Contents

Chapter 5

Statistical Thermodynamics

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Box 5.1
Reader's Guide

- Relativity enters into portions of this chapter solely via the relativistic energies and momenta of high-speed particles (Sec. 1.10.)
- This chapter relies in crucial ways on Secs. 3.2 and 3.3 of Chap. 3 and on Secs. 4.2–4.8 of Chap. 4.
- Portions of Chap. 6 rely on Sec. 5.6 of this chapter. Portions of Part V (Fluid Mechanics) rely on elementary thermodynamic concepts and equations of state treated in this chapter, but most readers will already have met these in a course on elementary thermodynamics.
- Other chapters do not depend strongly on this one.

5.1 Overview

In Chap. 4, 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* properties 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 macroscopic properties. Microphysics influences the macroscopic world 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 resulting 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 thermodynamic properties 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 $P = (N/V)k_BT$ 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 $P = (\bar{N}/V)k_BT$ 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. 5.10. 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 Secs. 5.2–5.5, we shall use the microcanonical, grand canonical, canonical and Gibbs ensembles to derive many useful results from statistical thermodynamics: fundamental potentials expressed as statistical sums over microstates, variants of the first law of thermodynamics, equations of state, Maxwell relations, Euler's equation, ... Table 5.1 summarizes the most important of 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. 4, 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. 5.5 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 applications, we learn how chemical potentials drive chemical reactions and phase transitions. In Sec. 5.6 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

Representation & Ensemble	**First Law**	**Bath**	**Distribution Function ρ**
Energy & Microcanonical (Secs. 4.5 and 5.2)	$d\mathcal{E} = TdS + \tilde{\mu}dN - PdV$	none	const $= e^{-S/k_B}$ $\mathcal{E}$ const in $\delta\mathcal{E}$
Enthalpy (Exs. 5.5 and 5.13)	$dH = TdS + \tilde{\mu}dN + VdP$	V & $\mathcal{E}$ $d\mathcal{E} = -PdV$	const $= e^{-S/k_B}$ Hconst
Physical-Free-Energy & Canonical (Secs. 4.4.1 and 5.4)	$dF = -SdT + \tilde{\mu}dN - PdV$	$\mathcal{E}$	$e^{(F-\mathcal{E})/k_BT}$
Gibbs (Secs. 4.4.2 and 5.5)	$dG = -SdT + \tilde{\mu}dN + VdP$	$\mathcal{E}$ & V	$e^{(G-\mathcal{E}-PV)/k_BT}$
Grand Canonical (Secs. 4.4.2 and 5.3)	$d\Omega = -SdT - Nd\tilde{\mu} - PdV$	$\mathcal{E}$ & N	$e^{(\Omega-\mathcal{E}+\tilde{\mu}N)/k_BT}$

Table 5.1: Representations and Ensembles for Statistical Equilibrium; cf. Table 5.2.

(evolution toward equilibrium and fluctuations away from equilibrium) are summarized in Table 5.2, 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 from their microscopic statistical properties 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 occurring configurations. Direct summation over states is hopelessly impractical for most real systems. We meet an example in Sec. 5.3.2: a derivation of the van der Waal's equation of state for a dilute high-temperature gas, where the interaction energy between gas molecules is a weak perturbation. Even here, at leading order in perturbation theory, the derivation by a statistical sum over grand canonically distributed quantum states is somewhat complex and tricky. When the interactions are stronger, straightforward methods can become prohibitively difficult.

However, in recent years a number of powerful approximation techniques have been devised for performing the statistical sums. In Secs. 5.7 and 5.8 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.*

5.2 Microcanonical Ensemble and the Energy Representation of Thermodynamics

5.2.1 Extensive and Intensive Variables; Fundamental Potential

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. These variables can be divided into two classes: *extensive variables* (Sec. 4.4.1) which double if one doubles the system's size (volume, mass, ...), and *intensive variables* whose magnitudes are independent of the system's size. Examples of extensive variables are a system's total energy $\mathcal{E}$, entropy S, volume V, magnetization $\mathbf{M}$, and 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.

For a large, closed system, there is a *complete set of extensive variables that we can specify independently* — usually its volume V, total energy $\mathcal{E}$ *or* entropy S, and number N_I of particles of each species I. The values of the other extrinsic variables and all the intrinsic variables are determined in terms of this complete set by methods that we shall derive.

The particle species I in the complete set must only include those 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, if one includes N_p and N_α in one's complete set of extensive variables, one must omit N_e.

As in Chap. 4, 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 $\mathcal{E}$ and in the chemical potentials $\tilde{\mu}_I$. For very nonrelativistic systems, however, we shall usually replace $\mathcal{E}$ by the nonrelativistic energy $E \equiv \mathcal{E} - \sum_I N_I m_I c^2$, 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. 5.5 when studying chemical reactions, the identification of the appropriate rest mass m_I to subtract is occasionally a delicate issue.)

For simplicity, we shall temporarily specialize to a microcanonical ensemble of unmagnetized one-species systems, which all have identically the same values of a complete set of *three* extrinsic variables: the energy $\mathcal{E}$,[1] number of particles N, and volume V. Suppose that the microscopic nature of the ensemble's systems 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 $\mathcal{E}$, 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 $S = k_B \ln N_{\rm states}$ [cf Eq. (4.34)]. The resulting entropy can be regarded as a function of the complete set of extensive variables,

$$S = S(\mathcal{E}, N, V) \ , \tag{5.1}$$

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

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[1] In practice, as was illustrated in Ex. 4.7, one must allow $\mathcal{E}$ to fall in some tiny but finite range $\delta\mathcal{E}$ rather than constraining it precisely, and one must then check to be sure that the results of one's analysis are independent of $\delta\mathcal{E}$.

the other extensive variables

$$\boxed{\mathcal{E} = \mathcal{E}(S, N, V)}\ . \tag{5.2}$$

We call the energy $\mathcal{E}$, viewed as a function of S, N, and V, the *fundamental thermodynamic potential for the microcanonical ensemble.* When using this fundamental potential, we regard S, N and V as our complete set of extensive variables rather than $\mathcal{E}$, N and V. From the fundamental potential, as we shall see, one can deduce all other thermodynamic properties of the system.

5.2.2 Intensive Variables Identified Using Measuring Devices; First Law of Thermodynamics

In Sec. 4.4.1, we used kinetic theory considerations to identify the thermodynamic temperature T of the canonical ensemble [Eq. (4.19)]. 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 $\mathcal{E}_0$ and $\mathcal{E}_1 = \mathcal{E}_0 + \Delta\mathcal{E}$. 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. 4.5) 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

$$\frac{\rho_1}{\rho_0} = \frac{e^{-\mathcal{E}_1/k_B T}}{e^{-\mathcal{E}_0/k_B T}} = e^{-\Delta\mathcal{E}/k_B T}\ . \tag{5.3a}$$

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 $\mathcal{E} + \mathcal{E}_0$, 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 $N_0 = e^{S(\mathcal{E},N,V)/k_B}$; and those with the atom in the excited state constitute a total number $N_1 = e^{S(\mathcal{E}-\Delta\mathcal{E},N,V)/k_B}$. 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. (5.1). 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

$$\frac{\rho_1}{\rho_0} = \frac{N_1}{N_0} = \frac{e^{S(\mathcal{E}-\Delta\mathcal{E},N,V)/k_B}}{e^{S(\mathcal{E},N,V)/k_B}} = \exp\left[-\frac{\Delta\mathcal{E}}{k_B}\left(\frac{\partial S}{\partial\mathcal{E}}\right)_{N,V}\right]\ . \tag{5.3b}$$

By equating Eqs. (5.3a) and (5.3b), we obtain an expression for the original system's temperature T in terms of the partial derivative $(\partial\mathcal{E}/\partial S)_{N,V}$ of its fundamental potential $\mathcal{E}(S,N,V)$

$$T = \frac{1}{(\partial S/\partial\mathcal{E})_{N,V}} = \left(\frac{\partial\mathcal{E}}{\partial S}\right)_{N,V} , \tag{5.3c}$$

where we have used Eq. (1) of Box 5.2.

Box 5.2
Two Useful Relations between Partial Derivatives

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

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

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

$$\begin{aligned} d\mathcal{E} = \left(\frac{\partial\mathcal{E}}{\partial S}\right)_{N,V}\left(\frac{\partial S}{\partial\mathcal{E}}\right)_{N,V} d\mathcal{E} \quad &+ \quad \left[\left(\frac{\partial\mathcal{E}}{\partial S}\right)_{N,V}\left(\frac{\partial S}{\partial N}\right)_{E,V} + \left(\frac{\partial\mathcal{E}}{\partial N}\right)_{S,V}\right] dN \\ &+ \quad \left[\left(\frac{\partial\mathcal{E}}{\partial S}\right)_{N,V}\left(\frac{\partial S}{\partial V}\right)_{N,E} + \left(\frac{\partial\mathcal{E}}{\partial V}\right)_{S,N}\right] dV \ , \end{aligned}$$

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

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

$$\left(\frac{\partial\mathcal{E}}{\partial N}\right)_{S,V} = -\left(\frac{\partial\mathcal{E}}{\partial S}\right)_{N,V}\left(\frac{\partial S}{\partial N}\right)_{\mathcal{E},V} \ , \tag{2}$$

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.

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"):

$$\begin{aligned} \frac{\rho_1}{\rho_0} &= e^{\tilde{\mu}\Delta N/k_B T} \\ &= \frac{e^{S(\mathcal{E},N-\Delta N,V)/k_B}}{e^{S(\mathcal{E},N,V)/k_B}} = \exp\left[-\frac{\Delta N}{k_B}\left(\frac{\partial S}{\partial N}\right)_{\mathcal{E},V}\right] \ . \end{aligned} \tag{5.4a}$$

Here the first expression is computed from the viewpoint of the measuring device's equilibrium ensemble,[2] and the second from the viewpoint of the combined system's microcanonical ensemble. Equating these two expressions, we obtain

$$\tilde{\mu} = -T\left(\frac{\partial S}{\partial N}\right)_{\mathcal{E},V} = \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{S,V} . \tag{5.4b}$$

In the last step we have used Eq. (5.3c) and Eq. (4) of Box 5.2. The reader should be able to construct a similar thought experiment involving an idealized pressure transducer (Ex. 5.1), which yields the following expression for the system's pressure:

$$P = -\left(\frac{\partial \mathcal{E}}{\partial V}\right)_{S,N} . \tag{5.5}$$

Having identifed the three intensive variables T, $\tilde{\mu}$, and P as partial derivatives [Eqs. (5.3c), (5.4b), (5.5)], we now see that the fundamental potential's differential relation

$$d\mathcal{E}(S,N,V) = \left(\frac{\partial \mathcal{E}}{\partial S}\right)_{N,V} dS + \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{V,S} dN + \left(\frac{\partial \mathcal{E}}{\partial V}\right)_{S,N} dV . \tag{5.6}$$

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

$$\boxed{d\mathcal{E} = TdS + \tilde{\mu}dN - PdV} ; \tag{5.7}$$

cf. Table 5.1 above.

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 $\mathcal{E}$ to $E \equiv \mathcal{E} - \sum N_I m_I c^2$ and from $\tilde{\mu}_I$ to $\mu_I = \tilde{\mu}_I - m_I c^2$). The result is the nonrelativistic, extended first law

$$\boxed{dE = TdS + \sum_I \mu_I dN_I - PdV + \sum_A X_A dY_A} \tag{5.8}$$

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

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[2] an ensemble with $\rho = \text{constant}\ e^{-\tilde{\mu}N/k_B T}$, since only particles can be exchanged with the device's heat bath (our system).

5.2.3 Euler's Equation and Form of the Fundamental Potential

We can integrate the differential form of the first law to obtain a remarkable, though essentially trivial relation known as *Euler's equation.* 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 $d\mathcal{E}$ to obtain $\mathcal{E}$, their entropies dS to obtain S, etc., we obtain from the first law (5.7) [3]

$$\boxed{\mathcal{E} = TS + \tilde{\mu}N - PV} \, . \tag{5.9a}$$

Since the energy $\mathcal{E}$ is itself extensive, Euler's equation (5.9a) must be expressible as

$$\boxed{\mathcal{E} = Nf(V/N, S/N)} \tag{5.9b}$$

for some function f. This is a useful functional form for the fundamental potential $\mathcal{E}(N, V, S)$. For example, for a monatomic ideal gas, the Sackur-Tetrode equation (4.41) can be solved for E to get the following form of the fundamental potential:

$$E(V, S, N) = N\left(\frac{3h^2}{4\pi m}\right)\left(\frac{V}{N}\right)^{-2/3} \exp\left(\frac{2}{3k_B}\frac{S}{N} - \frac{5}{3}\right) . \tag{5.9c}$$

Here m is the mass of an atom and h is Planck's constant.

5.2.4 Everything Deducible from First Law; Maxwell Relations

There is no need to memorize a lot of thermodynamic relations; most all relations can be deduced almost trivially from the functional form of the first law of thermodynamics — the main formula shown on the first line of Table 5.1.

For example, in the case of our simple one-species system, the first law $d\mathcal{E} = TdS + \tilde{\mu}dN - PdV$ tells us that the system energy $\mathcal{E}$ should be regarded as a function of the things that appear as differentials on the right hand side: S, N and V; i.e., the fundamental potential must have the form $\mathcal{E} = \mathcal{E}(S, N, V)$. By thinking about building up our system from smaller systems by adding entropy dS, particles dN and volume dV at fixed values of the intensive variables, we immediately deduce, from the first law, the Euler equation $\mathcal{E} = TS + \tilde{\mu}N - PV$. By writing out the differential relation (5.6), which is just elementary calculus, and comparing with the first law, we immediately read off the intensive variables in terms of partial derivatives of the fundamental potential:

$$T = \left(\frac{\partial \mathcal{E}}{\partial S}\right)_{V,N} , \quad \mu = \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{V,S} , \quad P = -\left(\frac{\partial \mathcal{E}}{\partial V}\right)_{S,N} . \tag{5.10a}$$

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[3] 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. 4.10.2). 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_H; and instead of being independent of the hole's mass, the intensive variables T_H = (temperature) and Ω_H = (angular velocity) scale as $1/M_H$. See, e.g., Tranah & Landsberg (1980) and see Sec. 4.10.2 for some other aspects of black-hole thermodynamics.

We 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., $\partial^2E/\partial V\partial S = \partial^2E/\partial S\partial V$) together with Eqs. (5.10a) implies that they must satisfy the following *Maxwell relations*:

$$\left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{N,V}, \quad -\left(\frac{\partial P}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial V}\right)_{S,N}, \quad \left(\frac{\partial \mu}{\partial V}\right)_{N,S} = -\left(\frac{\partial P}{\partial N}\right)_{V,S}. \tag{5.10b}$$

Additional relations can be generated using the types of identities proved in Box 5.2 — or they can be generated more easily by applying the above procedure to the fundamental potentials associated with other ensembles; see Secs. 5.3, 5.4 and 5.5. 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. (5.9c)] into Eqs. (5.10a) to obtain

$$\begin{aligned}
P(V,S,N) &= \left(\frac{h^2}{2\pi m}\right)\left(\frac{N}{V}\right)^{5/3}\exp\left(\frac{2S}{3k_BN}-\frac{5}{3}\right), \\
T(V,S,N) &= \left(\frac{h^2}{2\pi m k_B}\right)\left(\frac{N}{V}\right)^{2/3}\exp\left(\frac{2S}{3k_BN}-\frac{5}{3}\right), \\
\mu(V,S,N) &= \left(\frac{h^2}{4\pi m}\right)\left(\frac{N}{V}\right)^{2/3}\left(5-2\frac{S}{k_BN}\right)\exp\left(\frac{2S}{3k_BN}-\frac{5}{3}\right)
\end{aligned} \tag{5.11}$$

[Ex. 5.2]. These clearly do satisfy the Maxwell relations.

5.2.5 Mechanism of Entropy Increase When Energy is Injected

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 $\Delta\mathcal{E} = \Delta Q$; and correspondingly, according to the first law (5.7), the added heat must increase the system's entropy by an amount

$$\Delta S = \frac{\Delta Q}{T}. \tag{5.12}$$

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.[4] 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

$$\Delta S = \frac{\Delta \mathcal{E}}{T} \,. \tag{5.13}$$

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. 4.7, and it is responsible for the thermal equilibration and the entropy increase.

5.2.6 Representations of Thermodynamics

The treatment of thermodynamics given in this section is called the *energy representation* because it is based on the fundamental potential $\mathcal{E}(S, V, N)$ in which the energy is expressed as a function of the complete set of extensive variables $\{S,\ V,\ N\}$. This energy representation, as we have seen, is intimately related to the microcanonical ensemble. In Sec. 5.3, we shall meet the *grand-potential representation* for thermodynamics, which is 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 $\tilde\mu$. Then in Secs. 5.4 and 5.5, 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. And in Ex. 5.5 we shall meet a representation and ensemble based on *enthalpy*. These five representations and their ensembles are summarized in Table 5.1 above.

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EXERCISES

Exercise 5.1 *Problem: Pressure-Measuring Device*
For the microcanonical ensemble considered in Sec. 5.2, derive Eq. (5.5) for the pressure using a thought experiment involving a pressure-measuring device.

Exercise 5.2 *Derivation: Energy Representation for a Nonrelativistic Monatomic Gas*

(a) Use the fundamental potential $E(V, S, N)$ for the nonrelativistic, monatomic gas [Eq. 5.9c] to derive Eq. (5.11) for the the pressure, temperature, and chemical potential.

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[4] 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.

(b) Show that these equations of state satisfy the Maxwell relations (5.10b).

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

$$P = \frac{N}{V} k_B T \,, \tag{5.14}$$

which we derived in Ex. 3.7 using kinetic theory

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5.3 Grand Canonical Ensemble and the Grand Potential Representation of Thermodynamics

We now turn to the grand canonical ensemble, and its associated grand-potential representation of thermodynamics, for a semi-closed system that can exchange heat and particles with an enveloping bath. For simplicity, we shall assume that all the particles are identical (just one particle species), but we shall allow them to be relativistic (speeds comparable to the speed of light) or not, and allow them to have nontrivial internal degrees of freedom (e.g., vibrations or rotations), and allow them to exert forces on each other via an interaction potential that appears in their Hamiltonian (e.g. van der Waals forces; Sec. 5.3.2 and Ex. 5.12). We shall refer to these particles as a gas, though our analysis is more general than gases.

We shall begin in Subsec. 5.3.1 by deducing the grand-potential representation of thermodynamics from the grand canonical ensemble, and by deducing a method for computing the thermodynamic properties of our gas from a grand-canonical sum over the quantum states available to the system. In Ex. 5.3, the reader will apply this grand canonical formalism to an ideal gas of noninteracting particles, thereby deriving explicit equations for the gas's thermodynamic properties. In Subsec. 5.3.2 of the text, we shall apply the formalism to a nonrelativistic gas of particles that interact via van der Waals forces, and we shall thereby derive the van der Waals equation of state, which is surprisingly accurate for many non-ionized gases.

5.3.1 The Grand Potential Representation, and Computation of Thermodynamic Properties as a Grand Canonical Sum

Figure 5.1 illustrates the ensemble of systems that we are studying, and its bath. Each system is a cell of fixed volume V, with imaginary walls, inside a huge thermal bath of identical particles. Since the cells' walls are imaginary, the cells can and do exchange energy and particles with the bath. The bath is characterized by a chemical potential $\tilde{\mu}$ for these particles and by a temperature T. Since we allow the particles to be relativistic, we include the rest mass in the chemical potential $\tilde{\mu}$.

We presume that our ensemble of cells has reached statistical equilibrium with the bath, so its probabilistic distribution function has the grand canonical form (4.24c):

$$\boxed{\rho_n = \frac{1}{Z}\exp\left(\frac{-\mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right) = \exp\left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right)} . \tag{5.15}$$

Here the index n labels the quantum state $|n\rangle$ of a cell, N_n is the number of particles in that quantum state, $\mathcal{E}_n$ is the total energy of that quantum state (including each particle's rest mass, its energy of translational motion, its internal energy if it has internal vibrations or rotations or other internal excitations, and its energy of interaction with other particles), and $1/Z \equiv e^{\Omega/k_B T}$ is the normalization constant that guarantees $\sum_n \rho_n = 1$; i.e.,

$$\boxed{Z \equiv \exp\left(\frac{-\Omega}{k_B T}\right) \equiv \sum_n \exp\left(\frac{-\mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right)} . \tag{5.16}$$

This normalization constant, whether embodied in Z or in Ω, is a function of the bath's temperature T and chemical potential $\tilde{\mu}$, and also of the cells' common volume V (which influences the set of available states $|n\rangle$). When regarded as a function of T, $\tilde{\mu}$, and V, the quantity $Z(V, \tilde{\mu}, T)$ is called the gas's *grand partition function*, and $\Omega(T, \tilde{\mu}, V)$ is called its *grand potential*. The following general argument shows that, *once one has computed the explicit functional form for the grand potential*

$$\boxed{\Omega(V, \tilde{\mu}, T)} , \tag{5.17}$$

or equally well for the grand partition function $Z(V, \tilde{\mu}, T)$, *one can then derive from it all the thermodynamic properties of the thermally equilibrated system.* The argument is so general that it applies to *every* grand canonical ensemble of systems, not just to our chosen gas of identical particles.

We introduce, as key quantities in the argument, the mean energy and mean number of particles in the ensemble's systems (cells of Fig. 5.1):

$$\overline{\mathcal{E}} \equiv \sum_n \rho_n \mathcal{E}_n \ , \quad \text{and } \overline{N} \equiv \sum_n \rho_n N_n \ . \tag{5.18}$$

(We denote these with bars $\bar{\mathcal{E}}$ rather than brackets $\langle\mathcal{E}\rangle$ for ease of notation.) We now ask how the grand potential will change if the temperature T and chemical potential $\tilde{\mu}$ of the

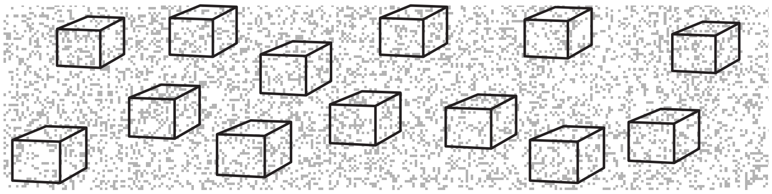

Fig. 5.1: An ensemble of gas cells, each with volume V, inside a heat and particle bath.

bath and therefore of the ensemble are slowly altered, with the common volume V of the cells held fixed. The answer for the change $d\Omega$ produced by changes dT and $d\tilde{\mu}$ can be derived from the normalization equation (5.16), which we rewrite as

$$1 = \sum_n \rho_n = \sum_n \exp\left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu} N_n}{k_B T}\right) \; . \tag{5.19a}$$

Since the normalization condition must continue to hold as T and $\tilde{\mu}$ change, the sum in Eq. (5.19a) must be left unchanged, which means that

$$0 = \sum_n \left(\frac{d\Omega + N_n d\tilde{\mu} - (\Omega - \mathcal{E}_n + \tilde{\mu} N_n) T^{-1} dT}{k_B T}\right) \rho_n \; . \tag{5.19b}$$

Using $\sum_n \rho_n = 1$ and expressions (5.18) for the mean energy and the mean number of particles, and rearranging terms, we obtain

$$d\Omega = -\overline{N} d\tilde{\mu} + (\Omega - \overline{\mathcal{E}} + \tilde{\mu}\overline{N}) T^{-1} dT \; . \tag{5.19c}$$

This change can be reexpressed in a more useful form by introducing the ensemble's entropy. Inserting expression (5.15) for ρ_n into the log term in the definition of entropy $S = -k \sum_n \rho_n \ln \rho_n$, we obtain

$$S = -k \sum_n \rho_n \ln \rho_n = -k \sum_n \rho_n \left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu} N_n}{k_B T}\right) = -\frac{\Omega - \overline{\mathcal{E}} + \tilde{\mu}\overline{N}}{T} ; \tag{5.19d}$$

or, equivalently

$$\boxed{\Omega = \overline{\mathcal{E}} - TS - \tilde{\mu}\overline{N}} \; . \tag{5.20}$$

This equation can be regarded as a *Legendre transformation* that leads from the energy representation of thermodynamics to the grand-potential representation. (Legendre transformations are a common tool, e.g., in classical mechanics[5], for switching from one set of independent variables to another.)

By inserting expression (5.20) into Eq. (5.19c), we obtain

$$d\Omega = -\overline{N} d\tilde{\mu} - S dT \; . \tag{5.21}$$

Equation (5.21) is the *First Law of Thermodynamics* in disguise. To see this, insert expression (5.20) for Ω into (5.21), thereby bringing it into the form

$$d\overline{\mathcal{E}} = \tilde{\mu} d\overline{N} + T dS, \tag{5.22}$$

which is the familiar form of the first law of thermodynamics, but with the "$-PdV$" work, associated with a change in a cell's volume, omitted because the cells have fixed volume V. If we (momentarily) pass from our original grand canonical ensemble, all of whose cells have the same V, $\tilde{\mu}$, and T, to another grand canonical ensemble whose cells have the same $\tilde{\mu}$

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[5] For example, Goldstein (1980).

and T as before, but have slightly larger volumes, $V + dV$, then according to Eq. (5.20) with $\tilde{\mu}$ and T fixed, Ω will change by $d\Omega = d\overline{\mathcal{E}} - TdS - \tilde{\mu}d\overline{N}$ (where dS and $d\overline{N}$ are the changes of entropy and mean number of particles induced by the volume change). Then by the elementary first law of thermodynamics (5.7), rewritten in the form appropriate for a grand canonical ensemble ($\mathcal{E} \rightarrow \bar{\mathcal{E}}$, $N \rightarrow \bar{N}$),

$$d\overline{\mathcal{E}} = -PdV + \tilde{\mu}d\overline{N} + TdS \, , \tag{5.23}$$

this change of Ω at fixed $\tilde{\mu}$ and T is simply $-PdV$. Combining with Eq. (5.21), this gives for the change of Ω when all of $\tilde{\mu}$, T, and V change:

$$\boxed{d\Omega = -PdV - \overline{N}d\tilde{\mu} - SdT} \, . \tag{5.24}$$

Equation (5.24) contains the same information as the first law of thermodynamics and can be thought of as the first law rewritten in the *grand-potential representation.* The quantities P, $\bar{N}$, S paired with the independent variables V, $\tilde{\mu}$, and T can be thought of as *generalized forces* that push on the independent variables as they change, to produce changes of the grand potential.

From this version of the first law (the key grand-canonical equation listed in the last line of Table 5.1), we can easily deduce almost all other equations of the grand-potential representation of thermodynamics. We just follow the same procedure as we used for the energy representation (Sec. 5.2.4):

The grand-potential representation's complete set of independent variables is those that appear as differentials on the right side of the first law (5.24): V, $\tilde{\mu}$, and T. From the form (5.24) of the first law we see that Ω is being regarded as a function of these three independent variables $\Omega = \Omega(V, \tilde{\mu}, T)$. This is the fundamental potential.

The Euler equation of this representation is deduced by building up a system from small pieces that all have the same values of the intensive variables $\tilde{\mu}$, T and P. The first law (5.24) tells us that this buildup will produce

$$\Omega = -PV \, . \tag{5.25}$$

Thus, if we happen to know P as a function of this representation's independent variables $P(V, \tilde{\mu}, T)$ (actually, P it cannot depend on V because $\tilde{\mu}$ and T are intensive, and there is nothing to divide V by so as to produce an intensive P), then we can simply multiply by V to get the functional form of the Grand potential: $\Omega(V, \tilde{\mu}, T) = P(\tilde{\mu}, T)V$; see Eqs. (5.44) and (5.45) below as a concrete example.

By comparing the grand-potential version of the first law (5.24) with the elementary calculus equation $d\Omega = (\partial\Omega/\partial V)dV + (\partial\Omega/\partial\tilde{\mu})d\tilde{\mu} + (\partial\Omega/\partial T)dT$, we infer equations for the system's "generalized forces", the pressure P, mean number of particles $\bar{N}$, and entropy S:

$$\overline{N} = -\left(\frac{\partial\Omega}{\partial\tilde{\mu}}\right)_{V,T} \, , \quad S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\tilde{\mu}} \, , \quad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{\tilde{\mu},T} \, . \tag{5.26}$$

By differentiating these relations and equating mixed partial derivatives, we can derive Maxwell relations analogous to those, (5.10b), of the energy representation; for example, $(\partial\bar{N}/\partial T)_{V,\tilde{\mu}} = (\partial S/\partial\tilde{\mu})_{V,T}$. Equations of state are constrained by these Maxwell relations.

If we had begun with a specific functional form of the fundamental potential as a function of this representation's complete set of independent variables $\Omega(V, T, \tilde{\mu})$ [e.g. Eq. (5.44) below], then Eqs. (5.26) would tell us the functional forms of almost all the other dependent thermodynamic variables. The only one we are missing is the mean energy $\bar{\mathcal{E}}(V, \tilde{\mu}, T)$ in a cell. If we have forgotten Eq. (5.20) (the Legendre transformation) for that quantity, we can easily rederive it from the grand canonical distribution function $\rho = \exp[(\Omega - \mathcal{E} + \tilde{\mu}N)/k_BT]$ (the other key equation, besides the first law, on the last line of Table 5.1), via the definition of entropy as $S = -k_B \sum_n \rho_n \ln \rho_n = -k_B \overline{\ln \rho}$, as we did in Eq. (5.19d) above.

This illustrates the power of the sparse information in Table 5.1. From it and little else we can deduce all of the thermodynamic equations for each of the representations of thermodynamics.

5.3.2 Nonrelativistic van der Waals Gas

The statistical sum $Z \equiv e^{-\Omega/k_BT} = \sum_n e^{(-\mathcal{E}_n + \tilde{\mu}N_n)/k_BT}$ is a powerful method for computing the grand potential $\Omega(V, \tilde{\mu}, T)$, a method often used in condensed matter physics. In this section we shall present a non-trivial example: a nonrelativistic, monatomic gas made of atoms or molecules (we shall call them particles) that interact with so-called *van der Waals forces*. In Ex. 5.3, the reader will explore a simpler example: an ideal gas (no interaction forces) that can be relativistic or nonrelativistic.

We shall assume that the heat and particle bath that bathes the cells of Fig. 5.1 has sufficiently low temperature that the gas's particles are not ionized (and therefore that they are also nonrelativistic, $k_BT \ll mc^2$), and that the bath has a sufficiently low chemical potential that the mean occupation number η of the particles' quantum states is small compared to unity, so they behave classically, $\mu \equiv \tilde{\mu} - mc^2 \ll -k_BT$ [Eq. (3.22d)].

The orbital electron clouds attached to each of the particles repel each other when the distance r between the particles' centers of mass is smaller than about the diameter of the particles. At larger separations, the particles' electric dipoles (intrinsic or induced) attract each other weakly. The interaction energy (potential energy) $u(r)$ associated with these forces has a form well approximated by the "Lennard-Jones" potential

$$u(r) = \varepsilon_o \left[\left(\frac{r_o}{r}\right)^{12} - \left(\frac{r_o}{r}\right)^{6} \right] , \tag{5.27a}$$

where (when a gradient is taken) the first term gives rise to the small-r repulsive force and the second to the larger-r attactive force. For simplicity of analytic calculations, we shall use the cruder approximation

$$u(r) = \infty \text{ for } r < r_o \; , \quad u(r) = -\varepsilon_o (r_o/r)^6 \text{ for } r > r_o \; , \tag{5.27b}$$

which has an infinitely sharp repulsion at $r = r_o$ (a *hard wall*). For simplicity, we shall assume that the mean interparticle separation is much larger than r_o (*dilute gas*) so it is highly unlikely that three or more particles are close enough together simultaneously, $r \sim r_o$, to interact; i.e., we shall confine ourselves to 2-particle interactions.

We shall compute the grand potential $\Omega(V, \mu, T)$ for an ensemble of cells embedded in a bath of these particles (Fig. 5.1), and from $\Omega(V, \mu, T)$ we shall compute how the particles' interaction energy $u(r)$ alters the gas's equation of state from the form $P = (\bar{N}/V)k_BT$ for an ideal, interaction-free gas [Eq. (3.37b)]. Since this is our objective, any internal degrees of freedom that the particles might have are irrelevant and we shall ignore them.

For this ensemble, the nonrelativistic grand partition function $Z = \sum_n \exp[(-E_n + \mu N_n)/k_BT]$ is

$$Z = \sum_{N=0}^{\infty} \frac{e^{\mu N/k_BT}}{N!} \int \frac{d^{3N}x d^{3N}p}{h^{3N}} \exp\left[-\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2mk_BT} - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=i+1}^{N} \frac{u_{ij}}{k_BT} \right] . \tag{5.28}$$

Here we have used Eq. (4.8b) for the sum over states $\sum_n$ (with $\mathcal{M} = N!$, $W = 3N$ and $d\Gamma_W = d^{3N}xd^{3N}p$; cf. Ex. 5.3), and we have written E_n as the sum over the kinetic energies of the N particles in the cell and the interaction energies

$$u_{ij} \equiv u(r_{ij}), \quad r_{ij} \equiv |\mathbf{x}_i - \mathbf{x}_j| \tag{5.29}$$

of the $\frac{1}{2}N(N-1)$ pairs of particles. In Eq. (5.28) the momentum integrals and the space integrals separate, and the N momentum integrals are identical, so Z takes the form

$$\begin{aligned} Z &= \sum_{N=0}^{\infty} \frac{e^{\mu N/k_BT}}{N!h^{3N}} \left[\exp\left(-\int_0^{\infty} \frac{4\pi p^4 dp}{2mk_BT} \right) \right]^N J_N \\ &= \sum_{N=0}^{\infty} \frac{(\zeta/\lambda^3)^N}{N!} J_N \ , \end{aligned} \tag{5.30}$$

where

$$\zeta \equiv e^{\mu/k_BT} \ , \quad \lambda \equiv \frac{h}{(2\pi m k_BT)^{1/2}} \tag{5.31}$$

(the particles' thermal deBroglie wavelength), and J_N is the space integral

$$J_N = \int d^{3N}x \exp\left[-\sum_{i=1}^{N}\sum_{j=i+1}^{N} \frac{u_{ij}}{k_BT} \right] . \tag{5.32}$$

The Boltzmann factor e^{-u_{ij}/k_BT} for the interaction energy is unity for large interparticle separations $r_{ij} \gg r_o$, so we write

$$e^{-u_{ij}/k_BT} \equiv 1 + f_{ij} \ , \tag{5.33}$$

where f_{ij} is zero except when $r_{ij} \lesssim r_o$. Using this definition and rewriting the exponential of a sum as the products of exponentials, we bring Eq. (5.32) into the form

$$J_N = \int d^{3N}x \prod_{i=1}^{N} \prod_{j=i+1}^{N} (1 + f_{ij}) \ . \tag{5.34}$$

The product contains (i) terms linear in f_{ij} that represent the influence of pairs of particles that are close enough ($r_{ij} \lesssim r_o$) to interact, plus (ii) quadratic terms such as $f_{14}f_{27}$ that are nonzero only if particles 1 and 4 are near each other and 2 and 7 are near each other (there are so many of these terms that we cannot neglect them!), plus (iii) quadratic terms such as $f_{14}f_{47}$ that are nonzero only if particles 1, 4, and 7 are all within a distance $\sim r_o$ of each other (because our gas is dilute, it turns out these three-particle terms can be neglected), plus (iv) cubic and higher-order terms. At *all* orders ℓ (linear, quadratic, cubic, quartic, ...) for our dilute gas, we can ignore terms that require three or more particles to be near each other, so we shall focus only on terms $f_{ij}f_{mn}...f_{pq}$ where all indices are different. Eq. (33) then becomes

$$J_N = \int d^{3N}x[1 + \underbrace{(f_{12} + f_{13} + ...)}_{n_1 \text{ terms}} + \underbrace{(f_{12}f_{34} + f_{13}f_{24} + ...)}_{n_2 \text{ terms}} + \underbrace{(f_{12}f_{34}f_{56} + f_{13}f_{24}f_{56} + ...)}_{n_3 \text{ terms}} ...] \ , \tag{5.35}$$

where n_ℓ is the number of terms of order ℓ with all 2ℓ particles different. Denoting

$$V_o \equiv \int f(r) d^3r \sim r_o^3 \ , \tag{5.36}$$

and performing the integrals, we bring Eq. (5.35) into the form

$$J_N = \sum_{\ell=0}^{\infty} n_l V^{N-\ell} V_o^\ell \ . \tag{5.37}$$

At order ℓ the number of unordered sets of 2ℓ particles that are all different is $N(N-1)\cdots(N-2\ell+1)/\ell!$. The number of ways that these 2ℓ particles can be assembled into unordered pairs is $(2\ell-1)(2\ell-3)(2\ell-5)\cdots 1 \equiv (2\ell-1)!!$. Therefore, the number of terms of order ℓ that appear in Eq. (5.37) is

$$n_\ell = \frac{N(N-1)\cdots(N-2\ell+1)}{\ell!}(2\ell-1)!! = \frac{N(N-1)\cdots(N-2\ell+1)}{2^\ell \ell!} \ . \tag{5.38}$$

Inserting Eqs. (5.37) and (5.38) into Eq. (5.30) for the partition function, we obtain

$$Z = \sum_{N=0}^{\infty} \frac{(\zeta/\lambda^3)^N}{N!} \sum_{\ell=0}^{[N/2]} \frac{N(N-1)\cdots(N-2\ell+1)}{2^\ell \ell!} V^{N-\ell} V_o^\ell \ , \tag{5.39}$$

where $[N/2]$ means the largest integer less than or equal to $N/2$. Performing a little algebra and then reversing the order of the summations, we obtain

$$Z = \sum_{\ell=0}^{\infty} \sum_{N=2\ell}^{\infty} \frac{1}{(N-2\ell)!} \left(\frac{\zeta V}{\lambda^3}\right)^{N-2\ell} \frac{1}{\ell!} \left(\frac{\zeta V}{\lambda^3} \frac{\zeta V_o}{2\lambda^3}\right)^\ell \ . \tag{5.40}$$

By changing the summation index from N to $N' = N - 2\ell$, we decouple the two summations. Each of sums is equal to an exponential, giving

$$Z = e^{-\Omega/k_B T} = \exp\left(\frac{\zeta V}{\lambda^3}\right) \exp\left(\frac{\zeta V}{\lambda^3}\frac{\zeta V_o}{\lambda^3}\right) = \exp\left[\frac{\zeta V}{\lambda^3}\left(1 + \frac{\zeta V_o}{2\lambda^3}\right)\right] \ . \tag{5.41}$$

Therefore, the grand potential for our van der Waals gas is

$$\Omega = \frac{-k_B T \zeta V}{\lambda^3}\left(1 + \frac{\zeta V_o}{2\lambda^3}\right) . \tag{5.42}$$

From kinetic theory [Eq. (3.37a)] we know that for an ideal monatomic gas, the mean number density is $\bar{N}/V = \zeta/\lambda^3$, and this will be a good first approximation also for our van der Waals gas, which differs from an ideal gas only by the weakly perturbative interaction energy $u(r)$. This means that $\zeta V_o/2\lambda^3$ is equal to $\frac{1}{2}V_o/$(mean volume per particle), which is $\ll 1$ by our dilute-gas assumption. If we had kept three-particle interaction terms such as $f_{14}f_{47}$, they would have given rise to fractional corrections of order $(\zeta V_o/\lambda^3)^2$, which are much smaller than the leading-order fractional correction $\zeta V_o/2\lambda^3$ that we have computed [Eq. (5.44)]. The higher-order corrections are derived in statistical mechanics textbooks such as Pathria (1972, Chap. 9) and Kardar (2007, Chap. 5) using a technique called *the cluster expansion.*

For the "hard-wall" potential (5.27b), f is -1 at $r < r_o$, and assuming that the temperature is high enough that $\varepsilon_o/k_B T \ll 1$, then at $r > r_o$, f is very nearly $-u/k_B T = (\varepsilon_o/k_B T)(r_o/r)^6$; therefore

$$\frac{V_o}{2} \equiv \frac{1}{2}\int f(r) d^3 r = \frac{a}{k_B T} - b\ , \quad \text{where} \quad b = \frac{2\pi r_o^3}{3}\ , \quad a = b\varepsilon_o\ . \tag{5.43}$$

Inserting this expression for $V_o/2$ and Eqs. (5.31) for ζ and λ into Eq. (5.44), we find the following explicit form for the grand potential of a van der Waals gas:

$$\Omega = -k_B T V \frac{(2\pi m k_B T)^{3/2}}{h^3} e^{\mu/k_B T}\left[1 + \frac{(2\pi m k_B T)^{3/2}}{h^3} e^{\mu/k_B T}\left(\frac{a}{k_B T} - b\right)\right] . \tag{5.44}$$

By differentiating this grand potential, we obtain the following expressions for the pressure P and mean number of particles $\bar{N}$ in a volume-V cell:

$$\begin{aligned} P &= -\left(\frac{\partial\Omega}{\partial V}\right)_{\mu,T} = -k_B T \frac{(2\pi m k_B T)^{3/2}}{h^3} e^{\mu/k_B T}\left[1 + \frac{(2\pi m k_B T)^{3/2}}{h^3} e^{\mu/k_B T}\left(\frac{a}{k_B T} - b\right)\right] , \\ \bar{N} &= -\left(\frac{\partial\Omega}{\partial \mu}\right)_{V,T} = V \frac{(2\pi m k_B T)^{3/2}}{h^3} e^{\mu/k_B T}\left[1 + 2\frac{(2\pi m k_B T)^{3/2}}{h^3} e^{\mu/k_B T}\left(\frac{a}{k_B T} - b\right)\right] \end{aligned} \tag{5.45}$$

Notice that, when the interaction energy is turned off so $a = b = 0$, the second equation gives our standard ideal-gas particle density $\bar{N}/V = (2\pi m k_B T)^{3/2} e^{\mu/k_B T}/h^3 = \zeta/\lambda^3$. Inserting this into the square bracketed expression in Eqs. (5.45), taking the ratio of expressions (5.45) and multiplying by V and expanding to first order in $a/k_B T - b$, we obtain $PV/\bar{N} = k_B T[1 + (\bar{N}/V)(b - a/k_B T)]$. Bringing the a term to the left side, multiplying both sides by $[1 - (\bar{N}/V)b]$ and linearizing in b, we obtain the standard *van der Waals equation of state*

$$\left(P + \frac{a}{(V/\bar{N})^2}\right)(V/\bar{N} - b) = k_B T\ . \tag{5.46}$$

The quantity $V/\bar{N}$ is called the *specific volume* (volume per particle).

We shall study this van der Waals equation of state in Ex. 5.12 below, focusing on the phase transition that it predicts and on fluctuations of thermodynamic quantities associated with that phase transition.

In this section we have presented the grand-canonical analysis for a van der Waals gas not because such a gas is important (though it is), but rather as a concrete example of how one uses the formalism of statistical mechanics to explore the behavior of realistic systems made of interacting particles.

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EXERCISES

Exercise 5.3 *Derivation and Example: Grand Canonical Ensemble for a Relativistic Ideal Gas*

Consider cells of ideal, classical gas (particles with no internal degrees of freedom and no interaction energies) that reside in the heat and particle bath of Fig. 5.1. Each cell has the same volume V and imaginary walls. Assume that the bath's temperature T has an arbitrary magnitude relative to the rest mass-energy mc^2 of the particles, so the thermalized particles might have relativistic velocities, but require $k_BT \ll -\mu$ so all the particles behave classically. Ignore the particles' spin degrees of freedom, if any.

(a) The number of particles in a chosen cell can be anything from $N = 0$ to $N = \infty$. Restrict attention, for the moment, to a situation in which the cell contains a precise number of particles, N. Explain why the multiplicity is $\mathcal{M} = N!$ even though the density is so low that the particles' wave functions do not overlap, and they are behaving classically; cf. Ex. 4.8 above.

(b) Still holding fixed the number of particles in the cell, show that the number of degrees of freedom W, the number density of states in phase space $\mathcal{N}_{\rm states}$ and the energy $\mathcal{E}_N$ in the cell are

$$W = 3N \ , \quad \mathcal{N}_{\rm states} = \frac{1}{N!h^{3N}} \ , \quad \mathcal{E}_N = \sum_{j=1}^{N} ({\bf p}_j{}^2 + m^2)^{\frac{1}{2}} \ , \tag{5.47a}$$

where ${\bf p}_j$ is the momentum of classical particle number j.

(c) Using Eq. (4.8b) to translate from the formal sum over states $\sum_n$ to a sum over $W = 3N$ and an integral over phase space, show that the sum over states (5.16) for the grand partition function becomes

$$Z = e^{-\Omega/k_BT} = \sum_{N=0}^{\infty} \frac{V^N}{N!h^{3N}} e^{\tilde\mu N/k_BT} \left[\int_0^\infty \exp\left(-\frac{(p^2+m^2)^{\frac{1}{2}}}{k_BT} \right) 4\pi p^2 dp \right]^N \ . \tag{5.47b}$$

(d) Evaluate the momentum integral in the nonrelativistic limit, and thereby show that

$$\Omega(T,\mu,V) = -k_BTV \frac{(2\pi m k_BT)^{3/2}}{h^3} e^{\mu/k_BT} \ , \tag{5.48a}$$

where $\mu = \tilde{\mu} - m$ is the nonrelativistic chemical potential. This is the interaction-free limit $V_o = a = b = 0$ of our grand potential (5.44) for a van der Waals gas.

(e) Show that in the extreme relativistic limit, Eq. (5.47b) gives

$$\Omega(T, \tilde{\mu}, V) = -\frac{8\pi V (k_B T)^4}{h^3} e^{\tilde{\mu}/k_B T} . \tag{5.48b}$$

(f) For the extreme relativistic limit use your result (5.48b) for the grand potential $\Omega(V, T, \tilde{\mu})$ to derive the mean number of particles $\overline{N}$, the pressure P, the entropy S, and the mean energy $\overline{\mathcal{E}}$ as functions of V, $\tilde{\mu}$, and T. Note that for a photon gas, because of the spin degree of freedom, the correct values of $\overline{N}$, $\overline{\mathcal{E}}$ and S will be twice as large as you obtain in this calculation. Show that $\overline{\mathcal{E}}/V = 3P$ (a relation valid for any ultrarelativistic gas); and that $\overline{\mathcal{E}}/\overline{N} = 3k_B T$ (which is higher than the $2.70 \ldots k_B T$ for black-body radiation, as derived in Ex. 2.5, because in the classical regime of $\eta \ll 1$ photons don't cluster in the same states at low frequency; that clustering lowers the mean photon energy for black-body radiation.)

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5.4 Canonical Ensemble and the Physical-Free-Energy Representation of Thermodynamics

In this section we turn to 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 $\mathcal{E}$, but they all have the same, fixed values of the two remaining extensive variables N and V. (Generalization to additional particle species and additional means of performing work on the system, e.g. magnetic coupling, 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 $\mathcal{E}$) given by Eq. (4.19)

$$\boxed{\rho_n = \frac{1}{z} e^{-\mathcal{E}_n/k_B T} \equiv e^{(F-\mathcal{E}_n)/k_B T}} . \tag{5.49}$$

Here, as in the grand canonical ensemble [Eq. (5.15)], we have introduced special notations for the normalization constant: $1/z = e^{F/k_B T}$, 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 $\mathcal{E}$ have been identified, the functions $z(N, V, T)$ and $F(N, V, T)$ can be computed from the normalization relation $\sum_n \rho_n = 1$:

$$\boxed{e^{-F/k_B T} \equiv z(T, N, V) = \sum_n e^{-\mathcal{E}_n/k_B T}} . \tag{5.50}$$

This canonical sum over states, like the grand canonical sum (5.16) that we used for the van der Waals gas, is a powerful tool in statistical mechanics. As an example, in Secs. 5.7 and 5.8 we shall use the canonical sum to evaluate the physical free energy F for a model of ferromagnetism, and we shall then use the resulting F to explore a ferromagnetic phase transition.

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 $S = -k_B \sum_n \rho_n \ln \rho_n = -k_B \overline{\ln \rho}$, together with Eq. (5.49) for ρ_n:

$$S = \frac{\bar{\mathcal{E}} - F}{T} \;, \tag{5.51a}$$

It is helpful to rewrite Eq. (5.51a) as an equation for the physical free energy F

$$\boxed{F = \bar{\mathcal{E}} - TS} \;. \tag{5.51b}$$

This is the Legendre transformation that leads from the energy representation of thermodynamics to the *physical-free-energy representation*:

Suppose that the canonical ensemble's parameters $T,\ N,\ V$ are changed slightly. By how much will the physical free energy change? Equation (5.51b) tells us that

$$dF = d\bar{\mathcal{E}} - TdS - SdT \;. \tag{5.51c}$$

Because macroscopic thermodynamics is independent of the statistical ensemble being studied, we can evaluate $d\bar{\mathcal{E}}$ using the first law of thermodynamics (5.7) with the microcanonical exact energy $\mathcal{E}$ replaced by the canonical mean energy $\bar{\mathcal{E}}$. The result is

$$\boxed{dF = -SdT + \tilde{\mu}dN - PdV} \;. \tag{5.52}$$

Equation (5.52) contains the same information as the first law of thermodynamics and can be thought of as the first law rewritten in the physical-free-energy representation. From this form of the first law, we can deduce the other equations of the physical-free-energy representation, by the same procedure as we used for the energy representation in Sec. 5.2.4 and the grand-potential representation in Sec. 5.3.1:

If we have forgotten our representation's independent variables, we read them off the first law (5.52); they appear as differentials on the right hand side: T, N and P. The fundamental potential is the quantity that appears on the left side of the first law: $F(T, N, P)$. By building up a full system from small subsystems that all have the same intensive variables $T, \tilde{\mu}, P$, we deduce from the first law the Euler relation for this representation:

$$\boxed{F = \tilde{\mu}N - PV} \;. \tag{5.53}$$

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. By comparing the first law with the elementary calculus relation $dV = (\partial F/\partial T)dT + (\partial F/\partial N)dN + (\partial F/\partial V)dV$, we obtain equations for this representation's generalized forces

$$-P = \left(\frac{\partial F}{\partial V}\right)_{T,N} \;, \quad -S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \;, \quad \tilde{\mu} = \left(\frac{\partial F}{\partial N}\right)_{V,T} \;; \tag{5.54}$$

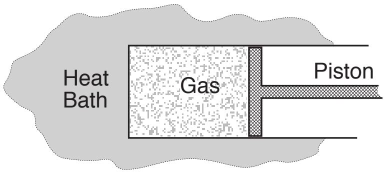

Fig. 5.2: Origin of the name *physical free energy* for $F(V,T,N)$.

These plus the Legendre transformation (5.51b) for $\bar{\mathcal{E}}$ (derivable from the canonical distribution function $\rho = \exp(-\mathcal{E}/k_BT)$ via the definition of entropy, $S = -k_B\overline{\ln\rho}$), give us all the thermodynamic quantities of interest as functions of the independent variables. Maxwell relations can be derived from the equality of mixed partial derivatives in Eqs. (5.54); for example, $(\partial P/\partial T)_{V,N} = (\partial S/\partial V)_{T,N}$.

Thus, as for the energy and grand-potential representations, all the equations of the physical-free-energy representation are easily deducible from the minimal information in Table 5.1: this representation's first law of thermodynamics, and its equilibrium distribution function.

5.4.1 Experimental Meaning of Physical Free Energy

The name *physical free energy* for F can be understood using the idealized experiment shown in Fig. 5.2. 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

$$\mathcal{E}_{\rm extracted} = \int_{V_i}^{V_f} -PdV \; . \tag{5.55a}$$

Using the first law $dF = -SdT + \tilde{\mu}dN - PdV$ and remembering that T and N are kept constant, Eq. (5.55a) becomes

$$\mathcal{E}_{\rm extracted} = F(V_f,T,N) \;-\; F(V_i,T,N) \equiv \Delta F \; . \tag{5.55b}$$

Thus, *F is the energy that is "free to be extracted" in an isothermal, physical expansion of the gas.*[6]

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. (5.12) tells us that there would have been no entropy change. Correspondingly, with S and N held fixed but V changing during the expansion,

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[6] More generally, the phrase "free energy" means the energy that can be extracted in a process that occurs in contact with some sort of environment. The nature of the free energy depends on the nature of the contact. We will meet "chemical free energy" in the next section.

the natural way to analyze the expansion would have been in the energy representation; and that representation's first law $d\mathcal{E} = -PdV + TdS + \tilde{\mu}dN$ would have told us that the total energy extracted, $\int -PdV$, was the change $\Delta\mathcal{E}$ of the gas's total energy. Such a process, which occurs without any heat flow or entropy increase, is called *adiabatic.* Thus, *the energy* $\mathcal{E}$ *(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.*

5.4.2 Ideal Gas with Internal Degrees of Freedom

As an example of the canonical distribution, we shall explore the influence of internal molecular degrees of freedom on the properties of a nonrelativistic, ideal gas. This example is complementary to the van der Waals gas that we analyzed in Sec. 5.3.2 using the grand canonical distribution. There we assumed no internal degrees of freedom, but we allowed each pair of particles to interact via an interaction potential $u(r)$ that depended on the particles' separation r. Here, because the gas is ideal, there are no interactions, but we allow for internal degrees of freedom — rotational, vibrational, and electron excitations.

(We have previously studied internal degrees of freedom in Sec. 4.4.4, where we proved the equipartition theorem for those whose generalized coordinates and/or momenta are quadratic in the Hamiltonian and are classically excited, e.g. the vibrations and rotations of a diatomic molecule. Here we allow the internal degrees of freedom to have any form whatsoever and to be excited or nonexcited arbitrarily.)

Our gas is confined to a fixed volume V, it has a fixed number of molecules N, it is in contact with a heat bath with temperature T, and its equilibrium distribution is therefore grand canonical, $\rho_n = e^{(F-E_n)/k_BT}$. The quantum states $|n\rangle$ available to the gas can be characterized by the locations $\{\mathbf{x}_i, \mathbf{p}_i\}$ in phase space of each of the molecules $i = 1, ..., N$, and by the state $|K_i\rangle$ of each molecule's internal degrees of freedom. Correspondingly, the partition function and physical free energy are given by

$$z = e^{-F/k_BT} = \frac{g_s}{N!}\int \frac{d^{3N}x d^{3N}p}{h^{3N}} \sum_{K_1,K_2,...K_N} \exp\left[-\sum_{i=1}^{N}\left(\frac{\mathbf{p}_i^2}{2mk_BT} + \frac{E_{K_i}}{k_BT}\right)\right] . \tag{5.56}$$

It is instructive to compare this with Eq. (5.28) for the grand partition function of the van der Waals gas. Here there is no sum over N and no $e^{\mu N/k_BT}$ because because N is fixed, and there is no interaction energy u_{ij} between molecules. However, we now have sums over the internal states K_i of each of the molecules, and a factor g_s to allow for the molecules' g_s different spin states in the multiplicity

Because there are no interactions between molecules, the partition function can be split up into products of independent contributions from each of the molecules; and because there are no interactions between a molecule's internal and translational degrees of freedom, the partition function can be split into a product of tranlational and internal terms; and because the molecules are all identical, their contributions are all identical, leading to

$$z = e^{-F/k_BT} = \frac{g_s}{N!}\left[\int \frac{d^3x d^3p}{h^3} e^{-\mathbf{p}^2/k_BT}\right]^N \left[\sum_K e^{-E_K/k_BT}\right]^N . \tag{5.57}$$

The $\int d^3x d^3p\, h^{-3} e^{-\mathbf{p}^2/k_BT}$ integral is the same as we encountered in the grand-canonical analysis; it gives V/λ^3 where $\lambda = 2\pi m k_B T/h$. The sum over internal states gives a contribution that is some function of temperature,

$$f(T) \equiv \sum_K e^{-E_K/k_BT} \; . \tag{5.58}$$

Correspondingly [using Stirling's approximation $N! \simeq 2\pi N^{1/2}(N/e)^N$] the physical free energy becomes

$$F(N,V,T) = Nk_BT \ln\left[\frac{N}{e}\frac{h^3}{(2\pi m k_BT)^3 V}\right] - Nk_BT\ln f(T) \; . \tag{5.59}$$

Note that because the molecules' translational and internal degrees of freedom are decoupled, their contributions to the free energy are additive We could have computed them separately, and then simply added their free energies.

Notice that, because the contribution of the internal degrees of freedom depends only on temperature and not on volume, the ideal gas's pressure

$$P = -(\partial F/\partial V)_{N,T} = (N/V)k_BT \tag{5.60}$$

is unaffected by the internal degrees of freedom. By contrast, the entropy and the total energy in the box do have internal contributions, which depend on temperature but not on the gas's volume and thence not on its density N/V:

$$S = -\left(\partial F/\partial T\right)_{N,V} = S_{\rm translational} + Nk_B(\ln f + d\ln f/d\ln T) \; , \tag{5.61}$$

where the entropy $S_{\rm translational}$ can straightforwardly be shown to be equivalent to the Sackur-Tetrode formula (4.41)[7]; and

$$\bar{E} = F + TS = Nk_BT\left(\frac{3}{2} + \frac{d\ln f}{d\ln T}\right) \; . \tag{5.62}$$

For degrees of freedom that are classical and quadratic, the internal contribution $Nk_BT d\ln f/d\ln T$ gives $\frac{1}{2}k_BT$ for each quadratic term in the Hamiltonian, in accord with the equipartition theorem (Sec. 4.4.4).

If there is more than one particle species present (e.g. electrons and protons at high temperatures so hydrogen is ionized), then the contributions of the species to F, P, S, and E simply add, just as the contributions of internal and translational degrees of freedom added in Eq. (5.59) above.

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[7] except that the factor g_s in that formula is an internal-degree-of-freedom factor and so appears in f.

Exercise 5.4 *Example and Derivation: Adiabatic Index for Ideal Gas*
In Part V, when studying fluid dynamics, we shall encounter an *adiabatic index*

$$\gamma \equiv -\left(\frac{\partial \ln p}{\partial \ln V}\right)_S \tag{5.63}$$

that describes how the pressure p of a fluid changes when it is compressed adiabatically, i.e. compressed at fixed entropy (with no heat being added or removed). Derive an expression for γ for an ideal gas that may have internal degrees of freedom, e.g., the Earth's atmosphere. More specifically:

(a) Consider a fluid element (a small sample of the fluid) that contains N molecules. These molecules can be of various species; all species contribute equally to the ideal gas's pressure $P = (N/V)k_BT$ and contribute additively to its energy. Define the fluid element's specific heat at fixed volume to be the amount of heat TdS that must be inserted to raise its temperature by an amount dT while the volume V is held fixed:

$$C_V \equiv T(\partial S/\partial T)_{V,N} = (\partial E/\partial T)_{V,N} \ . \tag{5.64}$$

Deduce the second equality from the first law of thermodynamics. Show that in an adiabatic expansion the temperature T drops at a rate given by $C_V dT = -pdV$. [Hint: use the first law of thermodynamics and the fact that for an ideal fluid the energy of a fluid element depends only on its temperature and not on its volume (or density), Eq. (5.62).]

(b) Combine the temperature change $dT = (-p/C_V)dV$ for an adiabatic expansion with the equation of state $PV = Nk_BT$ to obtain $\gamma = (C_V + Nk_B)/C_V$.

(c) To interpret the numerator $C_V + Nk_B$, imagine adding heat to a fluid element while holding its pressure fixed (which requires a simultaneous volume change). Show that in this case the ratio of heat added to temperature change is

$$C_p \equiv T(\partial S/\partial T)_{p,N} = C_V + Nk_B \ . \tag{5.65}$$

Combining with (b), conclude that the adiabatic index for an ideal fluid is given by

$$\gamma = C_p/C_V \ , \tag{5.66}$$

a standard result in elementary thermodynamics.

Exercise 5.5 ***Example: The Enthalpy Representation of Thermodynamics*

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

$$\boxed{H \equiv \mathcal{E} + PV} \ . \tag{5.67}$$

Show that this definition can be regarded as a Legendre transformation that converts from the energy representation of thermodynamics with $\mathcal{E}(V, S, N)$ 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

$$\boxed{dH = VdP + TdS + \tilde{\mu} dN}\;; \tag{5.68}$$

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. Show that each system of this ensemble (fluctuationally) exchanges volume and energy with a surrounding bath but does not exchange heat or particles, so the exchanged energy is solely that associated with the exchanged volume, $d\mathcal{E} = -PdV$, and the enthalpy H does not fluctuate.

(c) Show that this ensemble's distribution function is $\rho = e^{-S/k_B}$ =constant for those states in phase space that have a specified number of particles N and a specified enthalpy H. Why do we not need to allow for a small range δH of H, by analogy with the small range $\mathcal{E}$ for the microcanonical ensemble (Sec. 4.5 and Ex. 4.7).

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

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

(f) Show that the system's enthalpy is equal to its total inertial mass (multiplied by the speed of light squared); cf. Exs. 2.26 and 2.27.

(g) 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: $\Delta V/V = \Delta\mathcal{E}/\mathcal{E} = \Delta S/S \ll 1$. 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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5.5 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.

Each of the systems, in this case, has a fixed number of particles N_I for the various independent species I N_I, and it can exchange heat and volume with its surroundings. (We shall explicitly allow for more than one particle species because a major application of the Gibbs representation will be to chemical reactions.) There might be a membrane separating each system from its bath — a membrane impermeable to particles but through which heat can pass, and with negligible surface tension so the system and the bath can buffet each other freely, causing fluctuations in the system's volume. This is the case, e.g., for a so-called "constant-pressure balloon" of the type used to lift scientific payloads into the upper atmosphere. Usually, however, there is no membrane between system and bath. Instead, gravity might hold the system together because it has higher density than the bath (e.g. a liquid in a container), or solid-state forces might hold the system together (e.g. a crystal), or we might just introduce a conceptual, imaginary boundary around the system of interest — one that comoves with some set of particles.

The equilibrium ensemble, for this type of system, is that of Gibbs, with distribution function

$$\boxed{\rho = e^{G/k_BT} e^{-(\mathcal{E}+PV)/k_BT}}\,, \tag{5.69}$$

[Eq. (4.24b) to which we have added the normalization constant e^{G/k_BT}]. As for the canonical and grand canonical distributions, the quantity G in the normalization constant becomes the fundamental potential for the Gibbs representation of thermodynamics. It is called the *Gibbs potential*, and it is a function of the systems' fixed numbers of particles N_I and of the bath's temperature T and pressure P, which appear in the Gibbs distribution function: $G = G(N_I, T, P)$.

The Gibbs potential can be evaluated by a sum over quantum states that follows from $\sum_n \rho_n = 1$:

$$\boxed{e^{-G/k_BT} = \sum_n e^{-(\mathcal{E}_n+PV_n)/k_BT}}\,. \tag{5.70}$$

See Ex. 5.6 for an example. This sum has proved to be less useful than the canonical and grand canonical sums, so in most statistical mechanics textbooks there is little or no discussion of the Gibbs ensemble. By contrast, the Gibbs representation of thermodynamics is extremely useful as we shall see, so textbooks pay a lot of attention to it.

We can deduce the equations of the Gibbs representation by the same method as we used for the canonical and grand canonical representations:

We begin by writing down a Legendre transformation that takes us from the energy representation to the Gibbs representation. As for the canonical and grand canonical cases, that Legendre transformation can be inferred from the equilibrium ensemble's entropy, $S =$

$-k_B\overline{\ln\rho} = -(G - \bar{\mathcal{E}} + P\bar{V})/T$ [cf. Eq. (5.69) for ρ]. Solving for G, we get

$$\boxed{G = \bar{\mathcal{E}} + P\bar{V} - TS}\ . \tag{5.71}$$

Once we are in the thermodynamic domain (as opposed to statistical mechanics), we can abandon the distinction between expectation values of quantities and fixed values, i.e. we can remove the bars and write this Legendre transformation as $G = \mathcal{E} - TS + PV$.

Differentiating this Legendre transformation and combining with the energy representation's first law (5.8), we obtain the first law in the Gibbs representation:

$$\boxed{dG = VdP - SdT + \sum_I \tilde{\mu}_I dN_I\ .} \tag{5.72}$$

From this first law we read out the independent variables of the Gibbs representation, namely $\{P, T, N_I\}$ (in case we have forgotten them!) and the values of its generalized forces

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N_I}\ , \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N_I}\ , \quad \tilde{\mu}_I = \left(\frac{\partial G}{\partial N_I}\right)_{P,T}\ ; \tag{5.73}$$

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, intensive variables P, T and $\tilde{\mu}_I$) and applying the first law (5.72) to this buildup, we obtain the Euler relation

$$\boxed{G = \sum_I \tilde{\mu}_I N_I\ .} \tag{5.74}$$

This Euler relation will be very useful in Sec. 5.5.3, when we discuss chemical reactions.

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Exercise 5.6 *Problem and Practice: Ideal Gas Equation of State from Gibbs Ensemble*
For a nonrelativistic monatomic ideal gas (non interactions between particles), evaluate the statistical sum (5.70) to obtain G(P,T,N), and from it deduce the standard formula for the ideal-gas equation of state $P\bar{V} = Nk_BT$.

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5.5.1 Minimum Principles for Gibbs and Other Fundamental Thermodynamic Potentials

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 $\bar{\mathcal{E}} \equiv \sum_n \rho_n \mathcal{E}_n$ and volume $\bar{V} \equiv \sum_n \rho_n V_n$, and the ensemble will have some entropy $S = -k_B \sum_n \rho_n \ln \rho_n$. 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 *out-of-equilibrium* G is defined by the analog of the equilibrium definition (5.71)

$$G \equiv \bar{\mathcal{E}} + P\bar{V} - TS \ , \tag{5.75}$$

where P and T are the pressure and temperature of the identical baths with which the ensemble's systems are interacting.[8] 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 $\Delta\bar{\mathcal{E}}$, 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

$$\Delta\bar{\mathcal{E}}_{\rm bath} = -\Delta\bar{\mathcal{E}} \ , \quad \Delta\bar{V}_{\rm bath} = -\Delta\bar{V} \ . \tag{5.76a}$$

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

$$\Delta\bar{\mathcal{E}}_{\rm bath} = -P\Delta\bar{V}_{\rm bath} + T\Delta S_{\rm bath} + \tilde{\mu}\Delta N_{\rm bath} \ . \tag{5.76b}$$

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 Eqs. (5.76a), Eq. (5.76b) tells us that the baths' entropy changes by

$$\Delta S_{\rm bath} = \frac{-\Delta\bar{\mathcal{E}} - P\Delta\bar{V}}{T} \ . \tag{5.76c}$$

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

$$\Delta S_{\rm bath} + \Delta S = \frac{-\Delta\bar{\mathcal{E}} - P\Delta\bar{V} + T\Delta S}{T} \geq \ 0 \ . \tag{5.76d}$$

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

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[8] Notice that, because the number N of particles in the system is fixed as is the bath temperature T, the evolving Gibbs potential is proportional to

$$g \equiv \frac{G}{Nk_BT} = \frac{\bar{E}}{Nk_BT} + \frac{P\bar{V}}{Nk_BT} - \frac{S}{Nk_B} \ .$$

This quantity is dimensionless and generally of order unity. Note that the last term is the dimensionless entropy per particle [Eq. (4.43) and associated discussion].

any significant effect on the baths' intensive variables), the numerator of expression (5.76d) is equal to the evolutionary change in the ensemble's out-of-equilibrium Gibbs potential (5.75):

$$\boxed{\Delta S_{\rm bath} + \Delta S = \frac{-\Delta G}{T} \geq \ 0 \ .} \tag{5.77}$$

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' out-of-equilibrium 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 might be very short compared to the timescale for interaction with the heat and volume bath): The system's time-averaged energy $\bar{\mathcal{E}}$ 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 an out-of-equilibrium Gibbs potential $G = \bar{\mathcal{E}} + P\bar{V} - TS$. 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 $\mathcal{E}(V,S,N)$, one focuses on closed systems and switches to $S(V,\mathcal{E},N)$; and the extremum principle is then the standard second law of thermodynamics: An ensemble of closed systems of fixed $\mathcal{E}$, 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 $F(T,V,N)$ 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 out-of-equilibrium physical free energy* $F = \bar{\mathcal{E}} - TS$ *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. 5.3) satisfies the analogous minimum principle: *For an ensemble of systems interacting with a heat and particle bath, the out-of-equilibrium grand potential* $\Omega = \bar{\mathcal{E}} - \tilde{\mu}\bar{N} - TS$ *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. 5.5) the analogous extremum principle is a bit more tricky; see Ex. 5.13: *For an ensemble of systems interacting with a volume bath, as for an ensemble of closed systems, the bath's entropy remains constant, so the systems' entropy* S *will always increase, ultimately reaching a maximum when the ensemble reaches its final equilibrium distribution.*

In Table 5.2 we summarize these extremum principles. The first column lists the quantities that a system exchanges with its bath. The second column shows the out-of-equilibrium fundamental potential for the system, which depends on the bath variables and the system's out-of-equilibrium distribution function ρ (shown explicitly) and also on whatever quanti-

Bath	**Fundamental Potential**	**Total Entropy** $S+S_b$	**Second Law**	**Fluctuational Probability**
None	$S(\rho)$ with $\mathcal{E}$ const	$S+$ const	$dS \geq 0$	$\propto e^{S/k_B}$
V & $\mathcal{E}$ with $d\mathcal{E} = -PdV$	$S(P;\rho)$ with $H = \mathcal{E} + PV$ const	$S+$ const (see Ex. 5.13)	$dS \geq 0$	$\propto e^{S/k_B}$
Heat	$F(T;\rho) = \bar{\mathcal{E}} - TS$	$-F/T +$ const	$dF \leq 0$	$\propto e^{-F/k_BT}$
Heat & Volume	$G(T,P;\rho) = \bar{\mathcal{E}} + P\bar{V} - TS$	$-G/T+$ const	$dG \leq 0$	$\propto e^{-G/k_BT}$
Heat & Particle	$\Omega(T,\tilde{\mu},\rho) = \bar{\mathcal{E}} - \tilde{\mu}\bar{N} - TS$	$-\Omega/T +$ const	$d\Omega \leq 0$	$\propto e^{-\Omega/k_BT}$

Table 5.2: Deviations from Statistical Equilibrium; cf. Table 5.1.

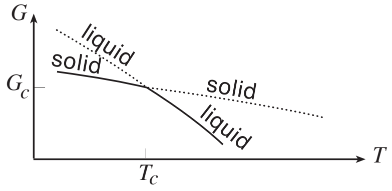

Fig. 5.3: The Gibbs potential $G(T,P,N)$ for H_2O as a function of temperature T with fixed P and N, near the freezing point 273K. The solid curves correspond to the actual path traversed by the H_2O if the phase transition is allowed to go. The dotted curves correspond to superheated solid ice and supercooled liquid water that are unstable against the phase transition because their Gibbs potentials 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 $G = E + PV - TS$.

ties are fixed for the system (e.g. its volume V and/or number of particles N; not shown explicitly). The third column expresses the total entropy of system plus bath in terms of the bath's out-of-equilibrium fundamental potential. The fourth column expresses the second law of thermodynamics for bath plus system in terms of the fundamental potential. We shall discuss the fifth column when we study fluctuations away from equilibrium, in Sec. 5.6.

5.5.2 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 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 nonrelativistic, 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

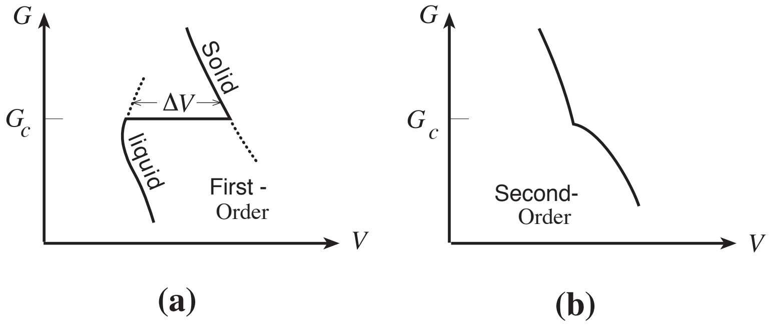

Fig. 5.4: The changes of volume (plotted rightward) with increasing Gibbs function (plotted upward) at fixed P and N for a first-order phase transition [diagram (a)] and a second-order phase transition [diagram (b)]. G_c is the critical value of the Gibbs potential at which the transition occurs.

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, for all relevant purposes. 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. 5.3. 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. 5.4(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 during the freezing (the *latent heat*) and the volume change ΔV are related to each other in a simple way; see Ex. 5.7, which focuses on the latent heat per unit mass Δq and the density change $\Delta\rho$ instead of on ΔQ and ΔV.

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

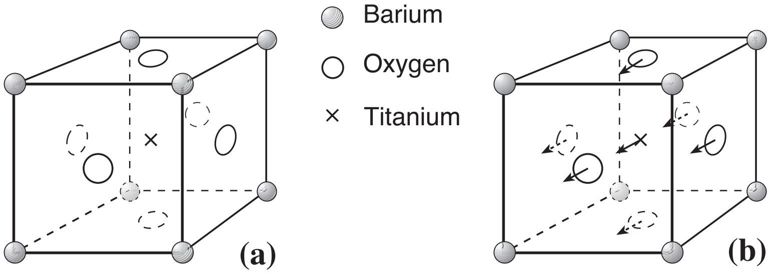

Fig. 5.5: (a) The unit cell for a $BaTiO_3$ crystal at relatively high temperatures. (b) The displacements of the titanium and oxygen ions relative to the corners of the unit cell, that occur in this crystal with falling temperature when it undergoes its second-order phase transition. The magnitudes 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 $T_c - T$.

as G decreases or holds T fixed or holds some combination of P and T fixed); see Fig. 5.4(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. 5.5(a) 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. 5.5(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. 5.5(a). The result is a discontinuity, at the critical temperature, in the rate of change of volume dV/dG [Fig. 5.4(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.

Bose-Einstein condensation of a bosonic atomic gas in a magnetic trap is another example of a second-order phase transition; see Sec. 4.9. As we saw in Ex. 4.12, for Bose condensation the specific heat of the atoms changes discontinuously (in the limit of an arbitrarily large number of atoms) at the critical temperature.

5.5.3 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

$$2\mathrm{H_2O} \ \leftrightarrow 2\mathrm{H_2} + \mathrm{O_2} \ . \tag{5.78}$$

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 (5.78) but long compared to the kinetic relaxation time, then we can regard the system as in ***partial*** *statistical equilibrium*, with fixed numbers of water molecules $N_{\rm H_2O}$, hydrogen molecules $N_{\rm H_2}$, and oxygen molecules $N_{\rm O_2}$, and with a Gibbs potential whose value is given by the Euler relation (5.74)

$$G = \tilde\mu_{\rm H_2O} N_{\rm H_2O} + \tilde\mu_{\rm H_2} N_{\rm H_2} + \tilde\mu_{\rm O_2} N_{\rm O_2} \ . \tag{5.79}$$

(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 (5.78), thereby changing the value of the Gibbs potential (5.79). 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 (5.79); 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

$$dN_{\rm H_2} = -dN_{\rm H_2O} \ , \qquad dN_{\rm O_2} = -\frac{1}{2} dN_{\rm H_2O} \ , \tag{5.80a}$$

we obtain

$$dG = (2\tilde\mu_{\rm H_2O} - 2\tilde\mu_{\rm H_2} - \tilde\mu_{\rm O_2})\frac{1}{2} dN_{\rm H_2O} \ . \tag{5.80b}$$

The reactions (5.78) 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 (i.e., increases the entropy of the molecules and their bath). Thus, if $2\tilde{\mu}_{\mathrm{H_2O}}$ is larger than $2\tilde{\mu}_{\mathrm{H_2}} + \tilde{\mu}_{\mathrm{O_2}}$, then water molecules preferentially break up to form hydrogen plus oxygen; but if $2\tilde{\mu}_{\mathrm{H_2O}}$ is less than $2\tilde{\mu}_{\mathrm{H_2}} + \tilde{\mu}_{\mathrm{O_2}}$, 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 the intimate connection

$$N_I = \frac{(2\pi m_I k_B T)^{3/2}}{h^3} e^{\mu_I / k_B T} V \tag{5.81}$$

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 (5.78) can no longer reduce G. In this final state of ***full** statistical equilibrium*, the dG of expression (5.80b) must be zero; and correspondingly, the combination of chemical potentials appearing in it must vanish:

$$2\tilde{\mu}_{\mathrm{H_2O}} = 2\tilde{\mu}_{\mathrm{H_2}} + \tilde{\mu}_{\mathrm{O_2}} \ . \tag{5.82}$$

The above analysis shows that *the "driving force" for the chemical reactions is the combination of chemical potentials in the dG of Eq. (5.80b).* Notice that *this combination has coefficients in front of the $\tilde{\mu}_I$'s that are identical to the coefficients in the reactions (5.78) themselves; and the equilibrium relation (5.82) also has the same coefficients as the reactions (5.80b).* It is easy to convince oneself that this is true in general:

Consider any chemical reaction. Write the reaction in the form

$$\sum_j \nu_j^L A_j^L \ \leftrightarrow \ \sum_j \nu_j^R A_j^R \ . \tag{5.83}$$

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 occurring in an environment of fixed temperature and pressure. Then to determine the direction in which the reaction preferentially goes, examine the chemical-potential sums for the two sides of the reaction,

$$\sum_j \nu_j^L \tilde{\mu}_j^L \ , \qquad \sum_j \nu_j^R \tilde{\mu}_j^R \ . \tag{5.84}$$

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 full statistical equilibrium. Exercises 5.8 and 5.9 illustrate this.

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 $dG = (2\mu_{\mathrm{H_2O}} - 2\mu_{\mathrm{H_2}} - \mu_{\mathrm{O_2}})\frac{1}{2} dN_{\mathrm{H_2O}}$

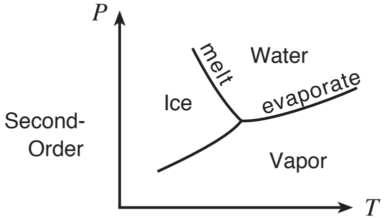

Fig. 5.6: Phase diagram for H_2O.

[Eq. (5.80b) 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 (Ex. 5.9) is an example.

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EXERCISES

Exercise 5.7 *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.5.6. 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. 5.6 (the "melting curve") is given by the "Clausius-Clapeyron equation"

$$\left(\frac{dP}{dT}\right)_{\rm melt} = \frac{\Delta q_{\rm melt}}{T}\left(\frac{\rho_{\rm ice}\;\rho_{\rm water}}{\rho_{\rm ice} - \rho_{\rm water}}\right), \tag{5.85a}$$

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

$$\frac{dP_{\rm vapor}}{dT} = \frac{\Delta q_{\rm evaporate}}{T}\left(\frac{\rho_{\rm water}\ \rho_{\rm vapor}}{\rho_{\rm water} - \rho_{\rm vapor}}\right) . \tag{5.85b}$$

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:

$$\left(\frac{dP_{\rm vapor}}{dP_{\rm total}}\right)_{T\ {\rm fixed}} = \frac{\rho_{\rm vapor}}{\rho_{\rm water}} > 0 \ , \tag{5.85c}$$

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

Exercise 5.8 *Example: Electron-Positron Equilibrium at "Low" Temperatures*

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

$$e^- + p \rightarrow e^- + p + e^- + e^+ \ . \tag{5.86}$$

[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 $\tilde\mu_+$ (with rest masses included)?

(b) Although these reactions require an e^- that is relativistic in energy, almost all the electrons and positrons will have kinetic energies of magnitude $\mathcal{E} - mc^2 \sim k_B T \ll mc^2$, and thus will have $\mathcal{E} \simeq mc^2 + \mathbf{p}^2/2m$. 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 $\eta \ll 1$ 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

$$n_\pm = \frac{2}{h^3}(2\pi m k_B T)^{3/2} \exp\left(\frac{\tilde\mu_\pm - mc^2}{k_B T}\right) . \tag{5.87}$$

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

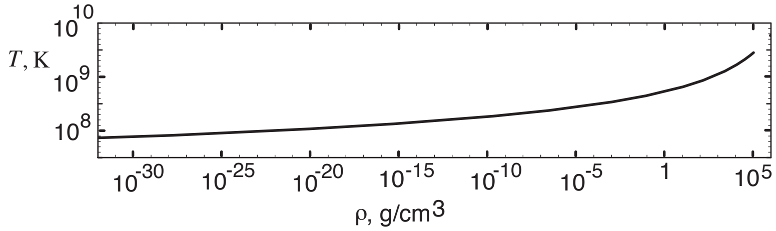

Fig. 5.7: The temperature T_p at which electron-positron pairs form in a dilute hydrogen plasma, plotted as a function of density ρ. This is the correct upper limit (upper dashed curve in Fig. 3.7) on the region where the plasma can be considered fully nonrelativistic. Above this curve, although T may be $\ll m_e c^2/k_B \simeq 6 \times 10^9$ K, a proliferation of electron-positron pairs radically changes the properties of the plasma.

(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

$$\frac{n_+}{n} = \frac{1}{2y[y + (1+y^2)^{\frac{1}{2}}]} \tag{5.88a}$$

where

$$y \equiv \frac{1}{4} n \lambda^3 e^{mc^2/k_B T} \ , \qquad \text{and} \quad \lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}} \tag{5.88b}$$

is the thermal deBroglie wavelength of the electrons. Fig. 5.7 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 $T \sim 10^8\,\mathrm{K} \simeq 0.02 m_e c^2/k_B$. Explain in terms of "available phase space" why the formation temperature is so low.

Exercise 5.9 *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 $\tilde{\mu}_\gamma$, $\tilde{\mu}_{\rm H}$, $\tilde{\mu}_e$, and $\tilde{\mu}_p$ be the chemical potentials *including rest mass-energies*; let $m_{\rm H}$, m_e, m_p be the rest masses; denote by $I \equiv$ (13.6 electron volts) the ionization energy of hydrogen, so that $m_{\rm H} c^2 = m_e c^2 + m_p c^2 \ - \ I$; denote

$\mu_j \equiv \tilde{\mu}_j - m_j c^2$; and assume that $T \ll m_e c^2/k_B \simeq 6 \times 10^9\,\mathrm{K}$, 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 $\tilde{\mu}_\gamma$, $\tilde{\mu}_{\rm H}$, $\tilde{\mu}_e$, and $\tilde{\mu}_p$?

(b) What are the number densities $n_{\rm H}$, n_e, and n_p expressed in terms of T and $\tilde{\mu}_{\rm H}$, $\tilde{\mu}_e$, $\tilde{\mu}_p$—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

$$\frac{n_e n_p}{n_{\rm H}} = \frac{(2\pi m_e k_B T)^{3/2}}{h^3} e^{-I/k_B T} \ . \tag{5.89}$$

This equation is widely used in astrophysics and elsewhere.

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5.6 Fluctuations of Systems in Statistical Equilibrium

As we saw in Chap. 4, statistical mechanics is built on a distribution function ρ that 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 system's interactions with its surroundings. Classical thermodynamics makes use of only a tiny portion of the information in this probability distribution: the mean values of a few macroscopic parameters (energy, entropy, volume, pressure, ...). Also contained in the distribution function, but ignored by classical thermodynamics, is detailed information about fluctuations of a system away from its mean values.

As a simple example, consider fluctuations of the number of particles in one of the cells with volume V depicted in Fig. 5.1. The cell has imaginary walls and is immersed in a bath of identical, nonrelativistic, noninteracting, classical particles (ideal gas) with temperature T and chemical potential μ. We want to know the probability p_N that the cell has N particles in it.

That probablility can be deduced from the cell's grand canonical distribution function $\rho_n = \exp[(\Omega - E_n - \mu N_n)/k_B T]$. All we need to do is identify those quantum states for the cell that have precisely N particles, and then sum ρ_n over those states. This is easy. Our standard expression for summing ρ_n over all states $|n\rangle$,

$$1 = \sum_n \rho_n = \frac{1}{\exp(-\Omega/k_B T)} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{d^{3N}x\, d^{3N}p}{h^{3N}} \exp\left[\frac{-E_n - \mu N_n}{k_B T}\right] \ , \tag{5.90}$$

is already broken down explicitly into contributions from states with fixed numbers N of particles in the cell. The portion with fixed N is the probability we seek. It is instructive to write that portion of the sum in the following form:

$$p_N = \frac{\exp[-\Omega(N;V,T,\mu)/k_BT)]}{\exp[-\Omega(V,T,\mu)/k_BT]} \ , \tag{5.91a}$$

where

$$\exp\left[\frac{-\Omega(N;V,T,\mu)}{k_BT}\right] \equiv \frac{1}{N!}\int \frac{d^{3N}xd^{3N}p}{h^{3N}} \exp\left[\frac{-E_n - \mu N_n}{k_BT}\right] \tag{5.91b}$$

is the N-particle portion of the statistical sum (5.16) by which we compute $\exp[-\Omega(V,T,\mu)/k_BT]$.

The quantity $\Omega(N;V,T,\mu)$, in fact, is the out-of-equilibrium grand potential discussed briefly in Sec. 5.5.1 and summarized on the bottom line of Table 5.2. As indicated in that table (bottom row, third entry), the total entropy of the bath plus our cell, when our cell is known to contain N particles and we view the bath plus cell to be a closed system, is $S_N^{\rm tot} = -\Omega(N;V,T,\mu)/T$, aside from an additive constant. By the relationship $p \propto e^{S/k_B}$ between probability and entropy for closed systems, $e^{S_N^{\rm tot}/k_B} \propto e^{-\Omega(N;V,T,\mu)/k_BT}$ must be proportional to the probability p_N that our cell contains N particles. This is a second way to understand Eq. (5.91a).

The last entry in Table 5.2 summarizes the general form of this result: *For any system in contact with a heat and particle bath, the probability of some fluctuation away from equilibrium is proportional to* $e^{-\Omega/k_BT}$, *where* Ω *is the out-of-equilibrium grand potential for the system, in that out-of-equilibrium macrostate,* e.g., in the *macrostate* where there are N particles in our cell.

For our cell immersed in a heat and particle bath, the probability p_N [Eqs. (5.91)] is evaluated explicitly in Ex. 5.10, with the result that p_N is a Poisson distribution:

$$p_N = e^{-\bar N}\frac{\bar N^N}{N!} \ . \tag{5.92a}$$

The mean $\bar N$ of this distribution is equal to the number predicted by thermodynamics or kinetic theory, $\bar N/V = P/k_BT =$ expression (3.37a), and its root-mean-square fluctuation away from the mean (i.e., the square root of its variance) 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 (5.92a) is extremely well approximated by a Gaussian. To convert to that Gaussian, take the logarithm of Eq. (5.92a), 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

$$p_N = \frac{1}{\sqrt{2\pi\bar N}}\exp\left[-\frac{(N-\bar N)^2}{2\bar N}\right] \ . \tag{5.92b}$$

In the next chapter (Sec. 5.2) we shall learn that the probability distribution (5.92a) *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.

As another example of fluctuations away from statistical equilibrium, consider a microcanonical ensemble of boxes, each with volume V and each containing precisely N identical, dilute ($\eta \ll 1$), 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. 4.7). Focus attention on a set of quantities y_j that characterize these boxes of gas and that are *not* fixed by the set $E,\ V,\ N$. For example, y_1 might be the total number N_R of particles in the right half of a box, and y_2 might be the total energy E_R 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., $y_1 = N_R$), 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

$$N_{\rm states}(y_j; E, V, N) = \exp[S(y_j; E, V, N)/k_B]\ ; \tag{5.93}$$

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

$$p(y_j; E, V, N) = \frac{N_{\rm states}(y_j; E, V, N)}{\sum_{y_j} N_{\rm states}(y_j; E, V, N)} = \text{const} \times \exp\left[\frac{S(y_j; E, V, N)}{k_B}\right]. \tag{5.94a}$$

Similarly, if the y_j take on a continuous range of values (e.g., $y_2 = E_R$), then the probability of finding y_j in some tiny, fixed range dy_j is proportional to $\exp[S(y_j; E, V, N)/k_B]$, and correspondingly the probability per unit y_j interval of finding a system to have specific values is

$$\frac{dp(y_j; E, V, N)}{dy_1 dy_2 \ldots dy_r} = \text{const} \times \exp\left[\frac{S(y_j; E, V, N)}{k_B}\right]. \tag{5.94b}$$

In expressions (5.94a) and (5.94b), the entropy $S(y_j; E, V, N)$ is 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.

The probability distributions (5.94a) and (5.94b), though "exact," are not terribly instructive. To get better insight we expand S 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. (5.94a) and Eq. (5.94b) become

$$p(y_j; E, V, N) \text{ or } \frac{dp(y_j; E, V, N)}{dy_1 dy_2 \ldots dy_r} = \text{const} \times \exp\left[\frac{1}{2k_B}\left(\frac{\partial^2 S}{\partial y_j \partial y_k}\right)(y_j - \bar{y}_j)(y_k - \bar{y}_k)\right]. \tag{5.94c}$$

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 (5.94c) 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.

The last entry in the first line of Table 5.2 summarizes the above equations: *For a closed system, the probability of some fluctuation away from equilibrium is proportional to* e^{S/k_B}, *where S is the total entropy for the out-of-equilibrium fluctuational macrostate*, e.g., the macrostate with N_R particles in the right half box.

For the specific example where $y_1 \equiv N_R$ =(number of particles in right half of box) and $y_2 \equiv E_R$ =(amount of energy in right half of box), and assuming the gas is ideal (no interactions between particles), we can infer $S(N_R, E_R; N, E, V)$ from Eq. (4.41) as applied to the two halves of the box and then added:

$$\begin{aligned} S(N_R, E_R; N, E, V) &= k_B N_R \ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} e^{5/2} \frac{V}{2} \frac{E_R^{3/2}}{N_R^{5/2}}\right] \\ &+ k_B (N - N_R) \ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} e^{5/2} \frac{V}{2} \frac{(E - E_R)^{3/2}}{(N - N_R)^{5/2}}\right] . \end{aligned} \tag{5.95a}$$

It is straightforward to compute the values $\bar{E}_R$ and $\bar{N}_R$ of E_R and N_R that maximize this entropy:

$$\bar{E}_R = \frac{E}{2}, \qquad \bar{N}_R = \frac{N}{2}. \tag{5.95b}$$

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 (5.95a) the second partial derivatives of the entropy with respect to E_R and N_R, evaluate them at $E_R = \bar{E}_R$ and $N_R = \bar{N}_R$, and plug them into the probability distribution (5.94c). The result is

$$\frac{dp_{N_R}}{dE_R} = \text{const} \times \exp\left(\frac{-(N_R - N/2)^2}{2(N/4)} + \frac{-[(E_R - E/2) - (E/N)(N_R - N/2)]^2}{2(N/6)(E/N)^2}\right) . \tag{5.95c}$$

[There is no dN_R in the denominator of the left side because N_R is a discrete variable.] This Gaussian distribution has the following interpretation: (*i*) there is a correlation between the energy E_R and the particle number N_R 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_R is $E_R - (E/N)N_R$, as one might have expected. (*iii*) For fixed N_R, dp_{N_R}/dE_R is Gaussian with mean $\bar{E}_R = E/2 + (E/N)(N_R - N/2)$ and with rms fluctuation (square root of variance) $\sigma_{E_R} = (E/N)\sqrt{N/6}$. (*iv*) After integrating over E_R, we obtain

$$p_{N_R} = \text{const} \times \exp\left[\frac{-(N_R - N/2)^2}{2N/4}\right] . \tag{5.95d}$$

This is Gaussian with mean $\bar{N}_R = N/2$ and rms fluctuation $\sigma_{N_R} = \sqrt{N/4}$. By contrast, if the right half of the box had been in equilibrium with a bath far larger than itself, N_R would have had an rms fluctuation equal to the square root of its mean, $\sigma_{N_R} = \sqrt{N/2}$ [the Poisson distribution (5.11)]. 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 rms fluctuation 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. (5.92), (5.95c), and (5.95d) 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^{26} for a cubic meter of the Earth's atmosphere, and thus the fractional fluctuations of thermodynamic quantities are of order

10^{-13}.) 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.

The generalization of our two examples (cell in a heat and particle bath, and closed box) to other situations should be fairly obvious. The generalization is summarized in Table 5.2. When a system is in some out-of-equilibrium macrostate, the total entropy $S + S_b$ of the system and any bath with which it may be in contact is, up to an additive constant, either the system's entropy S, or the negative of its out-of-equilibrium potential divided by the bath's temperature ($-F/T$+const, $-G/T$+const, or $= -\Omega/T$+const (column 3 of Table 5.2). Correspondingly, the probability of a fluctuation into this out-of-equilibrium macrostate is proportional to the exponential of this quantity in units of Boltzmann's constant (e^{-S/k_B}, e^{-F/k_BT}, e^{-G/k_BT} or $e^{-\Omega/k_BT}$; column 5 of Table 5.2). By expanding the quantity in the exponential around the equilibrium state, to second order in the fluctuations, one obtains a Gaussian probability distribution for the fluctuations.

In Ex. 5.11, the reader can work out the example of temperature and volume fluctuations for a system in contact with a heat and volume bath; in this case the starting point (next to last line in Table 5.2) is a fluctuational probability proportional to e^{-G/k_BT}, where G is the out-of-equilibrium Gibbs function.

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EXERCISES

Exercise 5.10 ***Example: Probability Distribution for the Number of Particles in a Cell*

Suppose that we make a large number of measurements of the number of atoms in one of the cells of Fig. 5.1, and that from those measurements we compute the probability p_N for that cell to contain N particles.

(a) How widely spaced in time must the measurements be to guarantee that the measured probability distribution is the same as that which one computes from the ensemble of cells at a specific moment of time?

(b) Assume that the measurements are widely enough separated for this criterion to be satisfied. Use Eqs. (5.91) to show that the probability p_N for the cell to contain N particles is given by the *Poisson distribution*

$$p_N = e^{-\bar{N}}(\bar{N}^N/N!) \ , \tag{5.96a}$$

where $\bar{N}$ is given by the standard equation for the mean number of particles in a cell, $\bar{N} = (\sqrt{2\pi m k_B T}/h)^3 e^{\mu/k_BT} V$ [Eq. (3.37a)].

(c) Show that for the Poisson distribution (5.96a), the expectation value is $\langle N \rangle = \bar{N}$, and the root mean square deviation from this is

$$\sigma_N \equiv \langle (N - \bar{N})^2 \rangle^{\frac{1}{2}} = \bar{N}^{\frac{1}{2}} \ . \tag{5.96b}$$

Exercise 5.11 *Example: Fluctuations of Temperature and Volume in an Ideal Gas*
Consider a gigantic container of gas made of identical particles that might or might not interact. Regard this gas as a bath, with temperature T_b and pressure P_b. Pick out at random a sample of the bath's gas containing precisely N particles, with $N \gg 1$. Measure the volume V of the sample and the temperature T inside the sample. Then pick another sample of N particles and measure its V and T, and repeat over and over again. Thereby map out a probability distribution $dp/dTdV$ for V and T of N-particle samples inside the bath.

(a) Explain in detail why

$$\frac{dp}{dTdV} = \text{const}\times\exp\left[-\frac{1}{2k_BT_b}\left(\frac{\partial^2 G}{\partial V^2}(V-\bar{V})^2+\frac{\partial^2 G}{\partial T^2}(T-T_b)^2+2\frac{\partial^2 G}{\partial T\partial V}(V-\bar{V})(T-T_b)\right)\right] , \tag{5.97a}$$

where $G(T,V,N)$ is the equilibrium Gibbs function for a sample of N particles interacting with this bath, $\bar{V}$ is the equilibrium volume of the sample when its temperature and pressure are those of the bath, and the double derivatives in Eq. (5.97a) are evaluated at the equilibrium temperature T_b and pressure P_b.

(b) Show that the derivatives are given by

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{V,N} = \frac{C_V}{T_b}, \quad \left(\frac{\partial^2 G}{\partial V^2}\right)_{T,N} = \frac{1}{\kappa}, \quad \left(\frac{\partial^2 G}{\partial T\partial V}\right)_{N} = 0 , \tag{5.97b}$$

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

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_{V,N} , \quad \kappa \equiv -\left(\frac{\partial V}{\partial P}\right)_{T,N} , \tag{5.97c}$$

both evaluated at temperature T_b and pressure P_b. Thereby conclude that

$$\frac{dp}{dTdV} = \text{const} \times \exp\left[-\frac{(V-\bar{V})^2}{2k_BT_b\kappa} - \frac{C_V(T-T_b)^2}{2k_BT_b^2}\right] . \tag{5.97d}$$

(d) This probability distribution says that the temperature and volume fluctuations are uncorrelated. Is this physically reasonable? Why?

(e) What are the rms fluctuations of the sample's temperature and volume, σ_T and σ_V. Show that these both scale as $1/\sqrt{N}$, where N is the number of particles in the samples. Is this physically reasonable? Why?

Exercise 5.12 *Example: Fluctuations and Phase Transitions in a van der Waals Gas*
Consider the van der Waals gas studied in Sec. 5.3.2, for which the equation of state is

$$\left(P + \frac{a}{(V/N)^2}\right)(V/N - b) = k_BT , \tag{5.98}$$

where a and b are constants [Eq. (5.46)].

(a) Show that the equation of state has the form depicted in Fig. 5.8a. What is the critical temperature $T_{\rm crit}$ below which the curve in Fig. 5.8a has a local maximum and a local minimum?

(b) Where along the curves in Fig. 5.8a is the gas stable against volume fluctuations, and where is it unstable? [Hint, see Ex. 5.11.] 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. 5.8b to another point B. Use the principle of minimum Gibbs potential (Sec. 5.5) to prove that the straight line from A to B in Fig. 5.8b 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 5.13 *Example: Evolution and Fluctuations of a System in Contact with a Volume Bath*

Exercise 5.5 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 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 $d\mathcal{E} = -P_b dV$. This implies that the system's enthalpy $H = \mathcal{E} + P_b V$ is conserved. All systems in the ensemble are assumed to have the same enthalpy H and the same number of particles N.

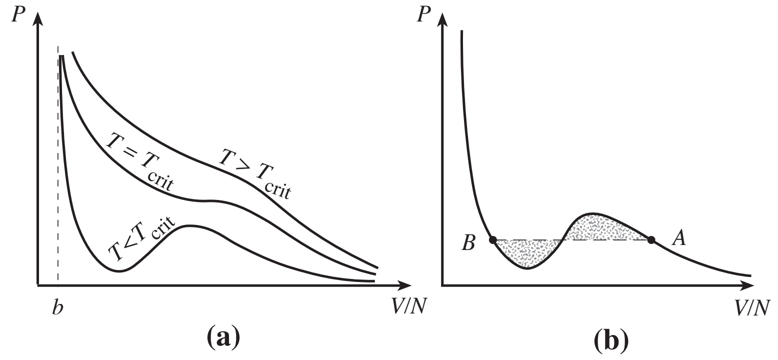

Fig. 5.8: (a) The van der Waals equation of state $P(N, V, T)$ plotted as pressure P versus specific volume V/N at fixed temperature T, for various values of the temperature T. (b) The route of a phase transition in the van der Waals gas. The transition is a discontinuous jump from point A to point B.

(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 5.1): $\rho = e^{-S/k_B} =$ const for all regions of phase space that have the specified particle number N and enthalpy H.

(d) Show that fluctuations away from equilibrium are described by the probability distributions (5.94a) and (5.94b), but with the system energy E replaced by the system enthalpy H; cf. Table 5.2.

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5.7 $\boxed{\text{T2}}$ Renormalization Group Methods for The Ising Model of a Ferromagnetic Phase Transition

In Sec. 5.5.2 we 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 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 methods by two examples: the *renormalization group*, and *Monte Carlo* techniques.[9]

We shall illustrate these methods using the so-called Ising model[10] 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 $-Jss'$ (where $J > 0$) that is attractive if the spins are aligned ($s = s'$) and repulsive if they are opposite ($s = -s'$). The Ising model does not explicitly include more distant interactions, though they are surely present, because they are unnecessary for a phase transition: the "knock-on" effect from one spin to the next, as we shall see, introduces an indirect long range organization that propagates across the lattice when the temperature is reduced below a critical value, inducing the transition.

The interaction's proportionality constant J depends on V/N, $J = \mathcal{F}(V/N)$, where N is the total number of spins and V is the lattice's 2-dimensional volume (i.e. its area), which are both held constant. (Recall from Sec. 5.5 that the volume does not change at a second order phase transition.) For later use, we introduce a dimensionless, positive parameter

$$K \equiv \frac{J}{k_B T} = \frac{\mathcal{F}(V/N)}{k_B T} \,. \tag{5.99}$$

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

[10] After E. Ising, who first investigated it, in 1925.

The actual functional form of $\mathcal{F}$ will be unimportant.

When the temperature is so high that $J \ll k_B T$, i.e. 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 approaches $-2NJ$. 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 paper by Lars Onsager (1944).

The key idea behind the renormalization group approach to the Ising model is to try to replace the full lattice by a sparser lattice that has similar thermodynamic properties, and then to iterate, making the lattice more and more sparse; cf Fig. 5.9. 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 $e^{-F/k_B T} \equiv z = \sum_n e^{-E_n/k_B T}$. For our Ising model with its nearest-neighbor interaction energies, Eq. (5.99), this sum becomes

$$z = \sum_{\{s_1=\pm1, s_2=\pm1, \ldots\}} e^{K\Sigma^1 s_i s_j} . \tag{5.100a}$$

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. (5.100a) so that each of the open-circle spins of Fig. 5.9, 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:

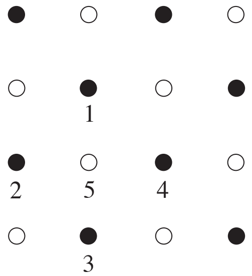

Fig. 5.9: Partition of a square lattice into two interlaced square lattices (solid circles and open circles). In the renormalization group approach, the open-circle spins are removed from the lattice, and all their interactions are replaced by modified interactions between the remaining solid-circle spins. The new lattice is rotated by $\pi/4$ with respect to the original lattice and the lattice spacing increases by a factor $\sqrt{2}$.

$$\begin{aligned} z &= \sum_{\{\ldots,s_4=\pm1,s_5=\pm1,s_6=\pm1,\ldots\}} \cdots e^{K(s_1+s_2+s_3+s_4)s_5} \ldots \\ &= \sum_{\{\ldots s_4=\pm1,s_6=\pm1\ldots\}} \cdots \left[e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)}\right] \cdots . \end{aligned} \tag{5.100b}$$

(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:

$$\begin{aligned} &\left[e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)}\right] \\ &= f(K) e^{\frac{1}{2}K_1(s_1s_2+s_2s_3+s_3s_4+s_4s_1)+K_2(s_1s_3+s_2s_4)+K_3s_1s_2s_3s_4} . \end{aligned} \tag{5.100c}$$

We can determine the four functions $K_1(K), K_2(K), K_3(K), f(K)$ by substituting each of the four possible distinct combinations of $\{s_1, s_2, s_3, s_4\}$, into Eq. (5.100b). Those four combinations, arranged in the pattern of the solid circles of Fig. YYY, are $+\overset{+}{\underset{+}{}}+$, $-\overset{+}{\underset{+}{}}-$, $+\overset{+}{\underset{-}{}}-$, and $+\overset{+}{\underset{+}{}}-$. [Rotating the pattern or changing all signs leaves both sides of Eq. (5.100c) unchanged.] By inserting these combinations into Eq. (5.100c)) and performing some algebra, we obtain

$$\begin{aligned} K_1 &= \frac{1}{4}\ln\cosh(4K) , \\ K_2 &= \frac{1}{8}\ln\cosh(4K) , \\ K_3 &= \frac{1}{8}\ln\cosh(4K) - \frac{1}{2}\ln\cosh(2K) , \\ f(K) &= 2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8} . \end{aligned} \tag{5.100d}$$

By inserting expression (5.100c) and the analogous expressions for the other terms into Eq. (5.100b), 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:

$$z(N,K) = [f(K)]^{N/2} \sum e^{[K_1\Sigma^1 s_is_j + K_2\Sigma^2 s_is_j + K_3\Sigma^3 s_is_js_ks_l]} . \tag{5.100e}$$

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. (5.100c) 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. (5.100e).]

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 (5.100e), we drop completely the quadruple interaction (i.e. 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

$$K' = K_1 + K_2 = \frac{3}{8} \ln \cosh(4K). \tag{5.101}$$

(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 $-(K_1 + K_2)Nk_BT$, is the same as that of a lattice in which we just include the nearest neighbor bonds, but strengthen the interaction from K_1 to K'. Clearly this will be unsatisfactory at high temperature, but we only need it to be true near the phase transition's critical temperature.

These approximations bring the partition function (5.100e) into the form

$$z(N, K) = [f(K)]^{N/2} z(N/2, K') \;, \tag{5.102a}$$

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, $F = -k_BT \ln z$, is an extensive variable, $\ln z$ must increase in direct proportion to the number of spins; i.e, it must have the form

$$-F/k_BT \equiv \ln z(N, K) = Ng(K) \tag{5.102b}$$

for some function $g(K)$. By combining Eqs. (5.102a) and (5.102b), we obtain a relation for the function $g(K)$ (the free energy, aside from constants) in terms of the function $f(K)$:

$$g(K') = 2g(K) - \ln f(K) \;, \quad \text{where} \quad f(K) = 2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8} \tag{5.103}$$

[cf. Eq. (5.100d)].

Equations (5.101) and (5.103) are the fundamental equations that allow us to calculate thermodynamic properties. They are called the *renormalization group equations* because their transformations form a mathematical group, and they are a scheme for determining how the effective coupling parameter K changes (gets renormalized) when one views the lattice on larger and larger distance scales. Renormalization group equations like these have been widely applied in elementary particle theory, condensed matter theory, and elsewhere. Let us examine them in detail.

The iterative map (5.101) expresses the coupling constant K' for a lattice of enlarged physical size and reduced number of particles $N/2$ in terms of K for the smaller lattice with N particles. (And the associated map (5.103) expresses the free energy when the lattice is viewed on the larger scale in terms of that for a smaller scale.) The map (5.101) has a fixed point that is obtained by setting $K' = K$; i.e., $K_c = \frac{3}{8}\ln\cosh(4K_c)$, which implies

$$K_c = 0.507\ . \tag{5.104}$$

This fixed point corresponds to the critical point for the phase transition, with critical temperature T_c such that $K_c = J/k_B T_c$. We can infer that this is the critical point by the following physical argument: Suppose that T is slightly larger than T_c, so K is slightly smaller than K_c. Then, when we make successive iterations, because $dK'/dK > 1$ at $K = K_c$, K decreases with each step, moving farther from K_c; the fixed point is unstable. What this means is that, when $T > T_c$, as we look on larger and larger scales, the effective coupling constant K becomes weaker and weaker, so the lattice becomes more disordered. Conversely, below the critical temperature ($T < T_c$ and $K > K_c$), 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 outside inward (at high temperature) to inside outward (at low temperature).

To demonstrate more explicitly that $K = K_c$ is the location of a phase transition, we shall compute the lattice's specific heat in the vicinity of K_c. The first step 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. (5.99)] and using expression (5.102b) for F, we see that

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = N k_B \left[g - K\left(\frac{dg}{dK}\right)\right]\ . \tag{5.105a}$$

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

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = N k_B K^2 \frac{d^2 g}{dK^2}\ . \tag{5.105b}$$

Next we note that, because the iteration (5.101) is unstable near K_c, the inverse iteration

$$K = \frac{1}{4}\cosh^{-1}[\exp(8K'/3)] \tag{5.105c}$$

is stable. The corresponding inverse transformation for the function $g(K)$ is obtained from Eq. (5.103), with f from (5.100d) and K in that f converted to K' using (5.100d):

$$g(K) = \frac{1}{2}g(K') + \frac{1}{2}\ln\{2\exp(2K'/3)[\cosh(4K'/3)]^{1/4}\} \tag{5.105d}$$

Now, we know that at low temperature, $T \ll T_c$ and $K \gg K_c$, all the spins are aligned; correspondingly, in the statistical sum (5.100a) the two terms with all s's identical dominate, giving $z = e^{-F/k_B T} = e^{Ng} = 2e^{2NK}$, whence $g(K) \simeq 2K$. Conversely, at high temperature, there is complete disorder and $K \to 0$. This means that every one of the 2^N terms in the statistical sum (5.100a) is unity, giving $z = e^{Ng} = 2^N$, whence $g(K) \simeq \ln 2$. We can therefore use the iterative map, Eqs. (5.105c), (5.105d), to approach $K = K_c$ from either side starting with the high temperature and low temperature limits of $g(K)$ and evaluating thermodynamic quantities at each step. More specifically, at each step, we evaluate $g(K)$, dg/dK

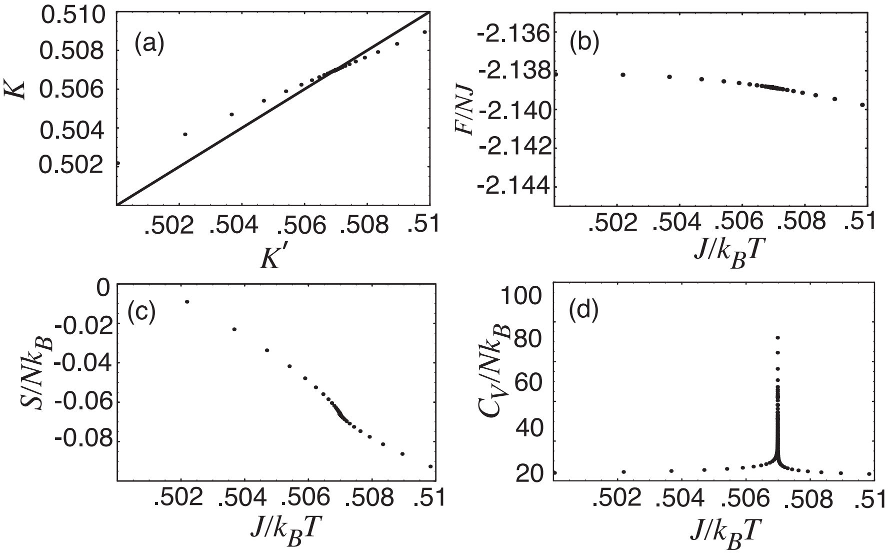

Fig. 5.10: (a) Iteration map $K(K')$ in the vicinity of the critical point. (b) Free energy per spin (c) Entropy per spin, (d) Specific heat per spin. Recall that $J/k_B T = K$.

and d^2g/dK^2 numerically, and from them we compute F, S and C_V using Eqs. (5.102b), (5.105a), and (5.105b).

The iterated values of these quantities are plotted as points in Fig. 5.10. Note that the specific heat [panel (d)] diverges at K_c, as $K \to K_c$ from either side, verifying that this is a second order phase transition.

In order to calculate the explicit form of this divergence, suppose that $g(K)$ is a sum of an analytic (infinitely differentiable) function and a non-analytic part. Suppose that near the critical point, the nonanalytic part behaves as $g(K) \sim |K - K_c|^{2-\alpha}$ for some "critical exponent" α. This implies that C_V diverges $\propto |K - K_c|^{-\alpha} \propto |T - T_c|^{-\alpha}$. Now, from Eq. (5.105d), we have that

$$|K' - K_c|^{2-\alpha} = 2|K - K_c|^{2-\alpha}, \tag{5.106a}$$

or equivalently,

$$\frac{dK'}{dK} = 2^{1/(2-\alpha)}. \tag{5.106b}$$

Evaluating the derivative at $K = K_c$ from Eq. (5.105c), we obtain

$$\alpha = 2 - \frac{\ln 2}{\ln(dK'/dK)_c} = 0.131\ , \tag{5.106c}$$

which is consistent with the numerical calculation.

The exact Onsager (1944) analysis of the Ising model gives $K_c = 0.441$ compared to our $K_c = 0.507$, and $C_V \propto -\ln|T - T_c|$ compared to our $C_V \propto |T - T_c|^{-0.131}$. Evidently, our renormalization group approach gives a fair approximation to the correct answers, but not a good approximation.

Our approach appears to have a serious problem in that it predicts a negative value for the entropy in the vicinity of the critical point [panel (c) of Fig. 5.10]. This is surely unphysical. (The entropy becomes positive further away, on either side of the critical point.) This is an artificiality associated with our approach's ansatz [i.e., associated with our setting $K_2 = K_3 = 0$ and $K' = K_1 + K_2$ in Eq. (5.101)]. It does not seem easy to cure this within a renormalization group approach. Nonetheless, our calculations exhibit the physical essentials of the renormalization group approach to phase transitions.

Why did we bother to go through this cumbersome procedure when Onsager has given us an exact analytical solution to the Ising model? 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 an Onsager-like solution to the three-dimensional Ising model. 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 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 5.14 *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

$$z(N, K) = f(K)^{N/2} z(N/2, K') \tag{5.107}$$

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.

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5.8 T2 Monte Carlo Methods for the Ising Model

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.[11] It will be instructive to tackle the same two dimensional Ising problem that we discussed in the last section.

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[11] The name "Monte Carlo" is a laconic reference to the casino whose patrons believe they will profit by exploiting random processes.

The Monte Carlo approach is much more straightforward in principle than the renormalization group approach. We set up a square lattice of spins as in Sec. 5.7 and initialize the spins randomly. (This calculation will be performed numerically and requires 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 imagine that our lattice is in contact with a thermal bath with a fixed temperature T – it is one member of a canonical ensemble of systems – and we allow it to approach equilibrium by changing the orientations of its spins in a prescribed, random manner. Our goal is to compute thermodynamic quantities using $\bar{X} = z^{-1}\sum_n e^{-E_n/k_BT}X_n$ where the sum is over all states of the lattice spins. For example we can compute the specific heat (at constant volume) from

$$C_V = \frac{d\bar{E}}{dT} = \frac{\partial}{\partial T}\left(\frac{\sum_n e^{-E_n/k_BT}E_n}{\sum_n e^{-E_n/k_BT}}\right) = \frac{\overline{E^2} - \bar{E}^2}{k_BT^2}.$$

(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. 5.6.)

In order to compute quantities like C_V, we replace ensemble averages by averages over successive configurations $|n\rangle$ of the lattice. Clearly, we cannot visit every one of the lattice's 2^N configurations and so we must sample these fairly. How do we prescribe the rules for changing the spins when going from one configuration in our sample to the next? There are many answers to this question; we shall just describe and use one of the simplest, due to Metropolis et al (1953). In order to understand this, we must appreciate that we don't need to comprehend the detailed dynamics by which a spin in a lattice actually flips. All that is required is that the rule we adopt should maintain thermodynamic equilibrium.

Let us label by $|n\rangle$ a single lattice state, specified by a matrix whose entries are ± 1, and denote by E_n its total energy. In addition, let us denote by $p_{nn'}$ the probability of making a transition from a state $|n\rangle$ to a new state $|n'\rangle$. Now, in a steady state, the probability of transitions into state $n\rangle$ is equal to the probability of transitions out of that state:

$$\sum_{n'} \rho_{n'} p_{n'n} = \rho_n \sum_{n'} p_{nn'} \; . \tag{5.108a}$$

However, we know that in equilibrium,

$$\rho_{n'} = \rho_n \exp[(E_n - E_{n'})/k_BT] \; . \tag{5.108b}$$

The Metropolis rule is simple:

$$\text{if } E_n > E_m, \text{ then } p_{nm} = 1; \text{ and if } E_n < E_m, \text{ then } p_{nm} = \exp[(E_n - E_m)/k_BT]. \tag{5.109}$$

It is easy to show that this satisfies statistical equilibrium [Eq. (5.108a)] and that it drives 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 $\exp[-\Delta E/k_BT]$, where $\Delta E > 0$ is the energy change. (Actually, there is a small subtlety here. The probability of making a given transition is actually the product of the probability of making the trial flip and of accepting the trial. However, the probability of making a trial flip is the same for all the spins that we might flip ($1/N$), and these trial probabilities cancel, so 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 a particularly convenient procedure for the Ising problem because, by changing just one spin at a time, ΔE can only take one of 5 values ($-4, -2, 0, +2, +4$ in units of J), and it is possible to change from one state to the next very quickly. (It also helps to store the two acceptance probabilities e^{-2J/k_BT} and e^{-4J/k_BT} for making an energy-gaining transition, so as to avoid evaluating exponentials at every step.)

How big a lattice do we need 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 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 compute 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 for Monte Carlo simulation that can be used for variance reduction and estimation, but we only concern ourselves here with the general method.

Returning to the Ising problem, we show in Fig. 5.11 typical equilibrium lattices for three temperatures (measured in units of J/k_B). Recall that the critical temperature is $T_c = J/k_BK_c = 2.268J/k_B$. Note the increasingly long range order as the temperature is reduced beyond T_c.

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

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EXERCISES

Exercise 5.15 *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.

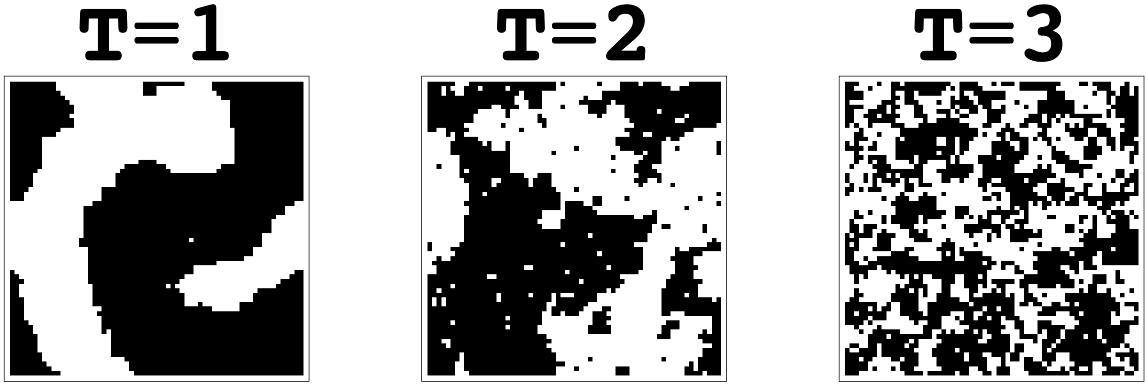

Fig. 5.11: Typical equilibrium Ising lattices for temperatures $T = 1, 2, 3$ in units of J/k_B. The black regions have spins $s = +1$; the white, $s = -1$.

Exercise 5.16 *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 5.17 *Problem: Ising Lattice with an Applied Magnetic Field*
It is straightforward to generalize our approach to the problem of a lattice placed in a uniform magnetic field B. This adds a term $\propto -Bs$ to the spin energy $-Jss'$. Modify the computer program from Ex (5.16) to include this term, and compute the magnetization and the magnetic susceptibility.

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Bibliographic Note

Most statistical mechanics textbooks include much detail on statistical thermodynamics. Among those we have found useful are Chandler (2007), Kardar (2007), Pathria (1972), and Reif (1965). Chandler (2007) gives a particularly nice treatment of phase transitions, on which Sec. 5.7 is largely based.

Bibliography

Binney, J. J., Dowrick, N. J., Fisher, A. J. & Newman, M. E. J. 1992 *The Theory of Critical Phenomena* Oxford: Oxford University Press

Chandler, D. 1987 *Introduction to Modern Statistical Mechanics*Oxford: Oxford University Press

Box 5.3
Important Concepts in Chapter 5

- **Representations of thermodynamics and their equilibrium ensembles and distributions**
  - Summary: Table 5.1, Sec. 5.2.6
  - Thermodynamic concepts: extensive and intensive variables, fundamental potential and its independent variables, Legendre transformations, generalized forces, Euler's equation, Maxwell relations, Secs. 5.2–5.5
  - Measuring devices for intensive variables, Sec. 5.2.2
  - Energy representation and microcanonical distribution, Sec. 5.2
  - Grand-potential representation and grand-canonical distribution, Sec. 5.3
  - Physical Free-energy representation and canonical distribution, Sec. 5.4
  - Gibbs representation and Gibbs distribution, Sec. 5.5
  - Enthalpy representation and enthalpy distribution: Ex. 5.5
- **Systems out of equilibrium**
  - Entropy increase $\Delta S = \Delta Q/T$ when energy is added in arbitrary way to an equilibrium system, Sec. 5.2.5
  - Entropy increase for each ensemble, expressed in terms of out-of-equilibrium fundamental potential, Table 5.2, Sec. 5.5.1
  - Partial statistical equilibrium, Sec. 5.5.3
  - Fluctuations away from statistical equilibrium, Table 5.2, Sec. 5.6, Exs. 5.10 and 5.11
- **Computational techniques**
  - most important statistical sums for fundamental potentials, Eqs. (5.19d), (5.50)
  - thermodynamic equations deduced from first law in each representation, Sec. 5.2.4, ends of Secs. 5.3.1, 5.4, 5.5
  - renormalization group, Sec. 5.7
  - Monte Carlo calculations, Sec. 5.8
- **Important applications**
  - phase transitions; first order and second order, Sec. 5.5.2
  - Chemical reactions–the direction they go and their equilibria, Sec. 5.5.3
  - Saha equation for ionization equilibrium, Ex. 5.9
  - van der Waals gas, Sec. 5.3.2; its fluctuations and phase transition, Ex. 5.12
  - Ferromagnetic phase transition, Secs. 5.7, 5.8

Goldstein, H. 1959 *Classical Mechanics* New York: Addison Wesley

Kardar, M. 2007. *Statistical Physics of Particles*, Cambridge: Cambridge University Press

Kittel, Charles 1958 *Elementary Statistical Physics*New York: Wiley

Maris, H. J. & Kadanoff, L. J. 1978 Am. J. Phys. 46 652

Metropolis, N., Rosenbluth, A., Rosenbluth, M., Teller, A. & Teller, E. 1953 J Chem. Phys. 21 1087

Onsager, L. 1944. "Crystal statistics. I. A two-dimensional model with an order-disorder transition", Phys. Rev. **65**, 117149,

Pathria, R. K. 1972 Statistical Mechanics Oxford: Oxford University Press

Press, W. H., Teukolsky, S. A., Vetterling, W. T. & Flannery, B. P. 1992 *Numerical Recipes*Cambridge: Cambridge University Press

Reif, F. 1965. *Fundamentals of Statistical and Thermal Physics,* New York: McGraw-Hill.

Tranah, D. & Landberg, P. T. 1980 Collective Phenomena 3 81

Zel'dovich, Ya. B. & Novikov, I. D. 1971 *Relativistic Astrophysics. Volume 1, Stars and Relativity*Chicago: University of Chicago Press