0.05–10. Use of a different approximation for σ_i , σ_x and σ_{xx} produces essentially the same curves for values of δ_x which differ by at most a factor of 2. The calculated values of the coverage (at the maximum cluster density) agrees with the published micrographs, as well as one can establish by simple inspection. At the highest temperatures this coverage can be less than 1%. The NaF data does not encourage us greatly to look in detail for a solution involving mobile clusters, although the coverage at the maximum cluster density is clearly low as in the KCl case, and the rate dependence in the data of fig. 7 (b) is somewhat higher than that calculated ignoring cluster mobility.

As explained in § 5.4, small mobile clusters would produce similar curves for $n_x(R, T)$ with values E_m and δ_m which are related to E_x and δ_x . Values of E_m would be in the range 0.60–0.75 eV to give essentially the same curves as in figs. 7 and 8, though the predicted coverages are somewhat higher in this case. Although these curves can be satisfactorily predicted there are definitely some unsolved problems as regards cluster mobility. In particular, the cluster diffusion coefficients needed to explain the $n_x(R, T)$ curves are probably the values for epitaxial clusters and are not directly comparable with the diffusion coefficients measured by Masson *et al.* (1971). This discrepancy is examined briefly in Appendix D.

Despite the fact that the drawing of parameters out of experiments without any justification, other than that they fit the data, feels unsatisfactory, it should be emphasized that the values of the parameters obtained in the above analysis are indeed physically reasonable. First, the values of E_a , E_d and ν are similar in order of magnitude for gold on both NaF and KCl. Second, if the high temperature data were determined by *small* cluster mobility the E_m values for Au/KCl would be a few times (i.e. $2\text{--}3 \times$) E_d . If the cluster primarily responsible is the stable pair of gold atoms, it is difficult to see how E_m can be more than 2 or $3 \times E_d$, and it might have been thought to be considerably less. If the data were determined by *large* cluster mobility then E_x must be less than about $4E_d$. This being so, it is fairly clear that cluster mobility must be rather generally important in nucleation experiments, as has been emphasized by Lewis (1970). Third, for the critical nucleus size to be equal to one atom up to

the highest temperatures investigated E_2 must be high (≥ 1 eV). Gas phase experiments enable E_2 to be determined and the value for Au quoted by Zinsmeister (1966) is 2.23 eV. It is highly likely that this high binding energy is hardly altered by the presence of the much weaker binding energy E_a to the substrate. In fact it may be that condensation cannot take place at the highest temperatures because stable pairs evaporate directly into the vapour with activation energy $\sim 2E_a$ (≈ 1.4 eV). Fourth, the cluster size distribution becomes broader at high temperatures (and changes with the onset of cluster mobility) as remarked by Robinson and Robins. The discussion of § 5.6 would enable this qualitative observation to be used more quantitatively.

Fig. 8



Maximum cluster density versus $(1/T)$ for Au/KCl. Curves (E) and (F): as for fig. 7.

Finally, it is clear from this analysis that extraordinarily detailed and precise measurements are required if one is to be able both to make unambiguous statements about the mechanisms involved and to extract reasonably accurate values for the material parameters. It is hoped that in future nucleation experiments the maximum cluster density, the time and coverage at this maximum, the cluster-cluster correlation function and the cluster size distribution will all be measured in order that the theory may be more fully tested and that better parameter values may be obtained from the data.

§ 7. CONCLUSIONS

It has been shown that a good understanding of many processes occurring in the early stages of growth of crystals on a perfect substrate can be understood in terms of a simplified set of rate equations for the cluster densities as a function of time. These processes included coalescence effects and cluster mobility. Using auxiliary diffusion equations, approximations for the capture numbers (appearing in the rate equations) have been obtained which bracket the true solution. Using these capture numbers, solutions of the rate equations have been obtained and expressions are given for experimentally observable quantities including the initial nucleation rate and condensation coefficient, the maximum cluster density and the corresponding times and substrate coverages. General equations have been given to describe the maximum cluster density in transition regions, especially at the onset of incomplete condensation and of cluster mobility. Particular attention has been drawn to the fact that expressions for the cluster-cluster correlation function and the size distribution of clusters can be discussed using this formulation, and that these quantities are readily measurable experimentally.

The equations were applied to recent experimental data on gold deposited on alkali halides. It was shown that the material parameters obtained were reasonable and that cluster mobility was required in order to understand the behaviour of the maximum cluster density and coverage at high temperatures.

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APPENDIX A

The Constants C_i

As mentioned in § 3.1, the values of the constants C_i were overestimated by Frankl and Venables (1970). This is because they used a kinetic argument which allowed for all growth modes but not all the decay modes

of small clusters. However, since we are interested in the C_i for small clusters in equilibrium with the single population, the statistical mechanical argument contained in their § 3.3 is quite sufficient.

The number of states at energy zero is as given previously, $Q_1 = N_0$. However, the number of states at energy $-E_i$ depends on the lattice geometry of the substrate and the cluster. For i -sized clusters of configuration j we may write

$$Q_i/N_0 = \sum_j C_i(j) \exp \beta E_i(j),$$

where C_i is the multiplicity (degeneracy) of orientations of clusters associated with a given substrate lattice position. All configurations j of a given sized cluster should be considered, though in most cases only the most strongly bound cluster in its ground state will be important because of the exponential weighting factor. If these less strongly bound clusters are not important, the C_i for the first seven clusters considered by Frankl and Venables (1970) are as follows: $C_1=1$, $C_2=3$, $C_3=2$, $C_4=3$, $C_5=6$, $C_6=6$ and $C_7=1$.

All these numbers are of order of magnitude unity, and the most symmetrical clusters have the lowest values of C_i . In general, however, the equilibrium relation used in the eqn. (5) should be of the form

$$(n_i/N_0) = (n_1/N_0)^i \sum_j C_i(j) \exp \beta E_i(j),$$

so that the C_i in (5) is $\simeq C_i$ (ground state) but increases slowly with increasing temperature.

APPENDIX B

U_m for Small Mobile Clusters

The term U_m can be written

$$U_m = \sum_k \sigma_{kx} D_k n_x n_x$$

when small k -sized clusters are mobile. For immobile small clusters of size $k > i$ we can write

$$dn_k/dt = \sigma_{k-1} D_{k-1} n_{k-1} - \sigma_k D_k n_k, \quad . \quad . \quad . \quad (B\ 1)$$

since the clusters do not decay and direct impingement is not important. Except for very short times the population n_k will be in steady state with the two terms on the right-hand side of (B 1) balanced. Since $\sigma_k \simeq \sigma_{k-1}$ this means $n_k \simeq n_{k-1}$ and by iteration $n_k \simeq n_{k-1} \dots \simeq n_i$. Thus if the values of D_k decrease fairly quickly with increasing size k , and if this steady state is not altered drastically by cluster mobility, then U_m can be written as $U_m \simeq \text{const.} \sigma_{mx} D_{(i+1)} n_i n_x$. The constant may be incorporated into the factor δ_m contained in $D_{(i+1)}$, giving $U_m \simeq \sigma_{mx} D_{(i+1)} n_i n_x$, as in the text of § 5.4.

APPENDIX C

The Value of Z_1 in the Mobile Cluster Case

The following argument is intended to show that eqn. (51) is a reasonable approximation.

In any of the well-defined regimes of condensation (§ 5.2.2), eqn. (30) for $\mathcal{N}(Z)$ can be reasonably approximated, over a large range of Z , by

$$d\mathcal{N}/dZ = bZ^p\mathcal{N}^{-q}(1 - U_m/U_i) - 2\mathcal{N}, \quad \text{. . . (C 1)}$$

where b contains material parameters and p and q are indices depending on the regime considered. Equation (C 1) can be integrated analytically in the initial stages where U_m/U_i and \mathcal{N} are small. This solution is

$$\mathcal{N} = (b(1+q)/(1+p))^{1/(1+q)} \cdot Z^{(1+p)/(1+q)}. \quad \text{. . (C 2)}$$

Let us now apply this solution somewhat beyond its range of validity, i.e. to the maximum in $\mathcal{N}(Z)$. Equating the two terms on the right-hand side of (C 1) gives a value for Z at the maximum, where $d\mathcal{N}/dZ = 0$.

Without cluster mobility, $Z = Z_0$, and

$$Z_0 = (1+p)/(2(1+q)). \quad \text{. (C 3)}$$

With the cluster mobility term $(1 - U_m/U_i)$ present, the same procedure gives $Z = Z_1$, and

$$Z_1/Z_0 = (1 - U_m/U_i). \quad \text{. (C 4)}$$

Equation (C 4), however, gives consistently too low values of Z_1 when compared with direct integration of eqns. (35) and (36). A better idea can be obtained by setting

$$\mathcal{N} = AZ^\alpha(1 - BZ^\beta),$$

where A and α are given by (C 2) and BZ^β accounts for the cluster mobility. Then, by comparison with (C 1), BZ^β can be approximately replaced by $(\alpha/(\alpha+\beta))(U_m/U_i)$. The use of this form of \mathcal{N} in the second term of (C 1) gives

$$Z_1/Z_0 \simeq (1 - U_m/U_i)/(1 - \alpha U_m/(\alpha+\beta)U_i). \quad \text{. . . (C 5)}$$

If all the clusters are mobile, $U_m \sim \mathcal{N}^2$ and therefore $\beta \simeq 2\alpha$ and $\alpha/(\alpha+\beta) \simeq 1/3$. However, it is simpler to let $\alpha/(\alpha+\beta) = C$, and to determine C by comparison with a single direct integration of (35) and (36). In practice this has given values of C between $\frac{1}{3}$ and $\frac{1}{2}$ and yielded values of $\mathcal{N}(Z_1)$ accurate to better than 5% and Z_1/Z_0 values to better than 20%.

APPENDIX D

Cluster Diffusion Coefficients

At $T = 600^\circ\text{K}$ and $R = 3 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ the Au/KCl data of Robinson and Robins (1970) require a mobile cluster diffusion coefficient, D_x , in the range 4×10^{-15} to $4 \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}$ according to figs. 7 and 8. This means that the clusters moved an average of $\sim 2\sqrt{(D_x t)}$, where $t \simeq 2000 \text{ sec}$

(Robinson and Robins 1970, fig. 2) ; i.e. the root mean square distance moved is ~ 600 to 2000 \AA , which is of the order of the cluster spacing at the maximum density. On the other hand, Masson *et al.* (1971) measured diffusion coefficients in the region of 10^{-12} to $10^{-13} \text{ cm}^2 \text{ sec}^{-1}$ at temperatures between 340 and 400°K . Extrapolating their data to 600°K gives D_x in the range 10^{-7} to $10^{-8} \text{ cm}^2 \text{ sec}^{-1}$, i.e. more than five orders of magnitude greater. If their diffusion coefficients are used in the present nucleation theory the cluster density would be limited by cluster mobility at all temperatures above 250°K . This serious discrepancy seems to be explicable only on one or other of the following grounds :

1. Clusters are very mobile but have, in general, a very small chance ($\sim 10^{-5}$) of coalescing when they meet.
2. The conditions for observing very high cluster diffusion coefficients are rather specific to the experiments of Masson *et al.* (1971).

The second could be the explanation, since the clusters were first nucleated at 293°K , not in epitaxial orientation. The high diffusion coefficients were the initial values for these non-epitaxial (large) clusters, and the diffusion coefficients became effectively zero as the clusters reached epitaxial orientation. It could be that, in a nucleation experiment conducted entirely at a higher temperature, the epitaxial orientation (or in general, the orientation with a low diffusion coefficient) is reached very quickly, and that the cluster diffusion coefficient required to analyse the nucleation data has the low value characteristic of epitaxial clusters. Certainly, the clusters shown in Robinson and Robins (1970, fig. 1) are all in epitaxial orientation at all visible stages of the nucleation process at $T = 600^\circ\text{K}$.

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