Chapter 4

Statistical Thermodynamics

4.1 Overview

In Chap. 3, we introduced the concept of statistical equilibrium and studied, briefly, some of the properties of equilibrated systems. In this chapter we shall develop the theory of statistical equilibrium in a more thorough way. The title of this chapter, "Statistical Thermodynamics," emphasizes two aspects of the theory of statistical equilibrium. The term "thermodynamics" is an ancient one that predates statistical mechanics. It refers to a study of the *macroscopic* attributes of systems that are in or near equilibrium, such as their energy and entropy. Despite paying no attention to the microphysics, classical thermodynamics is a very powerful theory for deriving general relationships between these attributes. However, microphysics influences macroscopic properties in a statistical manner and so, in the late nineteenth century, Willard Gibbs and others developed *statistical mechanics* and showed that it provides a powerful conceptual underpinning for classical thermodynamics. The resultant synthesis, *statistical thermodynamics*, adds greater power to thermodynamics by augmenting to it the statistical tools of ensembles and distribution functions.

In our study of statistical thermodynamics we shall restrict attention to an ensemble of *large* systems that are in statistical equilibrium. By "large" is meant a system that can be broken into a large number $N_{\rm ss}$ of subsystems that are all macroscopically identical to the full system except for having $1/N_{\rm ss}$ as many particles, $1/N_{\rm ss}$ as much volume, $1/N_{\rm ss}$ as much energy, $1/N_{\rm ss}$ as much entropy, ... (Note that this constrains the energy of interaction between the subsystems to be negligible.) Examples are one kilogram of plasma in the center of the sun and a one kilogram sapphire crystal.

The equilibrium thermodynamics of any type of large system (e.g. a monatomic gas) can be derived using any one of the statistical equilibrium ensembles of the last chapter (microcanonical, canonical, grand canonical, Gibbs). For example, each of these ensembles will predict the same equation of state $P = (N/V)kT$ for an ideal monatomic gas, even though in one ensemble each system's number of particles N is precisely fixed, while in another ensemble N can fluctuate so that strictly speaking one should write the equation of state as $P = (\bar{N}/V)kT$ with $\bar{N}$ the ensemble average of N. (Here and throughout this chapter, for compactness we use bars rather than brackets to denote ensemble averages, i.e. $\bar{N}$ rather than $\langle N\rangle$.)

The equations of state are the same to very high accuracy because the fractional fluctuations of N are so extremely small, $\Delta N/N \sim 1/\sqrt{N}$; cf Ex. 3.5. Although the thermodynamic properties are independent of the equilibrium ensemble, specific properties are often derived most quickly, and the most insight usually accrues, from that ensemble which most closely matches the physical situation being studied.

In Sec. 3.7 we used the grand canonical ensemble, and in Secs. 4.2, 4.3, and 4.4 we shall use the microcanonical, canonical and Gibbs ensembles to derive many useful results from both classical and statistical thermodynamics: equations of state, Maxwell relations, Euler's equation, sum-over-states methods for computing fundamental potentials, applications of fundamental potentials, ... Table 4.2 summarizes those statistical-equilibrium results and some generalizations of them. Readers may wish to delay studying this table until they have read further into the chapter.

As we saw in Chap. 3, when systems are out of statistical equilibrium, their evolution toward equilibrium is driven by the law of entropy increase—the second law of thermodynamics. In Sec. 4.4 we formulate the fundamental potential (Gibbs potential) for an out-of-equilibrium ensemble that interacts with a heat and volume bath, we discover a simple relationship between that fundamental potential and the entropy of system plus bath, and from that relationship we learn that the second law, in this case, is equivalent to a law of decrease of the Gibbs potential. As an application, we learn how chemical potentials drive chemical reactions and also drive phase transitions. In Sec. 4.4 we study spontaneous fluctuations of a system away from equilibrium, when it is coupled to a heat and particle bath, and discover how the fundamental potential (in this case Gibbs potential) can be used to compute the probabilities of such fluctuations. These out-of-equilibrium aspects of statistical mechanics (evolution toward equilibrium and fluctuations away from equilibrium) are summarized in Table 4.2, not just for heat and volume baths, but for a wide variety of other baths. Again, readers may wish to delay studying the table until they have read further into the chapter.

Although the conceptual basis of statistical thermodynamics should be quite clear, deriving quantitative results for real systems can be formidably difficult. In a macroscopic sample, there is a huge number of possible microscopic arrangements (quantum states) and these all have to be taken into consideration via statistical sums if we want to understand the macroscopic properties of the most frequently occuring configurations. Direct summation over states is hopelessly impractical for real systems. However, in recent years a number of powerful approximation techniques have been devised for performing the statistical sums. In Secs. 4.6 and 4.7 we give the reader the flavor of two of these techniques: the *renormalization group* and *Monte Carlo methods*. We illustrate and compare these techniques by using them to study a phase transition in a simple model for Ferromagnetism called the *Ising model*.

4.2 Microcanonical Ensemble and the Energy Representation of Thermodynamics

Consider a microcanonical ensemble of large, closed systems that have attained statistical equilibrium. We can describe the ensemble macroscopically using a set of thermodynamic variables. As we saw in Chap. 3, these variables can be divided into two classes: *extensive variables* which double if one doubles the size (volume, mass, ...) of the system, and *intensive variables* whose magnitudes are independent of the system's size. Examples of extensive variables are a system's total energy $\tilde{E}$, entropy S, volume V, magnetization $\mathbf{M}$, and its number of conserved particles of various species N_I. Examples of intensive variables are temperature T, pressure P, the magnetic field strength $\mathbf{H}$ imposed on the system from the outside, and the chemical potentials $\tilde{\mu}_I$ for various species of particles.

The particle species I must only include those species whose particles are conserved on the timescales of interest. For example, if photons can be emitted and absorbed, then one must not specify N_γ, the number of photons; rather, N_γ will come to an equilibrium value that is governed by the values of the other extensive variables. Also, one must omit from the set $\{I\}$ any conserved particle species whose numbers are automatically determined by the numbers of other, included species. For example, gas inside the sun is always charge neutral to very high precision, and therefore the number of electrons N_e in a sample of gas is always determined by the number of protons N_p and the number of Helium nuclei (alpha particles) N_α: $N_e = N_p + 2N_\alpha$. Therefore, one includes N_p and N_α in one's complete set of extensive variables, but one omits N_e.

As in Chapter 3, we shall formulate the theory relativistically correctly, but shall formulate it solely in the mean rest frames of the systems and baths being studied. Correspondingly, in our formulation we shall generally include the particle rest masses m_I in the total energy $\tilde{E}$ and in the chemical potentials $\tilde{\mu}_I$. For highly nonrelativistic systems, however, we shall usually replace $\tilde{E}$ by the nonrelativistic energy $E \equiv \tilde{E} - \sum_I N_I m_I c^2$, and $\tilde{\mu}_I$ by the nonrelativistic chemical potential $\mu_I \equiv \tilde{\mu}_I - m_I c^2$ (though, as we shall see in Sec. 4.4 when studying chemical reactions, the identification of the appropriate rest mass m_I to subtract is occasionally a delicate issue.)

Let us now specialize to a microcanonical ensemble of one-species systems, which all have identically the same values of the energy $\tilde{E}$,[1] number of particles N, and volume V. Suppose that the microscopic nature of the systems in the ensemble is known. Then, at least in principle and often in practice, one can identify from that microscopic nature the quantum states that are available to the system (given its constrained values of $\tilde{E}$, N, and V); one can count those quantum states; and from their total number $N_{\rm states}$ one can compute the ensemble's total entropy $S = k \ln N_{\rm states}$ [cf Eq. (3.41)]. The resulting entropy can be regarded as a function of the complete set of extensive variables,

$$S = S(\tilde{E}, N, V) \; , \tag{4.1}$$

and this equation can then be inverted to give the total energy in terms of the entropy and the other extensive variables

$$\tilde{E} = \tilde{E}(S, N, V) \; . \tag{4.2}$$

We call the energy $\tilde{E}$, viewed as a function of S, N, and V, the *fundamental thermodynamic potential* for the microcanonical ensemble. From it, one can deduce all other thermodynamic properties of the system.

[1]In practice, as was illustrated in Sec. 3.6, one must allow $\tilde{E}$ to fall in some tiny but finite range $\delta\tilde{E}$ rather than constraining it precisely, and one must then check to be sure that the results of one's analysis are independent of $\delta\tilde{E}$.

In Sec. 3.4, we used kinetic theory considerations to identify the thermodynamic temperature T of the canonical ensemble [Eq. (3.25)]. It is instructive to discuss how this temperature arises in the microcanonical ensemble. Our discussion makes use of an idealized *thermometer* consisting of an idealized atom that has only two states, $|0\rangle$ and $|1\rangle$ with energies $\tilde{E}_0$ and $\tilde{E}_1 = \tilde{E}_0 + \Delta\tilde{E}$. The atom, initially in its ground state, is brought into thermal contact with one of the large systems of our microcanonical ensemble and then monitored over time as it is stochastically excited and de-excited. The ergodic hypothesis (Sec. 3.5) guarantees that the atom traces out a history of excitation and deexcitation that is governed statistically by the canonical ensemble for a collection of such atoms exchanging energy (heat) with our large system (the heat bath). More specifically, if T is the (unknown) temperature of our system, then the fraction of the time the atom spends in its excited state, divided by the fraction spent in its ground state, is equal to the canonical distribution's probability ratio

$$\frac{\rho_1}{\rho_0} = \frac{e^{-\tilde{E}_1/kT}}{e^{-\tilde{E}_0/kT}} = e^{-\Delta\tilde{E}/kT} \; . \tag{4.3}$$

This ratio can also be computed from the properties of the full system augmented by the two-state atom. This augmented system is microcanonical with a total energy $\tilde{E} + \tilde{E}_0$, since the atom was in the ground state when first attached to the full system. Of all the quantum states available to this augmented system, the ones in which the atom is in the ground state constitute a total number $N_0 = e^{S(\tilde{E},N,V)/k}$; and those with the atom in the excited state constitute a total number $N_1 = e^{S(\tilde{E}-\Delta\tilde{E},N,V)/k}$. Here we have used the fact that the number of states available to the augmented system is equal to that of the original, huge system (since the atom, in each of the two cases, is forced to be in a unique state); and we have expressed that number of states of the original system, for each of the two cases, in terms of the original system's entropy function, Eq. (4.1). The ratio of the number of states N_1/N_0 is (by the ergodic hypothesis) the ratio of the time that the augmented system spends with the atom excited, to the time spent with the atom in its ground state; i.e., it is equal to ρ_1/ρ_0

$$\frac{\rho_1}{\rho_0} = \frac{N_1}{N_0} = \frac{e^{S(\tilde{E}-\Delta\tilde{E},N,V)/k}}{e^{S(\tilde{E},N,V)/k}} = \exp\left[-\frac{\Delta\tilde{E}}{k}\left(\frac{\partial S}{\partial\tilde{E}}\right)_{N,V}\right] \; . \tag{4.4}$$

By equating Eqs. (4.3) and (4.4), we obtain an expression for the original system's temperature T in terms of the partial derivative $(\partial\tilde{E}/\partial S)_{N,V}$ of its fundamental potential $\tilde{E}(S,N,V)$

$$T = \frac{1}{(\partial S/\partial\tilde{E})_{N,V}} = \left(\frac{\partial\tilde{E}}{\partial S}\right)_{N,V} , \tag{4.5}$$

where we have used Eq. (1) of Box 4.1.

A similar thought experiment, using a highly idealized measuring device that can exchange one particle $\Delta N = 1$ with the system but cannot exchange any energy with it, gives for the fraction of the time spent with the extra particle in the measuring device ("state 1") and in the system ("state 0"):

$$\frac{\rho_1}{\rho_0} = e^{\tilde{\mu}\Delta N/kT} \tag{4.6}$$

Box 4.1
Box Two Useful Relations between Partial Derivatives

Expand a differential increment in the energy $\tilde{E}(S,N,V)$ in terms of differentials of its arguments S,N,V

$$d\tilde{E}(S,N,V) = \Big(\frac{\partial\tilde{E}}{\partial S}\Big)_{N,V} dS + \Big(\frac{\partial\tilde{E}}{\partial N}\Big)_{V,S} dN + \Big(\frac{\partial\tilde{E}}{\partial V}\Big)_{S,N} dV \ . \tag{1}$$

Next expand the entropy $S(\tilde{E},N,V)$ similarly and substitute the resulting expression for dS into the above equation to obtain

$$d\tilde{E} = \left(\frac{\partial\tilde{E}}{\partial S}\right)_{N,V} \left(\frac{\partial S}{\partial\tilde{E}}\right)_{N,V} d\tilde{E} \ + \ \left[\left(\frac{\partial\tilde{E}}{\partial S}\right)_{N,V} \left(\frac{\partial S}{\partial N}\right)_{E,V} + \left(\frac{\partial\tilde{E}}{\partial N}\right)_{S,V}\right] dN \tag{2}$$

$$+ \ \left[\left(\frac{\partial\tilde{E}}{\partial S}\right)_{N,V} \left(\frac{\partial S}{\partial V}\right)_{N,E} + \left(\frac{\partial\tilde{E}}{\partial V}\right)_{S,N}\right] dV \ , \tag{3}$$

Noting that this relation must be satisfied for all values of $d\tilde{E}$, dN, and dV, we conclude that

$$\left(\frac{\partial\tilde{E}}{\partial S}\right)_{N,V} = \frac{1}{(\partial S/\partial\tilde{E})_{N,V}} \ , \tag{4}$$

$$\left(\frac{\partial\tilde{E}}{\partial N}\right)_{S,V} = -\left(\frac{\partial\tilde{E}}{\partial S}\right)_{N,V} \left(\frac{\partial S}{\partial N}\right)_{\tilde{E},V} \ , \tag{5}$$

etc.; and similar for other pairs and triples of partial derivatives.

These equations, and their generalization to other variables, are useful in manipulations of thermodynamic equations.

$$= \ \frac{e^{S(\tilde{E},N-\Delta N,V)/k}}{e^{S(\tilde{E},N,V)/k}} = \exp\Big[-\frac{\Delta N}{k}\Big(\frac{\partial S}{\partial N}\Big)_{\tilde{E},V}\Big] \ , \tag{4.7}$$

Here the first expression is computed from the viewpoint of the measuring device's grand canonical ensemble, and the second from the viewpoint of the combined system's microcanonical ensemble. Equating these two expressions, we obtain

$$\tilde{\mu} = -T\Big(\frac{\partial S}{\partial N}\Big)_{\tilde{E},V} = \left(\frac{\partial\tilde{E}}{\partial N}\right)_{S,V} \ . \tag{4.8}$$

In the last step we have used Eq. (4.5) and Eq. (2) of Box 4.1. The reader should be able to construct a similar thought experiment involving an idealized pressure transducer, which yields the following expression for the system's pressure:

$$P = -\left(\frac{\partial \tilde{E}}{\partial V}\right)_{S,N} . \tag{4.9}$$

Having identifed the three intensive variables T, $\tilde{\mu}$, and P as partial derivatives [Eqs. (4.5), (4.7), (4.8)], we now see that the fundamental potential's differential relation

$$d\tilde{E}(S,N,V) = \left(\frac{\partial \tilde{E}}{\partial S}\right)_{N,V} dS + \left(\frac{\partial \tilde{E}}{\partial N}\right)_{V,S} dN + \left(\frac{\partial \tilde{E}}{\partial V}\right)_{S,N} dV . \tag{4.10}$$

is nothing more nor less than the ordinary first law of thermodynamics

$$d\tilde{E} = TdS + \tilde{\mu}dN - PdV . \tag{4.11}$$

Notice the "pairing" of intensive and extensive variables in this first law: Temperature T is paired with entropy S; chemical potential $\tilde{\mu}$ is paired with number of particles N; and pressure P is paired with volume V. We can think of each intensive variable as a "generalized force" acting upon its corresponding extensive variable to change the energy of the system. We can add additional pairs of intensive and extensive variables if appropriate, calling them X_A, Y_A (for example the externally imposed magnetic field $\mathbf{H}$ and the magnetization $\mathbf{M}$). We can also generalize to a multi-component system, i.e. one that has several types of conserved particles with numbers N_I and associated chemical potentials $\tilde{\mu}_I$. We can also convert to nonrelativistic language by subtracting off the rest-mass contributions (switching from $\tilde{E}$ to $E \equiv \tilde{E} - \sum N_I m_I c^2$ and from $\tilde{\mu}_I$ to $\mu_I = \tilde{\mu}_I - m_I c^2$). The result is the nonrelativistic, extended first law

$$dE = TdS + \sum_I \mu_I dN_I - PdV + \sum_A X_A dY_A . \tag{4.12}$$

(e.g., Sec. 18 of Kittel 1958).

We can integrate the differential form of the first law to obtain a remarkable, though essentially trivial relation known as *Euler's equation*. More specifically, we decompose our system into a large number of subsystems in equilibrium with each other. As they are in equilibrium, they will all have the same values of the intensive variables $T, \tilde{\mu}, P$; and therefore, if we add up all their energies $d\tilde{E}$ to obtain $\tilde{E}$, their entropies dS to obtain S, etc., we obtain from the first law (4.11) [2]

$$\tilde{E} = TS + \tilde{\mu}N - PV . \tag{4.13}$$

Since the energy $\tilde{E}$ is itself extensive, Euler's equation (4.13) must be expressible in the functional form

$$\tilde{E} = Nf(V/N, S/N) \tag{4.14}$$

[2]There are a few (very few!) systems for which some of the thermodynamic laws, including Euler's equation, take on forms different from those presented in this chapter. A black hole is an example (cf Sec. 3.8). A black hole cannot be divided up into subsystems, so the above derivation of Euler's equation fails. Instead of increasing linearly with the mass M_H of the hole, the hole's extensive variables S_H = (entropy) and J_H = (spin angular momentum) increase quadratically with M; and instead of being independent of the hole's mass, the intensive variables T_H = (temperature) and Ω_H = (angular velocity) scale as $1/M$. (See, e.g., Tranah & Landsberg 1980.)

for some function f. For example, for a monatomic ideal gas, the non-relativistic version of Eq. (4.14) is

$$E(V,S,N) = N\left(\frac{3h^2}{4\pi m}\right)\left(\frac{V}{N}\right)^{-2/3}\exp\left(\frac{2}{3k}\frac{S}{N}-\frac{5}{3}\right)\,; \tag{4.15}$$

cf Eq. (3.69). Here m is the mass of an atom and h is Planck's constant.

There is no need to memorize a lot of thermodynamic relations; most all relations can be deduced almost trivially from the fundamental potential plus the first law. For example, if one remembers only that the nonrelativistic fundamental relation expresses E as a function of the other extensive variables S, N, V, then by writing out the differential relation (4.12) and comparing with the first law $dE = TdS + \mu dN - PdV$, one can immediately read off the intensive variables in terms of partial derivatives of the fundamental potential:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}\,, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{V,S}\,, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}\,. \tag{4.16}$$

One can then go on to notice that the resulting $P(V,S,N)$, $T(V,S,N)$, and $\mu(V,S,N)$ are not all independent. The equality of mixed partial derivatives (e.g., $\partial^2 E/\partial V\partial S = \partial^2 E/\partial S\partial V$) together with Eqs. (4.16) implies that they must satisfy the following *Maxwell relations*:

$$\left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{N,V}\,, \quad -\left(\frac{\partial P}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial V}\right)_{S,N}\,, \quad \left(\frac{\partial \mu}{\partial V}\right)_{N,S} = -\left(\frac{\partial P}{\partial N}\right)_{V,S}\,. \tag{4.17}$$

Additional relations can be generated using the types of identities proved in Box 4.1 — or they can be generated more easily by applying the above procedure to the fundamental potentials associated with other ensembles; see, e.g., Secs. 3.7, 4.3 and 4.4. All *equations of state*, i.e. all relations between intensive and extensive variables, must satisfy the Maxwell relations. For our simple example of a nonrelativistic, monatomic gas we can substitute our fundamental potential E [Eq. (4.15)] into Eqs. (4.16) to obtain

$$P(V,S,N) = \left(\frac{h^2}{2\pi m}\right)\left(\frac{N}{V}\right)^{5/3}\exp\left(\frac{2S}{3kN}-\frac{5}{3}\right)\,, \tag{4.18}$$

$$T(V,S,N) = \left(\frac{h^2}{2\pi m k}\right)\left(\frac{N}{V}\right)^{2/3}\exp\left(\frac{2S}{3kN}-\frac{5}{3}\right)\,, \tag{4.19}$$

$$\mu(V,S,N) = \left(\frac{h^2}{4\pi m}\right)\left(\frac{N}{V}\right)^{2/3}\left(5-2\frac{S}{kN}\right)\exp\left(\frac{2S}{3kN}-\frac{5}{3}\right)\,. \tag{4.20}$$

(4.21)

These clearly do satisfy the Maxwell relations.

Turn, now, from formalism to a simple thought experiment that gives insight into entropy. Consider a single, large, closed system (not an ensemble), which has evolved for a time far longer than $\tau_{\rm int}$ and thereby has reached statistical equilibrium. Let $T(V,\ S,\ N)$ be the temperature that characterizes this system's grand-canonically-distributed subsystems. Now add a small amount ΔQ of thermal energy (heat) to the system, without changing its volume V or its number of conserved particles N. The added heat, being on an equal footing with any other kind of energy in the law of energy conservation, must appear in the first law as a $\Delta\tilde{E} = \Delta Q$; and correspondingly, according to the first law (4.11), the added heat must increase the system's entropy by an amount

$$\Delta S = \frac{\Delta Q}{T} . \tag{4.22}$$

This can be generalized: The energy need not be inserted into the system in the form of heat. Rather, one can add the energy mechanically, e.g., if the system is a liquid by stirring it; or one can add it optically by shining a laser beam into it and letting a few of the system's atoms absorb the laser light. In either case the system, immediately after energy insertion, will be far from statistical equilibrium; i.e., its macroscopic properties such as the number of atoms with energies far higher than the mean (i.e. it's *macrostate*) will be highly improbable according to the microcanonical distribution.[3] However, if one waits long enough ($\Delta t \gg \tau_{\rm int}$) after the energy addition, the system will thermalize; i.e., it will evolve into a macrostate that is rather probable according to the microcanonical distribution, and thereafter it will wander ergodically through system quantum states that correspond, more or less, to this macrostate. This final, thermalized macrostate and the initial macrostate, before energy insertion, both have the same volume V and the same number of conserved particles N; but they differ in energy by the amount ΔE that was inserted. Correspondingly, they also differ in entropy by

$$\Delta S = \frac{\Delta\tilde{E}}{T} . \tag{4.23}$$

Where did this entropy come from? Suppose that the energy was injected by a laser. Then initially the energy went into those specific atoms that absorbed the photons. Subsequently, however, those atoms randomly exchanged and shared the energy with other atoms. This exchange and sharing is a variant of the phase mixing of Sec. 3.6, and it is responsible for the thermal equilibration and the entropy increase.

The treatment of thermodynamics given in this section is called the *energy representation* because it is based on the fundamental potential $\tilde{E}(S, V, N)$ in which the energy is expressed as a function of the complete set of extensive variables $\{S,\ V,\ N\}$. This energy representation is intimately related to the microcanonical ensemble, as the discussion near the beginning of this section shows. In Sec. 3.7 of the last chapter we met a *grand-potential representation* for thermodynamics, which was based on the grand potential $\Omega(T, \tilde{\mu}, V)$ and was intimately related to the grand canonical ensemble for systems of volume V in equilibrium with a heat and particle bath that has temperature T and chemical potential $\tilde{\mu}$. In the next two sections we shall meet the two representations of thermodynamics that are intimately related to the canonical and Gibbs ensembles, and shall discover their special power at handling certain special issues.

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EXERCISES

[3]We use the word "macrostate" to distinguish clearly from the quantum states available to the system as a whole, which in equilibrium are all equally likely. The probability for a macrostate is proportional to the number of system quantum states that correspond to it.

Representation & Ensemble	**First Law**	**Bath**	**Distribution Function** ρ
Energy & Microcanonical	$d\tilde{E} = TdS + \tilde{\mu}dN - PdV$	none	const $= e^{-S/k}$ $\tilde{E}$ const in $\delta\tilde{E}$
Enthalpy	$dH = TdS + \tilde{\mu}dN + VdP$	V & $\tilde{E}$ $d\tilde{E} = -PdV$	const $= e^{-S/k}$ Hconst in δH
Free-Energy & Canonical	$dF = -SdT + \tilde{\mu}dN - PdV$	$\tilde{E}$	$e^{(F-\tilde{E})/kT}$
Gibbs	$dG = -SdT + \tilde{\mu}dN + VdP$	$\tilde{E}$ & V	$e^{(G-\tilde{E}-PV)/kT}$
Grand Canonical	$d\Omega = -SdT - Nd\tilde{\mu} - PdV$	$\tilde{E}$ & N	$e^{(\Omega-\tilde{E}+\tilde{\mu}N)/kT}$

Table 4.1: Representations and Ensembles for Statistical Equilibrium.

Exercise 4.1 *Problem: Pressure-Measuring Device*
For the microcanonical ensemble considered in Sec. 4.2, derive Eq. (4.9) for the pressure using a thought experiment involving a pressure-measuring device.

Exercise 4.2 *Derivation: Energy Representation for a Nonrelativistic Monatomic Gas*

(a) Use the fundamental potential $E(V, S, N)$ for the nonrelativistic, monatomic gas to derive Eq. (4.21) for the the pressure, temperature, and chemical potential.

(b) Show that these equations of state satisfy the Maxwell relations (4.17).

(c) Combine these equations of state to obtain the perfect-gas equation of state

$$P = \frac{N}{V}kT \,. \tag{4.24}$$

Note that this is the same equation as we obtained using the grand canonical ensemble, Eq. (3.64), except that the average pressure and particle number are replaced by their exact microcanonical equivalents. As we discussed in Sec. 4.1, this is no coincidence.

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4.3 Canonical Ensemble and the Free-Energy Representation of Thermodynamics

In this section we focus attention on an ensemble of systems that can exchange energy but nothing else with a heat bath at temperature T. The systems thus have variable total energy $\tilde{E}$, but they all have the same, fixed values of the two remaining extensive variables N and V. (Once again generalization to additional particle species and additional means of performing work on the system is straightforward.) We presume that the ensemble has reached statistical equilibrium, so it is canonical with distribution function (probability of occupying any quantum state of energy $\tilde{E}$) given by the analog of Eq. (3.44)

$$\rho = \frac{1}{z} e^{-\tilde{E}/kT} \equiv e^{(F-\tilde{E})/kT} \; . \tag{4.25}$$

Here, as in the grand canonical ensemble (Sec. 3.7), we have introduced special notations for the normalization constant: $1/z = e^{F/kT}$, where z (the *partition function*) and F (the *physical free energy* or *Helmholtz free energy*) are functions of the systems' fixed N and V and the bath's temperature T. Once the microscopic configurations (quantum states $|n\rangle$) of fixed N and V but variable $\tilde{E}$ have been identified, the functions $z(N, V, T)$ and $F(N, V, T)$ can be computed from the normalization relation $\sum_n \rho_n = 1$:

$$e^{-F/kT} \equiv z(T, N, V) = \sum_n e^{-\tilde{E}_n/kT} = \int \left[e^{-\tilde{E}(\mathbf{q},\mathbf{p})/kT} \right] \frac{d^W q d^W p}{\mathcal{M} h^W} \; , \tag{4.26}$$

Having evaluated $z(T, N, V)$ or equivalently $F(T, N, V)$, one can then proceed as follows to determine other thermodynamic properties of the ensemble's systems.

The entropy S can be computed from the standard expression $S = -k\overline{\ln \rho}$, together with Eq. (4.25) for ρ:

$$S = \frac{\bar{\tilde{E}} - F}{T} \; , \tag{4.27}$$

It is helpful to rewrite Eq. (4.27) as an equation for the free energy F

$$F = \bar{\tilde{E}} - TS \; . \tag{4.28}$$

Suppose, now, that the canonical ensemble's parameters T, N, V are changed slightly. By how much will the free energy change? Equation (4.28) tells us that

$$dF = d\bar{\tilde{E}} - TdS - SdT \; . \tag{4.29}$$

Because macroscopic thermodynamics is independent of the statistical ensemble being studied, we can evaluate $d\bar{\tilde{E}}$ using the first law of thermodynamics (4.11) with the microcanonical exact energy $\tilde{E}$ replaced by the canonical mean energy $\bar{\tilde{E}}$. The result is

$$dF = -SdT + \tilde{\mu} dN - PdV \; . \tag{4.30}$$

Equation (4.30) contains the same information as the first law of thermodynamics and can be thought of as the first law rewritten in a new mathematical representation, the *free-energy representation*. In the original energy representation we regarded $\tilde{E}(S, N, V)$ as the fundamental potential, and the first law described how $\tilde{E}$ changes when its independent variables S, N, V are changed. In the free-energy representation we regard $F(T, N, V)$ as the fundamental potential, and the first law (4.30) describes how F changes when its independent variables T, N, V change. Because the microcanonical ensemble deals with systems of fixed $\tilde{E}$, N, V, it is the foundation that underlies the energy representation. Because the canonical ensemble deals with systems of fixed T, N, V, it is the foundation that underlies the free-energy representation. Eq. (4.28), which leads mathematically from the energy representation to the free-energy representation, is called a *Legendre transformation* and is a common tool (e.g. in classical mechanics[4]) for switching from one set of independent

[4]For example, Goldstein (1980).

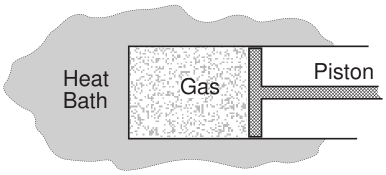

Fig. 4.1: Origin of the name "physical free energy" for $F(V, T, N)$.

variables to another.

The independent variables in the free-energy representation are the differentials on the right hand side of the first law (4.30), namely T, N, V. The "generalized forces" paired with these independent variables, $-S$, $\tilde{\mu}$, $-P$ respectively, are the coefficients of the first-law changes. The corresponding Euler equation can be inferred from the first law by thinking of building up the full system, piece-by-piece, with the extensive variables growing in unison and the intensive variables held fixed; the result is

$$F = -PV + \tilde{\mu}N \ . \tag{4.31}$$

Note that the temperature is present in this relation only implicitly, through the dependence of F, P, and $\tilde{\mu}$ on the representation's independent variables T, N, V.

We can use the free-energy form of the first law to read off equations of state for the generalized forces,

$$-P = \left(\frac{\partial F}{\partial V}\right)_{T,N} , \quad -S = \left(\frac{\partial F}{\partial T}\right)_{V,N} , \quad \tilde{\mu} = \left(\frac{\partial F}{\partial N}\right)_{V,T} ; \tag{4.32}$$

Finally, Maxwell relations can be derived from the equality of mixed partial derivatives, as in the energy representation; for example, $(\partial P/\partial T)_{V,N} = (\partial S/\partial V)_{T,N}$.

The name "physical free energy" for F can be understood using the idealized experiment shown in Fig. 4.1. Gas is placed in a chamber, one wall of which is a piston; and the chamber comes into thermal equilibrium with a heat bath, with which it can exchange heat but not particles. The volume of the chamber has some initial value V_i; and correspondingly, the gas has some initial physical free energy $F(V_i, T, N)$. The gas is then allowed to push the piston to the right sufficiently slowly for the gas to remain always in thermal equilibrium with the heat bath, at the bath's temperature T. When the chamber has reached its final volume V_f, the total work done on the piston by the gas, i.e., the total energy extracted by the piston from this "engine", is

$$\tilde{E}_{\rm extracted} = \int_{V_i}^{V_f} -PdV \ . \tag{4.33}$$

Using the first law $dF = -SdT + \tilde{\mu}dN - PdV$ and remembering that T and N are kept constant, Eq. (4.33) becomes

$$\tilde{E}_{\rm extracted} = F(V_f, T, N) \ - \ F(V_i, T, N) \equiv \Delta F \ . \tag{4.34}$$

Thus, F is the energy that is "free to be extracted" in an isothermal, physical expansion of the gas.

If the expansion had been done in a chamber that was perfectly thermally insulated, so no heat could flow in or out of it, Eq. (4.22) tells us that there would have been no entropy change. Correspondingly, with S and N held fixed but V changing during the expansion, the natural way to analyze the expansion would have been in the energy representation; and that representation's first law $d\tilde{E} = -PdV + TdS + \tilde{\mu}dN$ would have told us that the total energy extracted, $\int -PdV$, was the change $\Delta\tilde{E}$ of the gas's total energy. Such a process, which occurs without any heat flow or entropy increase, is called *adiabatic*. Thus, the energy $\tilde{E}$ (or in the nonrelativistic regime E) measures the amount of energy that can be extracted from an adiabatic engine, by contrast with F which measures the energy extracted from an isothermal engine.

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EXERCISES

Exercise 4.3 *Example: The Enthalpy Representation of Thermodynamics*

(a) Enthalpy H is a macroscopic thermodynamic variable defined by

$$H = \tilde{E} + PV \; . \tag{4.35}$$

Show that this definition can be regarded as a Legendre transformation that converts from the energy representation of thermodynamics with $\tilde{E}(V, S, N)$ as the fundamental potential, to an *enthalpy representation* with $H(P, S, N)$ as the fundamental potential. More specifically, show that the first law, reexpressed in terms of H, takes the form

$$dH = VdP + TdS + \tilde{\mu}dN \; ; \tag{4.36}$$

and then explain why this first law dictates that $H(P, S, N)$ be taken as the fundamental potential.

(b) There is an equilibrium statistical mechanics ensemble associated with the enthalpy representation. What extensive quantities do the systems of this ensemble exchange with their surrounding bath? Describe a physical situation that could produce this ensemble.

(c) What equations of state can be read off from the enthalpy first law? What are the Maxwell relations between these equations of state?

(d) What is the Euler equation for H in terms of a sum of products of extensive and intensive variables?

(e) Show that the system's enthalpy is equal to its total inertial mass (multiplied by the speed of light squared); cf Ex. 2.4.

(f) As another interpretation of the enthalpy, think of the system as enclosed in an impermeable box of volume V. You are asked to inject into the box a "sample" of additional material of the same sort as is already there. (It may be helpful to think of the material as a gas.) The sample is to be put into the same thermodynamic state, i.e. macrostate, as that of the box's material; i.e., it is to be given the same values of temperature T, pressure P, and chemical potential $\tilde{\mu}$. Thus, the sample's material is indistinguishable in its thermodynamic properties from the material already in the box, except that its extensive variables (denoted by Δ's) are far smaller: $\Delta V/V = \Delta\tilde{E}/\tilde{E} = \Delta S/S \ll 1$. Perform the injection by opening up a hole in one of the box's walls, pushing aside the box's material enough to make a little cavity of volume ΔV equal to that of the sample, inserting the sample into the cavity, and then closing the hole in the wall. The box now has the same volume V as before, but its energy has changed. Show that the energy change, i.e., the energy required to create the sample and perform the injection, is equal to the enthalpy ΔH of the sample. Thus, *enthalpy has the physical interpretation of "energy of injection at fixed volume V"*.

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4.4 The Gibbs Representation of Thermodynamics; Phase Transitions and Chemical Reactions

Turn attention, next, to the most important of the various representations of thermodynamics: the one appropriate to systems in which the temperature T and pressure P are both being controlled by an external environment (bath) and thus are treated as independent variables in the fundamental potential. This is the situation in most laboratory experiments. This representation can be obtained from the energy representation using a Legendre transformation

$$G \equiv \tilde{E} - TS + PV \; . \tag{4.37}$$

We call the quantity G the *Gibbs potential* (it is also known as the *chemical free-energy* or the *Gibbs free-energy*), and we call the representation of thermodynamics based on it the *Gibbs representation.*

Differentiating Eq. (4.37) and combining with the energy representation's first law (4.11), we obtain the first law in the Gibbs representation:

$$dG = VdP - SdT + \tilde{\mu}dN \; . \tag{4.38}$$

From this first law we read out the independent variables of the Gibbs representation, namely $\{P, T, N\}$ and the equations of state:

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} , \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad \tilde{\mu} = \left(\frac{\partial G}{\partial N}\right)_{P,T} ; \tag{4.39}$$

and from the equality of mixed partial derivatives, we read off Maxwell relations. By imagining building up a large system from many tiny subsystems (all with the same, fixed P and T) and applying the first law (4.38) to this buildup, we obtain the Euler relation

$$G = \tilde{\mu}N \; . \tag{4.40}$$

The energy representation (Sec. 4.2) is intimately associated with the microcanonical ensemble, the physical-free-energy representation (Sec. 4.3) is intimately associated with the canonical ensemble, and the grand-potential representation (Sec. 3.7) is intimately associated with the grand-canonical ensemble. What, by analogy, is the ensemble associated with the Gibbs representation? In general, those independent variables of a representation that are intensive are properties of the bath with which the ensemble's systems interact, the extensive variables paired with those independent intensive variables are the quantitites exchanged with the bath, and the independent extensive variables are the quantities held fixed in the ensemble's systems. For the Gibbs representation the independent intensive variables are pressure P and temperature T, and therefore the bath must be characterized by fixed P and T. Paired with P and T are the extensive variables V and $\tilde{E}$, and therefore the systems exchange volume and energy with the bath. The only independent extensive variable is N, and thus the systems in the ensemble must have fixed N.

A little thought then leads to the following conclusion: The bath can be regarded (for pedagogical purposes) as an enormous, closed system, of fixed volume, fixed energy and fixed number of particles. Each system in our ensemble can be thought of as immersed in this bath (or in a separate but identical bath). The system's particles are prevented from escaping into the bath and the bath's particles are prevented from entering the system, e.g., by a membrane that is impermeable to particles. However, the membrane must have negligible surface tension so the system and the bath can buffet each other freely; and the membrane must conduct heat freely. The system's volume will then fluctuate stochastically as its boundary membrane is buffeted by fluctuating forces from particles hitting it; and the system's energy will fluctuate stochastically as heat stochastically flows back and forth through the membrane between bath and system. Correspondingly, we can think of the bath as a "heat and volume bath"; it freely exchanges heat and volume with the system, and exchanges nothing else.

In Chap. 3 we showed that an ensemble of systems in equilibrium with such a heat and volume bath (a Gibbs ensemble) is described by the distribution function $\rho = \text{const} \times e^{-\tilde{E}/kT} e^{-PV/kT}$. By analogy with Eq. (4.25) for the canonical ensemble's distribution function and (3.44) for the grand canonical ensemble's distribution function, it is reasonable to expect the normalization constant to be the exponential of the Gibbs potential $G(P, T, N)$; i.e.,

$$\rho = e^{G/kT} e^{-(\tilde{E}+PV)/kT} , \tag{4.41}$$

where T and P are the temperature and pressure of the bath, and $\tilde{E}$ and V are the energy and volume of a specific system in the Gibbs ensemble. We can verify this by computing the entropy $S = -k\overline{\ln \rho}$ using expression (4.41) for ρ, and getting $S = -(G - \bar{\tilde{E}} - P\bar{V})/T$, which agrees with the definition (4.37) of G when we identify the ensemble-averaged energy $\bar{\tilde{E}}$ with the "precise" energy $\tilde{E}$ and the ensemble-averaged volume $\bar{V}$ with the "precise" volume V.

While this Gibbs ensemble is conceptually interesting, it is not terribly useful for computing the fundamental potential $G(T, P, N)$, because evaluating the normalization sum

$$e^{-G/kT} = \sum_n e^{-(\tilde{E}_n + PV_n)/kT} \tag{4.42}$$

is much more difficult than computing the physical free energy $F(T, V, N)$ from the sum over states (4.26), or than computing the grand potential $\Omega(T, V, \tilde{\mu})$ from the sum over states (3.45). Correspondingly, in most statistical mechanics textbooks there is little or no discussion of the Gibbs ensemble.

Despite its lack of usefulness in computing G, the Gibbs ensemble plays an important conceptual role in a "minimum principle" for the Gibbs potential, which we shall now derive.

Consider an ensemble of systems, each of which is immersed in an identical heat and volume bath, and assume that the ensemble begins with some arbitrary distribution function, one that is not in equilibrium with the baths. As time passes each system will interact with its bath and will evolve in response to that interaction; and correspondingly the ensemble's distribution function ρ will evolve. At any moment of time the ensemble's systems will have some mean (ensemble-averaged) energy $\bar{\tilde{E}} \equiv \sum_n \rho_n \tilde{E}_n$ and volume $\bar{V} \equiv \sum_n \rho_n V_n$, and the ensemble will have some entropy $S = -k \sum_n \rho_n \ln \rho_n$. From these quantities (which are well defined even though the ensemble may be very far from statistical equilibrium), we can compute a Gibbs potential G for the ensemble. This G is defined by the analog of the equilibrium definition (4.41)

$$G \equiv \bar{\tilde{E}} + P\bar{V} - TS , \tag{4.43}$$

where P and T are the pressure and temperature of the identical baths with which the ensemble's systems are interacting. Now, as the evolution proceeds, the total entropy of the baths' ensemble plus the systems' ensemble will continually increase, until equilibrium is reached. Suppose that during a short stretch of evolution the systems' mean energy changes by $\Delta\bar{\tilde{E}}$, their mean volume changes by $\Delta\bar{V}$, and the entropy of the ensemble changes by ΔS. Then, by conservation of energy and volume, the baths' mean energy and volume must change by

$$\Delta\bar{\tilde{E}}_{\rm bath} = -\Delta\bar{\tilde{E}} , \quad \Delta\bar{V}_{\rm bath} = -\Delta\bar{V} . \tag{4.44}$$

Because the baths (by contrast with the systems) are in statistical equilibrium, we can apply to them the first law of thermodynamics for equilibrated systems

$$\Delta\bar{\tilde{E}}_{\rm bath} = -P\Delta\bar{V}_{\rm bath} + T\Delta S_{\rm bath} + \tilde{\mu}\Delta N_{\rm bath} . \tag{4.45}$$

Since $N_{\rm bath}$ is not changing (the systems cannot exchange particles with their baths) and since the changes of bath energy and volume are given by Eq. (4.44), Eq. (4.45) tells us that the baths' entropy changes by

$$\Delta S_{\rm bath} = \frac{-\Delta\bar{\tilde{E}} - P\Delta\bar{V}}{T} . \tag{4.46}$$

Correspondingly, the sum of the baths' entropy and the systems' entropy changes by the following amount, which cannot be negative:

$$\Delta S_{\rm bath} + \Delta S = \frac{-\Delta\bar{\tilde{E}} - P\Delta\bar{V} + T\Delta S}{T} \geq 0 . \tag{4.47}$$

Because the baths' pressure P and temperature T are not changing (the systems are so tiny compared to the baths that the energy and volume they exchange with the baths cannot have any significant effect on the baths' intensive variables), the numerator of expression (4.47) is equal to the evolutionary change in the ensemble's Gibbs potential (4.43):

$$\Delta S_{\rm bath} + \Delta S = \frac{-\Delta G}{T} \geq \ 0 \ . \tag{4.48}$$

Thus, *the second law of thermodynamics for an ensemble of arbitrary systems in contact with identical heat and volume baths is equivalent to the law that* **the systems' Gibbs potential can never increase**. As the evolution proceeds and the entropy of baths plus systems continually increases, the Gibbs potential G will be driven smaller and smaller, until ultimately, when statistical equilibrium with the baths is reached, G will stop at its final, minimum value.

The ergodic hypothesis guarantees that this minimum principle applies not only to an ensemble of systems, but also to a single, individual system when that system is averaged over times long compared to its internal timescales $\tau_{\rm int}$ (but times that may be very short compared to the timescale for interaction with the heat and volume bath): The system's time-averaged energy $\bar{\tilde{E}}$ and volume $\bar{V}$, and its entropy S (as computed, e.g., by examining the temporal wandering of its state on timescales $\sim \tau_{\rm int}$), combine with the bath's temperature T and pressure P to give a Gibbs function $G = \bar{\tilde{E}} + P\bar{V} - TS$. This G evolves on times long compared to the averaging time used to define it; and that evolution must be one of continually decreasing G. Ultimately, when the system reaches equilibrium with the bath, G achieves its minimum value.

At this point we might ask about the other thermodynamic potentials. Not surprisingly, associated with each of them there is an extremum principle analogous to "minimum G": (*i*) For the energy potential $\tilde{E}(V, S, N)$, one focuses on closed systems and switches to $S(V, \tilde{E}, N)$; and the extremum principle is then the standard second law of thermodynamics: An ensemble of closed systems of fixed $\tilde{E}$, V, N must evolve always toward increasing entropy S; and when it ultimately reaches equilibrium, the ensemble will be microcanonical and will have maximum entropy. (*ii*) For the physical free energy $F(V, T, N)$ one can derive, in a manner perfectly analogous to the Gibbs derivation, the following minimum principle: For an ensemble of systems interacting with a heat bath the physical free energy F will always decrease, ultimately reaching a minimum when the ensemble reaches its final, equilibrium, canonical distribution. (*iii*) The grand-potential $\Omega(V, T, \tilde{\mu})$ (Sec. 3.7) satisfies the analogous minimum principle: For an ensemble of systems interacting with a heat and particle bath the grand potential Ω will always decrease, ultimately reaching a minimum when the ensemble reaches its final, equilibrium, grand-canonical distribution. (*iv*) For the enthalpy $H(P, S, N)$ (Ex. 3.2) the analogous minimum principle should be obvious: For an ensemble of systems interacting with a volume bath the enthalpy H will always decrease, ultimately reaching a minimum when the ensemble reaches its final equilibrium distribution.

4.4.1 Phase Transitions

The minimum principle for the Gibbs potential G is a powerful tool in understanding *phase transitions*: "Phase" in the phrase "phase transitions" refers to a specific pattern into which the atoms or molecules of a substance organize themselves. For the substance H_2O there are

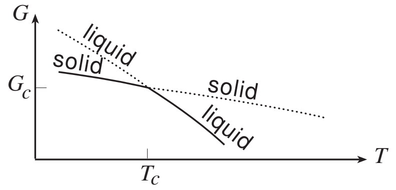

Fig. 4.2: The Gibbs potential $G(T, P, N)$ for H_2O as a function of temperature T with fixed P and N, near the freezing point 273K. The solid curves correspond to the actual path traversed by the H_2O if the phase transition is allowed to go. The dotted curves correspond to superheated solid ice and supercooled liquid water that are unstable against the phase transition because their Gibbs functions are higher than those of the other phase. Note that G tends to decrease with increasing temperature. This is caused by the $-TS$ term in $G = E + PV - TS$.

three familiar phases: water vapor, liquid water, and solid ice. Over one range of pressure P and temperature T, the H_2O molecules prefer to organize themselves into the vapor phase; over another, the liquid phase; and over another, the solid ice phase. It is the Gibbs potential that governs their preference.

To understand this role of the Gibbs potential, consider a cup of water in a refrigerator (and because the water molecules are highly norelativistic, adopt the nonrelativistic viewpoint with the molecules' rest masses removed from their energy E and chemical potential μ_{H_2O} and also from their Gibbs potential). The refrigerator's air forms a heat and volume bath for the water in the cup (the system). There is no membrane between the air and the water, but none is needed. Gravity, together with the density difference between water and air, serves to keep the water molecules in the cup and the air above the water's surface. Allow the water to reach thermal and pressure equilibrium with the refrigerator's air; then turn down the refrigerator's temperature slightly and wait for the water to reach equilibrium again; and then repeat the process. Pretend that you are clever enough to compute from first-principles the Gibbs potential G for the H_2O at each step of the cooling, using two alternative assumptions: that the H_2O molecules organize themselves into the liquid water phase; and that they organize themselves into the solid ice phase. Your calculations will produce curves for G as a function of temperature T at fixed (atmospheric) pressure that are shown in Fig. 4.2. At temperatures $T > 273$K the liquid phase has the lower Gibbs potential G; and at $T < 273$K the solid phase has the lower G. Correspondingly, when the cup's temperature sinks slightly below 273K, the H_2O molecules have a statistical preference for reorganizing themselves into the solid phase. The water freezes, forming ice.

It is a familiar fact that ice floats on water, i.e. ice is less dense than water, even when they are both precisely at the phase-transition temperature of 273K. Correspondingly, when our sample of water freezes, its volume increases discontinuously by some amount ΔV; i.e., when viewed as a function of the Gibbs potential G, the volume V of the statistically preferred phase is discontinous at the phase-transition point; see Fig. 4.3 (a). It is also a familiar fact that when water freezes, it releases heat into its surroundings. This is why the freezing requires a moderately long time: the solidifying water can remain at or below its freezing point and continue to solidify only if the surroundings carry away the released heat, and the surroundings typically cannot carry it away quickly. The heat ΔQ released

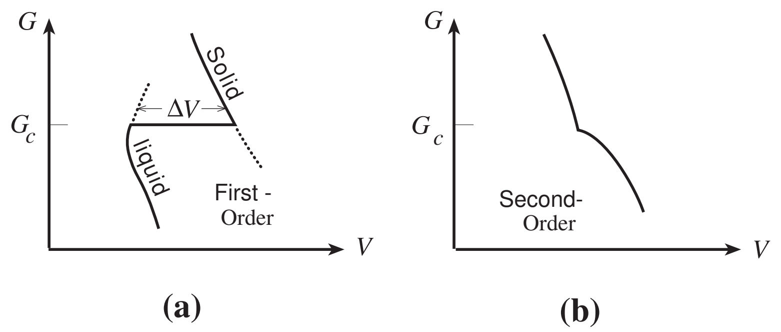

Fig. 4.3: The changes of volume (plotted rightward) with increasing Gibbs function (plotted upward) at fixed P and N for a first-order phase transition [diagram (a)] and a second-order phase transition [diagram (b)]. G_c is the critical value of the Gibbs potential at which the transition occurs.

during the freezing (the *latent heat*) and the volume change ΔV are related to each other in a simple way; see Ex. 4.3.

Phase transitions with finite volume jumps $\Delta V \neq 0$ and finite latent heat $\Delta Q \neq 0$ are called *first-order*. Less familiar, but also important, are *second-order phase transitions*. In such transitions the volumes V of the two phases are the same at the transition point, but their rates of change with decreasing G are different (and this is so whether one holds P fixed as G decreases or holds T fixed or holds some combination of P and T fixed); see Fig. 4.3 (b).

Crystals provide examples of both first-order and second-order phase transition. A crystal can be characterized as a 3-dimensional repetition of a "unit cell", in which ions are distributed in some fixed way. For example, Fig. 4.4 shows the unit cell for a $BaTiO_3$ crystal at relatively high temperatures. This unit cell has a cubic symmetry. The full crystal can be regarded as made up of such cells stacked side by side and one upon another. A first-order phase transition occurs when, with decreasing temperature, the Gibbs potential G of some other ionic arrangement, with a *distinctly different* unit cell, drops below the G of the original arrangement. Then the crystal can spontaneously rearrange itself, converting from the old unit cell to the new one with some accompanying release of heat and some discontinuous change in volume.

$BaTiO_3$ does not behave in this way. Rather, as the temperature falls a bit below a critical value, all the Titanium and Oxygen ions get displaced a bit in their unit cells parallel to one of the original crystal axes; see Fig. 4.4 (b). If the temperature is only a tiny bit below critical, they are displaced by only a tiny amount. When the temperature falls further, their displacements increase. If the temperature is raised back up above critical, the ions return to the standard, rigidly fixed positions shown in Fig. 4.4 (a). The result is a discontinuity, at the critical temperature, in the rate of change of volume dV/dG [Fig. 4.2 (b)], but no discontinuous jump of volume and no latent heat.

This $BaTiO_3$ example illustrates a frequent feature of phase transitions: When the transition occurs, i.e., when the titanium and oxygen atoms start to move, the cubic symmetry gets broken. The crystal switches, discontinuously, to a "lower" type of symmetry, a "tetragonal" one. Such symmetry breaking is a common occurence in phase transitions.

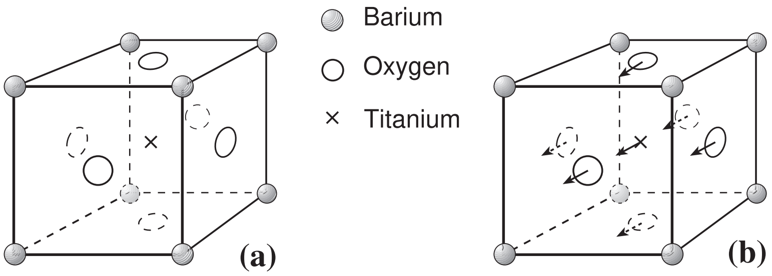

Fig. 4.4: (a) The unit cell for a $\mathrm{BaTiO_3}$ crystal at relatively high temperatures. (b) The displacements of the titanium and oxygen ions relative to the corners of the unit cell, that occur in this crystal with falling temperature when it undergoes its second-order phase transition. The magnitudes of the displacements are proportional to the amount $T_c - T$ by which the temperature T drops below the critical temperature T_c, for small $T_c - T$.

4.4.2 Chemical Reactions

A second important application of the Gibbs potential is to the study of *chemical reactions*. Under the term "chemical reactions" we include any change in the constituent particles of the material being studied, including the joining of atoms to make molecules, the liberation of electrons from atoms in an ionization process, the joining of two atomic nuclei to make a third kind of nucleus, the decay of a free neutron to produce an electron and a proton, ... In other words, the "chemical" of chemical reactions encompasses the reactions studied by nuclear physicists and elementary particle physicists as well as those studied by chemists. The Gibbs representation is the appropriate one for discussing chemical reactions, because such reactions generally occur in an environment ("bath") of fixed temperature and pressure.

As a specific example, consider in the earth's atmosphere the breakup of two molecules of water vapor to form two hydrogen molecules and one oxygen molecule, $2\mathrm{H_2O} \to 2\mathrm{H_2} + \mathrm{O_2}$. The inverse reaction $2\mathrm{H_2} + \mathrm{O_2} \to 2\mathrm{H_2O}$ also occurs in the atmosphere, and it is conventional to write down the two reactions simultaneously in the form

$$2\mathrm{H_2O} \ \leftrightarrow 2\mathrm{H_2} + \mathrm{O_2}\ . \tag{4.49}$$

A chosen (but arbitrary) portion of the atmosphere, with idealized walls to keep all its molecules in, can be regarded as a "system". (The walls are unimportant in practice, but are pedagogically useful.) The kinetic motions of this system's molecules reach and maintain statistical equilibrium, at fixed temperature T and pressure P, far more rapidly than chemical reactions can occur. Accordingly, if we view this system on timescales short compared to that $\tau_{\rm react}$ for the reactions (4.49) but long compared to the kinetic relaxation time, then we can regard the system as in statistical equilibrium with fixed numbers of water molecules $N_{\mathrm{H_2O}}$, hydrogen molecules $N_{\mathrm{H_2}}$, oxygen molecules $N_{\mathrm{O_2}}$, and nitrogen molecules $N_{\mathrm{N_2}}$, and with a Gibbs potential whose value is given by the Euler relation (4.40) generalized to a system with several conserved species: $G = \sum_I \tilde\mu_I N_I$, i.e.

$$G = \tilde\mu_{\mathrm{H_2O}} N_{\mathrm{H_2O}} + \tilde\mu_{\mathrm{H_2}} N_{\mathrm{H_2}} + \tilde\mu_{\mathrm{O_2}} N_{\mathrm{O_2}} + \tilde\mu_{\mathrm{N_2}} N_{\mathrm{N_2}}\ . \tag{4.50}$$

(Here, even though the Earth's atmosphere is highly nonrelativistic, we include rest masses in the chemical potentials and in the Gibbs potential; the reason will become evident at the end of this section.) When one views the sample over a longer timescale, $\Delta t \sim \tau_{\rm react}$, one discovers that these molecules are not inviolate; they can change into one another via the reactions (4.49), thereby changing the value of the Gibbs potential (4.50). The changes of G are more readily computed from the Gibbs representation of the first law $dG = VdP - SdT + \sum_I \tilde\mu_I dN_I$ than from the Euler relation (4.50); taking account of the constancy of P and T and the fact that the reactions entail transforming two water molecules into two hydrogen molecules and one oxygen molecule (or conversely) so

$$dN_{\rm H_2} = -dN_{\rm H_2O} \ , \qquad dN_{\rm O_2} = -\frac{1}{2}dN_{\rm H_2O} \ , \tag{4.51}$$

we obtain

$$dG = (2\tilde\mu_{\rm H_2O} - 2\tilde\mu_{\rm H_2} - \tilde\mu_{\rm O_2})\frac{1}{2}dN_{\rm H_2O} \ . \tag{4.52}$$

The reactions (4.49) proceed in both directions, but statistically there is a preference for one direction over the other. The preferred direction, of course, is the one that reduces the Gibbs potential. Thus, if $2\tilde\mu_{\rm H_2O}$ is larger than $2\tilde\mu_{\rm H_2}+\tilde\mu_{\rm O_2}$, then water molecules preferentially break up to form hydrogen plus oxygen; but if $2\tilde\mu_{\rm H_2O}$ is less than $2\tilde\mu_{\rm H_2}+\tilde\mu_{\rm O_2}$, then oxygen and hydrogen preferentially combine to form water. As the reactions proceed, the changing N's produce changes in the chemical potentials $\tilde\mu_I$. [Recall from Eq. (3.57) the intimate connection

$$N_I = \frac{(2\pi m_I kT)^{3/2}}{h^3} e^{\mu_I/kT} V \tag{4.53}$$

between $\mu_I = \tilde\mu_I - m_I c^2$ and N_I for a gas in the nonrelativistic regime]. These changes in the N_I's and $\tilde\mu_I$'s lead ultimately to a macrostate (thermodynamic state) of minimum Gibbs potential G—a state in which the reactions (4.49) can no longer reduce G. In this final, equilibrium macrostate the dG of expression (4.52) must be zero; and correspondingly, the combination of chemical potentials appearing in it must vanish:

$$2\tilde\mu_{\rm H_2O} = 2\tilde\mu_{\rm H_2} + \tilde\mu_{\rm O_2} \ . \tag{4.54}$$

The above analysis shows that the "driving force" for the chemical reactions is the combination of chemical potentials in the dG of Eq. (4.52). Notice that this combination has coefficients in front of the $\tilde\mu_I$'s that are identical to the coefficients in the reactions (4.49) themselves; and the equilibrium relation (4.54) also has the same coefficients as the reactions (4.52). It is easy to convince oneself that this is true in general:

Consider any chemical reaction. Write the reaction in the form

$$\sum_j \nu_j^L A_j^L \ \leftrightarrow \ \sum_j \nu_j^R A_j^R \ . \tag{4.55}$$

Here the superscripts L and R denote the "left" and "right" sides of the reaction, the A_j's are the names of the species of particle or atomic nucleus or atom or molecule involved in the reaction, and the ν_j's are the number of such particles (or nuclei or atoms or molecules) involved. Suppose that this reaction is occuring in an environment of fixed temperature and

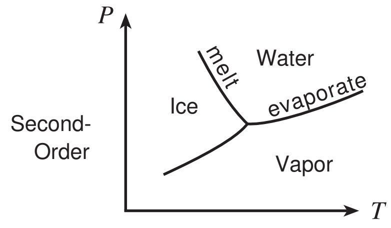

Fig. 4.5: Phase diagram for H_2O.

pressure. Then to determine the direction in which the reaction preferentially goes, examine the chemical-potential sums for the two sides of the reaction,

$$\sum_j \nu_j^L \tilde{\mu}_j^L \,, \quad \sum_j \nu_j^R \tilde{\mu}_j^R \,. \tag{4.56}$$

The reaction will proceed from the side with the larger chemical-potential sum to the side with the smaller; and ultimately the reaction will bring the two sides into equality. That final equality is the state of statistical equilibrium. Exercises 4.4 and 4.5 illustrate this analysis of chemical equilibrium.

When dealing with chemical reactions between highly nonrelativistic molecules and atoms—e.g. water formation and destruction in the Earth's atmosphere—one might wish to omit rest masses from the chemical potentials. If one does so, and if one wishes to preserve the criterion that the reaction goes in the direction of decreasing $dG = (2\mu_{\rm H_2O} - 2\mu_{\rm H_2} - \mu_{\rm O_2})\frac{1}{2}dN_{\rm H_2O}$ [Eq. (4.52) with tildes removed], then one must choose as the "rest masses" to be subtracted values that do not include chemical binding energies; i.e. one must define the rest masses in such a way that $2m_{\rm H_2O} = 2m_{\rm H_2} + m_{\rm O_2}$. One can avoid this delicacy by simply using the relativistic chemical potentials. The derivation of the Saha equation (Exercise 4.5) is an example.

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EXERCISES

Exercise 4.4 *Example: Latent Heat and the Clausius-Clapeyron Equation*

(a) Consider H_2O in contact with a heat and volume bath of temperature T and pressure P. For certain values of T and P the H_2O will be water; for others, ice; for others, water vapor—and for certain values it may be a two- or three-phase mixture of water, ice, and/or vapor. Show, using the Gibbs potential, that *if two phases a and b are present and in statistical equilibrium with each other, then their chemical potentials must be equal*: $\mu_a = \mu_b$. Explain why, for any phase a, μ_a is a unique function of T and P. Explain why the condition $\mu_a = \mu_b$ for two phases to be present implies that the two-phase regions of the $T - P$ plane are lines and the three-phase regions are points; see Fig.4.5. The three-phase region is called the "triple point". The volume V of the two- or three-phase system will vary depending on how much of each phase is present, since the density of each phase (at fixed T and P) is different.

(b) Show that the slope of the ice-water interface curve in Fig. 4.5 (the "melting curve") is given by the "Clausius-Clapeyron equation"

$$\left(\frac{dP}{dT}\right)_{\rm melt} = \frac{\Delta q_{\rm melt}}{T}\left(\frac{\rho_{\rm ice}\,\rho_{\rm water}}{\rho_{\rm ice}-\rho_{\rm water}}\right) , \tag{4.57}$$

where ρ is density (mass per unit volume) and $\Delta q_{\rm melt}$ is the latent heat per unit mass for melting (or freezing), i.e., the amount of heat required to melt a unit mass of ice, or the amount released when a unit mass of water freezes. Notice that, because ice is less dense than water, the slope of the melting curve is negative. [*Hint*: compute dP/dT by differentiating $\mu_a = \mu_b$, and then use the thermodynamic properties of $G_a = \mu_a N_a$ and $G_b = \mu_b N_b$.]

(c) Suppose that a small amount of water is put into a closed container of much larger volume than the water. Initially there is vacuum above the water's surface, but as time passes some of the H_2O evaporates to give vapor-water equilibrium. The vapor pressure will vary with temperature in accord with the Clausius-Clapeyron equation

$$\frac{dP_{\rm vapor}}{dT} = \frac{\Delta q_{\rm evaporate}}{T}\left(\frac{\rho_{\rm water}\,\rho_{\rm vapor}}{\rho_{\rm water}-\rho_{\rm vapor}}\right) . \tag{4.58}$$

Now, suppose that a foreign gas (not water vapor) is slowly injected into the container. Assume that this gas does not dissolve in the liquid water. Show that, as the pressure $P_{\rm gas}$ of the foreign gas gradually increases, it does *not* squeeze water vapor into the water, but rather it induces more water to vaporize:

$$\left(\frac{dP_{\rm vapor}}{dP_{\rm total}}\right)_{T\ {\rm fixed}} = \frac{\rho_{\rm vapor}}{\rho_{\rm water}} > 0 , \tag{4.59}$$

where $P_{\rm total} = P_{\rm vapor} + P_{\rm gas}$.

Exercise 4.5 *Example: Electron-Positron Equilibrium at "Low" Temperatures*

Consider hydrogen gas in statistical equilibrium at a temperature $T \ll m_e c^2/k \simeq 6 \times 10^9\,{\rm K}$. Electrons at the high-energy end of the Boltzmann energy distribution can produce electron-positron pairs by scattering off protons

$$e^- + p \rightarrow e^- + p + e^- + e^+ . \tag{4.60}$$

[There are many other ways of producing pairs, but in analyzing statistical equilibrium we get all the information we need (a relation among the chemical potentials) by considering just one way.]

(a) In statistical equilibrium the above reaction and its inverse must proceed at the same rate, on average. What does this imply about the relative magnitudes of the electron and positron chemical potentials $\tilde\mu_-$ and $\tilde\mu_+$ (where the rest mass-energies are included in the $\tilde\mu$'s)?

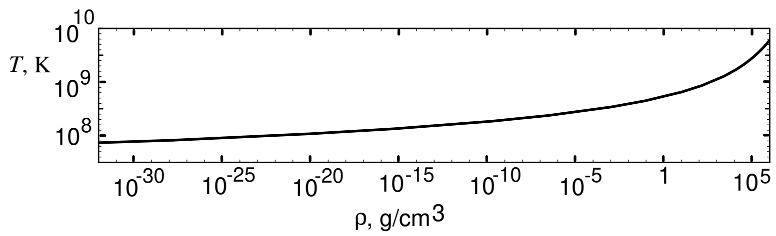

Fig. 4.6: The temperature T_p at which electron-positron pairs form in a dilute hydrogen plasma, plotted as a function of density ρ. This is the correct upper limit (upper dashed curve in Fig. 2.5) on the region where the plasma can be considered fully nonrelativistic. Above this curve, although kT may be $\ll m_e c^2 \simeq 6 \times 10^9$ K, a proliferation of electron-positron pairs radically changes the properties of the plasma.

(b) Although these reactions require an e^- that is relativistic in energy, almost all the electrons and positrons will have kinetic energies of magnitude $\tilde{E} - mc^2 \sim kT \ll mc^2$, and thus will have $\tilde{E} \simeq mc^2 + \mathbf{p}^2/2m$. What are the densities in phase space $\mathcal{N}_\pm = dN_\pm/d^3x d^3p$ for positrons and electrons in terms of $\mathbf{p}$, $\tilde{\mu}_\pm$, and T? Explain why for a hydrogen gas we must have $\tilde{\mu}_- > 0$ and $\tilde{\mu}_+ < 0$.

(c) Assume that the gas is very dilute so that $\bar{\eta} \ll 1$ for both electrons and positrons. Then integrate over momenta to obtain the following formula for the number densities in physical space of electrons and positrons

$$n_\pm = \frac{2}{h^3}(2\pi mkT)^{3/2} \exp\left(\frac{\tilde{\mu}_\pm - mc^2}{kT}\right) . \tag{4.61}$$

In cgs units, what does the dilute-gas assumption $\bar{\eta} \ll 1$ correspond to in terms of $n_\pm$? What region of hydrogen mass density ρ and temperature T is the dilute-gas region?

(d) Let n be the number density of protons. Then by charge neutrality $n = n_- - n_+$ will also be the number density of "ionization electrons" (i.e., of electrons that have been ionized off of hydrogen). Show that the ratio of positrons (and hence of pairs) to ionization electrons is given by

$$\frac{n_+}{n} = \frac{1}{2y[y + (1+y^2)^{\frac{1}{2}}]} \tag{4.62}$$

where

$$y \equiv \frac{1}{4} n\lambda^3 e^{mc^2/kT} , \quad \text{and} \quad \lambda \equiv \frac{h}{\sqrt{2\pi mkT}} \tag{4.63}$$

is the thermal deBroglie wavelength of the electrons. Fig. 4.6 shows the temperature T_p at which, according to this formula, $n_+ = n$ (and $y = 0.354$), as a function of mass density $\rho \simeq m_{\rm proton} n$. This T_p can be thought of as the "temperature at which pairs form" in a dilute plasma. Somewhat below T_p there are hardly any pairs; somewhat above, the pairs are profuse.

(e) Note that at low densities pairs form at temperatures $T \sim 10^8\,$K $\simeq 0.02 m_e c^2/k$. Explain in terms of "available phase space" why the formation temperature is so low.

Exercise 4.6 *Example: Saha Equation for Ionization Equilibrium*

Consider an optically thick hydrogen gas in statistical equilibrium at temperature T. (By "optically thick" is meant that photons can travel only a distance small compared to the size of the system before being absorbed, so they are confined by the hydrogen and kept in statistical equilibrium with it.) Among the reactions that are in statistical equilibrium are $\mathrm{H} + \gamma \leftrightarrow e + p$ [ionization and recombination of Hydrogen H, with the H in its ground state] and $e + p \leftrightarrow e + p + \gamma$ [emission and absorption of photons by "bremsstrahlung", i.e., by the coulomb-force-induced acceleration of electrons as they fly past protons]. Let $\tilde{\mu}_\gamma$, $\tilde{\mu}_\mathrm{H}$, $\tilde{\mu}_e$, and $\tilde{\mu}_p$ be the chemical potentials *including rest mass-energies*; let m_H, m_e, m_p be the rest masses; denote by $I \equiv$ (13.6 electron volts) the ionization energy of hydrogen, so that $m_\mathrm{H}c^2 = m_e c^2 + m_p c^2 - I$; denote $\mu_j \equiv \tilde{\mu}_j - m_j c^2$; and assume that $T \ll m_e c^2/k \simeq 6 \times 10^9\,\mathrm{K}$, and that the density is low enough that the electrons, protons, and Hydrogen atoms can be regarded as nondegenerate (i.e., as distinguishable, classical particles).

(a) What relationships hold between the chemical potentials $\tilde{\mu}_\gamma$, $\tilde{\mu}_\mathrm{H}$, $\tilde{\mu}_e$, and $\tilde{\mu}_p$?

(b) What are the number densities n_H, n_e, and n_p expressed in terms of T and $\tilde{\mu}_\mathrm{H}$, $\tilde{\mu}_e$, $\tilde{\mu}_p$—taking account of the fact that the electron and proton both have spin $\frac{1}{2}$, and including in H all possible electron and nuclear spin states?

(c) Derive the Saha equation for ionization equilibrium

$$\frac{n_e n_p}{n_\mathrm{H}} = \frac{(2\pi m_e k T)^{3/2}}{h^3} e^{-I/kT} . \tag{4.64}$$

This equation is widely used in astrophysics and elsewhere.

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4.5 Fluctuations of Systems in Statistical Equilibrium

As we saw in Chap. 3, statistical mechanics is built on a distribution function ρ, which is equal to the probability of finding a chosen system in a quantum state at some chosen location in the system's phase space. For systems in statistical equilibrium this probability is given by the microcanonical or canonical or grand canonical or Gibbs or ... distribution, depending on the nature of the interaction of the system with its surroundings. Classical thermodynamics, as studied in this chapter, makes use of only a tiny portion of the information in this probability distribution: the mean values of a few macroscopic parameters (energy, volume, pressure, ...) and the entropy. Also contained in the distribution function, but ignored by classical thermodynamics, is detailed information about fluctuations of a system away from its mean values.

We studied a simple example of this in Ex. 3.5: fluctuations in the number of particles in some chosen volume V of a dilute, nonrelativistic gas. The chosen volume, regarded as

Bath	Fundamental Potential	Total Entropy $S + S_b$	Second Law	Fluctuational Probability
None	$S(\rho)$ with $\tilde{E}$ const	$S+$ const	$dS \geq 0$	$\propto e^{S/k}$
V & $\tilde{E}$	$S(P;\rho)$	$S+$ const	$dS \geq 0$	$\propto e^{S/k}$
$d\tilde{E} = -PdV$	with $H = \tilde{E} + PV$ const			
Heat	$F(T;\rho) = \bar{\tilde{E}} - TS$	$-F/T +$ const	$dF \leq 0$	$\propto e^{-F/kT}$
Heat & Volume	$G(T,P;\rho) = \bar{\tilde{E}} + P\bar{V} - TS$	$-G/T+$ const	$dG \leq 0$	$\propto e^{-T/kT}$
Heat & Particle	$\Omega(T,\tilde{\mu},\rho) = \bar{\tilde{E}} - \tilde{\mu}\bar{N} - TS$	$-\Omega/T +$ const	$d\Omega \leq 0$	$\propto e^{-\Omega/kT}$

Table 4.2: Deviations from Statistical Equilibrium.

a system, was described by the grand canonical ensemble because it could freely exchange heat and particles with its surroundings (i.e. it had imaginary walls); and from the grand-canonical probability distribution we found that the number of particles in the volume V was described by a Poisson distribution

$$p_N = e^{-\bar{N}} \frac{\bar{N}^N}{N!} \ . \tag{4.65}$$

The mean $\bar{N}$ of this distribution is equal to the number predicted by thermodynamics [Eq. (3.57)], and the root-mean-square deviation from the mean, σ_N, is equal to $\sqrt{\bar{N}}$.

When $\bar{N}$ is huge, as it is for all the systems studied in this chapter, the Poisson distribution (4.65) is extremely well approximated by a Gaussian. To convert to that Gaussian, take the logarithm of Eq. (4.65), use Stirling's formula $N! \simeq \sqrt{2\pi N}(N/e)^N$, and expand in powers of $N - \bar{N}$ keeping only terms up through quadratic order. The result, after exponentiating, is

$$p_N = \frac{1}{\sqrt{2\pi\bar{N}}} \exp\left[-\frac{(N-\bar{N})^2}{2\bar{N}}\right] \ . \tag{4.66}$$

In the next chapter (Sec. 5.2) we shall learn that the probability distribution (4.65) *had to be* very nearly Gaussian: Any probability distribution that is produced by a superposition of the influences of many independent, random variables (in this case the independent, random motions of many gas particles) must be Gaussian to very high precision.

In this section we shall sketch the general theory of fluctuations of large systems in statistical equilibrium—a theory of which the above example is a special case. We begin by confining attention to a second specific case, and we then shall generalize.

Our second specific case is a microcanonical ensemble of boxes, each with volume V and each containing precisely N identical, dilute ($\bar{\eta} \ll 1$), nonrelativistic gas particles and containing energy (excluding rest mass) between E and $E + \delta E$, where $\delta E \ll E$. (Remember the "kludge" that was necessary in Ex. 3.6). Focus attention on a set of quantities y_j which characterize these boxes of gas and which are *not* fixed by the set E, V, N. For example, y_1 might be the total number n of particles in the right half of a box, and y_2 might be the total energy ε in the right half. We seek a joint probability distribution for these y_j's.

If the y_j's can take on only discrete values (e.g., $y_1 = n$), then the total number of quantum states that correspond to specific values of the y_j's is related to the entropy S by the standard microcanonical relation

$$N_{\text{states}}(y_j;E,V,N)=\exp[S(y_j;E,V,N)/k]\ ; \tag{4.67}$$

and correspondingly, since all states are equally probable in the microcanonical ensemble, the probability of finding a system of the ensemble to have the specific values y_j is

$$p(y_j;E,V,N)=\frac{N_{\text{states}}(y_j;E,V,N)}{\sum_{y_j}N_{\text{states}}(y_j;E,V,N)}=\text{const}\times\exp\Big[\frac{S(y_j;E,V,N)}{k}\Big]\ . \tag{4.68}$$

By a similar, but slightly more delicate argument one can show that, if the y_j take on a continuous range of values (e.g., $y_2=\varepsilon$) then the probability per unit y_j interval of finding a system to have specific values is

$$\frac{dp(y_j;E,V,N)}{dy_1dy_2\ldots dy_r}=\text{const}\times\exp\Big[\frac{S(y_j;E,V,N)}{k}\Big]\ . \tag{4.69}$$

In expressions (4.68), (4.69) the entropies $S(y_j;E,V,N)$ are to be computed via statistical mechanics (or, when possible, via thermodynamics) not for the original ensemble of boxes in which the y_j were allowed to vary, but rather for an ensemble in which the y_j's are fixed at the chosen values.

In our example where there are just two y_j's [$y_1\equiv n=$(number of particles in right half of box) and $y_2\equiv\varepsilon=$(amount of energy in right half of box)], we can infer $S(n,\varepsilon;N,E,V)$ from Eq. (3.60) as applied to the two halves of the box and then added:

$$\begin{aligned}S(n,\varepsilon;N,E,V) &= kn\ln\Big[\Big(\frac{4\pi m}{3h^2}\Big)^{3/2}e^{5/2}\frac{V}{2}\frac{\varepsilon^{3/2}}{n^{5/2}}\Big] && (4.70)\\ &+\ k(N-n)\ln\Big[\Big(\frac{4\pi m}{3h^2}\Big)^{3/2}e^{5/2}\frac{V}{2}\frac{(E-\varepsilon)^{3/2}}{(N-n)^{5/2}}\Big]\ . && (4.71)\end{aligned}$$

The probability distributions (4.68), (4.69), though "exact," are not terribly instructive. To get better insight we expand the S of Eq. (4.68), (4.69) in powers of the deviation of y_j from its mean. Denote by $\bar{y}_j$ the value of y_j that maximizes the entropy (this will turn out also to be the mean of the distribution). Then for small $|y_j-\bar{y}_j|$, Eq. (4.69) becomes

$$\frac{dp(y_j;E,V,N)}{dy_1dy_2\ldots dy_r}=\text{const}\ \times\ \exp\Big[\frac{1}{2k}\Big(\frac{\partial^2S}{\partial y_j\partial y_k}\Big)(y_j-\bar{y}_j)(y_k-\bar{y}_k)\Big] \tag{4.72}$$

and similarly for Eq. (4.68). Here the second partial derivative of the entropy is to be evaluated at the maximum-entropy location, where $y_j=\bar{y}_j$ for all j. Expression (4.72) is a (multidimensional) Gaussian probability distribution, as expected. Moreover, for this distribution the values $\bar{y}_j$ that were defined to give maximal entropy (i.e., the "most probable" values) are also the means.

For our example, it is straightforward to compute from expression (4.71) the values $\bar{\varepsilon}$ and $\bar{n}$ of ε and n that maximize the entropy:

$$\bar{\varepsilon}=\frac{E}{2},\qquad \bar{n}=\frac{N}{2}. \tag{4.73}$$

Thus, in agreement with intuition, the mean values of the energy and particle number in the right half box are equal to half of the box's total energy and particle number. It is also straightforward to compute from expression (4.71) the second partial derivatives of the entropy with respect to ε and n, evaluate them at $\varepsilon = \bar{\varepsilon}$ and $n = \bar{n}$, and plug them into the probability distribution (4.72). The result is

$$\frac{dp_n}{d\varepsilon} = \text{const} \times \exp\left(\frac{-(n - N/2)^2}{2(N/4)} + \frac{-[(\varepsilon - E/2) - (E/N)(n - N/2)]^2}{2(N/6)(E/N)^2}\right) . \tag{4.74}$$

[There is no dn in the denominator of the left side because n is a discrete variable; cf Eqs. (4.68) and (4.69).] This Gaussian distribution has the following interpretation: (i) there is a correlation between the energy ε and the particle number n in the right half of the box, as one might have expected: If there is an excess of particles in the right half, then we must expect an excess of energy there as well. (ii) The quantity that is not correlated with n is $\varepsilon - (E/N)n$, as one might have expected. (iii) For fixed n, $dp_n/d\varepsilon$ is Gaussian with mean $\bar{\varepsilon} = E/2 + (E/N)(n - N/2)$ and with variance $\sigma_\varepsilon = (E/N)\sqrt{N/6}$. ($iv$) After integrating over ε we obtain

$$p_n = \text{const} \times \exp\left[\frac{-(n - N/2)^2}{2N/4}\right] . \tag{4.75}$$

This is Gaussian with mean $\bar{n} = N/2$ and variance $\sigma_n = \sqrt{N/4}$. By contrast, if the right half of the box had been in equilibrium with a bath far larger than itself, n would have had a variance equal to the square root of its mean, $\sigma_n = \sqrt{N/2}$. The fact that the "companion" of the right half has only the same size as the right half, rather than being far larger, has reduced the variance of the number of particles in the right half from $\sqrt{N/2}$ to $\sqrt{N/4}$.

Notice that all the concrete probability distributions we have derived, Eqs. (4.65), (4.74), and (4.75) are exceedingly sharply peaked about their means: Their variances ("half-widths") divided by their means, i.e., the magnitude of their fractional fluctuations, are all of order $1/\sqrt{\bar{N}}$, where $\bar{N}$ is the mean number of particles in a system; and in realistic situations $\bar{N}$ is very large. (For example, $\bar{N}$ is of order 10^{29} for a cubic meter of gas inside the sun, and thus the fractional fluctuations of thermodynamic quantities are of order 10^{-14}.) It is this extremely sharp peaking that makes classical thermodynamics insensitive to the choice of type of equilibrium ensemble—i.e., sensitive only to means and not to fluctuations about the means.

How does the above, microcanonical, analysis generalize to ensembles of systems in equilibrium with various kinds of baths? Consider, as a specific example, a Gibbs ensemble of identical systems in equilibrium with a set of identical heat and volume baths. The systems all contain the same number of particles N, but they have a spread of energies $\tilde{E}$ and volumes V, as well as a spread of some set of variables y_i that interest us. (For example, one of the y_i's might be the energy in the right half of a system.) For ease of notation and presentation we shall assume that $\tilde{E}$ and V are completely determined by the full set of chosen y_i's together with N. Suppose that we pick a system at random from our equilibrium ensemble. We would like to know the probability $p(y_i)$ that it has a specific set of values of its variables y_i (or, for those variables that can vary continuously, the probability it has the specific values y_i in a chosen, fixed, tiny range dy_i). Because each system plus bath is closed, the systems plus their baths are microcanonically distributed. Therefore, the probability $p(y_i)$ is proportional to the total number of quantum states that a system plus its bath can have when the system is constrained to the values y_i in dy_i, $p(y_i) \propto N_{\rm states}$; the total number of quantum states in turn is related to the entropy of system plus bath by $N_{\rm states} = e^{(S_{\rm system}+S_{\rm bath})/k}$; and the entropy of system plus bath in turn is related to the Gibbs potential of the system by

$$S_{\rm system} + S_{\rm bath} = -T_b G + \text{constant} \tag{4.76}$$

[Eq. (4.48)]. Thus,

$$p(y_i) = \text{const} \ \times \ e^{-G(y_i,N,T_b,P_b)/kT_b} \ . \tag{4.77}$$

Here the Gibbs potential is *not* that of the equilibrium Gibbs ensemble; rather, in accord with the derivation of Eq. (4.48), it is a potential constructed from the bath temperature (denoted T in (4.48) but here and below denoted T_b), the bath pressure P_b, the energy $\tilde{E}(y_i,N)$ of the system, the volume $V(y_i,N)$ of the system, and the entropy $S(y_i,N)$ of a microcanonical subensemble of systems that have the specified values of the y_i's, and the same value of N as all the systems in the original equilibrium ensemble:

$$G(y_i,N,T_b,P_b) = \tilde{E}(y_i,N) + P_b V(y_i,N) \ - \ T_b S(y_i,N) \ . \tag{4.78}$$

As a specific example of the probability distribution (4.77), consider a monatomic gas and examine its fluctuations of temperature and volume. More specifically, inside a huge bath of monatomic gas that is in statistical equilibrium pick out at random a small sample containing precisely N atoms (with $N >>> 1$). That sample (the system) will have, because of statistical fluctuations, a temperature T that differs slightly from T_b and a volume V that differs slightly from the equilibrium value $\bar{V}$ predicted by the Gibbs ensemble. We want to know the probability that it will have specific values of T and V in specific ranges dT and dV. The answer is given by Eq. (4.77) with $y_1 = T$ and $y_2 = V$. Expanding the G of that answer in powers of $V - \bar{V}$ and $T - T_b$, setting $p(y_i) = dp$ (a mere change of notation) and dividing by $dTdV$, we obtain

$$\frac{dp}{dTdV} = \text{const} \times \exp\Big[-\frac{1}{2kT_b}\Big(\frac{\partial^2 G}{\partial V^2}(V-\bar{V})^2 + \frac{\partial^2 G}{\partial T^2}(T-T_b)^2 \, + 2\frac{\partial^2 G}{\partial T \partial V}(V-\bar{V})(T-T_b)\Big)\Big] \ . \tag{4.79}$$

Here the Gibbs function to be differentiated is [cf the nonrelativistic version of Eq. (4.78)]

$$G = E(T,V,N) + P_b V \ - \ T_b S(T,V,N) \ , \tag{4.80}$$

with $E(T,V,N)$ and $S(T,V,N)$ being the energy and entropy of the system (gas cell with N particles) at its specified values of T, V, and N; and the derivatives are to be evaluated at $T = T_b$ and $V = \bar{V}$. The terms linear in $V - \bar{V}$ and $T - T_b$ in the expansion (4.79) have been omitted because (as we shall see) their coefficients $\partial G/\partial V$ and $\partial G/\partial T$ vanish when $V = \bar{V}$ and $T = T_b$.

By straightforwardly differentiating Eq. (4.80) once with respect to T and V (while holding N fixed) and invoking the first law of thermodynamics $dE = -PdV + TdS + \mu dN$, we obtain

$$\left(\frac{\partial G}{\partial T}\right)_{V,N} = (T-T_b)\left(\frac{\partial S}{\partial T}\right)_{V,N} \ , \quad \left(\frac{\partial G}{\partial V}\right)_{T,N} = (P_b - P) + (T-T_b)\left(\frac{\partial S}{\partial V}\right)_{T,N} \ . \tag{4.81}$$

These quantities vanish when $V = \bar{V}$ and $T = T_b$, as promised. Their vanishing, in fact, is guaranteed by the statistical equilibrium of the bath. The second derivatives of G, evaluated for $V = \bar{V}$ and $T = T_b$, are readily computed from expressions (4.81) to be

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{V,N} = \frac{C_V}{T_b}, \quad \left(\frac{\partial^2 G}{\partial V^2}\right)_{T,N} = \frac{1}{\kappa}, \quad \left(\frac{\partial^2 G}{\partial T \partial V}\right)_N = 0 \,, \tag{4.82}$$

where C_V is the gas sample's specific heat at fixed volume and κ is its compressibility at fixed temperature:

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_{V,N} , \quad \kappa \equiv -\left(\frac{\partial V}{\partial P}\right)_{T,N} . \tag{4.83}$$

Inserting these relations into expression (4.79) we obtain the final form of the probability distribution for temperature and volume fluctuations in the monatomic gas:

$$\frac{dp}{dTdV} = \text{const} \times \exp\left(-\frac{(V-\bar{V})^2}{2kT_b\kappa} - \frac{C_V(T-T_b)^2}{2kT_b^2}\right) . \tag{4.84}$$

Not surprisingly, this probability distribution is Gaussian. Notice that the root-mean-square fluctuations of the volume are $\sigma_V = \sqrt{kT_b\kappa}$, and those of the temperature are $\sigma_T = kT_b^2/C_V$. Since C_V and κ are proportional to the number of atoms, N, in the sample of gas, σ_T scales as $1/\sqrt{N}$, and σ_V scales as $\sqrt{N}$, as one might expect. Because there are no cross terms, $(V-\bar{V})(T-T_b)$, in the probability distribution (4.84), the volume and temperature fluctuations are uncorrelated.

It is straightforward to generalize the probability distribution (4.77) to other kinds of baths. In general, the quantity that replaces G in (4.77) is the fundamental potential for the chosen kind of bath: the physical free energy F in the case of a heat bath, the enthalpy H in the case of a volume bath, and the grand potential Ω in the case of a heat and particle bath.

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EXERCISES

Exercise 4.7 *Example: Fluctuations and Phase Transitions in a Van der Waals Gas*

A real monatomic gas exhibits attractive forces between its atoms (or molecules) when the atoms are moderately far apart, and repulsive forces when they are close together. These forces modify expression (4.15) for the gas's nonrelativistic energy E in terms of its volume V, entropy S, and number of atoms N. A simple analytic approximation to these modifications is given by the van der Waals equation

$$E(V,S,N) = N\frac{3h^2}{4\pi m}\left(\frac{V}{N} - b\right)^{-2/3} \exp\left(\frac{2}{3k}\frac{S}{N} - \frac{5}{3}\right) - \frac{aN^2}{V} . \tag{4.85}$$

Here b is the specific volume (volume per particle) at which the repulsion becomes so strong that this approximation idealizes it as infinite. The term $-aN^2/V$ is associated with the attractive force at moderate distances, and a characteristic temperature below which this attractive force is important is given by $T_o \equiv a/bk$.

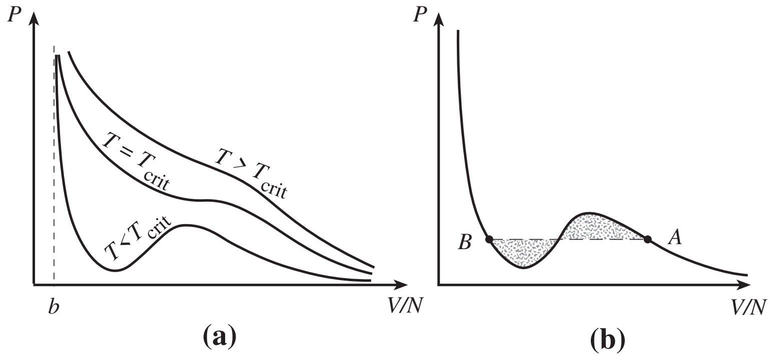

Fig. 4.7: (a) The van der Waals equation of state $P(N, V, T)$ plotted as pressure P versus specific volume V/N at fixed temperature T, for various values of the temperature T. (b) The route of a phase transition in the van der Waals gas. The transition is a discontinuous jump from point A to point B.

(a) Derive the equation of state $P = P(N, V, T)$ for this gas, and compare it with that of an ideal gas. Show that the equation of state has the form depicted in Fig. 4.7. What is the critical temperature $T_{\rm crit}$ below which the curve in Fig. 4.7 (a) has a local maximum and a local minimum?

(b) Where along the curves in Fig. 4.7(a) is the gas stable against volume fluctuations, and where is it unstable? For what range of T and P can there be two different phases that are both stable against volume fluctuations?

(c) Let the temperature T be fixed at $T < T_{\rm crit}$, and gradually increase the density from zero (decrease the volume from infinity). At low densities the gas will be vaporous, and at high densities it will be liquid. The phase transition from vapor to liquid involves a discontinuous jump from some point A in Fig. 4.7 (b) to another point B. Use the principle of minimum Gibbs potential (Sec. 4.4) to prove that the straight line from A to B in Fig. 4.7 (b) is horizontal and has a height such that the areas of the two stippled regions are equal.

(d) At what values of the pressure P and specific volume V/N does the gas exhibit huge volume fluctuations?

Exercise 4.8 *Example: Fluctuations of Systems in Contact with a Volume Bath* Exercise 4.3 explored the enthalpy representation of thermodynamics for an equilibrium ensemble of systems in contact with a volume bath. Here we extend that analysis to an ensemble out of equilibrium. We denote by P_b the bath pressure.

(a) The systems are free to exchange volume with the bath but not heat or particles. Explain why, even though the ensemble may be far from equilibrium, any system's volume change dV must be accompanied by an energy change $d\tilde{E} = -P_b dV$. This implies that the system's enthalpy $H = \tilde{E} + P_b V$ is conserved. All systems in the ensemble are assumed to have the same enthalpy H (within some very small range δH

analogous to that for energy in the microcanonical ensemble; Ex. 3.8) and all have the same number of particles N.

(b) Using equilibrium considerations for the bath, show that *interaction with a system cannot change the bath's entropy.*

(c) Show that the ensemble will always evolve toward increasing entropy S, and that when the ensemble finally reaches statistical equilibrium with the bath, its distribution function will be that of the enthalpy ensemble (Table 4.2): $\rho = e^{-S/k} = \text{const}$ for all regions of phase space that have the specified particle number N and enthalpy H in the small range δH.

(d) Show that fluctuations away from equilibrium are described by the probability distributions (4.68) and (4.69), but with the system energy E replaced by the system enthalpy H; cf. Table 4.2.

****

4.6 The Ising Model and Renormalization Group Methods

Having presented a thermodynamic description and classification of phase transitions, we now seek microphysical insight into them. After a little contemplation, one discovers that this is an extremely challenging problem because a phase change is an intrinsically non-perturbative process. Perhaps for this reason, the statistical mechanics of phase transitions has inspired the development of some of the most beautiful and broadly applicable methods in modern theoretical physics. In this section and the next we shall give the flavor of these developments by presenting simple examples of two methods of analysis: the *renormalisation group*, and *Monte Carlo* techniques.[5]

We shall illustrate these methods using a simplified model of a second order ferromagnetic phase transition, which involves spins arranged on a two dimensional square lattice. Each spin s can take on the discrete values $+1$ ("up") and -1 ("down"), and it is idealized as interacting solely with each of its four nearest neighbors, with an interaction energy $-Jss'$ that is attractive if the spins are aligned and repulsive if they are opposite. (Note that we do not explicitly include more distant interactions although these are surely present. As we shall see, these are not essential to give us a model of a phase transition. However, as we shall also see the "knock-on" effect from one spin to the next does introduce an indirect long range organization which can propagate across the lattice as the temperature is reduced below its critical value.) The proportionality constant in the interaction energy depends on V/N, where N is the total number of spins and V is the lattice's 2-dimensional volume (i.e. its area). We assume that these are both held constant. (Recall from section 4.4 that the volume does not change at a second order phase transition.)

[5]Our presentation is based in part on Maris and Kadanoff (1978) and in part on Chandler (1987).

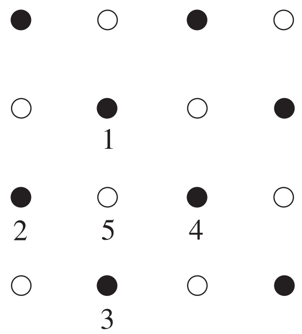

Fig. 4.8: Partition of a square lattice into two interlaced square lattices (solid circles and open circles). In the renormalisation group approach, the open-circle spins are removed from the lattice, and all their interactions are replaced by modified interactions between the remaining solid-circle spins. The new lattice is rotated by $\pi/4$ with respect to the original lattice and the lattice spacing increases by a factor $2^{1/2}$.

For ease of later notation, we shall write the interaction energy between two neighboring spins as

$$-Jss' = -kTKss' \ , \quad \text{where } K = \frac{\mathcal{F}(V/N)}{kT} \ , \tag{4.86}$$

with $\mathcal{F}$ a function whose actual form will be unimportant. Note that $K = \mathcal{F}/kT$ is dimensionless. As the interaction is attractive, $K > 0$. This is the *Ising model* after E. Ising who first investigated it in 1925.

When the temperature is so high that $J \ll kT$, ie when $K \ll 1$, the spins will be almost randomly aligned and the total interaction energy will be close to zero. Conversely, at low temperatures, where $K \gg 1$, the strong coupling will make it energetically favorable for most of the spins to be aligned over large volumes. In the limit, the total interaction energy $\to -2NJ$. At some critical intermediate temperature T_c and corresponding value K_c of K, there will be a phase transition. We shall compute the critical K_c and the dependence of the lattice's specific heat on T near T_c, using renormalization group methods in this section and Monte Carlo methods in the next; and we shall examine the accuracy of these methods by comparing our results with an exact solution for the Ising model, derived in a celebrated 1944 paper by Lars Onsager.

The key idea behind the renormalisation group approach is to try to replace the full lattice by a sparser lattice that has similar thermodynamic properties and then to interate, making the lattice more and more sparse; cf Fig. 4.8. In implementing this procedure, we shall embody all the lattice's thermodynamic properties in its physical free energy $F(N, V, T)$ (the appropriate fundamental potential for our situation of fixed N and V and interaction with a heat bath); and we shall evaluate F using the canonical-ensemble sum over states $e^{-F/kT} \equiv z = \sum_n e^{-\tilde{E}_n/kT}$. For our Ising model with its nearest-neighbor interaction energies, Eq. (4.86), this sum becomes

$$z = \sum_{\{s_1=\pm1, s_2=\pm1, \ldots\}} e^{K\Sigma^1 s_i s_j} \ . \tag{4.87}$$

Here in the exponential Σ^1 means a sum over all pairs of nearest neighbor sites $\{i, j\}$.

The first step in the renormalization group method is to rewrite Eq. (4.87) so that each of the open-circle spins of Fig. 4.8, e.g. s_5, appears in only one term in the exponential, and then explicitly sum each of those spins over ± 1 so they no longer appear in the summations:

$$\begin{aligned} z &= \sum_{\{\ldots, s_4=\pm 1, s_5=\pm 1, s_6=\pm 1, \ldots\}} \cdots e^{K(s_1+s_2+s_3+s_4)s_5} \cdots \\ &= \sum_{\{\ldots s_4=\pm 1, s_6=\pm 1 \ldots\}} \cdots \left[e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)}\right] \cdots . \end{aligned} \tag{4.88}$$

(This rewriting of z is possible because each open-circle spin interacts only with solid-circle spins.) The partition function is now a product of terms like those in the square brackets, one for each open-circle lattice site that we have "removed". We would like to rewrite each square bracketed term in a form involving solely nearest-neighbor interactions of the solid-circle spins, so that we can then iterate our procedure. Such a rewrite, however, is not possible; after some experimentation, one can verify that the rewrite also requires next-nearest-neighbor interactions and four-site interactions:

$$\begin{aligned} &\left[e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)}\right] \\ &= f(K) e^{\frac{1}{2}K_1(s_1s_2+s_2s_3+s_3s_4+s_4s_1)+K_2(s_1s_3+s_2s_4)+K_3s_1s_2s_3s_4} \end{aligned} \tag{4.89}$$

where we can determine the functions $K_1(K), K_2(K), K_3(K), f(K)$ by substituting each of the three distinct combinations of $\{s_1, s_2, s_3, s_4\}$ into Eq. (4.88). The result is

$$K_1 = \frac{1}{4} \ln \cosh(4K) \tag{4.90}$$

$$K_2 = \frac{1}{8} \ln \cosh(4K) \tag{4.91}$$

$$K_3 = \frac{1}{8} \ln \cosh(4K) - \frac{1}{2} \ln \cosh(2K) \tag{4.92}$$

$$f(K) = 2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8} \tag{4.93}$$

By inserting expression (4.89) and the analogous expressions for the other terms into Eq. (4.88), we obtain the partition function for our original N-spin lattice of open and closed circles, expressed as a sum over the $N/2$-spin lattice of closed circles:

$$z(N, K) = [f(K)]^{N/2} \sum e^{[K_1\Sigma^1 s_is_j + K_2\Sigma^2 s_is_j + K_3\Sigma^3 s_is_js_ks_l]} \tag{4.94}$$

Here the symbol Σ^1 still represents a sum over all nearest neighbors but now in the $N/2$ lattice, Σ^2 is a sum over the four next nearest neighbors and Σ^3 is a sum over spins located at the vertices of a unit cell. (The reason we defined K_1 with the 1/2 in Eq. (4.89) was because each nearest neighbor interaction appears in two adjacent squares of the solid-circle lattice, thereby converting the 1/2 to a 1 in Eq. (4.94).)

So far, what we have done is exact. We now make two drastic approximations that are designed to simplify the remainder of the calculation and thereby elucidate the renormalization group method. First, in evaluating the partition function (4.94), we drop completely the quadruple interaction (ie we set $K_3 = 0$). This is likely to be decreasingly accurate as we lower the temperature and the spins become more aligned. Second, we assume that near the critical point, in some average sense, the degree of alignment of next nearest neighbors (of which there are as many as nearest neighbors) is "similar" to that of the nearest neighbors, so that we can set $K_2 = 0$ but increase K_1 to

$$K' = K_1 + K_2 = \frac{3}{8} \ln \cosh(4K). \tag{4.95}$$

(If we simply ignored K_2 we would not get a phase transition.) This substitution ensures that the energy of a lattice with $N/2$ aligned spins, and therefore N nearest neighbor and N next nearest neighbor bonds, namely $-(K_1 + K_2)NkT$, is the same as that of a lattice in which we just include the nearest neighbor bonds, but strengthen the interaction. Clearly this will be unsatisfactory at high temperature.

These approximations bring the partition function (4.94) into the form

$$z(N, K) = [f(K)]^{N/2} z(N/2, K') \ , \tag{4.96}$$

which relates the partition function for our original Ising lattice of N spins and interaction constant K to that of a similar lattice with $N/2$ spins and interaction constant K'.

As the next key step in the renormalization procedure, we note that because the free energy, $F = -kT \ln z$, is an extensive variable, $\ln z$ must increase in direct proportion to the number of spins; i.e, it must have the form

$$-F/kT \equiv \ln z(N, K) = Ng(K) \tag{4.97}$$

defining the function $g(K)$. By combining Eqs. (4.96) and (4.97) we obtain a relation for the function $g(K)$ in terms of the function $f(K)$:

$$g(K') = 2g(K) - \ln f(K) \ . \tag{4.98}$$

Here K' is given by Eq. (4.95) and $f(K)$ by Eq. (4.93). Eq. (4.95), (4.98) are the fundamental equations that allow us to calculate thermodynamic properties under this approximation. Let us examine them more carefully.

The iterative map (4.95) which expresses the coupling constant K' for a lattice of size $N/2$ in terms of K for a lattice of size N, has a fixed point which is obtained by setting $K' = K$, or $K_c = \frac{3}{8} \ln \cosh(4K_c)$; i.e.

$$K_c = 0.507 \ . \tag{4.99}$$

This fixed point corresponds to the critical point for the lattice. We can make the identification on physical grounds. Suppose that K is slightly smaller than K_c and we make successive iterations. As $dK/dK'(K_c) < 1$ the difference increases with each step - the fixed point is unstable. What this means is that as we look on larger and larger scales, the lattice becomes more disordered. Conversely, at low temperature, when $K > K_c$, the lattice become more ordered with increasing scale. Only when $K = K_c$ does the lattice appear to be comparably disordered on all scales. It is here that the increase of order with length scale changes from the inside out (high temperature) to the outside in (low temperature).

To demonstrate that $K = K_c$ is indeed the location of a phase transition, we shall compute the lattice's specific heat in the vicinity of K_c. The first step in the computation is to compute the lattice's entropy, $S = -(\partial F/\partial T)_{V,N}$. Recalling that $K \propto 1/T$ at fixed V, N [Eq. (4.86)] and using expression (4.97) for F, we see that

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk\left[g - K\left(\frac{dg}{dK}\right)\right] . \tag{4.100}$$

The specific heat at constant volume is then, in turn, given by

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = NkK^2\frac{d^2g}{dK^2} . \tag{4.101}$$

Next we note that, as the iteration Eq. (4.95) is unstable near K_c, the inverse iteration

$$K = \frac{1}{4}\cosh^{-1}[\exp(8K'/3)] \tag{4.102}$$

is stable. The corresponding inverse transformation for the function $g(K)$ is

$$g(K) = \frac{1}{2}g(K') + \frac{1}{2}\ln\{2\exp(2K'/3)[\cosh(4K'/3)]^{1/4}\} \tag{4.103}$$

Now we know that at low temperature $K >> K_c$, all the spins are aligned and $g(K) \simeq 2K$. Conversely, at high temperature, there is complete disorder and $K \to 0$. This means that every one of the 2^N terms in the partition function is unity and $g(K) \simeq \ln 2$. We can therefore use the iterative map, Eq. (4.102),(4.103) to approach $K = K_c$ from either side starting with the high temperature and low temperature limits. This allows us to compute thermodynamic quantities, Fig. 4.9. For each value of K, we evaluate $g(K), g'(K)$ and $g''(K)$ numerically and use the results to compute F, S and C_V using Eq. (4.97),(4.100),(4.101). Note that the specific heat diverges at K_c, as $K \to K_c$, verifying that this is a second order phase transition.

In order to calculate the form of this divergence, suppose that $g(K)$ is a sum of an analytic (infinitely differentiable) function and a non-analytic part, the latter being designated with a $\sim$. Suppose that $\tilde{g}(K) \sim |K - K_c|^{2-\alpha}$ for some "critical exponent" α. This implies that C_V diverges $\propto |K - K_c|^{-\alpha} \propto |T - T_c|^{-\alpha}$, where T_c is the critical temperature. Now, from Eq. (4.103), we have that

$$|K' - K_c|^{2-\alpha} = 2|K - K_c|^{2-\alpha}, \tag{4.104}$$

or equivalently,

$$\frac{dK'}{dK} = 2^{1/(2-\alpha)}. \tag{4.105}$$

Evaluating the derivative at $K = K_c$ from Eq. (4.102), we obtain

$$\alpha = 2 - \frac{\ln 2}{\ln(dK'/dK)_c} = 0.131 \tag{4.106}$$

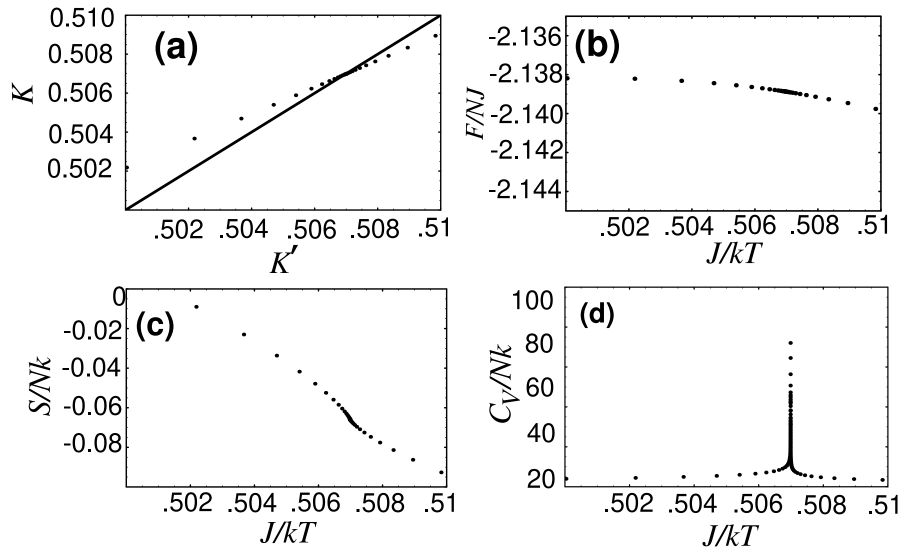

Fig. 4.9: a. Iteration map $K(K')$ in the vicinity of the critical point. b. Free energy per spin c. Entropy per spin, d. Specific heat per spin.

which is consistent with the numerical calculation. For comparison, the exact Onsager analysis gives $K_c = 0.441$ and $C_V \propto -\ln|T - T_c|$.

This analysis appears to have a serious problem in that it gives a negative value for the entropy in the vicinity of the critical point. This is surely unphysical. (The entropy becomes positive on either side of the critical point.) This is an artificiality associated with our particular ansatz which it does not seem easy to cure. For example, if we write $h(K) = \ln f(K)$ in Eq. (4.98), then the entropy at the critical point is given by

$$S_c = \frac{Nkh(K)}{2 - d\ln K'/d\ln K}\left(2 - \frac{d\ln K'}{d\ln K} - \frac{d\ln h}{d\ln K}\right) \tag{4.107}$$

all evaluated at $K = K_c$. Simply multiplying $K'(K)$ and $h(K)$ by different coefficients cannot change the sign of S_c. Nonetheless this procedure does exhibit the physical essentials of the renormalization group approach to critical phenomena.

Why did we bother to go through this cumbersome procedure when Onsager has given us an exact analytical solution? The answer is that it is not possible to generalize the Onsager solution to more complex and realistic problems. In particular, it has not even been possible to find a three dimensional counterpart. However, once the machinery of the renormalization group has been mastered, it can produce approximate answers, with an accuracy that can be estimated, for a whole variety of problems. In the following section we shall look at a quite different approach to the same 2D Ising problem with exactly the same motivation in mind.

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EXERCISES

Exercise 4.9 *Example: One Dimensional Ising Lattice*

(a) Write down the partition function for a one dimensional Ising lattice as a sum over terms describing all possible spin organisations.

(b) Show that by separating into even and odd numbered spins, it is possible to factorize the partition function and relate $z(N, K)$ exactly to $z(N/2, K')$. Specifically show that

$$z(N, K) = f(K)^{N/2} z(N/2, K') \tag{4.108}$$

where $K' = \ln[\cosh(2K)]/2$ and $f(K) = 2[\cosh(2K)]^{1/2}$.

(c) Use these relations to demonstrate that the one dimensional Ising lattice does not exhibit a second order phase transition.

Exercise 4.10 *Derivation: One Dimensional Ising Lattice*
Derive Eq. 4.107 (or show that it is incorrect).

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4.7 Monte Carlo Methods

We now turn to our second general method for approximately analyzing phase transitions (and a much larger class of problems in statistical physics). This is the *Monte Carlo* approach.[6] It will be instructive to tackle the same two dimensional Ising problem that we discussed in the last section.

The approach is much more straightforward in principle. We set up a square lattice of spins as in Sec. 4.6 and initialize the spins randomly. (This calculation will be performed numerically and will need a (pseudo) random number generator. Most programming languages now supply this utility which is mostly used uncritically, occasionally with unintended consequences. Defining and testing randomness is an important topic which unfortunately, we shall not address. See, for example, Press et al 1992.) We now imagine that this lattice is in contact with a thermal bath with a fixed temperature T – it is one member of a canonical ensemble of systems – and allow it to approach equilibrium by changing the orientiations of the spins in a prescribed manner. Our goal is to compute thermodynamic quantities using $\bar{X} = z^{-1}\Sigma e^{-E/kT}X$ where the sum is over all states. For example we can compute the specific heat (at constant volume) from

$$\begin{aligned} C_V &= \frac{d\bar{E}}{dT} && (4.109) \\ &= \frac{\partial}{\partial T}\left(\frac{\Sigma e^{-E/kT}E}{\Sigma e^{-E/kT}}\right) && (4.110) \\ &= \frac{\overline{E^2} - \overline{E}^2}{kT^2}. && (4.111) \end{aligned}$$

[6] This is a laconic reference to the casino whose patrons believe that they will profit by exploiting random processes.

(Note how a singularity in the specific heat at a phase transition will be associated with large fluctuations in the energy as we discussed in Sec. 4.5.)

In order to compute quantities like C_V, we replace ensemble averages by averages over successive configurations of the lattice. Clearly, we cannot visit every one of the 2^N configurations and so we must sample these fairly. How do we prescribe the rules for changing the spins? It turns out that there are many answers to this question and we shall just give one of the simplest, due to Metropolis et al (1953). In order to understand this, we must appreciate that we don't need to understand the detailed dynamics through which a spin in a lattice flips. All that is required is that the prescription we adopt should maintain thermodynamic equilibrium.

Let us label a single lattice state, specified by a matrix whose entries are ± 1, S_i and let its total energy be E_i. In addition, let us assign the probability of making a transition from a state S_i to a new state $S_{i'}$ to be $p_{ii'}$. Now, in a steady state,

$$\Sigma_{i'}\rho_{i'}p_{i'i} = \rho_i \Sigma_{i'} p_{ii'} \tag{4.112}$$

However, we know that in equilibrium,

$$\rho_{i'} = \rho_i \exp[(E_i - E_{i'})/kT] \tag{4.113}$$

The Metropolis rule is simple: if $E_i > E_{i'}$, then $p_{ii'} = 1$, but if $E_i < E_{i'}$, then $p_{ii'} = \exp[(E_i - E_{i'})/kT]$. This will maintain thermodynamic equilibrium and, as can easily be shown, drive an out of equilibrium system towards equilibrium.

The numerical expression of this procedure is to start with a random lattice and then choose one spin, at random, to make a trial flip. If the new configuration has a lower energy, we always accept the change. If it has a higher energy we only accept the change with a probability given by $\exp[-\Delta E/kT]$, where $\Delta E > 0$ is the energy change. (Actually, there is a small subtlety here. The probability of making a given transition is the product of the probability of making the trial flip and of accepting the trial. However the probability of making a trial flip from up to down is the same as that for down to up. and these trial probabilities cancel and it is only the ratio of the probabilities of acceptance that matters.) In this way, we choose a sequence of states that will ultimately have the equilibrium distribution function, and we can perform our thermodynamic averages using this sequence in an unweighted fashion. This is particularly convenient procedure for the Ising problem because, by changing one spin at a time, ΔE can only take one of 5 values and it is possible to change from one state to the next very quickly. (It also helps to store the two threshold probabilities for making an energy-gaining transition and avoid evaluating exponentials every step.)

How big a lattice need be used and how many states should we consider. The lattice size can be surprisingly small to get qualitatively correct results, if we adopt periodic boundary conditions. That is to say, we imagine an infinite tiling of our actual lattice and every time we need to know the spin at a site beyond the last column, we use the corresponding spin in the first column, and so on. This device minimizes the effects of the boundary on the final answer. Lattices as small as 32×32 can be useful. The length of the computation depends upon the required accuracy. (In practice, this is usually implemented the other way

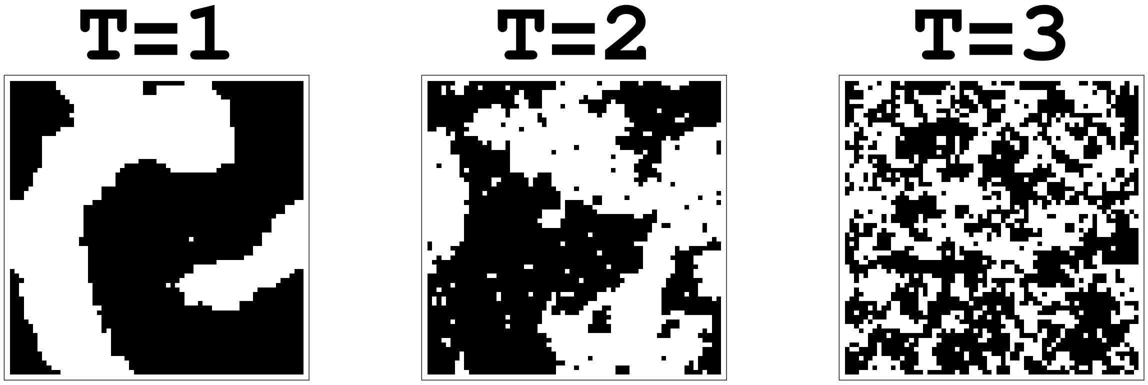

Fig. 4.10: Typical Ising lattices for $T = 1, 2, 3J/k$.

round. The time available on a computer of given speed determines the accuracy.) One thing, should be clear. It is necessary that we explore a reasonable volume of state space in order to be able to sample it fairly and computer meaningful estimates of thermodynamic quantities. The final lattice should exhibit no vestigial patterns from the configuration when the computation was half complete. In practice, it is this consideration that limits the size of the lattice and it is one drawback of the Metropolis algorithm that the step sizes are necessarily small. There is a large bag of tricks used in Monte Carlo simulation that can be used for variance reduction and estimation but we shall only concern ourselves here with the general method.

Returning to the Ising problem, we show typical equilibrium lattices for three temperatures (measured in units of J/k) in Fig. 4.10. Recall that the critical temperature is $T_c = J/kK_c = 2.268J/k$. Note the increasingly long range order as the temperature is reduced.

We have concluded this chapter with an examination of a very simple system that can approach equilibrium according to specified rules and which can exhibit strong fluctuations. In the following chapter, we shall examine these matters more systematically.

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EXERCISES

Exercise 4.11 *Practice: Direct Computation of Thermodynamic Integrals*
Estimate how long it would take a PC to compute the partition function for a 32×32 Ising lattice by evaluating every possible configuration.

Exercise 4.12 *Example: Monte Carlo Approach to Phase Transition*
Write a simple computer program to compute the energy and the specific heat of a 2 dimensional Ising lattice as described in the text. Examine the accuracy of your answers by varying the size of the lattice and the number of states sampled. (You might also try to compute a formal variance estimate.)

Exercise 4.13 *Problem: Ising Lattice with an Applied Field*

It is straightforward to generalize our approach to the problem of a lattice place in a uniform magnetic field B. This adds a term $\propto -Bs$ to the energy Eq. (4.86). Modify the computer program from Ex (4.12) to include this term and compute the magnetization and the magnetic susceptibility.

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There is no shortage of textbooks on Statistical Thermodynamics. A particularly useful treatment of phase transitions, on which Sec. 4.6 is based is Chandler (1987).

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