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 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, 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. an ideal gas[1]) 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 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. 5.11.

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 quantum states, 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 are advised 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 discover how the Gibbs potential can be used to study spontaneous fluctuations of a system away from equilibrium, when it is

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[1] An *ideal gas* is one with neglible interactions between its particles.

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 $= e^{-S/k_B}$ H const
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 systems in statistical equilibrium, in relativistic notation. The nonrelativistic formulae are the same but with the rest masses of particles removed from the chemical potentials, ($\tilde{\mu} \to \mu$) and from all fundamental potentials except Ω ($\mathcal{E} \to E$ but no change of notation for H, F, G). This table will be very hard to understand until after reading the sections referenced in column one.

coupled to a heat and particle bath. In Sec. 5.7, we employ these tools to explore fluctuations and the gas-to-liquid phase transition for a model of a real gas due to van der Waals. Out-of-equilibrium aspects of statistical mechanics (evolution toward equilibrium and fluctuations away from equilibrium) are summarized in Table 5.2 and discussed in Secs. 5.5.1 and 5.6, not just for heat and volume baths, but for a variety of baths.

Deriving the macroscopic properties of real materials by statistical sums over thgeir quantum states can be formidably difficult. Fortunately, in recent years a number of powerful approximation techniques have been devised for performing the statistical sums. In Secs. 5.8.3 and 5.8.4, 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* (Sec. 4.4.2) whose magnitudes are independent of the system's size. Familiar examples of extensive variables are a system's total energy $\mathcal{E}$, entropy S, volume V, and number of conserved particles of various species N_I. Corresponding examples of intensive variables are temperature T, pressure P, 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 extensive variables and all the intensive 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 a delicate issue.)

For simplicity, we now shall specialize, temporarily, to a microcanonical ensemble of one-species systems, which all have identically the same values of a complete set of *three* extensive variables: the energy $\mathcal{E}$,[2] 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 $S = k_B \ln N_{\rm states}$ [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 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

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[2] 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 $\delta\mathcal{E}$.

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 quantum 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

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

[cf. Eq. (4.14)].

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 with energy $\mathcal{E}$ or $\mathcal{E} - \Delta\mathcal{E}$ (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 $\mathcal{E}(S,N,V)$

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

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

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

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.

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

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,[3] and the second from the viewpoint of the combined system's microcanonical

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[3] 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).

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 an externally imposed magnetic field $\mathbf{B}$ and a material's magnetization $\mathbf{M}$; Sec. 5.8). 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

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

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EXERCISES

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

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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.* We discuss this for the one-species system whose first law is $d\mathcal{E} = TdS + \tilde{\mu}dN - PdV$. The generalization to other systems should be obvious.

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) [4]

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

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 nonrelativistic, classical, perfect gas,[5] 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 each of the gas's particles 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

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[4] There are a few (but 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 $\Omega_H =$ (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.

[5] Recall (Ex. 4.6) that a *perfect gas* is one that is ideal (i.e., has negligible interactions between its particles) and whose particles have no excited internal degrees of freedom. The phrase "perfect gas" must not be confused with "perfect fluid": a fluid whose viscosity is negligible so its stress tensor, in its rest frame, consists solely of an isotropic pressure.

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:

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

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., $\partial^2 E/\partial V \partial S = \partial^2 E/\partial S \partial V$) 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 such as Eqs. (4.14) between intensive and extensive variables, must satisfy the Maxwell relations. For our simple example of a nonrelativistic, classical, perfect 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.

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EXERCISES

Exercise 5.2 *Derivation: Energy Representation for a Nonrelativistic, Classical, Perfect Gas*

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

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

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

$$P = \frac{N}{V} k_B T \,, \tag{5.12}$$

which we derived in Ex. 3.7 using kinetic theory

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5.2.5 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.

5.3 Grand Canonical Ensemble and the Grand Potential Representation of Thermodynamics

We now turn to the grand canonical ensemble, and its grand-potential representation of thermodynamics, for a semi-closed system that exchanges heat and particles with a thermalized bath. For simplicity, we shall assume that all the particles are identical (just one particle species), but wecshall 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 and rotations, Sec. 5.4.2), and allow them to exert forces on each other via an interaction potential that appears in their Hamiltonian (e.g. van der Waals forces; Secs. 5.3.2 and 5.7). We shall refer to these particles as a gas, though our analysis is more general than gases. The nonrelativistic limit of all our fundamental equations is trivially obtained by removing particle rest masses from the chemical potential ($\tilde{\mu}$ gets replaced by $\mu = \tilde{\mu} - m$), but not from the Grand potential as it never has rest masses in it [see, e.g., Eq. (5.18) below]

We shall begin in Sec. 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 a relativistic perfect gas. In Sec. 5.3.2, 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):

$$\boxed{\rho_n = \frac{1}{Z}\exp\left(\frac{-\mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right) = \exp\left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right)}\,. \tag{5.13}$$

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.,

$$\boxed{Z \equiv \exp\left(\frac{-\Omega}{k_B T}\right) \equiv \sum_n \exp\left(\frac{-\mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right)}\,. \tag{5.14}$$

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*

$$\boxed{\Omega(V, \tilde{\mu}, T)}\,, \tag{5.15}$$

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

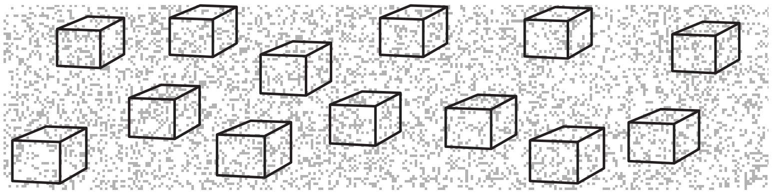

Fig. 5.1: An ensemble of cells, each with volume V and imaginary walls, inside a heat and particle bath.

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):

$$\overline{\mathcal{E}} \equiv \sum_n \rho_n \mathcal{E}_n \ , \quad \text{and } \overline{N} \equiv \sum_n \rho_n N_n \ . \tag{5.16}$$

(We denote these with bars $\bar{\mathcal{E}}$ rather than brackets $\langle \mathcal{E} \rangle$ for ease of notation.) Inserting expression (5.13) for ρ_n into the log term in the definition of entropy $S = -k_B \sum_n \rho_n \ln \rho_n$ and using Eqs. (5.16), we obtain

$$S = -k_B \sum_n \rho_n \ln \rho_n = -k_B \sum_n \rho_n \left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu} N_n}{k_B T} \right) = -\frac{\Omega - \overline{\mathcal{E}} + \tilde{\mu}\overline{N}}{T} ; \tag{5.17}$$

or, equivalently

$$\boxed{\Omega = \overline{\mathcal{E}} - TS - \tilde{\mu}\overline{N}} \ . \tag{5.18}$$

This 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[6], for switching from one set of independent variables to another.) Note that removing rest masses from $\bar{\mathcal{E}} = \bar{E} + Nm$ and from $\tilde{\mu} = \mu + m$ to get a nonrelativistic formula leaves Ω unchanged.

We now ask how the grand potential will change if the temperature T and chemical potential $\tilde{\mu}$ of the bath and therefore of the ensemble are slowly altered, and the volumes V of all the ensemble's boxes are slowly altered. Differentiating Eq. (5.18), we obtain $d\Omega = d\bar{\mathcal{E}} - TdS - SdT - \tilde{\mu} d\bar{N} - \bar{N} d\tilde{\mu}$. Expressing $d\mathcal{E}$ in terms of the energy representation's first law of thermodynamics (5.7) (with $\mathcal{E}$ replaced by $\bar{\mathcal{E}}$ and N replaced by $\bar{N}$), we bring this into the form

$$\boxed{d\Omega = -PdV - \overline{N} d\tilde{\mu} - SdT} \ . \tag{5.19}$$

This is the *grand potential representation* of the first law of thermodynamics. 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 (5.19): V, $\tilde{\mu}$, and T. From the form (5.19) 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.

---

[6] For example, Goldstein, Poole and Safko (2002).

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 (5.19) tells us that this buildup will produce

$$\boxed{\Omega = -PV}\ . \tag{5.20}$$

Thus, if we happen to know P as a function of this representation's independent variables $P(V, \tilde{\mu}, T)$ (actually, P 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. (5.24a) and (5.25) below as a concrete example.

By comparing the grand-potential version of the first law (5.19) 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:

$$\overline{N} = -\left(\frac{\partial\Omega}{\partial\tilde{\mu}}\right)_{V,T}\ , \quad S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\tilde{\mu}}\ , \quad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{\tilde{\mu},T}\ . \tag{5.21}$$

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. (5.24a) below], then Eqs. (5.21) 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. (5.18) (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. (5.17) 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.

It should be easy to convince oneself that *the nonrelativistic versions of all the above equations in this section can be obtained by the simple replacements $\mathcal{E} \to E$ (removal of rest masses from total energy) and $\tilde{\mu} \to \mu$ (removal of rest mass from chemical potential).*

5.3.2 Nonrelativistic van der Waals Gas

The statistical sum $Z \equiv e^{-\Omega/k_BT} = \sum_n e^{(-\mathcal{E}_n + \tilde{\mu}N_n)/k_BT}$ [Eq. (5.14)] 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: a relativistic, perfect gas.

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 r_o 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

$$u(r) = \varepsilon_o \left[\left(\frac{r_o}{r}\right)^{12} - \left(\frac{r_o}{r}\right)^{6} \right] , \tag{5.22a}$$

where ε_o is a constant energy. 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

$$u(r) = \infty \text{ for } r < r_o \ , \quad u(r) = -\varepsilon_o (r_o/r)^6 \text{ for } r > r_o \ , \tag{5.22b}$$

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 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

$$Z = e^{-\Omega/k_BT} = \sum_{N=0}^{\infty} \frac{e^{\mu N/k_BT}}{N!} \int \frac{d^{3N}x d^{3N}p}{h^{3N}} \exp\left[-\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2mk_BT} - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{u_{ij}}{k_BT} \right] . \tag{5.23a}$$

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

$$u_{ij} \equiv u(r_{ij}), \quad r_{ij} \equiv |\mathbf{x}_i - \mathbf{x}_j| \tag{5.23b}$$

of the $\frac{1}{2}N(N-1)$ pairs of particles.

The evaluation of the integrals and sum in Eq. (5.23a), with the particles' interaction energies given by Eqs. (5.23b) and (5.22b), is a rather complex task, which we relegate to the Track-Two Box 5.3. The result for the Grand potential $\Omega = -k_BT \ln Z$, accurate to first order in the particles' interactions (in the parameters a and b below) is:

$$\Omega = -k_BTV \frac{(2\pi mk_BT)^{3/2}}{h^3} e^{\mu/k_BT} \left[1 + \frac{(2\pi mk_BT)^{3/2}}{h^3} e^{\mu/k_BT} \left(\frac{a}{k_BT} - b \right) \right] . \tag{5.24a}$$

Box 5.3

$\boxed{\text{T2}}$ Derivation of van der Waals Grand Potential

In Eq. (5.23a) the momentum integrals and the space integrals separate, and the N momentum integrals are identical, so Z takes the form

$$Z = \sum_{N=0}^{\infty} \frac{e^{\mu N/k_B T}}{N! h^{3N}} \left[\exp\left(- \int_0^\infty \frac{4\pi p^4 dp}{2mk_B T} \right) \right]^N J_N = \sum_{N=0}^{\infty} \frac{(\zeta/\lambda^3)^N}{N!} J_N \ , \tag{1}$$

where

$$\zeta \equiv e^{\mu/k_B T} \ , \quad \lambda \equiv \frac{h}{(2\pi m k_B T)^{1/2}} \ , \quad J_N = \int d^{3N}x \exp\left[- \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{u_{ij}}{k_B T} \right] \ . \tag{2}$$

Note that λ is the particles' thermal deBroglie wavelength. The Boltzmann factor $e^{-u_{ij}/k_B T}$ is unity for large interparticle separations $r_{ij} \gg r_o$, so we write

$$e^{-u_{ij}/k_B T} \equiv 1 + f_{ij} \ , \tag{3}$$

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 J_N into the form

$$J_N = \int d^{3N}x \prod_{i=1}^{N} \prod_{j=i+1}^{N} (1 + f_{ij}) \ . \tag{4}$$

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

$$J_N = \int d^{3N}x [1 + \underbrace{(f_{12} + f_{13} + ...)}_{n_1 \text{ terms}} + \underbrace{(f_{12}f_{34} + f_{13}f_{24} + ...)}_{n_2 \text{ terms}} + \underbrace{(f_{12}f_{34}f_{56} + f_{13}f_{24}f_{56} + ...)}_{n_3 \text{ terms}} ...] \ , \tag{5}$$

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

$$V_o \equiv \int f(r) d^3 r \sim r_o^3 \ , \tag{6}$$

and performing the integrals, we bring Eq. (5) into the form

$$J_N = \sum_{\ell=0}^{\infty} n_l V^{N-\ell} V_o^\ell \ . \tag{7}$$

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. (7) is

$\boxed{\text{T2}}$ Box 5.3 Continued

$$n_\ell = \frac{N(N-1)\cdots(N-2\ell+1)}{\ell!}(2\ell-1)!! = \frac{N(N-1)\cdots(N-2\ell+1)}{2^\ell \ell!} \; . \tag{8}$$

Inserting Eqs. (7) and (8) into Eq. (1) for the partition function, we obtain

$$Z = \sum_{N=0}^{\infty} \frac{(\zeta/\lambda^3)^N}{N!} \sum_{\ell=0}^{[N/2]} \frac{N(N-1)\cdots(N-2\ell+1)}{2^\ell \ell!} V^{N-\ell} V_o^\ell \; , \tag{9}$$

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

$$Z = \sum_{\ell=0}^{\infty} \sum_{N=2\ell}^{\infty} \frac{1}{(N-2\ell)!} \left(\frac{\zeta V}{\lambda^3}\right)^{N-2\ell} \frac{1}{\ell!} \left(\frac{\zeta V}{\lambda^3} \frac{\zeta V_o}{2\lambda^3}\right)^{\ell} \; . \tag{10}$$

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

$$Z = e^{-\Omega/k_B T} = \exp\left(\frac{\zeta V}{\lambda^3}\right) \exp\left(\frac{\zeta V}{\lambda^3}\frac{\zeta V_o}{\lambda^3}\right) = \exp\left[\frac{\zeta V}{\lambda^3}\left(1 + \frac{\zeta V_o}{2\lambda^3}\right)\right] \; . \tag{11}$$

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

$$\Omega = \frac{-k_B T \zeta V}{\lambda^3}\left(1 + \frac{\zeta V_o}{2\lambda^3}\right) \; . \tag{12}$$

From kinetic theory [Eq. (3.37a)], we know that for an ideal 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. (12)]. The higher-order corrections are derived in statistical mechanics textbooks such as Pathria and Beale (2011, Chap. 10) and Kardar (2007, Chap. 5) using a technique called *the cluster expansion.*

For the "hard-wall" potential (5.22b), 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

$$\frac{V_o}{2} \equiv \frac{1}{2}\int f(r) d^3 r = \frac{a}{k_B T} - b \; , \quad \text{where} \quad b = \frac{2\pi r_o^3}{3} \; , \quad a = b\varepsilon_o \; . \tag{13}$$

Inserting this expression for $V_o/2$ and Eqs. (2) for ζ and λ into Eq. (12), we obtain Eqs. (5.24) for the grand potential of a van der Waals gas.

Here b is four times the volume of each hard-sphere particle, and a is that volume times the interaction energy ϵ_o of two hard-sphere particles when they are touching:

$$b = \frac{16\pi}{3}\left(\frac{r_o}{2}\right)^3 \ , \quad a = b\epsilon_0 \ . \tag{5.24b}$$

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:

$$\begin{aligned} P &= -\left(\frac{\partial\Omega}{\partial V}\right)_{\mu,T} = k_BT\frac{(2\pi m k_BT)^{3/2}}{h^3}e^{\mu/k_BT}\left[1 + \frac{(2\pi m k_BT)^{3/2}}{h^3}e^{\mu/k_BT}\left(\frac{a}{k_BT} - b\right)\right] \ , \\ \bar{N} &= -\left(\frac{\partial\Omega}{\partial \mu}\right)_{V,T} = V\frac{(2\pi m k_BT)^{3/2}}{h^3}e^{\mu/k_BT}\left[1 + 2\frac{(2\pi m k_BT)^{3/2}}{h^3}e^{\mu/k_BT}\left(\frac{a}{k_BT} - b\right)\right] \end{aligned} \tag{5.25}$$

Notice that, when the interaction energy is turned off so $a = b = 0$, the second equation gives our standard ideal-gas particle density $\bar{N}/V = (2\pi m k_BT)^{3/2}e^{\mu/k_BT}/h^3 = \zeta/\lambda^3$. Inserting this into the square bracketed expression in Eqs. (5.25), taking the ratio of expressions (5.25) and multiplying by V and expanding to first order in $a/k_BT - b$, we obtain $PV/\bar{N} = k_BT[1 + (\bar{N}/V)(b - a/k_BT)]$ — accurate to first order in $(b - a/k_BT)$. 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*

$$\boxed{\left(P + \frac{a}{(V/\bar{N})^2}\right)(V/\bar{N} - b) = k_BT} \ . \tag{5.26}$$

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

Comments: (i) The factor $(V/\bar{N} - b)$ in the equation of state corresponds to an excluded volume $b = (16\pi/3)(r_o/2)^3$ that is four times larger than the actual volume of each hard-sphere particle (whose radius is $r_o/2$). (ii) The term linear in a, $P = -a\bar{N}/V = -\epsilon_o\bar{N}/V$ is a pressure reduction due to the attactive force between particles. (iii) Our derivation is actually only accurate to first order in a and b, so it does not justify the quadratic term $P = ab(\bar{N}/V)^2$ in the equation of state (5.26). That quadratic term, however, does correspond to the behavior of real gases: a sharp rise in pressure at high densities due to the short-distance repulsion between particles.

We shall study this van der Waals equation of state in Sec. 5.7 below, focusing on the gas-to-liquid 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 Classical, Relativistic, Perfect Gas*
Consider cells that reside in a heat and particle bath of a classical, relativistic, perfect gas (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

$$W = 3N \ , \quad \mathcal{N}_{\rm states} = \frac{1}{N!h^{3N}} \ , \quad \mathcal{E}_N = \sum_{j=1}^{N} ({\bf p}_j{}^2 + m^2)^{\frac{1}{2}} \ , \tag{5.27a}$$

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 (5.14) for the grand partition function becomes

$$Z = e^{-\Omega/k_BT} = \sum_{N=0}^{\infty} \frac{V^N}{N!h^{3N}} e^{\tilde\mu N/k_BT} \left[\int_0^\infty \exp\left(-\frac{(p^2+m^2)^{\frac{1}{2}}}{k_BT} \right) 4\pi p^2 dp \right]^N \ . \tag{5.27b}$$

(d) Evaluate the momentum integral in the nonrelativistic limit $k_BT \ll m$, and thereby show that

$$\Omega(T,\mu,V) = -k_BTV\frac{(2\pi m k_BT)^{3/2}}{h^3} e^{\mu/k_BT} \ , \tag{5.28a}$$

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 (5.24a) for a van der Waals gas.

(e) Show that in the extreme relativistic limit $k_BT \gg m$, Eq. (5.27b) gives

$$\Omega(T,\tilde\mu,V) = -\frac{8\pi V (k_BT)^4}{h^3} e^{\tilde\mu/k_BT} \ . \tag{5.29}$$

(f) For the extreme relativistic limit use your result (5.29) 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 the energy density is $\overline{\mathcal{E}}/V = 3P$ (a relation valid for any ultrarelativistic gas); and that $\overline{\mathcal{E}}/\overline{N} = 3k_BT$ (which is higher than the $2.7011780\ldots k_BT$ for black-body radiation, as derived in Ex. 3.12, 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 single-species 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. 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)

$$\boxed{\rho_n = \frac{1}{z} e^{-\mathcal{E}_n/k_BT} \equiv e^{(F-\mathcal{E}_n)/k_BT}} \, . \tag{5.30}$$

Here, as in the grand canonical ensemble [Eq. (5.13)], we have introduced special notations for the normalization constant: $1/z = e^{F/k_BT}$, 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 systems' quantum states $|n\rangle$ (with 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 $\sum_n \rho_n = 1$:

$$\boxed{e^{-F/k_BT} \equiv z(T,N,V) = \sum_n e^{-\mathcal{E}_n/k_BT}} \, . \tag{5.31}$$

This canonical sum over states, like the grand canonical sum (5.14) that we used for the van der Waals gas, is a powerful tool in statistical mechanics. As an example, in Secs. 5.8.3 and 5.8.4 we shall use the canonical sum to evaluate the physical free energy F for a model of ferromagnetism, and shall 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 $S = -k_B \sum_n \rho_n \ln \rho_n = -k_B \overline{\ln \rho}$, which, with Eq. (5.30) for ρ_n, implies $S = (\bar{\mathcal{E}} - F)/T$. It is helpful to rewrite this as an equation for the physical free energy F

$$\boxed{F = \bar{\mathcal{E}} - TS} \, . \tag{5.32}$$

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

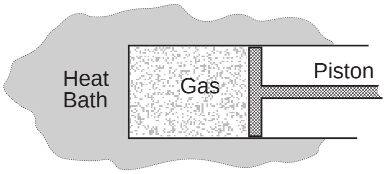

Fig. 5.2: Origin of the name *physical free energy* for $F(V,T,N)$.

Suppose that the canonical ensemble's parameters T, N, V are changed slightly. By how much will the physical free energy change? Equation (5.32) tells us that $dF = d\bar{\mathcal{E}} - TdS - SdT$. 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

$$\boxed{dF = -SdT + \tilde{\mu}dN - PdV} . \tag{5.33}$$

Equation (5.33) 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 (5.33); they appear as differentials on the right hand side: T, N and V. The fundamental potential is the quantity that appears on the left side of the first law: $F(T,N,V)$. 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:

$$\boxed{F = \tilde{\mu}N - PV} . \tag{5.34}$$

From the first law (5.33) we read off equations of state for this representation's generalized forces, e.g. $-S = (\partial F/\partial T)_{N,V}$. Maxwell relations can be derived from the equality of mixed partial derivatives.

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. And as for those representations, *the Newtonian version of this representation's fundamental equations (5.30)–(5.34) is obtained by simply removing rest masses from* $\tilde{\mu}$ *(which becomes* μ*),* $\mathcal{E}$ *(which becomes* E*), and* F *(whose notation does not change.)*

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

$$\mathcal{E}_{\rm extracted} = \int_{V_i}^{V_f} -PdV \; . \tag{5.35a}$$

Using the first law $dF = -SdT + \tilde\mu dN - PdV$ and remembering that T and N are kept constant, Eq. (5.35a) becomes

$$\mathcal{E}_{\rm extracted} = F(V_f, T, N) \; - \; F(V_i, T, N) \equiv \Delta F \; . \tag{5.35b}$$

Thus, *F is the energy that is "free to be extracted" in an isothermal, physical expansion of the gas.*[7]

If the expansion had been done in a chamber that was perfectly thermally insulated, so no heat could flow in or out of it, then there would have been no entropy change. Correspondingly, with S and N held fixed but V changing during the expansion, the natural way to analyze the expansion would have been in the energy representation; and that representation's first law $d\mathcal{E} = -PdV + TdS + \tilde\mu dN$ 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

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[7] 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 Sec. 5.5, and the free energy of a body on which a steady force is acting in Sec. 11.8.

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

$$z = e^{-F/k_BT} = \frac{g_s}{N!} \int \frac{d^{3N}x d^{3N}p}{h^{3N}} \sum_{K_1,K_2,...K_N} \exp\left[-\sum_{i=1}^{N} \left(\frac{\mathbf{p}_i^2}{2mk_BT} + \frac{E_{K_i}}{k_BT} \right) \right] . \tag{5.36a}$$

It is instructive to compare this with Eq. (5.23a) for the grand partition function of the van der Waals gas. Here there is no interaction energy u_{ij} between molecules, and there is no sum over N and no $e^{\mu N/k_BT}$ because N is fixed and there is no bath. 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

$$z = e^{-F/k_BT} = \frac{g_s}{N!} \left[\int \frac{d^3xd^3p}{h^3} e^{-\mathbf{p}^2/k_BT} \right]^N \left[\sum_K e^{-E_K/k_BT} \right]^N . \tag{5.36b}$$

The $\int d^3xd^3p\, h^{-3} e^{-\mathbf{p}^2/k_BT}$ integral is the same as we encountered in the grand-canonical analysis; it gives V/λ^3 where $\lambda = h/(2\pi mk_BT)$ [cf. Eq. (1)]. The sum over internal states gives a contribution that is some function of temperature,

$$f(T) \equiv \sum_K e^{-E_K/k_BT} . \tag{5.37}$$

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

$$F(N,V,T) = Nk_BT \ln\left[\frac{N}{e} \frac{h^3}{(2\pi mk_BT)^3 V} \right] - Nk_BT \ln f(T) . \tag{5.38}$$

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

$$P = -(\partial F/\partial V)_{N,T} = (N/V)k_BT \tag{5.39}$$

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:

$$S = -\left(\partial F/\partial T\right)_{N,V} = S_{\text{translational}} + Nk_B(\ln f + d\ln f/d\ln T) , \tag{5.40}$$

where the entropy $S_{\rm translational}$ can straightforwardly be shown to be equivalent to the Sackur-Tetrode formula (4.41)[8]; and

$$\bar{E} = F + TS = Nk_BT\left(\frac{3}{2} + \frac{d\ln f}{d\ln T}\right) \; . \tag{5.41}$$

For degrees of freedom that are classical and quadratic, the internal contribution $Nk_BTd\ln f/d\ln T$ 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. (5.38) above.

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EXERCISES

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

$$\Gamma \equiv -\left(\frac{\partial \ln P}{\partial \ln V}\right)_S \tag{5.42}$$

[Eq. (13.2)] 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:

$$C_V \equiv T(\partial S/\partial T)_{V,N} = (\partial E/\partial T)_{V,N} \; . \tag{5.43}$$

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 $C_VdT = -PdV$. [Hint: use the first law of thermodynamics and the fact that for an ideal gas the energy of a fluid element depends only on its temperature and not on its volume (or density), Eq. (5.41).]

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

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

(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

$$C_P \equiv T(\partial S/\partial T)_{P,N} = C_V + Nk_B \; . \tag{5.44}$$

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

$$\Gamma = \gamma \equiv C_P/C_V \; , \tag{5.45}$$

a standard result in elementary thermodynamics.

Exercise 5.5 $\boxed{T2}$ *Example: The Enthalpy Representation of Thermodynamics*

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

$$\boxed{H \equiv \mathcal{E} + PV} \; . \tag{5.46}$$

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

$$\boxed{dH = VdP + TdS + \tilde{\mu}dN} \; ; \tag{5.47}$$

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

(b) For a nonrelativistic system, it is conventional to remove the particle rest masses from the enthalpy just as one does from the energy, but by contrast with energy, we do not change notation for the enthalpy:

$$H_{\text{nonrelativistic}} \equiv H_{\text{relativistic}} - Nm = E + PV \; . \tag{5.48}$$

What, is the form of the first law (5.47) for the nonrelativistic H?

(c) 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.

(d) 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)?

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

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

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

(h) 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 Gibbs Ensemble and Representation of Thermodynamics; Phase Transitions and Chemical Reactions

Turn attention, next, 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 and geophysical situations.

Each of the systems, in this case, has a fixed number of particles N_I for the various independent species 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

$$\boxed{\rho = e^{G/k_BT} e^{-(\mathcal{E}+PV)/k_BT}}\,, \tag{5.49}$$

[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 also, sometimes, the *Gibbs free energy* or *chemical free energy*; 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 $\sum_n \rho_n = 1$:

$$\boxed{e^{-G/k_BT} = \sum_n e^{-(\mathcal{E}_n+PV_n)/k_BT}}\,. \tag{5.50}$$

See Ex. 5.7 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. (5.49) for ρ]. Solving for G, we get

$$\boxed{G = \bar{\mathcal{E}} + P\bar{V} - TS}\,. \tag{5.51}$$

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:

$$\boxed{dG = VdP - SdT + \sum_I \tilde{\mu}_I dN_I\,.} \tag{5.52}$$

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 (equations of state), e.g. $V = (\partial G/\partial P)_{T,N_I}$; 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 (5.52) to this buildup, we obtain the Euler relation

$$\boxed{G = \sum_I \tilde{\mu}_I N_I \ .} \tag{5.53}$$

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

As with previous representations of thermodynamics, to obtain the Newtonian version of all of this section's equations, we simply remove the particle rest masses from $\tilde{\mu}_I$ *(which then becomes* μ_I*), from* $\mathcal{E}$ *(which then becomes* E*), and from* G *(which does not change notation).*

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EXERCISES

Exercise 5.6 *Problem: Gibbs Free Energy*
In Sec. 5.4.1, we explained the experimental meaning of the physical free energy F. Give a similar experimental interpretation of the Gibbs free energy (chemical free energy) G.

Exercise 5.7 *Problem and Practice: Ideal Gas Equation of State from Gibbs Ensemble*
For a nonrelativistic, classical, ideal gas (no interactions between particles), evaluate the statistical sum (5.50) 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 Out-of-Equilibrium Ensembles and their Fundamental Thermodynamic Potentials and Minimum Principles

Despite its lack of usefulness in practical computations of the Gibbs potential G, the Gibbs ensemble plays an important conceptual role in a *minimum principle for G,* 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 ρ_n, 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 (5.51)

$$G \equiv \bar{\mathcal{E}} + P_b \bar{V} - T_b S \ , \tag{5.54}$$

where P_b and T_b are the pressure and temperature of the identical baths with which the ensemble's systems are interacting.[9] 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

$$\Delta\bar{\mathcal{E}}_b = -\Delta\bar{\mathcal{E}} \ , \quad \Delta\bar{V}_b = -\Delta\bar{V} \ . \tag{5.55a}$$

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

$$\Delta\bar{\mathcal{E}}_b = -P_b\Delta\bar{V}_b + T_b\Delta S_b + \tilde{\mu}\Delta N_b \ . \tag{5.55b}$$

Since N_b is not changing (the systems cannot exchange particles with their baths) and since the changes of bath energy and volume are given by Eqs. (5.55a), Eq. (5.55b) tells us that the baths' entropy changes by

$$\Delta S_b = \frac{-\Delta\bar{\mathcal{E}} - P_b\Delta\bar{V}}{T_b} \ . \tag{5.55c}$$

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

$$\Delta S_b + \Delta S = \frac{-\Delta\bar{\mathcal{E}} - P_b\Delta\bar{V} + T_b\Delta S}{T_b} \geq \ 0 \ . \tag{5.55d}$$

Because the baths' pressure P_b and temperature T_b are not changing (the systems are so tiny compared to the baths that the energy and volume they exchange with the baths cannot have any significant effect on the baths' intensive variables), the numerator of expression (5.55d) is equal to the evolutionary change in the ensemble's out-of-equilibrium Gibbs potential (5.54):

$$\boxed{\Delta S_b + \Delta S = \frac{-\Delta G}{T_b} \geq \ 0 \ .} \tag{5.56}$$

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

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

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

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].

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_b and pressure P_b to give an out-of-equilibrium Gibbs potential $G = \bar{\mathcal{E}} + P_b\bar{V} - T_bS$. 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 $F(T_b, V, N)$ 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* $F = \bar{\mathcal{E}} - T_bS$ *will always decrease, ultimately reaching a minimum when the ensemble reaches its final, equilibrium, canonical distribution.* (iii) The grand-potential $\Omega(V, T_b, \tilde{\mu}_b)$ (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* $\Omega = \bar{\mathcal{E}} - \tilde{\mu}_b\bar{N} - T_bS$ *will always decrease, ultimately reaching a minimum when the ensemble reaches its final, equilibrium, grand-canonical distribution.* (iv) For the enthalpy $H(P_b, S, N)$ (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 quantities 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.

Bath	**Fundamental Potential**	**Total Entropy** $\mathbf{S + S_b}$	**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 $d\mathcal{E} = -P_b dV$	$S(\rho)$ with $H = \mathcal{E} + P_b V$ const	$S+$ const (see Ex. 5.13)	$dS \geq 0$	$\propto e^{S/k_B}$
Heat	$F(T_b; \rho) = \bar{\mathcal{E}} - T_b S$	$-F/T_b +$ const	$dF \leq 0$	$\propto e^{-F/k_B T_b}$
Heat & Volume	$G(T_b, P_b; \rho) = \bar{\mathcal{E}} + P_b \bar{V} - T_b S$	$-G/T_b+$ const	$dG \leq 0$	$\propto e^{-G/k_B T_b}$
Heat & Particle	$\Omega(T_b, \tilde{\mu}_b, \rho) = \bar{\mathcal{E}} - \tilde{\mu}_b \bar{N} - T_b S$	$-\Omega/T_b +$ const	$d\Omega \leq 0$	$\propto e^{-\Omega/k_B T_b}$

Table 5.2: Descriptions of out-of-equilibrium ensembles with distribution function ρ, from which one computes $S = -k_B \sum_n \rho_n \ln \rho_n$, $\bar{\mathcal{E}} = \sum_n \rho_n \mathcal{E}_n$, $\bar{V} = \sum_n \rho_n V_n$, and $\bar{N}_n = \sum_n \rho_n N_n$. The systems of each ensemble are in contact with the bath shown in column one, and T_b, P_b, $\tilde{\mu}_b$ are the bath's temperature, pressure and chemical potential. For ensembles in statistical equilibrium see Table 5.1. As there, so also here, the nonrelativistic formulae are the same as above but with the rest masses of particles removed from the chemical potentials, ($\tilde{\mu} \to \mu$) and from all fundamental potentials except Ω ($\mathcal{E} \to E$ but no change of notation for H, F, G).

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 $\mu_{\mathrm{H_2O}}$ and also from their Gibbs potential). The refrigerator's air forms a heat and volume bath for the water in the cup (the system). There is no membrane between the air and the water, but none is needed. Gravity, together with the density difference between water and air, serves to keep the water molecules in the cup and the air above the water's surface, 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 the common bath and H_2O temperature $T_b = T$ at fixed (atmospheric) pressure, with the shapes shown in Fig. 5.3. At temperatures $T > T_c = 273$K the liquid phase has the lower Gibbs potential G, and at $T < T_c$ the solid phase has the lower G. Correspondingly, when the cup's temperature sinks slightly below 273K, the H_2O molecules

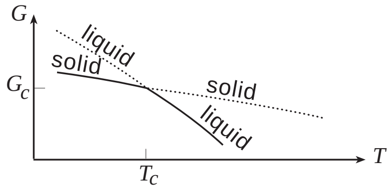

Fig. 5.3: The Gibbs potential $G(T, P, N)$ for H_2O as a function of temperature T with fixed P and N, near the freezing point $T = T_c = 273$K. The solid curves correspond to the actual path traversed by the H_2O if the phase transition is allowed to proceed. The dotted curves correspond to superheated 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 $G = E + PV - TS$.

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. 5.4a. 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. 5.8, which focuses on the latent heat per unit mass Δq and the density change $\Delta\rho$ instead of on ΔQ and ΔV.

Phase transitions like this one, with finite volume jumps $\Delta V \neq 0$ and finite latent heat $\Delta Q \neq 0$, are called *first-order*. The van der Waals gas (Sec. 5.3.2) provides an analytic model for another first-order phase transition: that from water vapor to liquid water; but we shall

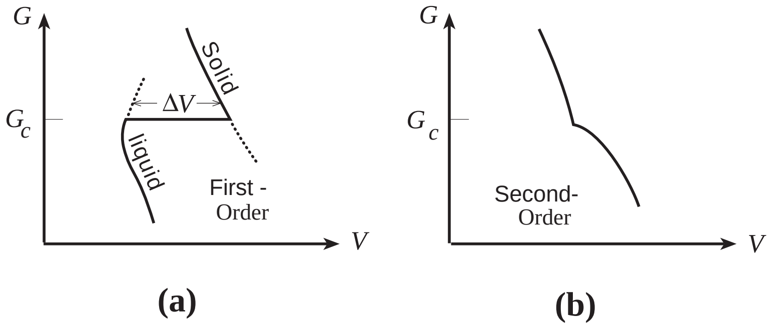

Fig. 5.4: The changes of volume (plotted rightward) with increasing Gibbs function (plotted upward) at fixed P and N for a first-order phase transition [diagram (a)] and a second-order phase transition [diagram (b)]. G_c is the critical value of the Gibbs potential at which the transition occurs.

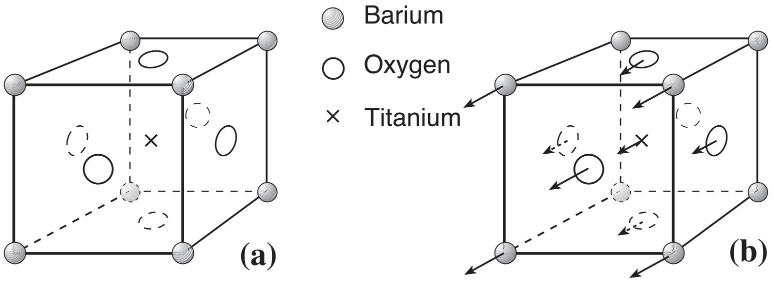

Fig. 5.5: (a) The unit cell for a $\mathrm{BaTiO_3}$ crystal at relatively high temperatures. (b) The displacements of the titanium and oxygen ions relative to the corners of the unit cell, that occur in this crystal with falling temperature when it undergoes its second-order phase transition. The magnitudes of the displacements are proportional to the amount $T_c - T$ by which the temperature T drops below the critical temperature T_c, for small $T_c - T$.

delay studying this model (Sec. 5.7) until we have learned about fluctuations of systems in statistical equilibrium (Sec. 5.6), which the van der Waals gas also illustrates.

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 dV/dG are different (and this is so whether one holds P fixed as G decreases, or holds T fixed, or holds some combination of P and T fixed); see Fig. 5.4b.

Crystals provide examples of both first-order and second-order phase transitions. 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. 5.5a shows the unit cell for a $\mathrm{BaTiO_3}$ (barium titanate) 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.

$\mathrm{BaTiO_3}$ does not behave in this way. Rather, as the temperature falls a bit below a critical value, the unit cell begins to elongate parallel to one of its edges; i.e., the cell's atoms get displaced as indicated in Fig. 5.5b. 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. 5.5a. The result is a discontinuity, at the critical temperature, in the rate of change of volume dV/dG (Fig. 5.4b), but no discontinuous jump of volume and no latent heat.

This $\mathrm{BaTiO_3}$ example illustrates a frequent feature of phase transitions: When the transition occurs, i.e., when the atoms start to move, the unit cell's cubic symmetry gets broken. The crystal switches, discontinuously, to a lower type of symmetry, a tetragonal one in this case. Such symmetry breaking is a common occurence in phase transitions.

Bose-Einstein condensation of a bosonic atomic gas in a magnetic trap (Sec. 4.9) is another example of a phase transition. As we saw in Ex. 4.13, 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; this, or often a mild divergence of the specific heat, is characteristic of second-order phase transitions. Ferromagnetism also exhibits a second-order phase transition, which we shall explore in Secs. 5.8.3 and 5.8.4 using two powerful computational techiques: the renormalization group, and Monte Carlo methods.

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EXERCISES

Exercise 5.8 *Example: The Clausius-Clapeyron Equation for Two Phases in Equilibrium with Each Other*

(a) Consider H_2O in contact with a heat and volume bath with temperature T and pressure P. For certain values of T and P the H_2O will be liquid 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 and its Euler equation, that, *if two phases a and b are present and in 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"

$$\left(\frac{dP}{dT}\right)_{\rm melt} = \frac{\Delta q_{\rm melt}}{T}\left(\frac{\rho_{\rm ice}\,\rho_{\rm water}}{\rho_{\rm ice} - \rho_{\rm water}}\right) , \tag{5.57a}$$

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 $G_b = \mu_b N_b$.]

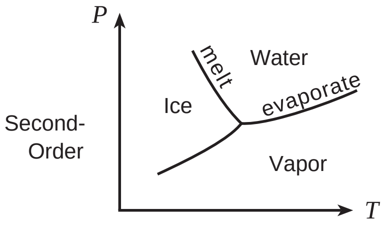

Fig. 5.6: Phase diagram for H_2O.

(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

$$\frac{dP_{\rm vapor}}{dT} = \frac{\Delta q_{\rm evaporate}}{T}\left(\frac{\rho_{\rm water}\;\rho_{\rm vapor}}{\rho_{\rm water}-\rho_{\rm vapor}}\right) . \tag{5.57b}$$

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:

$$\left(\frac{dP_{\rm vapor}}{dP_{\rm total}}\right)_{T\ {\rm fixed}} = \frac{\rho_{\rm vapor}}{\rho_{\rm water}} > 0 \; , \tag{5.57c}$$

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

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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, $2H_2O \to 2H_2 + O_2$. The inverse reaction $2H_2 + O_2 \;\to\; 2H_2O$ also occurs in the atmosphere, and it is conventional to write down the two reactions simultaneously in the form

$$2H_2O \;\leftrightarrow 2H_2 + O_2 \; . \tag{5.58}$$

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 (5.58) 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 $N_{\mathrm{H_2O}}$, hydrogen molecules $N_{\mathrm{H_2}}$, and oxygen molecules $N_{\mathrm{O_2}}$, and with a Gibbs potential whose value is given by the Euler relation (5.53)

$$G = \tilde{\mu}_{\mathrm{H_2O}} N_{\mathrm{H_2O}} + \tilde{\mu}_{\mathrm{H_2}} N_{\mathrm{H_2}} + \tilde{\mu}_{\mathrm{O_2}} N_{\mathrm{O_2}} \ . \tag{5.59}$$

(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, $\Delta t \sim \tau_{\mathrm{react}}$, one discovers that these molecules are not inviolate; they can change into one another via the reactions (5.58), thereby changing the value of the Gibbs potential (5.59). 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 (5.59). 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

$$dN_{\mathrm{H_2}} = -dN_{\mathrm{H_2O}} \ , \qquad dN_{\mathrm{O_2}} = -\frac{1}{2} dN_{\mathrm{H_2O}} \ , \tag{5.60a}$$

the first law says

$$dG = (2\tilde{\mu}_{\mathrm{H_2O}} - 2\tilde{\mu}_{\mathrm{H_2}} - \tilde{\mu}_{\mathrm{O_2}}) \frac{1}{2} dN_{\mathrm{H_2O}} \ . \tag{5.60b}$$

The reactions (5.58) 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_I's produce changes in the chemical potentials $\tilde{\mu}_I$. [Recall the intimate connection

$$N_I = \frac{(2\pi m_I k_B T)^{3/2}}{h^3} e^{\mu_I / k_B T} V \tag{5.61}$$

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 (5.58) can no longer reduce G. In this final state of ***full*** *statistical equilibrium*, the dG of expression (5.60b) must be zero; and correspondingly, the combination of chemical potentials appearing in it must vanish:

$$2\tilde{\mu}_{\mathrm{H_2O}} = 2\tilde{\mu}_{\mathrm{H_2}} + \tilde{\mu}_{\mathrm{O_2}} \ . \tag{5.62}$$

The above analysis shows that *the "driving force" for the chemical reactions is the combination of chemical potentials in the dG of Eq. (5.60b).* Notice that *this combination has coefficients in front of the $\tilde{\mu}_I$'s that are identical to the coefficients in the reactions (5.58) themselves; and the equilibrium relation (5.62) also has the same coefficients as the reactions (5.60b).* It is easy to convince oneself that this is true in general:

Consider any chemical reaction. Write the reaction in the form

$$\sum_j \nu_j^L A_j^L \leftrightarrow \sum_j \nu_j^R A_j^R \ . \tag{5.63}$$

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,

$$\sum_j \nu_j^L \tilde{\mu}_j^L \ , \quad \sum_j \nu_j^R \tilde{\mu}_j^R \ . \tag{5.64}$$

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 5.9 and 5.10 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 $dG = (2\mu_{\rm H_2O} - 2\mu_{\rm H_2} - \mu_{\rm O_2})\frac{1}{2}dN_{\rm H_2O}$ [Eq. (5.60b) 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. 5.10) is an example.

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EXERCISES

Exercise 5.9 ***Example: Electron-Positron Equilibrium at "Low" Temperatures*

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

$$e^- + p \rightarrow e^- + p + e^- + e^+ \ . \tag{5.65}$$

[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)?

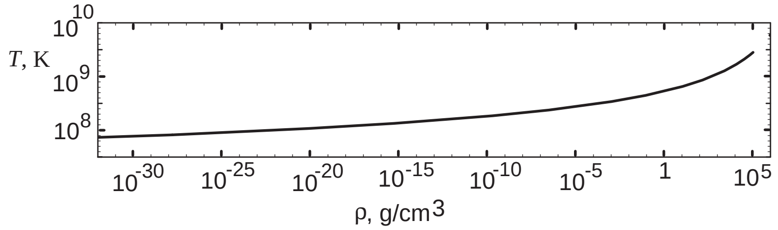

Fig. 5.7: The temperature T_p at which electron-positron pairs form in a dilute hydrogen plasma, plotted as a function of density ρ. This is the correct upper limit (upper dashed curve in Fig. 3.7) on the region where the plasma can be considered fully nonrelativistic. Above this curve, although T may 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.

(b) Although these reactions require an e^- that is relativistic in energy, almost all the electrons and positrons will have kinetic energies of magnitude $E \equiv \mathcal{E} - mc^2 \sim k_B T \ll mc^2$, 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

$$n_\pm = \frac{2}{h^3}(2\pi m k_B T)^{3/2} \exp\left(\frac{\tilde{\mu}_\pm - mc^2}{k_B T}\right) . \tag{5.66}$$

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?

(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

$$\frac{n_+}{n} = \frac{1}{2y[y + (1+y^2)^{\frac{1}{2}}]} \tag{5.67a}$$

where

$$y \equiv \frac{1}{4} n \lambda^3 e^{mc^2/k_B T} , \qquad \text{and} \quad \lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}} \tag{5.67b}$$

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 $\rho \simeq m_{\text{proton}} n$. 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 5.10 ***Example: Saha Equation for Ionization Equilibrium*

Consider an optically thick hydrogen gas in statistical equilibrium at temperature T. (By "optically thick" is meant that photons can travel only a distance small compared to the size of the system before being absorbed, so they are confined by the hydrogen and kept in statistical equilibrium with it.) Among the reactions that are in statistical equilibrium are $\mathrm{H} + \gamma \leftrightarrow e + p$ (ionization and recombination of Hydrogen H, with the H in its ground state) and $e + p \leftrightarrow e + p + \gamma$ (emission and absorption of photons by "bremsstrahlung", i.e., by the coulomb-force-induced acceleration of electrons as they fly past protons). Let $\tilde\mu_\gamma$, $\tilde\mu_{\mathrm{H}}$, $\tilde\mu_e$, and $\tilde\mu_p$ be the chemical potentials *including rest mass-energies*; let m_{H}, m_e, m_p be the rest masses; denote by $\phi \equiv$ (13.6 electron volts) the ionization energy of hydrogen, so that $m_{\mathrm{H}}c^2 = m_e c^2 + m_p c^2 - \phi$; 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 $\tilde\mu_\gamma$, $\tilde\mu_{\mathrm{H}}$, $\tilde\mu_e$, and $\tilde\mu_p$?

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

(c) Derive the Saha equation for ionization equilibrium

$$\frac{n_e n_p}{n_{\mathrm{H}}} = \frac{(2\pi m_e k_B T)^{3/2}}{h^3} e^{-\phi/k_B T} . \tag{5.68}$$

This equation is widely used in astrophysics and elsewhere.

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5.6 Fluctuations Away From 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 an example, consider a microcanonical ensemble of boxes, each with volume V and each containing precisely N identical, nonrelativistic, classical 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 quantity y that is not fixed by the set $E,\ V,\ N$. That quantity might be discrete; e.g., the total number N_R of particles in the right half of the box. Alternatively, it might be continuous; e.g., the total energy E_R in the right half.

In the discrete case, the total number of quantum states that correspond to specific values of y is related to the entropy S by the standard microcanonical relation $N_{\rm states}(E, V, N; y) = \exp[S(E, V, N; y)/k_B]$; 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 value y is

$$p(E, V, N; y) = \frac{N_{\rm states}(E, V, N; y)}{\sum_y N_{\rm states}(E, V, N; y)} = \text{const} \times \exp\left[\frac{S(E, V, N; y)}{k_B}\right] . \tag{5.69a}$$

Here the entropy S is to be computed via statistical mechanics (or, when possible, via thermodynamics) not for the original ensemble of boxes in which y was allowed to vary, but for an ensemble in which y is fixed at a chosen value.

The continuous case (e.g., $y = E_R$) can be converted into the discrete case by dividing the range of y into intervals that all have the same infinitesimal width δy. Then the probability of finding y in one of these intervals is $[dp(E, V, N; y \text{ in } \delta y)/dy]\delta y = \text{const} \times \exp[S(E, V, N, y \text{ in } \delta y)]$. Dividing both sides by δy and absorbing δy on the right side into the constant, we obtain

$$\frac{dp(E, V, N; y)}{dy} = \text{const} \times \exp\left[\frac{S(E, V, N; y \text{ in } \delta y)}{k_B}\right] . \tag{5.69b}$$

Obviously, if we are interested in the joint probability for a set of y's, some discrete (e.g. $y_1 = N_R$) and some continuous (e.g. $y_2 = E_R$), that will be given by

$$\frac{dp(E, V, N; y_1, y_2, ...y_r)}{dy_q...dy_r} = \text{const} \times \exp\left[\frac{S(E, V, N; y_j)}{k_B}\right] , \tag{5.69c}$$

where we keep in mind, but now omit from our notation, the fact that continous variables are to be given values y_j in some arbitrary but fixed infinitesimal range δy_j.

The probability distribution (5.69c), though "exact," is not terribly instructive. To get better insight we expand S in powers of the deviations of the y_j from the values $\bar{y}_j$ that maximize the entropy (these will turn out also to be the means of the distribution). Then for small $|y_j - \bar{y}_j|$, Eq. (5.69c) becomes

$$\frac{dp(E, V, N; y_j)}{dy_q \ldots dy_r} = \text{const} \times \exp\left[\frac{1}{2k_B}\left(\frac{\partial^2 S}{\partial y_j \partial y_k}\right)(y_j - \bar{y}_j)(y_k - \bar{y}_k)\right] . \tag{5.69d}$$

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 (5.69d) is a (multidimensional) Gaussian probability distribution for which the means are obviously $\bar{y}_j$ as predicted. (That this had to be Gaussian follows from the central limit theorem, Sec. 6.3.2.)

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 perfect-gas particles in right half of box) and $y_2 \equiv E_R =$(amount of energy in right half of box), we can infer $S(E,V,N;N_R,E_R)$ from the Sackur-Tetrode equation (4.41) as applied to the two halves of the box and then added:[10]

$$\begin{aligned} S(E,V,N;E_R,N_R) &= k_B N_R \ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} e^{5/2}\frac{V}{2}\frac{E_R^{3/2}}{N_R^{5/2}}\right] \\ &+ k_B(N-N_R)\ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} e^{5/2}\frac{V}{2}\frac{(E-E_R)^{3/2}}{(N-N_R)^{5/2}}\right] . \end{aligned} \tag{5.70a}$$

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

$$\bar{E}_R = \frac{E}{2}, \qquad \bar{N}_R = \frac{N}{2}. \tag{5.70b}$$

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 (5.70a) 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 (5.69d). The result is

$$\frac{dp_{N_R}}{dE_R} = \text{const} \times \exp\left(\frac{-(N_R - N/2)^2}{2(N/4)} + \frac{-[(E_R - E/2) - (E/N)(N_R - N/2)]^2}{2(N/6)(E/N)^2}\right) . \tag{5.70c}$$

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 (standard deviation; square root of variance) $\sigma_{E_R} = (E/N)\sqrt{N/6}$. (*iv*) After integrating over E_R, we obtain

$$p_{N_R} = \text{const} \times \exp\left[\frac{-(N_R - N/2)^2}{2N/4}\right] . \tag{5.70d}$$

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

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[10] Note that the derivation of Eq. (4.41), as specialized to the right half of the box, requires the same kind of infinitesimal range $\delta y_2 = \delta E_R$ as we utilized above in deriving our fluctuational probability equation (5.69d)].

have had an rms fluctuation equal to the square root of its mean, $\sigma_{N_R} = \sqrt{N/2}$ [see Ex. 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 the probability distributions (5.70c), and (5.70d) are exceedingly sharply peaked about their means: Their standard deviations 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 this example to other situations should be fairly obvious; see 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 ($-F/T_b$+const, $-G/T_b$+const, or $= -\Omega/T_b$+const (column 3 of Table 5.2). Correspondingly, the probability of a fluctuation, from statistical equilbrium, 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_b}, e^{-G/k_BT_b} or $e^{-\Omega/k_BT_b}$; 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.

As examples: in Ex. 5.11 we study fluctuations in the number of particles in a cell that is immersed in a heat and particle bath, so the starting point is the out-of-equilibrium grand potential Ω. And in Ex. 5.12, we study temperature and volume fluctuations for a system in contact with a heat and volume bath; so the starting point is the out-of-equilibrium Gibbs function G.

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EXERCISES

Exercise 5.11 *Example: Probability Distribution for the Number of Particles in a Cell*

Consider a cell with volume V, like those of Fig. 5.1, that has imaginary walls and is immersed in a bath of identical, nonrelativistic, classical, perfect-gas particles with temperature T and chemical potential μ. Suppose that we make a large number of measurements of the number of particles in the cell 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, by the methods of this section, from an ensemble of cells (Fig. 5.1) at a specific moment of time?

(b) Assume that the measurements are widely enough separated for this criterion to be satisfied. Show that p_N is given by

$$p_N \propto \exp\left[\frac{-\Omega(V,T_b,\mu_b;N)}{k_BT_b}\right] \equiv \frac{1}{N!}\int\frac{d^{3N}xd^{3N}p}{h^{3N}}\exp\left[\frac{-E_n-\mu_bN_n}{k_BT_b}\right] \tag{5.71}$$
$$= \frac{1}{N!}\int\frac{d^{3N}xd^{3N}p}{h^{3N}}\exp\left[\frac{(\sum_{i=1}^N \mathbf{p}_i^2/2m)-\mu_bN}{k_BT_b}\right] ,$$

where $\Omega(V,T_b,\mu_b;N)$ is the grand potential for the ensemble of cells, with each cell constrained to have precisely N particles in it (cf. the last entry in Table 5.2).

(c) By evaluating Eq. (5.71) exactly and then computing the normalization constant, show that the probability p_N for the cell to contain N particles is given by the *Poisson distribution*

$$p_N = e^{-\bar{N}}(\bar{N}^N/N!) , \tag{5.72a}$$

where $\bar{N}$ is given is the mean number of particles in a cell, $\bar{N} = (\sqrt{2\pi mk_BT_b}/h)^3e^{\mu/k_BT_b}V$ [Eq. (3.37a)].

(c) Show that for the Poisson distribution (5.72a), the expectation value is $\langle N\rangle = \bar{N}$, and the root mean square deviation from this is

$$\sigma_N \equiv \langle(N-\bar{N})^2\rangle^{\frac{1}{2}} = \bar{N}^{\frac{1}{2}} . \tag{5.72b}$$

(d) Show that for $N-\bar{N} \lesssim \sigma_N$, this Poisson distribution is exceedingly well approximated by a Gaussian with mean $\bar{N}$ and variance σ_N.

Exercise 5.12 *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

$$\frac{dp}{dTdV} = \text{const}\times\exp\left[-\frac{1}{2k_BT_b}\left(\frac{\partial^2G}{\partial V^2}(V-\bar{V})^2+\frac{\partial^2G}{\partial T^2}(T-T_b)^2+2\frac{\partial^2G}{\partial T\partial V}(V-\bar{V})(T-T_b)\right)\right] , \tag{5.73a}$$

where $G(N,T_b,P_b;T,V) = E(T,V,N)+P_bV-T_bS(T,V,N)$ is the out-of-equilibrium Gibbs function for a sample of N particles interacting with this bath (next to last line of Table 5.2), $\bar{V}$ is the equilibrium volume of the sample when its temperature and pressure are those of the bath, and the double derivatives in Eq. (5.73a) are evaluated at the equilibrium temperature T_b and pressure P_b.

(b) Show that the derivatives, evaluated at $T = T_b$ and $V = \bar{V}$, are given by

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{V,N} = \frac{C_V}{T_b}, \quad \left(\frac{\partial^2 G}{\partial V^2}\right)_{T,N} = \frac{1}{\kappa}, \quad \left(\frac{\partial^2 G}{\partial T \partial V}\right)_{N} = 0 \,, \tag{5.73b}$$

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

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} \,, \quad \kappa \equiv -\left(\frac{\partial V}{\partial P}\right)_{T,N} \,, \tag{5.73c}$$

both evaluated at temperature T_b and pressure P_b. [Hint: Write $G = G_{\rm eq} + (P_b - P)V - (T_b - T)S$, where $G_{\rm eq}$ is the equilibrium Gibbs function for the gas samples.] Thereby conclude that

$$\frac{dp}{dTdV} = \text{const} \times \exp\left[-\frac{(V-\bar{V})^2}{2k_B T_b \kappa} - \frac{C_V (T - T_b)^2}{2 k_B T_b^2}\right] . \tag{5.73d}$$

(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 samples' temperature and volume, σ_T and σ_V? Show σ_T scales as $1/\sqrt{N}$ and σ_V as $\sqrt{N}$, where N is the number of particles in the samples. Are these physically reasonable? Why?

Exercise 5.13 $\boxed{T2}$ *Example and Derivation: 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.

(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): $\rho = e^{-S/k_B} = \text{const}$ 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 (5.69a) and (5.69c), but with the system energy E replaced by the system enthalpy H; cf. Table 5.2.

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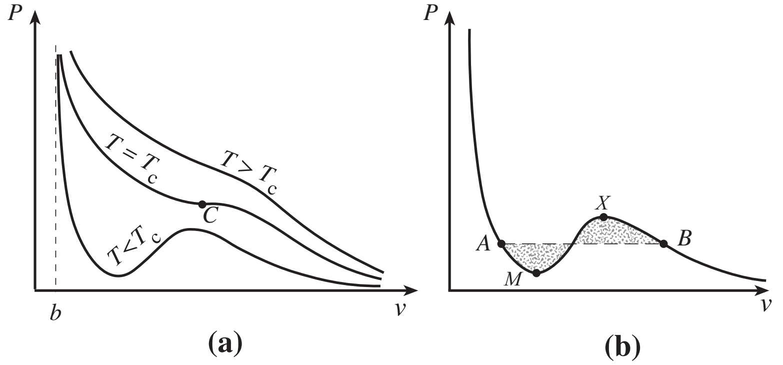

Fig. 5.8: (a) The van der Waals equation of state $P(N, V, T)$ plotted as pressure P versus specific volume V/N at fixed temperature T, for various values of the temperature T. (b) The route of a phase transition in the van der Waals gas. The transition is a discontinuous jump from point A to point B.

5.7 Van der Waals Gas: Volume Fluctuations, and Gas-To-Liquid Phase Transition

The van der Waals gas studied in Sec. 5.3.2 provides a moderately realistic model for real gases such as H_2O and their condensation (phase transition) into liquids such as water.

The equation of state for a van der Waals gas is

$$\left(P + \frac{a}{v^2}\right)(v - b) = k_B T \tag{5.74}$$

[Eq. (5.26)]. Here a and b are constants and $v \equiv V/N$ is the specific volume (the inverse of the number density of gas particles). In Fig. 5.8a we depict this equation of state as curves (*isotherms*) of pressure P versus specific volume v at fixed temperature T. Note [as one can easily show from Eq. (5.74)] that there is a critical temperature $T_c = 8a/27bk_B$ such that, for $T > T_c$ the isotherms are monotonic decreasing; for $T = T_c$ they have an inflection point (at $v = v_c \equiv 3b$ and $P = P_c = a/27b^2$); and for $T < T_c$ they have a maximum and a minimum.

From Eq. (5.73d), derived in Ex. 5.12, we can infer that the probability dp/dv for fluctuations of the specific volume of a portion of this gas containing N particles is

$$\frac{dP}{dv} = \text{const} \times \exp\left[\frac{N(\partial P/\partial v)_T}{2k_B T}(v - \bar{v})^2\right] . \tag{5.75}$$

This probability is controlled by the slope $(\partial P/\partial v)_T$ of the isotherms. Where the slope is negative, the volume fluctuations are small; where it is positive, the fluid is unstable: its volume fluctuations grow. Therefore, for $T < T_c$, the region of an isotherm between its minimum M and its maximum X (Fig. 5.8b) is unphysical; the fluid cannot exist stably there. Evidently, at $T < T_c$ there are two phases: one with low density ($v > v_X$) is gaseous; the other with high density ($v < v_M < v_c = 3b$) is liquid. [Recall, from comment (i) at the end of Sec. 5.3.2, that $b/4$ is the volume of each of the material's particles, so in the high-density phase the particles' separations are not much larger than their diameter; this is characteristic of a fluid.]

Hold the temperature T fixed at $T < T_c$, and gradually increase the density from zero (decrease the specific volume v from infinity). At low densities, the material will be gaseous, and at high densities, it will be liquid. The phase transition from gas to liquid involves a discontinuous jump from some point B in Fig. 5.8b to another point A. The Gibbs potential controls the location of those points:

Since the two phases are in equilibrium with each other at A and B, their Gibbs potential $G = \mu N$ must be the same, which means their chemical potentials must be the same, $\mu_A = \mu_B$—as, of course must be their temperatures $T_A = T_B$ (they lie on the same isotherm); and this in turn implies their pressures must be the same, $P_A = P(\mu_A, T) = P(\mu_B, T) = P_B$. Therefore, the points A and B in Fig 5.8b are connected by a horizontal line (the dashed line). Let us use the first law of thermodynamics in the Gibbs representation to compute the change in the chemical potential μ as one moves along the isotherm from point A to point B. The first law says $dG = -SdT + VdP + \mu dN$. Focusing on a sample of the material containing N particles, and noting that along the isotherm the sample has $G = \mu N$, $dN = 0$, $dT = 0$ and $V = vN$, we obtain $d\mu = vdP$. Integrating this along the isotherm from A to B, we obtain

$$0 = \mu_B - \mu_A = \int_A^B d\mu = \int_A^B vdP \ . \tag{5.76}$$

This integral is the area of the right stippled region in Fig. 5.8b minus the area of the left stippled region. Therefore, these two areas must be equal—and this tells us the location of the points A and B that identify the two phases, liquid and gaseous, when the phase transition occurs.

Returning to volume fluctuations: wherever an isotherm is flat, there are large volume fluctuations. For $T < T_c$, it is flat at the minimum M and the maximum X, but these do not occur in nature—unless the phase transition is somehow delayed as one compresses or expands the material. However, for $T = T_c$, the isotherm is flat at its inflection point $v = v_c$, $P = P_c$ (the material's "critical point" C in Fig. 5.8a); so the volume fluctuations will be very large there.

At some termperatures and pressures, T and P, it is possible for two phases, liquid and gas, to exist; and at other T and P, only one phase. The dividing line, in the $T - P$ plane between these two regions is called a *catastrophe* — a term that comes from *catastrophe theory.* We shall explore this in Ex. 7.13, after first introducing some ideas of catastrophe theory in the context of optics.

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EXERCISES

Exercise 5.14 ****Example: Out-of-Equilibrium Gibbs Potential for Water; Surface Tension and Nucleation*

[Exercise adapted from Ex. 11.3 and Sec. 11.3 of Sethna (2006).] Water and its vapor (liquid and gaseous H_2O) can be described moderately well by the van der Waals model, with the parameters $a = 1.52 \times 10^{-38}\text{J m}^3$ and $b = 5.05 \times 10^{-29}\text{m}^3$ determined by fitting to the measured pressure and temperature at the critical point (inflection point C in Fig. 5.8a:

$P_c = a/27b^2 = 22.09$MPa, $T_c = 8a/27bk_B = 647.3$K. [Note: MPa is 10^6 Pascal; and one Pascal is the SI unit of pressure, $1\text{kg}\,\text{m}\,\text{s}^{-2}$.]

(a) For an out-of-equilibrium sample of N atoms of H_2O at tempature T and pressure P, which has fluctuated to a specific volume v, the van-der-Waals-modeled Gibbs potential is

$$G(N,T,P;v) = N[-k_BT+Pv-a/v+k_BT\ln[\lambda^3/(v-b)]\ , \quad \lambda \equiv h/\sqrt{2\pi m k_B T}\ . \tag{5.77}$$

Verify that this Gibbs potential is minimized when v satisfies the van der Waals equation of state (5.74).

(b) Plot the chemical potential $\mu = G/N$ as a function of v at room temperature, $T = 300K$, for various pressures in the vicinity of one atmosphere $= 0.1013$MPa. Adjust the pressure so that the two phases, liquid and gaseous, are in equilibrium, i.e. so the two minima of the curve have the same height. [Answer: the required pressure is about 3.6 atmospheres, and the chemical-potential curve is shown in Fig. 5.9. If the gas is a mixture of air and H_2O rather than pure H_2O, then the required pressure will be lower.]

(c) Compare the actual densities of liquid water and gaseous H_2O with the predictions of Fig. 5.9. They agee moderately well but not very well.

(d) At the liquid's surface there is a surface layer, a few molecules thick, in which the attractive force between the water molecules, $F = -6\varepsilon_o r_o^6/r^7 = -(27/2\pi^2)ab/r^7$ [Eqs. (5.22b) and (5.24b)], produces surface tension. This surface tension is a force per unit length, γ, that the surface molecules on one side of any line lying in the surface exert on the molecules on the other side (Box 16.4). Explain by a simple physical argument

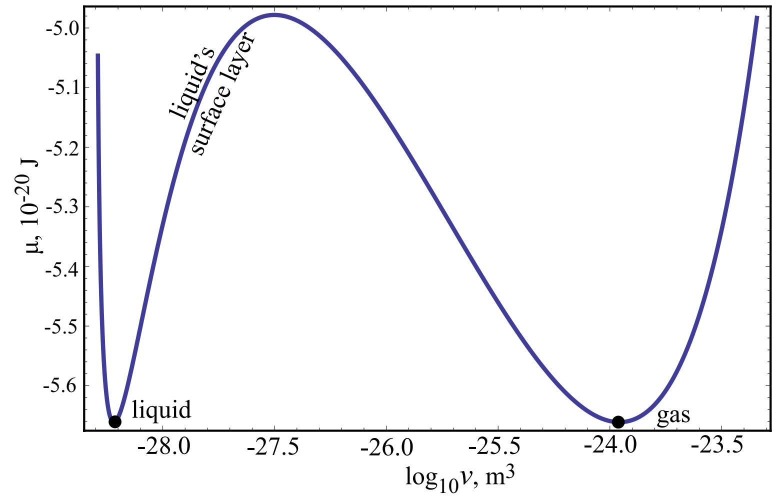

Fig. 5.9: The out-of-equilibrium chemical potential for a van der Waals gas, with its parameters fitted to the properties of H_2O, and with temperature $T = 300$K and pressure $P = 3.6$atm at the liquid-gas interface.

why there is an energy γA associated with this surface tension, stored in any area A of the surface. This is a free energy at fixed T, P (a Gibbs free energy) in excess of the free energy that the surface's water molecules would have, if they were in the bulk liquid or the bulk gas. This excess free energy shows up in the chemical potential of Fig. 5.9, and the numbers in that figure can be used to estimate the water's surface tension γ. Show that $\gamma \sim \Delta\mu h/v$, where h and v are the thickness and specific volume of the surface layer, and $\Delta\mu$ is the difference between the chemical potential in the surface layer and in the bulk water and gas. Estimate γ using numbers from Fig. 5.9 and compare with the measured surface tension, $\gamma \simeq 0.0723\text{N/m}$ at $T = 300\text{K}$.

(e) In a cloud or fog, when water vapor is cooled below its equilibrium temperature with liquid water T_e, water drops try to form, i.e. *nucleate*. However, there is a potential barrier against nucleation due to the surface tension of an incipient drop: If R is the drop's radius, show that the Gibbs free energy of a droplet (sum of contributions from its surface layer and its interior), minus the free energy that the droplet's molecules will have if they remain gaseous, is

$$\Delta G = 4\pi R^2\gamma - \left(\frac{4\pi}{3}R^3\right)\frac{q\Delta T}{v_\ell T_e} \,. \tag{5.78}$$

Here q is the latent heat per molecule that is released when the vapor liquifies, v_ℓ is the liquid's specific volume, and ΔT is the amount by which the temperature has dropped below the equilibrium point T_e for the two phases. Plot this $G(R)$, and explain why (i) there is a minimum droplet radius $R_{\rm min}$for nucleation to succeed, and (ii) for the droplet to form with this minimum size, thermal fluctuations must put into it some excess energy, B, above statistical equilibrium. Derive these formulas:

$$R_{\rm min} = \frac{2\gamma T_e v_\ell}{q\Delta T}\,, \quad B = \frac{16\pi\gamma^3 T_e^2 v_\ell^2}{3q^2\Delta T^2}\,. \tag{5.79}$$

Explain why the rate at which nucleation occurs must scale as $\exp(-B/k_BT)$, which is generally an exceedingly small number. Show that, if the nucleation occurs on a leaf or blade of grass or on the surface of a dust grain, so the drop's interface with the vapor is a hemisphere rather than a sphere, then the energy barrier B is reduced by a factor 8, and the rate of nucleation is enormously increased. That is why nucleation of water droplets almost always occurs on solid surfaces.

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5.8 $\boxed{\text{T2}}$ Magnetic Materials: Paramagnetism, Ising Model for Ferromagnetism, Renormalization Group and Monte Carlo Methods

The methods we have developed in this chapter can be applied to systems very different from the gases and liquids we have studied thus far. In this section, we focus on magnetic materials as an example, and we use this example to illustrate two powerful, modern computational techniques: the renormalization group, and Monte Carlo methods.

We consider, for concreteness, the simplest type of magnetic material: one consisting of a cubic lattice of N identical atoms, each with spin $1/2$ and magnetic moment m_o. The material is immersed in a uniform external magnetic field $\mathbf{B}$, so each atom (labeled by an index i) has two possible quantum states: one with its spin parallel to $\mathbf{B}$ (quantum number $s_i = +1$), the other antiparallel to $\mathbf{B}$ ($s_i = -1$). The energies of these states are $E_{s_i} = -m_o B s_i$. The atoms interact with each others' magnetic fields with a pairwise interaction energy $E_{s_i s_j}$ that we shall make more concrete in Sec. 5.8.2 below. The material's total energy, when the atoms are in the state $|n\rangle = |s_1, s_1, \ldots, s_n\rangle$ is $E_n - M_n B$, where

$$E_n = \sum_{i\neq j}^{N} \sum_{j=1}^{N} E_{s_i s_j} \ , \quad M_n = m_o \sum_{j=1}^{N} s_j \ . \tag{5.80a}$$

are the material's self-interaction energy (internal energy) and *magnetization.*

The atoms interact with a heat bath that has temperature T and with the external magnetic field B which can be thought of as part of the bath. When they reach statistical equilibrium with this heat and magnetic bath, the probability for the material (all N atoms) to be in state $|n\rangle = |s_1, s_1, \ldots, s_n\rangle$ is, of course,

$$p_n = e^{G(N,B,T)/k_B T} e^{-(E_n - BM_n)/k_B T} \ . \tag{5.80b}$$

Here the first term is the normalization constant, which depends on the number N of atoms in the sample and the bath's B and T, and $G(N, B, T)$ is the fundamental thermodynamic potential for this system, which acts as the normalizing factor for the probability:

$$e^{-G(N,B,T)/k_B T} = \sum_n e^{-(E_n - BM_n)/k_B T} \ . \tag{5.80c}$$

We have denoted this potential G because it is analogous to the Gibbs potential for a gas, but with the gas's volume V_n replaced by minus the magnetization $-M_n$, and the gas bath's pressure P replaced by the material bath's magnetic field strength B. Not surprisingly, the Gibbs thermodynamic formalism for this magnetic material is essentially the same as for a gas, but with $V \to -M$ and $P \to B$.

5.8.1 $\boxed{\text{T2}}$ Paramagnetism; the Curie Law

Paramagnetic materials have sufficiently weak self-interaction that we can set $E_n = 0$ and focus solely on the atoms' interaction with the external B field. The magnetic interaction tries to align each atom's spin with B, while thermal fluctuations try to randomize the spins. As a result, the stronger is B (at fixed temperature), the larger will be the mean magnetization $\bar{M}$. From Eq. (5.80b) for the spins' probability distribution we can compute the mean magnetization:

$$\bar{M} = \sum_n p_n M_n = E^{G/k_B T} \sum_n e^{BM_n/k_B T} = e^{G/k_B T} \left(\frac{\partial}{\partial B}\right)_{N,T} \sum_n e^{BM_n/k_B T} \ . \tag{5.81a}$$

The last sum is equal to e^{-G/k_BT} [Eq. (5.80c) with $E_n = 0$, so Eq. (5.81a) becomes

$$\bar{M} = -\left(\frac{\partial G}{\partial B}\right)_{N,T} . \tag{5.81b}$$

This is obviously our material's analog of $\bar{V} = (\partial G/\partial P)_{N,T}$ for a gas [which follows from the Gibbs representation of the first law, Eq. (5.52)].

To evaluate $\bar{M}$ explicitly in terms of B, we must first compute the Gibbs function from the statistical sum (5.80c) with $E_n = 0$. Because the magnetization M_n in state $|n\rangle = |s_1, s_2, \ldots, s_N\rangle$ is the sum of contributions from individual atoms [Eq. (5.80a)], this sum can be rewritten as the product of identical contributions from each of the N atoms:

$$e^{-G/k_BT} = \left(e^{-Bm_o} + e^{+Bm_o}\right)^N = [2\cosh(Bm_o/k_BT)]^N . \tag{5.81c}$$

(In the second expression, the first term is from state $s_i = +1$ and the second from $s_i = -1$.) Taking the logarithm of both sides, we obtain

$$G(B, T, N) = -k_BT \ln[2\cosh(Bm_o/k_BT)] . \tag{5.82}$$

Differentiating with respect to B [Eq. (5.81b)], we obtain for the mean magnetization

$$\bar{M} = Nm_o \tanh(Bm_o/k_BT) . \tag{5.83}$$

At high temperatures, $k_BT \gg Bm_o$, the magnetization increases linearly with the applied magnetic field (the atoms begin to align with $\mathbf{B}$) so the magnetic susceptibility is independent of B,

$$\chi_M \equiv \left(\frac{\partial \bar{M}}{\partial B}\right)_{T.N} \simeq Nm_o^2/k_BT ; \tag{5.84}$$

This $\chi_M \propto 1/T$ for a paramagnetic material at high temperature is called *Curie's law.* At low termperatures $k_BT \ll Bm_o$, the atoms are essentially all aligned with $\mathbf{B}$ and the magnetization saturates at $\bar{M} = Nm_o$.

5.8.2 **T2** Ferromagnetism: The Ising Model

Turn now to a magnetic material for which the spins' interactions are strong, and there is no external B field. In such a material, at high temperatures the spin directions are random, while at low enough temperatures, the interactions drive neighboring spins to align with each other, producing a net magnetization. This is called ferromagnetism because it occurs rather strongly in iron. The transition between the two regimes is sharp, i.e., it is a phase transition.

In this section, we introduce a simple model for the spins' interaction: the Ising model.[11] For simplicity, we shall idealize to two spatial dimensions. The corresponding three-dimensional model is far more difficult to analyze.

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[11] Named for E. Ising, who first investigated it, in 1925.

In this model, the atoms are confined to a square lattice that lies in the x, y plane, and their spins can point up (along the $+z$ direction) or down. The pairwise interaction energy is nonzero only for nearest neighbor atoms:

$$E_{s_i,s_j} = -J s_i s_j \quad \text{for nearest neighbors} \; ; \tag{5.85}$$

it vanishes for all other pairs. Here J is a positive constant (which depends on the lattice's specific volume $v = V/N$, but that will not be important for us). Note that the interaction energy $-Js_is_j$ is negative if the spins are aligned ($s_i = s'_j$) and positive if they are opposite ($s_i = -s_j$), so like spins attract and opposite spins repel. Although the Ising model does not explicitly include more distant interactions, they are present indirectly: the "knock-on" effect from one spin to the next, as we shall see, introduces long range organization that propagates across the lattice when the temperature is reduced below a critical value T_c, inducing a second-order phase transition.

We will use the dimensionless parameter

$$K \equiv J/k_BT \tag{5.86}$$

to characterize the phase transition. For $K \ll 1$ (i.e., $k_BT \gg J$), the spins will be almost randomly aligned and the total interaction energy will be close to zero. When $K \gg 1$ (i.e., $k_BT \ll J$), the strong coupling will drive the spins to align over large (2-dimensional) volumes. At some critical intermediate temperature $K_c \sim 1$ (and corresponding temperature $T_c = J/k_BK_c$), the phase transition will occur.

We shall compute this critical K_c, and macroscopic properties of the material near it, using two modern, sophisticated computatioal techniques: renormalization methods in Sec. 5.8.3, and Monte Carlo methods in Sec. 5.8.4; and we shall examine the accuracy of these methods by comparing our results with an exact solution for the 2-dimensional Ising model, derived in a celebrated paper by Lars Onsager (1944).

5.8.3 $\boxed{\text{T2}}$ Renormalization Group Methods for The Ising Model

[This section is based in part on Maris and Kadanoff (1978) and on Sec. 5.7 of Chandler (1987).]

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; see Fig. 5.10.

We shall implement this procedure using the statistical sum (5.80c) for the Gibbs potential, except that here the external magnetic field B vanishes, so the bath is purely thermal and its potential is $F(N, V, T)$, the *physical free energy*, not G; and the statistical sum (5.80c) reads $e^{-F/k_BT} \equiv z = \sum_n e^{-E_n/k_BT}$. For our Ising model, with its nearest-neighbor interaction energies (5.85), this becomes

$$e^{-F(N,V,T)/k_BT} \equiv z = \sum_{\{s_1=\pm1, s_2=\pm1, \ldots\}} e^{K\Sigma^1 s_i s_j} \; . \tag{5.87a}$$

Here in the exponential Σ^1 means a sum over all pairs of nearest neighbor sites $\{i,j\}$. The dependence on the material's number of atoms N appears in the number of terms in the big sum; and the dependence on V/N and on T is contained in the parameter $K = J(V/N)/k_BT$.

The first step in the renormalization group method is to rewrite Eq. (5.87a) so that each of the open-circle spins of Fig. 5.10, e.g. s_5, appears in only one term in the exponential, and then explicitly sum each of those spins over ±1 so they no longer appear in the summations:

$$\begin{aligned} z &= \sum_{\{\dots,s_4=\pm1,s_5=\pm1,s_6=\pm1,\dots\}} \cdots e^{K(s_1+s_2+s_3+s_4)s_5} \cdots \\ &= \sum_{\{\dots s_4=\pm1,s_6=\pm1\dots\}} \cdots \left[e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)}\right] \cdots . \qquad (5.87b) \end{aligned}$$

(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:

$$\begin{aligned} &\left[e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)}\right] \\ &= f(K) e^{\frac{1}{2}K_1(s_1s_2+s_2s_3+s_3s_4+s_4s_1)+K_2(s_1s_3+s_2s_4)+K_3s_1s_2s_3s_4} . \qquad (5.87c) \end{aligned}$$

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. (5.87c). Those four combinations, arranged in the pattern of the solid circles of Fig. 5.10, are $+{}^{+}_{+}+$, $-{}^{+}_{+}-$, $+{}^{+}_{-}-$, and $+{}^{+}_{+}-$. [Rotating the pattern or changing all signs leaves both sides of Eq. (5.87c) unchanged.] By inserting these combinations into Eq. (5.87c)) and performing some algebra,

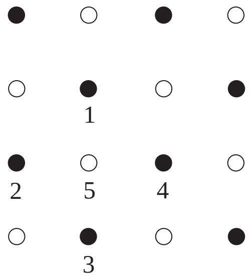

Fig. 5.10: Partition of a square lattice into two interlaced square lattices (solid circles and open circles). In the renormalization group approach, the open-circle spins are removed from the lattice, and all their interactions are replaced by modified interactions between the remaining solid-circle spins. The new lattice is rotated by $\pi/4$ with respect to the original lattice and the lattice spacing increases by a factor $\sqrt{2}$.

we obtain

$$\begin{aligned}
K_1 &= \frac{1}{4}\ln\cosh(4K) , \\
K_2 &= \frac{1}{8}\ln\cosh(4K) , \\
K_3 &= \frac{1}{8}\ln\cosh(4K) - \frac{1}{2}\ln\cosh(2K) , \\
f(K) &= 2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8} . \qquad (5.87\text{d})
\end{aligned}$$

By inserting expression (5.87c) and the analogous expressions for the other terms into Eq. (5.87b), 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:

$$z(N,K) = [f(K)]^{N/2}\sum e^{[K_1\Sigma^1 s_i s_j + K_2\Sigma^2 s_i s_j + K_3\Sigma^3 s_i s_j s_k s_l]} . \qquad (5.87\text{e})$$

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. (5.87c) 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. (5.87e).]

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 (5.87e), 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

$$K' = K_1 + K_2 = \frac{3}{8}\ln\cosh(4K). \qquad (5.88)$$

(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 (5.87e) into the form

$$z(N,K) = [f(K)]^{N/2}z(N/2,K') , \qquad (5.89\text{a})$$

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

$$-F/k_BT \equiv \ln z(N, K) = Ng(K) \ , \tag{5.89b}$$

for some function $g(K)$. By combining Eqs. (5.89a) and (5.89b), we obtain a relation for the function $g(K)$ (the free energy, aside from constants) in terms of the function $f(K)$:

$$g(K') = 2g(K) - \ln f(K) \ , \quad \text{where} \quad f(K) = 2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8} \tag{5.90}$$

[cf. Eq. (5.87d)].

Equations (5.88) and (5.90) 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 these in detail.

The iterative map (5.88) 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 (5.90) expresses the free energy when the lattice is viewed on the larger scale in terms of that for a smaller scale.) The map (5.88) has a fixed point that is obtained by setting $K' = K$; i.e., $K_c = \frac{3}{8} \ln \cosh(4K_c)$, which implies

$$K_c = 0.507 \ . \tag{5.91}$$

This fixed point corresponds to the critical point for the phase transition, with critical temperature T_c such that $K_c = J/k_BT_c$.

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 greater order at smaller scales (for high temperature) to greater order at larger scales (for 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. (5.86)] and using expression (5.89b) for F, we see that

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B\left[g - K\left(\frac{dg}{dK}\right)\right] \ . \tag{5.92a}$$

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

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = Nk_B K^2 \frac{d^2 g}{dK^2}\ . \tag{5.92b}$$

Next we note that, because the iteration (5.88) is unstable near K_c, the inverse iteration

$$K = \frac{1}{4}\cosh^{-1}[\exp(8K'/3)] \tag{5.92c}$$

is stable. The corresponding inverse transformation for the function $g(K)$ is obtained from Eq. (5.90), with f from (5.87d) and K in that f converted to K' using (5.87d):

$$g(K) = \frac{1}{2}g(K') + \frac{1}{2}\ln\{2\exp(2K'/3)[\cosh(4K'/3)]^{1/4}\}\ . \tag{5.92d}$$

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 (5.87a) the two terms with all s's identical dominate, giving $z = e^{-F/k_BT} = e^{Ng} = 2e^{2NK}$, 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 (5.87a) is unity, giving $z = e^{Ng} = 2^N$, whence $g(K) \simeq \ln 2$. We can therefore use the iterative map, Eqs. (5.92c), (5.92d), 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 and d^2g/dK^2 numerically, and from them we compute F, S and C_V using Eqs. (5.89b), (5.92a), and (5.92b).

The iterated values of these quantities are plotted as points in Fig. 5.11. Note that the entropy S is continuous at K_c [panel (c)], but its derivative, the specific heat [panel (d)], diverges at K_c, as $K \to K_c$ from either side. This is characteristic of 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. (5.92d), we have that

$$|K' - K_c|^{2-\alpha} = 2|K - K_c|^{2-\alpha}, \tag{5.93a}$$

or equivalently,

$$\frac{dK'}{dK} = 2^{1/(2-\alpha)}. \tag{5.93b}$$

Evaluating the derivative at $K = K_c$ from Eq. (5.92c), we obtain

$$\alpha = 2 - \frac{\ln 2}{\ln(dK'/dK)_c} = 0.131\ , \tag{5.93c}$$

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. 5.11]. 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. (5.88)]. 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 5.15 $\boxed{T2}$ *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.

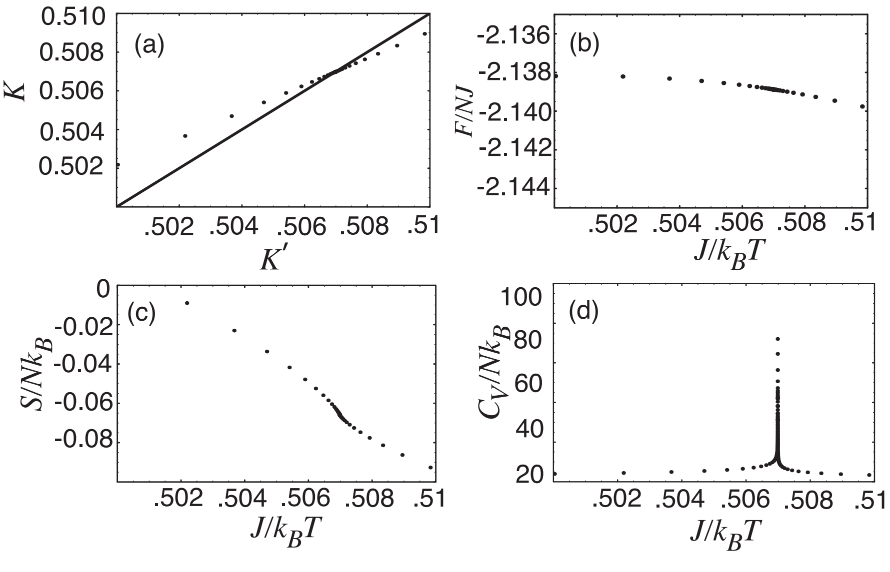

Fig. 5.11: (a) Iteration map $K(K')$ in the vicinity of the critical point. (b) Free energy per spin (c) Entropy per spin, (d) Specific heat per spin. Recall that $J/k_BT = K$.

(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

$$z(N, K) = f(K)^{N/2} z(N/2, K') \tag{5.94}$$

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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5.8.4 $\boxed{\text{T2}}$ Monte Carlo Methods for the Ising Model

In this section, we shall explore the phase transition of the 2-dimensional Ising model using our second general method: the *Monte Carlo* approach.[12] This method, like the renormalization group, is a powerful tool for a much larger class of problems than just phase transitions.

The Monte Carlo approach is much more straightforward in principle than the renormalization group. We set up a square lattice of atoms and initialize their spins randomly.[13] We imagine that our lattice is in contact with a heat bath with a fixed temperature T (it is one member of a canonical ensemble of systems), and we drive it to approach statistical equilibrium and then wander onward through an equilibrium sequence of states $|n_1\rangle$, $|n_2\rangle$, ... in a prescribed, ergodic manner. Our goals are to visualize typical equilibrium states (Fig. 5.12 below), and to compute thermodynamic quantities using $\bar{X} = z^{-1} \sum_n e^{-E_n/k_B T} X_n$, where the sum is over the sequence of states $|n_1\rangle$, $|n_2\rangle$, ... For example, we can compute the specific heat (at constant volume) from

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

[Note that a singularity in the specific heat at a phase transition will be associated with large fluctuations in the energy, just as it is associated with large fluctuations of temperature; Eq. (5.73d)].

In constructing our sequence of lattice states $|n_1\rangle$, $|n_2\rangle$, ... , we obviously cannot visit every all 2^N states even just once; so we must sample them fairly. How can we prescribe the rule for changing the spins when going from one state in our sample to the next, so as to produce a “fair” sampling? 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

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

[13] This and other random steps that follow are performed numerically and require a (pseudo) random number generator. Most programming languages 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 (2007).

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, for going from one state to the next, should produce a sequence that is in statistical equilibrium.

Let us denote by $p_{nn'}$ the conditional probability that, if the lattice is in state $|n\rangle$, then the next step will take it to state $|n'\rangle$. For statistical equlilibrium, it must be that the probability that any randomly observed step takes us out of state $|n\rangle$ is equal to the probability that it takes us into that state:

$$\rho_n \sum_{n'} p_{nn'} = \sum_{n'} \rho_{n'} p_{n'n} \ . \tag{5.95}$$

(Here ρ_n is the probability that the lattice was is state $|n\rangle$ just before the transition.) Now, we know that in equilibrium, $\rho_{n'} = \rho_n \ e^{(E_n - E_{n'})/k_BT}$, so our conditional transition probabilities must satisfy

$$\sum_{n'} p_{nn'} = \sum_{n'} p_{n'n} e^{(E_n - E_{n'})/k_BT} \ . \tag{5.96}$$

The Metropolis rule is simple:

$$\text{if } E_n > E_m, \text{ then } p_{nm} = 1; \text{ and if } E_n < E_m, \text{ then } p_{nm} = \exp[(E_n - E_m)/k_BT]. \tag{5.97}$$

It is easy to show that this satisfies the statistical equilibrium condition (5.96) and that it drives an initial out-of-equilibrium system towards equilibrium.

The numerical implementation of the Metropolis rule (5.97) is this: Start with the lattice in an initial, random state, 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.[14] In this way, we produce 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 a finite tiling of our actual finite lattice and every time we need to know the spin at a site beyond the tiling's last column (or row), we use the corresponding spin an equal distance beyond the first column (or row). 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 on 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

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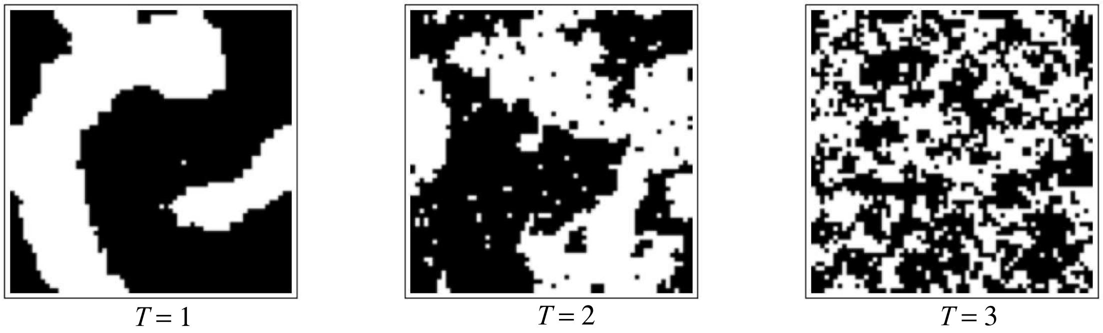
[14] Actually, there is a small subtlety here. The probability of making a given transition is actually the product of the probability of making the trial flip and of accepting the trial. However, the probability of making a trial flip is the same for all the spins that we might flip ($1/N$), and these trial probabilities cancel, so it is only the ratio of the probabilities of acceptance that matters.



$T = 1$ $T = 2$ $T = 3$

Fig. 5.12: 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, $s = -1$.

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 state 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 simulations that can be used for variance reduction and estimation, but we only concern ourselves here with the general method.

Returning to the Ising model, we show in Fig. 5.12 typical equilibrium states (snapshots) for three temperatures, measured in units of J/k_B). Recall that the critical temperature is $T_c = J/(k_B K_c) = 2.268 J/k_B$. Note the increasingly long range order as the temperature is reduced below 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 5.16 $\boxed{T2}$ *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 state.

Exercise 5.17 $\boxed{T2}$ *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 5.18 $\boxed{T2}$ *Problem: Ising Lattice with an Applied Magnetic Field*
Modify your computer program from Ex 5.17 to deal with the 2-dimensional Ising model augmented by an externally imposed, uniform magnetic field [Eqs. (5.80)]. Compute the

magnetization and the magnetic susceptibility for wisely selected values of $m_o B/J$ and $K = J/k_B T$.

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Bibliographic Note

Most statistical mechanics textbooks include much detail on statistical thermodynamics. Among those we have found useful at an elementary level are Kittel and Kroemer (1980), and at more advanced levels, Chandler (2007), Kardar (2007), Pathria and Beale (2011), Reif (1965), and Sethna (2006). Chandler (2007) and Sethna (2006) are particularly good for phase transitions; our treatment of the renormalization group in Sec. 5.8.3 is adapted in part from Chandler.

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Box 5.4
Important Concepts in Chapter 5

- **Representations of thermodynamics and their equilibrium ensembles and distributions**
  - Summary: Table 5.1, Sec. 5.2.5
  - 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
  - $\boxed{\textbf{T2}}$ Enthalpy representation and enthalpy distribution: Ex. 5.5
- **Systems out of equilibrium**
  - Entropy increase for each ensemble, expressed in terms of out-of-equilibrium fundamental potentials, 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. 5.11 and 5.12
- **Computational techniques**
  - most important statistical sums for fundamental potentials, Eqs. (5.17), (5.31)
  - thermodynamic equations deduced from first law in each representation, Sec. 5.2.4, ends of Secs. 5.3.1, 5.4, 5.5
  - $\boxed{\textbf{T2}}$ renormalization group, Sec. 5.8.3
  - $\boxed{\textbf{T2}}$ Monte Carlo calculations, Sec. 5.8.4
- **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
  - Electron-positron pairs in thermal equilibrium, Ex. 5.9
  - Saha equation for ionization equilibrium, Ex. 5.10
  - van der Waals gas, Sec. 5.3.2; its fluctuations, gas-to-liquid phase transition, surface tension and nucleation of droplets, Sec. 5.7 and Ex. 5.14
  - $\boxed{\textbf{T2}}$ Paramagnetism and Curie's law, Secs. 5.8 and 5.8.1
  - $\boxed{\textbf{T2}}$ Ferromagnetic phase transition and Ising model, Secs. 5.8.2, 5.8.3 and 5.8.4