Thermal Physics

Entropy and Free Energies

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Preface

Thermodynamics does not appeal to young sensitive minds for several reasons. First, there appear to be no glamorous concepts in thermodynamics; the prospect of learning about things like heat, temperature, and pressure hold little appeal. Second, there is a tendency, especially in older textbooks of general physics, to make it appear that thermodynamics is exclusively concerned with heat engines. In this day and age, no one can be expected to become very excited about heat engines. All these give many people the mistaken notion that thermodynamics is easy and trivial. This is decidedly not so. The underlying ideas are so subtle that they are hard to learn even with the proper attitude. This book attempts to make the subject more accessible and even enjoyable. This book can be used as a supplementary textbook, or preferably, even before taking the course, as an introduction. This book is also for some graduate students who wish to take a crash course in the basics of thermodynamics.

So that mathematics and quantum mechanics will not be a hindrance, I briefly review some prerequisite material on mathematics and quantum mechanics in Chapter 2. I assume that you have completed the usual series of introductory physics and are reasonably familiar with the basic ideas of modern physics such as the de Broglie wave length and the uncertainty principle of Heisenberg.

It is true that thermdynamics started as a science of heat engine, but it has a far wider application, and, when combined with basic statistical mechanics, is as interesting as any other branch of physics; thermal physics = thermodynamics + Δ statistical mechanics. As we shall see, thermal physics begins with a simple postulate. The postulate has an immediate, and al-

most obvious, consequence which introduces the idea of entropy and the second law of thermodynamics, i.e, the maximum entropy principle. For systems in contact with various types of reservoir, the entropy principle is then transformed into various minimum free energy principles. This is the essential and underlying theme of thermal physics. We will sing this theme in several different variations. —Molecules do X to maximize their entropy. Molecules do XX to minimize their free energy. Spins do Y to maximize their entropy. Spins do YY to minimize their free energy. In order to make this theme resound as clearly as possible, I will concentrate on those subjects where it is reasonably obvious how the entropy and free energy principle governs the behavior of thermal systems.

Our goal is to become comfortable with these extremum principles and ultimately to understand the meaning of the Landau-Ginzburg free energy functional which appears at the beginning of Chapter 9, but I have added more material in the remainder of Chapter 9 and through Chapter 10. This additional material (the phase separation dynamics and the renormalization group theory) is there only to give the reader an idea of how useful the free energy functional is.

This book has been written in a relaxed and informal style. It is meant to read like an informal chat or essay. I frequently employ analogies between what goes on in the thermal world and what goes on in the human world. These analogies are, however, never perfect, and should be taken only in the context in which they are presented.

Let me thank my wife Hye-Sook Lee for her support without which I would not have written this book. Our two daughters, Mi-Kyoung Lee and Sue-Kyoung Lee, graciously undertook the arduous task of checking my English. I thank Stanley Liu of World Scientific for his patient and skillful guidance during the course of writing this book. Peter Hunt and John Pojman offered several helpful suggestions. Inspite of all this help, the reader will find defects in my English composition, graphics and LaTEX skill. My incorrect English has been checked over and over again, but because I kept on revising the manuscript until the last minute, some errors are likely to remain in this final version. Needless to say, they are mine.

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October, 2001

Chapter 1

Introduction to Thermal Physics

1.1 Bird's-Eye View of Thermal Physics

To get a sense of how thermal physics works, consider a man coming to the greater Hattiesburg area for the first time. The area consists of Oak Grove, Hattiesburg, and Petal. All three sections are connected and it is difficult for a newcomer to tell which is which. This man arrives in the area from I-59 entering into Oak Grove and thinks that if he drives around a few blocks he will find his destination in no time. That is not so. He has no map and soon becomes lost. Hattiesburg has about 500 blocks, Petal and Oak Grove each about 50 blocks. He does not know where he is. He tries this block and that, turns left and then right, goes under this bridge and over that one. Twelve hours go by, but he is still wandering around. He is so overwhelmed by the charm of this city that he has forgotten why he came here in the first place. He wants to remain lost for another twelve hours, and more. Question (1): what are his chances of being in Hattiesburg after this many hours of wandering around? ANS: 500/(500+50+50)=0.83. Question (2): If he is in Hattiesburg right now, what are his chances of getting back to Oak Grove after another 12 hours, or, say, 24 hours? ANS: 50/(500+50+50)=0.083. The odds are in favor of "yes" for the first question and "no" for the second question, but not overwhelmingly.

Let us now exaggerate and suppose that Hattiesburg has a total of 10^{10} blocks while Oak Grove and Petal still have 50 blocks each. The odds are then near hundred percent for the first question and near zero for the second question. Why are the odds of his getting back to Oak Grove so overwhelmingly small? Remember that this man is lost but has no desire

to go to any particular place. From his starting position on the map, draw all the paths that he can potentially follow in 12 hours. The probability of his following any one of these paths is the same as for the others, but an overwhelmingly large number of the paths end up in Hattiesburg.

Since we gave Hattiesburg enough blocks to make it the largest city in the world, we might as well give its police department a patrol helicopter. A patrol officer has been following our traveler. The officer sees the traveler quite differently. He is not lost; he has a definite purpose. The more blocks there are for him to wander around, the more he seems to enjoy it. He arrived in Oak Grove, but he soon began moving around in Hattiesburg with so many blocks to wander around. The officer invents the term "tropy" for the number of city blocks the traveler may visit, or rather its logarithm. "The man in the brown Pontiac station wagon is in pursuit of tropy, which is why he traveled from Oak Grove to Hattiesburg. This man is after tropy and tropy alone." If there were another city in the area which offered him even more "tropy", he would move to that city in due time. His tropy therefore never decreases! If you can imagine the kind of world described by this example, you have entered the world of thermal physics.

There are $10^{10} + 50 + 50$ blocks in the area, and our traveler's location at each block constitutes the microstate of his whereabouts. If we describe him as being in Petal, we will have specified his macrostate since he can be in Petal by being in any of its 50 blocks. He started his journey from one of the two smaller macrostates; after a while it is overwhelmingly probable that he will end up in the largest macrostate. The movement is one-way. He will not go back. There are too many ways to remain lost in Hattiesburg to prevent him from returning to Oak Grove. Of course, there is nothing special about being in Hattiesburg. If we were to arbitrarily designate 50 blocks of Hattiesburg including the block in which he currently is located and give this area a new name, everything we have said about the chances of our traveler returning to Oak Grove would apply to the chances of his getting back to these 50 blocks as well.

Let us consider another analogy. Hattiesburg is not only a pleasant city to be lost in, it is also home to one of the best student symphony orchestras in the country. Indeed, they have had the privilege of performing with superstars like Yo-Yo Ma and Itzhak Perlman. Consider the repertoire that these student musicians can play, say, at two hours' notice. At the beginning of each year, their repertoire starts at zero, since they have not learned any music yet. Once they learn a piece, it remains a part of their

repertoire and they treasure it just as much as any other pieces they have learned. Suppose that their repertoire reaches 30 pieces at the end of the year. Due to various constraints such as their time and ability, this is the maximum size that their repertoire can reach. When they reach this point, the orchestra is so positioned to play any one of the 30 pieces of music. Now imagine that we give the musicians a stage and assist them so that they can play their thirty pieces of music hour after hour, day after day, repeating their entire repertoire as many times as they please. By the end of the year, these student musicians have gone through two different periods and two different states of musical adventure: the early transient period during which their repertoire kept increasing, and the final period during which they enjoyed playing what they had learned during the course of the year, without showing any preference for one piece over the others. Although the analogy of this to thermal systems is highly limited, the former depicts what a thermal system does in a non-equilibrium state, and the latter depicts what the system does while it is in an equilibrium state.

Are the atoms and molecules in the real thermal systems really lost? The answer is no. Given the initial conditions for molecules and atoms, one can in principle calculate their exact state at a later time. All thermal systems are subject to some constraints and therefore the system is limited to a certain portion of the phase space. According to what is known as Liouville's theorem, the system may start from any initial state (condition) to reach any other state, or infinite vicinity of any other state. Moreover, if we imagine putting dots in the phase space where the system has visited over a long span of time, the dots cover the allowed phase space with equal density. Thus we can assume with no harm that the system is lost in its phase space. The following is the synopsis of the book.

1.2 Synopsis

We begin with isolated thermal systems. Each system has many many microstates and these microstates may conveniently be grouped into macrostates. The fundamental postulate states that thermal systems get lost in the sea of their microstates just like the man lost in the Hattiesburg area. However, in the manner of the Hattiesburg helicopter officer, we will dignify the lost systems and say that they are in pursuit of the largest macrostate,

or that they are after entropy and entropy only. They will do whatever they can to increase their entropy, and they will continue to do so until their entropy finally reaches the maximum possible value; their entropy will therefore never decrease spontaneously. This is called the second law of thermodynamics or the maximum entropy principle. For molecular systems, entropy is a function of energy, volume and the number of molecules. Since the maximum entropy principle is the lone guiding principle, it is crucial that we know how much entropy will change if energy, volume and the number of molecules change in a certain way. Emerging for this purpose are three crucial thermodynamic variables: temperature, pressure and chemical potential. These variables direct the change that thermal systems have to make to maximize their entropy. They are to thermal systems what economic indices are to the investors on Wall Street.

When thermal systems are brought into contact with a large reservoir, the two "conspire" to maximize their combined total entropy, not their own. The system and the reservoir play different roles to achieve this "grand" goal. The system has to visit each of its microstates with frequency proportional to the Boltzmann factor; this will be called the modified postulate. This is quite different from staying "lost", but it too leads to an extremum principle. Depending on the nature of the reservoir, an appropriate kind of free energy exists which the system has to minimize. For a thermal reservoir, the appropriate free energy is called the Helmholtz free energy. It is the net entropy cost that the reservoir pays for sharing energy with the system, which is why it has to be minimized. The best example that illustrates this minimum principle is the van der Waals theory of gas-liquid phase transition.

The minimum free energy principle would be of no help if we had no idea what the free energy would be among the competing macrostates. We therefore have to make a model to estimate the free energy cost of each macrostate. We will learn how Landau performed this important task for his mean field theory and its extended version, the Landau-Ginzburg free energy functional. Getting there is our goal, but we will attempt to go further. We will see two examples which illustrate how useful the free energy model is. In one, we will put a system in an unduly high free energy state, and let the free energy minimum principle guide the molecules to reduce the free energy. In another, we will use it to study second-order phase transitions where all macrostates have to be allowed to play a role. The Landau-Ginzburg free energy model accommodates this unique situation

quite well and helps solve a puzzle which baffled physicists and chemists for nearly a century.

1.3 Notations

Several symbols are used to represent more than one variable. Although such multiple usages are never made at the same time, it may be helpful to be warned in advance.

- P represents both probability and pressure. When it represents a certain probability, it comes with the word "probability" and as a function of one or two variables, like $P(U_s)$. Although pressure is dependent on many factors, it is plainly written as P.
- t represents time except when we talk about static critical phenomena in Chap. 8 where it represents the relative distance to the critical temperature, $t = |T - T_C|/T_C$.
- m represents both molecular mass and magnetic dipole moments, but nowhere do we talk about molecular systems and spin systems at the same time.
- $\beta = 1/k_B T$ appears in all Boltzmann factors like $\exp(-\beta E_\nu)$. In Chap. 8, it represents the order parameter exponent.
- S represents entropy everywhere except briefly in Sec. 8.2 where $S(q)$ represents a structure factor. Similarly, G represents the Gibbs free energy everywhere except briefly in Sec. 8.2 where $G(r)$ represents a correlation function. C represents the heat capacity everyewhere except briefly in Sec. 4.8 where it represents the electric charge capacitance. There are a few more of this type.

Chapter 2

All You Need to Know to Read the Rest

2.1 Introduction

For some undergraduate readers who have not yet learned much mathematics and quantum mechanics, some preparation may be required before we proceed. More advanced readers may skip this chapter and proceed to Chapter 3.

2.2 Energy Eigenvalues

According to quantum mechanics, if you measure the energy of an object, the outcome can only be one of the energy eigenvalues $\{\epsilon_1, \epsilon_2, \epsilon_3, \ldots\}$. These eigenvalues are the only values of energy that the object is allowed to have by quantum mechanics. The corresponding states are called energy eigenstates. All the information about the physical properties that the object is expected to exhibit when it is in eigenstate j is contained in the energy eigenfunction $\phi_j(\vec{r})$. For example, when the object is in its 7th eigenstate, its energy is ϵ_7 and its energy eigenfunction is $\phi_7(\vec{r})$.

2.2.1 *A single Particle of Mass m*

For a particle of mass m confined to a cubic box with impenetrable walls of size $L \times L \times L = V$, the energy eigenvalues are given by

$$\epsilon_\nu = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2), \tag{2.1}$$

where n_x, n_y, and n_z can be any positive integers, including zero. The different eigenstates may be distinguished from one another with

$$\nu = \vec{n} = (n_x, n_y, n_z). \tag{2.2}$$

Consider the three eigenstates corresponding to $(n_x = 1, n_y = 0, n_z = 0)$, $(n_x = 0, n_y = 1, n_z = 0)$, and $(n_x = 0, n_y = 0, n_z = 1)$. These eigenstates are different because $\vec{n}$ is different for each, but the corresponding energies are the same. The three eigenstates are said to be degenerate. Corresponding to the energy $\epsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \times 1$, there are three degenerate states.

The index ν is only symbolic. Suppose that we arrange these eigenvalues in increasing order and label them with index i (which goes as 1, 2, 3, etc.) and make a list: $\epsilon_1, \epsilon_2, \epsilon_3, \ldots, \epsilon_\infty$. We will refer to these energies as single-particle energies. The corresponding states will simply be called single-particle states or orbitals. For the single-particle state (orbital) $i = 7$, the single-particle energy is ϵ_7.

2.2.2 *N Distinguishable Particles*

For N distinguishable, non-interacting particles confined to the same box, the energy eigenvalues are given by

$$E_\nu = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \sum_{\vec{n}_1}\sum_{\vec{n}_2}\cdots\sum_{\vec{n}_N}(n_1^2 + n_2^2 + n_3^2 + \cdots + n_N^2), \tag{2.3}$$

where $n_i^2 = n_{i,x}^2 + n_{i,y}^2 + n_{i,z}^2$ and $n_{i,x}$ refers to the x-component of $\vec{n}_i$ and can be any positive integer, including zero. The N-particle states may be indexed with

$$\nu = \{\vec{n}_1, \vec{n}_2, \vec{n}_3, \ldots,\}. \tag{2.4}$$

Clearly, the N-particle energy given by Eq. (2.3) is the sum of N single-particle energies, one for each particle. N is a very large number here, but

just as an exercise, let $N = 10$ and list the N-particle states and their corresponding N-particle energies. Observe how rapidly the degeneracy of their energy increases with increasing energy. Now let $N = 20$. How does the increase in N affect the degeneracy? What if $N = 10^{23}$? The degeneracy is truly awesome when N is this large.

2.2.3 *N Indistinguishable Particles*

If particles in a physical system are indistinguishable, quantum mechanics demands that we treat them accordingly. We cannot tag them and treat them as if they were carrying registration numbers; they cannot be distinguished from one another. If we do tag them, then we will commit the error of grossly overcounting them. It is important to understand the nature of this error so that we can find a way to correct it.

If we tag the molecules and let each $\vec{n}_i$ take on any allowed value and direction irrespective of the others, the N-particle states generated would include $A = (19, 1, 13, 12, \ldots)$ which says that the first particle is in the 19-th single-particle orbital, the second in the first orbital, the third in the 13-th orbital, and so on. Also included is $B = (1, 19, 12, 13, \ldots)$ where the first four molecules have exchanged their orbitals while all the other molecules remain in the same orbitals. If the N molecules are distinguishable, A and B are two distinct N-particle states. However, if these N molecules are indistinguishable, A and B do not constitute different N-particle states. The fact that the first four orbitals are occupied by "different" molecules is an artifact of our tagging action; the four molecules are identical molecules. We will discuss under what circumstances the overcounting error can be corrected in Chapter 3.

We will find a more sensible way to handle identical particles without tagging them in Chap. 5. The idea there is to focus on each orbital and count the occupation number and not to try to identify the specific molecules occupying that orbital.

2.3 Fluctuations

Imagine a yardstick placed at a certain spot in a lake so that we can read the water level. Record the height at a fixed time interval over a long time. The time series would look like $(y_1, y_2, y_3, \ldots, y_N)$. The average is

$$< y >= \frac{1}{N}\sum_{i=1}^{N} y_i. \tag{2.5}$$

The fluctuation is defined as

$$\delta y^2 = \frac{1}{N}\sum_{i=1}^{N} (y_i - < y >)^2. \tag{2.6}$$

By squaring the deviation from the average, we do not allow an upward deviation to cancel a downward deviation but allow both to contribute.

Expand the square and obtain

$$\delta y^2 = < y^2 > - < y >^2, \tag{2.7}$$

where

$$< y^2 >= \frac{1}{N}\sum_{i=1}^{N} y_i^2. \tag{2.8}$$

The fluctuation of the water level may be regarded as a measure of the strength of wind. Likewise, thermodynamic quantities fluctuate and their fluctuations are not merely insignificant ripples, but carry important signatures, as we will see later.

2.4 The Central Limit Theorem

The central limit theorem is a useful theorem which comes from probability theory. Suppose that you collect N samples, and each of them is a sum of something random. For example, suppose that you can only move sideways along a line and you take a step to the left or right randomly. You repeat this N times, with N being very large. Record your movements x_1, x_2, etc. and add them together to get $x = \sum_{i=1}^{N} x_i$, which gives the final position after N random movements. Suppose $N = 100$. You can guess that most of the times you will end up near $x = 0$; on some rare occasions you may get a result like $x = 80$ to the right or left, but $x = 100$ is utterly unlikely. If you plot the number of times you ended up with each value of x, the graph

should give you the probability for each value of x occurring. When such curves are appropriately normalized, it is called a distribution function.

Let

$$y = y_1 + y_2 + y_3 + y_4 + \cdots + y_N, \tag{2.9}$$

where y_i is random in magnitude, in sign, or in both, and N is large. According to the central limit theorem, the distribution function of y is given by

$$P(y) = \frac{1}{(2\pi\delta y^2)^{1/2}} e^{-(y-<y>)^2/2\delta y^2}. \tag{2.10}$$

Here δy^2 represents the fluctuation of y, i.e.,

$$\delta y^2 =< (y- < y >)^2 >=< y^2 > - < y >^2, \tag{2.11}$$

and is given by

$$\delta y^2 = \sum_{i=1}^{N} \delta y_i^2, \tag{2.12}$$

where δy_i^2 represents the fluctuation of y_i.

This theorem is powerful for two reasons. First, the Gaussian function, which is very easy to work with, follows, no matter what kind of distribution function is distributing each of the variables y_i. Second, since y is a sum of N variables, its full range should go like N, and therefore it may appear that its fluctuation should go like N^2. But it does not; according to Eq. (2.12), it goes like N. Thus the fluctuation is vastly reduced. If this is not clear, take instead of the raw sum y, the average, namely, y/N. The fluctuation of the average then goes like $N^{-1/2}$, which vanishes with increasing N. The peak of $P(y)$ becomes very narrow for large N.

2.5 Hypersphere in d-Dimensional Space

Consider the volume and the surface area of a sphere in various dimensions. Let us see how they are related to the radius r. In $d = 1$ space, the volume is equal to $2r$, and the "surface area" consists of 2 points and hence is 2.

In $d = 2$, the volume is πr^2 and the surface area is $2\pi r$. In $d = 3$, the volume is $4\pi r^3/3$, and the surface area is $4\pi r^2$. If we extrapolate this to dimensions $d > 3$, the surface area of a hypersphere of radius r is

$$A_d(r) = \frac{2\pi^{d/2} r^{d-1}}{\left(\frac{d}{2} - 1\right)!}. \tag{2.13}$$

For a derivation, see the book by Schroeder.

2.6 A Few Mathematical Identities

(1) Stirling's Approximation.
When N is very large, $N!$ may be approximated with

$$N! = \left(\frac{N}{e}\right)^N, \tag{2.14}$$

and thus

$$\ln N! = N \ln N - N. \tag{2.15}$$

(2) Taylor series expansion.
The following expansion will be used quite often for small x:

$$\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{2.16}$$

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^3}{4} + \cdots \tag{2.17}$$

If a function has two independent variables, the expansion is given by

$$f(x+a, y+b) = f(x, y) + f_x a + f_y b + \frac{1}{2}\left(f_{xx} a^2 + f_{yy} b^2 + 2 f_{xy} a\, b\right) + \cdots \tag{2.18}$$

(3) The Gaussian integral

$$Z(a) = \int_0^\infty dx \exp(-ax^2) = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}. \tag{2.19}$$

Many other Gaussian-related integrals may be obtained from $Z(a)$. A good example is

$$\int_0^\infty dx\, x^2 \exp(-ax^2) = \frac{\partial Z(a)}{\partial(-a)}. \tag{2.20}$$

We will make use of this trick many times in Chapters 4 and 5.

The goal of this book is to understand the maximum entropy principle and its equivalence, the minimum free energy principle. If you read up to Chap. 8 and the second section of Chap. 9, the Landau-Grinzburg (LG) free energy functional, we will have met our goal. However, I found it difficult to stop there without showing how useful the LG free energy functional has proven to be. Therefore I have expanded Chap. 9 and added Chap. 10. Unfortunately, the bulk of the material in these last two chapters requires more than just introductory physics, but you may still read them for a conceptual understanding without worrying about the mathematical details of each step. For such a moderate purpose, the following two additional items of preparation should be sufficient.

2.7 Fourier Transformations

Let $g(\vec{r})$ be a function of position vector $\vec{r}$. Its Fourier transform $h(\vec{q})$ is defined by

$$h(\vec{q}) = \frac{1}{(2\pi)^{3/2}} \int d^3r\, g(\vec{r}) \exp(i\vec{r}\cdot\vec{q}), \tag{2.21}$$

where $\vec{q}$ is called a wave vector, and

$$\exp(ix) = \cos(x) + i\sin(x), \tag{2.22}$$

and $i = \sqrt{-1}$.

The transform $h(\vec{q})$ tells us how much of a pattern there is which tends to repeat itself in the direction of $\vec{q}$ with the periodicity of $\lambda = 2\pi/q$. To see this, consider the following simple case in one dimension. Suppose that $g(x_n) = g(x_0)$ where $x_n = x_0 + n\lambda$ and $n = 1, 2, 3, \ldots$ Now let $q = q_0 = 2\pi/\lambda$ and examine how $g(x_0), g(x_1), g(x_2)$, etc. contribute to $h(q)$. Since all $q_0 x_n$'s differ from each other only by an integer multiple of 2π which amounts to no difference for trigonometric functions, their contributions add up to make a large net contribution.

Given $h(\vec{q})$, we may find $g(\vec{r})$ by inverting the transformation,

$$g(\vec{r}) = \frac{1}{(2\pi)^{3/2}} \int d^3q\, h(\vec{q}) \exp(-i\vec{r}\cdot\vec{q}). \tag{2.23}$$

This equation says that the function $g(\vec{r})$ may be regarded as a superposition of many trigonometric functions. Each of the trigonometric functions maintains a different repeating pattern which contributes to $g(\vec{r})$ with a weight given by $h(\vec{q})$. Thus, if $h(\vec{q})$ is very large compared to the rest, it simply means that *there is a recurring spatial pattern of length scale of* $\lambda = 2\pi/q$. This is all we need to remember. I do not expect you to carry out any Fourier transformations while reading this book.

2.8 Complete Sets for Vectors and Functions

Consider the set of three vectors $\{\vec{i}, \vec{j}, \vec{k}\}$ where $\vec{i}$, $\vec{j}$, and $\vec{k}$ are the unit vectors directed along the $x-$, $y-$ and $z-$ axes, respectively. The set is said to be complete in the sense that, given any vector $\vec{A}$, one can represent it as an appropriate sum of these three unit vectors, $\vec{A} = A_x\vec{i} + A_y\vec{j} + A_z\vec{k}$. Since the totality of all vectors $\vec{A}$ constitutes the three-dimensional vector space, we say that the three vectors span the three-dimensional vector space. We may extend this idea to functions in a multi-dimensional space of functions. A set of functions, $\{f_i(x), i = 1, 2, 3, \ldots\}$ is said to be complete if all well-behaving functions may be represented as an appropriately constructed sum of these functions, namely, given a function $g(x)$, it can be written as $g(x) = \sum_i A_i f_i(x)$. This is all we need to remember and we need not worry about how to calculate the coefficient A_i at the moment. As an example, the set of functions $\{\exp(-i\vec{q}\cdot\vec{r})\}$ is complete, as Eq. (2.23) claims.

Chapter 3

Isolated Thermal Systems

3.1 Introduction

We will consider in this chapter physical systems isolated from the rest of the Universe. Once we learn how to handle isolated systems, we will be ready to move on to systems coupled to the atmosphere or other large reservoirs. The systems we shall study consist of extremely large numbers of particles, as many as 10^{23} or more. This is a very large number indeed. The total number of temporal ticks (say, once per second) since the Big Bang is estimated to be on the order of 10^{18}. Because these systems consist of such a large number of particles, they can exist in many different ways, each of which may be regarded as a microstate. The number of possible microstates is very large. The systems are not "stuck" in any one of the microstates. Each system has something "thermal" in it which causes the system to move from one microstate to another. We need not know the exact nature of the mechanism responsible for this, but merely assume that such a mechanism exists for each thermal system. Since we know what the system does in each microstate, the only additional information we need in order to proceed is the number of times the system visits each microstate. That is where thermal physics takes off.

3.2 The Fundamental Postulate

The fundamental postulate says:

An isolated thermal system visits all of its accessible microstates with equal frequency, i.e., without preferring any single one over the others. The

system may be regarded as being "lost" in the sea of microstates, like the man lost in Hattiesburg discussed in Chap. 1.

The postulate is based on the assumption that we are only interested in what goes on in the system over time scales much larger than atomic time scales. Atomic time scales are on the order of 10^{-15} seconds. When we make measurements of thermodynamic quantities, the measurement may take only a small fraction of a second, but this is an eternity on an atomic time scale. The instruments measure the average of all the microstates that the system has visited during the measurement time.

3.3 Microcanonical Ensemble

Let us imagine what the instruments do when they take measurements of thermodynamic quantities. The instruments observe the system visiting different microstates and take an average over what the system shows in each microstate. If we imagine making a record of what the instruments observe even over a short measurement time span, it would still give us a very long time series of the microstates that the system visits in succession during the specified measurement time span. All equilibrium properties may be written as an average over this time series. Suppose that the microstates have been defined with respect to quantity A. The equilibrium average of A is then given by

$$< A >= \frac{1}{\hat{N}} \sum_j A(j), \tag{3.1}$$

where $A(j)$ is what A is in the microstate that the system visits at time j, and $\hat{N}$ is the total number of entries in the series. If we had this time series, we could calculate not only the equilibrium properties but also all nonequilibrium properties as well, but we do not. Notice, however, that as far as the equilibrium properties are concerned, the order in which the $A(j)$s' are added in the above sum is immaterial. We also know that all the microstates show up in this series with equal frequency. These two facts make it possible for us to mimic what the instruments do without having to know the exact time series.

Since the frequency of seeing microstate i is given by $f_j = 1/\Gamma$ where Γ is the total number of microstates, make as many replicas of the system as

there are microstates. Each replica represents the same system but frozen in a different microstate. We have Γ such replicas, one for each microstate. For the average of quantity A, we can go through the ensemble of replicas and find out what A is in each member and then take the average:

$$< A >= \sum_i f_i A(i) = \frac{1}{\Gamma} \sum_i A(i), \tag{3.2}$$

where the sum is over all the replicas, the microstates. The ensemble representing an isolated system is called a microcanonical ensemble.

In general, molecules act differently in different microstates. Fortunately for us, there are always an extremely large number of "typical" microstates. They are typical because they come in an overwhelmingly large number and share common characteristics. Let us call this group of microstates collectively macrostate A. Other groups of different microstates exist, but they come in much smaller numbers. Let us call them macrostates B, C, etc. These macrostates are smaller than macrostate A by many orders of magnitude. The system visits all the microstates of all macrostates with equal frequency, but since those belonging to macrostate A constitute such an overwhelming majority, it is safe to ignore those in the smaller macrostates. In fact, the system does not visit all of the microstates in A during a typical measurement time span. It visits only a fraction of them, but this fraction is large enough to represent the average of all the microstates in A. Since we know what the system does in each of these typical microstates, we can predict the average values, or the thermal properties of equilibrium states.

The term "equilibrium state" should be understood carefully. Contrary to what it means in mechanics, here an equilibrium state contains many events involving many different microstates. What then is "non-equilibrium state"? On an infinite time scale, any microstate can be reached from any other. This is not always true on a finite time scale. Suppose that we initially force the system to be in a microstate in macrostate B. The system will in due time move to macrostate A, but it may take longer than the finite observation time scale. If so, the transient process is a non-equilibrium process. While the system is in the transient period, the system is said to be in a non-equilibrium state. Once it reaches A, because A has so many microstates, it is safe to say that the system will not go back to B spontaneously. It is now in an equilibrium state.

3.4 Entropy and the Second Law of Thermodynamics

That being the case, the only thing that truly matters for determining how a thermal system will behave is Γ, the multiplicity (the number of microstates) of each macrostate. The natural logarithm of Γ of the macrostate that the system is in is called entropy:

$$S = k_B \ln \Gamma, \tag{3.3}$$

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. It contains a temperature unit which we have not yet discussed, but for now simply regard it as a constant. Put the thermal system in a small macrostate. It will spontaneously move from the small macrostate towards the largest macrostate (equilibrium), but not the other way around. If you observe the time evolution in terms of entropy, you will see a distinctive pattern of change. The entropy only increases and never spontaneously decreases. When it no longer increases because it has reached the largest macrostate, we say that the system has reached its equilibrium state. This is called the second law of thermodynamics or the maximum entropy principle; the first law will be introduced later.

Thermal systems are, so to speak, after entropy and entropy only. This is the only principle that guides thermal systems. Entropy reaches its maximum possible value when the system finally reaches its dominant macrostate; when that happens, we say that the system has reached an equilibrium state. Displace the system from the equilibrium state with a brief external interference. The displaced system will again find its way towards the dominant macrostate. As we will find out shortly, thermal systems have a built-in control system which does just that.

Another way of displacing a thermal system from its equilibrium is to impose a different set of constraints on the system. This demands the system to change its behavior. For example, consider a gas confined to a cylinder by a mobile piston. Fix the piston position, let the gas reach its equilibrium state, and then displace the gas from the equilibrium by moving the piston so as to allow more space for the molecules. The typical microstates in the largest macrostate before the system was displaced are no longer typical. For the displaced system, there are new typical microstates consistent with the changed constraint. Once the system reaches its new largest macrostate, it never spontaneously returns to the initial macrostate

as it is no longer the largest macrostate. If the system did, it would be quite spectacular as the molecules would then appear as if they wanted to stay away from a certain volume of space even though there is no dividing wall.

Several features about entropy should be noted. The multiplicity that defines entropy may be thought of as the number of different ways the system can do what it does. For example, suppose that a system consisting of non-interacting molecules are confined to a box and do two unrelated things α and β at the same time; let α represent the action of arranging themselves in various parts of the box and β the action of distributing energy among themselves. The total number of ways of doing both α and β is given by $\Gamma = \Gamma_\alpha \Gamma_\beta$, where Γ_α represents the number of ways of doing α and Γ_β represents the number of ways of doing β. Upon taking the logarithm, we get

$$S = S_\alpha + S_\beta. \tag{3.4}$$

The additivity also holds if the system consists of two uncoupled parts A and B. The multiplicity for the total is given by $\Gamma = \Gamma_A \Gamma_B$, and therefore $S = S_A + S_B$.

Carrying out an exact calculation for Γ can be quite difficult, but we can get away with large errors because Γ is so large and what is meaningful is its logarithm, not Γ itself. We should take advantage of this to the fullest extent, and we will. Suppose that $\Gamma = 10^{10^{23}}$, but we have overestimated it 100-fold, 1000-fold, or even 10^{23}-fold. What is the consequent error in the entropy? Since $\ln[10^{23} \times \Gamma] = 23 \times \ln 10 + \ln \Gamma$, the error is $23 \times \ln 10$. While the error is large compared to unity, it is negligible compared to $\ln \Gamma = 10^{23} \times \ln 10$. This should not deter you from doing your best to calculate Γ. Rather you should take this as saying "You do not have to be a math wizard. Just do your best; everything will be fine."

3.5 Entropy of Ideal Gas

The idea of entropy was recognized before Boltzmann, but its physical meaning was far from clear. Boltzmann clarified its meaning, but much of his thermal physics was based on an atomistic view of matter. This is remarkable because Boltzmann worked before the time of Rutherford

and Schrödinger. Boltzmann's atomistic point of view ran contrary to the prevailing tendency in his time to think of everything, except falling apples, as a kind of hydrodynamic phenomenon. He was clearly ahead of his time, and for that reason, his idea met with vicious attacks from some of his contemporaries. If he had lived just three more years, he would have seen his ideas vindicated. As it turns out, Boltzmann left behind him a powerful new science. Equation (3.3) is his masterpiece. Let us pay tribute to him by using it to calculate the entropy of an ideal gas.

Ideal gas molecules do not interact with one another. Real molecules do, but in the gas phase, because they are so far away from one another, it makes no difference if we ignore the molecular interactions. They are "ideal" because we can calculate lots of things that we would unable to calculate if they were interacting with one another.

To calculate entropy, we have to set up the appropriate microstates. We will do this in two ways. We will first do it using position- and momentum-definite microstates. We will then repeat the calculation using energy-definite microstates. The results for entropy turn out to be the same with both sets of microstates.

3.5.1 *With Position- and Momentum- Definite Microstates*

Let us construct microstates the more classical way by using position- and momentum-definite microstates for ideal gas molecules. In this scheme, we characterize each microstate by specifying where the molecules are and how fast they are moving, all within the limitations set by the Heisenberg uncertainty principle.

3.5.1.1 *One Molecule*

We begin by learning how to construct microstates for just one molecule in a box of volume V. This is hardly a thermal system, but we had better learn how to handle one molecule before tackling N of them. To specify the position of the molecule, divide the volume of the box into three-dimensional cubic blocks, each with volume $(\Delta x)^3$. The molecule could be found in any one of the blocks, and therefore the total number of the positional microstates is equal to the number of the blocks,

$$\Gamma_{\vec{r}} = \frac{V}{(\Delta x)^3}. \tag{3.5}$$

Next, turn to the momentum of the molecule. If the molecule has energy U, the momentum must satisfy

$$U = (p_x^2 + p_y^2 + p_z^2)/2m, \tag{3.6}$$

where m is the mass of the molecule. Written as $p_x^2+p_y^2+p_z^2 = 2mU$, it tells us that the momentum vector must lie on the surface of a sphere of radius $p = (2mU)^{1/2}$. We cannot construct microstates using the surface because we would then be specifying certain components of momentum precisely without acknowledging any uncertainty. This would be inconsistent with what we did in the spatial cubic blocks above. So we multiply the surface by Δp_x to make a shell. We then make three-dimensional momentum blocks in the shell. The number of momentum blocks in the shell is:

$$\Gamma_{\vec{p}} = \frac{4\pi p^2 \Delta p_x}{(\Delta p_x)^3} = \frac{8\pi m U \Delta p_x}{(\Delta p_x)^3}. \tag{3.7}$$

We can now specify the microstates by indicating the spatial block and the momentum block the particle is in. The total number of the microstates is

$$\Gamma = \Gamma_{\vec{r}}\Gamma_{\vec{p}} = V 8\pi m U \Delta p_x/\hbar^3, \tag{3.8}$$

where we have used the uncertainty principle $\Delta x \Delta p_x = \hbar$. The presence of Δp_x in this final result for Γ is disturbing. When we take the natural logarithm, it will remain as a block-size-dependent constant, but it is canceled out whenever we ask whether entropy increases or decreases under various circumstances, and that is the only relevant question to be answered by Eq. (3.8).

Equation (3.8) shows two different sources of entropy. We call the part coming from $\Gamma_{\vec{r}}$ spatial (positional) entropy, and the part coming from $\Gamma_{\vec{p}}$ kinetic entropy.

3.5.1.2 *N Identical Ideal Gas Molecules*

Let us now put N ideal gas molecules in the box. Draw the cubic blocks just as we did above, and place the molecules in them one by one. Because the particles do not interact with one another, it is also possible to put them all in one block. The total number of ways to accommodate N guests in the spatial blocks is

$$\Gamma_{\vec{r}} = \left[\frac{V}{(\Delta x)^3}\right]^N \tag{3.9}$$

Turning now to the momentum, write

$$(p_{1,x}^2+p_{1,y}^2+p_{1,z}^2+p_{2,x}^2+p_{2,y}^2+p_{3,z}^2+\cdots+p_{N,x}^2+p_{N,y}^2+p_{N,z}^2)/2m = U, \tag{3.10}$$

which calls for the surface area of a sphere in $3N$-dimensional momentum space of radius $p = (2mU)^{1/2}$. It can be calculated using Eq. (2.13). We then multiply the area by Δp_x to make a shell, divide the shell into blocks, and then count the number of blocks.

This calculation. however, has a problem. In Eq. (3.10), we tagged each molecule as 1,2, etc. This is illegal because according to quantum mechanics identical particles must be treated as such and cannot be tagged. For convenience, we tagged the molecules against the rule in Eq. (3.10), which results in an overcounting error. Let us see whether the error can be corrected. When the N momenta in Eq. (3.10) are all different, we overcount the number of blocks by a factor of $N!$. When the N momenta are the same, tagging the molecules does no harm. If we assume that U is very large, the latter kind of microstates are in a very small minority and may be ignored. For the remaining N momenta which are all different from each other, the error is systematic and may be corrected by dividing the count by $N!$. The result is

$$\Gamma_{\vec{p}} = \frac{1}{N!}\frac{2}{(3N/2)!}(2\pi mU)^{3N/2}\frac{\Delta p_x}{(\Delta p_x)^{3N}}. \tag{3.11}$$

Combining this with the result for the spatial part, we obtain

$$\Gamma = \frac{1}{N!}\frac{V^N}{(3N/2)!}\left(\frac{2\pi mU}{\hbar^2}\right)^{3N/2} 2\Delta p_x, \tag{3.12}$$

where we have used the uncertainty principle. As before, one factor of Δp_x remains, but it is inconsequential for the reason given earlier.

Now take the logarithm, and while doing so, use the Stirling approximation and throw away insignificant terms like -1 in $3N - 1$. The final result for the entropy is:

$$S = k_B N\left\{\ln\left[\frac{V}{N}\left(\frac{mU}{3\pi\hbar^2 N}\right)^{3/2}\right] + \frac{5}{2}\right\} + \ln(2\Delta p_x). \tag{3.13}$$

Ignoring the last term, this is the Sackur-Tetrode equation. We will rederive it later. Equations (3.11), (3.12) and (3.13) are valid only when U is large. As we will soon find out, a large amount of energy means a high temperature.

3.5.2 *With Energy-Definite Microstates*

The first way of calculating the entropy of an ideal gas uses the position- and momentum-definite microstates. Let us now calculate it a second way using the energy-definite microstates.

3.5.2.1 *Single Particle*

For a single particle, the possible values of energy are given by

$$\epsilon_\nu = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2). \tag{3.14}$$

Here ν is the index that specifies the microstates and represents

$$\nu = (n_x, n_y, n_z), \tag{3.15}$$

where each component of $\vec{n}$ can be any positive integer including zero. The calculation for Γ proceeds in the same manner as before. We calculate the surface area of the 3-dimensional $\vec{n}$ space, convert it into a shell, make blocks, and then count them. The only difference is that the components

of $\vec{n}$ are discrete with $\Delta n_x = 1$, which makes the calculation easier than before. The final result is the same as Eq. (3.8) but without the factor of Δp_x.

3.5.2.2 *N Identical Ideal Gas Molecules*

For N identical molecules in a box of dimension $L \times L \times L$, the possible values of energy are the energy eigenvalues given by

$$E_\nu = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \sum_{\vec{n}_1}\sum_{\vec{n}_2}\cdots\sum_{\vec{n}_N}(n_1^2 + n_2^2 + n_3^2 + \cdots + n_N^2), \tag{3.16}$$

where $n_i^2 = n_{i,x}^2 + n_{i,y}^2 + n_{i,z}^2$ and $n_{i,x}$ refers to the x-component of $\vec{n}_i$ and can be any positive integer, including zero. The index ν represents

$$\nu = \{\vec{n}_1, \vec{n}_2, \vec{n}_3, \ldots, \vec{n}_N\}. \tag{3.17}$$

We have no uncertainty principle to worry about. We calculate the surface area of a sphere in $3N$-dimensional $\vec{n}$ space. Since $\Delta n_x = 1$, we can still pretend to turn it into a shell, make blocks of size $\Delta n_x^3 = 1$, and count them. In the first step, each component of $\vec{n}$ is restricted to positive integers, but it is easier to ignore this restriction and calculate a much more expanded surface by doubly overcounting each microstate, and then dividing the final result by 2 for each component of $\vec{n}$.

We have again tagged the molecules. The resulting overcounting error is of the same nature as before, and may therefore be corrected as in Eq. (3.11) simply by dividing the count by $N!$. The final result is:

$$\Gamma = \frac{1}{N!}\frac{2V^N}{(3N/2)!}\left(\frac{2\pi m U}{\hbar^2}\right)^{3N/2} \tag{3.18}$$

which is the same as obtained previously using the position- and momentum-definite microstates, but we no longer have the annoying "leftover" from the uncertainty principle. Remember that Γ is proportional to V^N and $U^{3N/2}$.

3.6 Macrostates

3.6.1 *The Largest Macrostate*

With Γ as a function of N, V and U, we are ready to construct macrostates for our ideal gas system and study the largest one. Macrostates may be constructed in a number of ways. One way would be as follows. Divide the box into two parts with an imaginary mobile partition which keeps N_A molecules in part A and the remainder $N_B = N - N_A$ in part B. Macrostates may then be defined according to the way the two parts share the total available volume and energy. Consider a macrostate in which chamber A holds energy U_A and volume V_A while chamber B holds $U - U_A$ and $V - V_A$. Using Eq. (3.18), the multiplicity of that macrostate is given by

$$\Gamma_{AB}(U, V, U_A, V_A) \sim V_A^{N_A}(V - V_A)^{N_B} U_A^{3N_A/2}(U - U_A)^{3N_B/2}. \tag{3.19}$$

Is there a particular value of U_A for which the value of Γ is maximum? Differentiating Eq. (3.19) with respect to U_A, we find that the answer is yes, and that the maximum occurs when

$$\frac{U_A}{N_A} = \frac{U_B}{N_B}. \tag{3.20}$$

Is there an optimum value for V_A which maximizes Γ? The answer is again yes; the maximum occurs when

$$\frac{V_A}{N_A} = \frac{V_B}{N_B}. \tag{3.21}$$

In the largest macrostate, energy and volume are divided between the two parts in proportion to their respective numbers N_A and N_B. We may repeat this argument with more partitions for further refinement. We conclude that in the largest macrostate, energy and volume are more or less uniformly distributed in all parts of the system.

3.6.2 *How Dominant?*

Next, let us find out how dominant the largest macrostate is. This question can easily be answered if we assume that $N_A = N_B = N/2$. We do not lose any generality with this assumption since each of the halves can be divided into halves again and again. In the largest macrostate, $U_A = U/2 \equiv \hat{U}$ and $V_A = V/2 \equiv \hat{V}$. Now consider a macrostate in which U_A deviates from $\hat{U}$ by x, namely,

$$U_A = \hat{U} + x, \qquad U_B = \hat{U} - x. \tag{3.22}$$

The size of the corresponding macrostate is

$$\begin{aligned} \Gamma_{AB}(x) &\sim \left(\hat{U} + x\right)^{3N/4} \left(\hat{U} - x\right)^{3N/4} \\ &= (\hat{U}^2 - x^2)^{3N/4} \end{aligned} \tag{3.23}$$

Because N is very large, Γ_{AB} decreases quite rapidly with increasing x. When a function changes this rapidly, it is difficult to approximate the function with a Taylor series. To make the function vary less rapidly, take the logarithm and rewrite the result in the form of $\ln(1 - x^2/\hat{U}^2)$. It may now be approximated with its first order Taylor series. Next, exponentiate the result. The final result is

$$\Gamma_{AB}(x) \sim \exp\left(\frac{-x^2}{2\delta x^2}\right), \tag{3.24}$$

where $\delta x^2 = \hat{U}^2/(3N/2)$. The deviation x is distributed in a Gaussian form with a peak at $x = 0$. The width of the peak is given by

$$\delta x = \frac{\hat{U}}{(3N/2)^{1/2}}, \tag{3.25}$$

which is extremely small because N is so large. We may argue likewise for the volume.

Let us consider the macrostate defined by $x = 1.14 \times 10^{-11}\hat{U}$ and compare it with that of the largest macrostate corresponding to $x = 0$. The multiplicity of the former is given by

$$\Gamma_{AB}(x = 1.14 \times 10^{-11}\hat{U}) = \Gamma_{AB}(x = 0)e^{-10}, \tag{3.26}$$

which is smaller than the largest one by a factor of e^{10}. Therefore the chance of the system visiting it is e^{-10}, or one out of 22026. If we check the system once every second for 6 hours, we have a chance of witnessing the deviation. That is not bad, but the deviation is only one part out of 10^{11} which is hardly much of a deviation. That is the largest deviation that we have any chance of observing. Observing a larger deviation would be fun, but do not try it—we really have no chance. As this example illustrates, there can be macrostates which are large enough to compete with the largest one, but they are hardly different from the largest macrostate, and therefore it does no harm if we simply ignore them.

When a gas is given a certain volume, it takes up all the given space, no matter how large the volume may be. Why? Why do the molecules not reserve some part of the space for guests or for some special purpose like we do? Let us define the macrostates according to y, the amount of space left vacant out of the given volume V. Since the size of the macrostate corresponding to y goes like $(V - y)^N$, $y = 0$ clearly constitutes the largest macrostate. Let us consider the macrostate B in which molecules occupy only 99.9 percent of the given volume leaving 0.1 percent empty, i.e., $y = 0.001V$. How small is this macrostate compared to the largest one? Eq. (3.18) says that the multiplicity ratio is $(0.999V/V)^N = 0.999^N$. With $N = 10^{23}$, the ratio is 4.3×10^{-19}. Do we have a chance of observing the system in B? That is, is there any chance of seeing the molecules spontaneously staying away from 0.1 percent of the available volume? To have any reasonable chance of seeing this, we would have to devote at least the length of time since the Big Bang checking the system once every second.

To summarize, at the thermodynamic limit of large N, it is safe to take the largest macrostate and ignore the rest. This is a virtue; if it were not true, thermal physics would not be a predictable science.

3.7 Fundamental Thermodynamic Equations

According to Eq. (3.13), entropy is a function of U, V, and N. Let us more closely examine why it depends on each of these variables.

(1) Energy

First, consider energy U. U can only be one of the eigenvalues E_ν which is a sum of N ϵ's. Given energy U for N molecules, the multiplicity Γ is simply the number of ways of dividing it up into N ϵ's. Given more energy, there are more ways to divide it up. Thus entropy is a monotonically increasing function of U.

(2) Volume

If we take the position- and momentum-definite microstates, the reason for V is clear; the larger the volume, the more blocks we can make and therefore the more ways to accommodate the molecules. If we take the energy-definite microstates, the reason is somewhat subtle. To see this, suppose that a person has a bag containing 100 dollars, and that he distributes its contents to 10 people. How many ways can the money be distributed? The answer depends on whether the money in the bag consists of one hundred-dollar bill, 10 ten-dollar bills, 100 one-dollar bills, or 1000 dimes. If the money comes in smaller units, there are more ways to distribute it among the ten people. Likewise, energy can be distributed differently depending on the units in which the energy is given, namely the values of ϵ's. When volume is large, Eq. (3.14) shows that the energy comes in smaller units, and therefore there are more ways to divide the given energy between the molecules. Entropy is a monotonically increasing function of the volume $V = L^3$.

(3) Number N

In the above arguments, the number of molecules N has been invoked more than once. We need not argue any further why N should be one of the variables.

Thus we may write

$$S = S(U, V, N). \tag{3.27}$$

Since S is a monotonic function of U, it may be inverted to give

$$U = U(S, V, N). \tag{3.28}$$

These two equations will be referred to as the fundamental thermodynamic equations. For idal gases, the Sackur-Tetrode equation, i.e., the logarithm

of Eq. (3.18), is the most fundamental thermodynamic relationship. It carries the grand title because all thermodynamic properties may be calculated from it, as we will see below.

3.8 Temperature, Pressure and Chemical Potential

Let us now see how entropy is affected when the variables change under various circumstances. To that end, take the differential of Eq. (3.28):

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN, \tag{3.29}$$

The three partial derivatives are abbreviated as follows with names:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} \equiv T, \quad \text{Temperature;} \tag{3.30}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} \equiv -P, \quad \text{Pressure;} \tag{3.31}$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} \equiv \mu, \quad \text{Chemical Potential.} \tag{3.32}$$

I urge you to pretend like you have never heard of these names before. With these abbreviations, Eq. (3.29) can be written as follows

$$dU = TdS - PdV + \mu dN, \tag{3.33}$$

or

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN, \tag{3.34}$$

where the coefficients may be identified with

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \tag{3.35}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \tag{3.36}$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{3.37}$$

3.9 The Approach to Equilibrium

The coefficients $1/T$, p/T, and $-\mu/T$ play very important roles because they determine how much the entropy is affected when U, V and N change. To see this important point which we are going to dramatize in length, consider a gas in a cylinder with an insulating partition which divides the gas into two uncoupled systems. Let A represent the gas on the left and B the gas on the right. The two parts are at their respective equilibrium states. The piston is insulating, impermeable and fixed at a position. Let us now suppose that we have a way of changing these characteristics of the piston one by one to disrupt the equilibrium and then see what roles these coefficients play while the system is moving toward its new equilibrium state.

3.9.1 *Temperature*

The position of the partition remains fixed, but now imagine it turning into a thermally conducting wall which allows an exchange of energy between the two sides. What happens then? Assume that A is initially at a higher temperature than B. Since entropy is a monotonic function of energy, both A and B will want to increase their energy to increase their own entropy. However, since the combined system is isolated, one part can increase its energy only at the expense of the other part. It is then crucial that the side receiving energy increases its entropy more than the donor loses. Which side must give and which side must receive? From Eqs. (3.35) and (3.13), we have

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3N}{2}\frac{k_B}{U} = \frac{1}{T}. \tag{3.38}$$

Equation (3.38) gives us the answer. The side for which $\partial S/\partial U$ is larger should receive energy, namely the one at a lower T. **If a system at a low temperature receives energy, the resultant increase in entropy is huge. If such a system loses energy, the resultant loss in entropy can be devastating. By contrast, if a system at a high temperature receives that same amount of energy, the resultant increase in entropy is very small, and if it loses that amount of energy, the resultant loss in entropy is hardly noticeable.**

As energy flows from A to B, Eq. (3.38) tells us what happens to each part. It says: T increases with U; a small amount of energy means a small value of T, a low temperature, and a large amount of U means a large value of T, a high temperature. Therefore the receiving side will increase its temperature while the donor side lowers its temperature. The energy flow will stop when the two temperatures match; it has now reached thermal equilibrium.

Think of $1/T$ as the molecules' appetite for energy. When two different systems, or two different parts of the same system, have different degrees of appetite for energy, the party with more appetite takes energy from the party with less appetite. This is not a runaway process, however. As the energy is exchanged, the receiving party loses its appetite while the donor party gains it, which ultimately leads to an equilibrium state where both parties have the same amount of appetite. This built-in safety system brings displaced thermal systems back to equilibrium and is called the Le Châtelier theorem. Molecules know when to receive energy and when to give it, all for the good of the total system to which they belong. Moreover, they know when to increase their appetite and when to decrease their appetite. We may say that thermal physics is a science of giving and receiving.

3.9.2 *Pressure*

If we leave the system as it is, nothing will happen and the two parts will remain in their respective equilibrium states. Suppose that the partition becomes mobile so that the volume for the two sides, A and B, can be exchanged. What then happens? Assume that the pressure, p, is higher for A than for B. Entropy is a monotonically increasing function of volume, and therefore each side will want to increase its volume to increase its own entropy. But since the total volume of the cylinder is fixed, one can increase its volume only at the expense of the other. In order to ensure that the

total entropy will increase, the receiving side must increase its entropy more than the donor loses. Which side must give and which side must receive?

From Eqs. (3.36) and (3.13), it follows that

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{k_B N}{V} = \frac{P}{T}. \tag{3.39}$$

Equation (3.39) gives us the answer. The side for which $\partial S/\partial V$ is larger should receive, i.e., A, which has the higher pressure. In order to increase their combined total entropy, B should shrink so that A can expand. **If a system at a high pressure is given more volume to expand into, the resultant increase in entropy is huge. If such a system loses volume, the resultant loss in entropy can be devastating. By contrast, if a system at a low pressure receives that same amount of volume, the resultant increase in entropy is very small, and if it loses that amount of volume, the resultant loss in entropy is hardly noticeable.**

Equation (3.39) also tells us that the exchange of volume results in a change in pressure. It says that the pressure p decreases with increasing volume. As the partition moves to increase A's volume, A's pressure decreases while B's increases. The volume exchange, or the volume "flow", will continue until the two pressures match; the system has now reached mechanical equilibrium. Think of p as the molecules' appetite for volume.

3.9.3 *Chemical Potential*

To repeat the story for N, imagine that the partition now becomes a permeable wall through which molecules on one side can migrate to the other. After both thermal and mechanical equilibriums have been reached, suppose that μ is higher for B than for A. Since molecules are neither annihilated nor created in the cylinder, if one side is to increase its population, it can do so only at the expense of the other. To ensure that the total entropy increases as a result of the migration, which side should give and which side should receive?

From Eqs. (3.37) and (3.13), it follows that

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = k_B \ln\left[\frac{V}{N}\left(\frac{mU}{3\pi\hbar^2 N}\right)^{3/2}\right] = -\frac{\mu}{T}. \tag{3.40}$$

The minus sign calls for some caution. Suppose that $\mu > 0$. Each party can increase its entropy by decresing its N and decrease its entropy by increasing its N. Think of μ/T as the molecular analogue of the "unlivability" of each geographic region which tends to encourage its population to leave. **If a system at a high chemical potential decreases its population, its entropy goes up by a huge amount. Should such a system increase its population, it will suffer a devastating loss in entropy. By contrast, if a system at a low chemical potential receives that same number of molecules, the resultant loss in entropy is hardly noticeable, and if it loses its population by that number of molecules, the resultant gain in entropy is very small.** The answer is clear. The side for which μ is larger should give, i.e., B should give, and the side for which μ is less should receive, i.e., A should receive. The migration should be directed from a high μ/T to a low μ/T.

Equation (3.40) then says that, as molecules migrate into a region of lower unlivability, the unlivability of that region increases. Thus as molecules migrate from B to A, the chemical potential increases in A and decreases in B. When the two chemical potentials match, the systematic migration will stop, and the system will reach diffusive equilibrium.

If μ is negative, the above description has to be revised, but it remains true that the migration should be directed from a high μ/T to a low μ/T.

3.9.4 *Multiple Traffic Control Systems*

We have changed the nature of the partition stage by stage in order to highlight the individual roles of T, P, and μ, respectively. What would happen if we were to convert the insulating, fixed, and impermeable partition all at once into a conducting, mobile and permeable wall? The three kinds of flow will take place simultaneously. The energy traffic will be controlled by $1/T$, the volume traffic by p/T, and the particle traffic by $-\mu/T$. The energy traffic is coupled to the concurrent volume and particle traffic, and therefore all three traffics are coupled to each other.

What we called A and B up to this point can be viewed as two adjacent parts of a large thermal system out of equilibrium. What takes a system

out of its equilibrium state? The answer: U, V, and N are not properly distributed among the different parts of the system. To deal with this situation, we have to regard T, P and μ as representing local properties. There may be too much energy in one part; if so, energy must flow from that part to the rest. Molecules in one part may be unduly compressed; if so, that part needs to expand at the expense of the rest. There may be too many molecules in one part; if so, they must diffuse away from that part. The traffic should be directed to increase the total entropy. Energy should flow along the direction in which T decreases most rapidly, namely, $-\nabla T$. Volume should flow along the direction in which P/T increases most rapidly, namely, $\nabla(P/T)$. Particles should migrate along the direction in which μ/T decreases most rapidly, namely, $-\nabla(\mu/T)$.

Draw a map showing the equi-surfaces of T, P/T, and $-\mu/T$. We have three topographic maps, one for the energy traffic, one for the volume traffic, and one for the particle traffic. The three equi-surfaces are constantly changing to ensure that the traffic will result in increasing the entropy and guide the system to its new equilibrium state. In other words, the molecules have built-in safety control systems: automated thermostats for temperature control, automated valves for pressure control, and automated border control systems for migration control. This is again the Le Châtelier theorem.

What would it be like if molecules were in a state in which they did not have this built-in control system? The temperature would decrease with increasing amount of energy, the pressure would increase with increasing volume, and the chemical potential would decrease with increasing population. Their appetite for energy would increase with increasing amount of energy, and their appetites for V and N would increase likewise. These molecules would then gobble up everything in the universe. Worse yet, should the safety system be restored after a while, their return to a normal state would be dangerously explosive. To give a human analogue, think of a man whose appetite increases with an increasing amount of food in his stomach. Molecules will never lose the safety system, but we can force the molecules into such a state. In Section 7.5 we will see what the molecules do under such a condition.

3.10 Summary: Ideal Gas

Rewrite Eq. (3.38) as

$$U = 3N \times \frac{k_B T}{2}. \tag{3.41}$$

We can see where this equation comes from. Each component of momentum contributes $k_B T/2$ to the energy and there are $3N$ such components. This is called the equipartition theorem. We will see more on this later.

From Eq. (3.39), we may write

$$PV = N k_B T, \tag{3.42}$$

which should look familiar. It is called the ideal gas equation of state.

Rewriting Eq. (3.18) along with the corresponding entropy is worthwile here:

$$\Gamma = \frac{1}{N!} \frac{2V^N}{(3N/2)!} \left(\frac{2\pi m U}{\hbar^2} \right)^{3N/2} \tag{3.43}$$

$$S = k_B N \left\{ \ln \left[\frac{V}{N} \left(\frac{mU}{3\pi\hbar^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}. \tag{3.44}$$

Finally, to make the list complete, we also rewrite Eq. (3.40):

$$\mu = k_B T \ln \left[\frac{N}{V} \left(\frac{3\pi\hbar^2 N}{mU} \right)^{3/2} \right], \tag{3.45}$$

or by replacing U with T using Eq. (3.41), we may write

$$\mu = k_B T \ln \left[\frac{N}{V} \left(\frac{2\pi\hbar^2}{m k_B T} \right)^{3/2} \right]. \tag{3.46}$$

Thinking again of μ/T as the molecular analogue of "unlivability", notice how the unlivability changes with N and V. It increases with increasing

N and decreases with increasing V. Is this not similar to the way the unlivability of human communities change? For example, Hattiesburg was at the top of many lists of the most livable small cities in the U.S. about 10 years ago. Since then it has experienced a steady increase in population. It is still a very livable small city, but not as much as it used to be. Needless to say, the brown Pontiac contributed to the increased volume of traffic.

Exercise *Equation (3.46) shows how the chemical potential changes with the concentration $n = N/V$ and the temperature T. Because $\mu = \partial U/\partial N$, anything that contributes to U also contributes to μ. The chemical potential that we have calculated for the ideal gas only takes into account the kinetic energy of the molecules. If the molecules are subject to an external potential such as the gravitational potential energy in the atmosphere, the potential may be added to what we have in Eq. (3.46). With this in mind, consider the atmosphere on a calm day when there is no organized migration of molecules. Assume that the temperature is the same everywhere. State that the unlivability right above the ground is the same as at altitude h, and find out how the concentration and pressure change with height h.*

3.11 First Law of Thermodynamics

Let us write Eq. (3.33) once more

$$dU = TdS - PdV + \mu dN. \tag{3.47}$$

It is called the First Law of thermodynamics. It is simply a statement of the energy conservation law for a system. Examine how each term contributes to a change in energy. The system can receive or give away energy in three different ways: (a) by changing its entropy for the TdS term, (b) by changing its volume for the PdV term, or (c) by changing its population number for the μdN term. It is important to understand the difference between (a) and (b).

When energy increases via (a), we say that heat has entered the system. The energy increases without any change in volume and therefore without any change in the energy units. There is now more energy in the same

units to be divided up among the same number of molecules, which means an increase in entropy. The increased entropy is kinetic entropy. If we put a hot brick next to another physical system, the vibrational kinetic energy of the brick molecules is transferred to the system for TdS. If we send a light beam into a cup of water so that the water molecules absorb the light energy, the light energy is transferred to the water for TdS.

When energy changes via (b), we say that work has been done to the system. It is important to note that this occurs **without changing entropy** or N. How can energy change without changing entropy? Consider a gas held in a cylinder by a piston. Imagine that we push the piston very slowly. We are performing work to the system. What happens to the work? The change in volume causes a change in all the ϵ's. When energy changes in this way, entropy does not change. To see this, imagine that we have 1111 dollars in a bag to be divided up among 4 people. In the bag are one 1000-dollar bill, one 100-dollar bill, one 10-dollar bill, and one 1 dollar bill. Suppose that you are going to just grab whatever you can in the bag and hand it over to one of the four, and repeat the action until there is nothing left in the bag. How many different ways are there to divide up the money? Hold your answer for a moment and let me ask you one more question. What if the bag has one 100-dollar bill, one 10-dollar bill, one 1 dollar bill, and one dime? It is clear that the answer is the same for both questions. Equations (3.13) and (3.16) confirm this intuition. Notice that V and U enter as $VU^{3/2}$ into Eq. (3.13) to determine S. Since Eq. (3.16) says that U scales with V like $V^{-2/3}$, $VU^{3/2}$ does not change when V changes.

If we compare our wealth with energy, we may also say that our wealth can change in two similar ways. At this very moment I have in my pocket one ten dollar bill, one 1-dollar bill, two quarters, two dimes, and four pennies. I can become richer in two ways. (a) I may win a prize to bring a few more quarters and dimes into my pocket, the "heat" way. (b) No additional money goes into my pocket, but thanks to the hard *work* of the nation's economy, I may find one day that each of my four pennies can buy what costs today one dollar, and likewise each of my two dimes can buy what costs today ten dollars, and so on, the "work" way. I rely on the "work" way, namely (b), which is why I have two large jars full of pennies. A better way is to buy some stocks and let the company do the *work*, but we know that this is a risky proposition because the company may do the work in the wrong direction, decreasing their ϵ instead of increasing it. I have just read a physicist's autobiography. Apparently he was brilliant

with stocks and rare art pieces because his stock broker once proposed that they exchange roles! It is good to know that some of us can do better than collecting pennies.

3.12 Extensive and Intensive Variables

All thermodynamic quantities may be divided into two groups, extensive and intensive. Examples of extensive quantities are U, S, V, and N. They are called extensive because if we add two systems, the extensive variables of the two systems add for the combined total. Energy is additive as are entropy, volume, and particle numbers. We can speak of a total for these quantities. By contrast, the temperatures of two added systems do not add, nor do P and μ. Temperature, pressure, and chemical potential are called intensive variables. The product of an extensive variable and an intensive variable is extensive; PV, TS, and μN are extensive quantities.

Bearing this in mind, rewrite the first law of thermodynamics for a system,

$$dU = TdS - PdV + \mu dN. \tag{3.48}$$

Now increase the size of the system λ times. The corresponding first law should read

$$d(U\lambda) = Td(S\lambda) - Pd(V\lambda) + \mu\, d(N\lambda). \tag{3.49}$$

Carrying out the differentials one step further, we have

$$\lambda dU + U\, d\lambda = \lambda(TdS - P\,dV + \mu\, dN) + (TS - PV + \mu N)d\lambda. \tag{3.50}$$

Since λ is arbitrary, the coefficients of $d\lambda$ must match to give the following useful relationship

$$U = TS - PV + \mu N. \tag{3.51}$$

We can obtain one more useful relationship. Consider Eq. (3.51) for a system. Suppose that the system goes through a process which changes everything, T, S, p, V, N and μ. Take the differential of Eq. (3.51) allowing

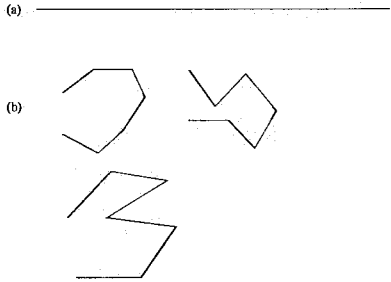

Fig. 3.1 A rubber band consisting of 6 elementary segments: (a) completely stretched, (b) partially curled.

all the variables to change on the right hand side. No matter what that process is, however, the first law must hold. Therefore dU can only be what Eq. (3.48) says; the rest must go. In other words,

$$SdT - VdP + Nd\mu = 0, \tag{3.52}$$

which is called the Gibbs-Duhem relationship. It says that changes can occur in temperature, pressure, and chemical potential, but they are subject to this constraint.

3.13 Entropy-Driven Forces

Think of entropy as something thermal systems always thirst for. No matter how much they may have, they always want more. Their never-ending thirst for entropy can be strong enough to manifest itself as a force. In other words, we must exert force to suppress what molecules do out of their desire for more entropy. Let me give you three examples.

3.13.1 *Rubber bands*

Rubber bands consist of long flexible chain molecules. A good simple model for each chain is to regard it as a large number of elementary, non-

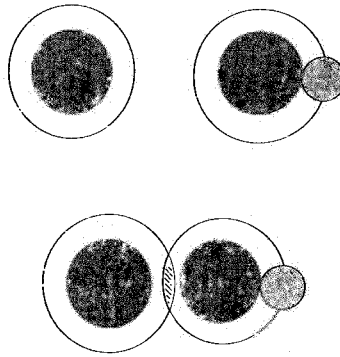

Fig. 3.2 Large molecules (shaded dark) and small molecules (shaded gray). Around each large molecule is a shell into which no small molecule can put its center. When two large molecules come close to each other as shown in the bottom figure, the two shells overlap. The cross-hatched area is the saved space which results in reducing the loss of entropy.

interacting segments. Take one long chain and stretch it to its maximum possible length. This can be done in only one way: all the elementary segments have to be aligned parallel to each other so that they do not bend, as shown in Fig. 3.1(a). Now bring the two ends closer to each other to a certain distance. As Fig. 3.1(b) shows, this can be done in many different ways. Thus it is sensible to define the macrostates according to the end-to-end length. Clearly the macrostates become larger with decreasing end-to-end length. Therefore the entropy-hungry chains will want to curl for greater entropy. When we stretch a rubber band, we feel the counterforce of the rubber band that opposes our action. It is a force whose origin lies in nature's attempt to maximize entropy. We will know how to model this thermodynamic force by the end of Sec. 3.15.

3.13.2 *Colloidal Suspensions*

Colloidal particles are very large hard-sphere molecules. If these large particles are suspended in a solution of small molecules, the size difference

creates another entropy-driven force. Suppose that we add one such large molecule to a solution of small molecules. Since the volume of the space occupied by the large molecule is no longer available for the small molecules, the large molecule is depriving the small molecules of some of their positional entropy. The large molecule or the small molecules can do nothing about it. Now add one more large molecule to the solution. The small molecules lose even more positional entropy. This time, however, they can do something together to minimize the loss of entropy. Since the small molecules also have a certain size, the volume of the space that each of the large molecules takes away is the volume of the large molecule plus a shell-shaped space covering the large sphere. The thickness of the shell is equal to the radius of the small molecules, and therefore no small molecule can put its center within the shell shown in the top of Fig. 3.2. If all the small molecules and the two large molecules conspire to bring the two large molecules close to each other so that the two shells overlap even slightly as shown in the bottom of Fig. 3.2, they can reduce the wasted space and the resultant loss in entropy. For this entropy incentive. will the two large molecules come towards each other? Yes! When colloidal particles are put in a solution, they spontaneously aggregate. This provides one of the most dramatic examples of entropy-driven forces. When the colloidal particles are charged, this entropy-driven force can overcome the electric force, and when one colloidal particle is held below another, it can overcome the gravitational force.

3.13.3 *Ideal Gas*

Figure 3.3 shows a gas held in a cylinder with a mobile piston on its right end. If we wish to keep the volume fixed, we know that we have to push the piston to the left to keep the gas from expanding, but never to the right to keep it from shrinking. The gas always pushes the piston to the right for more volume. They want more volume for more positional entropy. After all, Eq. (3.13) says "if you want more entropy, expand your volume". These molecules are banging on the wall with their own body, the only tool they have, for more entropy, just like the Germans who banged on the Berlin Wall with a sledge hammer for more freedom. We will find in Sec. 6.3 that this force is not only a real force, it has a potential energy associated with it. The work that we do when we push the piston to the left to reduce the volume goes into this potential.

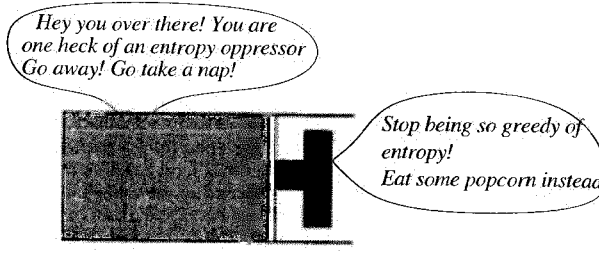

Fig. 3.3 The gas molecules inside the cylinder always want to push the piston out to increase their entropy, but the piston does not let them do that. The gas molecules do not like that.

Both rubber bands and the ideal gas exhibit elasticity for the same reason, but their manifestations are different; rubber bands do not want to be stretched, while the ideal gas does not want to be squeezed. The origin of the elasticity of springs is entirely mechanical.

3.14 Ising Model

Until now, we have studied the thermal behavior of molecules. We now turn to another thermal system, namely magnets using the Ising model. The Ising model was originally designed to study uniaxial ferromagnets, but it can actually represent a host of other thermal systems such as binary atomic mixtures. Draw any lattice, and put (Ising) spins on the lattice sites. A spin can only be +1 or -1. If $s = +1$, it is said to be "up", and if $s = -1$, it is said to be "down". Let us assume for now that the spins do not interact with each other; they are ideal spins. The spins are, however, coupled to the external magnetic field $\vec{H}$. Always assume that $\vec{H}$ is directed in the z-direction. Then s is the z-component of $\vec{m}/m$, where $\vec{m}$ is the magnetic dipole moment represented by the spins. When $s = 1$, its energy is $-mH$. When $s = -1$, its energy is mH. It costs energy to be directed opposite to the direction of $\vec{H}$. There are only two single-spin energy states with energy

$$\epsilon_s = -smH. \tag{3.53}$$

Since the spins are localized on the lattice sites, they can be treated as distinguishable objects. We may therefore tag them with no concern for an overcounting error. The microstates of N such spins may be indexed with ν,

$$\nu = \{s_1, s_2, s_3, \ldots, s_N\}, \tag{3.54}$$

where s_i represents the spin located at site i. For a given spin microstate, let us call the total spin

$$M = (s_1 + s_2 + s_3 + \cdots + s_N) \tag{3.55}$$

the magnetization. The N-spin energy is then given by

$$E_\nu = -mMH. \tag{3.56}$$

Notice that M is unitless. We should actually put m in the definition of M, but then m would follow everywhere in our analysis for M, which is why we leave it out; we put it back for energy in Eq. (3.56) which is the only place where m matters. The ideal spins do not interact with one another and are only coupled to the external magnetic field, but something thermal within the system makes the spins flip and the fundamental postulate says that the system will visit all the microstates with equal frequency.

The spin´system is different from the ideal gas in three important ways. First, the energy is not kinetic in origin. It may be regarded as an orientational potential energy. Thus the spin system provides an example of a thermal system in which the constituent members are not themselves moving around. Second, the total number of microstates is not infinite as it is for the ideal gas. This has an interesting consequence which we will explore shortly. Third, the N-spin microstate energy is dependent on two variables M and H in a remarkably simple manner. However, thermodynamics of magnetism can be quite confusing; it is not a trivial matter to write down the magnetic work because it is different depending on who does the work and how the experiment is set up. We will limit ourselves to what we can do on the basis of Eq. (3.56).

Let us calculate the total number of microstates Γ as a function of M and N. The task here is much easier than before because each spin has only two microstates, up or down. Calculating Γ as a function of M and N is not difficult. It is a factorial problem which we will work out in Sec. 4.6. Here we will take a shortcut and use the central limit theorem.

Notice that M is the sum of a very large number of spins each of which can be either +1 or -1. To make use of the central limit theorem, disregard for a moment that M is related to the energy, and let each spin be randomly +1 or -1, regardless of what the others are. Then M is the sum of a large number of randomly changing variables and, as such, its statistics can be obtained from the central limit theorem. Imagine a computer monitor screen which tells you what the total magnetization is at each moment while the individual spins are changing randomly. You would see something like: $1, -5, 200, 3, 40, -76, 12, \ldots, 7$. Call the time series $M_1, M_2, M_3, \ldots, M_N$. The central limit theorem provides us with the frequency, or the probability, of seeing a particular value M in this long time series. We may then obtain $\Gamma(M, N)$ by multiplying the probability by the total number of microstates (corresponding to all values of M) which is 2^N.

The probability $P(M, N)$ is obtained by replacing y in Eq. (2.10) with M:

$$P(M, N) = \frac{1}{(2\pi\delta M^2)^{1/2}} e^{-(M-<M>)^2/2\delta M^2}. \tag{3.57}$$

Here δM^2 represents the fluctuation of M,

$$\delta M^2 =< M^2 > - < M >^2 . \tag{3.58}$$

According to the central limit theorem, the fluctuation of M is given by

$$\delta M^2 = \sum_i \delta s_i^2, \tag{3.59}$$

where δs_i^2 represents the fluctuation of s_i,

$$\delta s_i^2 =< s_i^2 > - < s_i >^2 . \tag{3.60}$$

Since s_i is +1 or -1, $< s_i >= 0$. Also, since s_i^2 is always +1, $< s_i^2 >= 1$, and therefore $\delta s_i^2 = 1$. It follows that

$$\delta M^2 = N. \tag{3.61}$$

It is a good exercise to obtain this result directly. Go to Eq. (3.55), square both sides, and then put a big average sign on both ends. To be averaged are terms like $s_5 s_{17}$ and $s_5 s_5$. Of course, the spins do not know what the others are doing; they are just having a great time flipping up and down. So if you just focus on the 5th and 17th spins, there will be no compelling reason for the 17th spin to be like or unlike the 5th spin. When $s_5 = 1$, s_{17} will be +1 as often as it will be -1. So the average of these cross terms vanishes, leaving only the self-terms. The self-terms are all 1, and there are N of them, which gives Eq. (3.61).

To obtain Γ, multiply Eq. (3.57) with the total number of microstates 2^N which gives:

$$\Gamma(M, N) = \Gamma_0(N) e^{-M^2/2N} \tag{3.62}$$

where

$$\Gamma_0(N) = \frac{2^N}{(2\pi N)^{1/2}}. \tag{3.63}$$

There is a sharp peak at $M = 0$, and Γ decreases exponentially with increasing M.

In the above, we let the spins flip randomly. This was solely to calculate Γ as a function of M using the central limit theorem. When N ideal spins are isolated with energy U in an external field $\vec{H}$, the spins flip but not randomly; their total must remain fixed to satisfy Eq. (3.56).

With $\Gamma(M, N)$ in hand, let us construct macrostates for the system and examine whether or not there is a dominant one. As we did for ideal gases, we construct macrostates according to the way magnetization and energy are distributed in the system. Thus divide the spins into two groups, A and B. There are N_A spins in A and $N_B = N - N_A$ spins in B. We give the system a total energy of $U = -mMH$ and then isolate it. Since it is isolated, the energy and the total magnetization remain fixed. The total number of microstates may be written as

$$\Gamma_{AB}(M,N) = \sum_{M_A} \Gamma_A(M_A,N_A)\Gamma_B(M-M_A,N_B), \tag{3.64}$$

where each term defines a different macrostate. Let us find the largest one and see whether it dominates. By partially differentiating the summand with respect to M_A, we identify the largest term or the largest macrostate as corresponding to

$$\begin{aligned} \hat{M}_A &= \frac{N_A M}{N_A+N_B}, \\ \hat{M}_B &= \frac{N_B M}{N_A+N_B}. \end{aligned} \tag{3.65}$$

In the largest macrostate, the magnetization is divided between the two parts according to the spin numbers.

Now we let M_A deviate from $\hat{M}$ to

$$M_A = \hat{M}_A + \delta, \quad M_B = \hat{M}_B - \delta, \tag{3.66}$$

and find out how the size of the smaller macrostate decreases with increasing δ. Using Eq. (3.62), we find

$$\Gamma_{AB}(\delta) = \Gamma_A(\hat{M}_A+\delta)\Gamma_B(\hat{M}_B-\delta) = \Gamma_{mx}\exp\left(-\frac{\delta^2}{2N_A}-\frac{\delta^2}{2N_B}\right), \tag{3.67}$$

where Γ_{mx} is the size of the largest macrostate corresponding to $M_A = \hat{M}_A$ and $M_B = \hat{M}_B$. Let $N_A = N_B = 10^{23}$, and try $\delta = 10^{12}$. The ratio of this term to Γ_{mx} is e^{-10} or $10^{-3.343}$. If we checked the system 22,026 times, we would have some chance of seeing the system visit this macrostate. But $\delta/N_A = 10^{-9}$, which says that the deviation is no more than one spin flipped to the "wrong" direction out of 10^9 spins, which is hardly much of a deviation. Ignoring such macrostates does no harm. For $\delta > 10^{12}$, the corresponding macrostates are so small compared to the largest one that there is no point bothering with them.

Thus the story is the same for spins as for ideal gases. We can represent the equilibrium state with the largest macrostate and ignore the rest.

3.15 The Temperature of Spins

The temperature of ideal spins in an external magnetic field has something unique which cannot be found in molecular systems. To see this, write the entropy using Eq. (3.62) as follows

$$S(M,H,N) = k_B \left\{ \ln \Gamma_0(N) - \frac{M^2}{2N} \right\} \tag{3.68}$$

or by using Eq. (3.56)

$$S(U,H,N) = k_B \left\{ \ln \Gamma_0(N) - \frac{U^2}{2Nm^2H^2} \right\}. \tag{3.69}$$

Examine how entropy changes with energy here. M ranges between $+Nm$, which occurs when all the spins are up, and $-Nm$, which occurs when all the spins are down. The energy is therefore limited between $-mNH$ and $+mNH$. As the energy increases from the lowest possible value $-mNH$, entropy increases reaching its maximum when $U = 0$. As U further increases into its positive region, entropy decreases, as depicted in Fig. 3.4. Let us explore this anomalous relationship between entropy and energy.

Differentiating Eq. (3.69) with respect to U, the temperature is given by

$$\frac{1}{T} = -\frac{k_B U}{Nm^2H^2}, \tag{3.70}$$

which becomes negative when U is positive. The negative temperature simply means that entropy decreases with increasing energy or that the system can actually increase its entropy by losing energy. As the energy increases from the lowest possible value $-mNH$ to $U = 0$, the temperature increases from $+0$, reaching $+\infty$ when $U = 0$. Once U enters its positive range, the temperature starts from $-\infty$ and then increases, reaching $T = -0$ when U reaches mNH. There are therefore four limit temperatures. In order of increasing U, they are: $+0$, $+\infty$, $-\infty$, -0.

Are the four limit temperatures listed in order of increasing "hotness" as well? If B is hotter than A, it means that if A and B come into thermal contact, B will be the donor of energy. Assume that A is a normal thermal

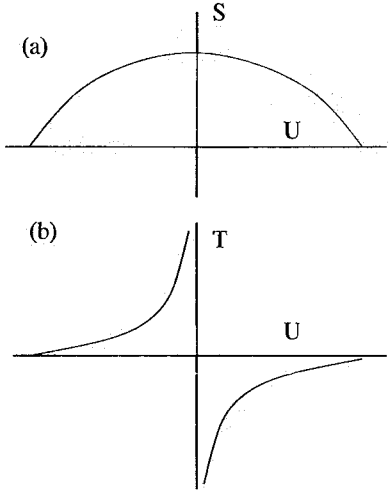

Fig. 3.4 Figure (a) depicts the relationship between entropy and energy while that in (b) depicts the relationship between temperature and energy.

system like an ideal gas while B is a spin system at a negative temperature. If A and B are brought into thermal contact, which one should be the donor of energy? The answer is clear: B should be the donor. This is true, no matter how high A's temperature is as long as it is positive. When B gives energy to A, it is not just A that benefits in terms of entropy; B also increases its entropy by doing so. What a happy situation! Thus the spin system at a negative temperature is always the donor which means that it is actually "hotter" than even the normal system at $T = +\infty$! Therefore, the answer to the question is "yes", and the spin system at $T = -0$ is at the hottest temperature. There is no significant physical difference between $T = +\infty$ and $T = -\infty$ for the spin system; the spin system only needs to lose an infinitesimal amount of energy to "cool" its temperature from $T = -\infty$ to $T = +\infty$.

For a real laboratory spin system driven into the negative-temperature region, one does not actually need another normal system to cool it down to a positive temperature. The crystal lattice has a vibrational mode of energy for which the N-particle energies have no limit and therefore the temperature is always positive.

Finally, return to Eq. (3.68) and regard the entropy as a function of M, H and N, and differentiate it with respect to M. Then combine the result with Eqs. (3.56) and (3.70) to obtain

$$\frac{\partial S}{\partial M} = -\frac{k_B M}{N} = -\frac{mH}{T}. \tag{3.71}$$

Comparing this with Eq. (3.36) of an ideal gas, it is clear that M is to spins what V is to an ideal gas, and $-mH$ is to spins what pressure P is to an ideal gas.

The example of negative temperature illustrates how sound the definition of temperature is. It applies to all systems regardless of whether the constituent elements are wiggling (the usual perception of temperature) or not.

Exercise *Suppose that we have N parking spots each of which can be occupied by a student's car or by a professor's car. Assuming that N is very large, what is the multiplicity of accommodating n students and $N - n$ professors? How does the entropy associated with these arrangements change with n?*

Exercise *Suppose that we are raising funds to promote thermal physics. We have N potential donors each of whom may donate 0, 1, 2, 3, $\cdots$ or as much as ∞ dollars. What is the multiplicity of raising n dollars from this group? How does the entropy change with n? This is a difficult counting problem, but we will need to know the answer for a real physics problem in Sec. 4.10. For a trick, examine carefully*

$$\left(\frac{1}{1-t}\right)^N = \left(\sum_{s=0}^{\infty} t^s\right)^N \equiv \sum_n g(N,n)t^n. \tag{3.72}$$

The multiplicity that we seek is given by $g(N,n)$. To obtain $g(N,n)$, differentiate $\sum_n g(N,n)t^n = [1/(1-t)]^N$ n times and then set $t = 0$, which

gives

$$g(N,n) = \frac{(N+n-1)!}{n!(N-1)!} \tag{3.73}$$

Exercise *There is a significant problem which we can work out using the results that we have already worked out for the Ising model. It is the one-dimensional model for a long flexible polymer chain. The chain consists of N elementary segments each of length l. The end-to-end length L can only be Ml where M is an integer less than N. Representing the macrostate of the chain with L, the counting for Γ is essentially the same as for the Ising spins. Draw the first segment starting from the coordinate origin. The next one can either be directed forward or be folded backward, and likewise for the third and the others. In this one-dimensional world, L plays the role of volume, and the tension plays the role of pressure. The exercise is to calculate the multiplicity as a function of L, the entropy, and then the tension $f/T = -\partial S/\partial L$. Observe that the tension increases with L as we know from rubber bands, and most interestingly, it increases with temperature!*

Chapter 4

Systems in Contact with a Thermal Reservoir

4.1 Introduction

So far we have studied isolated thermal systems. We are now ready to move on to study thermal systems exposed to the atmosphere or other forms of thermal reservoirs with which the system can exchange energy. Since the combined system, namely, the system of interest plus the reservoir, is isolated from the rest of the Universe, the fundamental postulate still guides the thermal behavior of the combined system. But we only wish to study the system of interest without getting involved with the microscopic details of the reservoir. Could this be too much to ask?

To what extent should the reservoir influence the thermal behavior of the system? When the combined system (the system plus the reservoir) is in equilibrium, the total energy should be distributed more or less uniformly throughout both the reservoir and the system, as we argued in Chap. 3. Then, since the reservoir is so much larger than the system, it should always hold the bulk of the total energy and therefore maintain a fixed temperature. The energy in the system is no longer fixed because energy may flow out of the reservoir into the system or into the reservoir from the system. The fundamental thermodynamic equation still holds but only for the combined system. The same is also true for the fundamental postulate and the maximum entropy principle. Thus the big question is: what do the system and the reservoir do to maximize the total entropy of the combined system? Could it be that the system may still remain lost among its own microstates? If not, is there a certain recipe that the system may follow to do its part to help maximize the total entropy?

The fundamental postulate and the fundamental thermodynamic equation served us well for isolated thermal systems. But even for isolated systems, everything was not as rosy as we may have painted. The fundamental thermodynamic equation states that the energy of an isolated system is a function of S, V, and N. Among the three variables, entropy is the most difficult to control. This is so not only in the laboratory but conceptually as well. It is therefore desirable to work with another function, if there is one, for which entropy is not one of the independent variables. As far as isolated thermal systems are concerned, there is no other function to work with. No matter how inconvenient the situation may be, we cannot get rid of entropy because it is the heart of thermal physics; without it there is no thermal physics. For systems in thermal contact with a reservoir, on the other hand, it turns out that we have legitimate grounds for asking for another function to work with. This does not mean that we can completely get rid of entropy. We will be able to work with a different "energy-like" function for which entropy is not one of the independent variables. Entropy can be calculated from the energy-like function if we wish, and of course we do. We have a lot to find out in this chapter. Let us begin.

4.2 Helmholtz Free Energy

A simple idea attributed to Legendre provides the function that we are searching for. From a function $f(x,y)$, we can switch to $g(u,y)$ where the unwanted variable x is replaced by $u = (\partial f/\partial x)_y$. The procedure is simple:

$$g(u,y) = f(x,y) - ux. \tag{4.1}$$

Now differentiate g to obtain

$$dg = v\,dy - x\,du, \tag{4.2}$$

which shows that g is indeed a function of u and y. Here $v = (\partial f/\partial y)_x$. So we do have the option of removing entropy, but then we have no choice but to introduce $(\partial U/\partial S)_{V,N} = T$ as a new variable. This is what we wanted because T is determined by the reservoir and we do not wish to know any thing about the reservoir except that it maintains a constant temperature. The new energy-like function that we wish to have is

$$F = U - TS, \tag{4.3}$$

which is called the Helmholtz free energy. So far this is all mathematics. We shall examine what the entropy principle says about it.

4.3 The Minimum Free Energy Principle

Let us write the total entropy of the combined system as follows

$$S_{R+s}(U_R, U_s) = S_R(U_R - U_s) + S_s(U_s), \tag{4.4}$$

where the subscript symbol s represents the system and R the reservoir. A total amount of energy U_R is to be shared between the reservoir and the system, and Eq. (4.4) represents what the total entropy of the combined systems would be if the reservoir allowed the system to have energy U_s. Let us now find out what the maximum entropy principle says about the idea of the reservoir sharing energy with the system. Assume that both the reservoir and the system are normal in the sense that entropy is a monotonically increasing function of energy. The two terms on the right side of Eq. (4.4) are then in competition: maximizing S_s requires a large U_s while maximizing S_R requires a large $U_R - U_s$ or a small U_s. We appear to have here a delicate optimization problem.

Since $U_R \gg U_s$, we may safely approximate the reservoir term in Eq. (4.4) with the first two terms of the Taylor series to obtain

$$\begin{aligned} S_{R+s}(U_R, U_s) &= S_R(U_R) + \left(\frac{\partial S_R}{\partial U_R}\right)(-U_s) + S_s(U_s) \\ &= S_R(U_R) - [U_s/T - S_s], \end{aligned} \tag{4.5}$$

where we recognize $U_s/T - S_s = F/T$. Notice that the two extensive variables appearing in F/T are both those of the system. This means that we can enforce the maximum entropy principle by simply minimizing the Helmholtz free energy of the system without having to know anything about the reservoir except that it maintains a fixed temperature. In this way, the maximum entropy principle of the combined system is transformed into a minimum free energy principle of the system.

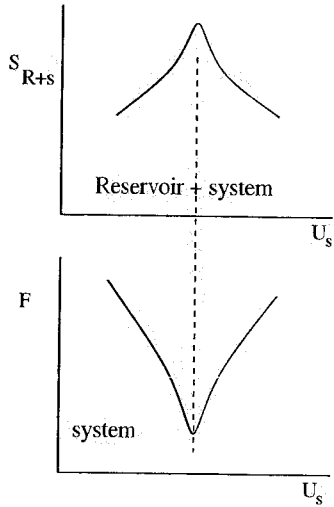

Fig. 4.1 The top figure shows the total entropy of the combined system vs. the system energy U_s while the bottom figure shows the free energy of the system vs. U_s. The two figures are equivalent.

Let us examine Eq. (4.5) and clarify the two terms in F/T. The first term U_s/T comes from the reservoir and represents the entropy that the reservoir loses by allowing the system to have energy U_s. It is the price in entropy that the reservoir pays for sharing the energy with the system. The second term S_s, on the other hand, represents the entropy contribution that the system is able to offer in return thanks to the energy U_s it is given. Thus F/T is the net cost, which is why F should be minimized. Figure 4.1 depicts how the maximum entropy principle is transformed into the minimum free energy principle.

In Eq. (4.4), we speak of a specific value of reservoir energy $U_R - U_s$ and a specific value of system energy U_s as if the system and the reservoir were two disconnected systems. This is based on what we learned in

the previous chapter. There are many macrostates of the combined system corresponding to many different distributions of the total energy U_R between the reservoir and the system. Among them we only need to worry about the largest macrostate. The system energy U_s appearing in Eq. (4.4) may be regarded as the system energy in the largest macrostate. This does not mean that we will ignore the fluctuations in the system energy; U_s is actually the average energy of the system.

The free energy of the system, F, is an energy-like function for which entropy is not one of its independent variables. Entropy is therefore a quantity to be calculated from F along with pressure and chemical potential. To this end, we take a differential for F:

$$dF = dU - T\,dS - S\,dT = -S\,dT - P\,dV + \mu\,dN, \tag{4.6}$$

where the first law has been used. It follows that

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \tag{4.7}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{4.8}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}. \tag{4.9}$$

Since $F(T, V, N)$ provides a complete description of the thermodynamic state in this way, and needs to be minimized for the equilibrium states, it may be regarded as a thermodynamic potential. This will be discussed in detail in Sec. 6.3.

Exercise *When a system in thermal contact with a reservoir is pushed out of equilibrium, the three partial derivatives S, p, and μ play crucial roles in guiding the system towards its new equilibrium state. Carry out the argument which may proceed as in Section 3.9.*

4.4 The Modified Postulate and the Boltzmann Factor

In the previous section, we transformed the maximum entropy principle that applies to the combined system, i.e., the system of our interest plus the reservoir, into a minimum free energy principle that applies only to the system. We now wish to repeat this at a deeper level. The fundamental postulate states that the combined system visits every one of its microstates with equal frequency. We wish to translate this fundamental postulate which applies to the combined system into a statement which is only true of the system. Thus, we ask: how often does the system visit each of its microstates irrespective of what the reservoir does?

Since the reservoir and the system are two different systems, we may characterize the microstates of the combined system as (i, j), where i refers to the microstate of the system of interest and j the microstate of the reservoir. Let the microstate energies corresponding to i and j be E_i and $\tilde{E}_j$, respectively. Since the combined system is isolated, the total energy must remain fixed at U_R, that is,

$$E_i + \tilde{E}_j = U_R. \tag{4.10}$$

For a given microstate i for the system, all the microstates of the combined system satisfying this condition are visited with equal frequency. Therefore the frequency of the system visiting i is given by the number of the combined microstates (i, j) that satisfy Eq. (4.10), namely, the size of the macrostate of the reservoir corresponding to $U_R - E_i$, or the number of ways the reservoir can accommodate what the system wants to do,

$$f(E_i) \sim \Gamma_R(U_R - E_i). \tag{4.11}$$

Let us examine $\Gamma_R(U_R - E_i)$ in detail. It decreases quite rapidly with increasing E_i, and therefore it is wise to convert it into a more slowly changing function by taking the logarithm,

$$\begin{aligned} \Gamma_R(U_R - E_i) &= \exp[\ln \Gamma_R(U_R - E_i)] \\ &= \exp[S_R(U_R - E_i)/k_B]. \end{aligned} \tag{4.12}$$

Since $U_R \gg E_i$, the reservoir entropy $S_R(U_R - E_i)$ may be approximated with the first two terms of its Taylor series

$$\begin{aligned} S_R(U_R - E_i) &= S_R(U_R) + \left(\frac{\partial S_R}{\partial U_R}\right)(-E_i) \\ &= S_R(U_R) - E_i/T. \end{aligned} \tag{4.13}$$

Substituting Eq. (4.13) into Eq. (4.12), we find

$$\Gamma_R(U_R - E_i) \sim \exp[-E_i/k_B T], \tag{4.14}$$

where the first term of Eq. (4.13) has been dropped because it is a constant independent of E_i which we do not have to display in a proportionality statement. The frequency of the system visiting its microstate i is therefore

$$f(E_i) \sim \exp[-E_i/k_B T], \tag{4.15}$$

where $\exp(-E_i/k_B T)$ is called the Boltzmann factor. This result again shows that we do not have to know anything about the reservoir except that it maintains a constant temperature T.

Finally, converting the proportionality relationship into an equality relationship, we may write

$$f(E_i) = \exp[-E_i/k_B T]/Z, \tag{4.16}$$

where the normalization factor

$$Z = \sum_i \exp[-E_i/k_B T] \tag{4.17}$$

is called the partition function. The fundamental postulate for the combined system has been transformed into the following statement which involves only the system. **The system visits each microstate with a frequency proportional to the Boltzmann factor.** For the purpose of reference, this will be called the modified postulate. Apparently this is what the system actually does, but from the macroscopic point of view of thermodynamics, it appears as if the system is trying to minimize its free energy. Or conversely, we may state that this is what the system has to do

in order to minimize its free energy. The visiting frequency is substantial for all states up to k_BT, but drops off quite rapidly for $E_i > k_BT$. Since we will often have to write the Boltzmann factor, let us write it as $\exp(-\beta E_i)$ where $\beta = 1/k_BT$. This also facilitates the idea of Eq. (2.20) in Chapter 2.

We may take the average of the energies of the visited microstates according to the frequency of visits as follows:

$$< U >= \sum_i E_i \exp[-\beta E_i]/Z, \tag{4.18}$$

which may be rewritten as

$$\begin{aligned} < U > &= \frac{1}{Z}\frac{\partial Z}{\partial(-\beta)} \\ &= k_BT^2\frac{\partial}{\partial T}(\ln Z). \end{aligned} \tag{4.19}$$

The average energy $< U >$ may be identified with what we called U_s in the previous section.

Let us now try to relate F to Z. Since we have already related energy to Z, we may start from

$$\begin{aligned} < U > &= F + TS \\ &= F - T\frac{\partial F}{\partial T} \\ &= T^2\left(\frac{F}{T^2} - \frac{1}{T}\frac{\partial F}{\partial T}\right) \\ &= T^2\frac{\partial}{\partial T}\left(\frac{-F}{T}\right). \end{aligned} \tag{4.20}$$

Comparing the last line with Eq. (4.19), the free energy F may be identified with $-k_BT\ln Z$. In other words,

$$Z = \exp[-\beta F]. \tag{4.21}$$

Thus if we know Z, we have in hand everything we want to know about the thermal behavior of a system. Equation (4.21) may be regarded as

connecting the microscopic world which we specify with microstates and the macroscopic world which we describe with F.

Entropy was introduced originally for isolated systems to reflect the number of accessible microstates. The fundamental postulate states that an isolated system visits its microstates with equal frequency. Since systems do not visit all of their microstates with equal frequency when they are in thermal contact with a reservoir, can we construct a new notion of entropy appropriate for the revised fundamental postulate? Because we have just identified F in terms of Z, entropy is not actually anything for us to construct here. It can only be what Eq. (4.7) gives, and Eq. (4.7) gives

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\ &= k_B \sum_i [\ln Z + \frac{E_i}{k_B T}] \frac{\exp(-E_i/k_B T)}{Z} \\ &= -k_B \sum_i f(E_i) \ln f(E_i). \end{aligned} \tag{4.22}$$

As a consistency check, substitute Eq. (4.16) for f along with $Z = \exp(-\beta F)$ into Eq. (4.22). The result is:

$$S = (-F + < U >)/T. \tag{4.23}$$

The relationship between the entropy given by Eq. (4.22) and the free energy we identified as $-k_B T \ln Z$ is the same as that between the entropy S_s we associated in the previous section with U_s and the free energy we introduced there as the net entropy cost. With $< U >$ identified as U_s, this means that the entropy given by Eq. (4.23) is the same as $k_B \ln \Gamma_s(U_s)$. This is remarkable because Eq. (4.22) refers to all microstates of different energies while the latter, $k_B \ln \Gamma_s(U_s)$, only refers to those of energy U_s. It again shows that although the system visits all macrostates, we can still meaningfully single out one value of energy and one macrostate which dominates over the rest. We will further discuss this point later.

In the meantime, I would like to make sure that you are convinced that Eq. (4.22) does give the only correct description of entropy for systems in contact with a thermal reservoir. I will do so by having you consider a plausible and seemingly logical idea of entropy and then argue why it must

be rejected. I shall argue as follows. It is true that these systems do not visit their microstates with equal frequency. However, we can still proceed in the same spirit as we did for isolated systems; we can still count the microstates but weigh each count according to the frequency with which the system visits it. The weighted sum is none other than the partition function Z. Since Z is to the present systems what Γ is to isolated systems, and since $S = k_B \ln \Gamma$ for isolated systems, it seems logical to say that entropy should be given by $k_B \ln Z$ for the present systems. Entropy thus defined would, however, be inconsistent with F because the logarithm of Z does not give entropy; instead it gives the free energy F. The idea sounded logical but has to be rejected.

Rather, we should say that the role played by $\ln \Gamma$ for isolated systems is played by $\ln Z$ for the present system. Indeed, $\ln \Gamma$ gives the entropy whose "maximum" principle guides isolated systems, while $\ln Z$ gives the free energy whose "minimum" principle guides systems in thermal contact with a reservoir. The change from "maximum" to "minimum" is not significant; had we defined the free energy as the net gain rather than the net cost, we would be speaking of a maximum free energy principle instead of the minimum free energy principle. Bearing that in mind, look at Eq. (4.22). It is a weighted sum, but the logarithm is taken for each weighted count of the microstates before they are summed. This should sound just as "logical" as the false idea we just dispelled above.

Moreover, Eq. (4.22) may be applied to isolated systems as well as to those in contact with a thermal reservoir. For isolated systems, the sum is limited to the particular value of energy that the isolated system has, and the visiting frequency of each microstate is $f_i = 1/\Gamma$, and therefore $\ln f_i = -\ln \Gamma$. Substituting these values into Eq. (4.22), we find $S = k_B \ln \Gamma$. Thus Eq. (4.22) may be regarded as a generalized definition of entropy.

4.5 Entropy as a Measure of Disorder

There is a description of entropy and the second law of thermodynamics which is very popular among the general public. According to this description, entropy is a measure of **disorder** and nature tends to change irreversibly from an ordered state to a more disordered state. The usual examples given include the way unruly children mess up neatly ordered chairs in their classroom and the way monkeys might mess up a well ordered li-

brary catalogue. This description associates disorder with a state of affair which can be realized in many different ways, that is, a large number of microstates, and it associates order with a state of affair which can be realized only in a small number of ways, that is, a small number of microstates. According to the film "Amadeus", Mozart effectively said that there is in fact only one way to compose an opera based on the story of Marriage of Figaro, namely, the way he composed it. In other words, there is only one microstate which achieves the maximum musical order possible for the story. To the emperor who ordered Mozart to change the composition, he said, "Your Majesty, it cannot be changed because it is perfect". Likewise, there are fewer ways to arrange chairs in straight lines than there are to arrange them in crooked lines or with no geometrical pattern whatsoever.

This is not, however, how the average person thinks of disorder. Most people assume that if things are left to themselves, they will tend towards a state of confusion and chaos, and therefore for the worse. This is totally inappropriate for molecules and spins. Recall the "orderly" manner in which molecules direct their traffic of energy flow, for example, when we disrupt them by adding an excessive amount of energy to a certain region. When the same type of circumstances arise for humans with, say, gridlocked cars in one area, we need traffic-control officers, but molecules do not. Even for human affairs, who is to say that crooked lines are necessarily worse than straight lines, or that the absence of a prominently visible geometric pattern necessarily means artistic disorder? In the case of the monkey and the library cards, I would challenge the perception even more firmly. Suppose that the monkey mixed the cards for thermal physics books with those for sociology. Perhaps the monkey saw a connection between thermal physics and sociology and wanted to say that sociology is a highly sophisticated kind of thermal physics.

This is typical of the confusion which arises when a scientific term defined with a specific meaning is taken in the context of words used in our daily life. We just poked fun at it. The term "disorder" was introduced by Shannon with the following specific meaning in his information theory. Suppose that we are to make a decision based on several pieces of information we have been given. When the information is incomplete, as is often the case, it is helpful if the uncertainty or poverty of information can be quantified. This is the purpose of Shannon's information theory. He introduces the term "disorder" as a measure of incompleteness of the given information. For example, suppose that a message written by someone for

you to tell you his favorite subject in physics has been muddied and you can only tell that the message has 14 letters and one space. A man is trapped in a burning house and the firefighter needs to decide which room he should try first. The only information the firefighter has is that there are N rooms in the house. Shannon constructs the measure to meet all conceivable criteria. In the example of the firefighter, the measure should increase with N. Should the firefighter be given a further piece of information, say, that the man spends approximately half his time in the kitchen, the measure should reduce significantly. If he is told the precise room in which the man is trapped, the measure should reduce to zero. Shannon argues that the best definition of disorder which meets these and other criteria that he demands is:

$$\text{Disorder} = -C \sum_i f_i \ln f_i, \tag{4.24}$$

where C can be any positive constant, and f_i is the likelihood of "microstate" i. For the muddied message, one possible microstate is the words "thermal physics". For the man trapped in the burning house, one microstate is his being in his bedroom. Thus Eq. (4.24) is essentially the same as Eq. (4.22).

4.6 Canonical Ensembles

When a system is in contact with a thermal reservoir, the system and the reservoir play different roles to maximize the entropy of the combined system. The system has to minimize its free energy. To this end, the system can no longer remain lost among its microstates. Instead it has to visit its microstates discriminately according to their Boltzmann factors. The reservoir, on the other hand, maintains a fixed temperature for the system.

Let us construct the appropriate ensemble method to carry out this recipe. Since the system now visits each of its microstates with different frequencies, we need to replicate the system for each microstate as many "times" as the frequency of visit. Although the Boltzmann factor $\exp(-E_i/k_BT)$ is not an integer, think of it as the number of replicas that represents microstate i. The equilibrium average of quantity A is then given

by

$$< A >= \sum_i A(i) \exp(-E_i)/Z, \tag{4.25}$$

where Z may now be regarded as the total number of replicas over which the average is taken, and $A(i)$ is what A takes on when the system is in microstate i. It is important to recognize that the index i represents the microstates; each of the degenerate microstates corresponding to the same value of energy has the same representation in the ensemble with the same number of replicas. The ensemble of replicas constructed in this way for systems in thermal contact with a reservoir is called the canonical ensemble. Like the microcanonical ensemble, they are replicas of the same system but frozen in different microstates. Think of the ensemble of replicas as the Congress of the molecular world. In the microcanonical ensemble, each microstate sends one representative to Congress. In the canonical ensemble, each microstate can send more than one representative depending on its Boltzmann factor; the larger the Boltzmann factor is, the larger is the delegation. In Sec. 10.2, we will actually find a way to construct such an ensemble.

We will carry out the two ensemble methods with Ising spins in Sec. 4.6.1 and with ideal gas molecules in Sec 4.7. This will give us a chance to check the results of the central limit theorem which we worked out earlier. There is actually a more important purpose in doing this. In order to introduce the notion of free energy, we argued earlier that although a system in thermal contact with a reservoir visits all microstates of different values of energy, we may still pick up a single value of energy and then using the entropy associated with it we may define the free energy. We adopted essentially this sort of idea for isolated systems, namely, that although the system visits all macrostates we may select just one and ignore the rest. By comparing the predictions of the two ensemble methods, we can effectively test this important idea which will resurface again and again.

4.6.1 *Ising Model in a Microcanonical Ensemble*

In microcanonical ensemble, the energy is first given and then the temperature is determined according to the multiplicity that the energy allows. Out of N total spins, suppose that N_{up} spins are up and $N - N_{\text{up}}$ spins

are down. It is convenient to express everything, M, U, and S in terms of N_{up}. We have

$$M = N_{\text{up}} - (N - N_{\text{up}}) = 2N_{\text{up}} - N, \tag{4.26}$$

and

$$U = -mH(2N_{\text{up}} - N). \tag{4.27}$$

Since N_{up} does not ask which spins are up and which are down, N_{up} has a large number of multiplicity. Let us calculate it directly without using the central limit theorem. The multiplicity is given by

$$\Gamma(N_{\text{up}}) = \frac{N!}{N_{\text{up}}!(N - N_{\text{up}})!}. \tag{4.28}$$

Assuming that N, N_{up} and $N - N_{\text{up}}$ are all large, we approximate the three factorials using the Stirling formula to obtain

$$\begin{aligned} S(N_{\text{up}}) &= k_B \ln \Gamma(M) \\ &= N \ln N - N - N_{\text{up}} \ln N_{\text{up}} \\ &\quad - (N - N_{\text{up}}) \ln(N - N_{\text{up}}). \end{aligned} \tag{4.29}$$

Strictly speaking, when N_{up} is near N this is a rather rough approximation, but as we have already seen, we can get away with big errors for Γ. Temperature can be calculated as follows.

$$\begin{aligned} \frac{1}{T} &= \frac{\partial N_{\text{up}}}{\partial U} \left(\frac{\partial S(N_{\text{up}})}{\partial N_{\text{up}}} \right) \\ &= \frac{k_B}{2mH} \ln \left(\frac{N + M}{N - M} \right), \end{aligned} \tag{4.30}$$

where we used Eq. (4.26) to express the final result in terms of M. Equation (4.30) can be solved for M to give

$$M = N \frac{\exp(2mH/k_B T) - 1}{\exp(2mH/k_B T) + 1}$$

$$= N \tanh(mH/k_BT), \tag{4.31}$$

and

$$U = -mHN \tanh(mH/k_BT). \tag{4.32}$$

According to Eq. (4.31), the magnetization is small when mH/k_BT is small. When mH/k_BT is small, $\tanh(mH/k_BT) \approx mH/k_BT$, and Eq. (4.32) reduces to Eq. (3.70).

4.6.2 *Ising Model in a Canonical Ensemble*

In the canonical ensemble, the temperature T is first given, and from it, we calculate the average energy $< U >$. Let us now assume that the same spin system is in contact with a thermal reservoir at temperature T and calculate the average energy.

The microstate energies may be written as

$$E_{s_1,s_2,s_3,\ldots,s_N} = -(s_1 + s_2 + s_3 + \cdots + s_N)mH, \tag{4.33}$$

and the partition function as

$$\begin{aligned} Z &= \sum_{s_1,s_2,s_3,\ldots} e^{(s_1+s_2+s_3+\cdots)\beta mH} \\ &= \left(e^{\beta mB} + e^{-\beta mH}\right) \sum_{s_2,s_3,\ldots} e^{(s_2+s_3+\cdots)\beta mH} \\ &= \left(e^{\beta mH} + e^{-\beta mH}\right)^N . \end{aligned} \tag{4.34}$$

With Z in hand, we can calculate $< M >$ and $< U >$ via

$$\begin{aligned} < M > &= \sum_{s_1,s_2,s_3\ldots} (s_1 + s_2 + s_3 + \cdots)e^{(s_1+s_2+s_3+\cdots)\beta mH}/Z \\ &= \frac{1}{Z}\frac{\partial Z}{\partial(\beta mH)} \\ &= N \tanh(\beta mH). \end{aligned} \tag{4.35}$$

and

$$
\begin{aligned}
< U > &= \frac{1}{Z} \sum_{s_1, s_2, s_3 \ldots} -(s_1 + s_2 + s_3 + \cdots) mH e^{(s_1+s_2+s_3+\cdots)\beta mH} \\
&= \frac{-1}{Z} \frac{\partial Z}{\partial \beta} \\
&= -NmH \tanh(\beta mH),
\end{aligned} \tag{4.36}
$$

in agreement with Eq. (4.32). The two ensemble methods give the same result.

Finally, the free energy may be obtained from Eq. (4.34) with the result

$$
F = -k_B T \ln(e^{\beta mH} + e^{-\beta mH}). \tag{4.37}
$$

4.7 Ideal Gas in a Canonical Ensemble

Let us now repeat for the ideal gas what we did above for the ideal spins, and confirm that the two ensemble methods give the same result for the ideal gas as well. To calculate the partition function of an ideal gas, write the N-particle microstate energies in the form of

$$
E_\nu = \sum_{n_{ix}} \sum_{n_{iy}} \sum_{n_{iz}} \alpha^2 (n_{ix}^2 + n_{iy}^2 + n_{iz}^2), \tag{4.38}
$$

where n_{ix}, n_{iy}, and n_{iz} can be any positive integer including zero, and

$$
\alpha^2 = \left(\frac{\hbar^2}{2m}\right) \left(\frac{\pi}{V^{1/3}}\right)^2. \tag{4.39}
$$

The single particle microstate energy may then be written as

$$
\epsilon_n = \alpha^2 n^2, \tag{4.40}
$$

where $n^2 = n_x^2 + n_y^2 + n_z^2$, and $n_x = 0, 1, 2, \ldots$, and likewise for n_y and n_z.

4.7.1 *With One Molecule*

We should begin with the thermal system consisting of one molecule. Then the partition function is given by

$$Z_1 = \sum_{n_x,n_y,n_z} \exp(-\epsilon_n/k_BT) = \sum_{n_x}\sum_{n_y}\sum_{n_z} \exp[-\alpha^2(n_x^2+n_y^2+n_z^2)/k_BT]. \tag{4.41}$$

Let us assume that k_BT is much larger than α^2 and replace the three sums with Gaussian integrals. We find that

$$\begin{aligned} Z_1 &= \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \exp[-\alpha^2(n_x^2+n_y^2+n_z^2)/k_BT] \\ &= \left(\frac{1}{2}\right)^3 \left(\frac{\pi}{\alpha^2/k_BT}\right)^{3/2} \end{aligned} \tag{4.42}$$

First, notice that the contributions from the three integrals are factorized out. In general, contributions from different and unrelated modes of energy are partitioned into products. Second, examine what the Boltzmann factor has done for Eq. (4.42). All single particle orbitals enter into the sum, but the Boltzmann factor cuts the spectrum off at the upper end starting approximately from

$$n_c = \sqrt{k_BT/\alpha^2}. \tag{4.43}$$

Roughly speaking, the larger the n_c is, the more single-particle states are included in the partition function. We assume, as we effectively did previously for Eq. (4.42), that n_c is large.

4.7.2 *With N Molecules*

Now we are ready to consider N identical ideal molecules. If we tag the molecules and treat them for a moment as if they were distinguishable from one another, then the N-particle partition function turns into a product of N single particle partition functions,

$$Z^{(1)} \times Z^{(2)} \times Z^{(3)} \cdots \tag{4.44}$$

where $Z^{(1)} = Z^{(2)} = Z^{(3)} = \cdots = Z_1$. We have calculated the partition function at a lightning speed, which was why we wanted to tag the molecules, but we have to pay a price: Eq. (4.44) puts all molecules indiscriminately in single-particle orbitals, resulting in an overcounting error.

Let us explore the nature of the error in some detail so that we may correct it. Let us look at what Eq. (4.44) does explicitly:

$$\begin{aligned}
&\{\exp(-\epsilon_1/k_BT) + \exp(-\epsilon_2/k_BT) + \exp(-\epsilon_3/k_BT) + \cdots\} \times \\
&\{\exp(-\epsilon_1/k_BT) + \exp(-\epsilon_2/k_BT) + \exp(-\epsilon_3/k_BT) + \cdots\} \times \\
&\{\exp(-\epsilon_1/k_BT) + \exp(-\epsilon_2/k_BT) + \exp(-\epsilon_3/k_BT) + \cdots\} \times \\
&\cdots
\end{aligned} \tag{4.45}$$

where the first bracket represents $Z^{(1)}$ for the first molecule, the second bracket $Z^{(2)}$ for the second molecule, and so on. All the single-particle energies appearing here are assumed to have survived the cuts by the Boltzmann factor. When the brackets are opened up, Eq. (4.45) consists of many terms, each of which looks like

$$\begin{aligned}
A &= \exp(-\epsilon_{46}/k_BT)\exp(-\epsilon_3/k_BT)\exp(-\epsilon_{17}/k_BT), \ldots \\
&= (46, 3, 17, \ldots),
\end{aligned} \tag{4.46}$$

which says that the first molecule is in the 46th orbital, the second molecule in the 3rd orbital, the third in the 17th orbital, and so on. This is one of many N-particle microstates counted by Eq. (4.44). In addition to A, Eq. (4.44) also counts microstates such as

$$B = (3, 17, 46, \ldots), \tag{4.47}$$

which is the same as A except that the first three registries have been swapped around while keeping the rest as they are in A. As we may see by writing B like the first line of Eq. (4.46), B does not constitute a microstate different from A. Counting such terms in addition to A constitutes an overcounting error. How many times does Eq. (4.44) overcount A in this way? That depends on the registries in A. If they are all different from each other, then A is overcounted $N!$ times. As another example, if the other registries not explicitly shown in A and B are all, say, 8, then A is

overcounted 3! times. Thus the overcounting error is different depending on whether all the registries in A are different or include some orbitals more than once. Under these circumstances, the best we can do is to assume that the overwhelming majority of the N-particle microstates fall into the former category, and try to see if we may justify the assumption under a certain easily realizable condition.

The assumption that the majority of the single-particle states surviving the Boltzmann cut are all different from one another may be justified if the cutoff n_c is large. In fact we assumed this condition for Eq. (4.42) before we worried about overcounting. If the number of surviving orbitals is much larger than N, then there are far more orbitals than there are molecules to populate them. The chances of any single-particle orbital appearing more than once would be very slim.

With this in mind, let us examine the cutoff. According to Eqs. (4.43) and (4.39), n_c is large when the temperature is very high, or when the volume is very large (low density), or when the mass is very large. In the meantime, what does a large n_c mean? To find an answer, return to Eq. (3.41) where U is the total kinetic energy of all molecules. It says that the kinetic energy per molecule is proportional to k_BT. Thus we may replace k_BT in Eq. (4.43) with mv^2 where v is the root-mean-squared average speed, i.e., $(\sum_i v_i^2/N)^{1/2}$. The cutoff may then be written in the following form

$$n_c \sim \left(\frac{L}{\lambda_d}\right)^2, \tag{4.48}$$

where $\lambda_d = h/mv$, the de Broglie wavelength. By assuming a large cutoff, we effectively assume that the de Broglie wavelength is negligible compared to the dimensions of the box, i.e., $L \gg \lambda_d$. Then all quantum mechanical effects should disappear leaving the system in the classical regime. That is exactly what we were hoping for, but we did not have the luxury to ask for it. Such luck!

In the classical regime, the N-particle partition function is therefore given by

$$Z = \frac{Z_1^N}{N!}. \tag{4.49}$$

Substituting Eq. (4.42) into Eq. (4.49), we find

$$Z = \frac{1}{N!}\frac{1}{2^{3N}}\left(\frac{k_B T 2mV^{2/3}}{\hbar^2 \pi}\right)^{3N/2} \tag{4.50}$$

Upon taking the logarithm, we have for the free energy

$$F = -k_B T N \ln\left[\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} V\right] + k_B T N \ln N - k_B T N. \tag{4.51}$$

All other quantities of interest are obtained by taking the appropriate partial differentiations. The results are:

$$U = 3N\frac{k_B T}{2}, \tag{4.52}$$

$$P = \frac{Nk_B T}{V}, \tag{4.53}$$

$$S = N\left\{\ln\left[\frac{V}{N}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\right] + \frac{5}{2}\right\}, \tag{4.54}$$

$$\mu = k_B T \ln\left\{\frac{N}{V}\left(\frac{2\pi\hbar^2}{mk_B T}\right)^{3/2}\right\}. \tag{4.55}$$

These results are the same as those we obtained earlier for isolated systems. All four quantities exhibit the same temperature dependence as they do in isolated systems!

Exercise *Consider a system consisting of just one particle which can exist only in one of two states, one of energy $-\epsilon/2$ and one of energy $\epsilon/2$, where ϵ is a constant. Calculate the average energy U and the heat capacity $C = \partial U/\partial T$. Show that the heat capacity vanishes both at the high and low temperature limits with a hump in the mid range of temperature. This is called a Schottky anomaly. The vanishing heat capacity at the low temperature limit is due to the gap between the lowest (ground) state energy*

and the next one while the vanishing heat capacity at the high temperature limit is due to the absence of sufficiently high energy states comparable to $k_BT \gg \epsilon$; the reservoir provides plenty of energy, but the system cannot take it in the two limits. We will see similar examples in Secs. 4.1 and 5.4. As this example shows, we can learn a great deal about the atomic and molecular details of a system by measuring its heat capacity.

Exercise *Consider a paramagnet consisting of non-interacting magnetic dipole moments in external field $\vec{H}$. Unlike in the uniaxial ferromagnets, the dipole moments can point in any direction. The energy of a single moment $\vec{m}$ is given by $\epsilon = -\vec{m} \cdot \vec{H}$. Since there is no coupling between different moments, each moment may be treated as an independent system. The total magnetization is given by $M = Nm < cos(\theta) >$ where θ is the angle between $\vec{m}$ and $\vec{H}$. Calculate $< cos(\theta) >$ and the susceptibility $\chi = \partial M/\partial H$ in the high temperature limit. Observe that the susceptibility goes like $1/T$. This is called the Curie Law.*

4.8 Equipartition Theorem

In the case of energy, the role of temperature warrants an additional comment. Examine Eq. (4.52). All those factors entering into α, namely, m, h, and V do affect the microstate energies, but they disappear in the final expression for the average energy! This may be attributed to the fact that the mode of energy is quadratic in n, and n can be anything from zero to infinity. Each of the $3N$ Gaussian integrals has resulted in $k_BT/2$, whence Eq. (4.52). This is called the equipartition theorem. What if the molecules interact with each other? As we will discuss in Chap. 7, there is no quadratic pattern in the interaction energy and therefore the equipartition theorem does not apply to the interaction energy, but the theorem still applies to the kinetic energy part. Thus we may write as a general statement,

$$< \frac{mv^2}{2} >= \frac{3}{2}k_BT, \tag{4.56}$$

which provides us with an idea of how temperature affects molecular motions, but unfortunately many people take it as the definition of temperature which is of course quite inappropriate.

As another example, consider an RC circuit with no voltage applied. Although there is no externally applied voltage across the capacitor, there is still fluctuating charge on the capacitor due to thermal fluctuations. What would be the average energy due to this fluctuating charge? When a capacitor is charged to Q, its energy is $Q^2/2C$, a quadratic function of Q and Q can be anything from zero to infinity. The equipartition theorem gives $< Q^2/2C >= k_BT/2$. Similarly, there will be a current through an inductor even when there is no external driving voltage. The thermal energy that the reservoir provides for the thermal current is $< LI^2/2 >= k_BT/2$.

Exercise. *Consider an oscillator in equilibrium with a thermal reservoir at temperature T. The energy of the oscillator is given by $U = mv^2/2 + Kr^2/2$. What is the average energy at temperature T?*

4.9 Light

Light is all around us at all times, but because it is so different from gases and other forms of matter, it is an exotic thermal system to study. Make a cavity of dimension $L \times L \times L$ using any material and keep it at temperature T. The electromagnetic waves radiated by the wall form various standing waves in the cavity. The intensity of the radiation is distributed over all modes of frequency in a certain pattern which changes only with temperature independently of the makeup of the cavity wall. Considerable efforts were made during the early part of the 20th century to find out why, but it proved to be one of the most difficult problems that faced physicists at that time. The key to solving the puzzle was a powerful idea of Planck's, that, in order to account for the thermal behavior of the radiation in the cavity, the radiation in the cavity must be regarded as a collection of particles called photons. A photon in the mode of angular frequency ω carries energy $\hbar\omega$. There can only be an integer number of photons in each mode, not, e.g., 0.5 photon or 126.7 photons. High intensity simply means that there is a large number of photons.

Let us study the radiation as a thermal system with the cavity walls serving as a reservoir. The reservoir exchanges energy with the system by emitting photons into the cavity or by absorbing the photons from the cavity. Thus the number of photons does not remain fixed. Let us focus on the mode of radiation of angular frequency ω. The microstates of the

radiation may be indexed with the number of photons s,

$$E_s = s\hbar\omega, \tag{4.57}$$

where $s = 0, 1, 2, 3 \cdots \infty$. The partition function is given by adding the Boltzmann factors for all microstates, i.e., by adding the Boltzmann factors over all s,

$$Z = \sum_{s=0}^{\infty} \exp[-\beta\hbar\omega s] = \frac{1}{1 - \exp[-\beta\hbar\omega]}. \tag{4.58}$$

The average energy is then given by

$$U = \frac{1}{Z}\sum_s s\hbar\omega e^{-\beta s\hbar\omega} = \frac{1}{Z}\frac{\partial Z}{\partial(-\beta)} = \frac{\hbar\omega}{\exp[\beta\hbar\omega] - 1}, \tag{4.59}$$

and the average photon number by

$$< s >= \frac{1}{\exp[\beta\hbar\omega] - 1}. \tag{4.60}$$

If you have read this book this far, here is a reward for you: we can calculate the pressure of light. If a person were to try to calculate this without any knowledge of thermal physics, he would have to ask: how much momentum does a photon carry? What atoms make up the cavity wall? How does a photon interact with the atoms? We do not have to answer any of these questions. According to Eq. (4.8), all we have to ask is: does the free energy depend on the volume of the space in which the photons are confined? If the answer is yes, it takes only one stroke of differentiation to find out the pressure.

The free energy is obtained from Eq. (4.58),

$$F = k_B T \ln[1 - e^{-\beta\hbar\omega}]. \tag{4.61}$$

The only factor in this equation that may depend on volume is ω, and ω does depend on V in the following way. For this purpose, regard the radiation as a wave. The electromagnetic waves exist in the cavity as a standing wave. In order to form a standing wave, the wavelength must fit in just

right with the cavity dimensions. To sort out the conditions for a standing wave, proceed just as you did in introductory physics for a standing wave on a string of length L, but at the end, declare that the integer n is actually $(n_x + n_y^2 + n_z^2)^{1/2}$. Thus, $\lambda = 2L/n$ where $n = (n_x + n_y^2 + n_z^2)^{1/2}$. The corresponding angular frequency is then given by

$$\omega(n) = \frac{n\pi c}{L} = \frac{n\pi c}{V^{1/3}}, \tag{4.62}$$

where c is the speed of light.

Now differentiate F with respect to V. The result is:

$$P = \frac{1}{3}\frac{U}{V}. \tag{4.63}$$

Compare this with the gas pressure which may be written as $P = 2U/3V$. Suppose that photons and molecules have the same amount of energy per volume. The light exerts half as much pressure as the molecules do. Considering the fact that photons do not give us the sensation of collision that molecules do on a windy day, I would say that half is a surprisingly high fraction.

Now that we have learned about each mode of frequency, let us add all of them to calculate the total average energy over all frequencies

$$U = 2\sum_n \frac{\hbar\omega(n)}{\exp[\beta\hbar\omega(n)] - 1}, \tag{4.64}$$

where the factor 2 takes into account the fact that each mode can be polarized in two different directions. Strictly speaking, n is limited to the grid points in the (n_x, n_y, n_z) space, but since $\omega(n)$ is multiplied by $\hbar$ which is very small, the discrete sum may be converted into an integral. We should remain in the first quadrant only, but since it is symmetric, we cover all 8 quadrants and then divide the result by 8. The result for U is

$$U = \frac{2}{8}\int_0^\infty dn\, 4\pi n^2 \frac{\hbar\omega(n)}{\exp[\hbar\omega(n)/k_BT] - 1}. \tag{4.65}$$

How does the total energy or the total intensity change with the temperature? Let $x = \hbar\omega/k_BT$, and write all n's and ω's appearing in the integral

in terms of x. Then the integral may be written entirely in terms of x (the integral converges), and all the things that get pushed out of the integral include 4 factors of T, two from n^2, one from dn and one from the $\hbar\omega$ in the numerator. Thus the total energy goes like T^4 which is called the Stefan-Boltzmann law. The heat capacity therefore goes like T^3 and vanishes at the low temperature limit. The vanishing heat capacity is a result of the gap between the lowest microstate energy and the next one, a phenomenon which we saw in an exercise problem in Sec. 4.7; we will see more of it later.

Next convert the integration over n to one over ω and represent U in the form of $\int d\omega u(\omega, T)$. The result for $u(\omega, T)$ is

$$u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp[\hbar\omega/k_B T] - 1}. \tag{4.66}$$

This is the famous Planck radiation law. It has had an enormous impact in all branches of physics, most notably in astrophysics. According to Eq. (4.66), the intensity reaches a maximum at

$$\hbar\omega_{mx}/k_B T \approx 2.82. \tag{4.67}$$

If the intensity is measured over a reasonably wide range of ω to specify ω_{mx}, Eq. (4.67) gives us the temperature of the cavity. The best known example of such a measurement is that of the cosmic background radiation, namely, the remnant radiation from the Big Bang. The cavity in this case, namely the Universe, has cooled down to approximately 2.9K.

4.10 Einstein's Solid

There is another model for which calculating Z is as easy as for light. It is the Einstein model of solid. In a solid phase, atoms are arranged on lattice sites, and each atom oscillates around its site. We would then have $3N$ coupled oscillators. In the Einstein model, we disregard the coupling between the oscillators and treat each atom as executing an independent simple harmonic motion around its lattice site. According to quantum mechanics, an oscillator can only have the following amount of energy:

$$\epsilon(n) = \left(\frac{1}{2} + n\right)\hbar\omega, \tag{4.68}$$

where $\omega = (K/m)^{1/2}$, and $n = 0, 1, 2, 3, \ldots$. Since the oscillators are localized on the lattice sites, we may tag them and treat them as distinguishable objects with no concern for overcounting errors. Each microstate of N oscillators may then be indexed with

$$\nu = (n_1, n_2, n_3, \ldots, n_N), \tag{4.69}$$

where the subscripts represent the oscillator tag numbers, and the corresponding microstate energy is given by

$$E(n_1, n_2, n_3, ..., n_N) = \epsilon(n_1) + \epsilon(n_2) + \cdots + \epsilon(n_N), \tag{4.70}$$

which shows no coupling between oscillators; there are no terms like $n_1 n_5$. The partition function for the N oscillators therefore partitions into N single-oscillator partition functions,

$$Z = z_1^N, \tag{4.71}$$

where the single-oscillator partition function z_1 is given by

$$z_1 = \sum_{n_1=0}^{\infty} \exp[-\epsilon(n_1)] = \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)}. \tag{4.72}$$

Exercise *Calculate the free energy and the entropy.*

Exercise *Show that*

$$\frac{< U >}{3N} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1}, \tag{4.73}$$

and then calculate $C = \partial U/\partial T$. Observe that the heat capacity vanishes exponentially as T approaches zero. Although the exponential vanishment

is an exaggeration of the model, the vanishing heat capacity is a very typical quantum effect at low temperatures.

Exercise *We treated the Einstein solid as a thermal system in contact with a reservoir. Now treat the system as an isolated thermal system. The necessary multiplicity factor can be obtained from the "fund raising" exercise that we did at the end of Chap. 3.*

4.11 Response Functions and Fluctuations

When a system is put in contact with a thermal reservoir, its energy fluctuates. All other extensive quantities fluctuate if conditions allow, and we wish to study these fluctuations. In the human world, we are accustomed to thinking of fluctuations as something bad. If your grades fluctuate widely between A and D, we assume that you are not a steady reliable worker, which is considered bad. As a scientist, we first learn the word "fluctuation" in an introductory laboratory course to learn how to analyze error. This leaves us with a long-lasting firm impression that fluctuation has something to do with error. Nature abounds with fluctuations and that is not a result of anybody's error. Actually nature's fluctuations carry useful signatures which we are about to learn how to read.

4.11.1 *Energy*

Let us start with energy. The fluctuation is defined as

$$\begin{aligned} \delta U^2 &= <(U-<U>)^2> \\ &= <U^2> - <U>^2 . \end{aligned} \tag{4.74}$$

Since

$$<U> = \sum_i E_i \exp[-\beta E_i]/Z, \tag{4.75}$$

and

$$< U^2 >= \sum_i E_i^2 \exp[-\beta E_i]/Z, \tag{4.76}$$

it follows that

$$\delta U^2 = \frac{1}{Z}\sum_i E_i^2 \exp[-\beta E_i] - \left(\frac{1}{Z}\sum_i E_i \exp[-\beta E_i]\right)^2. \tag{4.77}$$

The two terms may be combined to yield

$$\delta U^2 = \frac{\partial < U >}{\partial(-\beta)} = k_B T^2 \left(\frac{\partial < U >}{\partial T}\right)_V = k_B T^2 C_V, \tag{4.78}$$

where C_V is the heat capacity measured with the volume held fixed. The volume was held fixed during the differentiation because the differentiation did not alter E_i.

As Eq. (4.78) shows, the fluctuation is not just a set of insignificant ripples to be averaged out. It is a useful thermodynamic quantity in its own right; $C_V = (\partial U/\partial T)_V$ is a response function. It is a response of U against a change in T. Thanks to Eq. (4.78), although the definition of C_V requires a change in temperature and the consequent change in energy, we can measure it without changing the temperature at all. Keep the temperature where it is, and just watch how the energy fluctuates. In fact, this is how C_V is measured when one performs computer simulations. Because energy and temperature enter into the Boltzmann factor as $\exp(-E_i/k_B T)$, the temperature T dictates how much energy the system should have. When the dictator changes its message with a changed T, the dictatee has to respond. Is there something that the dictator can read before changing its message to find out how favorably the dictatee will respond? Yes. It is the fluctuation of the dictated quantity U.

There is something very similar to this in the human world. Generals are supposed to defend their government, but that is not always what they do. There are some generals who wait for a chance to topple their own government. Is there a sign in the government that such a general can read to find out how favorable the result of his action will be if and when he attempts it? Yes: fluctuations in the government. The more fluctuations

there are in the stability of the government, the more vulnerable is the government to a coup.

4.11.2 *Magnetization*

Similarly, let us return to Ising spins and calculate the fluctuation in the magnetization $M = m(s_1 + s_2 + s_3 + \cdots + s_N)$:

$$\delta M^2 = < M^2 > - < M >^2, \tag{4.79}$$

where

$$< M > = \sum_{s_1, s_2, \ldots} M \exp(\beta H M)/Z, \tag{4.80}$$

$$< M^2 > = \sum_{s_1, s_2, s_3, \ldots} M^2 \exp(\beta H M)/Z. \tag{4.81}$$

Following the same steps that we followed for δU^2, we find

$$\delta M^2 = k_B T \frac{\partial M}{\partial H} = k_B T \chi, \tag{4.82}$$

where χ is a response function called the susceptibility. Suppose we apply more magnetic field. In response the spins will further align along the direction of the magnetic field, resulting in more magnetization. Equations (4.78) and (4.82) are two examples of what is known as the fluctuation-dissipation theorem. It describes a relationship between the fluctuation of a quantity and its response against changes in the "field" that dictate the quantity. We have seen twice already how such a relationship arises. To generalize, if the Boltzmann factor has a term like $\exp(Aa)$ or $\exp(A/a)$, the fluctuation of A is a measure of how A will respond if a changes. Think of a as a field which tries to dictate A. By the way, the word "dissipation" in the fluctuation-dissipation theorem is somewhat misleading in the present context. The theorem actually covers more than what we have discussed. The name "fluctuation-dissipation" comes from the non-equilibrium statistical mechanics where the time-dependent fluctuations are related to the transport coefficients of dissipating quantities.

Chapter 5

Open Systems, Flexible Systems, and Two More Energy-like Functions

5.1 Introduction

So far we have only considered closed systems with a fixed number of molecules in a fixed volume. In this chapter we will study open systems in a fixed volume but with a variable number of molecules. We will also study systems with a fixed number of molecules but in a flexible volume. To give an example of an open system, designate somewhere in your room a volume of space of $1cm \times 1cm \times 1cm$. That designated volume of space is an open system. The space is wide open and molecules can enter or leave as they please. The rest of the room may be regarded as a reservoir as it is ready to exchange both energy and molecules with the designated space. We will study such open systems in Secs. 5.2 through 5.5. Section 5.6 is devoted to systems in a flexible (variable) volume. By then we will have introduced three different free energies or energy-like functions. In Sec. 5.7, we will study energy as an energy-like function.

5.2 Open Systems and Landau Free Energy

Consider an open system in a fixed volume but consisting of a variable number of molecules. The system is in contact with a reservoir which exchanges with the system not only energy but also molecules. What is the appropriate energy-like function? Since N is not fixed, we wish to remove it from F. Since $\partial F/\partial N = \mu$, the variable to replace N with is μ, the chemical potential. The energy-like function is

$$\Omega = F - \mu N = U - TS - \mu N, \tag{5.1}$$

which is called the Landau free energy. Substituting Eq. (3.51) for U, it follows that

$$\Omega = -PV. \tag{5.2}$$

The reservoir and the system are to share N_R molecules and U_R energy; both N_R and U_R are very large. Suppose that the system claims N_s molecules and energy U_s. The system is only a small part of the combined system, and the reservoir is large enough to guarantee $N_s \ll N_R$ and $U_s \ll U_R$. In order to maximize the total entropy of the combined system, how many molecules and how much energy should the system claim? The decision should be made so as to maximize the total entropy,

$$S_{R+s}(U_R, N_R, U_s, N_s) = S_R(U_R - U_s, N_R - N_s) + S_s(U_s, N_s). \tag{5.3}$$

Since $N_s \ll N_R$ and $U_s \ll U_R$, we may expand S_R to first order in U_s and N_s to obtain

$$\begin{aligned} S_{R+s}(U_R, N_R, U_s, N_s) &= S_R(U_R, N_R) - \frac{1}{T}U_s + \frac{\mu}{T}N_s + S_s \\ &= S_R(U_R, N_R) - \left(\frac{U_s}{T} - \frac{\mu N_s}{T} - S_s\right), \end{aligned} \tag{5.4}$$

where we recognize $U_s/T - \mu N_s/T - S_s = \Omega/T$. Two observations should be made here. First, both T and μ are determined by the reservoir and do not change with U_s and N_s because $U_R \gg U_s$ and $N_R \gg N_s$. Second, the three extensive quantities appearing in Ω, U_s, N_s and S_s, are all those of the system. How should N_s and U_s be chosen? Equation (5.4) says that the total entropy of the combined system may be maximized if U_s and N_s are chosen so as to minimize Ω. We do not have to know anything about the reservoir except that it imposes a fixed temperature T and a fixed chemical potential μ on the system. Once again everything has come out the way we wanted.

Examine where the three terms of Ω/T come from. The first two terms represent the entropy cost that the reservoir pays for allowing the system to

have N_s molecules and energy U_s while the third term is what the system brings to the total entropy in return. Therefore Ω/T is the net entropy cost. The reservoir and the system conspire to minimize it.

Taking the differential for Ω, we obtain

$$d\Omega = -SdT - P\,dV - Nd\mu, \tag{5.5}$$

and

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} \tag{5.6}$$

$$P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} \tag{5.7}$$

$$N = -\left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V} \tag{5.8}$$

The appropriate variables of Ω are T, V and μ, as we wanted. Given Ω as a function of T, V and μ, we may calculate S, P, and N via the above equations.

5.3 Grand Canonical Ensemble

What is the probability that N molecules will come into the open system to occupy the microstate $E_i(N)$? Because the combined system visits all of its microstates with equal frequency, the probability in question is proportional to the number of ways the reservoir can accommodate what the N molecules want to do:

$$\begin{aligned} P[E_i(N), N] &\sim \Gamma_R[U_R - E_i(N), N_R - N] \\ &= \exp\{S_R[U_R - E_i(N), N_R - N]/k_B\}. \end{aligned} \tag{5.9}$$

Upon expanding S_R to first order in E_i and N, we may write

$$S_R = S_R(U_R, N_R) - \frac{1}{T}E_i(N) + \frac{\mu}{T}N. \tag{5.10}$$

It then follows that

$$P[E_i(N), N] \sim \exp[-(E_i(N) - \mu N)/k_B T], \tag{5.11}$$

which is called the Gibbs factor. To normalize it for all microstates of all number of molecules, the normalization factor takes the form of

$$\Xi = \sum_i \sum_N \exp[-(E_i(N) - \mu N)/k_B T] \tag{5.12}$$

which is called the grand partition function. Just like its canonical-ensemble counterpart Z, Ξ becomes the "master" because everything that can be calculated using the Gibbs factor can be obtained directly from it. To see why, notice that

$$\begin{aligned} < U - \mu N > &= \frac{1}{\Xi}\sum_i \sum_N (E_i(N) - N\mu)\exp[-(E_i - \mu N)/k_B T] \\ &= kT^2 \frac{\partial \ln \Xi}{\partial T}. \end{aligned} \tag{5.13}$$

From Eqs. (5.1) and (5.6), we may also write

$$\begin{aligned} < U - \mu N > &= \Omega + TS \\ &= \Omega - T\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \\ &= T^2 \frac{\partial}{\partial T}\left(-\frac{\Omega}{T}\right)_{V,\mu}, \end{aligned} \tag{5.14}$$

which, by comparing with Eq. (5.13), gives us

$$\Xi = \exp(-\Omega/k_B T). \tag{5.15}$$

Everything we said earlier for Z and F can be reiterated here for Ξ and Ω.

Since the number of molecules N is not fixed, it is interesting to see how it is determined and how it fluctuates. To this end, rewrite Ξ as follows

$$\Xi = \sum_i \sum_N \exp[\mu N/k_B T] \exp[-E_i(N)/k_B T]. \tag{5.16}$$

It follows that

$$\begin{aligned} < N > &= \sum_i \sum_N N \exp[\mu N/k_B T] \exp[-E_i(N)/k_B T]/\Xi \\ &= k_B T \frac{1}{\Xi} \frac{\partial \Xi}{\partial \mu}. \end{aligned} \tag{5.17}$$

Thus $< N >$ is determined by the chemical potential that the reservoir imposes on the system. This is also true in the human world. The city of Hattiesburg is open to anyone who wishes to move in or out. There is no guard who controls the population count. However, the city can control its population by controlling the "unlivability" of the city. If they wish to accelerate the growth of population, they can help make it more livable in many different ways, which they do quite well. If they decide to slow down the growth, on the other hand, they have many ways of doing so. For example, they could make it very difficult to obtain a building permit.

In an open system, the number of molecules N fluctuates. To study it, let us first calculate

$$\begin{aligned} < N^2 > &= \sum_i \sum_N N^2 \exp[\mu N/k_B T] \exp[-E_i(N)/k_B T] \\ &= (k_B T)^2 \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial \mu^2}. \end{aligned} \tag{5.18}$$

It then follows that

$$\begin{aligned} \delta N^2 &= < N^2 > - < N >^2 \\ &= k_B T \left(\frac{\partial < N >}{\partial \mu} \right)_{V,T}. \end{aligned} \tag{5.19}$$

This is another example of the fluctuation-dissipation theorem. Because N and μ are coupled in the Gibbs factor, the fluctuation of N is related to

the response of N to a change in μ.

The response function in Eq. (5.19) is difficult to measure directly in the laboratory. To find a way to measure it more easily, we need to do some juggling. Invert the partial derivative and write it as $(\partial\mu/\partial N)_{V,T}$, where the volume V and T should be left untouched during the differentiation. Now invoke the Gibbs-Duhem relationship, Eq. (3.52). Since T must be held fixed, μ can only change via p. Thus

$$\begin{aligned}\left(\frac{\partial\mu}{\partial N}\right)_{V,T} &= \frac{V}{N}\left(\frac{\partial P}{\partial N}\right)_{V,T} \\ &= \frac{1}{N}\left(\frac{\partial p}{\partial n}\right)_{V,T},\end{aligned} \tag{5.20}$$

where $n = N/V$ represents the concentration. This calls for changing n and finding out the consequent change in P while holding V fixed, but P is blind and cannot tell whether n changes through V or through N. Thus we may replace $(\partial n)_{V,T}$ with $(-N/V^2)(\partial V)_{N,T}$ and write

$$\frac{1}{N}\left(\frac{\partial P}{\partial n}\right)_{V,T} = -\frac{V^2}{N^2}\left(\frac{\partial p}{\partial V}\right)_{N,T}. \tag{5.21}$$

Thus we finally arrive at

$$\begin{aligned}\delta N^2 &= k_B T\left(\frac{\partial N}{\partial \mu}\right)_{V,T} \\ &= k_B T N n K_T,\end{aligned} \tag{5.22}$$

where

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T} \tag{5.23}$$

is called the isothermal compressibility and may be measured more easily in the laboratory.

5.4 Two Examples of Open Systems

In the above section, $E_i(N)$ is the energy of the i-th microstate of N molecules, and contains many different single particle orbitals of different ϵ. The N-dependent microstates can be handled in this way for the purpose of understanding the general properties of open systems, but it is not the best way to take advantage of the grand canonical ensemble formalism. A much better way is to focus on a single particle orbital of energy, say ϵ, and just count the occupants. We need not worry about how other orbitals are occupied because the total number of occupants in all orbitals is a matter which the chemical potential takes care of automatically. This is great because we do not have to ask for the identity of the occupants, which makes us free of the overcounting problem. The total energy of all the occupants of an orbital may simply be written as ϵN. Think of the orbital as a SEAT waiting for particles to visit, like a flower garden waiting for bees and butterflies or a bench in a park waiting for us to sit on. It may sound odd, but the main focus is on the seat because the seat may not have any occupants. In the next section, we will handle cases where the seat is really a physical entity. After that, we will return to the ideal gas case for which a seat means a single particle orbital.

5.4.1 *Hemoglobin*

There are many exotic open systems, one of which is protein hemoglobin in blood cells. It looks like a winding self-closed tube and has four spots on it called hemes. The hemes pick up oxygen molecules in the lung and carry them to the rest of the body. Each heme can accommodate one oxygen molecule with energy ϵ or remain vacant with no energy. The oxygen molecules in the lung are the reservoir and impose a certain chemical potential on the hemes. The grand partition function consists of only two terms: $N = 0$ with no energy, and $N = 1$ with energy ϵ, and therefore

$$\Xi = 1 + \lambda \exp(-\epsilon/k_B T), \tag{5.24}$$

where

$$\lambda = \exp(\mu/k_B T). \tag{5.25}$$

The probability of a heme having one oxygen molecule, or the ratio of those hemes with one oxygen molecule to the total number of hemes is

$$f = \frac{\lambda \exp(-\epsilon/k_B T)}{1 + \lambda \exp(-\epsilon/k_B T)}. \tag{5.26}$$

Equation (5.26) can be written another way. Treating the oxygen gas as an ideal gas, $\lambda = P/k_B T n_Q$, where $n_Q = (mk_B T/2\pi\hbar^2)^{3/2}$, f can be written as

$$f = \frac{P}{P_0 + P}, \tag{5.27}$$

where $P_0 = n_Q k_B T \exp(\epsilon/k_B T)$. Written in this form, it is called the Langmuir adsorption isotherm. Consider a solid surface which provides "seats" waiting to absorb gas molecules. Equation (5.27) provides the ratio of those sites that have absorbed a gas molecule to the total sites.

5.4.2 *Quantum Ideal Gas*

The N-fixed formalism that we used for the closed systems of ideal gas was plagued with the overcounting error problem. We found a way to correct the problem for the classical regime, but the task of calculating the partition function in the quantum regime appeared bleak. The present μ-fixed formalism makes it possible to study the quantum regime. Focus on **each single-particle orbital** and count the occupation number without asking for the identity of the occupants. The occupation number is not free from the rule of quantum mechanics that identical particles should be treated as such. For particles of integer spins like helium-4 atoms, there is no restriction and the occupation number can be any positive integer. These particles are called bosons. For particles of non-integer spins like electrons and helium-3 atoms, on the other hand, the occupation number must be either zero or unity; each orbital can be occupied by no more than one particle. These particles are called fermions.

First, consider the fermions. Let us calculate the grand partition function of a single-particle state of energy ϵ. Here the single-particle orbital is the seat waiting for fermions to visit. Unlike the hemes in the Hemoglobin, it is not a physical seat, but the idea is the same. It is either empty of fermions with zero energy or occupied by one fermion with energy ϵ. Thus

the result for the partition function is the same as Eq. (5.24), and the probability of the orbital being occupied by a fermion is given by Eq. (5.26). We rewrite it in the form of

$$f_{\mathrm{FD}}(\epsilon, \mu, T) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}, \tag{5.28}$$

which is called the Fermi-Dirac distribution function.

Next, consider the bosons. Each orbital can be occupied by any number of bosons. Focusing on a particular orbital of energy ϵ,

$$\begin{aligned} \Xi_\epsilon &= \sum_{N=0}^{\infty} \lambda^N \exp(-N\epsilon/k_B T) \\ &= \frac{1}{1 - \lambda \exp(-\epsilon/k_B T} \\ &= \frac{1}{1 - \exp[-(\epsilon - \mu)/k_B T}. \end{aligned} \tag{5.29}$$

The average occupation number may be calculated using Eq. (5.17) with the result:

$$f_{\mathrm{BE}}(\epsilon, \mu, T) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] - 1}, \tag{5.30}$$

which is called the Bose-Einstein distribution function. It gives the expected number of occupants in the orbital.

Putting all of the orbitals together, the full partition functions are then given by

$$\Xi_{\mathrm{FD}} = \prod_{\epsilon_i} \{1 + \exp[-(\epsilon_i - \mu)/k_B T]\}, \tag{5.31}$$

and

$$\Xi_{\mathrm{BE}} = \prod_{\epsilon_i} \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}, \tag{5.32}$$

where the partition functions of different orbitals are multiplied because they are independent of one another. Think of the orbitals as different and

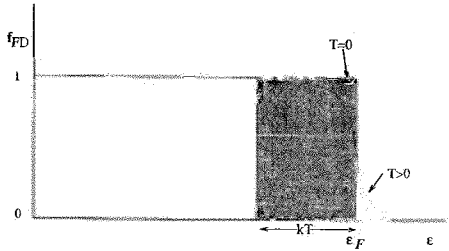

Fig. 5.1 Fermi gas near T=0. Those fermions in the shaded area can absorb the thermal energy, but those below cannot.

independent thermal systems, 1, 2, 3, and so on. The partition function then partitions into $Z_1 Z_2 Z_3 \cdots$, because what happens in one does not affect the others, a general property which we saw several times before.

With Eqs. (5.28) and (5.30), we can study the thermal behavior in the quantum regime. As an example, consider the heat capacity of metals at a low temperature. In the low temperature quantum regime, the thermal behavior of metals may be modeled as a non-interacting fermion gas of electrons. Examine how Eq. (5.28) distributes the electrons among the orbitals at low temperatures. Calling $\mu(T = 0) = \epsilon_F$, the Fermi energy, consider the orbitals whose energy is below the Fermi energy. When $k_B T < \epsilon_F$, it is safe to replace $\mu(T)$ with ϵ_F. At $T = 0$, Eq. (5.28) says that all the single particle states up to the Fermi level are occupied by electrons and all those above the Fermi level are vacant, as shown in Fig. 5.1.

Consider how this distribution changes as we raise the temperature. For temperatures in the range $\epsilon_F > k_B T > 0$, Fig. 5.1 shows that those electrons sitting on the orbitals approximately within the distance of $k_B T$ below ϵ_F (shaded in the figure) can take the thermal energy to move to a vacant seat above ϵ_F, but those electrons sitting further below this range (not shaded in the figure) cannot. The energy is available for them to absorb but they cannot take the energy because the orbitals where they need to land after absorbing the energy are already occupied. These electrons are doomed to remain buried in the Fermi sea. The fraction of those electrons that can absorb the thermal energy out of the total number of electrons is $k_B T/\epsilon_F$. Since each of these can absorb energy on the order of $k_B T$, the

total thermal energy that they can absorb goes like T^2. The heat capacity then goes like

$$C_V \sim T \tag{5.33}$$

and vanishes at $T = 0$. The fraction of those electrons that do not absorb the thermal energy and remain in the same orbitals as they do at $T = 0$ is $(\epsilon_F - k_B T)/\epsilon_F$ which becomes unity as T approaches zero. Contrast this behavior of electrons with that of the molecules in the classical regime

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= \frac{3Nk_B}{2}. \end{aligned} \tag{5.34}$$

The electrons behave in the quantum regime like picky eaters who refuse to eat unless what is on their plates satisfy about 500 conditions. This is in fact a general characteristics of quantum systems at low temperatures although the reason for their "pickiness" is different from system to system. For example, liquid helium-4 atoms in their superfluid phase cannot receive energy from a classical object unless the velocity of the latter is larger than a certain critical velocity. The atoms no longer behave individually; they behave collectively. The way they collectively possess energy and momentum is different from the way classical objects do. Consequently, it is not always possible for the two parties to exchange momentum and energy. When they cannot, the helium atoms behave as though the classical counterparts did not exist. This gives rise to their superfluid behavior.

5.5 The Classical Regime Revisited

Bosons and fermions differ in the quantum regime by the +1 and -1 factors in the denominator of their respective distribution functions, Eqs. (5.28) and (5.30). Let us see how this difference disappears in the classical regime. We can only blame $\exp(-\mu/k_B T)$. Assume that it is large enough in the classical regime to allow us to ignore the +1 and -1 factors. Then both Eq. (5.28) and Eq. (5.30) converge to

$$f(\epsilon_i, \mu, T) = \exp(\mu/k_B T)\exp(-\epsilon_i/k_B T). \tag{5.35}$$

This is still not the Boltzmann factor. It cannot be because we are in the μ-fixed formalism whereas the Boltzmann factor is the distribution function in the N-fixed formalism. To go to the N-fixed formalism, let us add Eq. (5.35) for all single-particle states and demand that the chemical potential be such that the total number of occupants in all the seats is equal to N:

$$\sum_i f(\epsilon_i, \mu, T) = N. \tag{5.36}$$

Upon carrying out the sum, we find that

$$\exp(\mu/k_B T) Z_1 = N. \tag{5.37}$$

Substituting Eq. (4.42) for Z_1, we find that

$$\exp(\mu/k_B T) = N/Z_1 = \frac{2N}{\pi k_B T/\alpha^2} = \frac{2N}{n_c^2}, \tag{5.38}$$

where we recognize the cutoff n_c. When we assumed in the above that $\exp(-\mu/k_B T) \gg 1$ or equivalently that $\exp(\mu/k_B T) \ll 1$, we effectively assumed that $n_c \gg 1$, namely, that the system is in the classical regime. The resulting chemical potential from Eq. (5.38) is the same as what we obtained in Sec. 4.7 for the classical regime. All results are consistent!

5.6 Systems Confined to a Flexible Volume and the Gibbs Free Energy

Systems which are closed for N but open for V, like gas in a balloon, are our subject in this section. Such systems are in contact with a reservoir to exchange not only energy but also volume. As an example, consider a gas confined to a cylinder equipped with a mobile piston which is designed to exert a constant pressure on the gas. If the gas pressure increases (or decreases) for any reason, the gas will expand (or shrink) until its pressure

matches the fixed reservoir pressure. Since $\partial F/\partial V = -P$, the appropriate energy-like function is

$$\begin{aligned} G &= F + PV \\ &= U - TS + PV, \end{aligned} \tag{5.39}$$

which is called the Gibbs free energy. For G, the appropriate independent variables are T, P, and N. Substituting Eq. (3.51) for U into Eq. (5.39), it follows that

$$G = \mu N. \tag{5.40}$$

The Gibbs free energy is a very useful thermodynamic potential. But after having gone through the details for F and Ω, there is no need to repeat the arguments again for G. Let me just briefly outline the rest of the story for G. G/T is the net entropy cost that the reservoir pays for allowing the system to have volume V and energy U, which is why minimizing it maximizes the total entropy of the whole combined system.

Differentiating G, we find

$$dG = -SdT - VdP + \mu dN, \tag{5.41}$$

where

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \tag{5.42}$$

$$V = -\left(\frac{\partial G}{\partial P}\right)_{T,N} \tag{5.43}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}. \tag{5.44}$$

The probability of finding that the system claims volume V and is in microstate $E_i(V)$ is given by

$$P\{V, E_i(V)\} = \frac{1}{\Psi} \exp\{-[E_i(V) + PV]/k_B T\}, \tag{5.45}$$

where the normalization factor

$$\Psi = \sum_V \sum_i \exp\{-[E_i(V) + PV]/k_B T\} \tag{5.46}$$

is again called the partition function.

The partition function is related to the free energy by

$$\Psi = \exp(-G/k_B T). \tag{5.47}$$

Since the volume is not held fixed, we have one more chance to see the fluctuation-dissipation theorem. Examine Eq. (5.45). Since P and V are coupled in the Boltzmann factor, the fluctuation of V is related to the response of V against a change in p:

$$\delta V^2 = k_B T \left(\frac{\partial V}{\partial P}\right)_{T,N}. \tag{5.48}$$

We see the same response function that we saw earlier for δN^2. This is not surprising since allowing V to vary with a fixed N is the same as allowing N to vary with a fixed volume.

The Gibbs free energy is particularly useful for magnetic systems. As we argued with Eq. (3.71), M and H are to magnetic systems what V and P are to molecular systems. The appropriate free energy for spins subject to a magnetic field is therefore the Gibbs free energy. Just as V is variable in flexible molecular systems, so is M in magnetic systems.

5.7 Two More Energy-like Functions: Energy and Enthalpy

5.7.1 *Energy*

We have examined so far three different energy-like functions. They all follow a minimum principle. It would be odd if energy itself did not behave

as energy-like functions do. It does, but in the following mathematical sense.

For energy, the independent variables are S, V, and N. The main actor S remains, and in the presence of the main actor, we can only attempt to translate what the main actor says in terms of energy. Entropy says that in the equilibrium state energy should be distributed such that the entropy is maximized. To put this more quantitatively, divide an isolated system into two parts. part 1 consists of N_1 molecules occupying volume V_1 while part 2 consists of N_2 molecules occupying volume V_2. The total entropy of the two-part system differs depending on how the total energy is distributed between the two parts. Suppose that the entropy is maximized when part 1 holds energy $\hat{U}_1$ and part 2 holds $\hat{U}_2$. Should U_1 and U_2 deviate from $\hat{U}_1$ and $\hat{U}_2$ by ΔU, the entropy must decrease, i.e.,

$$S(\hat{U}_1 + \Delta U, V_1, N_1) + S(\hat{U}_2 - \Delta U, V_2, N_2) < S(\hat{U}_1, V_1, N_1) + S(\hat{U}_2, V_2, N_2). \tag{5.49}$$

Let us invert this equation, allowing S and U to exchange their roles. The entropy must then be treated as a conserved quantity while the energy must follow whatever is necessary to invert the equation. Call the right-hand side of Eq. (5.49) $\hat{S}_1 + \hat{S}_2$. If we repartition this total entropy differently, how would the energy in each part have to change? Look at Eq. (5.49). Since the same amount of total entropy is going to be distributed into two parts, the total entropy on the left-hand side should be equal to that on the right-hand side. Our question is: how should the two energy arguments on the left-hand side change if we want to replace the inequality sign with an equality sign? Since S is a monotonically increasing function of U, and since what is on the left-hand side of the equation is not large enough to match what is on the right-hand side, the two energy arguments on the left-hand side have to be increased. Then the total of the energies to enter as arguments on the left-hand side of the equation must be larger than those on the right-hand side. Thus the inverted equation reads:

$$U(\hat{S}_1 + \Delta S, V_1, N_1) + U(\hat{S}_2 - \Delta S, V_2, N_2) > U(\hat{S}_1, V_1, N_1) + U(\hat{S}_2, V_2, N_2). \tag{5.50}$$

This equation says that the entropy should be distributed such that the energy is minimized. It is a useful mathematical property which we will

use in Sec. 5.7.2 and in Appendix C.

5.7.2 *Enthalpy*

Finally, consider the Legendre transformation,

$$W = U + PV, \tag{5.51}$$

which is called the enthalpy or heat function. Taking a differential for W,

$$dW = dU + PdV + VdP = TdS + VdP. \tag{5.52}$$

Thus for all processes taking place at a constant pressure, $dW = TdS$. The total change in W will tell us the total amount of heat transfer, which makes W a useful thermodynamic function.

We may argue for a minimum principle for W in the following way. Consider a flexible system in contact with a pressure reservoir. The system can only exchange volume with the reservoir and is insulated from the rest of the universe. Since changing volume requires work, the reservoir exchanges energy with the system by means of work and work only. Thus we may write

$$U_{R+s}(V_R, V_s) = U_R(V_R - V_s) + U_s(V_s), \tag{5.53}$$

where V_s is the volume of the system and V_R the total volume available for both. Since $V_R \gg V_s$, we may expand the reservoir term to first order in V_s to write

$$U_{R+s}(V_R, V_s) = U_R(V_R) + PV_s + U_s(V_s), \tag{5.54}$$

where $PV_S + U_s = W$. The work exchange process is an isentropic process, and therefore we may apply the minimum energy principle to it. To minimize the total energy of the combined system U_{R+s}, W needs to be minimized. This is a physically meaningful minimum principle, but because it stipulates thermal insulation, it has little or no practical utility. If we allow a heat exchange as well, then the appropriate free energy is G, the Gibbs free energy.

Chapter 6

Energy versus Free Energy

6.1 Introduction

To pursue thermal physics from a basic point of view, one only has to calculate the partition function which is a sum of Boltzmann factors which involve only energy, not free energy. Once the partition function is calculated, one can calculate free energy and all other thermodynamic quantities from it. In this approach, the key player is energy and the free energy minimum principle has no role to play, which is why the extremum principle of free energy is not even mentioned in many text books on statistical mechanics. Unfortunately, however, the partition function is in general very difficult to calculate. Under these circumstances, a wise alternate approach is to make a model for free energy and proceed from there, guided by the minimum free energy principle. Indeed, if many of our heros did not take this approach, we would not be where we are today, and the title "thermal physics" would have never been coined. The difference between energy and free energy is that free energy takes into account the multiplicity of macrostates. The purpose of this chapter is to highlight how the multiplicity factor replaces energy with free energy.

In Sec. 6.2, we will construct macrostates in terms of energy and look for the probability of the system visiting each macrostate. When all the Boltzmann factors in each macrostate are added to take into account the multiplicity factor, the result looks like a Boltzmann factor but with the microstate energy replaced by a free energy. Landau makes a model of this free energy in his celebrated mean field theory.

In Sec. 6.3, we will start from the work-energy relationship that we

have learned from mechanics and add to it the multiplicity factor. The multiplicity factor once again replaces energy with free energy and turns the work-energy relationship into one of thermodynamic work and free energy. We will see why free energy is also called thermodynamic potential.

6.2 Boltzmann Factor for Macrostates and Macrostate Free Energy

We introduced the notion of free energy as a gauge by which systems in contact with a thermal reservoir can decide how much energy to claim to help maximize the total entropy of the combined system. To go to a deeper level of thermal physics, since these systems follow the modified postulate, it is desirable to see the notion of free energy from the standpoint of the modified postulate. According to the modified postulate, the probability of finding the system in microstate j is proportional to the Boltzmann factor, i.e.,

$$\text{probability} \sim \exp(-E_j/k_BT). \tag{6.1}$$

The Boltzmann factor is a not-yet-normalized probability, but let us simply call it the "probability" without the qualifier. Their sum over all microstates, namely, the normalization factor

$$Z = \sum_j \exp(-E_j/k_BT) \tag{6.2}$$

is the partition function.

We now wish to construct a Boltzmann factor appropriate for macrostates, namely the probability of finding the system in a specified macrostate. Macrostates may be defined in many different ways. Let us first define it by specifying energy. In the sum in Eq. (6.2), the same term reappears many times with the same value of energy to account for the degenerate states. For example, suppose that the first three microstates are degenerate, i.e., $E_1 = E_2 = E_3 \equiv U_1$. We lump the three microstates together to define macrostate 1. We do likewise to define macrostates 2, 3, 4, etc. We may then write

$$Z = \sum_j \Gamma(U_j) \exp(-U_j/k_B T), \tag{6.3}$$

where $\Gamma(U_j)$ is the degeneracy (multiplicity) corresponding to U_j. Absorbing Γ into the exponential,

$$Z = \sum_j Z_j = \sum_j \exp(-F_j/k_B T), \tag{6.4}$$

where

$$F_j = U_j - T k_B \ln \Gamma(U_j) = U_j - T S_j. \tag{6.5}$$

The probability of finding the system in macrostate j, i.e., the probability of finding the system with energy U_j is given by

$$\text{Probability} \sim Z_j = \exp(-F_j/k_B T), \tag{6.6}$$

which differs from the Boltzmann factor of microstates in that E_j has been replaced with F_j.

S_j, Z_j, and F_j are inter-related attributes of macrostate j. Since j may or may not be the largest macrostate, S_j and F_j may or may not represent their respective equilibrium properties characteristic of the largesest macrostate. When we wish to make this distinction, we may call Z_j the partial partition function becuase it is only one term in Eq. (6.4), S_j the macrostaste entropy and F_j the macrostate free energy. In the literature, such distinctions are not made. The implication is that the difference is obvious, and it is. For example, suppose that we are given free energy $F(M,T)$ for an Ising model. This cannot be the equilibrium free energy because if it were, M should be a function of T and therefore has no business to be there. When free energy is given in this manner with a seemingly inappropriate variable, take it as a sign that what you are given is a macrostate free energy; in the above example M is there to specify the macrostate and therefore is an "independent" variable. All the free energies that carry the name Landau or Landau and Ginzburg in Sec. 8.6 and throughout Chap. 9 are all macrostate free energies.

From Eq. (6.6), it is apparent that **more probable macrostates are associated with a lower free energy, and less probable macrostates with a higher one.**

For isolated thermal systems, what matters for each macrostate is its size Γ_j. As we stated in Sec. 4.4, the role played by Γ for isolated systems is played by Z for systems in contact with a thermal reservoir. Here, the analogy is clearer. We may regard Z_j as representing the "size" of macrostate j.

A system in contact with a thermal reservoir visits all macrostates of different energies. How is it then that the most probable macrostate alone can represent the equilibrium state? Suppose that $j = 64$ is the most probable macrostate. The corresponding free energy F_{64} is the lowest that the free energy can be, i.e., the equilibrium free energy. Recall that F is an extensive quantity; it increases with N like $N\hat{f}$, where $\hat{f}$ is the free energy per molecule. Because N is so large, it is safe to approximate the partition function with Z_{64}, i.e.,

$$Z \approx Z_{64} = \exp(-N\hat{f}_s/k_BT). \tag{6.7}$$

For example, $\hat{f}_5$ may only be slightly larger than $\hat{f}_{64}$, but the factor N makes Z_5 look like an ant and Z_{65} a fully grown redwood tree. What if $\hat{f}_9$ is so close to $\hat{f}_{64}$ that F_9 is actually comparable to F_{64}? It could be, but do not worry about it. Suppose that there are not one but as many as N such macrostates. We should then instead write $Z \approx NZ_{64}$. But take the logarithm and see how much it adds to the free energy. The additional factor that we bring in to account for such macrostates is $\ln N$ which is negligible compared to what the largest state brings by itself, namely, $-N\hat{f}_s/k_BT$.

In the above analysis, we defined macrostates in terms of energy. We may define them in terms of any variable, say, A. The partial partition function corresponding to $A = a$, i.e., the probability of finding $A = a$ is

$$Z_a = \sum_i \Delta(A_i - a)\exp(-E_i/k_BT), \tag{6.8}$$

where A_i is what A would be when the system is in microstate i, and $\Delta(x)$ is unity when $x = 0$ and zero when x is not zero. The corresponding free energy is given by

$$F_a = -k_B T \ln \sum_i \Delta(A_i - a) \exp(-E_i/k_B T). \tag{6.9}$$

We shall return to this equation in Sec. 8.6 to learn Landau's mean field theory. In terms of F_a, Eq. (6.8) may be rewritten as

$$Z_a = \exp[-F_a/k_B T]. \tag{6.10}$$

The relationship between the probability Z_a and the corresponding free energy F_a is worth repeating. **More probable macrostates are associated with lower free energy while less probable macrostates are associated with higher free energy.**

In view of the parallel between Eqs. (6.1) and (6.10), the equipartition theorem applies to free energy just as well as it does to energy. To give an example, suppose that we define macrostates with a space-dependent function, say, $A(\vec{r})$ or its Fourier transform $A(\vec{q})$. F should then be a functional of $A(\vec{q})$, i.e., a function of a function. Furthermore, suppose that the corresponding free energy is given by

$$F\{A(\vec{q})\} = \sum_{\vec{q}} \frac{1}{2} K_{\vec{q}} |A(\vec{q})|^2, \tag{6.11}$$

where $|A(\vec{q})|^2$ can be anything from zero to infinity. The equipartition theorem gives us

$$< |A(\vec{q})|^2 > = \frac{k_B T}{K_{\vec{q}}}, \tag{6.12}$$

a result which appears quite often in advanced literatures.

6.3 Thermodynamic Work and Thermodynamic Potential

When we perform work on a thermal system, say a gas, we cannot guarantee that our work will be completely consumed for increasing their energy (by altering its microstate energies). Thermal systems are driven to increase their entropy or to decrease their free energy. If our action is contrary to this prevailing tendency of nature, our work may have to be consumed at least in part to overpower that tendency. To check this possibility on a more

rigorous basis than we argued in Sec. 3.13, let us assume for a moment that the gas is stuck in one microstate i of energy E_i. In order to change the volume by ΔV, the amount of work to be done is

$$\Delta W = \frac{\partial E_i(V)}{\partial V}\Delta V. \tag{6.13}$$

If our assumption that the gas is stuck in one microstate were true, the gas pressure $\partial E_i/\partial V$ would be a mechanical property. We know that the gas does not stay stuck in one microstate. This is the difference between mechanical systems and thermal systems. For mechanical systems, multiplicity plays no role because there is no pertinent degeneracy to speak of. By contrast, degeneracy or the multiplicity of macrostates is in fact the essential element of thermal systems. Let us take into account this crucial element and recognize that the gas visits all of its microstates according to the Boltzmann factor. Taking the average of Eq. (6.13) over all microstates, we arrive at

$$\Delta W = \frac{1}{Z}\sum_i \frac{\partial E_i(V)}{\partial V}\exp[-\beta E_i(V)]\Delta V. \tag{6.14}$$

Using the trick of Eq. (2.20), we can write this entirely in terms of Z, namely,

$$\Delta W = -\frac{1}{\beta}\frac{1}{Z}\frac{\partial Z}{\partial V}\Delta V = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial V}\Delta V, \tag{6.15}$$

Upon substituting $Z = \exp(-\beta F)$, we arrive at

$$\Delta W = \frac{\partial F}{\partial V}\Delta V. \tag{6.16}$$

In comparison with Eq. (6.13), it is notable the microstate energy has been replaced with free energy. Denoting the initial volume with V_1 and the final volume with V_2, we may write

$$\Delta W = F(V_2) - F(V_1). \tag{6.17}$$

The work is not consumed just to increase its energy. It is consumed to increase its free energy, and therefore the work may be called thermodynamic work and $-\partial F/\partial V = P$, the force against which we push the piston, may be called a thermodynamic force. In fact, since the temperature remains fixed (assuming that we pushed the piston very slowly), there is actually no change in energy and the change in free energy is entirely in entropy. To check this, use Eqs. (4.51) and (4.54) to obtain

$$\Delta W = -k_B T N[\ln V_2 - \ln V_1] = -k_B T(S_2 - S_1), \tag{6.18}$$

which confirms what we suspected. It takes work to increase free energy or to decrease entropy. If we wish to act against the "desire" of nature, we have to sweat. This is what we claimed in Section 3.13. The restoring force is entirely driven by entropy.

We may make Eq. (6.16) look just like an ordinary mechanical potential energy. Referring to Fig. 6.1, since $V = Ax$, the work that the gas does to the piston is given by

$$\Delta W_{\text{gas}\to\text{piston}} = -\frac{\partial F}{\partial x}\Delta x, \tag{6.19}$$

where the restoring force is

$$-\frac{\partial F}{\partial x} = \frac{\partial F}{\partial V}\frac{\partial V}{\partial x} = -k_B T N\frac{1}{x}. \tag{6.20}$$

The restoring force of the gas has a potential energy to associate with it, namely,

$$U_{\text{eff}}(x) = -k_B T N \ln x. \tag{6.21}$$

Written in this form, the free energy should be regarded as a thermodynamic potential.

Let us compare this to the way we describe a mechanical system, say, a rock of mass m. The earth pulls the rock with a force of mg. We describe this force as $-\partial mgz/\partial z$ where mgz is the gravitational potential energy. Personalizing the rock as we do for thermal systems, the rock really really wants to decrease its mgz. It takes work to move a rock from the bottom of a hill to the top against this nature's tendency. Once at the top, the

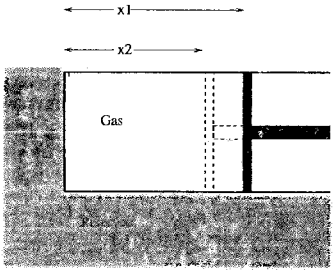

Fig. 6.1 A gas confined to a cylinder by a piston

rock is unstable because it really wants to come down. We have all seen rocks sliding down hills but none spontaneously sliding up. Similarly, try to increase the thermodynamic potential of a gas. It costs work as we have seen a moment ago. Once placed at a high thermodynamic potential, it is unstable because it really wants to decrease its thermodynamic potential.

Let us generalize Eq. (6.16) where V is the lone variable that determines the single particle microstate energy ϵ for molecular systems. Call such a parameter of other systems X. The amount of work that we have to do to change X by ΔX is given by

$$\Delta W = \frac{\partial F(X)}{\partial X}\Delta X, \tag{6.22}$$

where $-\partial F(X)/\partial X$ may be regarded as the corresponding thermodynamic force.

6.4 Is Some Energy Really Free?

The fact that ΔF has no energy component (at a fixed temperature) can be quite bewildering if one tries to focus on where the energy resides. To see this, push the piston from $x = x_1$ to $x = x_2$, as shown in Fig. 6.1. Do this very slowly to ensure that the process is isothermal, that is, to ensure that the gas remains in equilibrium with the reservoir at all times. By pushing

the piston, we will have performed work in the amount of

$$\Delta U = U_{\text{eff}}(x_2) - U_{\text{eff}}(x_1) \tag{6.23}$$

to the gas. But the gas has no more energy at the end than it had at the beginning because the total energy U does not depend on volume. What happened to the work? It has been transferred to the reservoir. By the way, the process does not have to be isothermal. If we perform the action quickly, the gas will have more energy at the end than at the beginning with increased temperature, but soon the energy will be transferred to the reservoir and the gas temperature will return to the reservoir temperature T. It is then interesting to ask: can the disposed energy be recovered as useful work for us? The answer is yes. If we allow the gas to push the piston back to x_1, it will perform exactly the same amount of work performed on it earlier, namely, ΔU, but again oddly enough, the gas has no less energy at the end of the expansion than it had at the beginning. At whose expense did the gas do the work if not its own? The disposed energy has been brought back from the reservoir. Here again the process does not have to be isothermal. If the gas is allowed to expand quickly, it will have less energy at the end than at the beginning of the expansion with a lower temperature, but soon the gas will replenish its depleted energy from the reservoir and the temperature will return back to T.

The relationship between the reservoir and the gas appears to be like that between a bank (reservoir) and a customer (system) who enjoys complete trust from his bank and never tries to take advantage of it. When the customer gets some extra money that he does not need, he deposits it in the bank, but the bank makes no record of the deposit. When the customer needs the money to pay a bill, he can go ahead and pay it out of his pocket because he knows that the bank will reimburse it without asking for any record. To a third party who does not understand the unusual business practice between the two parties, it would appear as if money were coming for free out of nowhere. But nothing in life is free. Neither the bank nor the customer gets anything for free.

Chapter 7

Phases and Phase Transitions

7.1 Introduction

We have seen how the extremum principles of entropy and free energies work to guide the thermal behavior of molecules in the gas phase. We now wish to extend this study to other phases, the liquid phase and the solid phase. These condensed phases are, however, a result of molecular interactions. Unfortunately, it is in general very difficult to calculate the partition function in the presence of molecular interactions. We will not study interacting molecules *per se*, but we will find a way to take a glimpse into the thermal world of interacting molecules and observe how the free energy is altered by the molecular interactions. We will then observe how the altered free energy alters molecular behavior. Here, molecules are effectively cornered so that the only way to minimize the free energy is to change their basic structure. That comes up in Sec. 7.5. In the meantime, we need to get used to the different phases.

7.2 Phase Diagrams

Figure 7.1 shows the phase diagram of a normal substance. In the low temperature and high pressure region, the substance is a solid (S). In the low pressure and high temperature region, it is a gas (G). In the intermediate region of p and T, it is a liquid (L). The sharp lines dividing different phases are called coexistence curves. When the system is placed exactly on these curves, the neighboring phases coexist. The coexistence curve of L and S is called the melting curve. The coexistence curve of G and L is called the

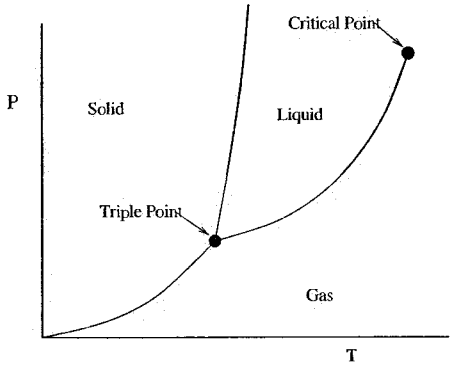

Fig. 7.1 A schematic phase diagram of a normal substance

vapor pressure curve. The coexistence curve between solid and gas is called the sublimation curve.

The fact that different phases are divided by a sharp line is remarkable because it means that even a small amount of change in temperature or pressure across the coexistence lines can drive the substance from one phase into another. Since we know that the minimum free energy principle is the lone guiding principle for the molecules, this means that the free energy landscape changes completely upon crossing the lines, forcing the molecules to change the way they aggregate, namely, their density. Such an abrupt transition is called a first-order phase transition; it occurs when we cross a coexistence line. When we cross a coexistence line from one phase to another, because molecules aggregate differently in the two phases requiring different amount of energy, we cannot just cross the line; we have to provide or remove the energy difference as needed. The energy difference is called the latent heat.

All three coexistence curves meet at the triple point which means that the three phases can coexist there. The vapor pressure curve ends at a point called the critical point, (P_C, T_C). As one moves along the vapor pressure curve toward the critical point, the distinction between the liquid phase

on one side and the gas phase on the other gradually decreases and finally disappears at the critical point. The phase transition that occurs exactly at the critical point but by changing T through T_C is called a second-order phase transition and all phenomena taking place near the critical point are called critical phenomena. Unlike in first-order transitions, the transition is continuous and does not require any latent heat.

The two types of phase transitions differ in a more important way. Second-order phase transitions are "stormy" in the sense that all the response functions diverge at $T = T_C$! This means large fluctuations in extensive quantities. The fluctuations grow larger and larger as T approaches T_C from either direction as if to warn us that a transition is forthcoming, and finally diverge at $T = T_C$. Ironically, the abrupt first-order phase transitions have no such warning signs.

We have a fairly good intuitive idea what molecules and atoms are doing in each phase. In the gas phase, they are moving around randomly and individually. In the solid phase, they are highly organized in the way they arrange themselves; they form various lattice structures. They are also highly organized in the way they are moving around; each is moving about its lattice site but in coordination with its neighbors. In the liquid phase, molecules are doing something in between, which is why the liquid state is more difficult to study than the other two states.

In some substances, molecules and atoms have some additional characteristic properties which lead to another type of phases. Two good examples are magnetic materials and liquid crystals. In magnetic materials, the atoms have magnetic dipole moments which give rise to magnetism. Depending on how the dipole moments are oriented with respect to each other, their magnetic properties are different and hence have different magnetic phases. In the case of liquid crystals, the molecules have various distinctive geometrical shapes. In some liquid crystals they look like a plate and in some others they look like a rod. Not surprisingly, the positional entropy is quite different depending on how they are oriented with respect to each other. The different orientational orders lead to different phases in which the molecules exhibit different electro-optical properties.

7.3 Coexistence Curves

The fact that molecules can coexist in two different phases, say 1 and 2, means that a molecule in phase 1 has no compelling reason to migrate to join those in phase 2, and vice versa. The "unlivability" must be the same in both phases:

$$\mu_1(P,T) = \mu_2(P,T). \tag{7.1}$$

Under this condition, the two phases are in a state of diffusive equilibrium; there are as many molecules migrating from phase 1 to phase 2 as there are migrating from phase 2 to phase 1. Now consider another adjacent point on the same coexistence line at $(P+dP, T+dT)$. The diffusive equilibrium exists there as well, whence

$$\mu_1(P+dP, T+dT) = \mu_2(P+dP, T+dT). \tag{7.2}$$

To prepare for the next step, since $\mu = G/N$, write Eqs. (5.42) and (5.43) in the form

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -\frac{S}{N} = -s, \tag{7.3}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = -\frac{V}{N} = -v. \tag{7.4}$$

Now expand the right hand side of Eq. (7.2) to first order in dp and dT. Remembering Eq. (7.1), the zeroth-order terms in the expansion cancel out. Separate the remaining terms involving dp from those involving dT to obtain

$$\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2}, \tag{7.5}$$

which is called the Clausius-Clapeyron equation.

The slope dP/dT of a coexistence line holds a rather precious piece of information. It tells us how entropy and volume change upon crossing the coexistence lines. Since the change in entropy is divided by the change

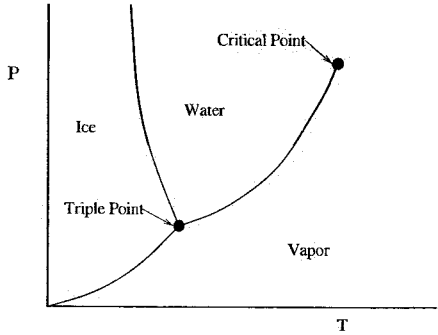

Fig. 7.2 A schematic phase diagram of water

in volume, the information is not as complete as it would be if the two came separately. But considering how little it costs to map the coexistence lines, what we get from Eq. (7.5) is a bargain. At a session of an American Physical Society meeting sometime ago, a speaker opened up his talk with the question "You have seen the Clausius-Clapeyron equation already six times. Would you like to see it once more?" That demonstrates how busy the equation was; it was during the period when the low temperature physics of helium was extremely intense. The equation is still busy.

For most normal substances, the slope of the melting curve is positive. The liquid phase requires more volume and more entropy than the solid phase. Water is not normal. The slope of the melting curve of water is negative, as shown in Fig. 7.2. The liquid phase (water) requires more entropy than the solid phase (ice) as in all normal substances, but the volume requirement is the other way around; the liquid phase (water) requires less volume than the solid phase (ice), which makes the slope negative.

Figure 7.3 shows the phase diagram of helium-3. The coexistence line between the solid phase and the liquid phase has a negative slope at very low temperatures. In this case, the liquid phase requires more volume than the solid phase does as in normal substances, but the liquid phase has less entropy than the solid phase. In other words, the liquid is more ordered than the solid, and therefore it takes heat to change the liquid to a solid!

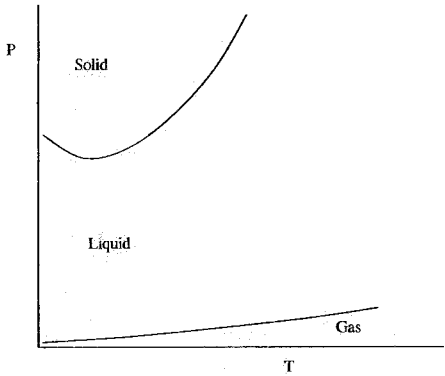

Fig. 7.3 A schematic phase diagram of Helium-3

The molecules do move around in the liquid phase, but not individually as they do in the normal liquid phase. They behave collectively in much the same way as the members of a flawless marching band do on a football field to execute a routine which allows little or no room for error. If you wish to break them up, give them a dose of highly disruptive heat. What do they do then? The atoms crystallize and all the energy is used to vibrate, which turns out to give them more entropy.

Exercise *Calculate the solid-gas coexistence curve using the Einstein model for a solid phase and the ideal gas model for a gas phase. For the solid phase, since it takes up only a small amount of volume, ignore the PV term in $G = N\mu = F + PV$.*

7.4 Interface

Two different phases can coexist, but their coexistence comes at a price. In order for two phases to coexist, there has to be a region where the two phases

meet. The key question is whether or not it is possible to make a sharp dividing surface so that all the extensive thermodynamic variables may be written as the sum of two bulk variables representing the two coexisting phases like

$$N = N_1 + N_2, \quad V = V_1 + V_2, \quad U = U_1 + U_2, \quad \text{etc.} \tag{7.6}$$

This can easily be done for N and V by exercising the spirit of give and take between the two phases, but not for U and S. For U and S, there is a leftover which cannot be attributed to the two bulk phases. One way to proceed under these circumstances is to envision a sharp dividing surface, the interface, and then attribute the leftover energy and entropy to the interface. We may then write

$$U = U_1 + U_2 + U^\sigma, \tag{7.7}$$

and

$$S = S_1 + S_2 + S^\sigma, \tag{7.8}$$

where σ refers to the interface.

The surface energy is a function of the surface entropy S^σ and the surface area σ. The interface has neither molecules nor volume because N and V have been completely allocated to the two bulk phases, leaving nothing for the interface. The first law for the interface is therefore

$$dU^\sigma = TdS^\sigma + \gamma d\sigma, \tag{7.9}$$

where

$$\gamma = \left(\frac{\partial U^{(\sigma)}}{\partial \sigma}\right)_{S^{(\sigma)}} \tag{7.10}$$

is called the surface tension. The surface tension is to the surface what the pressure is to the bulk phases.

The surface area σ, the surface energy $U^{(\sigma)}$, and the surface entropy $S^{(\sigma)}$ are all extensive quantities, and therefore the first law gives

$$U^\sigma = TS^\sigma + \gamma\sigma, \tag{7.11}$$

or equivalently

$$F^\sigma = U^\sigma - TS^\sigma = \gamma\sigma, \tag{7.12}$$

which says that the surface tension γ is equal to the surface free energy per area. What do molecules do to minimize the surface free energy? The molecules can do nothing to change the surface tension, but they can change the surface area. The molecules in the two coexisting phases will rearrange themselves so as to minimize the interface area σ to minimize the surface free energy. Consequently the interface acts like a stretched rubber sheet. This is why raindrops never come in a cubic or any other sharp-angled shape. If they did, it would be hazardous to go out on a rainy day without protection!

A study of the interface would not be complete without the following experiment. Fill a bowl with water and sprinkle black pepper onto the surface. The pepper grains float, thanks to the surface tension of the water. Now touch the surface with a soap bar near the middle. The detergent in the soap effectively punctures the "rubber sheet" of the interface. The broken sheet is then pulled towards the edge of the bowl, carrying the pepper grains with it. This happens very quickly– as soon as the soap bar touches the surface. Some insects living on water surfaces know how to take advantage of this phenomenon. When they are in dangerously close proximity to a predator, they shoot a drop of detergent-rich liquid to the surface in the direction of the predator. The punctured sheet quickly carries them away from the predator.

7.5 The van der Waals Theory

We will now study the van der Waals theory, which will be our first attempt to take intermolecular interactions into account. The theory can be presented in several different ways. We will stress how the interactions alter the ideal gas free energy.

For typical monatomic spherical molecules, the molecular interaction potential may be represented with the Lennard-Jones potential,

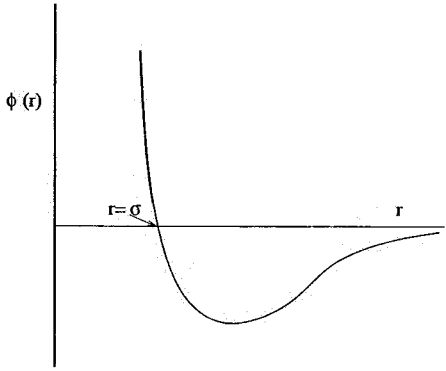

Fig. 7.4 The Lennard-Jones potential

$$\phi(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}, \tag{7.13}$$

which is sketched in Fig. 7.4. Two important ingredients to be captured are: (a) the strong short-range repulsion, and (b) the weak long-range attraction. Let us see how (a) and (b) affect the free energy.

Consider (a). For $r < \sigma$, the interaction is strongly repulsive. No molecules allow any other molecules to come within this range. When we have N such molecules, the effective volume of space in which the molecules can move around freely like an ideal gas is not V, but $V - Nb$ where b is approximately $4\pi\sigma^3/3$.

To consider (b), assume that a molecule is at the coordinate origin. Its interaction with all other molecules in the vicinity gives

$$\delta U = \int_0^\infty dr 4\pi r^2 n(r)\phi(r), \tag{7.14}$$

where $n(r)$ is the concentration of molecules at r given that a molecule is at the origin. The local concentration $n(r)$ is essentially zero for $r < \sigma$, and

is expected to rise and fall periodically with increasing r. If we ignore this local fluctuation of $n(r)$ and approximate it with its global average value, $n = N/V$, then δU may be approximated as

$$\delta U \approx n \int_{\sigma}^{\infty} 4\pi r^2 \phi(r). \tag{7.15}$$

Regard this as the weighted sum of $\phi(r)$ where $\phi(r)$ is weighted more and more heavily as r increases. Since $\phi(r)$ is negative for large r, it is clear that δU is a negative number which we will write as

$$\delta U \approx -2na, \tag{7.16}$$

where a is another constant.

Since the location of any one of the N molecules may be chosen as the coordinate origin, every molecule causes all other molecules to have the same amount of potential energy. Counting each pair twice in this way and then later dividing the result by 2, the total potential energy is

$$\Delta U = N\delta U/2 = -N^2 a/V. \tag{7.17}$$

The molecules have this much additional energy due to their interactions.

We may now modify the ideal gas free energy in order to take (a) and (b) into account. To that end, inspect the ideal gas free energy which we rewrite here:

$$\begin{aligned} F_{\text{ideal}} &= -k_B T N \ln\left\{(mk_B T/2\pi\hbar^2)^{3/2} V\right\} \\ &\quad + k_B T N \ln N - k_B T N. \end{aligned} \tag{7.18}$$

For (a), we merely replace V with $V - Nb$. For (b), the pertinent question is: in order for energy to change by ΔU, how much does the free energy have to change? Notice that ΔU is independent of temperature. According to Eq. (4.20), if we let F change by ΔU, energy would change by the same desired amount. Thus we merely add ΔU to F_{ideal}. The final result is:

$$F_{\text{vdw}} = -k_B T N \ln\left\{(mk_B T/2\pi\hbar^2)^{3/2}(V - Nb)\right\}$$

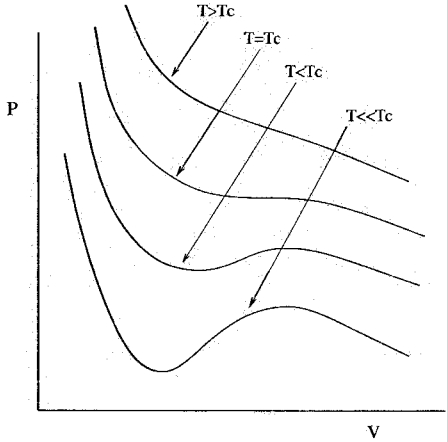

Fig. 7.5 The van der Waals pressure

$$+ k_B T N \ln N - k_B T N - N^2 a/V. \tag{7.19}$$

Let us calculate the pressure:

$$\begin{aligned} P_{\text{vdw}} &= -\left(\frac{\partial F}{\partial V}\right)_T \\ &= \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}. \end{aligned} \tag{7.20}$$

It is interesting that the molecular interactions have two opposite effects on the pressure: the first term shows that the reduced volume due to (a) increases the pressure, as anticipated, while the second term shows that the reduced energy due to (b) decreases the pressure. We may say that the effect of (b) was also anticipated. Because all molecules are pulling each other, they now tend to try to form a more bound state which effectively reduces their "appetite" for volume, namely, their pressure.

What is the net effect of (a) and (b)? With this question in mind, plot

p_{vdw} as a function of V with T fixed at various values. The results are as depicted in Fig. 7.5. At sufficiently high temperatures, there is no noticeable effect and molecules can exist in a single gas phase. There exists, however, a critical temperature T_C below which the molecular interactions have a noticeable effect. Figure 7.6 shows a typical pressure curve at $T < T_C$ along with the corresponding free energy curve given by Eq. (7.19). Examine the free energy curve. Unlike its ideal gas counterpart, there is a region in which F makes a concave protrusion, namely, $(\partial^2 F/\partial V^2) < 0$, in the middle of a convex curve. Due to this protrusion, it is possible to draw a common tangent line so that it just touches the bottom of the left dip at $V = V_1$ and another dip to the right at $V = V_2$; let F_1 denote the free energy at $V = V_1$ and F_2 the free energy at $V = V_2$.

The fact that the free energy curve allows a common tangent line has far reaching consequences. Suppose that the N molecules divide themselves into two groups, N_1 and $N_2 = N - N_1$, and that the size of the two groups changes in the following systematic way as V gradually changes from V_2 to V_1. At $V = V_2$, $N_1 = 0$ and $N_2 = N$. As V decreases toward V_1, N_1 progressively increases while N_2 decreases so that when V reaches V_1, $N_1 = N$ and $N_2 = 0$. In other words, N_1 and N_2 change with V via

$$\begin{aligned} \frac{N_1}{N} &= \frac{V_1 - V}{V_1 - V_2}, \\ \frac{N_2}{N} &= \frac{V - V_2}{V_1 - V_2}. \end{aligned} \tag{7.21}$$

Furthermore, suppose that the N_1 molecules behave like a part of an N-molecule system occupying volume V_1 (thus they are very compact) while the N_2 molecules behave like a part of another N-molecule system but occupying volume V_2 (thus they are much more loosely held together); since $V_2 > V_1$, the N_2 molecules are at a higher density than the N_1 molecules. The total free energy of the two groups would then be

$$\begin{aligned} F &= F_2 + \frac{F_1 - F_2}{V_1 - V_2}(V - V_2) \\ &= \frac{F_2(V_1 - V)}{V_1 - V_2} + \frac{F_1(V - V_2)}{V_1 - V_2}, \end{aligned} \tag{7.22}$$

which we recognize as the common tangent line.

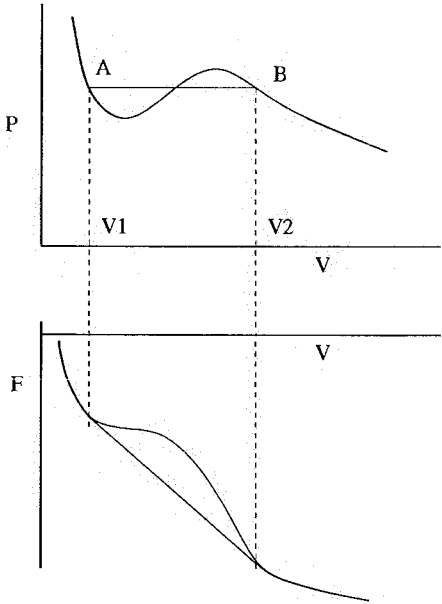

Fig. 7.6 The van der Waals pressure and free energy curves

Two important observations should be made. First, since the common tangent line lies below the van der Waals free energy curve, molecules follow it rather than the van der Waals free energy curve to save free energy. In this way, they refuse to be in a single homogeneous phase in the region between V_1 and V_2 and prefer to be in two coexisting phases, one in a gas phase and one in a liquid phase. The minimum free energy principle ordered the molecules to change the way they assemble together.

Second, since the common tangent line maintains a fixed slope between V_1 and V_2, the pressure remains constant between V_1 and V_2. In other

words, the line connecting points A and B in Fig. 7.6 is horizontal, and thus the two coexisting phases are in a mechanical equilibrium.

Is it possible to find points A and B directly from the van der Waals pressure curve without drawing the free energy curve? The answer is yes, thanks to the following curious geometrical property of the line connecting points A and B. Call the pressure corresponding to the horizontal line p_{12}. Due to Eq. (4.8), the area under this horizontal line is $p_{12}(V_2 - V_1) = -(F_2 - F_1)$. But $-(F_2 - F_1)$ is equal to the area under the van der Waals pressure curve, namely, $\int_{V_2}^{V_1} PdV$. This means that the area bound by the horizontal line and the van der Waals pressure curve above it is equal to the area bound by the left portion of the same horizontal line and the van der Waals pressure curve below it. The answer is simple: draw the horizontal line so that it encloses two equal areas as explained above. This is called the Maxwell construction.

Let us examine the van der Waals theory in terms of the Gibbs free energy G. Since $G = F + PV$, Eqs. (7.19) and (7.20) give

$$\begin{aligned} G &= -k_BTN\ln\left\{(mk_BT/2\pi\hbar^2)^{3/2}(V - Nb)\right\} \\ &\quad + k_BTN\ln N - k_BTN\frac{Nk_BTV}{V - Nb} - \frac{2N^2}{V}. \end{aligned} \tag{7.23}$$

Since V is not one of the proper variables of G, let us eliminate it in favor of p, in the following way. Choose a value for V, compute G and P, and then mark a point on a (p, G) plane. If this is repeated for many different values of V, the locus of the points on the (p, G) plane turn out to be as shown in Fig. 7.7.

Because of the triangular ribbon, G is not a single-valued function of P. Where do the points on the triangle come from? They are generated when V is between V_1 and V_2. If we replace G in this range of V with $G =$ Eq. (7.22) $+ PV$ while retaining the same G as given above by Eq. (7.23) in other ranges of V, then we get the same curve without the triangle. While V runs from V_1 to V_2, P and G do not change; the results repeatedly go to the vertex to which the triangle is attached. The free energy curve then consists of two line segments. Where the two lines meet, the slope changes abruptly. Here V and thus the concentration change abruptly, which makes the transition a first-order one.

As we move along the gas-liquid coexistence line toward the critical

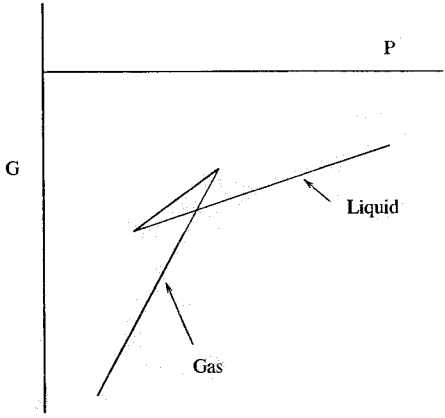

Fig. 7.7 Gibbs free energy as a function of p.

point in the P-T phase diagram, the first-order phase transition should become less and less abrupt. The critical point should mark the end point at which the abruptness finally disappears. Bearing this in mind, let us rearrange the van der Waals pressure equation in the form of

$$V^3 - \left(Nb + \frac{Nk_BT}{P}\right)V^2 + \frac{N^2aV}{P} - \frac{abN^3}{P} = 0. \tag{7.24}$$

Since this is a cubic equation, there are in general three solutions for V. Three solutions signify a first order phase transition and two coexisting phases. Since the critical point marks the end of the first order phase transition, the three solutions should merge into one at $T = T_C$. In other words, at the critical point, Eq. (7.24) should turn into

$$(V - V_C)^3 = 0. \tag{7.25}$$

If we expand this equation and then match it with Eq. (7.24) for each order

of V, we end up with three equations for V_C, P_C and T_C. Solving them simultaneously, we find

$$P_C = \frac{a}{27b^2}, \quad V_C = 3bN^2, \quad T_C = \frac{81}{27b}. \tag{7.26}$$

This does not say much about what really goes on at the critical point. Something interesting emerges if we scale p, V, and T by writing $P = \hat{P}P_C$, $V = \hat{V}V_C$, and $T = \hat{T}T_C$. Then the van der Waals pressure equation becomes

$$\left(\hat{P} + \frac{3}{\hat{V}^2}\right)\left(\hat{V} - \frac{1}{3}\right) = \frac{8\hat{T}}{3}, \tag{7.27}$$

where all the parameters that characterize different species, namely a and b, have disappeared. In other words, when p, V and T are viewed in such scales, all species of molecules look alike. This is called the law of corresponding states. It suggests that everything looks the same if we see them in the proper scales and offers a glimpse of a much broader scaling phenomenon which occurs in second-order phase transitions. We will discuss this in more detail in Sec. 8.7.

Finally, return to Eq. (7.14) and recall what we did for $n(\vec{r})$. The local density fluctuates because the Lennard-Jones force or the field that the molecule at the origin exerts on others changes with $\vec{r}$. When we replaced it with its global average value $n = N/V$, we ignored the fluctuation. For this reason, the van der Waals theory is called a mean field theory.

7.6 Phase Diagram in T-V Plane

Returning back to Fig. 7.6, let us summarize what the van der Waals theory has taught us for N interacting molecules. Their thermal behavior is different above and below T_C. At $T > T_C$, the N molecules can exist in a single phase in any volume V, namely, with any density $n = N/V$. At $T < T_C$, on the other hand, they can exist in a homogeneous phase either in volume $V < V_1$ with any density greater than $n_1 = N/V_1$, or in volume $V > V_2$ with any density less than $n_2 = N/V_2$. There is a gap in the density allowed for a homogeneous phase. Should we confine the N molecules at $T < T_C$ in volume V which lies between V_1 and V_2, the molecules then split

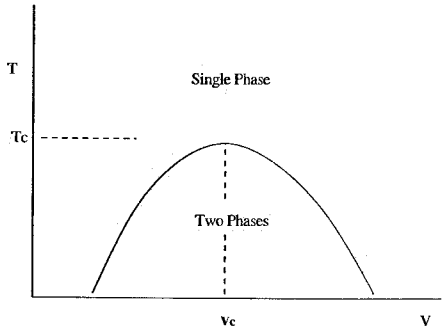

Fig. 7.8 Schematic T-V phase diagram

into two groups to form two coexisting phases, one in a liquid phase and one in a gas phase. Marking the point (V_1, T) and (V_2, T) for various T on a T-V plane, we may construct a phase diagram as depicted in Fig. 7.8. The density gap emerges at $T = T_C$ and widens as the temperature is further reduced. The two boundary lines, one on the gas side and one on the liquid side, are simply called the coexistence lines. The exterior of the "dome" bound by the two coexistence lines is called the one-phase region and the interior the two-phase region.

If the system enters the dome straight down through the appex where $V = V_C$, the transition is of second order; the phase diagram makes it clear that the density cannot change abruptly. If the entrance is anywhere else where $V \neq V_C$, the transition is of first order. For example, if the entrance is through the two-phase boundary line on the gas side, it is obvious that the emerging liquid phase requires an abrupt change in density.

If the entrance itself is abrupt, things become not only interesting but extremely useful. Prepare a system in equilibrium anywhere in a single homogeneous phase with density, say, between n_1 and n_2. Then "grab" it and suddenly change the temperature to displace it deep into the two-phase region where the chosen density is forbidden. What happens? Since the system is in the two-phase region, a phase separation has to occur, but the actual dynamics of the phase separation is different depending on exactly

what part of the two-phase region the molecules are thrown into. This seemingly "playful" question captivated scientists across a broad spectrum for nearly half a century and is still an active area of research.

The van der Waals pressure curve in Fig. 7.6 explains what happens when the molecules are thrown into the forbidden region. It is notable that as V increases from V_1 to V_2, the curve first goes down below the horizontal line, goes up above it, and then finally keeps going down. There is a valley and a peak. Call the volume corresponding to the bottom of the valley $\tilde{V}_1$ and that corresponding to the top of the peak $\tilde{V}_2$. At these two points,

$$\frac{\partial P}{\partial V} = 0, \tag{7.28}$$

or equivalently,

$$\frac{\partial^2 F}{\partial V^2} = 0, \tag{7.29}$$

where F is the van der Waals free energy. For $\tilde{V}_1 < V < \tilde{V}_2$, notice that

$$\frac{\partial P}{\partial V} > 0, \tag{7.30}$$

which suggests a negative isothermal compressibility

$$K_T < 0. \tag{7.31}$$

As we will argue shortly and in Appendix C, this means that the system has lost its stability.

The locus of $(\tilde{V}_1, T)$ and $(\tilde{V}_2, T)$ at various temperatures form two lines which divide the two-phase region into two parts as shown in Fig. 7.9; these lines are called spinodal lines and are chatacterized by Eqs. (7.28) and (7.29). When molecules are displaced into the central region bound by the two spinodal lines, they become **unstable** against the phase separation. When molecules are displaced into the outer region bound by the two spinodal lines and the two coexistence lines, they become **metastable** against the phase separation. Let us find out why.

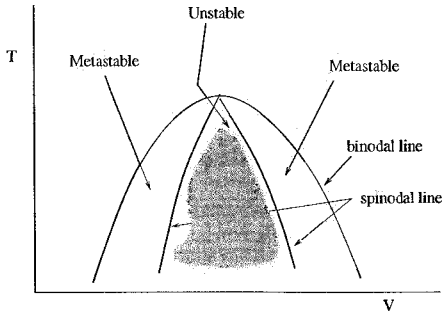

Fig. 7.9 The binodal and spinodal lines in the two-phase region

7.6.1 *Unstable Region*

When molecules are displaced into the unstable region, they become unstable against phase separation. To see why, examine Eq. (7.30). It says that **pressure increases with increasing volume and decreases with decreasing volume!** Since pressure represents the "appetite" for volume, this is a pathological feature and puts the molecules in a dangerously explosive condition. The molecules divide themselves into two groups. One group expands to turn into a further rarefied gas while the other compresses itself to turn into a more condensed liquid phase. One group wants more volume while the other wants less volume, and therefore there is no shortage or excess of volume. Each party can do what it wants to do at the courtesy of the other. This explains the instability. The initial prompt phase separation is not, however, a run-away process. Soon the molecules are no longer homogeneously mixed as they were at the beginning and therefore the pathological feature $\partial P/\partial V > 0$ no longer applies. The mechanism that drives the ensuing phase separation is called the spinodal decomposition which we will study in Sec. 9.3.

7.6.2 *Metastable Region*

Consider what happens when molecules are quenched into the metastable region, say, the one on the right hand side facing the gas phase in Fig. 7.9. The initial homogeneous mixture is to be transformed into two phases, a large gas phase and a small liquid phase. By doing so, they would save free energy by the amount of ΔF which is the difference between the van der Waals free energy and the common tangent line in Fig. 7.6. In order to do so, N_1 molecules should go into the liquid phase with density $n_1 = N_1/V_1$ while the rest should go into the vapor phase with density $n_2 = N_2/V_2$. Because the liquid phase constitutes only a small fraction, the liquid phase has to occur as droplets in the midst of a vapor. Thus immediately after the quench, many droplets are nucleated. To see what then happens to them, consider a droplet of radius R assuming that its density is $n_1 = N_1/V_1$. The free energy saved by the droplet is $(\Delta F/N)n_1 4\pi R^3/3$. Meanwhile, a liquid droplet in the midst of a vapor has an interface which costs free energy; the interface cost is proportional to the surface area of the droplet. Thus the net free energy cost is given by

$$\delta F = \gamma 4\pi R^2 - (\Delta F/N)n_1 4\pi R^3/4, \tag{7.32}$$

where the first term represents the interface cost and the second the savings.

Figure 7.10 shows how δF changes with R. For a small R, the surface term dominates and $\delta F > 0$. For a sufficiently large radius, the second term dominates and it pays to phase separate because $\delta F < 0$, but a barrier has to be overcome to get there, which explains the metastability. Most of the droplets fail to overcome the barrier and evaporate back into the vapor, but rare thermal fluctuations carry some of the droplets over the barrier for further growth. This process is called nucleation and growth.

7.7 Mixing and Demixing

Let us now study the phase-separation phenomenon with a different system. We know that water and oil do not mix at normal temperatures but they do at very high temperatures. We wish to find out how the free energy minimum principle causes this behavior. Mixing and demixing phenomena occur in all phases of matter, but if we choose atoms in a solid phase,

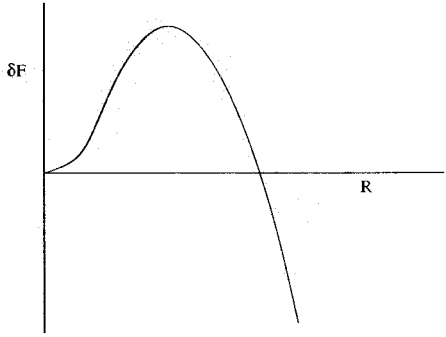

Fig. 7.10 The free energy cost for a droplet of radius R.

constructing a mean field theory is particularly simple.

Consider N_A atoms of species A and $N_B = N - N_A$ atoms of species B. Let $N_B/N = x$. For the sake of simplicity, assume that both species of atoms share the same lattice structure and that each atom supports p bonds irrespective of species. Let u_{AA}, u_{BB}, and u_{AB} represent the bond energy between $A-A$ pairs, $B-B$ pairs, and $A-B$ pairs, respectively. In the actual mixtures in a laboratory, the mixing would not be uniform throughout the sample. But in the spirit of mean field theory, let us ignore the local fluctuations. Then on average, an A-atom supports $p(1-x)$ bonds of $A-A$ type and px bonds of $A-B$ type. The average energy of an A atom is

$$u_A = p(1-x)u_{AA} + px\,u_{AB}, \tag{7.33}$$

and the average energy of a B atom is

$$u_B = p(1-x)u_{AB} + px\,u_{BB}. \tag{7.34}$$

The average energy per atom is given by

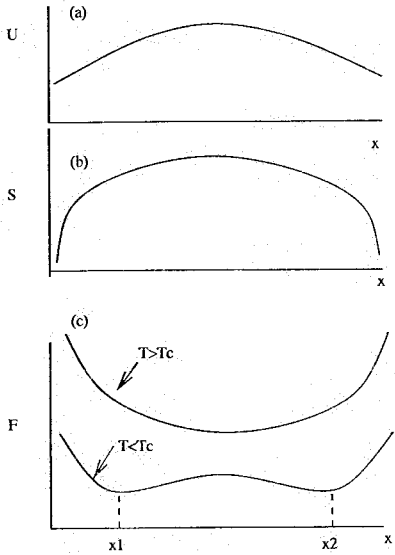

Fig. 7.11 (a) Energy, (b) Entropy, and (c) Free energy.

$$u = \frac{1}{2}\{(1-x)u_A + x\,u_B\}, \tag{7.35}$$

where the factor 1/2 corrects the fact that each bond has been doubly counted. The total energy is then

$$U = Nu = \frac{Np}{2}\{(1-x)^2 u_{AA} + 2x(1-x)u_{AB} + x^2 u_{BB}\}. \tag{7.36}$$

Assuming that $U_{AB} > U_{BB} = U_{AA}$, Fig. 7.11(a) depicts how U changes with x. It is significant that U has an upward bulge.

Let us now calculate the entropy. The total number of ways of distributing the two species of atoms over the lattice sites is given by

$$\Gamma = \frac{N!}{(N-N_B)!N_B!}. \tag{7.37}$$

Assuming that the three numbers are large, we may use the Stirling formula to obtain

$$\begin{aligned} S &= \ln\Gamma \\ &= (N-N_B+N_B)\ln N - (N-N_B)\ln(N-N_B) - N_B\ln N_B \\ &= (N-N_B)\ln\left(\frac{N-N_B}{N}\right) - N_B\ln\left(\frac{N_B}{N}\right) \\ &= -N\left((1-x)\ln(1-x) + x\ln x\right). \end{aligned} \tag{7.38}$$

This is a concave-downward function as shown in Fig. 7.11(b). Notice that the slope is infinite at both ends, and therefore the entropy of mixing is going to be the dominant factor near $x = 0$ and $x = 1$. As will become clear shortly, this means that the two species will always mix near $x = 0$ and $x = 1$.

Combining Eqs. (7.36) and (7.38), the free energy $F = U - TS$ takes the shape shown in Fig. 7.11(c). Starting from a temperature to be called T_C, there is an upward bulge in the mid range of x which suggests the same instability that we saw in the van der Waals theory. Draw a common tangent line which touches the F curve at x_1 and x_2. The two species of atoms do not mix in the range $x_1 < x < x_2$ to create a miscibility gap; instead they split into two different mixtures, one mixed at the ratio of x_1 and the other mixed at the ratio of x_2. The miscibility gap emerges at T_C and widens as the temperature is further lowered.

The primary thermodynamic variables are x, T and $\mu = (\partial F/\partial x)_T$. The variable x plays the same role for mixing and demixing atomic systems that V plays for liquid-gas systems, while μ plays the role that pressure plays for liquid-gas systems.

Figure 7.12 shows the chemical potential along with the corresponding free energy curve. The chemical potential curve looks like the van der Waals pressure curve flipped over. It has a peak at $x = \tilde{x}_1$ followed by a valley at $x = \tilde{x}_2$. At these two points of x,

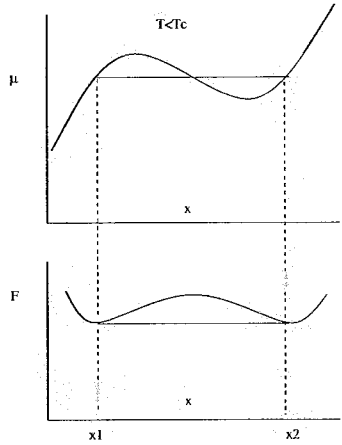

Fig. 7.12 The chemical potential and the free energy of binary atomic systems. Here x represents the ratio of one species to the total number of atoms.

$$\frac{\partial^2 F}{\partial x^2} = 0, \quad \text{or} \quad \frac{\partial \mu}{\partial x} = 0 \tag{7.39}$$

The locus of these two points for various temperatures define the spinodal lines which divide the two-phase region of the phase diagram into two parts, as shown in Fig. 7.13.

Returning back to Fig. 7.12, examine the chemical potential in the region of x between $\bar{x}_1$ and $\bar{x}_2$. In this region,

$$\frac{\partial \mu}{\partial x} < 0 \tag{7.40}$$

which says that the unlivability decreases with increasing population. Since $x = N_B/N$, this equation says that the livability increases for B atoms with an increasing fraction of B atoms. The same can be said for A atoms as well. As a result, the atoms split into two phases, one rich in B and one rich

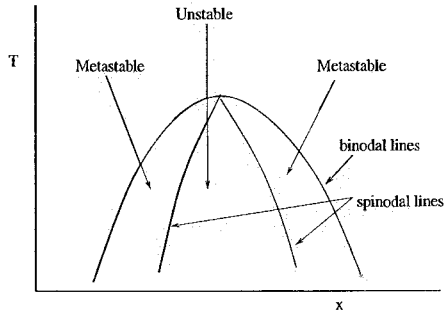

Fig. 7.13 The phase diagram in T-x plane

in A; once again, each group can form a more livable phase at the courtesy of the other. This explains the instability in the interior of the two-phase region. The word "segregation" is often used to describe this phenomenon, but it misleads. It is true that the atoms find it unduly expensive to be mixed at any mixing ratio between $\tilde{x}_1$ and $\tilde{x}_2$ and therefore they separate into two groups to reduce their free energy. However, the atoms also find it unduly expensive to be in two completely "segregated" phases, which they do not do spontaneously.

In the outer regions, the reason for the metastability is the same as before. Droplets rich in one species have to be formed in a sea of the phase rich in the other majority species, but the interface cost poses a free energy barrier which the droplets have to overcome for further growth. The phase diagram is as depicted in Fig. 7.13. In Sec. 9.3, we will find a way to study the actual phase separation process that happens when a homogeneous mixture is thrown into this forbidden region.

When the mixing-demixing phase diagram is as shown in Figure 7.13, the phase diagram is said to be normal with an upper critical temperature, which means that demixing occurs for $T < T_C$. Not all binary mixtures have this type of phase diagram. Some have an inverted phase diagram with a lower critical temperature, meaning that demixing occurs when $T > T_C$. Some have a closed phase diagram with both upper and lower critical

temperatures.

We have merely taken a glimpse at the mixing and demixing phenomena. The field is rich from the basic point of view as we have emphasized. It is also rich from the point of view of industrial applications. In fact the equation that we will derive in Sec. 9.3 to describe the dynamics of phase separation was obtained by workers from metallurgy. We hardly did justice to the field with the brief coverage, and that with the idealized model.

Chapter 8

Second-Order Phase Transitions

8.1 Introduction

In this chapter we will study second-order phase transitions in more detail. We should start by reexamining the Helmholtz free energy equation $F/T = U_s/T - S_s$. The first term U_s/T is an investment by the reservoir and S_s is the return. The investment is not U_s but U_s/T. Low temperature discourages investment, which results in a state of low energy and low entropy. High temperature encourages investment, which results in a state of high energy and large entropy. States of low entropy look like a bear stock market while states of high entropy look like a bull market. I do not know if there is a distinct pattern of business activities which may be taken as a warning sign of an upcoming transition from one market to the other. For thermal systems, the transition occurs at a well-defined temperature, namely T_C, and comes with a distinctive warning sign. As the temperature approaches the critical temperature, all extensive variables fluctuate wildly. At $T = T_C$, the fluctuations diverge. The divergence is characterized by various critical exponents. Just as the fluctuations in the stock market are difficult to study scientifically, critical phenomena has proved to be extremely difficult. This chapter describes the difficult state of affairs before the renormalization group theory emerged.

We will first discuss in Secs. 8.2 and 8.3 what has been learned about the transition by laboratory experiments. Section 8.2 covers liquid-gas molecular systems and Sec. 8.3 magnetic systems. Such studies for many different systems lead to the notion of universality in Sec. 8.4 and the scaling laws in Sec. 8.5. The much-anticipated Landau mean field theory appears in

Sec. 8.6. The static scaling hypothesis in Sec. 8.7 is an effort to explain the scaling laws.

8.2 Liquid-Gas Molecular Systems

Let us return to Fig. 7.8 and consider a molecular system in a fixed volume equal to V_C, the volume at the critical point. The molecules are in a homogeneous single phase at $T > T_C$ and in two distinctively different phases at $T < T_C$, a dense phase of liquid and a dilute phase of gas. Raise the temperature from slightly below T_C towards T_C. The difference between the densities of liquid and gas, ρ_L and ρ_G, becomes smaller and smaller and finally vanishes at T_C. At this point the system has reached the peak of the dome in the phase diagram where the two coexistence lines meet. The transition may thus be described by

$$\tilde{\rho} = \rho_L - \rho_G, \tag{8.1}$$

which is referred to as the order parameter; it is zero above T_C and non-zero below T_C. In the context of entropy as a measure of disorder, the transition marks an onset of order if we approach T_C from the high temperature side, or the disappearance of order if we approach it from the low temperature side. Experiments have shown that

$$\tilde{\rho} \sim t^{\beta}, \tag{8.2}$$

where $t = |T_C - T|/T_C$, the relative distance in temperature to the critical point. For most liquid-gas systems, the order-parameter exponent is approximately $\beta = 1/2.9$, regardless of the intermolecular interactions. From now on, the symbol β will be used solely to represent the order parameter exponent rather than $1/k_BT$.

The order parameter is just one of many variables which exhibit critical behavior. The critical behavior is very simple: the variables either diverge or vanish, with nothing in between. For these variables, the issue is how they diverge or how they vanish. For this reason, they are always presented with the symbol $\sim$ which should be read as "goes like".

The transition is accompanied by diverging response functions. The specific heat and the compressibility become larger and larger as T ap-

proaches T_C from either direction (from $T > T_C$ or $T < T_C$) and finally diverge at T_C. Experiments have shown that the specific heat diverges at T_C with exponent α

$$C \sim t^{-\alpha}, \tag{8.3}$$

and the compressibility diverges with exponent γ

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T} \sim t^{-\gamma}. \tag{8.4}$$

The diverging compressibility means that if V is allowed to vary with N held fixed, the density should exhibit large fluctuations. What does this indicate? If the local density fluctuations are random, then there should be as many localities where the density is above average as there are localities where it is below average. Therefore, there cannot be a large global or overall density fluctuation. The fact that there are large global density fluctuations means that the local density fluctuations are not random but correlated. Indeed, the local density fluctuations are correlated over a length scale which increases as T approaches T_C and finally diverges at $T = T_C$. To describe the correlated density fluctuations, define the local density deviation by

$$\delta\tilde{\rho}(\vec{r}) = \tilde{\rho}(\vec{r}) - <\rho>, \tag{8.5}$$

where $<\rho>$ is the average density over all different localities. The correlations may then be described by

$$G(r) = <\delta\tilde{\rho}(\vec{0})\delta\tilde{\rho}(\vec{r})>. \tag{8.6}$$

The correlation function questions whether or not distant localities tend to act in unison for fluctuations in the same direction. If they do, there are bound to be many patches of different densities, and the patches should be sized comparably to the length scale over which they act together. This assertion can be checked experimentally by observing how the sample scatters light. At T near T_C, experimental results suggest that

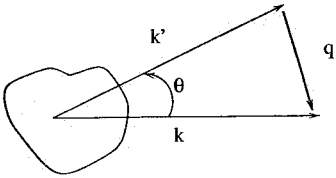

Fig. 8.1 Light scattering

$$G(r) \sim \frac{\exp(-r/\xi)}{r}, \tag{8.7}$$

which says that $G(r)$ is non-zero approximately up to $r = \xi$ and then drops off quite rapidly as r increases further. In other words, the correlation extends up to the length scale of ξ. Therefore, ξ is called the correlation length. It is the most important player in critical phenomena. Experiments have also shown that

$$\xi \sim t^{-\nu}, \tag{8.8}$$

where ν is called the correlation length exponent. The correlation length grows as T approaches T_C and diverges at T_C. This means that at exactly T_C, the patches are of all sizes up to infinity. This is why the compressibility diverges at T_C. Since the molecules spontaneously form patches of liquids (in which molecules are more compressed than in the gas phase) without any external force, not much change in pressure is required to force a large change in density.

This correlated fluctuation is not a result of an external force. Groups of molecules act together spontaneously. They are like good friends. When something happens to make one of them sad, it tends to also make the others sad, and when something good happens to make one of them happy, it tends to also make the others happy; their moods tend to fluctuate in a correlated fashion. How do we study this correlation in the laboratory? A monochromatic light beam of wavelength λ is sent into a sample and the intensity of the scattered light is measured at various angles with respect to the incoming light as depicted in Fig. 8.1. The triangle shows $\vec{k}$, the

wave vector (momentum divided by $\hbar$) of the incoming photons, $\vec{k}'$, the wave vector of the scattered photons, and $\vec{q}$, the wave vector transferred to the sample from the light. Here, the scattering is elastic and therefore $k = k' = 2\pi/\lambda$. It is clear from the triangle that the transferred wave vector q is given by

$$q = \frac{4\pi}{\lambda}\sin(\theta/2), \tag{8.9}$$

The intensity of the scattered light at the angle corresponding to the wave vector q is found to follow

$$\text{Intensity} \sim S(q) = \frac{k_B T \rho K_T}{1 + q^2\xi(T)^2}, \tag{8.10}$$

where $S(q)$ is the Fourier transform of the correlation function $G(r,T)$. It is called the structure factor and may be written as

$$S(q) =< |\delta\rho(\vec{q})|^2 >, \tag{8.11}$$

where $\delta\rho(\vec{q})$ is the Fourier transform of the local density fluctuations $\delta\rho(\vec{r})$.

By measuring the light intensity with the detector placed at an angle corresponding to q, we are probing the density fluctuation (df) in the length scale $\lambda_{\text{df}} = 2\pi/q$. If $S(q)$ is large for a particular value of q, it means that the density fluctuation has a prominent pattern which tends to repeat itself with the wavelength given by $2\pi/q$. As it turns out, there is not just one such pattern but rather many of them. Therefore, near $T = T_C$ the sample may be thought of as a "random" diffraction grating, as depicted in Fig. 8.2. Unlike a "uniform" diffraction grating where lines are drawn with the same spacing and in the same direction everywhere, many different groups of lines are drawn here and there with different spacings and in different directions. Such diffraction gratings would scatter white light in all directions. That is exactly what samples do near $T = T_C$. Away from the critical point, samples look transparent. But as the critical point is approached, samples look milky because all of the components of white light are scattered. This phenomenon is called critical opalescence. Watching this is great fun. Go to any physical chemistry laboratory and ask for a demonstration. A binary liquid mixture with an inverted phase diagram appears to be the easiest

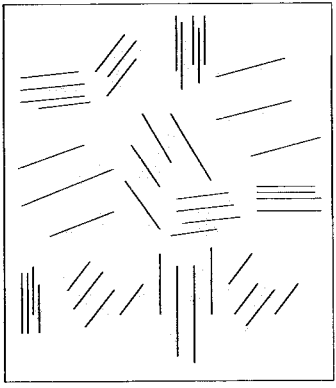

Fig. 8.2 An incomplete and random diffraction grating. Someone must have been drunk.

way to see it. If you are as lucky as I was, you will find someone to do this for you. My host poured a binary liquid mixture into a test tube and then put the tube on a Bunsen burner to raise the temperature. Initially the mixture looked transparent like a wine, but as the temperature approached the critical temperature, it turned into a white milk.

The fact that the patches come in many different length scales is the root of the difficulty of studying the critical point phenomena. No other physical phenomena involve such a vast range of different length scales. Examine the atomic physics of hydrogen. You will notice that in all of the energy eigenfunctions the variable r always appears in the form of r/a_0 where a_0 is the Bohr radius, and therefore a_0 is the unique characteristic length scale. Examine the electric field in the presence of, say, a conductor of radius R. Again, r appears in the electric field in the form of r/R, meaning that R is the lone characteristic length scale. Can you imagine how difficult it would be if there were an infinite number of Bohr radii? How would you then construct a Bohr theory? Critical opalescence was observed in the late 19th century, but a satisfactory explanation was not found for nearly a century. That explanation is given by the renormalization group theory.

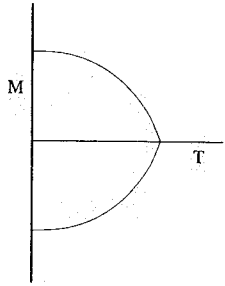

Fig. 8.3 The phase diagram of ferromagnets in an M-T plane.

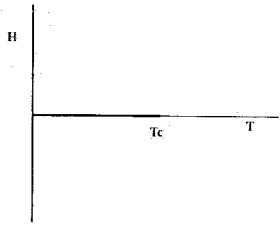

Fig. 8.4 The phase diagram of ferromagnets in a T-H plane

8.3 Spin Systems

Now consider uniaxial ferromagnets using Ising models. Above the transition temperature, the spins are oriented randomly with no net magnetization, and the system is in a paramagnetic phase. As the temperature is lowered below the critical temperature (called the Curie temperature), the spins spontaneously begin to align and go into a ferromagnetic phase. The net magnetization begins to become nonzero from $T = T_C$; upon passing through T_C, two symmetric phases emerge, one of M and the other of $-M$, as shown in Fig. 8.3. This is the magnetic analogue of Fig. 7.8. With a

magnetic field, the two coexisting phases can be turned into one. The phase behavior in an H-T plane is as shown in Fig. 8.4. This is the magnetic analogue of Fig. 7.1. The thick line represents the coexistence of up ($+M$) and down ($-M$) phases, and therefore is a line of first-order phase transitions. As we move on it towards the right, the difference between the up phase and the down phase becomes less and less and finally disappears at the critical temperature T_C; the end of the line is a point of second-order phase transition. Since M is zero above T_C and non-zero below T_C, it serves as the order parameter.

Even in the zero magnetic field, the two coexisting phases are actually only metastable. Given enough time, they will ultimately turn into one of the two phases. In the one-phase region above T_C, the spin orientations are symmetric under the reversal of spins, namely, s_i to $-s_i$ for all spins. Below T_C, however, the symmetry is broken spontaneously. Nothing in the spin interaction or in the microstate structure favors one spin direction over the other, and therefore an ordered phase of up spins should coexist with one of down spins. But they do not; the interface cost is too much for them to bear. In the presence of the up-down symmetry, how do they then decide which curve to choose?

A truly minuscule impurity in the sample which favors one direction over the other or a truly insignificant up-down asymmetry which may have existed while the system was in the homogeneous phase is now enough to break the symmetry and allows all the spins to turn in the favored direction. This symmetry breaking process is very slow. We can accelerate it with an external magnetic field. Suppose we apply a weak magnetic field. All spins align in the direction of the field. Now gradually remove the field. The spins **remain aligned** in the same direction even after the field has vanished. In this way, we can put the system on the $+M$ curve or on the $-M$ curve. In order to save the interface cost, the spins prefer to break the up-down symmetry.

We humans actually do something similar to this. In a typical old public building, when a man in search of a restroom sees one for ladies, he will rush to the opposite end of the building for a men's room and it is a good bet that he will find one there. In many modern buildings, the left-right symmetry is broken to save plumbing costs.

The transition to the ordered state at T_C is smooth in the sense that M changes continuously with the temperature. However, the continuous change at T_C is accompanied by diverging specific heat and diverging sus-

ceptibility, as in the liquid-gas system. Experiments have shown that the order parameter M vanishes, or begins to grow, like

$$M \sim t^{\beta}, \tag{8.12}$$

and the response functions diverge like

$$C \sim t^{-\alpha}, \tag{8.13}$$

and

$$\chi \sim t^{-\gamma}. \tag{8.14}$$

Notice that the susceptibility exponent shares the same symbol with that of the compressibility of liquid-gas systems. This is because they represent the fluctuation of their respective order parameters, and therefore they represent essentially the same critical property.

The spin correlation function may be defined by

$$G(r) = < (s_i - < s >)(s_j - < s >) >, \tag{8.15}$$

where r represents the distance between site i and site j. It exhibits the same pattern of correlation as in Eq. (8.7). In particular, the spins tend to act together in unison over long distances, i.e.,

$$\xi(r,t) \sim t^{-\nu}. \tag{8.16}$$

Exactly at $T = T_C$, the spatial correlation decays much more slowly,

$$G(r, t = 0) \sim \frac{1}{r^{d-2+\eta}}, \tag{8.17}$$

where d is the dimensionality of the space and η is yet another exponent.

Let us introduce one more exponent. At $T = T_C$, the magnetization follows the field like

$$M \sim H^{1/\delta}.$$

Many different systems exhibit critical point behavior. In general, the critical exponents are different for different systems; α, β, γ, etc., are in general different for different systems. However, for all systems the critical exponents satisfy certain relationships such as:

$$\alpha + 2\beta + \gamma = 2, \tag{8.19}$$

$$\gamma = \beta(\delta - 1), \tag{8.20}$$

$$\gamma = (2 - \eta)\nu, \tag{8.21}$$

$$\nu d = 2 - \alpha. \tag{8.22}$$

Such relationships among the critical exponents are called the scaling laws. We will return to these relationships in Sec. 8.7. In a way, aren't the scaling laws similar to the third law of Kepler? Different planets maintain different average distances (R) from the sun and take different amounts of time (T) to revolve around the sun, but for all planets, T^2/R^3 is the same. Just like Kepler's laws provided clues to the laws of motions and the law of gravitation, these scaling laws imply something rather startling and ultimately helped solve the puzzle of critical phenomena.

8.4 Universality

Many different systems exhibit second-order phase transitions. Experiments have shown that these systems form several universality classes. Those belonging to the same class share the same set of critical exponents. This is remarkable because the member systems belonging to the same class can be quite different from atomic and molecular points of view. For example, two-dimensional planar ferromagnets and liquid helium-4 belong to the same universality class. The former is a solid (in which the dipole moments are on a three-dimensional lattice but their direction vectors form a plane) while the latter is a liquid. The former is in its classical regime while the latter is in its quantum mechanical regime. But near the critical point the atomic and molecular characteristics do not seem to play a role in the critical behavior of these systems, and what determines the critical behavior are the spatial dimensionality of the system and the number of

components of the order parameter, or the dimensionality of the order parameter space. For both planar ferromagnets and liquid He-4, $d = 3$. The order parameter for planar ferromagnets has two components because the direction vectors of the magnetic dipole moments are restricted to lying on a plane and therefore the order parameter is a two-dimensional vector. The order parameter for liquid He-4 is given by the condensate wave function which has two components, the real and imaginary parts.

The liquid-gas molecular systems and the three-dimensional uniaxial ferromagnets (the Ising model) provide another example. They belong to the same class because their order parameters have only one component.

8.5 Mean-Field Theory

We observed earlier that the ideal Ising spins cannot support a ferromagnetic phase. Let us now add an interaction term and see whether it brings with it a ferromagnetic phase and critical behavior. The microstate energy depends on the spins in the following way:

$$E_\nu = -Hm \sum_i s_i - J \sum_{<i,j>} s_i s_j, \tag{8.23}$$

where $< i, j >$ means that, for a given lattice site i, the index j ranges over all the sites neighboring i. Thus the interaction is short-ranged and extends only to the nearest neighbors. The coupling constant J is positive, meaning that it costs energy for neighboring spins to oppose each other.

It is quite easy to work out the partition function for interacting Ising spins in one dimension, but the solution does not exhibit a phase transition at a finite temperature. The partition function has been worked out by Onsager in two dimensions, and the solution does exhibit a phase transition at a finite temperature. The solution for the three-dimensional Ising model has proven very illusive, and no one has been able to work it out. Let us try a simple mean field theory.

To apply the idea of a mean field, we rewrite Eq. (8.23) in the form of

$$E_\nu = -\sum_i s_i \Big\{ mH + J \sum_j s_j \Big\} = -\sum_i s_i m \hat{H}_i, \tag{8.24}$$

where $m\hat{H}_i = mH + J\sum_j s_j$. The effective field $\hat{H}_i$ acting on spin i consists of the external applied field plus the sum of its nearby spins. Because of the latter, the effective field differs from site to site, but in the spirit of mean field theory we ignore the local fluctuations and write the field in terms of the global average spin. Thus we write

$$m\hat{H}_i = mH + Jz < s >, \tag{8.25}$$

where z is the number of nearest neighbors (called the coordination number). Since the ferromagnetic phase transition takes place in the absence of an external magnetic field, we set $H = 0$. The effective field is $\hat{H}_i = Jz < s > /m$, where $< s >= \sum_i s_i/N$. We may then treat $\hat{H}_i$ like an external field for ideal spins. Using Eq. (4.31), the result for the magnetization is:

$$< s >= \tanh(m\hat{H}/k_BT). \tag{8.26}$$

Since $\hat{H}$ involves $< s >$, it has to be solved self-consistently. First, notice that since $\tanh(x) = 0$ for $x = 0$, $< s >= 0$ is a solution at any temperature.

Is there a nonzero solution? The best way to pursue the answer is to rewrite the right hand side of Eq. (8.26) in terms of $\exp(m\hat{H}/k_BT)$ and to solve Eq. (8.26) for it. This gives us

$$\frac{1+ < s >}{1- < s >} = \exp(2m\hat{H}/k_BT). \tag{8.27}$$

The fact that the transition is continuous proves to be handy for us here because we may assume that $< s >$ is very small. Take the logarithm of Eq. (8.27), and then expand $\ln(1+ < s >)$ and $\ln(1- < s >)$ to the second order in $< s >$. We find

$$< s >^2 = \frac{3}{T}(2Jz - T). \tag{8.28}$$

Identifying $2Jz$ with T_C, we see that there is a nontrivial solution for $T < T_C$. The spin interaction does bring a phase transition with the order parameter exponent $\beta = 1/2$. Although the mean field theory is good enough to detect the presence of a phase transition, $\beta = 1/2$ is incorrect.

While the exponent β is independent of the parameters characterizing each system, J and z, the transition temperature T_C is dependent on these atomic details. This turns out to be a general property.

8.6 Landau Mean Field Theory

Landau constructs a mean field theory in a different way. He proceeds as follows. How much free energy would it cost if the system claimed a total spin of M at temperature T? From Eq. (6.9), the answer is

$$F(M,T) = -k_B T \ln \sum_i \Delta(M - M_i) \exp(-E_i/k_B T), \tag{8.29}$$

where macrostates are defined in terms of M, and M_i is the net spin of the microstate i. By asking for $F_L(M,T)$, we are not just after the equilibrium free energy. Depending on what we choose for M, $F_L(M,T)$ could be the equilibrium free energy corresponding to the most probable macrostate or it could be a very expensive macrostate free energy corresponding to a less probable macrostate.

Imagine how nice it would be if we had this function in hand. The equilibrium free energy would be obtained by merely asking at what value of M it reaches its minimum. Should we substitute any other value for M in the same function, $F_L(M,T)$ would tell us exactly how costly it is not to be in the most probable macrostate. Should we put the system in such a macrostate, the system would know how to move to the most probable macrostate as we discussed in Chapter 3, and we would therefore be able to study the nonequilibrium process in which a displaced system, i.e., a system with an undue amount of free energy, searches for its equilibrium state. It is important that we may distinguish between the equilibrium state and the non-equilibrium states by using different values of M but still using the same function.

Unfortunately we do not know how to carry out the summation that Eq. (8.29) requires. We shall guess the answer. We have two clues. First, at the critical point, nothing changes abruptly. Therefore the free energy should be a smooth analytical function of both M and T. Second, the free energy should be an even function of M because in the absence of an external magnetic field, there is no difference between up and down for the

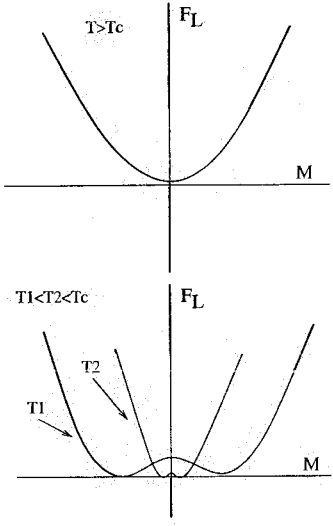

Fig. 8.5 The Landau mean-field free energy model

spins. Thus for small values of M, Landau assumes that $F_L(M,T)$ may be expanded as a power series in M, namely,

$$F_L(M,T) = g_0(T) + \frac{1}{2}g_2(T)M^2 + \frac{1}{4}g_4(T)M^4, \tag{8.30}$$

and lets each coefficient be a smooth function of T. Since $F_L(M,T)$ is written entirely in terms of the total spin M ignoring local fluctuations, it is a mean field theory.

We do not know what the coefficients are. We shall choose them so that when the system is at equilibrium near $T = T_C$, F_L can mimic the second order phase transition as best as it can within the limitation set by the functional form given by Eq. (8.30). To find out what M can be when the

system is at equilibrium, we set $\partial F_L/\partial M = 0$, which gives

$$g_2 M + g_4 M^3 = M(g_2 + g_4 M^2) = 0. \tag{8.31}$$

This equation determines the free energy minimum, i.e., the equilibrium state determined by the most probable macrostate that Eq. (8.30) allows. Obviously $M = 0$ is one solution, regardless of the temperature. It should remain as the lone solution for $T > T_C$. There should be a nontrivial solution for $T < T_C$. Let us seek it in

$$g_2 + g_4 M^2 = 0, \tag{8.32}$$

and try

$$g_2 = a(T - T_c), \qquad g_4 = b \tag{8.33}$$

where a and b are positive constants. The solution we seek is

$$M = (a/b)^{1/2}(T_C - T)^{1/2}. \tag{8.34}$$

Since M cannot be imaginary, it is a solution only for $T < T_C$ and the order parameter exponent $\beta = 1/2$ is in agreement with the previous mean field theory.

Notice that $g_0(T)$ is not coupled to the order parameter M, and therefore has no role to play; we will therefore omit it. The final result is

$$F_L(M,T)/k_B T = \frac{a}{2}(T - T_C)M^2 + \frac{b}{4}M^4. \tag{8.35}$$

Figure 8.5 depicts F_L plotted as a function of M at various temperatures. For $T > T_C$, the curve has one stable minimum at M=0. For $T < T_C$, the minimum at $M = 0$ becomes an unstable maximum while two stable minima emerge that favor nonzero M and hence a ferromagnetic phase. The minimum position starts from $M = 0$ at $T = T_C$ and increases continuously as T further decreases, as it should.

Exercise *Let us figure out what the following free energy model attempts to represent,*

$$F_L^2(M,T) = F_L^1 + \frac{1}{2}g_2M^2 - \frac{1}{4}g_4M^4 + \frac{1}{6}M^6, \tag{8.36}$$

where $F_L^2(M,T)$ is the macrostate free energy of phase 2 and $F_L^1(M,T)$ is that of phase 1; $g_2 = a(T-T_0)$, $a > 0$, $g_4 > 0$, and $g_6 > 0$. Notice that the g_4 term and the g_6 term compete against each other, the former in favor of phase 1 and the latter in favor of phase 2. The g_2 term sides with the g_6 term at $T > T_0$ and with the g_4 term at $T < T_0$. Plot the function for several values of T and observe that the model favors phase 1, namely, $F_L^2 > F_L^1$ with $M = 0$ at high temperatures. There exists, however, a temperature T_C below which the model favors phase 2 with an abrupt change in M. This is the Landau mean-field model for first-order phase transitions.

8.7 The Static Scaling Hypothesis

It is always a good idea to start with a mean field theory for any problem in thermal physics, but in the case of second-order phase transitions its validity is highly limited. This is because it ignores the fluctuations which are the heart of the phenomena. An intriguing idea of scaling was advanced in an effort to explain the scaling laws, and helped pave a way to the renormalization group theory. Someone once said that it would be impossible for anyone to walk through the halls of his physics department building without hearing the word "scaling". This points out how popular the idea of scaling is. We have already observed what might be called a primitive version while studying the van der Waals theory.

The static scaling hypothesis may be presented in several ways. We will first follow a version due to Widom. The hypothesis says that free energy is a homogeneous function of its proper variables. What does this mean? If a function $F(x,y)$ is homogeneous, the function is associated with two numbers p and q such that the following holds true, no matter what value is chosen for λ:

$$F(\lambda^p x, \lambda^q y) = \lambda F(x,y). \tag{8.37}$$

This means that if we know $F(x,y)$ for a limited range of x and y, say, $x < L$ and $y < L$, we can tell what the function is outside the range by

merely changing the scales (units) of x, y, and F. Suppose that we wish to know $F(x,y)$ for $x = X > L$ and $y = Y > L$. Then choose λ such that

$$\lambda^p X = x' < L, \tag{8.38}$$

and

$$\lambda^q Y = y' < L. \tag{8.39}$$

Then

$$F(X,Y) = \frac{F(x',y')}{\lambda}. \tag{8.40}$$

We do not even have to bother going outside the $x < L$ and $y < L$ range. We may stay inside the range and just change the unit of the x axis by λ^p, the y axis by λ^q, and the z axis (for F) by λ and then read the vertical reading! It is a lazy man's dream function!

Let us rephrase this fact in a more practical way. There are two independent variables x and y. Suppose that we plot F versus x with y fixed at various values. The plot is depicted in Fig. 8.6 The relationship between F and x seems to require an infinite number of curves. But notice the following. Since we may choose any value for λ, let us try $\lambda^q y = 1$ or $\lambda = y^{-1/q}$. Substituting this into Eq. (8.37), we find

$$F(y^{-p/q}x, 1) = y^{-1/q}F(x,y), \tag{8.41}$$

where the lefthand side is a function of one variable $z = y^{-p/q}x$. Therefore if we plot $F/y^{1/q}$ as a function of $x/y^{p/q}$, all of those scattered curves collapse into one, as depicted in Fig. 9.3(b). The implication is that x itself and F itself are meaningless. To be meaningful, x has to be measured in units of $y^{p/q}$, and likewise F has to be measured in units of $y^{1/q}$. When F and x are scaled in this way, they have a unique one-to-one relationship. Of course, we may say likewise for F and y in which case x will determine the proper scales.

There are many situations in life where different variables are interrelated in a similar fashion. When a person is stung by a bee, a doctor may say something similar. It is not the amount of poison itself that determines how critical the poison is going to be. It is the amount of poison that went into the blood stream divided by the total amount of blood in the body. The reader can add many more similar examples.

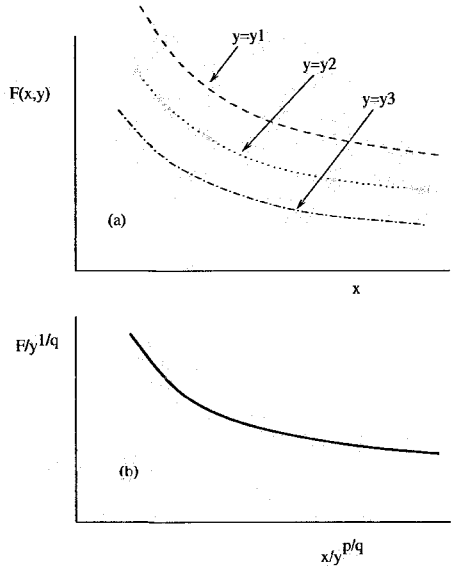

Fig. 8.6 (a) A homogeneous function F(x,y) plotted vs. x. (b) When F and x are properly scaled, all of the curves collapse into one.

Now let us apply the static scaling hypothesis to a ferromagnet in a magnetic field. The appropriate free energy is the Gibbs free energy, namely, $G(t, H)$, where the symbol t now represents $|T - T_C|/T_C$; in this section, we will not be speaking of time which t normally represents. Assume that $G(t, H)$ is a homogeneous function of t and H, namely,

$$G(\lambda^p t, \lambda^q H) = \lambda G(t, H). \tag{8.42}$$

What does the homogeneity assumption say about the magnetization, susceptibility, specific heat, and so on? Recall that M is to spins what V

is to molecules, and mH is to spins what $-P$ is to molecules. According to Eq. (5.43), M may be obtained from G by differentiating it with respect to H. By differentiating M with respect to H, we may then obtain the susceptibility χ. The specific heat C may be obtained from G by differentiating it twice with respect to t.

Differentiating Eq. (8.42) with respect to H, we obtain

$$\lambda^q M(\lambda^p t, \lambda^q H) = \lambda M(t, H). \tag{8.43}$$

Let $H = 0$ and, since we may choose anything for λ, let $\lambda^p t = 1$, i.e., $\lambda = t^{-1/p}$. Then Eq. (8.43) reduces to

$$M(t, H) = t^{-(q-1)/p} M(1, 0), \tag{8.44}$$

which gives

$$\beta = \frac{1-q}{p}. \tag{8.45}$$

To obtain the susceptibility exponent γ, differentiate Eq. (8.43) once more with respect to H to obtain

$$\lambda^{2q} \chi(\lambda^p t, \lambda^q H) = \lambda \chi(t, H). \tag{8.46}$$

Now let $H = 0$ and $\lambda^p t = 1$ to obtain

$$\chi(t, 0) = t^{-(2q-1)/p} \chi(1, 0), \tag{8.47}$$

which gives

$$\gamma = \frac{2q-1}{p}. \tag{8.48}$$

To obtain the specific heat exponent α, return to Eq. (8.42) and differentiate it twice with respect to t to obtain

$$\lambda^{2p} C(\lambda^p t, \lambda^q H) = \lambda C(t, H). \tag{8.49}$$

Let $H = 0$ and $\lambda^p t = 1$, which gives

$$C(t, 0) = t^{-(2p-1)/p} C(1, 0), \tag{8.50}$$

and thus

$$\alpha = \frac{2p - 1}{p}. \tag{8.51}$$

Since we do not know what p and q are, we have not really calculated these exponents. However, substitute the three exponents that we have obtained above into Eq. (8.19). All p's and q's are cancelled out, leaving us with the result 2 as the scaling law predicts!

The static scaling hypothesis has the following physical meaning. As Goodstein puts it, the system says to us: "I do not know anything but the correlation length ξ." I would add "Do not try to find out anything else from me because I know nothing more." This means that we can write the free energy only in terms of the correlation length. Under this restriction, what we can do for any quantity is totally dictated by its unit (dimension) and thermal physics becomes just a dimensional analysis. We wish to study G but we cannot just write $G =$ something. The only physically meaningful quantity that is related to G and is still amenable to the dimensional analysis is $G/(k_B T V)$: G has been divided by $k_B T$ to make it unitless and then by V so that we can say "free energy per volume" which is a physically meaningful quantity. Since its dimension is $-d = -3$, there is only one way it can depend on ξ, namely,

$$\frac{G}{k_B T V} \sim \frac{1}{\xi^d}, \tag{8.52}$$

where the simple power law is the result of the assumption that the sample only knows the correlation length; if it knew another pertinent length scale, the simple power law would no longer hold. Since the sample told us that it only knows ξ and did not say how much about it, we may assume that the correlation length depends on the temperature t and the magnetic field H also following a power law:

$$\xi(t, H = 0) \sim t^{-p}, \tag{8.53}$$

and

$$\xi(t=0,H) \sim H^{-q}. \tag{8.54}$$

This gives us free energy as a function of t and H, and therefore we may calculate M, C, and χ in terms of p and q, in the same way we did above. I will leave it for the reader to show that the scaling laws then follow.

All of these scaling analysis suggest that a successful theory of critical phenomena may have to involve some sort of scaling argument, and that scaling can make seemingly different things look alike. Notice that the hypothesis only recognizes the longest length scale, and not the others. This is a flaw.

Another important clue was provided by Kadanoff. In an effort to justify the scaling hypothesis, he introduced the notion of "coarse graining" or reducing the number of degrees of freedom. He did this with an Ising model by constructing block spins. The idea of a block spin is very simple. Consider Ising spins on a two-dimensional lattice. Group the spins into blocks of $a \times a$ spins and call the net spin in the block the block spin. Here the block size is assumed to be far less than the correlation length. Since we are adding the spins in each block, the details within the block are coarse grained out. Kadanoff argues that we should be able to treat the spins as block spins in the same manner as we treat the spins as site spins and that "the coarse graining" should leave the Ising model invariant except for a change in the parameters that appear in the Hamiltonian. As it turns out, the Ising model cannot always be invariant to the coarse graining, but nevertheless this idea proved to be an important clue. The clue is that a successful scaling argument may have to come with some sort of coarse graining. Wilson took these clues and constructed his Nobel Prize winning renormalization group theory. The theory is, however, based on the Landau-Ginzburg free energy functional which is the topic of Sec. 9.2.

The murky situation before the emergence of the renormalization group theory and the role that scaling played are well described in an extremely interesting "editorial" on page 487 in Goodstein's book which I urge the reader to read. In particular, he discusses the issue of "honesty" and "dishonesty" and what really drives scientific enterprises.

Chapter 9

Landau-Ginzburg Free Energy Functional and Applications

9.1 Introduction

The virtue of the Landau mean field model is that it can be modified quite easily to include local fluctuations. The resulting free energy model is called the Landau-Ginzburg free energy functional. With it we will study the non-equilibrium process that follows temperature quenches (first-order phase transition) in Sec. 9.3, and the equilibrium phenomena near the critical temperature (second-order phase transitions) in Sec. 9.4, all at a level beyond mean field theory.

9.2 Landau-Ginzburg Free Energy Functional

Let us see how we can include the local fluctuations ignored by the Landau mean field model given by Eq. (8.35). The order parameter M appearing in this equation is for the entire sample volume. To include the local fluctuations, we divide the volume into small cells. Each cell is small enough to be represented by a differential volume element d^3r but large enough to include many spins in it. Let $s(\vec{r})$ represent the average magnetization of the cell located at $\vec{r}$ and call it the order parameter function. Because $s(\vec{r})$ is the average of many spins, it is no longer limited to $+1$ and -1; it is a continuous function of $\vec{r}$. The free energy per volume in the cell at $\vec{r}$ is given by Eq. (8.35), namely,

$$f_L[s(\vec{r})] = \frac{1}{2}g_2 s(\vec{r})^2 + \frac{1}{4}g_4 s(\vec{r})^4, \tag{9.1}$$

where g_2 and g_4 are specified by Eq. (8.33). If there is an interface, it costs free energy. Since the order-parameter function $s(\vec{r})$ changes a great deal across the interface, a simple way of charging a hefty free energy penalty to such a rapidly changing order-parameter function is to add $K[\nabla s(\vec{r})]^2$ to the mean field part. The more rapidly the order parameter function changes, the more it costs.

Let us define a macrostate by specifying the order parameter function $s(\vec{r})$. How much free energy does it cost to be in that macrostate? The answer is obtained by integrating the cell free energy density over the volume of the sample, namely,

$$F_{LG}\left\{s(\vec{r})\right\}/k_BT = \int d^3r \left\{\frac{1}{2}K[\nabla s(\vec{r})]^2 + f_L[s(\vec{r})]\right\}, \tag{9.2}$$

which is called the Landau-Ginzburg (LG) free energy functional; it is a function of the order parameter function, whence the name "functional". It is without a doubt the most frequently used free energy model in the field of condensed matter physics and materials science. We have introduced it here as a model for ferromagnets, but it can also be used for many other systems including binary atomic mixtures, as we will argue later. In the literature, F_{LG}/k_BT is often called a Hamiltonian.

The probability of the system visiting the macrostate defined by $s(\vec{r})$ is given by the partial partition function

$$Z_{s(\vec{r})} = \exp(-F_{LG}\left\{s(\vec{r})\right\}/k_BT). \tag{9.3}$$

Notice here again that more probable macrostates are associated with smaller free energy while less probable macrostates are associated with larger free energy. The full partition function is obtained by integrating the probability over all macrostates,

$$Z = \int Ds(\vec{r}) \exp(-F_{LG}\left\{s(\vec{r})\right\}/k_BT), \tag{9.4}$$

which is the continuum counterpart of Eq. (6.4). Here, the functional integration, $\int Ds(\vec{r})$, covers all possible functional forms that the order parameter function can take and thus sums over all possible macrostates. We will use this model to study a non-equilibrium phenomenon in Section 9.3 and an equilibrium phenomenon in Sect. 9.4.

9.3 First-Order Phase Transitions

We wish to apply the Landau-Ginzburg model to study the non-equilibrium phenomenon of mixing and demixing in binary systems. We arrived at the L-G model with ferromagnets in mind, but the same model may be used for binary systems as well. Consider a binary system consisting of two species A and B. Divide the space into small cells. The cells are so small that the chance of more than one particle being in the same cell at the same time is negligible. If cell i is occupied by a particle of species A, the cell is associated with an Ising spin $s_i = 1$. If the cell is occupied by a particle of species B, then it is associated with $s_i = -1$. In this way, the distribution of molecules (atoms) may be described with Ising spins. Combine the cells to form blocks. The blocks are large enough to include many cells but still small enough to be represented by d^3r. Denote the average spin in each block with $c(\vec{r})$ which represents the local concentration of species A or the lack of species B. The order parameter function $c(\vec{r})$ is a continuous function of $\vec{r}$, and $c(\vec{r}) > 0$ means that species A is dominant at $\vec{r}$ while $c(\vec{r}) < 0$ means that species B is dominant. In this way, we again arrive at the Landau-Ginzburg free energy functional,

$$F\{c(\vec{r})\}/k_BT = \int d^3r \left\{ f_L[c(\vec{r})] + \frac{1}{2}K[\nabla c(\vec{r})]^2 \right\}. \tag{9.5}$$

Because the kinetic degrees of freedom are not included, the only role that k_BT plays is through g_2 which changes sign when T passes through T_C.

9.3.1 *The Time Evolution of the Order Parameter Function*

The question to answer is: given an initial order parameter function $c(\vec{r}, 0)$, how does it evolve as time progresses? Assume that the order parameter function initially given represents a small (not very probable) macrostate with an unduly large amount of free energy. We have to guide the order parameter function to change in a way that helps reduce the free energy. The task is easy here thanks to the nature of our model. There is only one reason for the unduly large amount of free energy: the two species are not mixed in the most optimal way. The atoms need to do some highly complex migration, some this way and some that way. To use the metaphor we introduced in Sec. 3.8, the traffic of atoms is controlled by the chemical

potential.

The question of whether $c(\vec{r})$ should increase (for more A) or decrease (for more B) at $\vec{r}$ depends on how the chemical potential at $\vec{r}$ compares with the chemical potential in the surrounding region. The chemical potential at $\vec{r}'$ is given by

$$\mu(\vec{r}') = \frac{\delta F}{\delta c(\vec{r}')}, \tag{9.6}$$

which is the continuum analogue of Eq. (4.9). The functional derivative asks: if the concentration changes at $\vec{r}'$ while remaining the same everywhere else, how much does the free energy change? Let $c(\vec{r})$ change by $\delta c(\vec{r})$ at $\vec{r}'$. To take the functional derivative, replace $c(\vec{r})$ in Eq. (9.5) with $\delta c(\vec{r})\delta(\vec{r}-\vec{r}')$. In this way, we ensure that the integral takes into account only the change in the block at $\vec{r}'$ and nothing from the other blocks. The interface term $[\nabla c(\vec{r})]^2$ requires an integration by parts, after which we find

$$\mu(\vec{r}) = g_2 c(\vec{r}) + g_4 c(\vec{r})^3 - K\nabla^2 c(\vec{r}). \tag{9.7}$$

Since $\nabla^2 c(\vec{r})$ involves not only $c(\vec{r})$ at $\vec{r}$ but also $c(\vec{r})$ at the surrounding blocks, the interface term provides a coupling between nearby blocks, as it should. Now we tell the particles to move in the direction in which the "unlivability" decreases most rapidly, namely along the direction of $-\nabla\mu(\vec{r})$, just like the earth's gravity does to rainwater on a mountain. Denoting the current density with $\vec{j}$, this means

$$\vec{j}(\vec{r}) = -M\nabla\mu(\vec{r}), \tag{9.8}$$

where M is the measure of mobility. Think of $-\nabla\mu$ as the thermodynamic force that drives the current $\vec{j}$, just like the electric field drives the charge current in Ohms law; the charge conductivity is an example of M.

If there is a current from point X to point Y, the current should reduce the concentration at X and increase it at Y. The order parameter conservation may be enforced with the continuity equation,

$$\frac{\partial c(\vec{r},t)}{\partial t} = \nabla\vec{j}(\vec{r},t), \tag{9.9}$$

where t represents time. Substituting Eq. (9.8) into Eq. (9.9), we finally obtain the Cahn-Hilliard equation

$$\frac{\partial c(\vec{r},t)}{\partial t} = M\nabla^2[g_2 c(\vec{r},t) + g_4 c(\vec{r},t)^3 - K\nabla^2 c(\vec{r},t)], \tag{9.10}$$

which instructs $c(\vec{r},t)$ how to change in order to reduce the free energy. We have just sung the last verse of our free energy song!

The Cahn-Hilliard equation is highly non-linear and cannot be solved analytically. That is not a problem. We can solve it on a computer by writing a program. We may start from an initial order parameter function and update it using the $\partial c(\vec{r})/\partial t$ that the Cahn-Hilliard provides. To that end, some preparations are necessary. First, notice that we need to specify three parameters, a, b and K to precisely define the system to be studied. In addition, we need to specify the temperature $T - T_C$. No one can possibly solve the equation for all possible sets of these parameters and the temperature. It would be nice if we could solve the equation just once in such a way that from that solution we could deduce the solution for any given set.

This is indeed possible. Change the three main variables, the local concentration c, the time t, and the position coordinate r, in the following way:

$$c = \left(\frac{|g_2|}{g_4}\right)^{1/2} \phi, \tag{9.11}$$

$$t = \frac{K}{2Mg_2^2}\tau, \ , \tag{9.12}$$

$$r = \left(\frac{K}{|g_2|}\right)^{1/2} R. \tag{9.13}$$

I will leave it as an exercise for the reader to prove that the rescaled variables, ϕ, τ, and R are all unitless. In terms of these unitless variables, the Cahn-Hilliard equation now reads

$$2\frac{\partial\phi(\vec{R},\tau)}{\partial\tau} = \nabla^2[\pm\phi(\vec{R},\tau) + \phi(\vec{R},\tau)^3 - \nabla^2\phi(\vec{R},\tau)], \qquad (9.14)$$

where the first term takes a plus sign for $T > T_C$ and a minus sign for $T < T_C$. All parameters have disappeared. After solving the equation for ϕ as a function of $\vec{R}$ and τ, the system-specific information can be put back, if you so desire, by merely scaling the three variables following Eqs. (9.11), (9.12) and (9.13).

For the purposes of learning, and for some more serious purposes as well, we can get a good sense of what the equation does by solving it in two dimensions. Make a square lattice with a small lattice spacing, and indicate the order parameter at each lattice site by $\phi(i,j)$. For the initial configuration at $T > T_C$, choose random values for $\phi(i,j)$ in the range between +1 and -1 so that $\sum_{i,j}\phi(i,j)$ is zero, which means a critical (50-50) mixture, or with a bias for plus (or minus) so that the sum is not zero, which means an off-critical mixture. Because the Cahn-Hilliard equation enforces the order parameter conservation, the mixing ratio remains constant throughout the ensuing time evolution.

Next, approximate the differentiation operators using the first order finite difference method. For example, $\partial\phi(x,y)/\partial x$ at the site (i,j) may be approximated as $\phi(i+1,j) - \phi(i,j)$. In this way, one can compute all the partial derivatives appearing in the right-hand side of Eq. (9.14), and then update $\phi(i,j)$ for each time increment $\delta\tau$. This completes our preparations. We are now ready to implement the equation, which we will do after a short break.

9.3.2 *Relocating Squirrels*

I live in a house next to a large vacant lot full of trees. This is home to a nation of squirrels. They seem to like all the fruits that I manage to grow in my backyard, even more than we do. Over the past five or six years, we have hardly tasted any; the squirrels wanted them all. If I could sit down with them and cut a deal, I would be happy for a mere one percent, but I know that they will not settle for anything less than one hundred percent. Thoughts of a violent solution, a BB gun, did flash through my mind but I could not do it. A more peaceful solution was suggested by a colleague of mine who is a master squirrel trapper. From a nearby farming

and home supply store, I bought a nice trap which is a wire cage of about $30cm \times 30cm \times 70cm$. It has a door and a seat. I invite them to enjoy some nuts on the seat. When they jump on the seat, the door closes. Not all members of the Lee family were thrilled with this idea of getting rid of the squirrels, and so we had some serious discussions and investigations on where to relocate them. Our first choice was the university campus because the campus is full of live oak trees, but we decided on a nearby forest about 20 minutes away. We thought that the forest should be large enough to accommodate plenty of newcomers and provide a more continuous supply of food throughout the year.

Whenever I find a trapped squirrel waiting for me, I take the cage to the forest, leave it on the ground, and then open the door. The way the squirrels run away from the cage is a truly heart-moving scene. There are two types of squirrels. The first type will run away from the cage at lightning speed and climb up a tree. The second type starts running just as fast, but seem to fear that I am watching them, and so they suddenly stop when they find something to hide under, wait a while, and then run again. I always wish them a happy new life in their new home. I would love to learn how they adjust to the new environment, but I will never know. I do know one thing for sure. They cherish their recovered freedom, and appreciate the wide open forest where they can roam about. I may have acted against some law of ecology, but I certainly did not act against the law that we treasure in this book.

It is actually much easier to relocate thermal systems from one part of their phase diagram to another across a coexistence line. Moreover, we can easily observe how the displaced thermal system adjusts to new conditions and searches for a new life, their new equilibrium state. We take an atomic binary system which is in equilibrium in the one phase region above T_C, and then quench the temperature into the two phase region. In the new environment, the thermal system can exist with less free energy than allowed before the quench, which should make our atomic squirrels very "happy". The Cahn-Hilliard equation tells them how to change their order parameter function to reduce their free energy.

Since the two species are initially mixed, we start out with an order parameter function which changes randomly with $\vec{r}$; it can be generated easily using a random number generator. Using the Cahn-Hilliard equation with the minus sign in front, we then update the order parameter function. The solution turns out to be different depending on the mixing ratio.

In the metastable region in which, say, A is the minority, the initial phase-separated domains are small droplets of A-dominated phase in a sea of of B-dominated majority phase, as we discussed in Sec. 7.6. Those droplets that overcome the barrier will grow for a while because there is enough imbalance in the chemical potential which pulls A atoms into the region surrounding the droplets, but the process cannot continue indefinitely because the available A atoms are soon depleted. Thereafter the droplets begin to merge to reduce the interface cost. The net effect is that big droplets grow at the expense of small droplets. This phase separation mechanism is called nucleation and growth.

In the unstable region where the mixing ratio of the two species is closer to 50/50, since neither of the two species are dominant, the phase-separated domains tend to grow into a shape resembling seaweeds, or a mesh of tunnels which seem to turn, merge, or close in an unpredictable manner. Immediately after the quench, all the initial thermal fluctuations (in local compositions) that existed before the quench stay and begin to grow; with no barrier to overcome, the phase separation begins immediately. In the end, one long wavelength mode dominates to form phase-separated domains which look like those shown in Fig. 9.1. As time further progresses, the pattern coarsens and the seaweeds grow bigger and bigger to reduce the interface cost. This process is called spinodal decomposition.

The morphology of the evolving phase-separated domains is a matter of great interest to materials scientists. Most useful materials are composite materials consisting of more than one component. The physical properties of the composites depend heavily on the morphology of the phase-separated domains. One wishes to learn how to manipulate the phase separating process to obtain the optimum morphology. In order to do so, one must first understand the morphology-forming process, and the Cahn-Hilliard equation serves that purpose very well.

Let us add one more feature to the equation. Suppose that the system has frozen impurities that prefer one of the two components more than the other. These impurity atoms are just sitting at certain randomly chosen locations and stay without compromising with the thermal fluctuations. Figure 9.2 shows the evolving pattern where the small dots represent the impurity atoms. The impurity atoms prefer to to be surrounded by one species over the other, which is an expensive proposition because granting this preference for every impurity atom would vastly increase the interface cost. The two competing factors, the need to please the impurity atoms

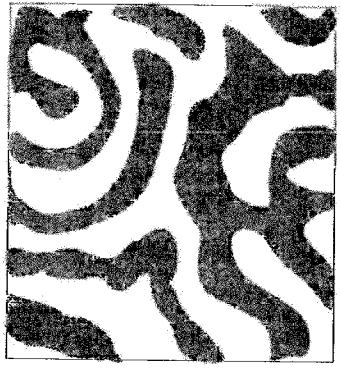

Fig. 9.1 A sketch of a very typical spinodal pattern

and the need to minimize the interface, must be optimally balanced. At the time the picture was taken, most of the dots were indeed surrounded by their preferred component (the gray), but notice that several dots have been abandoned in hostile territory. Do the resultant domains look like various animals to you?

Exercise *This exercise is for all computer and high-tech wizards which I am not. Suppose that we mix ink and water at a ratio of, say, 1 to 100. What would be the probability of finding the ink molecules spontaneously aggregating to write "THERMAL PHYSICS" in the middle of the water? I would suggest the following two-dimensional experiment. Write the letters on a piece of paper with a thick marker pen, and then make the letters bigger with a lighter pen to gradually mesh the letters into the white background which represents the water component. Digitize it and carry out the integration in Eq. (9.5). Repeat the experiment with "COMPUTER SCIENCE", and then "GREEK PHILOSOPHY". Which is more probable?*

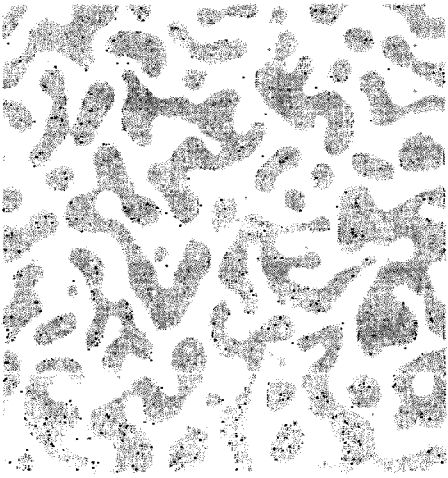

Fig. 9.2 A spinodal pattern in the presence of frozen impurity atoms which prefer the gray component. The small dots represents these impurity atoms

9.4 Second-Order Phase Transitions: The Renormalization Group Theory

In the previous section, we used the Landau-Ginzburg free energy functional to study a non-equilibrium process. In this section, we will use it to study the equilibrium properties near the critical point. Away from the critical point, equilibrium properties are determined by the sizes of the macrostates. Near the critical point, on the other hand, equilibrium states are in fact dominated by fluctuations which introduce many pertinent length scales, ranging from typical short-length scales to large ones, and therefore the issue is no longer finding the largest macrostate. The issue is how to recognize the presence of these multi-length scales in all macrostates. As we will find out shortly, the Landau-Ginzburg model has a structure which can accommodate such a need.

The critical point behavior was discovered during the latter part of the 19th century, but it took nearly a century to understand the essential physics involved in it. The renormalization group (RG) theory not only makes it possible to calculate the critical exponents but more importantly, it explains in a rather picturesque manner the universality of critical behavior. Our purpose here is not to go through the details of the RG theory which is beyond the scope of this book, but to highlight the essential elements of the theory so that the reader can get a feeling for the theory.

We start from the Landau-Ginzburg free energy functional which is written in the form of

$$F_{\mathrm{LG}}\{s(\vec{r})\}/k_BT$$
$$= \int d^dr \left\{ g_0 + g_2 s(r)^2 + g_4 s(r)^4 + \cdots + \frac{1}{2}K[\nabla s(\vec{r})]^2 + \cdots \right\}, \tag{9.15}$$

where d is the dimensionality of the space. The contents inside the large parenthesis represents the local free energy per volume and in general includes terms beyond the fourth order and more interface-related terms such as $[\nabla s(\vec{r})]^4$; it will become clear later why we have to be willing to include all of them. The coefficients, g_0, g_2, etc., define the sample, and as such, they become the main focus of the renormalization group theory. Think of them as a vector in a parameter space,

$$g = (g_0, g_2, g_4, \ldots K, \ldots). \tag{9.16}$$

Since g defines a **local** free energy, and since the singular critical behavior is a result of an infinite correlation length which requires a large system size, these coefficients have to be a smooth analytical function of temperature; the term "local" means a tiny system for which there is absolutely no singular behavior. In particular, we know that g_2 goes like $(T - T_C)$. Thus we start the theory with analytical functions.

Let us now switch from the position space $\vec{r}$ to the wave vector space of $\vec{k}$ by performing the Fourier transformations,

$$s(k) = L^{-d/2} \sum_r s(r) \exp(-i\vec{k} \cdot \vec{r}) \tag{9.17}$$

and

$$s(r) = L^{-d/2} \sum_{k<\Lambda} s(k) \exp(-i\vec{k} \cdot \vec{r}). \tag{9.18}$$

Using Eq. (9.18), we may express the free energy as a functional of $s(k)$, i.e., $F_{\mathrm{LG}}\left\{s(\vec{k})\right\}/k_BT$.

Examine Eq. (9.17) to see what $s(k)$ means. If $s(k)$ is very large for a particular wave vector k, then the order parameter distribution has a prominent pattern which tends to repeat itself with the wave vector k. In other words, there are many structures of size given by $\lambda = 2\pi/k$. Thus $s(k)$ reveals the length scales that characterize the order parameter distribution. All the features of long length scales are in the small k regime while all those of short length scales are in the large k regime. The statement $k < \Lambda$ in Eq. (9.18) says that the shortest length scale is $2\pi/\Lambda$.

We do not attempt to calculate the partition function. The heart of the renormalization group theory is the renormalization group transformation (RGT). Given a sample, namely, $g = (g_0, g_1, g_2, ...)$, we generate using RGT another sample, $g' = (g'_0, g'_1, g'_2, ...)$. We manipulate the transformation so that these samples mimic the way a laboratory sample changes its correlation length when we change its temperature near T_C. This manipulation is done in three steps.

(1) Given F_{LG}, perform the following integrations to define F'_{LG} given by

$$\exp(-F'_{\mathrm{LG}}) = \int \delta s' \exp(-F_{\mathrm{LG}}/k_BT), \tag{9.19}$$

where

$$\delta s' = \prod_{\Lambda/l<k<\Lambda} \delta s(k). \tag{9.20}$$

The integrations remove all the patterns in the short-length regime $\Lambda/l < k < \Lambda$ and therefore the remaining length scales extend only to $2\pi/(\Lambda/l) = 2\pi l/\Lambda$. By performing the integrations, we say that **we do not want to see any short-length details beyond the length scale of $2\pi l/\Lambda$.**

(2) All the remaining Fourier components corresponding to $k < \Lambda/l$ are now rescaled with $l^{1-\eta}$,

$$s(k) \to l^{1-\eta} s(k). \tag{9.21}$$

With this rescaling, we decrease (or increase) the "contrast" of what we see now. Assuming that we are looking at the sample under a light, this rescaling makes the light dimmer (or brighter).

(3) Shrink the sample by a factor of l. This can be done by changing k to lk, that is,

$$k \to lk \tag{9.22}$$

wherever we see k. All length scales are reduced by a factor of l, and therefore the shortest length scale is back to $2\pi/\Lambda$.

When RGT is performed on a properly chosen sample, it results in another sample which we may write symbolically as

$$R_l\, g = g'. \tag{9.23}$$

Let us see what RGT does. We remove the short-length details, change the contrast, and then shrink the sample. What good does this do? Exactly at the critical point, there are patterns of all length scales, from zero to infinity, and therefore the new sample should be indistinguishable from the old one. In other words, the parameter space should have fixed points g^* which remain invariant under RGT, namely,

$$R_l\, g^* = g^*. \tag{9.24}$$

Away from the critical point, on the other hand, since the longest length scale is not infinity, RGT should shorten the longest length scale. In other words, RGT should push the sample further away from the critical point. The result should then reveal how the correlation length becomes shorter and shorter as $t = (T - T_C)/T_C$ increases, namely, the correlation length exponent ν. These two expectations are borne out if we choose η properly.

The story goes like this. Consider a point $g^* + \delta g$ where δg is the vector drawn from the fixed point to g. Representing component α of g with g_α, we may linearize R_l and write

$$\delta g'_\alpha = \sum_\beta \left(R_l^L\right)_{\alpha\beta} \delta g_\beta, \tag{9.25}$$

where

$$\left(R_l^L\right)_{\alpha\beta} = \left(\frac{\partial g_\alpha}{\partial g_\beta}\right)_{g=g^*}, \tag{9.26}$$

where the differentiation is taken at $g = g^*$. The presence of the off-diagonal elements suggests that the parameters are tangled up after the action of RGT. The best way to handle this type of messy situation is to represent the vectors (points) in the parameter space in terms of the eigenvectors and represent the results of RGT in terms of the eigenvalues. The eigenvectors and eigenvalues are defined by

$$R_l^L e_j = \rho_j(l) e_j. \tag{9.27}$$

We demand that the operation of RGT is associative, i.e., $R_l R_{l'} = R_{ll'}$, from which it follows that

$$\rho_j(l) = l^{y_j}. \tag{9.28}$$

Using the fact that the set of eigenvectors span the parameter space, we may write

$$\delta g = \sum_j t_j e_j, \tag{9.29}$$

and

$$\delta g' = \sum_j t'_j e_j. \tag{9.30}$$

It then follows that

$$t_j' = t_j l^{y_j}. \tag{9.31}$$

The effect of RGT on a point near a fixed point is different depending on the direction of δg. Along the direction of those eigenvectors with $y_j < 0$, Eq. (9.31) says that RGT drives the point towards the fixed point. Think of the points in this path as the basin of the fixed point. All the points in the basin represent different samples but they differ from each other only in some irrelevant short-length atomic and molecular details which are washed away by RGT. Since RGT drives all of them into the same fixed point, these samples share the same critical behavior. This explains the universality of critical point phenomena. The eigenvectors corresponding to $y_i < 0$ represent properties irrelevant to critical point phenomena.

Now let δg be directed along the direction of an eigenvector with $y_j > 0$. Equation (9.31) now says that RGT pushes the point further away from the fixed point along the direction of that eigenvector. The eigenvectors corresponding to $y_i > 0$ represent relevant properties. Among the eigenvalues with $y_i > 0$, find the largest one and call it y_1. Since the temperature cannot be irrelevant, let us assume that it is represented by e_1. Concentrating on the temperature dependence,

$$R_l^L g(T) \approx g^* + t_1(T) l^{y_1} e_1 + \cdots \tag{9.32}$$

At the critical point $T = T_C$, $t_1(T) = 0$; if it were not, RGT would drive it away from the fixed point. This means that we can expand $t_1(T)$ near T_C to first order and write

$$t_1(T) = A(T - T_C). \tag{9.33}$$

The sample is now characterized by $(t_1, t_2, t_3 \cdots)$. These parameters contain highly coarse-grained yet local information, and therefore $t_1, t_2, t_3 \cdots$ must be a smooth function of temperature, as Eq. (9.33) claims for t_1. Substituting Eq. (9.33) into Eq. (9.32), we find

$$R_l^L g(T) \approx g^* \pm (l/\xi)^{1/\nu} e_1 + \cdots \tag{9.34}$$

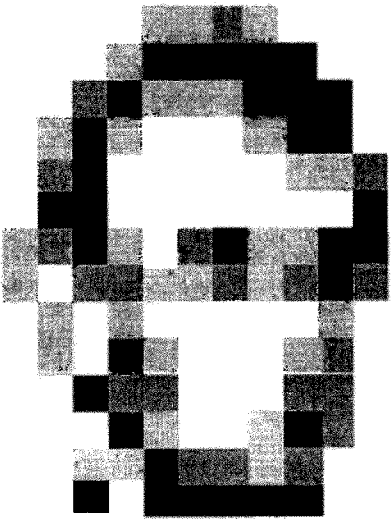

Fig. 9.3 A highly coarse-grained portrait of Lincoln

where $\nu = 1/y_1$ and $\xi = A|T - T_C|^{-\nu}$ is identified as the correlation length. The way t_1 changes by RGT reveals how the correlation length changes with the changing temperature!

There are many parallels between RGT and vision. Look at a picture which has objects of many different sizes. If you move further away from the picture, you lose small details; you get less light and thus lose contrast, and see the objects on a reduced scale. With this in mind, look at the portrait in Fig. 9.3. The portrait consists of blocks, and therefore it has no feature in length scales shorter than the block size. Walk away from it until you can no longer see the individual blocks. At this distance, even if there were short-length details in each block, you would not see them. You are now seeing only the features which come in length scales larger than the block size, and apparently there are enough of them to identify

the famous face. Do you see Lincoln? If you walk further away, this crucial feature is renormalized away and nothing is left. In the language of RGT, the portrait represents systems away from fixed points.

It is difficult to find a picture resembling a fixed point because the picture has to have features of all length scales including an infinite one. Straight railroad tracks as viewed from the back of a train come close, but only capture finite length scales. In order to have an infinite one as well, just imagine that the width of the railroad track is very very wide. Then one would see very long length scales right in front, the nearby railroad ties, and infinitely small ones far away on the horizon. As the train moves, the longest one turns into the next longest, and what was previously the next longest turns into the next-next longest, and ad infinitum. If the longest one were infinitely long, since half of infinity is still infinite, we would find the scene invariant against the RGT. My graphic skills are not good enough to draw this scene.

Chapter 10

Monte Carlo and Finite-Size Scaling

10.1 Introduction

It is easy to talk about the renormalization group theory as a story, but it is an entirely different matter to actually locate the fixed points and find out the associated critical behavior. That is a formidable task that lies beyond the scope of this introductory book. This is a pity because we would like to close this book with something we can do. I trust that the reader can write a simple computer program and run it on your computer. In Sec. 10.2, I will offer a crash course on the Monte Carlo computer simulation method. The computer simulation can only be performed for a finite system which does not support an infinite correlation length and therefore does not support the true critical behavior. This difficulty can be overcome thanks to the finite size scaling theory which is our last subject in Sec. 10.3.

10.2 The Master Equation and Monte Carlo Method

Suppose that we try to carry out the canonical ensemble average for a system as small as 100 Ising spins on a computer. A total of 2^{100} microstates need to be generated. This is far too many, even for the fastest computers today. Why not then randomly select a limited number of microstates and carry out the average over them, just like pollsters do when they take public opinion polls? Unfortunately this idea of random sampling does not work because the important microstates, namely, those that carry a substantial Boltzmann factor, are not distributed randomly in the microstate state space. Why does random sampling work so well for pollsters? Take any

city for an example. It is true that people living in a section of a city tend to share the same opinions, but their names do not appear together in the telephone book on the same page.

Is there still a way to generate just enough microstates over which the ensemble average can be carried out? The answer is yes. Many of the 2^{100} microstates, even if we have generated them, make little or no contribution towards the ensemble average because their Boltzmann factors are so small. What then is the purpose of generating them in the first place? Rather than generating all microstates indiscriminately and then later weighing them only to discard most of them, why not weigh the generating process itself so that a microstate corresponding to a large Boltzmann factor has a better chance of being generated than those corresponding to a small Boltzmann factor? In other words, why not generate the microstates according to their importance? A pool of microstates generated in this way (called importance sampling) can be as small as on the order of 10^6, but because they represent all the microstates in proportion to their Boltzmann factors, they give the correct ensemble average. We can generate such a pool of microstates in the following way.

Imagine that our system is moving around from one microstate to another in its microstate space following a transition probability function $W(x, x')$ which gives the probability that the system will move to microstate x' within one unit of time, given that it is now in microstate x. Given $W(x, x')$, we should be able to obtain the probability function $P(x, t)$, the probability of the system visiting microstate x at time t. How would the probability function $P(x, t)$ change after time dt? It is clear that

$$\frac{\partial P(x,t)}{\partial t} = -\sum_{x'} P(x,t)W(x,x') + \sum_{x'} P(x',t)W(x',x), \tag{10.1}$$

which is called the master equation. The first term accounts for all the processes in which the system moves out of x while the second term accounts for all the processes in which the system moves into x. The equation defines a dynamics by choosing $W(x, x')$, but the dynamics itself is not our purpose which is why I said just "imagine".

Since the transition probability density is independent of time, it is reasonable to expect that the probability function will ultimately reach a stationary state in which it no longer changes. Now, suppose that the stationary probability distribution is the Boltzmann distribution, and ask: what

is the transition probability density function $W(x, x')$ that has brought our system to this stationary state and is keeping it there? In this stationary state, the system is visiting each microstate according to its Boltzmann factor, i.e., a state corresponding to a large Boltzmann factor very often and a state corresponding to a small Boltzmann factor very rarely. The system would be sampling for us the microstates according to the Boltzmann factors. Therefore, the pool of the microstates visited by our system is exactly what we want in order to perform the proposed importance sampling!

Since $dP(x, \infty)/dt = 0$ in the stationary state, we have

$$\sum_{x'} P(x, \infty) W(x, x') = \sum_{x'} P(x', \infty) W(x', x), \tag{10.2}$$

where $P(x, \infty)$ is given by

$$P(x, \infty) \sim \exp(-E(x)/k_B T). \tag{10.3}$$

To solve Eq. (10.2) for $W(x, x')$, the left and right sides of the equation need not match (balance) term by term, but we demand that they do and rewrite the equation in the form

$$P(x, \infty) W(x, x') = P(x', \infty) W(x', x), \tag{10.4}$$

or

$$\frac{W(x, x')}{W(x', x)} = \frac{P(x', \infty)}{P(x, \infty)} = \exp(-\Delta U/k_B T), \tag{10.5}$$

where

$$\Delta U = U(x') - U(x). \tag{10.6}$$

Equation (10.4) is called the condition of "detailed balance". We adopted this condition because it gives us an easy solution as we will find below. We are not after the general solution to Eq. (10.2). We are only after a $W(x, x')$ which will guarantee us that **the system will visit the microstates according to their Boltzmann factors** and we are not concerned about the sequence taken by the system.

The simplest solution to Eq. (10.5) is

$$W(x,x') = \text{the smaller of } \exp(-\Delta U/k_BT) \text{ or } 1, \tag{10.7}$$

i.e.,

$$W(x,x') = \begin{cases} 1 & \text{when} \quad \Delta U \leq 0, \\ \exp(-\Delta U/k_BT) & \text{when} \quad \Delta U > 0. \end{cases}$$

This solution is known as the Metropolis algorithm.

It is important to notice that $W(x,x')$ is not symmetric for x and x'. To show that Eq. (10.7) solves Eq. (10.5), assume that $U(x') > U(x)$. Then, $\Delta U > 0$ for $W(x,x')$ and therefore $W(x,x') = 1$. For $W(x',x)$, on the other hand, $\Delta U < 0$ and therefore $W(x',x) = \exp(\Delta U)$; $W(x,x')/W(x',x) = \exp(-\Delta U/k + BT)$.

There are also two symmetric solutions,

$$W(x,x') = \frac{1}{2}(1 - \tanh \Delta U/2k_BT), \tag{10.8}$$

and

$$W(x,x') = \frac{\exp(-\Delta U/k_BT)}{1 + \exp(-\Delta U/k_BT)}. \tag{10.9}$$

The dynamics following Eq. (10.9) is known as the Glauber dynamics.

We assumed that the transition probability density $W(x,x')$ only depends on x and x' and not on the past history that has brought the system to x. Such a process is called a Markov process. The time series of the visited microstates is said to form a Markov chain.

The Metropolis algorithm works in the following steps.

(i) Choose an initial microstate x.
(ii) Choose randomly or sequentially another microstate x' which can easily be realized from x.
(iii) Calculate ΔU.
(iv) If ΔU is equal to or less than zero, the system moves to x'.
(v) If ΔU is greater than zero, the system moves to x' with probability $p = \exp(-\Delta U/k_BT)$. To perform this step, generate a random number r between zero and one. If r is truly random, then it is equally likely to be in one part of the range from zero to one as

another. For example, suppose that $p = 0.9$. What is the probability of generating a random number r which is less than 0.9? The answer is 90 percent! Thus we let the system move to x' if $p > r$. When the gamble fails, i,e., $p < r$, the system remains at x once more; the initial microstate x is recounted, i.e., $x' = x$.

We repeat this process on the order of 10^6 times to prepare a pool of microstates. We can then calculate all equilibrium averages as

$$< A >= \frac{1}{\hat{N}} \sum_x A(x), \tag{10.10}$$

where $\hat{N}$ is the number of microstates in the pool. Note that the sum in Eq. (10.10) does not have a Boltzmann factor. The transition probability $W(x, x')$ has been chosen such that microstates are sampled according to the Boltzmann factor, and therefore those important microstates corresponding to a large Boltzmann factor appear in the pool many many times while those corresponding to a small Boltzmann factor appear very few times.

To see this important point, examine how the trial ends in the Metropolis algorithm. If it ends at step (iv), the selection of x' is biased in favor of larger Boitzmann factor. The same is true when the gamling fails. Under these two scinarios, however, the system would be heading towards a local minimum energy state, which is not our purpose. The third scinario, namely, the selection of x' inspite of the fact that its Boltzmann facror is less than that of x is actually the most crucial element of the algorithm. It allows the system to venture out and explore all parts of the microstate space. Yes, the selection does apppear "unfair" and the intitial state x appears to have been denied its chance to enter into the pool once more for a "questionable" reason. However, see what happens thanks to its sacrifice. Not only states with a small Boltzmann factor get a chance to enter into the pool but many many states with a large Boltzmann factor get to enter into the pool more number of times than they would otherwise. Is it not nice? The method carries the name "Monte Carlo" because we gamble using random numbers.

Exercise *Let us try out this idea using a very simple example. Assume that microstates are distributed according to* $\exp(-x^2/2)$ *where* x *is*

no longer a symbol; it is a number which is distributed between $-\infty$ to $+\infty$. Calculate $< x^2 >$ using the Metropolis algorithm. We know the correct answer in advance by carrying out the integration,

$$< x^2 > = \int_{-\infty}^{\infty} dx x^2 \exp(-x^2/2)/Z, \tag{10.11}$$

where $Z = \int_{-\infty}^{\infty} dx \exp(-x^2/2)$. Random sampling does not work here because while x is distributed over an infinite range, the x's that contribute significantly to the average are in a relatively small range around $x = 0$. Make sure that you have an adequate random number generator on your computer. You may generate the Markov chain $(x_1, x_2, x_3 \cdots, x_N)$ in the following way. Imagine a walker who walks only on the x-axis. At each step, the walker can either move to the left to decrease its x-coordinate, move to the right to increase its x-coordinate, or stay at the same position. Choose any initial position x_1, and a small, but not too small, step size Δx. Generate a pair of random numbers, r_1 and r_2; r_1 is to be used to decide the direction of the next movement and r_2 is to be used in case the walker has to gamble. Try $x_1 - \Delta x$ for x_2 if $r_1 < 0.5$, but $x_1 + \Delta x$ if $r_1 > 0.5$. In either case, if $x_2^2/2 < x_1^2/2$, then select x_2 to enter the pool. Otherwise, gamble using r_2. This completes one Monte Carlo step. Generate another pair of random numbers and repeat the process for x_3, and so on. Now, take a look at the chain $(x_1, x_2, x_3 \cdots)$. It should look like footsteps taken by a drunken man who moves to the left and to the right in a seemingly unpredictable fashion. He lingers around $x = 0$ most of the time, but notice that once in a while he moves a good distance away. This is a crucial element of importance sampling. If the walker only lingers around $x = 0$ and never ventures far out, the result will not be correct. Plot the frequency at which each value of x is visited. Does it look like a "Boltzmann factor"? Compute $< x^2 >$. In this exercise problem, we can see without any effort where the important microstates are. In the real world problems, we cannot see it, but we do not have to because the Monte Carlo walker sees it for us.

Let us now apply the method to study a system of interacting Ising spins on a square lattice of 50×50. The microstate energies are given by

$$E_\nu = -J \sum_{<ij>} s_i s_j, \tag{10.12}$$

where $\nu = (s_1, s_2, ...)$, $J > 0$ is the coupling constant, and $< ij >$ means that the sum covers all pairs of spins i and j which are the nearest neighbor of each other. We need two parameters to specify the system to be studied, J and $k_B T$, but only one unitless parameter $\epsilon = k_B T/J$ enters into the Monte Carlo computer code. Run the simulation covering a range of ϵ. From the results, we can, if we wish, deduce what the results would be for any combination of $k_B T$ and J.

When a system is as small as 50×50, the ratio of the spins sitting on the edges to the total is not negligible. Let us represent their coordinates as $(x = 1, y)$, $(x = 50, y)$, $(x, y = 1)$, and $(x, y = 50)$. These spins have only three neighbors to interact with. To eliminate this finite size effect, we apply the periodic boundary condition. The spins at $(x = 1, y)$ and $(x = 50, y)$ become neighbors. Similarly, those at $(x, y = 1)$ and at $(x, y = 50)$ become neighbors.

Important microstates are hidden here and there in groups throughout the multi-dimensional ν space. Our Monte Carlo walker walks through this space and samples the microstates according to their importance. Choose a $(s_1, s_2, s_3, ...)$ for the initial microstate x. Next pick a spin, either sequentially or randomly, and flip it to generate x'. Calculate ΔU. The microstate x' is either selected as the next microstate to enter the pool or rejected. If it is the latter (the gamble failed), unflip the spin and let x enter the pool again. Repeat this process.

Prepare four storage "buckets" for U, U^2, M, and M^2. After each round, calculate these four quantities and dump them into their respective buckets. After $\hat{N}$ rounds, each bucket should have $\hat{N}$ entries. Calculate their average for $< U >$, $< U^2 >$, $< M >$, and $< M^2 >$. Finally, calculate the specific heat and the susceptibility by calculating δU^2 and δM^2.

If you have never written a computer program, your program may not be efficient, but do not worry about it now. It is far better to keep your computer busy than keeping it idle night after night. Let it run your program while you are away and get some results. After a few trials, you will understand how to improve your program.

10.3 Finite Size Scaling

If you actually carry out the Monte Carlo simulation, you will be disappointed because your results will not exhibit the expected singular behavior. You will only see a mild peak for the susceptibility and hardly anything that can be called a peak for the specific heat. This is a finite size effect. The singular behavior of the response functions is a result of the diverging correlation length which a finite system cannot support.

This impasse can be overcome, thanks to an idea known as finite-size scaling. Consider how the correlation length changes with temperature in a finite system of size L. As the temperature approaches T_C (the critical temperature of the infinite system), the correlation length ξ will grow and at some point reach L. Once it reaches this point, the temperature can get closer to T_C, but ξ will no longer grow. This is just like an indoor tree which can only grow as high as the room ceiling. The temperature at which the correlation length reaches its maximum possible value L depends on the system size. If the system's size is very small, the saturation of ξ will happen while the system is still far from T_C, but if the system size is large, it will happen when the temperature is much closer to T_C. Is there a temperature at which we can **absolutely and positively** guarantee that the correlation length has already saturated to the value of L regardless of the system size? Yes, $T = T_C$!

Now, compare a finite system of linear size L at $T = T_C$ with an infinite system at $T \neq T_C$. Suppose that we choose T such that the correlation length of the infinite system is $\xi(t) = L$ where $t = |T - T_C|/T_C$. Since the correlation length of the finite system is the same as that of the infinite system, we may state that the finite system is a faithful representation of the infinite system at that temperature. Therefore, what happens in the infinite system as the temperature T approaches T_C may be represented with a series of finite systems ordered in increasing size. For a given temperature of the infinite system, the system size of the corresponding finite system may be obtained from

$$\xi(t) \sim t^{-\nu} = L, \tag{10.13}$$

or

$$t = L^{-1/\nu}. \tag{10.14}$$

The criticality of χ and C in the infinite system, $\chi \sim t^{-\gamma}$ and $C \sim t^{-\alpha}$, may then be represented with finite systems at T_C in the form of

$$\chi \sim L^{\gamma/\nu}, \tag{10.15}$$

and

$$C \sim L^{\alpha/\nu}. \tag{10.16}$$

To implement this, compute C and χ starting from a small-sized system, such as $L = 5$, and repeat the computations with gradually increasing L. Plot the results for C and χ as a function of L on a log-log graph. The result should be a straight line. The good news is that L does not have to be infinite to reach this power law regime. The slopes may be identified as γ/ν and α/ν. This trick requires T_C to be known. The critical temperature of the two-dimensional Ising model is given by $J/k_B T_C = -(1/2)\ln(\sqrt{2} - 1)$.

It is late October here in Hattiesburg. While there remains a good deal more to learn, it is too nice to stay inside. There is going to be a festival downtown this weekend. I will stop the book here and join the crowd to roam the downtown blocks. The brown Pontiac still runs, but it will stay in the garage. If this book has been helpful and you wish to read more, consult the references in the reference section. We focused on the extremum principles and bypassed many useful topics. The Appendix covers the topics of heat engines, Maxwell relationships, and thermodynamic stability.

Appendix A

Heat Engines

In this appendix, we will explore how the second law of thermodynamics is involved in devices which we use for our day to day lives. Heat engines and refrigerators are two good examples. We can make some fairly important statements about these devices without knowing anything about the actual mechanical details.

A heat engine absorbs energy from a heat source and then converts it into work for us. We would of course like to get as much work as possible. Recall the first law which says that a closed thermal system (N=fixed) may increase its energy in two ways,

$$\begin{aligned} \Delta U &= T\Delta S + p\Delta V \\ &\equiv \Delta Q + \Delta W, \end{aligned} \tag{A.1}$$

where the first term represents the energy received in the form of heat and the second term the energy received in the form of work.

When the engine absorbs heat energy, the absorbed heat energy comes with entropy. When the engine performs work, on the other hand, no entropy leaves the engine. This is problematic. We would like the engine to repeat the process again and again to provide us with a steady work source instead of one gigantic burst of work like a bomb. In order to do so, the working substance inside the engine must return to its initial thermodynamic condition after a cycle, which requires to remove the remaining entropy. The engine can do this only in one way. It must let part of the absorbed heat energy leave without converting it into work. Therefore the engine cannot convert all of the input energy into work!

If the engine cannot convert 100 percent of the received heat energy into work, is there a limit to its efficiency? Since $\Delta S = \Delta Q/T$, the amount of wasted energy ΔQ is dependent on the temperature of the reservoir to which ΔQ is to be dumped away. The lower the temperature is, the less the waste is.

Consider the following ideal engine. It runs with two reservoirs, one at a high temperature T_h and one at a low temperature T_l. The working substance first draws energy from the high temperature reservoir. It then performs work, dumps the remaining heat energy to the low temperature reservoir, and then finally returns to its initial state. The process repeats.

Let ΔQ_h denote the energy drawn from the high temperature reservoir and ΔQ_l the energy dumped into the low temperature reservoir. Then the amount of work that the engine can deliver in one cycle is

$$\Delta W = \Delta Q_h - \Delta Q_l. \tag{A.2}$$

The efficiency of the engine is given by

$$\eta = \frac{\Delta W}{\Delta Q_h} = \frac{\Delta Q_h - \Delta Q_l}{\Delta Q_h}. \tag{A.3}$$

Let us apply the second law of thermodynamics to the whole combined system after once cycle. As Fig. A.1 shows, the combined system consists of the high temperature reservoir, the heat engine, the low temperature reservoir, and the work source to which work is delivered. The hot reservoir decreases its entropy by $\Delta Q_h/T_h$. Since the working substance returns back to its initial thermodynamic state, it does not change its entropy. The low temperature reservoir increases its entropy by Q_l/T_l. The work source suffers no change in entropy because work cannot change entropy. The net increase is $\Delta Q_l/T_l - \Delta Q_h/T_h$, and therefore the second law says that

$$\frac{\Delta Q_l}{T_l} - \frac{\Delta Q_h}{T_h} \geq 0. \tag{A.4}$$

Substituting Eq. (A.4) into Eq. (A.3), it follows that

$$\eta \leq \frac{T_h - T_l}{T_h} \equiv \eta_C, \tag{A.5}$$

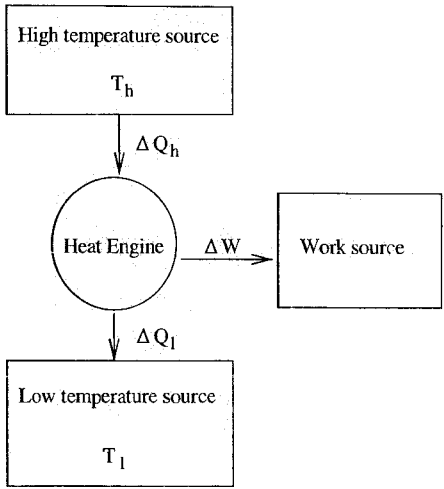

Fig. A.1 The high temperature heat sours, the low temperature heat source, the heat engine, and the work source to which work is being delivered

where η_C is called the Carnot efficiency.

The efficiency cannot surpass the Carnot efficiency. Actually, real engines cannot even reach the Carnot efficiency. This is because the Carnot efficiency requires zero entropy change in Eq. (A.4), namely, that the entire process take place while in equilibrium. In particular, the process of absorbing heat energy from the high temperature source should end in equilibrium so that when the engine is disconnected from the reservoir, the temperature of the working substance should be T_h. The process of dumping the heat energy to the low temperature reservoir should end in equilibrium so that when the engine is disconnected from the source, the temperature of the working substance should be T_l.

If the condition of equilibrium is unrealistic, it is not the only condition that the Carnot efficiency requires. The Carnot engine also requires that

the engine convert 100 % of $\Delta Q_h - \Delta Q_l$ into work and deliver it to the work source. This means that the engine should run with no friction anywhere. What if there is friction? Part of the converted work energy has to be wasted to overcome the friction. Worse yet, the wasted work energy is converted back into heat and therefore creates an additional amount of entropy to be removed, which means that even more heat energy has to be dumped away.

A refrigerator works in the reverse order. It absorbs energy from a low temperature reservoir (the interior of the refrigerator) and then dumps the heat energy to a high temperature reservoir (the kitchen room). We all painfully know that refrigerators do not work when electricity is out. When the motor does not work and the refrigerator is left alone, its preferred direction of heat transfer is from the kitchen room to the interior of the refrigerator. If it did the other way spontaneously, it would be a violation of the second law. I will leave it to you to show that

$$\eta \leq \frac{T_l}{T_h - T_l}. \tag{A.6}$$

Appendix B

Maxwell Relations

Consider the identity

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_{V,N} &= \frac{\partial}{\partial T}\left(-\left(\frac{\partial F}{\partial V}\right)_{T,N}\right)_{V,N} \\ &= \frac{\partial}{\partial V}\left(-\left(\frac{\partial F}{\partial T}\right)_{V,N}\right)_{T,N} \\ &= \left(\frac{\partial S}{\partial V}\right)_{T,N}. \end{aligned} \tag{B.1}$$

Suppose that we have to measure what is on the right-hand side, namely, $(\partial S/\partial V)_T$. For isolated systems, changing V does not change S, but notice that the system is in a thermal bath. In order to maintain T fixed, some energy must be absorbed from the reservoir or released to it, which changes the entropy. The task is to measure this heat exchange with the reservoir, which is not a trivial task to perform. With this in mind, examine what is on the left hand side; it calls for a much simpler task. The identity makes our task that much simpler.

Where does this useful relationship originate? We merely took a cross-derivative of $dF = -SdT - PdV + \mu dN$ with respect to T and V. The identity of such cross-derivatives are called a Maxwell relation. Taking cross-derivatives with the other two pairs, (T, N) and (V, N), we obtain

$$-\left(\frac{\partial S}{\partial N}\right)_{T,N} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N} \tag{B.2}$$

and

$$-\left(\frac{\partial P}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N} \tag{B.3}$$

Not everyone of them may be as useful as our first example, but knowing how useful they can be, we should construct as many such relationships as we can. We may do so using

$$dU = TdS - PdV + \mu dN, \tag{B.4}$$
$$d\Omega = -SdT - PdV - Nd\mu, \tag{B.5}$$
$$dG = -SdT + VdP + \mu dN, \tag{B.6}$$
$$dW = TdS + VdP + \mu dN. \tag{B.7}$$

Knowing how we constructed these energy-like functions, we carry out two more Legendre transformations:

$$U' = U - \mu N, \tag{B.8}$$
$$U'' = U + PV - \mu N, \tag{B.9}$$

which give us

$$dU' = TdS - PdV - Nd\mu, \tag{B.10}$$
$$dU'' = TdS + VdP + Nd\mu. \tag{B.11}$$

I will leave it to you to carry out the cross derivatives to complete the list.

Appendix C

Thermodynamic Stability

Recall the instability that develops when systems attempt to enter the two-phase region of their phase diagram as a single-phase system. We saw this in the van der Waals mean field theory for liquid-gas systems and again in a similar mean field theory for binary atomic systems. In liquid-gas systems, a pathological thermodynamic state develops in which one subsystem "wants" more and more of volume while the other subsystem "wants" less and less of volume and therefore each can do what it wants at the courtesy of the other. We wish to identify these pathological conditions, or rather the lack of such conditions, namely, conditions for stability without relying on any specific model.

Let us return to the fundamental equation $S(U, V, N)$. Let us see what we have to demand for stability. Consider two identical subsystems. The fundamental equation should be the same for both. Could it be that one wants more and more energy while the other wants less and less energy? Let one subsystem transfer a small amount of energy to the other. The answer is simple: if this transfer of energy increases their combined entropy, the answer will be yes. To make it sure that the answer is no, we tell them that "it will not pay", namely, that

$$S(U + \Delta U, V, N) + S(U - \Delta U, V, N) \leq 2S(U, V, N). \tag{C.1}$$

Expand the two terms on the left-hand side to second order. The first order terms are cancelled out as do the two $S(U, V, N)$'s. The final result is

$$S_{UU} \leq 0, \tag{C.2}$$

where

$$S_{UU} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{\partial}{\partial U}\left(\frac{1}{T}\right)_{V,N} = -\frac{1}{T^2}\frac{1}{C_V} \leq 0, \tag{C.3}$$

which gives

$$C_V \geq 0. \tag{C.4}$$

This simple condition guarantees that the system will remain stable energywise. Thermal fluctuations could cause some inhomogeneous energy distribution, but as long as the specific heat is positive, the system will by itself return to a more normal distribution. It is interesting to ask: what would it be like if $C_V \leq 0$? Upon receiving energy, the substance will lower its temperature, meaning more appetite for energy. The negative specific heat also means that upon losing energy, the substance will want to lose even more! This is exactly the scenario that we prevented from happening with Eq. (C.1).

Let us continue the argument for volume V. To ensure stability, we have to demand

$$S(U, V + \Delta V, N) + S(U, V - \Delta U, V, N) \leq 2S(U, V, N) \tag{C.5}$$

which gives

$$\begin{aligned} S_{VV} &= \left(\frac{\partial S^2}{\partial U^2}\right)_{U,N}, \\ &= \frac{\partial}{\partial V}\left(\frac{p}{T}\right)_{T,N}, \\ &= -\frac{1}{T}\frac{1}{VK_T} \leq 0, \end{aligned} \tag{C.6}$$

i.e.,

$$K_T \geq 0, \tag{C.7}$$

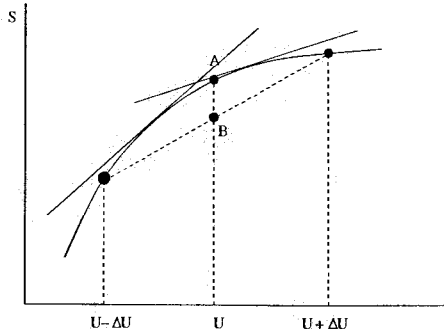

Fig. C.1 The basic equation depicted here represents a stable system. The fact that point A is above point B reflects the inequality in Eq. (C.5). Notice that all the tangent lines are above the curve, which does not allow a common tangent line anywhere.

where K_T is the isothermal compressibility. What would it be like if a substance did not have this property? We saw what happens in Chap. 7.

We may express Eqs. (C.1) and (C.5) graphically. The function $S(U,V,N)$ has to be concave; all tangential lines must lie above the curve, as demonstrated in Fig. C.1.

We have examined the function $S(U,V,N)$ first along the axis of U and then along the axis of V. For all intermediate directions, we have to demand

$$S(U+\Delta U, V+\Delta V, N) + S(U-\Delta U, V-\Delta V, N) \leq 2S(U,V,N). \quad \text{(C.8)}$$

Expand the two terms to second order using Eq. (2.18). The first order terms are all cancelled out as before and the final result is

$$\phi \equiv S_{UU}\Delta U^2 + 2S_{UV}\Delta U\Delta V + S_{VV}\Delta V^2 \leq 0. \quad \text{(C.9)}$$

This may be written in the form of

$$\phi S_{UU} = (S_{UU}\Delta U + S_{UV}\Delta V)^2 + (S_{UU}S_{VV} - S_{UV}^2)\Delta V^2 \geq 0, \quad \text{(C.10)}$$

which has to be positive because $S_{UU} \leq 0$. The condition that we seek is

$$S_{UU}S_{VV} - S_{UV}^2 \geq 0. \tag{C.11}$$

Apparently this is what it takes to ensure that $S(U,V,N)$ is concave-down in every intermediate direction.

Let us reformulate the stability arguments using $U(S,V,N)$. Since U follows a minimum principle, stability requires

$$U(S+\Delta S, V+\Delta V, N) + U(S-\Delta S, V-\Delta V, N) \geq 2U(S,V,N), \tag{C.12}$$

which gives three conditions:

$$\frac{\partial^2 U}{\partial S^2} = \frac{\partial T}{\partial S} \geq 0, \qquad \frac{\partial^2 U}{\partial V^2} = -\frac{\partial P}{\partial V} \geq 0, \tag{C.13}$$

and

$$U_{SS}U_{VV} - U_{SV}^2 \geq 0. \tag{C.14}$$

The function $U(S,V,N)$ must be convex in every direction. Thus the shapes of the two surfaces described by $S(U,V,N)$ and $U(S,V,N)$ are opposite.

It would be interesting to find out the shapes of all other energy-like functions. Since these functions are generated from $U(S,V,N)$ by various Legendre transformations, we should be able to obtain all of their second derivatives from Eq. (C.13). To this end, consider a function $A(x,y)$ or $dA = u\,dx + v\,dy$. Transform it to $B(u,y) = A(x,y) - ux$. Notice that

$$u = \frac{\partial A}{\partial x}, \qquad x = -\frac{\partial B}{\partial u}, \tag{C.15}$$

from which it follows that

$$-\frac{\partial^2 B}{\partial^2 u} = \left(\frac{\partial^2 A}{\partial x^2}\right)^{-1} \tag{C.16}$$

which tell us what to do: if the old function (A) is convex with respect to the old variable (x), the new function (B) is concave with respect to the new variable (u),

It then follows:

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \leq 0, \qquad \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq 0, \tag{C.17}$$

$$\left(\frac{\partial^2 W}{\partial S^2}\right)_{P,N} \geq 0, \qquad \left(\frac{\partial^2 W}{\partial P^2}\right)_{S,N} \leq 0, \tag{C.18}$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \leq 0, \qquad \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \leq 0. \tag{C.19}$$

We may conclude that for fixed N the energy and all of its Legendre transformations are convex functions of their extensive variables and concave functions of their intensive variables.

Bibliography

The literature on Thermodynamics and Statistical Mechanics is vast. I do not claim to have seen them all. I can only say that I consulted the books listed below while writing this book. I consider the first four books to be classics. They provided me with a crash course in thermal physics, and I wish to salute the authors for these excellent books. The rest are either more recent publications or deal with more advanced subjects of statistical mechanics.

States of Matter by David L. Goodstein (Dover, New York).

Fundamentals of Statistical and Thermal Physics by Frederick Reif (McGraw-Hill, 1985).

Thermodynamics and Introduction to Thermostatistics by Herbert B. Callen (John Wiley, 1985).

Thermal Physics by Charles Kittel and Herbert Kroamer (Freeman, New York, 1980).

Statistical Physics: An introductory course by Daniel J. Amit and Yosef Verbin (World Scientific, Singapore, 1995)

An Introduction to Thermal Physics by Daniel V. Schroeder (Addison Wiley, 2000)

Thermal Physics by Ralph Baierlein (Cambridge Press, 1999)

Statistical Thermodynamics by Robert P.H. Gasser and W. Graham Richards (Worlds Scientific, 1995)

Statistical Mechanics and Thermodynamics by Claude Garrod (Oxford, 1995)

A Modern Course in Statistical Physics by L.E. Reichel (U. of Texas Press, 1988)

Statistical Mechanics by Shang-Keng Ma (World Scientific, 1985)

Introduction to Modern Statistical Mechanics by David Chandler (Oxford, 1987)

Statistical Mechanics by Donald A. McQuarries (Harper Collins, 1976)

Statistical Mechanics by Kerson Huang (John Wiley, 1987)

Statistical Physics by L.D. Landau and E.M. Lifshitz (Pergamon, 1980)

Statistical Physics: Statics, Dynamics and Renormalization by Leo P. Kadanoff (World Scientific, 2001)

The book by Kittel and Kroemer has very nice problems, some solved and some not; we have borrowed some of them. Amit and Verbin and Garrod offer a wonderful collection of exercise problems with solutions.

A very detailed mathematical exposition of free energies can be found in the book by Callen. Callen also offers a more in-depth exposition of Shannon's information theory.

Except at the beginning, we covered little or no thermodynamics for spins; we heavily relied on statistical mechanics for spins. For an introduction to the thermodynamics of magnetism on a more general ground, a good book is **Statistical Physics** by F. Mandl (John Wiley, 1971). The brief section on magnetic work is superb.

We applied the Monte Carlo method only to a two-dimensional Ising model. The Monte Carlo method may be applied to liquid-gas molecular systems as well, but because the molecular interaction is not short-ranged, the simulation is not as straightforward as for the Ising spins. The actual molecular motions may be simulated using the method called Molecular Dynamics.

For both Monte Carlo and Molecular Dynamics for liquids, a good reference is **Computer Simulation of Liquids** by M.P. Allen and D.J. Tildesley (Oxford Press, 1994)

For a more intensive introduction to critical phenomena, you will do well to read "**Introduction to Phase Transitions and Critical Phenomena** by H.E. Stanley (Oxford, 1971).

If you would like the full account of the picture on the front cover, see J.C. Lee, Physica. A 210, 127 (1994).

For a coverage of non-equilibrium thermodynamics along the line discussed in Sec. 3.9, see **Nonequilibrium Thermodynamics** by Donald D. Fitts (McGraw-Hill, 1962) and **Thermodynamics of Irreversible Processes** by Rolf Haase (Dover, 1990).

If you wish to study how the partition function may be calculated for Ising models in one and two dimensions, see Stanley's book. Landau and Lifshitz present a slightly different version for the two-dimensional model.

If you wish to study the fluctuation-dissipation theorem in the context of transport phenomena (a subject which we did not cover), Chandler offers an excellent introduction to the vast subject area. McQuarries provides more extensive coverage of the subject.

For a full coverage of the renormalization group theory of second order phase transitions, I have two excellent books: **Modern Theory of Critical Phenomena** by Shang-keng Ma (W.A. Benjamin, 1976), and **Lectures on Phase Transitions and the Renormalization Group** by Nigel Goldenfeld (Addison Wesley, 1992). The latter book also covers first order phase transitions.

If the finite-size scaling fascinated you and you wish to read more, see **Finite Size Scaling and Numerical Simulation of Statistical Systems** edited by V. Privman (World Scientific, 1990).

Thermal physics is no longer a peripheral subject. It is everywhere, but its role is most prominent in condensed matter physics. When you feel you are ready, you may first start with the book by Goodstein and then **Principles of Condensed Matter Physics** by P.M. Chaikin and T.C. Lubensky (Cambridge University Press, 1997).

Finally, if you have difficulty writing code for the two-dimensional Ising model, Chandler has one in his book. Similar programs may also be found

in **Thermal and Statistical Physics Simulations** by H. Gould, L. Spornick, J. Tobochnik (Wiley, 1995), **Computational Physics** by N. Giordano (Prentice Hall, 1997), and **Computer Simulation Methods** by D.W. Heermann (Springer-Verlag, 1990).

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Thermal Physics

Entropy and Free Energies

This book is an informal, readable introduction to the basic ideas of thermal physics. It is aimed at making the reader feel comfortable with the extremum principles of entropy and free energies. There is a repeating theme: Molecules (spins) do X to maximize their entropy, and molecules (spins) do XX to minimize their free energy. This finally leads to the idea of the Landau–Ginzburg free energy functional. The author illustrates how powerful the idea is by using two examples from phase transitions.

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