Contents

Chapter 4

Statistical Mechanics

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Box 4.1
Reader's Guide

- Relativity enters into portions of this chapter solely via the relativistic energies and momenta of high-speed particles (Box 1.4.) We presume that all readers are familiar with at least this much relativity and accordingly, we do not provide a Newtonian track through this chapter. We will make occasional additional side remarks for the benefit of relativistic readers, but a Newtonian reader's failure to understand them will not compromise mastering all of this chapter's material.
- This chapter relies in crucial ways on Secs. 2.2 and 2.3 of Chap. 2.
- Chapter 4 is an extension of this chapter. To understand it and portions of Chap. 5, one must master the fundamental concepts of statistical mechanics (Secs. 4.2–4.4, 4.5–4.7, and 4.9), and also the application to an ideal, monatomic gas (Sec. 4.8).
- Other chapters do not depend strongly on this one.

4.1 Overview

While kinetic theory (Chap. 2) gives a powerful description of some statistical features of matter, other features are outside its realm and must be treated using the more sophisticated tools of statistical mechanics. Examples are:
(i) *Correlations*: Kinetic theory's distribution function $\mathcal{N}$ tells us, on average, how many particles will occupy a given phase-space volume, but it says nothing about whether the

particles like to clump, or avoid each other. It is therefore inadequate to describe the distribution of galaxies, which aggregate under their mutual gravitational attraction, or that of electrons (Chap. 21), which are mutually repulsive and thus are spatially anti-correlated.
(ii) *Fluctuations*: In experiments to measure a very weak mechanical force (e.g. tests of the equivalence principle and searches for gravitational waves), one typically monitors the motion of a pendulum's test mass, on which the force acts. Molecules of gas hitting the test mass also make it move. Kinetic theory predicts how many molecules will hit in one millisecond, on average, and how strong is the resulting pressure acting in all directions; but kinetic theory's distribution function $\mathcal{N}$ cannot tell us the probability that in one millisecond more molecules will hit one side of the test mass than the other, mimicking the force to be measured. The probability distribution for fluctuations is an essential tool for analyzing the noise in this and any other physical experiment, and it falls in the domain of statistical mechanics, not kinetic theory.
(iii) *Strongly interacting particles*: As should be familiar, the thermal motions of an ionic crystal are best described not in terms of individual atoms (as in the "Einstein theory"), but instead by decomposing the atoms' motion into normal modes (phonons; "Debye theory"). The thermal excitation of phonons is governed by statistical mechanics.
(iv) *Microscopic origin of thermodynamic laws*: The laws of classical thermodynamics can be (and often are) derived from a few elementary, macroscopic postulates without any reference to the microscopic, atomic nature of matter. Kinetic theory provides a microscopic foundation for some of thermodynamics' abstract macroscopic ideas (e.g. the first law of thermodynamics) and permits the computation of equations of state. However a full appreciation of entropy and the second law of thermodynamics, and of behavior at phase transitions requires the machinery of statistical mechanics.

In this chapter we shall develop the conceptual foundations for classical statistical mechanics and its interface with quantum physics, and we shall also delve deeply enough into the quantum world to be able to treat a few simple quantum problems. More specifically: In Sec. 3.2 we shall introduce the concepts of systems, ensembles of systems, and the distribution function for an ensemble. In Sec. 3.3 we shall use Hamiltonian dynamics to study the evolution of an ensemble's distribution function and derive the statistical mechanical version of Liouville's theorem. In Sec. 3.4, we shall develop the concept of statistical equilibrium and shall derive the general forms of distribution functions for ensembles of systems that have reached statistical equilibrium. In Sec. 3.5 we will study an illustrative example of statistical-equilibrium ensembles: the phenomenon of Bose-Einstein condensation. In Sec. 3.6 we shall explore a peculiar but important example of an equilibrium ensemble, one called (for historical reasons) *microcanonical*, and we shall learn its relationship to *ergodicity*. In Sec. 3.7 we shall introduce the concept of the *entropy* of an ensemble of systems and shall show that an ensemble of identical systems that are isolated from the external universe maximizes its entropy by evolving (via *phase mixing* and *coarse-graining*) into statistical equilibrium. Having laid all these foundations, we shall develop illustrative applications of them in Secs. 3.5, 3.8, 3.9 and a number of exercises. Our examples will include, in addition to Bose-Einstein condensation, a simple monatomic gas in both the nonrelativistic and ultrarelativistic domains, an ionized-hydrogen plasma, the mean occupation numbers of boson and fermion states, and stars, galaxies, black holes, and the universe as a whole.

For galaxies, black holes and the universe we will have to confront the role of gravity in statistical mechanics (Sec. 3.9). Finally, in Sec. 3.10 we will give a brief introduction to the concept of *information* and its connection to entropy.

4.2 Systems, Ensembles, and Distribution Function

4.2.1 Systems

Systems play in statistical mechanics the same role as is played by particles in kinetic theory. A system is *any physical entity.* (Obviously, this is an exceedingly general concept!) Examples are a galaxy, the sun, a sapphire crystal, the fundamental mode of vibration of that crystal, an aluminum atom in that crystal, an electron from that aluminum atom, a quantum state in which that electron could reside, ...

Statistical mechanics focuses special attention on systems that couple only weakly to the rest of the universe. Stated more precisely, we are interested in systems whose relevant "internal" evolution timescales, $\tau_{\rm int}$, are short compared with the "external" timescales, $\tau_{\rm ext}$, on which they exchange energy, entropy, particles, etc. with their surroundings. Such systems are said to be *semiclosed*, and in the idealized limit where one completely ignores their external interactions, they are said to be *closed.* The statistical-mechanics formalism for dealing with them relies on the assumption $\tau_{\rm int}/\tau_{\rm ext} \ll 1$; in this sense, it is a variant of a two-lengthscale expansion (Box 2.3).

Some examples will elucidate these concepts: For a galaxy of, say, 10^{11} stars, $\tau_{\rm int}$ is the time it takes a star to cross the galaxy, $\tau_{\rm int} \sim 10^8$ yr. The external timescale is the time since the galaxy's last collison with a neighboring galaxy or the time since it was born by separating from the material that formed neighboring galaxies; both these times are $\tau_{\rm ext} \sim 10^{10}$ yr, so $\tau_{\rm int}/\tau_{\rm ext} \sim 1/100$ and the galaxy is semiclosed. For a small volume of gas inside the sun, say 1 m on a side, $\tau_{\rm int}$ is the timescale for the constituent electrons, ions and photons to interact through collisions, typically $\tau_{\rm int} \sim 10^{-11}$ s; this is much smaller than the time for external heat or particles to diffuse from the cube's surface to its center, $\tau_{\rm ext} \sim 10^{-5}$ s, so the cube is semiclosed. An individual atom in a crystal is so strongly coupled to its neighboring atoms by electrostatic forces that $\tau_{\rm int} \sim \tau_{\rm ext}$, which means the atom is not semiclosed. By contrast, for a vibrational mode of the crystal, $\tau_{\rm int}$ is the mode's vibration period and $\tau_{\rm ext}$ is the time to exchange energy with other modes and thereby damp the chosen mode's vibrations; and quite generally, the damping time is far longer than the period, so the mode is semiclosed. (For a highly-polished, cold sapphire crystal, $\tau_{\rm ext}$ can be $\sim 10^9 \tau_{\rm int}$.) Therefore, it is the crystal's vibrational normal modes and not its atoms that are amenable to the statistical mechanical tools we shall develop.

When a semiclosed classical system is idealized as closed, so its interactions with the external universe are ignored, then its evolution can be described using Hamiltonian dynamics.[1] The system's classical state is described by *generalized coordinates* $\mathbf{q} \equiv \{q_j\}$ and *generalized momenta* $\mathbf{p} \equiv \{p_j\}$, where the index j runs from 1 to W = (the number of

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[1] See, for example, Goldstein et. al. (2002), or Thornton and Marion (2004).

degrees of freedom). The evolution of $\mathbf{q}, \mathbf{p}$ is governed by *Hamilton's equations*

$$\boxed{\frac{dq_j}{dt} = \frac{\partial H}{\partial p_j} , \quad \frac{dp_j}{dt} = -\frac{\partial H}{\partial q_j} ,} \tag{4.1}$$

where $H(\mathbf{q}, \mathbf{p})$ is the *Hamiltonian* and each equation is really W separate equations. Note that, because the system is idealized as closed, there is no explicit time dependence in the Hamiltonian. Of course, not all physical systems (e.g. not those with strong internal dissipation) are describable by Hamiltonian dynamics, though in principle this restriction can usually be circumvented by increasing the number of degrees of freedom to include the cause of the dissipation.

Let us return to our examples. For an individual star inside a galaxy, there are three degrees of freedom ($W = 3$) which we might choose to be the motion along three mutually orthogonal Cartesian directions so $q_1 = x$, $q_2 = y$, $q_3 = z$. Because the star's speed is small compared to light, it's Hamiltonian has the standard form for a nonrelativistic particle

$$H(\mathbf{q}, \mathbf{p}) = \frac{1}{2m}({p_1}^2 + {p_2}^2 + {p_3}^2) + m\Phi(q_1, q_2, q_3) \ . \tag{4.2a}$$

Here m is the stellar mass and $\Phi(q_1, q_2, q_3)$ is the galaxy's Newtonian gravitational potential (whose sign we take to be negative). Now make a *canonical transformation*[2] (in this case the same as a coordinate transformation) to new $Q_1 = r$, $Q_2 = \theta$, $Q_3 = \phi$, where (r, θ, ϕ) are the star's spherical polar coordinates with r measured from the center of the galaxy. The corresponding, *canonically conjugate* momenta turn out to be $P_1 = p_r$, $P_2 = rp_\theta$, $P_3 = r \sin\theta p_\phi$ where p_r, p_θ and p_ϕ are the components of the star's momentum along unit vectors that point in the r, θ, and ϕ directions. In terms of these new coordinates, the Hamiltonian (4.2a) takes the form

$$H = \frac{1}{2m}\left({P_1}^2 + \frac{{P_2}^2}{r^2} + \frac{{P_3}^2}{r^2 \sin^2\theta}\right) + m\Phi(r, \theta, \phi) \ , \tag{4.2b}$$

and Hamilton's equations with this Hamiltonian continue to govern the star's motion. Now consider not just one star, but $K \sim 10^{11}$ of them in a galaxy. There are now $W = 3K$ degrees of freedom and the Hamiltonian is simply the sum of the Hamiltonians for each individual star so long as we ignore interactions between stars.

If our system is the fundamental mode of a sapphire crystal, then the number of degrees of freedom is only $W = 1$ and we can take the single generalized coordinate q to be the displacement of one end of the crystal from equilibrium; there will be an "effective mass" M for the mode (approximately equal to the actual mass of the crystal) such that the mode's generalized momentum is $p = Mdq/dt$. The Hamiltonian will be the standard one for a harmonic oscillator:

$$H(p, q) = \frac{p^2}{2M} + \frac{1}{2}M\omega^2 q^2 \ , \tag{4.3a}$$

where ω is the mode's angular frequency of oscillation.

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[2] See Ex. 4.1; also Goldstein et. al. (2002) or Thornton and Marion (2004).

If we want to describe a whole crystal with $N \sim 10^{27}$ atoms, then we obtain H by summing over $W = 3N$ oscillator Hamiltonians for the crystal's W normal modes and adding an interaction potential $H_{\rm int}$ that accounts for the very weak interactions between modes:

$$H = \sum_{j=1}^{W} \left\{ \frac{p_j^2}{2M_j} + \frac{1}{2} M_j {\omega_j}^2 {q_j}^2 \right\} + H_{\rm int}(q_1, \ldots, q_W, p_1, \ldots, p_W) \; . \tag{4.3b}$$

Here M_j is the effective mass of mode jm and ω_j is the mode's angular frequency. This description of the crystal is preferable to one in which we use, as our generalized coordinates and momenta, the coordinate locations and momentum components of each of the 10^{27} atoms. Why? Because the normal modes are so weakly coupled to each other, that they are semiclosed *subsystems* of the crystal, whereas the atoms are so strongly coupled that they are not, individually, semiclosed. As we shall see, there is great power in decomposing a complicated system into semiclosed subsystems.

4.2.2 Ensembles

In kinetic theory we study, statistically, a collection of a huge number of *particles*. Similarly, in statistical mechanics, we study, statistically, a collection or *ensemble* of a huge number of *systems*. This ensemble is actually only a conceptual device, a foundation for statistical arguments that take the form of thought experiments. As we shall see, there are many different ways that one can imagine forming an ensemble and this freedom can be used to solve many different types of problems.

In some applications, we require that all the systems in the ensemble be *closed*, and be *identical* in the sense that they all have identically the same number of degrees of freedom W, and are governed by Hamiltonians with identically the same functional forms $H(\mathbf{q}, \mathbf{p})$, and have identically the same volume V and total internal energy $\mathcal{E}$. However, the values of the generalized coordinates and momenta at a specific time t, $\{\mathbf{q}(t), \mathbf{p}(t)\}$, need not be the same; i.e., the systems need not be in the same *state* at time t. If such a conceptual ensemble of identical closed systems (first studied by Boltzmann) evolves until it reaches "statistical equilibrium" (Sec. 3.4), it then is called *microcanonical*; see Table 4.1.

Ensemble	**Quantities Exchanged with Surroundings**
Microcanonical	nothing
Canonical	Energy $\mathcal{E}$
Gibbs	Energy $\mathcal{E}$ and Volume V
Grand Canonical	Energy $\mathcal{E}$ and number of particles N_I of various species I

Table 4.1: Statistical-equilibrium ensembles used in this chapter.

Sometimes we will deal with an ensemble of systems that can exchange energy (heat) with their identical surroundings so the internal energy of each system can fluctuate. If the surroundings (sometimes called *heat baths*) have far greater heat capacity than the individual systems, and if statistical equilibrium has been reached, then we call this sort of ensemble (introduced by Gibbs) *canonical*.

At the next level of freedom, the systems can also expand, i.e. they can exchange volume as well as energy with their identical surroundings. This was also studied by Gibbs and in equilibrium is known as the *Gibbs* ensemble. A fourth ensemble in common use is Pauli's *grand canonical* ensemble in which each system can exchange energy and particles (but not volume) with its surroundings; see Table 4.1. We will study these equilibrium ensembles in Sec. 4.4 below.

4.2.3 Distribution Function

In kinetic theory (Chap. 2), we described the statistical properties of a collection of identical particles by a distribution function, and we found it useful to tie that distribution function's normalization to quantum theory: $\eta(t; \mathbf{x}, \mathbf{p})$ = (mean number of particles that occupy a quantum state at location $\{\mathbf{x}, \mathbf{p}\}$ in 6-dimensional phase space at time t). In statistical mechanics, we will use the obvious generalization of this: η = (mean number of systems that occupy a quantum state at location $\{\mathbf{q}, \mathbf{p}\}$ in an ensemble's $2W$-dimensional phase space, at time t) — except that we need two modifications: *First*: This η is proportional to the number of systems $N_{\rm sys}$ in our ensemble. (If we double $N_{\rm sys}$, then η will double.) Because our ensemble is only a conceptual device, we don't really care how many systems it contains, so we divide η by $N_{\rm sys}$ to get a renormalized, $N_{\rm sys}$-independent distribution function, $\rho = \eta/N_{\rm sys}$, whose physical interpretation is

$$\rho(t; \mathbf{q}, \mathbf{p}) = \left(\begin{array}{c} \text{probability that a system, drawn randomly from our ensemble,} \\ \text{will be in a quantum state at location } (\mathbf{q}, \mathbf{p}) \text{ in phase space, at time } t \end{array} \right) . \tag{4.4}$$

Second: If the systems of our ensemble can exchange particles with the external universe (as is the case, for example, in the grand canonical ensemble of Table 4.1), then their number W of degrees of freedom can change, so ρ depends on W as well as on location in the $2W$-dimensional phase space: $\rho(t; W, \mathbf{q}, \mathbf{p})$.

In the sector of the system's phase space with W degrees of freedom, denote the number density of quantum states by

$$\mathcal{N}_{\rm states}(W, \mathbf{q}, \mathbf{p}) = \frac{dN_{\rm states}}{d^W q d^W p} \equiv \frac{dN_{\rm states}}{d\Gamma_W} . \tag{4.5}$$

Here

$$d^W q \equiv dq_1 dq_2 \cdots dq_W , \quad d^W p \equiv dp_1 dp_2 \cdots dp_W , \quad d\Gamma_W \equiv d^W q d^W p . \tag{4.6}$$

Then the sum of the occupation probability ρ over all quantum states, which must (by the meaning of probability) be unity, takes the following form:

$$\sum_n \rho_n = \sum_W \int \rho \mathcal{N}_{\rm states} d\Gamma_W . \tag{4.7}$$

Here, on the left side n is a formal index that labels the various quantum states $|n\rangle$ available to the ensemble's systems; and on the right side the sum is over all possible values of the system's dimensionality W, and the integral is over all of the $2W$-dimensional phase space, with $d\Gamma_W$ a short-hand notation for the phase-space integration element $d^W q d^W p$.

Equations (4.4)–(4.7) require some discussion:

Just as the event $\{t, \mathbf{x}\}$ and 4-momentum $\{\mathcal{E}, \mathbf{p}\}$ in relativistic kinetic theory are geometric, frame-independent objects, similarly *location in phase space* in statistical mechanics is a geometric, coordinate-independent concept (though our notation does not emphasize it). The quantities $\{\mathbf{q}, \mathbf{p}\} \equiv \{q_1, q_2, ...q_W, p_1, p_2, ...p_W\}$ are the coordinates of that phase-space location. When one makes a canonical transformation from one set of generalized coordinates and momenta to another, the q's and p's change but the geometric location in phase space does not. Moreover, just as the individual spatial and momentum volumes $d\mathcal{V}_x$ and $d\mathcal{V}_p$ occupied by a set of relativistic particles in kinetic theory are frame-dependent but their product $d\mathcal{V}_x d\mathcal{V}_p$ is frame-independent [cf. Eqs. (2.8a)–(2.8c)], so also in statistical mechanics the volumes $d^W q$ and $d^W p$ occupied by some chosen set of systems are dependent on the choice of canonical coordinates and they change under a canonical transformation, but the product $d^W q d^W p \equiv d\Gamma_W$ (the systems' total volume in phase space) is independent of the choice of canonical coordinates and is unchanged by a canonical transformation. Correspondingly, the number density of states in phase space $\mathcal{N}_{\rm states} = dN_{\rm states}/d\Gamma_W$ and the statistical mechanical distribution function $\rho(t; W, \mathbf{q}, \mathbf{p})$, like their kinetic-theory counterparts, are geometric, coordinate-independent quantities; i.e., they are unchanged by a canonical transformation. See Ex. 4.1.

Classical thermodynamics was one of the crowning achievements of nineteenth century science. However, thermodynamics was inevitably incomplete and had to remain so until the development of quantum theory. A major difficulty, one that we have already confronted in Chap. 2, was how to count the number of states available to a system. As we saw in Chap. 2, the number density of quantum mechanical states in the 6-dimensional, single-particle phase space of kinetic theory is (ignoring particle spin) $\mathcal{N}_{\rm states} = 1/h^3$, where h is Planck's constant. Generalising to the $2W$-dimensional phase space of statistical mechanics, the number density of states turns out to be $1/h^W$, (one factor of $1/h$ for each of the canonical pairs (q_1, p_1), (q_2, p_2) , $\cdots$, (q_W, p_W).) Formally, this follows from the canonical quantization procedure of elementary quantum mechanics.

There was a second problem in nineteenth century classical thermodynamics, that of *distinguishability*: If we swap two similar atoms in phase space do we have a new state or not? If we mix two containers of the same gas at the same temperature and pressure, does the entropy increase? This problem was recognized classically, but was not resolved in a completely satisfactory classical manner. When the laws of quantum mechanics were developed, it became clear that all identical particles are indistinguishable (Ex. 4.9 below), so having particle 1 at location $\mathcal{A}$ in phase space and an identical particle 2 at location $\mathcal{B}$ must be counted as the same state as particle 1 at $\mathcal{B}$ and particle 2 at $\mathcal{A}$. Correspondingly, if we attribute half the quantum state to the classical phase space location {1 at $\mathcal{A}$, 2 at $\mathcal{B}$} and the other half to {1 at $\mathcal{B}$, 2 at $\mathcal{A}$}, then the classical number density of states per unit volume of phase space must be reduced by a factor 2—and more generally by some *multiplicity factor* $\mathcal{M}$. In general, therefore, we can write the actual number density of states in phase space as

$$\boxed{\mathcal{N}_{\rm states} = \frac{dN_{\rm states}}{d\Gamma_W} = \frac{1}{\mathcal{M}h^W}\ ,} \tag{4.8a}$$

and correspondingly we can rewrite the normalization condition (4.7) for our probabilistic distribution function as:

$$\boxed{\sum_n \rho_n \equiv \sum_W \int \rho \mathcal{N}_{\rm states} d\Gamma_W = \sum_W \int \rho \frac{d\Gamma_W}{\mathcal{M}h^W} = 1\ .} \tag{4.8b}$$

This equation can be regarded, in the classical domain, as defining the meaning of the sum over states n. We shall make extensive use of such sums over states.

For N identical and indistinguishable particles with zero spin, it is not hard to see that $\mathcal{M} = N!$. If we include the effects of quantum mechanical spin, then there are g_s [Eq. (2.15)] more states present in phase space than we thought, so the multiplicity $\mathcal{M}$ (the number of different phase space locations to be attributed to each state) is reduced to

$$\boxed{\mathcal{M} = \frac{N!}{g_s} \quad \text{for a system of } N \text{ identical particles with spin } s.} \tag{4.8c}$$

This is the quantity that appears in the denominator of the sum over states, Eq. (4.8b).

Occasionally, for conceptual purposes, it is useful to introduce a renormalized distribution function analogous to kinetic theory's number density of particles $\mathcal{N}_{\rm sys}$ in phase space:

$$\mathcal{N}_{\rm sys} = N_{\rm sys}\, \mathcal{N}_{\rm states}\, \rho = \frac{d\text{number of systems}}{d\text{volume in } 2W\text{-dimensional phase space}}\ . \tag{4.9}$$

However, this version of the distribution function will rarely if ever be useful computationally.

Each system in an ensemble is endowed with a total energy that is equal to its Hamiltonian, $\mathcal{E} = H(\mathbf{q}, \mathbf{p})$ [or $E = H(\mathbf{q}, \mathbf{p})$ nonrelativistically]. Because different systems reside at different locations $(\mathbf{q}, \mathbf{p})$ in phase space, they typically will have different energies. A quantity of much interest is the *ensemble-averaged energy*, which is the average value of $\mathcal{E}$ over all systems in the ensemble

$$\langle \mathcal{E} \rangle = \sum_n \rho_n \mathcal{E}_n = \sum_W \int \rho \mathcal{E} \mathcal{N}_{\rm states} d\Gamma_W = \sum_W \int \rho \mathcal{E} \frac{d\Gamma_W}{\mathcal{M}h^W}\ . \tag{4.10a}$$

For any other function $A(\mathbf{q}, \mathbf{p})$ defined on the phase space of a system, for example the linear momentum or the angular momentum, one can compute an ensemble average by the obvious analog of Eq. (4.10a):

$$\boxed{\langle A \rangle = \sum_n \rho_n A_n\ .} \tag{4.10b}$$

Our probabilistic distribution function $\rho_n = \rho(t; W, \mathbf{q}, \mathbf{p})$ has deeper connections to quantum theory than the above discussion reveals: In the quantum domain, even if we start with a system whose wave function ψ is in a *pure* state (ordinary, everyday type of quantum state), the system may evolve into a *mixed state* as a result of (i) interaction with the rest of the universe and (ii) our choice not to keep track of correlations between the universe and the system; Box 4.2 and Sec. 4.7.2 below. The system's initial, pure state can be described in geometric, basis-independent quantum language by a state vector ("ket") $|\psi\rangle$; but its final, mixed state requires a different kind of quantum description: a *density operator* $\hat{\rho}$. In the classical limit, the quantum mechanical density operator $\hat{\rho}$ becomes our classical probabilistic distribution function $\rho(t, W, \mathbf{q}, \mathbf{p})$; see Box 4.2 for some details.

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EXERCISES

Exercise 4.1 *Derivation and Example: Canonical Transformation*[1]

Let (q_j, p_k) be one set of generalized coordinates and momenta for a given system and let (Q_j, P_k) be another set. Then (except in degenerate cases, for which a different generating function must be used) there is a generating function $F(q_j, P_k)$, which depends on the "old" coordinates q_j and "new" momenta P_k, such that

$$p_j = \frac{\partial F}{\partial q_j} \; , \quad Q_j = \frac{\partial F}{\partial P_j} \; . \tag{4.11}$$

(a) As an example, what are the new coordinates and momenta in terms of the old that result from

$$F = \sum_{i=1}^{W} f_i(q_j) P_i \; , \tag{4.12}$$

where f_i are arbitrary functions of the old coordinates?

(b) The canonical transformation generated by Eq. (4.11) for arbitrary $F(q_j, P_k)$ leaves unchanged the value, but not the functional form, of the Hamiltonian at each point in phase space, i.e., H is a geometric, coordinate-independent function (scalar field) of location in phase space. Show, for the special case of a system with one degree of freedom (one q, one p, one Q, and one P) that, if Hamilton's equations (4.1) are satisfied in the old variables (q, p), then they will be satisfied in the new variables (Q, P).

(c) Show, for a system with one degree of freedom, that although $dq \neq dQ$ and $dp \neq dP$, the volume in phase space is unaffected by the canonical transformation: $dpdq = dPdQ$.

(d) Hence show that for any closed path in phase space, $\oint pdq = \oint PdQ$.

(e) As a higher-dimensional example ($W = 3$), consider a star moving in a galaxy [Eqs. (4.2a), (4.2b) and associated discussion]. Show that $d^3q = dxdydz \neq d^3Q = drd\theta d\phi$, and $d^3p \neq d^3P$, but $d^3qd^3p = d^3Qd^3P$.

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Box 4.2

$\boxed{\text{T2}}$ Density Operator and Quantum Statistical Mechanics

For readers who know some quantum statistical mechanics, we here describe briefly the connection of our probabilistic distribution function ρ to the full quantum statistical theory as laid out, e.g., in Feynman (1972).

Consider a single quantum mechanical system that is in a *pure* state $|\psi\rangle$. One can formulate the theory of such a pure state equally well in terms of $|\psi\rangle$ or the *density operator* $\hat{\varrho} \equiv |\psi\rangle\langle\psi|$. For example, the expectation value of some observable, described by a Hermitian operator $\hat{A}$, can be expressed equally well as $\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle$ or as $\langle A\rangle = \text{Trace}(\hat{\varrho}\hat{A})$. (In any basis $|\phi_i\rangle$, "Trace" is just the trace of the matrix product $\sum_j \varrho_{ij}A_{jk}$, where $A_{jk} \equiv \langle\phi_j|\hat{A}|\phi_k\rangle$, and $\varrho_{ij} \equiv \langle\phi_i|\hat{\varrho}|\phi_j\rangle$ is called the *density matrix* in that basis.)

If our chosen system interacts with the external universe and we have no knowledge of the correlations that the interaction creates between the system and the universe, then the interaction drives the system into a mixed state, which is describable by a density operator $\hat{\varrho}$ but not by a ket vector $|\psi\rangle$. This $\hat{\varrho}$ can be regarded as a classical-type average of $|\psi\rangle\langle\psi|$ over an ensemble of systems, each of which has interacted with the external universe and then has been driven into a pure state $|\psi\rangle$ by a measurement of the universe. Equivalently, $\hat{\varrho}$ can be constructed from the pure state of universe plus system by "tracing over the universe's degrees of freedom".

If the systems in the ensemble behave nearly classically, then it turns out that in the basis $|\phi_n\rangle$, whose states are labeled by the classical variables $n = \{W, \mathbf{q}, \mathbf{p}\}$, the density matrix $\varrho_{nm} \equiv \langle\phi_n|\hat{\varrho}|\phi_m\rangle$ is very nearly diagonal. The classical probability ρ_n of classical statistical mechanics (and of this book when dealing with classical or quantum systems) is then equal to the diagonal value of this density matrix: $\rho_n = \varrho_{nn}$.

It can be demonstrated that the equation of motion for the density operator $\hat{\varrho}$, when the systems in the quantum mechanical ensemble are all evolving freely (no significant interactions with the external universe), is

$$\frac{\partial\hat{\varrho}}{\partial t} + \frac{1}{i\hbar}[\hat{\varrho}, \hat{H}] = 0 \ . \tag{1}$$

This is the quantum statistical analog of Liouville's equation (4.14), and the quantum mechanical commutator $[\hat{\varrho}, \hat{H}]$ appearing here is the quantum mechanical analog of the Poisson bracket $[\rho, H]_{\mathbf{q},\mathbf{p}}$, which appears in Liouville's equation. If the quantum systems are in eigenstates of their Hamiltonians, then $\hat{\varrho}$ commutes with $\hat{H}$ so the density matrix is constant in time and there will be no transitions. This is the quantum analog of the classical ρ being constant in time and thus a constant of the motion; Sec. 4.4 below.

4.3 Liouville's Theorem and the Evolution of the Distribution Function

In kinetic theory the distribution function $\mathcal{N}$ was not only a frame-independent entity; it was also a constant along the trajectory of any freely moving particle, so long as collisions between particles were negligible. Similarly, in statistical mechanics the probability ρ is not only coordinate-independent (unaffected by canonical transformations); *ρ is also a constant along the phase-space trajectory of any freely evolving system*, so long as the systems in the ensemble are not interacting significantly with the external universe, i.e. so long as they can be idealized as closed. This is the statistical mechanical version of *Liouville's theorem*, and its proof is a simple exercise in Hamiltonian mechanics, analogous to the "sophisticated" proof of the collisionless Boltzmann equation in Box 2.2:

Since the ensemble's systems are closed, no system changes its dimensionality W during its evolution. This permits us to fix W in the proof. Since no systems are created or destroyed during their evolution, the number density of systems in phase space, $\mathcal{N}_{\rm sys} = N_{\rm sys}\,\mathcal{N}_{\rm states}\,\rho$ [Eq. (4.9)] must obey the same kind of conservation law as we encountered in Eq. (1.73) for electric charge and particle number in Newtonian physics. For particle number, the conservation law is $\partial n/\partial t + \boldsymbol{\nabla}\cdot(n\mathbf{v}) = 0$, where n is the number density of particles in physical space, $\mathbf{v}$ is their velocity in physical space, and $n\mathbf{v}$ is their flux. Our ensemble's systems have velocity $dq_j/dt = \partial H/\partial p_j$ in physical space, and "velocity" $dp_j/dt = -\partial H/\partial q_j$ in momentum space, so the conservation law (valid for ρ as well as $\mathcal{N}_{\rm sys}$ since they are proportional to each other) is

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial q_j}\left(\rho\frac{dq_j}{dt}\right) + \frac{\partial}{\partial p_j}\left(\rho\frac{dp_j}{dt}\right) = 0\ . \tag{4.13}$$

Here the implicit sums over j are from 1 to W. Using Hamilton's equations, we can rewrite this as

$$0 = \frac{\partial\rho}{\partial t} + \frac{\partial}{\partial q_j}\left(\rho\frac{\partial H}{\partial p_j}\right) - \frac{\partial}{\partial p_j}\left(\rho\frac{\partial H}{\partial q_j}\right) = \frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial q_j}\frac{\partial H}{\partial p_j} - \frac{\partial\rho}{\partial p_j}\frac{\partial H}{\partial q_j} = \frac{\partial\rho}{\partial t} + [\rho, H]_{\mathbf{q},\mathbf{p}}\ ,$$

where $[\rho, H]_{\mathbf{q},\mathbf{p}}$ is the *Poisson bracket*.[1] By using Hamilton's equations once again in the third expression, we discover that this is the time derivative of ρ moving with a fiducial system through the $2W$-dimensional phase space:

$$\boxed{\frac{d\rho}{dt} \equiv \frac{\partial\rho}{\partial t} + \frac{dq_j}{dt}\frac{\partial\rho}{\partial q_j} + \frac{dp_j}{dt}\frac{\partial\rho}{\partial p_j} = \frac{\partial\rho}{\partial t} + [\rho, H]_{\mathbf{q},\mathbf{p}} = 0.} \tag{4.14}$$

Therefore, the probability ρ is constant along the system's phase space trajectory, as was to be proved.

We shall call Eq. (4.14), which embodies this Liouville theorem, the statistical mechanical *Liouville equation* or *collisionless Boltzmann equation.*

As a simple, qualitative example, consider a system consisting of hot gas expanding adiabatically so that its large random kinetic energy is converted into ordered radial motion. If we examine a set $\mathcal{G}$ of such systems very close to each other in phase space, then it is apparent that, as the expansion proceeds, the size of $\mathcal{G}$'s physical-space volume d^Wq increases and the size of its momentum-space volume d^Wp diminishes, so that the product d^Wqd^Wp remains constant (Fig. 4.1), and correspondingly $\rho \propto \mathcal{N}_{\rm sys} = dN_{\rm sys}/d^Wqd^Wp$ is constant.

What happens if the systems being studied interact weakly with their surroundings? We must then include an interaction term on the right hand side of Eq. (4.14), thereby converting

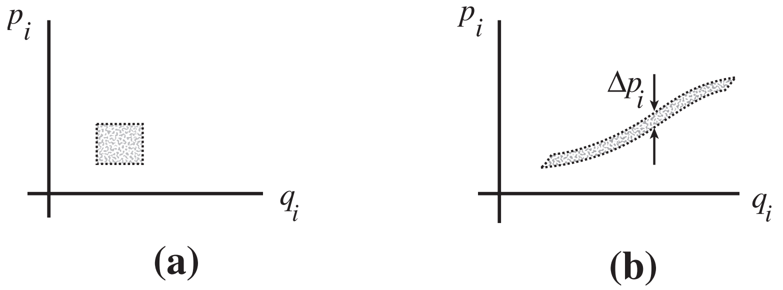

Fig. 4.1: Liouville's theorem: (a) The region in the $q_i - p_i$ part of phase space (with i fixed) occupied by a set $\mathcal{G}$ of identical, closed systems at time $t = 0$. (b) The region occupied by the same set of systems a short time later, $t > 0$. The Hamiltonian-generated evolution of the individual systems has moved them in such a manner as to skew the region they occupy, but the volume $\int dp_i dq_i$ is unchanged.

it into the statistical mechanical version of the Boltzmann transport equation:

$$\boxed{\left(\frac{d\rho}{dt}\right)_{\text{moving with a fiducial system}} = \left(\frac{d\rho}{dt}\right)_{\text{interactions}} .} \tag{4.15}$$

Here the time derivative on the left is taken moving through phase space with a fiducial system that does *not* interact with the external universe.

4.4 Statistical Equilibrium

4.4.1 Canonical Ensemble and Distribution

Consider an ensemble of identical systems, all of which have the same huge number of degrees of freedom (dimensionality $W \gg 1$). Put all the systems initially in identically the same state, and then let them exchange heat (but not particles or volume or anything else) with an external *thermal bath* that has a huge heat capacity and is in thermodynamic equilibrium at some temperature T. (For example, the systems might be impermeable cubes of gas 1 kilometer on a side near the center of the sun, and the thermal bath might be all the surrounding gas near the sun's center; or the systems might be identical sapphire crystals inside a huge cryostat, and the thermal bath might be the cryostat's huge store of liquid Helium.) After a sufficiently long time, $t \gg \tau_{\text{ext}}$, the ensemble will settle down into equilibrium with the bath, i.e. it will become the *canonical ensemble* mentioned in Table 4.1 above. In this final, canonical equilibrium state, the probability $\rho(t, \mathbf{q}, \mathbf{p})$ will be independent of time t, and it no longer will be affected by interactions with the external environment; i.e., the interaction terms in the evolution equation (4.15) will have ceased to have any net effect: on average, for each interaction event that feeds energy into a system there will be an interaction event that takes away an equal amount of energy. The distribution function, therefore, will satisfy the interaction-free, collisionless Boltzmann equation (4.14) with the time derivative $\partial\rho/\partial t$ removed:

$$[\rho, H]_{\mathbf{q},\mathbf{p}} \equiv \frac{\partial\rho}{\partial q_j}\frac{\partial H}{\partial p_j} - \frac{\partial\rho}{\partial p_j}\frac{\partial H}{\partial q_j} = 0 \tag{4.16}$$

We shall use the phrase *statistical equilibrium* to refer to any ensemble whose distribution function has attained such a state and thus satisfies Eq. (4.16).

Equation (4.16) is a well-known equation in Hamiltonian mechanics; it says that ρ is a function solely of constants of the individual systems' Hamiltonian-induced motions;[1] i.e., ρ can depend on location $(\mathbf{q}, \mathbf{p})$ in phase space only through those constants of the motion. Sometimes this goes by the name *Jeans' Theorem.* Among the constants of motion in typical situations (for typical Hamiltonians) are the system's energy $\mathcal{E}$, its linear momentum $\mathbf{P}$, its angular momentum $\mathbf{J}$, its number N_I of conserved particles of various types I (e.g. electrons, protons, ...), and its volume V. Note that these constants of motion are all additive: if we double the size of a system, they each double. We shall call such additive constants of the Hamiltonian-induced motion *extensive variables* (a term borrowed from thermodynamics) and we shall denote them by an enumerated list $K_1, K_2, ...$

Now, the systems that we are studying have exchanged energy $\mathcal{E}$ with their environment (the thermal bath) and thereby have acquired some range of $\mathcal{E}$'s; therefore, ρ can depend on $\mathcal{E}$. However, the systems have not exchanged anything else with their environment, and they all thus have retained their original (identical) values of the other extensive variables K_A; therefore, ρ must be a delta function in the others. We shall write

$$\rho = \rho(\mathcal{E})\ , \tag{4.17a}$$

and shall not write down the delta functions explicitly.

As an aid in discovering the form of the function $\rho(\mathcal{E})$, let us decompose each system in the ensemble into a huge number of subsystems. For example, each system might be a cube 1 km on a side inside the sun and its subsystems might be the 10^9 1-m cubes into which one can divide it, or the systems might be identical sapphire crystals each containing 10^{27} atoms, and the subsystems might be the crystals' 3×10^{27} normal modes of vibration. We shall label the subsystems of each system by an integer a in such a way that subsystem a in one system has the same Hamiltonian as subsystem a in any other system. (For the sapphire crystals, $a = 1$ could be the fundamental mode of vibration, $a = 2$ the first harmonic, $a = 3$ the second harmonic, etc.) The subsystems with fixed a make up a *subensemble* because of their relationship to the original ensemble.

Because the full ensemble is in statistical equilibrium, the subensembles will also be in statistical equilibrium; and therefore their probabilities must be functions of those extensive variables $\mathcal{E}, K_A$ that they can exchange with each other:

$$\rho_a = \rho_a(\mathcal{E}_a, K_{1\,a}, K_{2\,a}, ...)\ . \tag{4.17b}$$

(Although each system can exchange only energy $\mathcal{E}$ with its heat bath, the subsystems may be able to exchange other quantities with each other; for example, if subsystem a is a 1-meter cube inside the sun with permeable walls, then it can exchange energy $\mathcal{E}_a$ and particles of all species I, so $K_{I\,a} = N_{I\,a}$.)

Since there is such a huge number of subsystems in each system, it is reasonable to expect that in statistical equilibrium there will be no significant correlations at any given time between the actual state of subsystem a and the state of any other subsystem. In other words, the probability $\rho_a(W_{a,}\mathbf{q}_a, \mathbf{p}_a)$ that subsystem a is in a quantum state with W_a degrees of freedom and with its generalized coordinates and momenta near the values $(\mathbf{q}_a, \mathbf{p}_a)$ is independent of the state of any other subsystem. This lack of correlations, which has the mathematical statement

$$\rho(\mathcal{E}) = \prod_a \rho_a \ , \tag{4.17c}$$

is called *statistical independence*. (Statistical independence is actually a consequence of a "2-lengthscale approximation" [Box 2.3]. The size of each subsystem is far smaller than that of the full system, and precise statistical independence arises in the limit as the ratio of these sizes goes to zero.)

Statistical independence places a severe constraint on the functional forms of ρ and ρ_a, as the following argument shows. By taking the logarithm of Eq. (4.17c), we obtain

$$\ln \rho(\mathcal{E}) = \sum_a \ln \rho_a(\mathcal{E}_a, K_{1\,a}, ...) \ . \tag{4.17d}$$

We also know, since energy is a linearly additive quantity, that

$$\mathcal{E} = \sum_a \mathcal{E}_a. \tag{4.17e}$$

Now, we have not stipulated the way in which the systems are decomposed into subsystems. For our solar example, the subsystems might have been 2-m cubes or 7-m cubes rather than 1-m cubes. Exploiting this freedom, one can deduce that Eqs. (4.17d) and (4.17e) can be satisfied simultaneously if and only if $\ln \rho$ and $\ln \rho_a$ depend linearly on the energies $\mathcal{E}$ and $\mathcal{E}_a$, with the same proportionality constant $-\beta$:

$$\begin{aligned} \ln \rho_a &= -\beta \mathcal{E}_a + (\text{some function of } K_{1\,a}, K_{2\,a}, ...) \ , & (4.18\text{a}) \\ \ln \rho &= -\beta \mathcal{E} + \text{constant}. & (4.18\text{b}) \end{aligned}$$

Since the parameter β is the same for all the systems and their subsystems, it must be some characteristic of the thermal bath with which the systems and subsystems equilibrated. By exponentiating Eq. (4.18b) and noting that it has the same functional form as the Boltzmann distribution (2.22d) of kinetic theory, we infer that β must be $1/k_B T$, where T is the temperature of the thermal bath.

To summarize, an ensemble of identical systems with many degrees of freedom $W \gg 1$, which have reached statistical equilibrium by exchanging energy but nothing else with a huge thermal bath, has the following *canonical* distribution function:

$$\boxed{\rho_{\text{canonical}} = C \exp(-\mathcal{E}/k_B T) \ .} \tag{4.19}$$

Here $\mathcal{E}(\mathbf{q}, \mathbf{p})$ is the energy of a system at location $\{\mathbf{q}, \mathbf{p}\}$ in phase space, k is Boltzmann's constant, T is the temperature of the heat bath, and C is whatever normalization constant is required to guarantee that $\sum_n \rho_n = 1$.

Actually, we have proved more than this. Not only must the ensemble of huge systems ($W \gg 1$) have the energy dependence $\rho \propto \exp(-\mathcal{E}/k_BT)$, so must each subensemble of smaller systems, $\rho_a \propto \exp(-\mathcal{E}_a/k_BT)$, even if (for example) the subensemble's identical subsystems have only one degree of freedom $W_a = 1$. Thus, if the subsystems exchanged only heat with their parent systems, then they must have the same canonical distribution (4.19) as the parents. This shows that the canonical distribution is the equilibrium state independently of the number of degrees of freedom W.

4.4.2 General Equilibrium Ensemble and Distribution; Gibbs Ensemble; Grand Canonical Ensemble

We can easily generalize this canonical distribution to an ensemble of systems that exchange other additive conserved quantitities (extensive variables) $K_1, K_2, ...$, in addition to energy $\mathcal{E}$, with a huge, thermalized bath. By an obvious generalization of the above argument, the resulting statistical equilibrium distribution function must have the form

$$\rho = C \exp\left(-\beta\mathcal{E} - \sum_A \beta_A K_A\right) . \tag{4.20}$$

When the extensive variables K_A that are exchanged with the bath, and that thus appear explicitly in the distribution function ρ, are energy $\mathcal{E}$, and/or momentum $\mathbf{P}$, and/or angular momentum $\mathbf{J}$, and/or the number N_I of the species I of conserved particles, and/or volume V, it is conventional to rename the multiplicative factors β and β_A so that ρ takes on the following form

$$\boxed{\rho = C \exp\left[\frac{-\mathcal{E} + \mathbf{U}\cdot\mathbf{P} + \mathbf{\Omega}\cdot\mathbf{J} + \sum_I \tilde{\mu}_I N_I - PV}{k_BT}\right] .} \tag{4.21}$$

Here k_B is Boltzmann's constant; T, $\mathbf{U}$, $\mathbf{\Omega}$, $\tilde{\mu}_I$, and P are constants (called *intensive* variables) that are the same for all systems and subsystems, i.e., that characterize the full ensemble and all its subensembles and that therefore must have been acquired from the bath; and any extensive variable that is not exchanged with the bath must be omitted from the exponential and be replaced by an implicit delta function.

As we have seen, T is the *temperature* that the ensemble and subensembles acquired from the bath; i.e., it is the bath temperature. From the Lorentz transformation law for energy and momentum $[\mathcal{E}' = \gamma(\mathcal{E} - \mathbf{U}\cdot\mathbf{P})]$ we see that, if we were to transform to a reference frame that moves with velocity $\mathbf{U}$ with respect to our original frame, then the $\exp(\mathbf{U}\cdot\mathbf{P}/k_BT)$ term in ρ would disappear, and the distribution function would be isotropic in $\mathbf{P}$. This tells us that $\mathbf{U}$ is the *velocity* of the bath with respect to our chosen reference frame. By a similar argument, $\mathbf{\Omega}$ is the bath's *angular velocity* with respect to an inertial frame. By comparison with Eq. (2.22d) we see that $\tilde{\mu}_I$ is the *chemical potential* of the conserved species I. Finally, experience with elementary thermodynamics suggests (and it turns out to be true) that P is the bath's *pressure.*[3] Note that, by contrast with the corresponding extensive variables $\mathcal{E}$,

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[3] One can also identify these physical interpretations of T, $\tilde{\mu}_I$ and P by analyzing idealized measuring devices; cf. Sec. 4.2 of the next chapter.

$\mathbf{P}$, $\mathbf{J}$, N_I, and V, the intensive variables T, $\mathbf{U}$, $\mathbf{\Omega}$, $\tilde{\mu}_I$, and P do not double when the size of a system is doubled, i.e. they are not additive; rather, they are properties of the ensemble as a whole and thus are independent of the systems' sizes.

By removing the rest masses of all the particles from each system's energy and similarly removing the particle rest mass from each chemical potential,

$$E \equiv \mathcal{E} - \sum_I N_I m_I \ , \quad \mu_I \equiv \tilde{\mu}_I - m_I \tag{4.22}$$

[Eqs. (2.20) and (2.21)], we bring the distribution function into a form that is identical to Eq. (4.21) but with $\mathcal{E} \to E$ and $\tilde{\mu}_I \to \mu_I$:

$$\boxed{\rho = C \exp\left[\frac{-E + \mathbf{U}\cdot\mathbf{P} + \mathbf{\Omega}\cdot\mathbf{J} + \sum_I \mu_I N_I - PV}{k_B T}\right] .} \tag{4.23}$$

This is the form used in Newtonian theory, but it is also valid relativistically.

Henceforth (except in Sec. 3.8, when discussing black-hole atmospheres), we shall restrict our baths always to be at rest in our chosen reference frame and to be non-rotating with respect to inertial frames, so that $\mathbf{U} = \mathbf{\Omega} = 0$. The distribution function ρ can then either be a delta function in the system momentum $\mathbf{P}$ and angular momentum $\mathbf{J}$ (if momentum and angular momentum are not exchanged with the bath), or it can involve no explicit dependence whatsoever on $\mathbf{P}$ and $\mathbf{J}$ (if momentum and angular momentum *are* exchanged with the bath; cf. Eq. (4.21) with $\mathbf{U} = \mathbf{\Omega} = 0$). In either case, if energy is the only other quantity exchanged with the bath, then the distribution function is said to be *canonical* and has the form (4.19):

$$\rho_{\rm canonical} = C \exp\left[\frac{-\mathcal{E}}{k_B T}\right] = C' \exp\left[\frac{-E}{k_B T}\right] \ , \tag{4.24a}$$

where (obviously) the constants C and C' are related by $C' = C \exp[-\sum_I N_I m_I / k_B T]$.

If, in addition to energy, volume can also be exchanged with the bath (e.g., if the systems are floppy bags of gas whose volumes can change and through which heat can flow), then the equilibrium is the *Gibbs ensemble*, which has the distribution function

$$\boxed{\rho_{\rm Gibbs} = C \exp\left[\frac{-(\mathcal{E} + PV)}{k_B T}\right] = C' \exp\left[\frac{-(E + PV)}{k_B T}\right]} \tag{4.24b}$$

(and an implicit delta function in N_I and possibly in $\mathbf{J}$ and $\mathbf{P}$). The combination $\mathcal{E} + PV$ is known as the *enthalpy* H. If the exchanged quantities are energy and particles but not volume (e.g., if the systems are 1-m cubes inside the sun with totally imaginary walls through which particles and heat can flow), then the equilibrium is the *grand canonical ensemble*, with

$$\boxed{\rho_{\rm grand\ canonical} = C \exp\left[\frac{-\mathcal{E} + \sum_I \tilde{\mu}_I N_I}{k_B T}\right] = C \exp\left[\frac{-E + \sum_I \mu_I N_I}{k_B T}\right]} \tag{4.24c}$$

(and an implicit delta function in V and perhaps in $\mathbf{J}$ and $\mathbf{P}$). See the summary in Table 4.1.

We mention, as a preview of an issue to be addressed in Chap. 4, that an individual system, picked randomly from the ensemble and then viewed as a bath for its own tiny subsystems, will *not* have *identically* the same temperature T, and/or chemical potential $\tilde{\mu}_I$, and/or pressure P as the huge bath with which the ensemble has equilibrated; rather, the individual system's T, $\tilde{\mu}_I$, and/or P can fluctuate a tiny bit about the huge bath's values (about the values that appear in the above probabilities), just as its $\mathcal{E}$, N_I, and/or V fluctuate. We shall study these fluctuations in Chap. 4.

4.4.3 Bose-Einstein and Fermi-Dirac Distributions

The concepts and results developed in this chapter have enormous generality. They are valid (when handled with sufficient care) for quantum systems as well as classical, and they are valid for semiclosed or closed systems of any type whatsoever. The systems need not resemble the examples we have met in the text. They can be radically different, but so long as they are closed or semiclosed, our concepts and results will apply.

As an important example, let each system be a single-particle quantum state of some field, rather than a collection of particles or normal modes of a crystal. These quantum states can exchange particles (quanta) with each other. As we shall see, in this case the above considerations imply that, in statistical equilibrium at temperature T, the mean number of particles in a state, whose individual particle energies are $\mathcal{E}$, is given by the Fermi-Dirac formula (for fermions) $\eta = 1/(e^{(\mathcal{E}-\tilde{\mu})/k_BT}+1)$ and Bose-Einstein formula (for bosons) $\eta = 1/(e^{(\mathcal{E}-\tilde{\mu})/k_BT}-1)$, which we used in our kinetic-theory studies in the last chapter [Eqs. (2.22a), (2.22b)]. Our derivation of these mean occupation numbers will illustrate the closeness of classical statistical mechanics and quantum statistical mechanics: the proof is fundamentally quantum mechanical because the regime $\eta \sim 1$ is quantum mechanical (it violates the classical condition $\eta \ll 1$); nevertheless, the proof makes use of precisely the same concepts and techniques as we have developed for our classical studies.

As a conceptual aid in the derivation, consider an ensemble of complex systems in statistical equilibrium. Each system can be regarded as made up of a large number of fermions (electrons, protons, neutrons, neutrinos, ...) and/or bosons (photons, gravitons, alpha particles, phonons, ...). We shall analyze each system by identifying a complete set of single-particle quantum states (which we shall call *modes*) into which the particles can be inserted. (For photons, these "modes" are the normal modes of the classical electromagnetic field; for phonons in a crystal, they are the normal modes of the crystal's vibrations; for nonrelativistic electrons or protons or alpha particles, they are energy eigenstates of the nonrelativistic Schroedinger equation; for relativistic electrons, they are energy eigenstates of the Dirac equation.) A complete enumeration of modes is the starting point for the *second quantization* formulation of quantum field theory, and also the starting point for our far simpler analysis.

Choose one specific mode $\mathcal{S}$ [e.g., a nonrelativistic electron plane-wave mode in a box of side L with spin up and momentum $\mathbf{p} = (5, 3, 17)h/L$)]. There is one such mode $\mathcal{S}$ in each of the systems in our ensemble, and these modes (all identical in their properties) form a subensemble of our original ensemble. Our derivation focuses on this subensemble of identical modes $\mathcal{S}$. Because each of these modes can exchange energy and particles with all the other modes in its system, the subensemble is *grand canonically distributed*.

The (many-particle) quantum states allowed to the mode $\mathcal{S}$ are states in which $\mathcal{S}$ contains a finite number of particles (quanta), n. Denote by $\mathcal{E}_\mathcal{S}$ the energy of one particle residing in the mode $\mathcal{S}$. Then the mode's total energy when it is in the state $|n\rangle$ (when it contains n quanta) is $\mathcal{E}_n = n\mathcal{E}_\mathcal{S}$. [Note: for a freely traveling, relativistic electron mode, $\mathcal{E}_\mathcal{S} = \sqrt{m^2 + \mathbf{p}^2}$ where $\mathbf{p}$ is the mode's momentum, $p_x = jh/L$ (for j some integer) etc.; for a phonon mode with angular eigenfrequency of vibration ω, $\mathcal{E}_\mathcal{S} = \hbar\omega$; etc.] Since the distribution of the ensemble's modes among the allowed quantum states is grand canonical, the probability ρ_n of being in state $|n\rangle$ is [Eq. (4.24c)]

$$\rho_n = \text{const} \times \exp\left(\frac{-\mathcal{E}_n + \tilde{\mu} n}{k_B T}\right) = \text{const} \times \exp\left(\frac{n(\tilde{\mu} - \mathcal{E}_\mathcal{S})}{k_B T}\right) , \qquad (4.25)$$

where $\tilde{\mu}$ and T are the chemical potential and temperature of the bath of other modes, with which the mode $\mathcal{S}$ interacts.

Suppose that $\mathcal{S}$ is a fermion mode (i.e., its particles have half-integral spin). Then the Pauli exclusion principle dictates that $\mathcal{S}$ cannot contain more than one particle; i.e., n can take on only the values 0 and 1. In this case, the normalization constant in the distribution function (4.25) is determined by $\rho_0 + \rho_1 = 1$, which implies that

$$\rho_0 = \frac{1}{1 + \exp[(\tilde{\mu} - \mathcal{E}_\mathcal{S})/k_B T]} , \quad \rho_1 = \frac{\exp[(\tilde{\mu} - \mathcal{E}_\mathcal{S})/k_B T]}{1 + \exp[(\tilde{\mu} - \mathcal{E}_\mathcal{S})/k_B T]} . \qquad (4.26a)$$

This is the explicit form of the grand canonical distribution for a fermion mode. For many purposes (including all those in Chap. 2), this full probability distribution is more than one needs. Quite sufficient instead is the mode's mean occupation number

$$\boxed{\eta_\mathcal{S} \equiv \langle n \rangle = \sum_{n=0}^{1} n\rho_n = \frac{1}{\exp[(\mathcal{E}_\mathcal{S} - \tilde{\mu})/k_B T] + 1} = \frac{1}{\exp[(E_\mathcal{S} - \mu)/k_B T] + 1} .} \qquad (4.26b)$$

Here $E_\mathcal{S} = \mathcal{E}_\mathcal{S} - m$ and $\mu = \tilde{\mu} - m$ are the energy of a particle in the mode with rest mass removed, and the chemical potential with rest mass removed — the quantities used in the nonrelativistic (Newtonian) regime.

Equation (4.260 is the *Fermi-Dirac mean occupation number* asserted in Chap. 2 [Eq. (2.22a)], and studied there for the special case of a gas of freely moving, noninteracting fermions. Because our derivation is completely general, we conclude that this mean occupation number and the underlying grand canonical distribution (4.26a) are valid for any mode of a fermion field — for example, the modes for an electron trapped in an external potential well or a magnetic bottle, and the (single-particle) quantum states of an electron in a hydrogen atom.

Suppose that $\mathcal{S}$ is a boson mode (i.e., its particles have integral spin), so it can contain any nonnegative number of quanta; i.e., n can assume the values 0, 1, 2, 3, ... Then the normalization condition $\sum_{n=0}^{\infty} \rho_n = 1$ fixes the constant in the Grand canonical distribution (4.25), resulting in

$$\rho_n = \left[1 - \exp\left(\frac{\tilde\mu - \mathcal{E}_\mathcal{S}}{k_B T}\right)\right] \exp\left(\frac{n(\tilde\mu - \mathcal{E}_\mathcal{S})}{k_B T}\right) . \tag{4.27a}$$

From this grand canonical distribution we can deduce the mean number of bosons in mode $\mathcal{S}$:

$$\boxed{\eta_\mathcal{S} \equiv \langle n \rangle = \sum_{n=1}^{\infty} \rho_n = \frac{1}{\exp[(\mathcal{E}_\mathcal{S} - \tilde\mu)/k_B T] - 1} = \frac{1}{\exp[(E_\mathcal{S} - \mu)/k_B T] - 1}} \tag{4.27b}$$

in accord with Eq. (2.22b). As for fermions, this *Bose-Einstein mean occupation number* and underlying grand canonical distribution (4.27a) are valid generally, and not solely for the freely moving bosons of Chap. 2.

When the mean occupation number is small, $\eta_\mathcal{S} \ll 1$, both the bosonic and the fermionic distribution functions are well approximated by the classical *Boltzmann mean occupation number*

$$\boxed{\eta_{\rm S} = \exp[-(\mathcal{E}_\mathcal{S} - \tilde\mu)/k_B T] \; .} \tag{4.28}$$

In Sec. 4.10 below we shall explore an important modern application of the Bose-Einstein mean occupation number (4.27): *Bose-Einstein condensation* of bosonic atoms in a magnetic trap.

4.5 The Microcanonical Ensemble

Turn attention, now, from ensembles of systems that interact with an external, thermal bath (as discussed in Sec. 4.4.1), to an ensemble of identical, precisely closed systems, i.e. systems that have no interactions whatsoever with the external universe. By "identical" we mean that every system in the ensemble has (i) precisely the same set of degrees of freedom, and thus (ii) precisely the same number of degrees of freedom W, (iii) precisely the same Hamiltonian, and (iv) precisely the same values for all the additive constants of motion $(\mathcal{E}, K_1, K_2, \ldots)$ except perhaps total momentum $\mathbf{P}$ and total angular momentum $\mathbf{J}$[4]).

Suppose that these systems begin with values of $(\mathbf{q}, \mathbf{p})$ that are spread out in some (arbitrary) manner over a *hypersurface* in phase space that has $H(\mathbf{q}, \mathbf{p})$ equal to the common value of energy $\mathcal{E}$. Of course, we cannot choose systems whose energy is *precisely* equal to $\mathcal{E}$. For most $\mathcal{E}$ this would be a set of measure zero. Instead we let the systems occupy a tiny range of energy between $\mathcal{E}$ and $\mathcal{E} + \delta\mathcal{E}$ and then discover (in Ex. 4.8) that our results are highly insensitive to $\delta\mathcal{E}$ as long as it is extremely small compared with $\mathcal{E}$.

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[4] Exercise 4.8 below is an example of a microcanonical ensemble where $\mathbf{P}$ and $\mathbf{J}$ are not precisely fixed, though we do not discuss this in the exercise. The gas atoms in that example are contained inside an impermeable box whose walls cannot exchange energy or atoms with the gas, but obviously can and do exchange momentum and angular momentum when atoms collide with the walls. Because the walls are at rest in our chosen reference frame, the distribution function has $\mathbf{U} = \boldsymbol{\Omega} = 0$ and so is independent of $\mathbf{P}$ and $\mathbf{J}$ [Eq. (4.23) above] rather than having precisely defined values of them.

It seems reasonable to expect that this ensemble, after evolving for a time much longer than its longest internal dynamical time scale $t \gg \tau_{\rm int}$, will achieve statistical equilibrium, i.e. will evolve into a state with $\partial\rho/\partial t = 0$. (In the next section we will justify this expectation.) The distribution function ρ will then satisfy the collisionless Boltzmann equation (4.14) with vanishing time derivative, and therefore will be a function only of the Hamiltonian's additive constants of the motion $\mathcal{E}, K_A$. However, we already know that ρ is a delta function in K_A and a delta function with a tiny but finite spread in $\mathcal{E}$; and the fact that it cannot depend on any other phase-space quantities then implies *ρ is a constant over the hypersurface in phase space that has the prescribed values of K_A and $\mathcal{E}$, and is zero everywhere else in phase space.* This equilibrium ensemble is called *microcanonical*.

There is a subtle aspect of this microcanonical ensemble that deserves discussion. Suppose we split each system in the ensemble up into a huge number of subsystems that can exchange energy (but for concreteness nothing else) with each other. We thereby obtain a huge number of subensembles, in the manner of Sec. 3.4. The original systems can be regarded as a thermal bath for the subsystems, and correspondingly the subensembles will have canonical distribution functions, $\rho_a = Ce^{-\mathcal{E}_a/k_BT}$. One might also expect the subensembles to be statistically independent, so that $\rho = \prod_a \rho_a$. However, such independence is not possible, since together with additivity of energy $\mathcal{E} = \sum_a \mathcal{E}_a$, it would imply that $\rho = Ce^{-\mathcal{E}/k_BT}$, i.e. that the full ensemble is canonically distributed rather than microcanonical. What is wrong here?

The answer is that there in fact is a tiny correlation between the subensembles: If, at some moment of time, subsystem $a = 1$ happens to have an unusually large energy, then the other subsystems must correspondingly have a little less energy than usual; and this very slightly invalidates the statistical-independence relation $\rho = \prod_a \rho_a$, thereby enabling the full ensemble to be microcanonical even though all its subensembles are canonical. In the language of two-lengthscale expansions, where one expands in the dimensionless ratio (size of subsystems)/(size of full system) [Box 2.3], this correlation is a higher-order correction to statistical independence.

We are now in a position to understand more deeply the nature of the thermalized bath that we have invoked to drive ensembles into statistical equilibrium. That bath can be any huge system which contains the systems we are studying as subsystems; and the bath's *thermal equilibrium* can be either a microcanonical statistical equilibrium, or a statistical equilibrium involving exponentials of its extensive variables.

Exercise 4.8 gives a concrete illustration of the microcanonical ensemble, but we delay presenting it until we have developed some additional concepts that it also illustrates.

4.6 The Ergodic Hypothesis

The ensembles we have been studying are almost always just conceptual ones that do not exist in the real universe. We have introduced them and paid so much attention to them not for their own sake, but because, in the case of statistical-equilibrium ensembles, they can be powerful tools for studying the properties of a single, individual system that really does exist in the universe or in our laboratory.

This power comes about because a sequence of "snapshots" of the single system, taken at times separated by sufficiently large intervals Δt, has a probability distribution ρ (for the snapshots' instantaneous locations $\{\mathbf{q}, \mathbf{p}\}$ in phase space) that is the same as the distribution function ρ of some conceptual, statistical-equilibrium ensemble. If the single system is closed, so its evolution is driven solely by its own Hamiltonian, then the time between snapshots should be $\Delta t \gg \tau_{\rm int}$ and its snapshots will be (very nearly) microcanonically distributed. If the single system exchanges energy, and only energy, with a thermal bath, then the time between snapshots should be $\Delta t \gg \tau_{\rm ext}$ and its snapshots will be canonically distributed; and similarly for the other types of bath interactions. This property of snapshots is equivalent to the statement that for the individual system, *the long-term time average of any function of the system's location in phase space is equal to the statistical-equilibrium ensemble average:*

$$\boxed{\bar{A} \equiv \lim_{T\to 0} \int_{-T/2}^{+T/2} A(\mathbf{q}(t), \mathbf{p}(t)) = \langle A \rangle \equiv \sum_n A_n \rho_n \ .} \qquad (4.29)$$

This property comes about because of *ergodicity*: the individual system, as it evolves, visits each accessible quantum state n for a fraction of the time that is equal to the equilibrium ensemble's probability ρ_n. Or, stated more carefully, the system comes sufficiently close to each state n for a sufficient length of time that, for practical purposes, we can approximate it as spending a fraction ρ_n of its time at n.

At first sight, ergodicity may seem obvious. However, it is not a universal property of all systems: one can easily devise idealized examples of non-ergodic behavior (e.g., an elastic billiard ball bouncing around a square billiard table). On the other hand, generic systems, whose properties and parameters are not carefully fine tuned, do typically behave ergodically, but to prove so is one of the most difficult problems in statistical mechanics. We shall assume throughout this book's discussion of statistical physics that all the systems we study are indeed ergodic; this is called the *ergodic hypothesis*. Correspondingly, sometimes (for ease of notation) we shall denote the ensemble average with a bar.

One must be cautious in practical applications of the ergodic hypothesis: It can sometimes require much longer than one might naively expect for a system to wander sufficiently close to accessible states that $\bar{A} = \langle A \rangle$ for observables A of interest. [GIVE REFERENCES TO THE LITERATURE ON THE ERGODIC HYPOTHESIS? E.G. ter Haar (1955).]

4.7 Entropy and Evolution Into Statistical Equilibrium

4.7.1 Entropy and the Second Law of Thermodynamics

For *any* ensemble of systems, whether it is in statistical equilibrium or not, and also whether it is quantum mechanical or not, the ensemble's *entropy* S is defined, in words, by the following awful sentence: S is the mean value (ensemble average) of the logarithm of the probability that a random system in the ensemble occupies a given quantum state, summed over states and multiplied by $-k$. More specifically, denoting the probability that a system is in state n by ρ_n, the ensemble's entropy S is the following sum over quantum states (or the equivalent integral over phase space):

$$\boxed{S \equiv -k_B \sum_n \rho_n \ln \rho_n \ .} \tag{4.30}$$

Entropy is a measure of our lack of information about the state of any system chosen at random from an ensemble; see Sec. 4.12 below. In this sense, *the entropy can be regarded as a property of a random individual system in the ensemble*, as well as of the ensemble itself.

If all the systems are in the same quantum state, e.g. in the state $n = 17$, then $\rho_n = \delta_{n,17}$ so we know precisely the state of any system pulled at random from the ensemble, and Eq. (4.30) dictates that the entropy vanish. Vanishing entropy thus corresponds to a perfect knowledge of the system's quantum state; it corresponds to the quantum state being pure.

By contrast, consider a system in microcanonical statistical equilibrium. In this case, all states are equally likely (ρ is constant), so if there are $N_{\rm states}$ states altogether, then $\rho_n = 1/N_{\rm states}$ and the entropy (4.30) takes the form[5]

$$\boxed{S = k_B \ln N_{\rm states} \ .} \tag{4.31}$$

The entropy, so defined, has some important properties. One is that whenever the ensemble can be broken up into statistically independent subensembles of subsystems (as is generally the case for big systems in statistical equilibrium), so $\rho = \prod_a \rho_a$, then the entropy is additive, $S = \sum_a S_a$; see Ex. 4.3. This permits us to regard the entropy, like the systems' additive constants of the motion, as an *extensive variable.*

A second very important property is the fact that, as an ensemble of systems evolves, its entropy cannot decrease and it generally tends to increase. This is the statistical mechanical version of the *second law of thermodynamics.*

As an example of this second law, consider two different gases (e.g., nitrogen and oxygen) in a container, separated by a thin membrane. One set of gas molecules is constrained to lie on one side of the membrane; the other set lies on the opposite side. The total number of available states $N_{\rm states}$ is less than if the membrane is ruptured and the two gases are allowed to mix. The mixed state is accessible from the partitioned state and not vice-versa. When the membrane is removed, the entropy begins to increase in accord with the second law of thermodynamics.

Since any ensemble of identical, closed systems will ultimately, after a time $t \gg \tau_{\rm int}$, evolve into microcanonical statistical equilibrium, it must be that the microcanonical distribution function $\rho =$ constant has a larger entropy than any other distribution function that the ensemble could acquire. That this, indeed, is so, can be demonstrated formally as follows: Consider the class of all distribution functions ρ that: (i) vanish unless the constants of motion have the prescribed values $\mathcal{E}$ (in the tiny range $\delta\mathcal{E}$) and K_A, (ii) can be non-zero anywhere in the region of phase space, $\mathcal{S}_o$, where the prescribed values $\mathcal{E}$, K_A are taken on, and (iii) are correctly normalized so that

$$\sum_n \rho_n \equiv \int_{\mathcal{S}_o} \rho \mathcal{N}_{\rm states} d\Gamma = 1 \tag{4.32a}$$

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[5] This formula, with slightly different notation, can be found on Boltzmann's tomb.

[Eq. (4.8b)]. We ask which ρ in this class gives the largest entropy $S = -k\sum_n \rho_n \ln \rho_n$. The requirement that the entropy be extremal (stationary) under variations $\delta\rho$ of ρ that preserve the normalization (4.32a) is embodied in the variational principle[6]

$$\delta \int_{\mathcal{S}_o} (-k\rho\ln\rho - \Lambda\rho)\mathcal{N}_{\rm states} d\Gamma = 0 \; . \tag{4.32b}$$

Here Λ is a Lagrange multiplier that enforces the normalization (4.32a). Performing the variation, we find that

$$\int_{\mathcal{S}_o} (-k\ln\rho - k - \Lambda)\delta\rho\mathcal{N}_{\rm states} d\Gamma = 0 \; , \tag{4.32c}$$

which is satisfied if and only if ρ is a constant, $\rho = e^{-1-\Lambda/k}$, independent of location in the allowed region $\mathcal{S}_o$ of phase space; i.e., if and only if ρ is that of the microcanonical ensemble. This calculation actually only shows that the microcanonical ensemble has stationary entropy. To show it is a maximum, one must perform the second variation; i.e., one must compute the second-order contribution of $\delta\rho$ to $\delta S = \delta\int(-k\rho\ln\rho)\mathcal{N}_{\rm states} d\Gamma$. That second-order contribution is easily seen to be

$$\delta^2 S = \int_{\mathcal{S}_o} \left(-k\frac{(\delta\rho)^2}{\rho}\right)\mathcal{N}_{\rm states} d\Gamma < 0 \; . \tag{4.32d}$$

Thus, the microcanonical distribution does *maximize* the entropy, as claimed.

4.7.2 What Causes the Entropy to Increase?

There is an apparent paradox at the heart of statistical mechanics and, at various stages in the development of the subject it has led to confusion and even despair.[7] It still creates controversy.[8] Its simplest and most direct expression is to ask how can the time-reversible, microscopic laws, encoded in a time-independent Hamiltonian, lead to the remorseless increase of entropy?

In search of insight, consider, first, a classical, microcanonical ensemble of precisely closed systems (no interaction at all with the external universe). Assume, for simplicity, that at time $t = 0$ all the systems are concentrated in a small but finite region of phase space with volume $\Delta\Gamma$, as shown in Fig. 4.2(a), with $\rho = 1/\mathcal{N}_{\rm states}\Delta\Gamma$ in the occupied retion, and $\rho = 0$ everywhere else. As time passes each system evolves under the action of the systems' common Hamiltonian. As is depicted in Fig. 4.2(b), this evolution distorts the occupied region of phase space; but Liouville's theorem dictates that the occupied region's volume, $\Delta\Gamma$, remain unchanged and, correspondingly, that the ensemble's entropy

$$S = -k\int(\rho\ln\rho)\mathcal{N}_{\rm states} d\Gamma = k\ln(\mathcal{N}_{\rm states}\Delta\Gamma) \tag{4.33}$$

remain unchanged.

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[6] See, e.g., Mathews & Walker (1964), Chap. 12.

[7] Boltzmann committed suicide.

[8] See, e.g., Hawking (1989) and Penrose (1989).

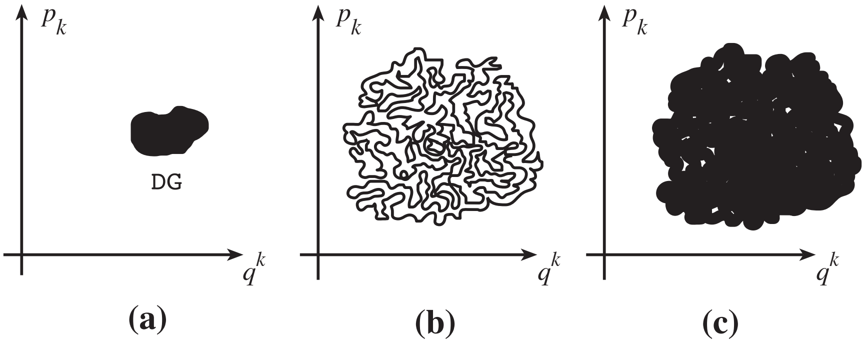

Fig. 4.2: Evolution of a classical ensemble into statistical equilibrium by means of phase mixing followed by coarse-graining of one's viewpoint.

How can this be so? The ensemble is supposed to evolve into statistical equilibrium, with its distribution function uniformly spread out over that entire portion of phase space allowed by the Hamiltonian's constants of motion—a portion of phase space far far larger than $\Delta\Gamma$—and in the process the entropy is supposed to increase.

Fig. 4.2(b,c) resolves the paradox. As time passes, the occupied region becomes more and more distorted. It retains its phase-space volume, but gets strung out into a winding, contorted surface [Fig. 4.2(b)] which (by virtue of the ergodic hypothesis) ultimately passes arbitrarily close to any given point in the region allowed by the constants of motion. This ergodic wandering is called *phase mixing*. Ultimately the physicist gets tired of keeping track of all these contortions of the occupied region and chooses instead to take a *coarse-grained* viewpoint that averages over scales larger than the distance between adjacent portions of the occupied surface and thereby regards the ensemble as having become spread over the entire allowed region [Fig. 4.2(c)]. More typically, the physicist will perform a coarse-grained smearing out on some given, constant scale at all times; and once the transverse scale of the ensemble's lengthening and narrowing phase-space region drops below the smearing scale, its smeared volume and its entropy start to increase. Thus, *for an ensemble of closed systems it is the physicist's choice to perform coarse-grain averaging that causes entropy to increase and causes the ensemble to evolve into statistical equilibrium.*

The situation is a bit more subtle for an ensemble of systems interacting with a thermal bath. The evolution into statistical equilibrium is driven by the interactions. Thus, it might appear at first sight that the physicist is not, this time, to blame for the entropy increase and the achievement of statistical equilibrium. A deeper examination, however, reveals the physicist's ultimate culpability. If the physicist were willing to keep track of all those dynamical degrees of freedom of the bath which are influenced by and influence the systems in the ensemble, then the physicist could incorporate these degrees of freedom into the description of the systems and define a phase space volume that obeys Liouville's theorem and thus does not increase, and an entropy that correspondingly remains constant. However, physicists instead generally choose to ignore the microscopic details of the bath, and that choice forces them to attribute a growing entropy to the ensemble and regard the ensemble as approaching statistical equilibrium.

When one reexamines these issues in quantum mechanical language, one discovers that the entropy increase is caused by the physicists' discarding the quantum mechanical correlations (the off-diagonal terms in the density matrix of Box 4.2) that get built up through the systems' interaction with the rest of the universe. This discarding of correlations is accomplished through a trace over the external universe's basis states (Box 4.2), and if the state of system plus universe was originally pure, this tracing (discarding of correlations) makes it mixed. From this viewpoint, then, *it is the physicist's choice to discard correlations with the external universe that causes the entropy increase and the evolution into statistical equilibrium.* Heuristically, we can say that the entropy does not increase *until* the physicist actually (or figuratively) chooses to let it increase by ignoring the rest of the universe. For a simple, pedagogical example, see Box 4.3 and Ex. 4.5.

This then raises a most intriguing question. What if we regard the universe as the ultimate microcanonical system? In this case, we might expect that the entropy of the universe will remain identically zero for all time, unless physicists (or other intelligent beings) perform some sort of coarse graining or discard some sort of correlations. However, such coarse graining or discarding are made deeply subtle by the fact that the physicists (or intelligent beings) are themselves part of the system being studied. Further discussion of these questions introduces fascinating, though ill-understood, quantum mechanical and cosmological considerations to which we shall briefly return in Sec. 27.6.

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EXERCISES

Exercise 4.2 *Practice: Estimating Entropy*
Make rough estimates of the entropy of the following systems, assuming they are in statistical equilibrium:

(a) An electron in a hydrogen atom at room temperature

(b) A glass of wine

(c) The Pacific ocean

(d) An ice cube

(e) The universe (This is mostly contained in the 3 K microwave background radiation.)

Exercise 4.3 *Derivation: Additivity of Entropy for Statistically Independent Systems*
Consider an ensemble of classical systems with each system made up of a large number of statistically independent subsystems, so $\rho = \prod_a \rho_a$. Show that the entropy of the full ensemble is equal to the sum of the entropies of the subensembles a: $S = \sum_a S_a$.

Exercise 4.4 ***Example: Entropy of a Thermalized Mode of a Field*
Consider a mode $\mathcal{S}$ of a fermionic or bosonic field, as discussed in Sec. 4.4.3 above. Suppose that an ensemble of identical such modes is in statistical equilibrium with a heat and particle bath and thus is grand-canonically distributed.

Box 4.3
Entropy Increase Due to Discarding Quantum Correlations

As an idealized, pedagogical example of entropy increase due to physicists' discarding quantum correlations, consider an electron that interacts with a photon. The electron's initial quantum state is $|\psi_e\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$, where $|\uparrow\rangle$ is the state with spin up, $|\downarrow\rangle$ is that with spin down, and α and β are complex probability amplitudes with $|\alpha|^2+|\beta|^2 = 1$. The interaction is so arranged that, if the electron spin is up then the photon is put into a positive helicity state $|+\rangle$, and if down, the photon is put into a negative helicity state $|-\rangle$. Therefore, after the interaction the combined system of electron plus photon is in the state $|\Psi\rangle = \alpha|\uparrow\rangle \otimes |+\rangle + \beta|\downarrow\rangle \otimes |-\rangle$.

The photon flies off into the universe leaving the electron isolated. Suppose that we measure some electron observable $\hat{A}_e$. The expectation values for the measurement result before and after the interaction with the photon are

$$\text{Before: } \langle\psi_e|\hat{A}_e|\psi_e\rangle = |\alpha|^2\langle\uparrow|\hat{A}_e|\uparrow\rangle + |\beta|^2\langle\downarrow|\hat{A}_e|\downarrow\rangle + \alpha^*\beta\langle\uparrow|\hat{A}_e|\downarrow\rangle + \beta^*\alpha\langle\downarrow|\hat{A}_e|\uparrow\rangle\ . \quad (1)$$

$$\begin{aligned} \text{After: } \langle\Psi|\hat{A}_e|\Psi\rangle &= |\alpha|^2\langle\uparrow|\hat{A}_e|\uparrow\rangle \underbrace{\langle+|+\rangle}_{1} + |\beta|^2\langle\downarrow|\hat{A}_e|\downarrow\rangle \underbrace{\langle-|-\rangle}_{1} \\ &\quad + \alpha^*\beta\langle\uparrow|\hat{A}_e|\downarrow\rangle \underbrace{\langle+|-\rangle}_{0} + \beta^*\alpha\langle\downarrow|\hat{A}_e|\uparrow\rangle \underbrace{\langle-|+\rangle}_{0} \\ &= |\alpha|^2\langle\uparrow|\hat{A}_e|\uparrow\rangle + |\beta|^2\langle\downarrow|\hat{A}_e|\downarrow\rangle\ . \end{aligned} \quad (2)$$

Comparing Eqs. (1) and (2), we see that *the correlations with the photon have removed the $\alpha^*\beta$ and $\beta^*\alpha$ quantum interference terms from the expectation value.* The two pieces $\alpha|\uparrow\rangle$ and $\beta|\downarrow\rangle$ of the electron's original quantum state $|\psi_e\rangle$ are said to have *decohered*. Since the outcomes of all measurements can be expressed in terms of expectation values, this *quantum decoherence* is "complete" in the sense that no quantum interference whatsoever between the $\alpha|\uparrow\rangle$ and $\beta|\downarrow\rangle$ pieces of the electron state $|\psi_e\rangle$ will ever be seen again in any measurement on the electron, unless the photon returns, interacts with the electron, and thereby removes its correlations with the electron state.

If physicists are confident the photon will never return and the correlations will never be removed, then they are free to change mathematical descriptions of the electron state: Instead of describing the post-interaction state as $|\Psi\rangle = \alpha|\uparrow\rangle \otimes |+\rangle + \beta|\downarrow\rangle \otimes |-\rangle$, *the physicists can discard the correlations with the photon, and regard the electron has having* **classical** *probabilities $\rho_\uparrow = |\alpha|^2$ for spin up and $\rho_\downarrow = |\beta|^2$ for spin down — i.e. as being in a* **mixed** *state.* This new, *mixed-state viewpoint* leads to the same expectation value (2) for all physical measurements as the old, correlated, *pure-state viewpoint* $|\Psi\rangle$.

The important point for us is that, when discarding the quantum correlations with the photon (with the external universe), the physicist changes the entropy from zero (the value for any pure state including $|\Psi\rangle$) to $S = -k(p_\uparrow \ln p_\uparrow + p_\downarrow \ln p_\downarrow) = -k(|\alpha|^2 \ln|\alpha|^2 + |\beta|^2 \ln|\beta|^2) > 0$. The physicist's change of viewpoint has increased the entropy.

In Ex. 4.5 this pedagogical example is reexpressed in terms of the density operator.

(a) Show that if $\mathcal{S}$ is fermionic, then the ensemble's entropy is

$$\begin{aligned} S_{\mathcal{S}} &= -k[\eta \ln \eta + (1-\eta)\ln(1-\eta)] \\ &\simeq -k\eta(\ln \eta - 1) \quad \text{in the classical regime } \eta \ll 1 \ , \end{aligned} \tag{4.34a}$$

where η is the mode's fermionic mean occupation number (4.26b).

(b) Show that if the mode is bosonic, then the entropy is

$$\begin{aligned} S_{\mathcal{S}} &= k[(\eta+1)\ln(\eta+1) - \eta \ln \eta] \\ &\simeq -k\eta(\ln \eta - 1) \quad \text{in the classical regime } \eta \ll 1 \ , \end{aligned} \tag{4.34b}$$

where η is the bosonic mean occupation number (4.27b). Note that in the classical regime, $\eta \simeq e^{-(\mathcal{E}-\tilde{\mu})/k_BT} \ll 1$, the entropy is insensitive to whether the mode is bosonic or fermionic.

(c) Explain why the entropy per particle in units of Boltzmann's constant (which we denote by σ) is $\sigma = S_{\mathcal{S}}/\eta k$. Plot σ as a function of η for fermions and for bosons. Show analytically that for degenerate fermions ($\eta \simeq 1$) and for the bosons' classical-wave regime ($\eta \gg 1$) the entropy per particle is small compared to unity.

Exercise 4.5 *Problem: Quantum Decoherence and Entropy Increase in terms of the Density Operator*
Reexpress Box 4.3's pedagogical example of quantum decoherence and entropy increase in the language of the quantum mechanical density operator $\hat{\rho}$ (Box 4.2). Use this example to explain the meaning of the various statements made in the next-to-last paragraph of Sec. 4.7.2.

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4.8 Grand Canonical Ensemble for an Ideal Monatomic Gas

We now turn to an example that illustrates the formalism we have developed: an ideal, relativistic, classical monatomic gas. In this section and Ex. 4.6 we shall use the grand canonical ensemble to compute the gas's statistical-equilibrium properties, and in doing so we shall elucidate the connections between statistical mechanics and thermodynamics. In Ex. 4.8 we shall compute this gas's entropy in the microcanonical ensemble. In Chap. 4 we shall see that the statistical-mechanics tools developed in this section have applicabilities that go

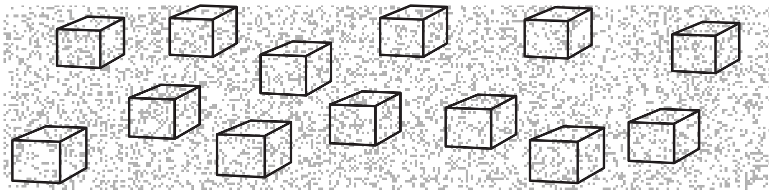

Fig. 4.3: An ensemble of gas cells, each with volume V, inside a heat and particle bath.

far beyond the ideal gas, and have straightforward analogs in other statistical-equilibrium ensembles.

We consider the ensemble of systems illustrated in Fig. 4.3. Each system in the ensemble is a cell of fixed volume V, with imaginary walls, inside a huge thermal bath of a monatomic gas (e.g. helium or atomic hydrogen or neutrons or photons or ...). Since the cells' walls are imaginary, the cells can and do exchange energy and atoms with the bath. We presume that the gas particles do not interact with each other (no potential energies in the Hamiltonian) so the gas is *ideal*. The bath is characterized by a chemical potential $\tilde{\mu}$ for these particles and by a temperature T, and each particle has rest mass m. In most textbooks on statistical mechanics one does not include the particles' rest mass in the chemical potential; however, we wish to allow the particles to be relativistic (e.g. they might be photons, which move at the speed of light), so we will be careful to include the rest mass in both the chemical potential $\tilde{\mu}$ and in the energy $\mathcal{E} = (m^2 + |\mathbf{p}|^2)^{1/2} = (m^2c^4 + |\mathbf{p}|^2c^2)^{1/2}$ of each particle. We assume that the chemical potential is sufficiently small (sufficiently few particles) that the mean occupation number of the particles' quantum states, η, is small compared to unity, so they behave classically, which means that

$$\mu \equiv \tilde{\mu} - mc^2 \ll -k_BT \tag{4.35}$$

[Eq. (2.22d)]. However, we do not require for now that k_BT be $\ll mc^2$, i.e., that the particles be nonrelativistic.

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):

$$\rho_n = \frac{1}{Z}\exp\left(\frac{-\mathcal{E}_n + \tilde{\mu}N_n}{k_BT}\right) = \exp\left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu}N_n}{k_BT}\right) \ . \tag{4.36}$$

Here $\mathcal{E}_n$ is the energy of a system that is in the many-particle quantum state $|n\rangle$, N_n is the number of particles in that quantum state, and $1/Z \equiv e^{\Omega/k_BT}$ is the normalization constant that guarantees $\sum_n \rho_n = 1$; i.e.,

$$\boxed{Z \equiv \exp\left(\frac{-\Omega}{k_BT}\right) \equiv \sum_n \exp\left(\frac{-\mathcal{E}_n + \tilde{\mu}N_n}{k_BT}\right) \ .} \tag{4.37}$$

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*

$$\boxed{\Omega(V,\tilde{\mu},T)\ ,} \tag{4.38}$$

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 gas. The argument is so general that it applies to *every* grand canonical ensemble of systems, not just to our chosen, monatomic gas; but for simplicity, we shall restrict ourselves to systems made of a single type of particle (which need not for now be monatomic or free of potential-energy interactions).

We introduce, as key quantities in the argument, the mean energy and mean number of particles in the ensemble's systems (cells of Fig. 4.3):

$$\overline{\mathcal{E}} \equiv \sum_n \rho_n \mathcal{E}_n\ , \quad \text{and}\ \overline{N} \equiv \sum_n \rho_n N_n\ . \tag{4.39}$$

(We denote these with bars $\bar{\mathcal{E}}$ rather than brackets $\langle\mathcal{E}\rangle$ for ease of notation.) We now ask how the grand potential will change if the temperature T and chemical potential $\tilde{\mu}$ of the bath and therefore of the ensemble are slowly altered with the common volume V of the cells held fixed. The answer for the change $d\Omega$ produced by changes dT and $d\tilde{\mu}$ can be derived from the normalization equation (4.37), which we rewrite as

$$1 = \sum_n \rho_n = \sum_n \exp\left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right)\ . \tag{4.40a}$$

Since the normalization condition must continue to hold as T and $\tilde{\mu}$ change, the sum in Eq. (4.40a) must be left unchanged, which means that

$$0 = \sum_n \left(\frac{d\Omega + N_n d\tilde{\mu} - (\Omega - \mathcal{E}_n + \tilde{\mu}N_n)T^{-1}dT}{k_B T}\right)\rho_n\ . \tag{4.40b}$$

Using $\sum_n \rho_n = 1$ and expressions (4.39) for the mean energy and the mean number of particles, and rearranging terms, we obtain

$$d\Omega = -\overline{N}d\tilde{\mu} + (\Omega - \overline{\mathcal{E}} + \tilde{\mu}\overline{N})T^{-1}dT\ . \tag{4.40c}$$

This change can be reexpressed in a more useful form by introducing the ensemble's entropy. Inserting expression (4.36) for ρ_n into the log term in the definition of entropy $S = -k\sum_n \rho_n \ln \rho_n$, we obtain

$$S = -k\sum_n \rho_n \ln\rho_n = -k\sum_n \rho_n\left(\frac{\Omega - \mathcal{E}_n + \tilde{\mu}N_n}{k_B T}\right) = -\frac{\Omega - \overline{\mathcal{E}} + \tilde{\mu}\overline{N}}{T}; \tag{4.40d}$$

or, equivalently

$$\boxed{\Omega = \overline{\mathcal{E}} - TS - \tilde{\mu}\overline{N}\ .} \tag{4.41}$$

By inserting expression (4.41) into Eq. (4.40c), we obtain

$$d\Omega = -\overline{N} d\tilde{\mu} - S dT \; . \tag{4.42}$$

Equation (4.42) has several important consequences. The first consequence is the fact that it is actually the *First Law of Thermodynamics* in disguise. To see this, insert expression (4.41) for Ω into (4.42), thereby bringing it into the form

$$d\overline{\mathcal{E}} = \tilde{\mu} d\overline{N} + T dS, \tag{4.43}$$

which is the familiar form of the first law of thermodynamics, but with the "$-PdV$" work, associated with a change in a cell's volume, omitted because the cells have fixed volume V. If we (momentarily) pass from our original grand canonical ensemble, all of whose cells have the same V, $\tilde{\mu}$, and T, to another grand canonical ensemble whose cells have the same $\tilde{\mu}$ and T as before, but have slightly larger volumes, $V + dV$, then according to Eq. (4.41) with $\tilde{\mu}$ and T fixed, Ω will change by $d\Omega = d\overline{\mathcal{E}} - TdS - \tilde{\mu} d\overline{N}$ (where dS and $d\overline{N}$ are the changes of entropy and mean number of particles induced by the volume change); and by the elementary first law of thermodynamics,

$$\boxed{d\overline{\mathcal{E}} = -PdV + \tilde{\mu} d\overline{N} + T dS \; ,} \tag{4.44}$$

this change of Ω at fixed $\tilde{\mu}$ and T is simply $-PdV$. Combining with Eq. (4.42), this gives for the change of Ω when all of $\tilde{\mu}$, T, and V change:

$$\boxed{d\Omega = -PdV - \overline{N} d\tilde{\mu} - S dT \; .} \tag{4.45}$$

A second consequence of Eq. (4.42), in the generalized form (4.45), is the fact that it tells us how to compute the mean number of particles, the entropy, and the pressure in terms of $\tilde{\mu}$, T, and V:

$$\overline{N} = -\left(\frac{\partial \Omega}{\partial \tilde{\mu}}\right)_{V,T} \; , \quad S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\tilde{\mu}} \; , \quad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{\tilde{\mu},T} \; . \tag{4.46}$$

A third consequence is the fact that Eqs. (4.46) and (4.41) determine the cell's full set of standard thermodynamic parameters, $\{\overline{\mathcal{E}}, T, \overline{N}, \tilde{\mu}, V, P, S\}$ in terms of the ensemble's three independent quantities T, $\tilde{\mu}$, V. Thus, as soon as the functional form of $\Omega(T, \tilde{\mu}, V)$ is known, from it we can generate all the thermodynamic properties of our equilibrated cells of gas. As we shall see in Chap. 4 and shall illustrate in Ex. 4.8, the resulting thermodynamic properties are independent of the equilibrium ensemble used to compute them: grand canonical, canonical, Gibbs, or microcanonical. This is completely general: *When confronted by a new type of system, one can compute its thermodynamic properties using whatever equilibrium ensemble is most convenient; the results will be ensemble-independent.*

Returning to the specific case of a monatomic, relativistic gas, we can compute $\Omega(T, \tilde{\mu}, V)$ by carrying out explicitly the sum over states of Eq. (4.37). We first fix (temporarily) the number of particles N in an individual system (cell) and its corresponding number of degrees of freedom $W = 3N$. We then perform the integral over phase space. Then we sum over all N from 1 to ∞. The details are spelled out in Ex. 4.6 below—*a very important exercise for readers who have never done computations of this sort.* In the non-relativistic limit, $k_BT \ll mc^2$, this calculation, with the aid of the "classical particles" condition (4.35), yields

$$\Omega(T, \mu, V) = -k_BTV\frac{(2\pi mk_BT)^{3/2}}{h^3}e^{\mu/k_BT}\ , \tag{4.47a}$$

where $\mu = \tilde{\mu} - mc^2$. In the ultra-relativistic limit, $k_BT \gg mc^2$ (e.g. for photons or neutrinos or an ultrarelativistic gas of electrons), the calculation gives

$$\Omega(T, \tilde{\mu}, V) = -\frac{8\pi V(k_BT)^4}{h^3}e^{\tilde{\mu}/k_BT}\ . \tag{4.47b}$$

In the non-relativistic limit, differentiation of the grand potential (4.47a) gives [with the aid of Eqs. (4.46) and (4.41)] the following thermodynamic relations

$$\begin{aligned}\overline{N} &= \tfrac{(2\pi mk_BT)^{3/2}}{h^3}e^{\mu/k_BT}V\ , \quad S = \left(\tfrac{5}{2} - \tfrac{\mu}{k_BT}\right)k\overline{N}\ , \\ P &= k_BT\tfrac{(2\pi mk_BT)^{3/2}}{h^3}e^{\mu/k_BT} = \tfrac{\overline{N}}{V}k_BT\ , \quad \overline{E} = \tfrac{3}{2}k_BT\overline{N}\ .\end{aligned} \tag{4.47c}$$

The corresponding ultrarelativistic expressions are derived in Ex. 4.6(e). Note that the first of the nonrelativistic expressions (4.47c) is the same number density of particles, $\overline{N}/V$, as we derived from kinetic theory in the last chapter [Eq. (2.37a)] but with $g_s = 1$ since we have ignored spin degrees of freedom in the above analysis. The second expression says that each particle in a nonrelativistic, thermalized, ideal, classical gas carries an entropy of $5/2 - \mu/k_BT$ in units of Boltzmann's constant. The third and fourth expressions are the standard, nonrelativistic ideal-gas equations of state, $P = (\overline{N}/V)k_BT$ and $\epsilon \equiv \overline{E}/V = \frac{3}{2}nk_BT$ [Eq. (2.37b)].

The statistical mechanical tools developed in this chapter not only can reproduce all the thermodynamic results that kinetic theory gives us; they can do much more. For example, as we shall see in the following two chapters (and we learn as a preview in Ex. 4.7), these tools can be used to study statistical fluctuations of the physical quanties, whose mean values we have computed.

4.9 Entropy Per Particle

The entropy per particle in units of Boltzmann's constant,

$$\boxed{\sigma \equiv S/Nk_B\ ,} \tag{4.48}$$

is a very useful concept in both quantitative analyses and order-of-magnitude analyses; see, e.g., Ex. 4.10 and the discussion of entropy in the expanding universe in Sec. 4.11.3. One reason is the second law of thermodynamics. Another is that in the real universe σ generally lies somewhere between 0 and 100 and thus is a natural quantity in terms of which to think and remember. For example, for ionized hydrogen gas in the nonrelativistic, classical

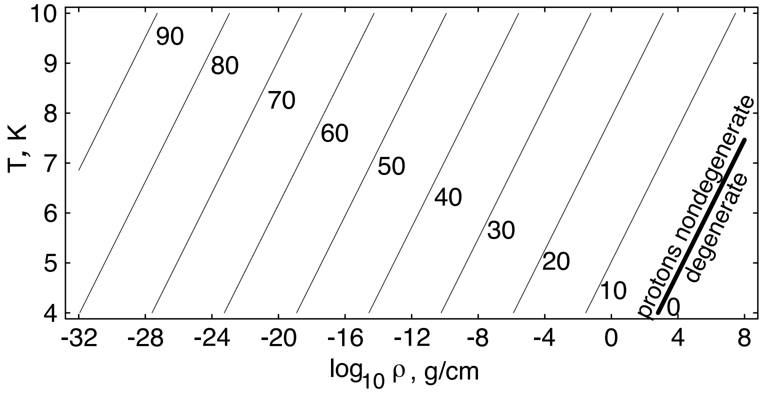

Fig. 4.4: The proton entropy per proton σ_p for an ionized hydrogen gas. The electron entropy per electron, σ_e, is a factor $\simeq 10$ smaller; the electrons are degenerate when $\sigma_e \simeq \sigma_p - 10 \lesssim 1$. The protons are degenerate when $\sigma_p \lesssim 1$.

domain, Eqs. (4.47c) with μ/k_BT from the first equation inserted into the second) say that the protons' entropy per proton is a factor $\simeq$ 10 higher than the electrons', $\sigma_p - \sigma_e = \frac{3}{2}\ln(m_p/m_e) = 11.27 \simeq 10$, and thus for an ionized hydrogen gas most of the entropy is in the protons. The proton entropy per proton grows logarithmically with decreasing density ρ,

$$\sigma_p = \frac{5}{2} - \frac{\mu_p}{k_BT} = \frac{5}{2} + \ln\left[\frac{2m_p}{\rho}\left(\frac{2\pi m_p k_B T}{h^2}\right)^{3/2}\right] \; ; \tag{4.49}$$

[Eqs. (4.47c) and (4.48)]. This entropy per proton is plotted as a function of density and temperature in Fig. 4.4. It ranges from $\sigma \ll 1$ in the regime of extreme proton degeneracy (lower right of Fig. 4.4; see Ex. 4.4) to $\sigma \sim 1$ near the onset of proton degeneracy (the boundary of the classical approximation), to about $\sigma \sim 100$ at the lowest density that occurs in the universe, $\rho \sim 10^{-29}$ g/cm^3. This range is an example of the fact that the logarithms of almost all dimensionless numbers that occur in nature lie between ~ -100 and $+100$.

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EXERCISES

Exercise 4.6 ***Derivation and Example: Grand Canonical Ensemble for Monatomic Gas* Consider the cells of ideal, classical, monatomic gas with volume V that reside in the heat and particle bath of Fig. 4.3. Assume initially that the bath's temperature T has an arbitrary magnitude relative to the rest mass-energy mc^2 of the particles, 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 given system 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. 4.9 below.

(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

$$W = 3N \ , \quad \mathcal{N}_{\rm states} = \frac{1}{N!h^{3N}} \ , \quad \mathcal{E}_N = \sum_{A=1}^{N} ({\mathbf{p}_A}^2 + m^2)^{\frac{1}{2}} \ , \qquad (4.50a)$$

where $\mathbf{p}_A$ is the momentum of classical particle number A.

(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 (4.37) for the grand partition function becomes

$$Z = e^{-\Omega/k_BT} = \sum_{N=0}^{\infty} \frac{V^N}{N!h^{3N}} e^{\tilde{\mu}N/k_BT} \left[\int_0^\infty \exp\left(-\frac{(p^2+m^2)^{\frac{1}{2}}}{k_BT} \right) 4\pi p^2 dp \right]^N \ . \qquad (4.50b)$$

(d) Show that in the nonrelativistic limit this gives Eq. (4.47a), and in the extreme relativistic limit it gives Eq. (4.47b).

(e) For the extreme relativistic limit use your result (4.47b) for the grand potential $\Omega(V, T, \tilde{\mu})$ to derive the mean number of particles $\overline{N}$, the pressure P, the entropy S, and the mean energy $\overline{\mathcal{E}}$ as functions of V, $\tilde{\mu}$, and T. Note that for a photon gas, because of the spin degree of freedom, the correct values of $\overline{N}$, $\overline{\mathcal{E}}$ and S will be twice as large as you obtain in this calculation. Show that $\overline{\mathcal{E}}/V = 3P$ (a relation valid for any ultrarelativistic gas); and that $\overline{\mathcal{E}}/\overline{N} = 3k_BT$ (which is higher than the 2.70 … k_BT for black-body radiation, as derived in Ex. 2.5, because in the classical regime of $\eta \ll 1$ photons don't cluster in the same states at low frequency; that clustering lowers the mean photon energy for black-body radiation.)

Exercise 4.7 ***Example: Probability Distribution for the Number of Particles in a Cell*
Suppose that we make a large number of measurements of the number of atoms in one of the systems of the ensemble of Fig. 4.3, (and Ex. 4.6), and that from those measurements we compute a probability p_N for that cell to contain N particles.

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

(b) Assume that the measurements are widely enough separated for this criterion [part (a)] to be satisfied. Use the grand canonical distribution to show that the probability p_N is given by the *Poisson distribution*

$$p_N = e^{-\overline{N}} (\overline{N}^N / N!) \ . \qquad (4.51a)$$

(c) Show that the mean number of particles in a single system, as predicted by this distribution, is $\langle N\rangle = \overline{N}$, and the root mean square deviation from this is

$$\Delta N \equiv \langle (N-\overline{N})^2\rangle^{\frac{1}{2}} = \overline{N}^{\frac{1}{2}} \ . \tag{4.51b}$$

Exercise 4.8 *Example: Entropy of a Classical, Nonrelativistic, Monatomic Gas in the Microcanonical Ensemble*

Consider a microcanonical ensemble of closed cubical cells with volume V, each containing precisely N particles of a monatomic, nonrelativistic, ideal, classical gas, and each containing a nonrelativistic total energy $E \equiv \mathcal{E} - Nmc^2$. For the moment (by contrast with the text's discussion of the microcanonical ensemble), assume that E is precisely fixed instead of being spread over some tiny but finite range.

(a) Explain why the region $\mathcal{S}_o$ of phase space accessible to each system is

$$|x^j_A| < L/2 \ , \quad \sum_{A=1}^{N} \frac{1}{2m}|\mathbf{p}_A|^2 = E \ , \tag{4.52a}$$

where A labels the particles and $L \equiv V^{1/3}$ is the side of the cell.

(b) In order to compute the entropy of the microcanonical ensemble, we compute the volume in phase space $\Delta\Gamma$ that it occupies, then multiply by the number density of states in phase space (which is independent of location in phase space), and then take the logarithm. Explain why

$$\Delta\Gamma \equiv \prod_{A=1}^{N} \int_{\mathcal{S}_o} dx_A dy_A dz_A dp^x_A dp^y_A dp^z_A \tag{4.52b}$$

vanishes. This illustrates the "set of measure zero" statement in the text (second paragraph of Sec. 4.5), which we used to assert that we must allow the systems' energies to be spread over some tiny but finite range.

(c) Now permit the energies of our ensemble's cells to lie in the tiny but finite range $E_o - \delta E_o < E < E_o$. Show that

$$\Delta\Gamma = V^N[\mathcal{V}_\nu(a) - \mathcal{V}_\nu(a-\delta a)] \ , \tag{4.52c}$$

where $\mathcal{V}_\nu(a)$ is the volume of a sphere of radius a in a Euclidean space with $\nu \gg 1$ dimensions, and where

$$a \equiv \sqrt{2mE_o} \ , \quad \frac{\delta a}{a} \equiv \frac{1}{2}\frac{\delta E_o}{E_o} \ , \quad \nu \equiv 3N \ . \tag{4.52d}$$

It can be shown (and you might want to try) that

$$\mathcal{V}_\nu(a) = \frac{\pi^{\nu/2}}{(\nu/2)!}a^\nu \quad \text{for } \nu \gg 1 \ . \tag{4.52e}$$

(d) Show that, so long as $1 \gg \delta E_o/E_o \gg 1/N$ (where N in practice is an exceedingly huge number),

$$\mathcal{V}_\nu(a) - \mathcal{V}_\nu(a-\delta a) \simeq \mathcal{V}_\nu(a)[1 - e^{-\nu\delta a/a}] \ \simeq \ \mathcal{V}_\nu(a) \ , \tag{4.52f}$$

which is independent of δE_o and thus will produce a value for $\Delta\Gamma$ and thence $N_{\rm states}$ and S independent of δE_o, as desired. From this and with the aid of Stirling's approximation, $n! \simeq 2\pi n^{1/2}(n/e)^n$ for large n, and taking account of the multiplicity $\mathcal{M} = N!$, show that the entropy of the microcanonically distributed cells is given by

$$S(V, E, N) = Nk_B \ln\left[\frac{V}{N}\left(\frac{E}{N}\right)^{3/2}\left(\frac{4\pi m}{3h^2}\right)^{3/2} e^{5/2}\right] \ . \tag{4.53}$$

This is known as the *Sackur-Tetrode* equation.

(e) Returning to the grand canonical ensemble of the text and Ex. 4.6, show that its entropy (4.47c), when expressed in terms of $V/\overline{N}$ and $\overline{E}/\overline{N}$, takes precisely the same form as this Sackur-Tetrode equation. This illustrates the fact that the thermodynamic properties of a thermally equilibrated system are independent of the nature of its statistical equilibrium, i.e. independent of the type of bath (if any) that has brought it to equilibrium.

Exercise 4.9 ***Example: Entropy of Mixing, Indistinguishability of Atoms, and the Gibbs Paradox*

(a) Consider two identical chambers, each with volume V, separated by an impermeable membrane. Into one chamber put energy E and N molecules of Helium, and into the other, energy E and N molecules of Xenon, with E/N and N/V small enough that the gases are nonrelativistic and nondegenerate. The membrane is ruptured, and the gases mix. Show that this mixing drives the entropy up by an amount $\Delta S = 2Nk_B \ln 2$. [Hint: use the Sackur-Tetrode equation (4.53).]

(b) Suppose that energy E and N atoms of Helium are put into both chambers (no Xenon). Show that, when the membrane is ruptured and the gases mix, there is no increase of entropy. Explain why this is reasonable, and explain the relationship to entropy being an extensive variable.

(c) Suppose that the N Helium atoms were distinguishable instead of indistinguishable. Show this would mean that, in the microcanonical ensemble, they have $N!$ more states available to themselves, and their entropy would be larger by $k_B \ln N! \simeq k_B(N\ln N - N)$; and as a result, the Sackur-Tetrode formula (4.53) would be

$$\text{Distinguishable particles: } S(V, E, N) = Nk_B \ln\left[V\left(\frac{E}{N}\right)^{3/2}\left(\frac{4\pi m}{3h^2}\right)^{3/2} e^{3/2}\right] \ . \tag{4.54}$$

Before the advent of quantum theory, physicists thought that atoms are distinguishable, and up to an additive multiple of N which they could not compute, they deduced this entropy.

(d) Show that if, as pre-quantum physicists believed, atoms were distinguishable, then when the membrane between two identical Helium-filled chambers is ruptured there would be an entropy increase identical to that when the membrane between Helium and Xenon is ruptured: $\Delta S = 2Nk_B \ln 2$ [cf. parts (a) and (b)]. This result, which made pre-quantum physicists rather uncomfortable, was called the *Gibbs paradox.*

Exercise 4.10 *Problem: Primordial Element Formation*
When the expanding universe was $t \sim 10^{-4}$ second old, it contained equal numbers of protons and neutrons, plus far more photons, electrons, and positrons, all in statistical equilibrium at a temperature $T \sim 10^{12}$ K. As the universe continued to expand, its temperature fell as $T \propto 1/\sqrt{t}$. Nuclear reactions in this expanding plasma were continually trying to make alpha particles (helium nuclei): $2n + 2p \rightarrow \alpha + 7$ Mev, with the 7 Mev of energy able to go into thermalized photons. Using an order-of-magnitude computation based on entropy per baryon, show that the second law of thermodynamics prevented this helium formation from occuring until the temperature had fallen to some critical value $T_{\rm crit}$, and thereafter the second law encouraged helium formation to occur. Compute $T_{\rm crit}$ and the corresponding time t at which helium could start to form. The fraction of the universe's protons and neutrons that actually became α's (about 25%) was controlled by the actual rates for the relevant nuclear reactions and by the complete shutoff of these reactions via beta decay of the neutrons at $t \sim$ (neutron half life) = 11 minutes. For further detail, see Chap. 27.

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4.10 $\boxed{\text{T2}}$ Bose-Einstein Condensate

In this section we shall explore an important modern application of the Bose-Einstein mean occupation number for bosons in statistical equilibrium. Our objectives are: (i) to present an important modern application of the tools developed in this chapter, and (ii) give a nice example of the connections between quantum statistical mechanics (which we shall use in the first 3/4 of this section) and classical statistical mechanics (which we shall use in the last 1/4).

For bosons in statistical equilibrium, the mean occupation number $\eta = 1/[e^{(E-\mu)/k_BT} - 1]$ diverges as $E \rightarrow 0$, if the chemical potential μ vanishes. This divergence is intimately connected to *Bose-Einstein condensation*, a phenomenon that provides a nice and important example of the concepts we are developing:

Consider a dilute atomic gas in the form of a large number N of bosonic atoms spatially confined by a magnetic trap. When the gas is cooled below some critical temperature T_c, μ is negative but gets very close to zero [Eq. (4.56d) below], causing η to become huge near zero energy. This huge η is manifest, physically, by a large number N_0 of atoms collecting into the trap's mode of lowest (vanishing) energy, the Schroedinger equation's ground state [Eq. (4.58a) and Fig. 4.5(a) below].

This *condensation* was predicted by Einstein (1925), but an experimental demonstration was not technologically feasible until 1995, when two research groups independently exhibited it: one at JILA (University of Colorado) led by Eric Cornell and Carl Wieman; the other at MIT led by Wolfgang Ketterle. For these experiments, Cornell, Ketterle and Wieman were awarded the 2001 Nobel Prize. Bose-Einstein condensates have great promise as tools for precision measurement technology and for nanotechnology.

As a concrete example of Bose-Einstein condensation, we shall analyze an idealized version of one of the early experiments by the JILA group (Ensher et. al. 1996): a gas of 40,000 ^{87}Rb atoms placed in a magnetic trap that we approximate as a spherically symmetric, harmonic oscillator potential[9]

$$V(r) = \frac{1}{2} m\omega_o^2 r^2 = \frac{1}{2} m\omega_o^2 (x^2 + y^2 + z^2) \ . \tag{4.55a}$$

Here x, y, z are Cartesian coordinates and r is radius. The harmonic-oscillator frequency ω_o and associated temperature $\hbar\omega_o/k$, the number N of Rubidium atoms trapped in the potential, and the atoms' rest mass m are

$$\omega_o/2\pi = 181\text{Hz} \ , \quad \hbar\omega_o/k = 8.7\text{nK} \ , \quad N = 40,000 \ , \quad m = 1.444 \times 10^{-25}\text{kg} \ . \tag{4.55b}$$

Each ^{87}Rb atom is made from an even number of fermions [$Z = 37$ electrons, $Z = 37$ protons, and $(A - Z) = 50$ neutrons], and the many-particle wave function Ψ for the system of $N = 40,000$ atoms is antisymmetric (changes sign) under interchange of each pair of electrons, each pair of protons, and each pair of neutrons. Therefore, when any pair of atoms is interchanged (entailing interchange of an even number of fermion pairs), there is an even number of sign flips in Ψ. This means that Ψ is symmetric (no sign change) under interchange of atoms; i.e., the atoms behave like bosons and must obey Bose-Einstein statistics.

Repulsive forces between the atoms have a moderate influence on the experiment, but only a tiny influence on the quantities that we shall compute (see, e.g., Dalfovo et. al. 1999). We shall ignore those forces and treat the atoms as noninteracting.

To make contact with our derivation, above, of the Bose-Einstein distribution, we must identify the *modes* $\mathcal{S}$ available to the atoms. Those modes are the energy eigenstates of the Schroedinger equation for a ^{87}Rb atom in the harmonic-oscillator potential $V(r)$. Solution of the Schroedinger equation [e.g., Complement B_{VII} (pp. 814ff) of Cohen-Tannudji et. al. 1977] reveals that the energy eigenstates can be labeled by the number of quanta of energy $\{n_x, n_y, n_z\}$ associated with an atom's motion along the x, y, and z directions; and the energy of the mode $\{n_x, n_y, n_z\}$ is $E_{n_x,n_y,n_z} = \hbar\omega_o[(n_x + 1/2) + (n_y + 1/2) + (n_z + 1/2)]$. We shall simplify subsequent formulas by subtracting $\frac{3}{2}\hbar\omega_o$ from all energies and all chemical potentials. This is merely a change in what energy we regard as zero, a change under which our statistical formalism is invariant. Correspondingly, we shall attribute to the mode $\{n_x, n_y, n_z\}$ the energy $E_{n_x,n_y,n_z} = \hbar\omega_o(n_x + n_y + n_z)$. Our calculations will be simplified by lumping together all modes that have the same energy, so we switch from $\{n_x, n_y, n_z\}$

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[9] In the actual experiment the potential was harmonic but prolate spheroidal rather than spherical, i.e. in Cartesian coordinates $V(x, y, z) = \frac{1}{2}m[\omega_\varpi^2(x^2 + y^2) + \omega_z^2 z^2]$ with ω_z somewhat smaller than ω_ϖ. For pedagogical simplicity we treat the potential as spherical, with ω_o set to the geometric mean of the actual frequencies along the three Cartesian axes, $\omega_o = (\omega_\varpi^2 \omega_z)^{1/3}$. This choice of ω_o gives good agreement between our model's predictions and the prolate-spheroidal predictions, for the quantities that we compute.

to $q \equiv n_x + n_y + n_z =$ (the mode's total number of quanta) as our fundamental quantum number, and we write the mode's energy as

$$E_q = q\hbar\omega_o \; . \tag{4.56a}$$

It is straightforward to verify that the number of independent modes with q quanta (the number of independent ways to choose $\{n_x, n_y, n_z\}$ such that their sum is q) is $\frac{1}{2}(q+1)(q+2)$.

Of special interest is the ground-state mode of the potential, $\{n_x, n_y, n_z\} = \{0, 0, 0\}$. This mode has $q = 0$ and it is unique: $(q+1)(q+2)/2 = 1$. Its energy is $E_0 = 0$, and its Schroedinger wave function is $\psi_o = (\pi\sigma_o^2)^{-3/4}\exp(-r^2/2\sigma_o^2)$, so for any atom that happens to be in this ground-state mode, the probability distribution for its location is the Gaussian

$$|\psi_o(r)|^2 = \left(\frac{1}{\pi\sigma_o^2}\right)^{3/2} \exp\left(-\frac{r^2}{\sigma_o^2}\right) \; , \quad \text{where } \sigma_o = \sqrt{\frac{\hbar}{m\omega_o}} = 0.800\mu\text{m} \; . \tag{4.56b}$$

The entire collection of N atoms in the magnetic trap is a system; it interacts with its environoment, which is at temperature T, exchanging energy but nothing else, so a conceptual ensemble consisting of this N-atom system and a huge number of identical systems has the canonical distribution, $\rho = C\exp(-\mathcal{E}_{\rm tot}/k_BT)$, where $\mathcal{E}_{\rm tot}$ is the total energy of all the atoms. The modes labeled by $\{n_x, n_y, n_z\}$ (or by q and two degeneracy parameters that we have not specified) are subsystems of this system, and because the modes can exchange atoms with each other as well as energy, a conceptual ensemble consisting of any chosen mode and its clones is grand canonically distributed [Eq. (4.27a)], and its mean occupation number is given by the Bose-Einstein formula (4.27b) with $E_{\mathcal{S}} = q\hbar\omega_o$:

$$\eta_q = \frac{1}{\exp[(q\hbar\omega_o - \mu)/k_BT] - 1} \; . \tag{4.56c}$$

The temperature T is inherited from the environment (heat bath) in which the atoms live. The chemical potential μ is common to all the modes, and takes on whatever value is required to guarantee that the total number of atoms in the trap is N — or, equivalently, that the sum of the mean occupation number (4.56c) over all the modes is N.

For the temperatures of interest to us: (i) The number $N_0 \equiv \eta_0$ of atoms in the ground-state mode $q = 0$ will be large, $N_0 \gg 1$, which permits us to expand the exponential in Eq. (4.56c) with $q = 0$ to obtain $N_0 = 1/[e^{-\mu/k_BT} - 1] \simeq -k_BT/\mu$, i.e.,

$$\mu/k_BT = -1/N_0 \; . \tag{4.56d}$$

And (ii) the atoms in excited modes will be spread out roughly uniformly over many values of q, so we can approximate the total number of excited-mode atoms by an integral:

$$N - N_0 = \sum_{q=1}^{\infty} \frac{(q+1)(q+2)}{2}\eta_q \simeq \int_0^\infty \frac{\frac{1}{2}(q^2 + 3q + 2)dq}{\exp[(q\hbar\omega_o/k_BT + 1/N_0)] - 1} \; . \tag{4.57a}$$

The integral is dominated by large q's, so it is a rather good approximation to keep only the q^2 term in the numerator and to neglect the $1/N_0$ in the exponential:

$$N - N_0 \simeq \int_0^\infty \frac{q^2/2}{\exp(q\hbar\omega_o/k_BT) - 1} = \zeta(3)\left(\frac{k_BT}{\hbar\omega_o}\right)^3 \; . \tag{4.57b}$$

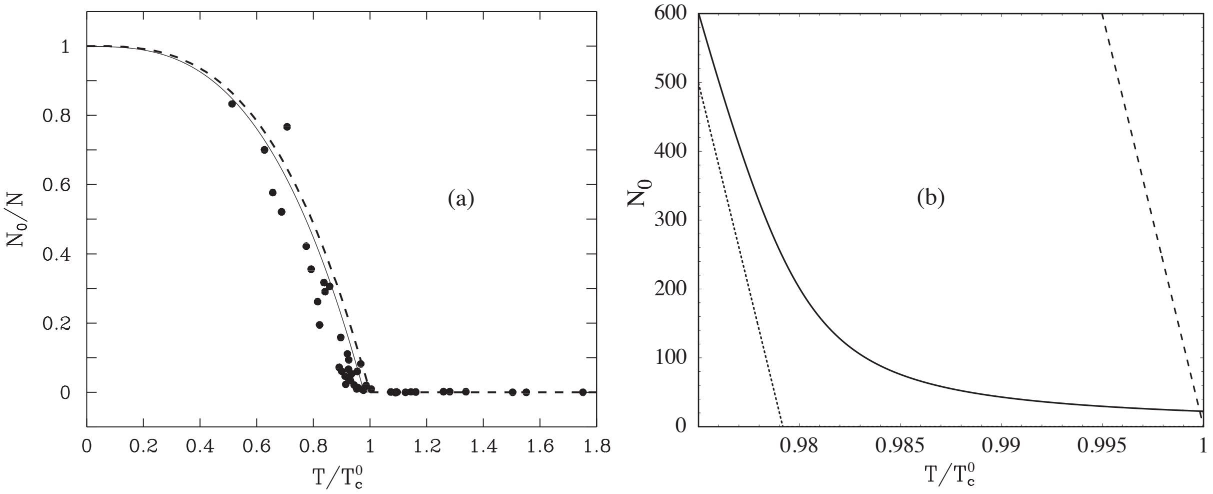

Fig. 4.5: The number N_0 of atoms in the Bose-Einstein condensate at the center of a magnetic trap as a function of temperature T; panel (a) — low resolution, panel (b) — high resolution. The dashed curve in each panel is the prediction (4.58a) of the simple theory presented in the text, using the parameters shown in Eq. (4.55b). The dotted curve in panel (b) is the prediction derived in Ex. 4.11(c). The solid curves are our most accurate prediction (4.63) [Ex. 4.11(d)] including details of the condensation turn on. The large dots are experimental data from Ensher et. al. (1996). The left panel is adapted from Dalfovo et. al. (1999).

Here $\zeta(3) \simeq 1.2020569...$ is the Riemann Zeta function [which also appeared in our study of the equation of state of thermalized radiation, Eq. (2.51b)]. It is useful to rewrite Eq. (4.57b) as

$$N_0 = N\left[1 - \left(\frac{T}{T_c^0}\right)^3\right] , \tag{4.58a}$$

where

$$T_c^0 = \frac{\hbar\omega_o}{k_B}\left(\frac{N}{\zeta(3)}\right)^{1/3} = 280\text{nK} \gg \hbar\omega_o/k_B = 8.7\text{nK} \tag{4.58b}$$

is our leading-order approximation to the critical temperature T_c. Obviously, we cannot have a negative number of atoms in the ground-state mode, so Eq. (4.58a) must fail for $T > T_c^0$. Presumably N_0 becomes so small there, that our approximation (4.56d) fails.

Figure 4.5(a), from a review article by Dalfovo et. al. (1999), compares our simple prediction (4.58a) for $N_0(T)$ (dashed curve) with the experimental measurements by the JILA group (Ensher et. al. 1996). Both theory and experiment show that, when one lowers the temperature T through a critical temperature T_c, the atoms suddenly begin to accumulate in large numbers in the ground-state mode. At $T \simeq 0.8T_c$, half the atoms have condensed into the ground state ("Bose-Einstein condensation"); at $T \simeq 0.2T_c$ almost all are in the ground state. The simple formula (4.58a) is remarkably good at $0 < T < T_c$; and, evidently, T_c^0 [Eq. (4.58b)] is a rather good "leading-order" approximation to the critical temperature T_c at which the Bose-Einstein condensate begins to form.

Exercise 4.11 and Fig. 4.5(b) use more accurate approximations to Eq. (4.57a) to explore the onset of condensation as T is gradually lowered through the critical temperature. The onset is actually continuous when viewed on a sufficiently fine temperature scale; but on scales $0.01T_c$ or greater, it appears truly discontinuous.

The onset of Bose-Einstein condensation is an example of a *phase transition*: a sudden (nearly) discontinuous change in the properties of a thermalized system. Among the sudden changes accompanying this phase transition is a (nearly) discontinuous change of the atoms' specific heat (Ex. 4.12). We shall study some other phase transitions in Chap. 4.

Notice that the critical temperature T_c^0 is larger, by a factor $\simeq N^{1/3} = 34$, than the temperature $\hbar\omega_o/k = 8.7$ nK associated with the harmonic-oscillator potential. Correspondingly, at the critical temperature there are significant numbers of atoms in modes with q as large as ~ 34 — which means that *the vast majority of the atoms are actually behaving rather classically at* $T \simeq T_c^0$*, despite our use of quantum mechanical concepts to analyze them!*

It is illuminating to compute the spatial distribution of these atoms at the critical temperature using classical techniques. (This distribution could equally well be deduced using the above quantum techniques.) In the near classical, outer region of the trapping potential, the atoms' number density in phase space $\mathcal{N} = (2/h^3)\eta$ must have the classical, Boltzmann-distribution form (4.28): $dN/d\mathcal{V}_x d\mathcal{V}_p \propto \exp(-E/k_BT) = \exp\{-[V(r) + p^2/2m]/k_BT_c\}$, where $V(r)$ is the harmonic-oscillator potential (4.55a). Integrating over momentum space, $d\mathcal{V}_p = 4\pi p^2 dp$, we obtain for the number density of atoms $n = dN/d\mathcal{V}_x$

$$n(r) \propto \exp\left(\frac{-V(r)}{k_BT_c}\right) = \exp\left(\frac{-r^2}{a_o^2}\right) , \quad \text{where} \tag{4.59a}$$

$$a_o = \sqrt{\frac{2k_BT_c}{m\omega_o^2}} = \frac{\sqrt{2}}{[\zeta(3)]^{1/6}} N^{1/6}\sigma_o = 1.371 N^{1/6}\sigma_o = 8.02\sigma_o = 6.4\mu\text{m} . \tag{4.59b}$$

Thus, at the critical temperature, the atoms have an approximately Gaussian spatial distribution with radius a_o eight times larger than the trap's 0.80μm ground-state Gaussian distribution. This size of the distribution gives insight into the origin of the Bose-Einstein condensation: The mean inter-atom spacing at the critical temperature T_c^0 is $a_o/N^{1/3}$. It is easy to verify that this is approximately equal to the typical atom's deBroglie wavelength $\lambda_{\rm dB} = \hbar/\sqrt{2mk_BT} = \hbar/(\text{typical momentum})$ — which is the size of the region that we can think of each atom as occupying. The atomic separation is smaller than this in the core of the atomic cloud, so the atoms there are beginning to overlap and feel each others' presence, and thereby want to accumulate into the same quantum state (i.e., want to begin condensing). By contrast, the mean separation is larger than $\lambda_{\rm dB}$ in the outer portion of the cloud, so the atoms there continue to behave classically.

At temperatures below T_c, the N_0 condensed, ground-state-mode atoms have a spatial Gaussian distribution with radius, σ_o, 8 times smaller than that, a_o, of the (classical) excited-state atoms, so the condensation is manifest, visually, by the growth of a sharply peaked core of atoms at the center of the larger, classical, thermalized cloud. In momentum space the condensed atoms and classical cloud also have Gaussian distributions, with rms momenta $p_{\rm cloud} \simeq 8p_{\rm condensate}$. In early experiments, the existence of the condensate was observed by suddenly shutting off the trap and letting the condensate and cloud expand ballistically to sizes $p_{\rm condensate}t/m$ and $p_{\rm cloud}t/m$, and then observing them visually. The condensate was

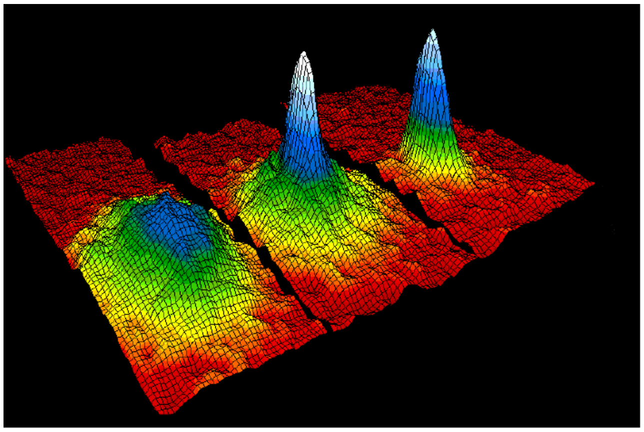

Fig. 4.6: Velocity distribution of rubidium atoms in a bose-condensate experiment by Anderson et. al. (1995), as observed by the ballistic expansion method described in the text. In the left frame T is slightly higher than T_c and there is only the classical cloud. In the center frame T is a bit below T_c and the condensate sticks up sharply above the cloud. The right frame, at still lower T, shows almost pure condensate. Figure from Cornell (1996).

revealed as a sharp Gaussian peak, sticking out of the ~ 8 times larger, classical cloud; Fig. 4.6.

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EXERCISES

Exercise 4.11 ***Example: Onset of Bose-Einstein Condensation*
By using more accurate approximations to Eq. (4.57a), explore the onset of the condensation near $T = T_c^0$. More specifically:

(a) Approximate the numerator in (4.57a) by $q^2 + 3q$ and keep the $1/N_0$ term in the exponential. Thereby obtain

$$N - N_0 = \left(\frac{k_B T}{\hbar\omega_o}\right)^3 \mathrm{Li}_3(e^{-1/N_0}) + \frac{3}{2}\left(\frac{k_B T}{\hbar\omega_o}\right)^2 \mathrm{Li}_2(e^{-1/N_0}) \; . \tag{4.60}$$

Here

$$\mathrm{Li}_n(u) = \sum_{p=1}^{\infty} \frac{u^p}{p^n} \tag{4.61a}$$

is a special function called the *polylogarithm* (Lewin 1981), which is known to *Mathematica* and other symbolic manipulation software, and has the properties

$$\mathrm{Li}_n(1) = \zeta(n) \; , \quad \frac{d\mathrm{Li}_n(u)}{du} = \frac{\mathrm{Li}_{n-1}(u)}{u} \; , \tag{4.61b}$$

where $\zeta(n)$ is the Riemann zeta function.

(b) Show that by setting $e^{-1/N_0} = 1$ and ignoring the second polylogarithm in Eq. (refeq3:NLi), we obtain the leading-order description of the condensation discussed in the text: Eqs. (4.57b) and (4.58).

(c) By continuing to set $e^{-1/N_0} = 1$ but keeping the second polylogarithm, obtain an improved equation for $N_0(T)$. Your answer should continue to show a discontinuous turn on of the condensation, but at a more accurate, slightly lower critical temperature

$$T_c^1 = T_c^0 \left[1 - \frac{\zeta(2)}{\zeta(3)^{2/3}} \frac{1}{N^{1/3}} \right] = 0.979 T_c^0 \ . \tag{4.62}$$

This equation illustrates the fact that the approximations we are making are a *large-N expansion*, i.e. and expansion in powers of $1/N$.

(d) By keeping all details of Eq. (4.60) but rewriting it in terms of T_c^0, show that

$$N_0 = N \left[1 - \left(\frac{T}{T_c^0} \right)^3 \frac{\mathrm{Li}_3(e^{-1/N_0})}{\zeta(3)} - \frac{3}{2\zeta(3)^{2/3}} \frac{1}{N^{1/3}} \left(\frac{T}{T_c^0} \right)^2 \mathrm{Li}_2(e^{-1/N_0}) \right] \ . \tag{4.63}$$

Solve this numerically to obtain $N_0(T/T_c^0)$ for $N = 40,000$ and plot your result graphically. It should take the form of the solid curves in Fig. 4.5: a continuous turn on of the condensation over the narrow temperature range $0.98 T_c^0 \lesssim T \lesssim 0.99 T_c^0$, i.e. a range $\Delta T \sim T_c^0 / N^{1/3}$. In the limit of an arbitrarily large number of atoms, the turn on is instantaneous, as described by Eq. (4.58a).

Exercise 4.12 ***Problem: Discontinuous change of Specific Heat*
Analyze the behavior of the atoms' total energy near the onset of condensation, in the limit of arbitrarily large N — i.e., keeping only the leading order in our $1/N^{1/3}$ expansion and approximating the condensation as turning on discontinuously at $T = T_c^0$. More specifically:

(a) Show that the total energy of the atoms in the magnetic trap is

$$\begin{aligned} E_{\rm total} &= \frac{3\zeta(4)}{\zeta(3)} N k_B T_c^0 \left(\frac{T}{T_c^0} \right)^4 \quad \text{when } T < T_c^0 \ , \\ E_{\rm total} &= \frac{3\mathrm{Li}_4(e^{\mu/k_B T})}{\zeta(3)} N k_B T_c^0 \left(\frac{T}{T_c} \right)^4 \quad \text{when } T > T_c^0 \ , \end{aligned} \tag{4.64a}$$

where (at $T > T_c$) $e^{\mu/k_B T}$ is a function of N, T determined by $N = (k_B T / \hbar\omega_o)^2 \mathrm{Li}_3(e^{\mu/k_B T})$, and $\mu = 0$ at $T = T_c^0$. Because $\mathrm{Li}_n(1) = \zeta(n)$, this energy is continuous across the critical temperature T_c.

(b) Show that the specific heat $C = (\partial E_{\rm total}/\partial T)_N$ is discontinuous across the critical temperature T_c^0:

$$\begin{aligned} C &= \frac{12\zeta(4)}{\zeta(3)} N k = 10.80 N k \quad \text{as } T \to T_c \text{ from below,} \\ C &= \left(\frac{12\zeta(4)}{\zeta(3)} - \frac{9\zeta(3)}{\zeta(2)} \right) N k = 4.227 N k \quad \text{as } T \to T_c \text{ from above.} \end{aligned} \tag{4.64b}$$

Note: for gas contained within the walls of a box, there are two specific heats: $C_V = (\partial E/\partial T)_{N,V}$ when the box volume is held fixed, and $C_P = (\partial E/\partial T)_{N,P}$ when the pressure exerted by the box walls is held fixed. For our trapped atoms, there are no physical walls; the quantity held fixed in place of V or P is the trapping potential $V(r)$.

Exercise 4.13 *Problem: Momentum Distributions in Condensate Experiments*
Show that in the Bose-Einstein condensate discussed in the text, the momentum distribution for the ground-state-mode atoms is Gaussian with rms momentum $p_{\rm condensate} = \hbar/\sigma_o = \sqrt{\hbar m\omega_o}$ and that for the classical cloud it is Gaussian with rms momentum $p_{\rm cloud} = \sqrt{2mk_BT_c} \simeq \sqrt{2N^{1/3}\hbar m\omega_o} \simeq 8p_{\rm condensate}$.

Exercise 4.14 *Problem: Bose-Einstein Condensation in a Cubical Box*
Analyze Bose-Einstein condensation in a cubical box with edge lengths L, i.e. for a potential $V(x,y,z)$ that is zero inside the box and infinite outside it. Show, in particular, using the analog of the text's simplest approximation, that the critical temperature at which condensation begins is

$$T_c = \frac{1}{2\pi m k_B}\left[\frac{2\pi\hbar}{L}\left(\frac{N}{\zeta(3/2)}\right)^{1/3}\right]^2 , \qquad (4.65a)$$

and the number of atoms in the ground-state condensate, when $T < T_c$, is

$$N_0 = N\left[1-\left(\frac{T}{T_c}\right)^{3/2}\right] . \qquad (4.65b)$$

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4.11 $\boxed{\text{T2}}$ Statistical Mechanics in the Presence of Gravity

Systems with significant gravity behave quite differently, statistical mechanically, than systems without gravity. This has led to much controversy as to whether statistical mechanics can really be applied to gravitating systems. Despite that controversy, statistical mechanics *has* been applied in the presence of gravity in a variety of ways, with great success, and with important, fundamental conclusions. In this section we sketch some of those applications: to galaxies, black holes, the universe as a whole, and the formation of structure in the universe. Our discussion is intended to give just the flavor of these subjects and not full details, so we shall state a number of things without derivation. This is necessary in part because many of the phenomena we shall describe rely for their justification on general relativity (Part VI) and/or quantum field theory in curved spacetime (not treated in this book).

4.11.1 $\boxed{\text{T2}}$ Galaxies

We shall idealize a galaxy as a spherically symmetric cluster of $N \sim 10^{11}$ stars each with mass m comparable to that of the sun, $m \sim 1M_\odot$.[10] The stars are bound under their collective self-gravity. (In fact we know that there is also dark matter present, but we will ignore its effects. In addition, most galaxies including our own are not spherical, a fact we shall also ignore.) Now the characteristic size of a galaxy is $R \sim 10$ kiloparsecs (kpc).[11] Therefore the magnitude of its Newtonian gravitational potential in units of c^2 is $|\Phi/c^2| \sim GNm/Rc^2 \sim 10^{-6} \ll 1$ (where G is Newton's gravitational constant) and the characteristic speed of the stars in the galaxy is $v \sim (GNm/R)^{1/2} \sim 200$ km s$^{-1} \ll c$, which means the gravity and stars can be analyzed in the nonrelativistic, Newtonian framework (cf. Fig. 1.1 and Part VI).

The time it takes stars to cross the galaxy is $\tau_{\rm int} \sim 2R/v \sim 10^8$ yr.[12] This time is short compared with the age of a galaxy, $\sim 10^{10}$ yr. Galaxies have distant encounters with their neighbors on timescales that can be smaller than their ages but still much longer than $\tau_{\rm int}$; in this sense, they can be thought of as semiclosed systems, weakly coupled to their environments. However, we shall idealize our chosen galaxy as fully closed (no interaction with its environment). Direct collisions between stars are exceedingly rare, and strong two-star gravitational encounters, which happen when the impact parameter is smaller than $\sim Gm/v^2 \sim R/N$, are also neglibibly rare. We can therefore regard each of our galaxy's stars as moving under a gravitational potential determined by the smoothed-out mass of all the other stars, and can use Hamiltonian dynamics to describe their motions.

We imagine that we have an ensemble of such galaxies, all with the same number of stars N, the same mass $M = Nm$, and the same energy E (in a tiny range δE), and we begin our study of that ensemble by making an order of magnitude estimate of the probability ρ of finding a chosen galaxy from the ensemble in some chosen (single-particle) quantum state. We compute that probability from the corresponding probabilities for its subsystems, individual stars: The phase-space volume available to each star in the galaxy is $\sim R^3(mv)^3$, the density of states in each star's phase space is $1/h^3$, the number of available states is the product of these $\sim (Rmv/h)^3$, and the probability of the star occupying the chosen state, or any other state, is the reciprocal of this, $\sim (h/Rmv)^3$. The probability of the galaxy occupying a state in its phase space is the product of the probabilities for each of its N stars [Eq. (4.17c)]:

$$\rho \sim \left(\frac{h}{Rmv}\right)^{3N} \sim 10^{-1000}. \tag{4.66}$$

This very small number suggests that it is somewhat silly of us to use quantum mechanics to normalize the distribution function (i.e., silly to use the probabilistic distribution function ρ), when dealing with a system as classical as a whole galaxy. Silly, perhaps; but dangerous, no. The key point is that, so far as classical statistical mechanics is concerned, the only important feature of ρ is that it is proportional to the classical distribution function $\mathcal{N}_{\rm sys}$; its

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[10] $1{\rm M}_\odot \equiv 2 \times 10^{30}$ kg.

[11] 1kpc$\equiv 3.1 \times 10^{16}$ km.

[12] 1 yr$\sim \pi \times 10^7$ s.

absolute normalization is usually not important, classically. It was this fact that permitted so much progress to be made in statistical mechanics prior to the advent of quantum mechanics.

Are real galaxies in statistical equilibrium? To gain insight into this question, we shall estimate the entropy of a galaxy in our ensemble and shall then ask whether that entropy has any chance of being the maximum value allowed to the galaxy's stars (as it must be if the galaxy is in statistical equilibrium).

Obviously, the stars (by contrast with electrons) are distinguishable, so we can assume multiplicity $\mathcal{M} = 1$ when estimating the galaxy's entropy. Ignoring the (negligible) correlations between stars, the entropy computed by integating $\rho \ln \rho$ over the galaxy's full $6N$ dimensional phase space is just N times the entropy associated with a single star, which is approximately $S \sim N k_B \ln(\Delta\Gamma/h^3)$ [Eqs. (4.33) and (4.8a)], where $\Delta\Gamma$ is the phase space volume over which the star wanders in its ergodic, Hamiltonian-induced motion, i.e. the phase space volume available to the star. We shall express this entropy in terms of the galaxy's total mass $M = Nm$ and its total nonrelativistic energy $E \equiv \mathcal{E} - Mc^2 \sim -GM^2/2R$. Since the characteristic stellar speed is $v \sim (GM/R)^{1/2}$, the volume of phase space over which the star wanders is $\Delta\Gamma \sim (mv)^3 R^3 \sim (GMm^2R)^{3/2} \sim (-G^2M^3m^2/2E)^{3/2}$, and the entropy therefore is

$$S_{\rm Galaxy} \sim (M/m) k_B \ln(\Delta\Gamma/h^3) \sim (3M/2m) k_B \ln(-G^2M^3m^2/2Eh^2)\ . \tag{4.67}$$

Is this the maximum possible entropy available to the galaxy, given the constraints that its mass be M and its nonrelativistic energy be E? No. Its entropy can be made larger by removing a single star from the galaxy to radius $r \gg R$, where the star's energy is negligible. The entropy of the remaining stars will decrease slightly since the mass M diminishes by m at constant E. However, the entropy associated with the removed star, $\sim (3/2)\ln(GMm^2r/h^2)$ can be made arbitrarily large by making its radius r arbitrarily large. Therefore, by this thought experiment we discover that galaxies cannot be in a state of maximum entropy at fixed $\mathcal{E}$ and M, and they therefore cannot be in a true statistical equilibrium state.[13] (One might wonder whether there is entropy associated with the galaxy's gravitational field, and whether that entropy invalidates our analysis. The answer is no. The gravitational field has no randomness , beyond that of the stars themselves, and thus no entropy; its structure is uniquely determined, via Newton's field equation, by the stars' spatial distribution.)

In a real galaxy or other star cluster, rare near-encounters between stars in the cluster core cause individual stars to be ejected from the core into distant orbits or be ejected from the cluster altogether. These ejections increase the cluster's entropy in just the manner of our thought experiment. The core of the galaxy shrinks, a diffuse halo grows, and the total number of stars in the galaxy gradually decreases. This evolution to ever larger entropy is demanded by the laws of statistical mechanics, but by contrast with systems without gravity, it does not bring the cluster to statistical equilibrium. The long-range influence of gravity prevents a true equilibrium from being reached. Ultimately, the cluster's core may collapse to form a black hole.

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[13] A true equilibrium *can* be achieved if the galaxy is enclosed in an idealized spherical box whose walls prevent stars from escaping, or if the galaxy lives in an infinite thermalized bath of stars so that, on average, whenever one star is ejected into a distant orbit in the bath, another gets injected into the galaxy; see, e.g., Ogorodnikov (1965) and Lynden-Bell (1967). However, in the real universe galaxies are not surrounded by walls or by thermalized star baths.

4.11.2 $\boxed{\text{T2}}$ Black Holes

Quantum field theory predicts that, near the horizon of a black hole, the vacuum fluctuations of quantized fields behave thermally, as seen by stationary (non-infalling) observers. More specifically, such observers see the horizon surrounded by an atmosphere that is in statistical equilibrium (a "thermalized" atmosphere) and that rotates with the same angular velocity $\mathbf{\Omega}_H$ as the hole's horizon.[14] The atmosphere contains all types of particles that can exist in nature. Very few of the particles manage to escape from the hole's gravitational pull; most emerge from the horizon, fly up to some maximum height, then fall back down to the horizon. Only if they start out moving almost vertically upward (i.e., with near zero angular momentum) do they have any hope to escape. The few that do escape make up a tiny trickle of "Hawking radiation" that will ultimately cause the black hole to evaporate, unless it grows more rapidly due to infall of material from the external universe.

In discussing the distribution function for the hole's thermalized, rotating atmosphere, one must take account of the fact (Part VI) that the locally measured energy of a particle decreases as it climbs out of the hole's gravitational field; one does so by attributing to the particle the energy that it would ultimately have if it were to escape from the hole's gravitational grip. This is called the particle's "redshifted" energy and is denoted by $\mathcal{E}_\infty$. This $\mathcal{E}_\infty$ is conserved along the particle's world line, as is the projection $\mathbf{j}\cdot\hat{\mathbf{\Omega}}_H$ of the particle's orbital angular momentum $\mathbf{j}$ along the hole's spin axis (unit direction $\hat{\mathbf{\Omega}}_H$).

The hole's horizon behaves like the wall of a black-body cavity: Into each upgoing mode a of any and every quantum field that can exist in nature, it deposits particles that are thrmalized with (redshifted) temperature T_H, vanishing chemical potential, and angular velocity $\mathbf{\Omega}_H$. As a result, the mode's distribution function (probability of finding N_a particles in it with net redshifted energy $\mathcal{E}_{a\,\infty} = N_a \times$ (redshifted energy of one quantum in the mode) and net axial component of angular momentum $\mathbf{j}_a \cdot \hat{\mathbf{\Omega}}_H = N_a \times$ (angular momentum of one quantum in the mode) is [Eq. (4.21)]

$$\rho_a = C \exp\left[\frac{-\mathcal{E}_{a\,\infty} + \mathbf{\Omega}_H \cdot \mathbf{j}_a}{k_B T_H}\right] . \tag{4.68}$$

The distribution function for the entire thermalized atmosphere (made of all modes that emerge from the horizon) is, of course, $\rho = \prod_a \rho_a$. ("Ingoing" modes, which originate at infinity, i.e. far from the black hole, are not thermalized; they contain whatever the Universe chooses to send toward the hole.) Because $\mathcal{E}_{a\,\infty}$ is the *redshifted* energy in mode a, T_H is similarly a *redshifted temperature*: it is the temperature that the Hawking radiation exhibits when it has escaped from the hole's gravitational grip. Near the horizon the locally measured atmospheric temperature is gravitationally blue-shifted to much higher values than T_H.

The temperature T_H and angular velocity $\mathbf{\Omega}_H$, like all properties of a black hole, are determined completely by the hole's spin angular momentum $\mathbf{J}_H$ and its mass M_H; and, to

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[14] This remarkable conclusion, due to Stephen Hawking, William Unruh, and Paul Davies, is discussed pedagogically in a book by Thorne, Price and Macdonald (1986) and more rigorously in a book by Wald (1994). For detailed but fairly brief analyses along the lines of this section, see Zurek and Thorne (1986) and Frolov and Page (1994). For a review of the literature on black-hole thermodynamics and of conundrums swept under the rug in our simple-minded discussion, see, Wald (2001),

within factors of order unity, they have magnitudes

$$T_H \sim \frac{\hbar}{8\pi G M_H/c^3} \simeq \frac{6\times 10^{-8}\mathrm{K}}{M_H/M_\odot}\ , \quad \Omega_H \sim \frac{J_H}{M_H(2GM_H/c^2)^2}\ . \tag{4.69}$$

Notice how small the hole's temperature is, if its mass is greater than or of order $M_\odot$. For such holes the thermal atmosphere is of no practical interest, though it has deep implications for fundamental physics. Only for tiny black holes (that might, e.g., have been formed in the big bang) is T_H high enough to be physically interesting.

Suppose that the black hole evolves much more rapidly by accreting matter than by emitting Hawking radiation. Then the evolution of its entropy can be deduced from the first law of thermodynamics for its atmosphere. By techniques analogous to those in Sec. 4.8 [Eqs. (4.36)–(4.45)] above, one can argue that the atmosphere's equilibrium distribution (4.68) implies the following form for the first law (where we set $c=1$):

$$dM_H = T_H dS_H + \mathbf{\Omega}_H \cdot d\mathbf{J}_H\ . \tag{4.70}$$

Here dM_H is the change of the hole's mass due to the accretion (with each infalling particle contributing its E_∞ to dM_H), $d\mathbf{J}_H$ is the change of the hole's spin angular momentum due to the accretion (with each infalling particle contributing its $\mathbf{j}$), and dS_H is the increase of the black hole's entropy.

Because this first law can be deduced (as described above) via the techniques of statistical mechanics, it can be argued (e.g. Zurek and Thorne 1986) that the hole's entropy increase has the standard statistical mechanical origin and interpretation: If $N_{\rm states}$ is the total number of quantum states that the infalling material could have been in (subject only to the requirement that the total infalling mass-energy be dM_H and total infalling angular momentum be $d\mathbf{J}_H$), then $dS_H = k_B \log N_{\rm states}$ [cf. Eq. (4.31)]. In other words, the hole's entropy increases by k_B times the logarithm of the number of quantum mechanically different ways that we could have produced its changes of mass and angular momentum, dM_H and $d\mathbf{J}_H$. Correspondingly, we can regard the hole's total entropy as k_B times the logarithm of the number of ways in which it could have been made. That number of ways is enormous, and correspondingly the hole's entropy is enormous: The above analysis, when carried out in full detail, reveals that the entropy is

$$S_H = k_B \frac{A_H}{4{l_P}^2} \sim 1\times 10^{77} k_B \left(\frac{M}{M_\odot}\right)^2 \tag{4.71}$$

where $A_H \sim 4\pi(2GM_H/c^2)$ is the surface area of the hole's horizon and $l_P = \sqrt{G\hbar/c^3} = 1.616\times 10^{-33}$ cm is the Planck length — a result first speculated by Bekenstein and proved by Hawking.

What is it about a black hole that leads to this peculiar thermal behavior and enormous entropy? Why is a hole so different from a star or galaxy? The answer lies in the black-hole horizon and the fact that things which fall inward through the horizon cannot get back out. In quantum field theory it is the horizon that produces the thermal behavior. In statistical mechanics it is the horizon that produces the loss of information about how the black-hole was made and the corresponding entropy increase. In this sense, the horizon for a black hole plays a role analogous to coarse graining in conventional classical statistical mechanics.[15]

The above statistical mechanical description of a hole's atmosphere and thermal behavior is based on the laws of quantum field theory in curved spacetime—laws in which the atmosphere's fields (electromagnetic, neutrino, etc.) are quantized but the hole itself is not governed by the laws of quantum mechanics. As of 2008, a much deeper understanding is arising from string theory—the most promising approach to quantum gravity and to quantization of black holes. Indeed, the thermal properties of black holes, and most especially their entropy, is a powerful testing ground for candidate theories of quantum gravity.

4.11.3 The Universe[16]

Observations and theory agree that the universe began in a highly thermalized state, with all types of particles (except gravitons) in mutual statistical equilibrium. As the universe expanded, the energies of the particles and the equilibrium temperature all got cosmologically redshifted by the same amount, thereby maintaining the equilibrium; see Part VI. In the absence of gravity, this expanding equilibrium state would have had maximum entropy, and the second law of thermodynamics would have forbidden the development of galaxies, stars, and people.

Fortunately, gravity exists and through its long-range force it produced condensations with an attendant *increase* of entropy. The enormous power of gravity to do this is epitomized by the following:

After an early epoch of "inflation" (Part VI), the universe's expansion settled into a more leisurely *radiation-dominated* form in which, when its age was t, a region with radius $R \sim t$ was able to communicate with itself. Here and below we set $c = 1$. As we shall show in Part VI, the temperature of this region, at time t, was given by $k_B T \sim E_P \sqrt{t_P/t}$, where $E_P = \sqrt{\hbar c^5/G} \sim 10^{19}$ Gev and $t_P = \sqrt{\hbar G/c^5} \sim 10^{-43}$ s are the Planck energy and Planck time.[17] As we shall also show in Part VI, the number of particles inside the communicable region was $N \sim (t/t_P)^{3/2}$ ($\sim 10^{91}$ today). Since each particle, in order of magnitude, carried an entropy k_B (cf. Sec. 4.9), the total entropy in the communicable region at time t was $S \sim k_B (t/t_P)^{3/2}$. This actual entropy should be compared with the maximum entropy that could be produced, in the communicable region, with the aid of gravity. That maximum entropy would arise if we were to collapse the entire mass $M \sim N k_B T \sim E_P (t/t_P)$ of the communicable region into a black hole, thereby giving up all information about the content of

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[15] It is not completely clear in 2008 whether the information about what fell into the hole gets completely lost, in principle as well as in practice, or whether—as with coarse-graining—the loss of information is the physicist's fault. There is strong evidence that the information is somehow retained in the black-hole atmosphere and we have just coarse-grained it away by our faulty understanding of the relevant black-hole quantum mechanics.

[16] This subsection is based on Frautschi (1982), which contains many fascinating ideas and facts about entropy in the expanding universe.

[17] This formula predicts a temperature today for the cosmic microwave radiation $T_o \sim 100$ K that is too high by a factor ~ 30 because the details of the expansion changed, altering this formula a bit, when the universe was about a million years old and nonrelativistic matter became the dominant source of gravity rather than radiation; see Part VI.

the communicable region except its mass and (approximately vanishing) angular momentum: $S_{\rm max} \sim k_B (GM)^2/{l_P}^2 \sim k_B(t/t_P)^2$.

Notice that near the Planck time (when space and time as we know them presumably were coming into existence), the actual entropy in the communicable region and the maximum achievable entropy were of the same order, $S \sim S_{\rm max} \sim k_B$, so it was difficult to produce gravitational condensations. However, as the universe expanded, the actual entropy $S \sim k_B(t/t_P)^{3/2}$ (in the radiation-dominated era) lagged further and further behind the maximum achievable entropy $S_{\rm max} \sim k_B(t/t_P)^2$, so gravitational condensations became more and more favorable, statistically. Ultimately, those condensations did occur under the inexorable driving force of gravity, producing (with aid from the other fundamental forces) galaxies, stars and people.

4.11.4 $\boxed{\text{T2}}$ Structure Formation in the Expanding Universe: Violent Relaxation and Phase Mixing

The formation of stars and galaxies ("structure") by gravitational condensation provides a nice illustration of the phase mixing and coarse graining that underly the second law of thermodynamics (Sec. 4.7.2 above):

It is believed that a galaxy's stars formed out of the universe's almost uniform, expanding gas, when slight overdensities (presumably irregular in shape) stopped expanding and began to contract under their mutual gravitational attraction. This gas had little internal motion, so the stars were formed with very small relative velocities. Correspondingly, although the physical volume $\mathcal{V}_x$ occupied by the galaxy's N stars was initially somewhat larger than its volume today, its stars' kinetic-theory momentum-space volume $\mathcal{V}_p$ was far smaller than today. Translated into the language of an ensemble of such galaxies, the initial coordinate-space volume $\int d^{3N}x \sim {\mathcal{V}_x}^N$ occupied by the ensemble's galaxies was moderately larger than today, while its momentum-space volume $\int d^{3N}p \sim {\mathcal{V}_p}^N$ was far smaller. The phase-space volume must therefore have increased considerably during the galaxy formation—with the increase due to a big increase in the relative momenta of neighboring stars. For this to occur, it was necessary that the stars changed their relative energies during the collapse, and this required a time-dependent Hamiltonian. In other words the gravitational potential Φ felt by the stars must have varied rapidly so that the individual stellar energies would vary according to

$$\frac{dE}{dt} = \frac{\partial H}{\partial t} = m\frac{\partial \Phi}{\partial t} \; . \tag{4.72}$$

The largest changes of energy occurred when the galaxy was collapsing dynamically, so the potential changed significantly on the time it took stars to cross the galaxy, $\tau_{\rm int} \sim R/v$. Numerical simulations show that this energy transfer was highly efficient. This process is known as *violent relaxation*. Although violent relaxation could create the observed stellar distribution functions, it was not by itself a means of diluting the phase-space density, since Liouville's theorem still applied.

The mechanism that changed the phase-space density was *phase mixing* and *coarse-graining* (Sec. 4.7.2 above). During the initial collapse, when the stars were newly formed, they could be thought of as following highly perturbed radial orbits. The orbits of nearby stars were somewhat similar, though not identical. This means that small elements of phase space became highly contorted as the stars moved along their phase-space paths. Let us make a simple model of this process by assuming the individual stars initially populated a fraction $f \ll 1$ of the final occupied phase-space volume $\mathcal{V}_{\rm final}$. After one dynamical timescale $\tau_{int} \sim R/v$, this small volume $f\mathcal{V}_{\rm final}$ is (presumably) deformed into a convoluted surface that folds back upon itself once or twice, while still occupying the same volume $f\mathcal{V}_{\rm final}$. After n dynamical times, there are $\sim 2^n$ such folds (cf. Fig. 4.2 (b) above). After $n \sim -\log_2 f$ dynamical timescales the spacing between folds becomes comparable with the characteristic thickness of this convoluted surface and it is no longer practical to distinguish the original distribution function. Coarse-graining has been accomplished for all practical purposes; only a pathological physicist would resist it and insist on trying to continue keeping track of which contorted phase-space regions have the original high density and which do not. For a galaxy we might expect that $f \sim 10^{-3}$ and so this natural coarse-graining can occur in a time $\sim -\log_2 10^{-3} \sim 10\,\tau_{int} \sim 10^9$ yr, which is 10 times shorter than the present age of galaxies. It need therefore not be a surprise that the galaxy we know best, our own Milky Way, exhibits no obvious vestigial trace of its initial high-density (low phase-space-volume) distribution function.

4.12 $\boxed{\text{T2}}$ Entropy and Information

4.12.1 $\boxed{\text{T2}}$ Information Gained When Measuring the State of a System in a Microcanonical Ensemble

In Sec. 4.7 above, we said that "Entropy is a measure of our lack of information about the state of any system chosen at random from an ensemble". In this section we shall make this heuristic statement precise by introducing a precise definition of *information.*

Consider a microcanonical ensemble of identical systems. Each system can reside in any one of a finite number, $N_{\rm states}$, of quantum states, which we label by integers $n = 1, 2, 3, \ldots, N_{\rm states}$. Because the ensemble is microcanonical, all $N_{\rm states}$ states are equally probable; they have probabilities $\rho_n = 1/N_{\rm states}$. Therefore, the entropy of any system chosen at random from this ensemble is $S = -k_B \sum_n \rho_n = k_B \ln N_{\rm states}$ [Eqs. (4.30) and (4.31)].

Suppose, now, that we measure the state of our chosen system, and find it to be (for example) state number 238 out of the $N_{\rm states}$ equally probable states. How much information have we gained? For this thought experiment, and more generally (see below), *the amount of information gained, expressed in* **bits***, is defined to be the minimum number of binary digits required to distinguish the measured state from all the other* $N_{\rm states}$ *states that the system could have been in.* To evaluate this information gain, we label each state n by the number $n-1$ written in binary code (state $n = 1$ is labeled by $\{000\}$, state $n = 2$ is labeled by $\{001\}$, 3 is $\{010\}$, 4 is $\{011\}$, 5 is $\{100\}$, 6 is $\{101\}$, 7 is $\{110\}$, 8 is $\{111\}$, etc.). If $N_{\rm states} = 4$, then the number of binary digits needed is 2 (the leading 0 in the enumeration above can be dropped), so in measuring the system's state we gain 2 bits of information. If $N_{\rm states} = 8$, the number of binary digits needed is 3, so our measurement gives us 3 bits of information. In general, we need $\log_2 N_{\rm states}$ binary digits to distinguish the states from each other, so *the* *amount of information gained in measuring the system's state is the logarithm to the base 2 of the number of states the system could have been in:*

$$I = \log_2 N_{\rm states} = (1/\ln 2) \ln N_{\rm states} = 1.4427 \ln N_{\rm states} \ . \tag{4.73a}$$

Notice that this information gain is proportional to the entropy $S = -k_B \ln N_{\rm states}$ of the system before the measurement was made:

$$I = S/(k_B \ln 2) \ . \tag{4.73b}$$

The measurement reduces the system's entropy from $S = -k_B \ln N_{\rm states}$ to zero (and increases the entropy of the rest of the universe by at least this amount), and it gives us $I = S/(k_B \ln 2)$ bits of information about the system. We shall discover below that this entropy/information relationship is true of measurements made on a system drawn from *any* ensemble, not just a microcanonical ensemble. But first we must develop a more complete understanding of information.

4.12.2 $\boxed{\text{T2}}$ Information in Communication Theory

The definition of "the amount of information I gained in a measurement" was formulated by Claude Shannon (1948) in the context of his laying the foundations of *communication theory.* Communication theory deals (among other things) with the problem of how, most efficiently, to encode a message as a binary string (a string of 0's and 1's) in order to transmit it across a communication channel that transports binary signals. *Shannon defined the information in a message as the number of bits required, in the most compressed such encoding, to distinguish this message from all other messages that might be transmitted.*

Shannon focused on messages that, before encoding, consist of a sequence of *symbols.* For an English-language message, each symbol might be a single character (a letter A B,C,...Z or a space, $N = 27$ distinct symbols in all), and a specific message might be the following sequence of "length" $L = 17$ characters: "I DO NOT UNDERSTAND". Alternatively, each symbol might be an English word (approximately $N = 12,000$ words in a person's vocabulary) and a specific message might be the following sequence of length $L = 4$ words: {I}{DO}{NOT}{UNDERSTAND}.

Suppose, for simplicity, that in the possible messages, all N distinct symbols appear with equal frequency (this, of course, is not the case for English-language messages), and suppose that the length of some specific message (its number of symbols) is L. Then, the number of bits needed to encode this message and distinguish it from all other possible messages of length L is

$$I = \log_2 N^L = L \log_2 N \ . \tag{4.74a}$$

In other words, the average number of bits per symbol (the average amount of information per symbol) is

$$\bar{I} = \log_2 N \ . \tag{4.74b}$$

If there are only 2 possible symbols, we have one bit per symbol in our message. If there are 4 possible (equally likely) symbols, we have two bits per symbol, etc.

It is usually the case that not all symbols occur with the same frequency in the allowed messages. For example, in English messages the letter “A” occurs with a frequency $p_{\rm A} \simeq 0.07$, while the letter “Z” occurs with the much smaller frequency $p_{\rm Z} \simeq 0.001$. All English messages, of character length $L \gg N = 27$, constructed by a typical English speaker, will have these frequencies of occurence for “A” and “Z”. Any purported message with frequencies for “A” and “Z” differing substantially from 0.07 and 0.001will not be real English messages, and thus need not be included in the binary encoding of messages. As a result, it turns out that the most efficient binary encoding of English messages (the most *compressed* encoding) will use an average number of bits per character somewhat less than $\log_2 N = \log_2 27 = 4.755$. In other words, the average information per character in English language messages is somewhat less than $\log_2 27$.

To deduce the average information per character when the characters do not all occur with the same frequency, we shall begin with a simple example, one where the number of distinct characters to be used in the message is just $N = 2$ (the characters “B” and “E”); and their frequencies of occurence in very long allowed messages are $p_{\rm B} = 3/5$, $p_{\rm E} = 2/5$. For example, in the case of messages with length $L = 100$, the message

$$\begin{array}{r} \text{EBBEEBBBBEBBBBBBBBBEBEBBBEEEEBBBEB} \\ \text{BEEEEEBEEBEEEEEEBBEBBBBBEBBBBBEBBE} \\ \text{BBBEBBBEEBBBEBBBBBBBEBBBEBBEEBEB} \end{array} \tag{4.75a}$$

contains 63 B’s and 37 E’s, and thus (to within statistical variations) has the correct frequencies $p_B \simeq 0.6$, $p_E \simeq 0.4$ to be an allowed message. By contrast, the message

$$\begin{array}{r} \text{BBBBBBBBBBBBBBBEBBBBBBBBBBBBBBBBBB} \\ \text{BBBBBBBBBBBEBBBBBBBBBBBBBBBBBBBBBB} \\ \text{BBBBBBBBBBBBBBBEBBBBBBBBBBBBBBBB} \end{array} \tag{4.75b}$$

contains 97 B’s and 3 E’s and thus is not an allowed message. To deduce the number of allowed messages and thence the number of bits required to encode them, distinguishably, we map this problem of 60% probable B’s and 40% probable E’s onto the problem of messages with 5 equally probable symbols, as follows: Let the set of distinct symbols be the letters “a”, “b”, “c”, “y”, “z”, all occuring in allowed messages equally frequently, $p_{\rm a} = p_{\rm b} = p_{\rm c} = p_{\rm y} = p_{\rm z} = 1/5$. An example of an allowed message, then, is

$$\begin{array}{r} \text{zcczzcaabzccbabcccczaybacyzyzcbbyc} \\ \text{ayyyyyayzcyzzzzzcczacbabybbbcczabz} \\ \text{bbbybaazybccybaccabazacbzbayycyc} \end{array} \tag{4.75c}$$

We map each such message from our new message set into one from the previous message set by identifying “a”, “b”, and “c” as from the Beginning of the alphabet (and thus converting them into “B”), and identifying “y” and “z” as from the End of the alphabet (and thus converting them into “E”). Our message (4.75c) from the new message set then maps into the message (4.75a) from the old set. This mapping enables us to deduce the number of bits required to encode the old messages, with their unequal frequencies $p_{\rm E} = 3/5$ and $p_{\rm B} = 2/5$, from the number required for the new messages, with their equal frequencies $p_{\rm a} = p_{\rm b} = \ldots = p_{\rm z} = 1/5$:

The number of bits needed to encode the new messages, with length $L \gg N_{\rm new} = 5$, is $I = L \log_2 5$. Now, the characters "a", "b", and "c" from the beginning of the alphabet occur $\frac{3}{5}L$ times in each new message (in the limit that L is arbitrarily large). When converting the new message to an old one, we no longer need to distinguish between "a", "b" and "c", so we no longer need the $\frac{3}{5}L \log_2 3$ bits that were being used to make those distinctions. Similarly, the number of bits we no longer need when we drop the distinction between our two end-of-alphabet characters "y" and "z" is $\frac{2}{5}L \log_2 2$. As a result, the number of bits still needed, to distinguish between old messages (messages with "B" occurring 3/5 of the time and "E" occurring 2/5 of the time) is

$$\begin{aligned} I &= L \log_2 5 - \frac{3}{2} L \log_2 3 - \frac{2}{5} \log_2 2 = L \left[-\frac{3}{5} \log_2 \frac{3}{5} - \frac{2}{5} \log_2 \frac{2}{5} \right] \\ &= L(-p_{\rm B} \log_2 p_{\rm B} - p_{\rm E} \log_2 p_{\rm E}) \qquad (4.75\text{d}) \end{aligned}$$

A straightforward generalization of this argument (Ex. 4.15) shows that, *whenever one constructs messages with very large length $L \gg N$ from a pool of N symbols that occur with frequencies p_1, p_2, ... , p_N, the minimum number of bits required to distinguish all the allowed messages from each other (i.e., the amount of information in each message) is*

$$I = L \sum_{n=1}^{N} -p_n \log_2 p_n \; ; \qquad (4.76)$$

so *the average information per symbol in the message is*

$$\boxed{\bar{I} = \sum_{n=1}^{N} -p_n \log_2 p_n = (1/\ln 2) \sum_{n=1}^{N} -p_n \ln p_n \; .} \qquad (4.77)$$

4.12.3 $\boxed{\text{T2}}$ Examples of Information Content

Notice the similarity of the general information formula (4.76) to the general formula (4.30) for the entropy of an arbitrary ensemble. This similarity has a deep consequence:

Consider an arbitrary ensemble of systems in statistical mechanics. As usual, label the quantum states available to each system by the integer $n = 1, 2, \ldots, N_{\rm states}$, and denote by p_n the probability that any chosen system in the ensemble will turn out to be in state n. Now, select one system out of the ensemble and measure its quantum state n_1; select a second system and measure its state, n_2; and continue this process until some large number $L >> N_{\rm states}$ of systems have been measured. The sequence of measurement results $\{n_1, n_2, \ldots, n_L\}$ can be regarded as a message. The minimum number of bits needed to distinguish this message from all other possible such messages is given by the general information formula (4.76). This is the total information in the L system measurements. Correspondingly, *the amount of information we get from measuring the state of one system (the average* *information per measurement) is given by Eq. (4.77).* This acquired information is related to the entropy of the system before measurement (4.30) by the same standard formula (4.73a) as we obtained earlier for the special case of the microcanonical ensemble:

$$\boxed{\bar{I} = S/(k_B \ln 2)\ .} \tag{4.78}$$

For another example of information content, we return to English-language messages (Shannon 1948). Evaluating the information content of a long English message is a very difficult task, since it requires figuring out how to compress the message most compactly. We shall make a sequence of estimates:

A crude initial estimate of the information per character is that obtained by idealizing all the characters as occurring equally frequently: $\bar{I} = \log_2 27 \simeq 4.76$ bits per character. This is an overestimate because the 27 characters actually occur with very different frequencies. We could get a better estimate by evaluating $\bar{I} = \sum_{n=1}^{27} -p_n \log_2 p_n$ taking account of the characters' varying frequencies p_n (the result is about $\bar{I} = 4.1$); but we can do even better by converting from characters as our symbols to words. The average number of characters in an English word is about 4.5 letters plus one space, or 5.5 characters per word. We can use this number to convert from characters as our symbols to words. The number of words in a typical English speaker's vocabulary is roughly 12,000. If we idealize these 12,000 words as occuring with the same frequencies, then the information per word is $\log_2 12,000 \simeq 13.6$, so the information per character is $\bar{I} = (1/5.5)\log_2 12,000 \simeq 2.46$. This is much smaller than our initial estimate. A still better estimate is obtained by using Zipf's (1935) approximation $p_n = 0.1/n$ to the frequencies of occurrence of the words in English-language messages. [The most frequently occuring word is "THE", and its frequency is about 0.1 (one in 10 words is "THE" in a long message). The next most frequent words are "OF", "AND", and "TO"; their frequencies are about 0.1/2, 0.1/3, and 0.1/4; and so forth.] To ensure that $\sum_{n=1}^{N} p_n = 1$ for Zipf's approximation, we require that the number of words be $N = 12,367$. We then obtain, as our improved estimate of the information per word, $\sum_{n=1}^{12,367} (-0.1/n)\log_2(0.1/n) = 9.72$, corresponding to an information per character $\bar{I} \simeq 9.72/5.5 = 1.77$. This is substantially smaller than our initial, crudest estimate of 4.76 .

4.12.4 $\boxed{\text{T2}}$ Some Properties of Information

Because of the similarity of the general formulas for information and entropy (both proportional to $\sum_n -p_n \ln p_n$), information has very similar properties to entropy. In particular (Ex. 4.16):

1. Information is additive (just as entropy is additive). The information in two successive, independent messages is the sum of the information in each message.

2. If the frequencies of occurrence of the symbols in a message are $p_n = 0$ for all symbols except one, which has $p_n = 1$, then the message contains zero information. This is analogous to the vanishing entropy when all states have zero probability except for one, which has unit probability.

3. For a message L symbols long, whose symbols are drawn from a pool of N distinct symbols, the information content is maximized if the probabilities of the symbols are all equal, $p_n = 1/N$; and the maximal value of the information is $I = L \log_2 N$. This is analogous to the microcanonical ensemble having maximal entropy.

4.12.5 $\boxed{\text{T2}}$ Capacity of Communication Channels; Erasing Information from Computer Memories

A noiseless communication channel has a maximum rate (number of bits per second) at which it can transport information. This rate is called the *channel capacity* and is denoted C. When one subscribes to a cable internet connection in the United States, one typically pays a monthly fee that depends on the connection's channel capacity; for example, in Pasadena, California in autumn 2003 the fee was \$29.99 per month for a connection with capacity C = 384 kilobytes per second = 3.072 megabits per second, and \$39.99 for C = 16.384 megabits per second.

It should be obvious from the way we have defined the information I in a message, that the maximum rate at which we can transmit optimally encoded messages, each with information content I, is C/I messages per second. This is called *Shannon's theorem*.

When a communication channel is noisy (as all channels actually are), for high-confidence transmission of messages one must put some specially designed redundancy into one's encoding. With cleverness, one can thereby identify and correct errors in a received message, caused by the noise ("error-correcting code"); see, e.g., Shannon (1948), Raisbeck (1963), and Pierce (1980).[18] The redundancy needed for such error identification and correction reduces the channel's capacity. As an example, consider a *symmetric binary channel*: one that carries messages made of 0's and 1's, with equal frequency $p_0 = p_1 = 0.5$, and whose noise randomly converts a 0 into a 1 with some small error probability p_e, and randomly converts a 1 into 0 with that same probability p_e. Then one can show (e.g., Raisbeck 1963, Pierce 1980) that the channel capacity is reduced, by the need to find and correct for these errors, by a factor

$$C = C_{\rm noiseless}[1 - \bar{I}(p_e)] \; , \quad \text{where} \quad \bar{I}(p_e) = -p_e \log_2 p_e - (1-p_e)\log_2(1-p_e) \; . \tag{4.79}$$

Note that the fractional reduction of capacity is by the amount of information per symbol in messages made from symbols with frequencies equal to the probabilities p_e of making an error and $1 - p_e$ of not making an error — a remarkable and nontrivial conclusion! This is one of many important results in communication theory.

Information is also a key concept in the theory of computation. As an important example of the relationship of information to entropy, we cite Landauer's (1961, 1991) theorem: In a computer, when one erases L bits of information from memory, one necessarily increases the entropy of the memory and its environment by at least $\Delta S = L k_B \ln 2$ and correspondingly one increases the thermal energy (heat) of the memory and environment by $\Delta Q = T \Delta S = L k_B T \ln 2$ (Ex. 4.19).

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[18] A common form of error-correcting code is based on "parity checks".

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EXERCISES

Exercise 4.15 *Derivation: Information Per Symbol When Symbols Are Not Equally Probable*
Derive Eq. (4.76) for the average number of bits per symbol in a long message constructed from N distinct symbols whose frequency of occurence are p_n. [Hint: generalize the text's derivation of Eq. (4.75d).]

Exercise 4.16 *Derivation: Properties of Information*
Prove the properties of entropy enumerated in Sec. 4.12.4.

Exercise 4.17 *Problem: Information Per Symbol for Messages Built from Two Symbols*
Consider messages of length $L \gg 2$ constructed from just two symbols, $N = 2$, which occur with frequencies p and $(1 - p)$. Plot the average information per symbol $\bar{I}(p)$ in such messages, as a function of p. Explain why your plot has a maximum $\bar{I} = 1$ when $p = 1/2$, and has $\bar{I} = 0$ when $p = 0$ and when $p = 1$. (Relate these properties to the general properties of information.)

Exercise 4.18 *Problem: Information in a Sequence of Dice Throws*
Two dice are thrown randomly, and the sum of the dots showing on the upper faces is computed. This sum (an integer n in the range $2 \le n \le 12$) constitutes a symbol, and the sequence of results of $L \gg 12$ throws is a message. Show that the amount of information per symbol in this message is $\bar{I} \simeq 3.2744$.

Exercise 4.19 *Derivation: Landauer's Theorem*
Derive, or at least give a plausibility argument for, Landauer's theorem (stated at the end of Sec. 4.12.5).

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Bibliographic Note

Statistical Mechanics has inspired a variety of readable and innovative texts. The classic treatment is Tolman (1938). Among more modern approaches that deal in much greater depth with the topics covered by this chapter are Lifshitz & Pitaevski (1980), Pathria (1972), Reichl (1980), Riedi (1988) and Reif (1965). A highly individual and advanced treatment, emphasizing quantum statistical mechanics is Feynman (1972). A particularly readable account in which statistical mechanics is used heavily to describe the properties of solids, liquids and gases is Goodstein (1985). Readable, elementary introductions to information theory are Pierce (1980), and Raisbeck (1963); an advanced, recent text is McEliece (2002).

Box 4.4
Important Concepts in Chapter 3

- **Foundational Concepts**
  - A system, its phase space, its Hamiltonian and canonical transformations - Sec. 4.2.1 and Ex. 4.1.
  - Ensemble of systems, Sec. 4.2.2, its distribution function ρ or ρ_n, and ensemble averages $\langle A \rangle$, Sec. 4.2.3.
    - Concepts underlying the notation ρ_n: multiplicity $\mathcal{M}$ and number density of states in phase space $\mathcal{N}_{\rm states}$, Sec. 4.2.3.
  - Evolution of distribution functions: Liouville's theorem - Sec. 4.3.
  - Statistical Equilibrium, Sec. 4.4.
  - Ergodic Hypothesis $\bar{A} = \langle A \rangle$, Sec. 4.6.
  - Entropy, Sec. 4.7.1; its connection to information, Sec 4.12 and Eq. (4.78); entropy per particle as a useful tool, Sec. 4.9 .
  - Second law of thermodynamics: law of entropy increase, Secs. 4.7.1 and 4.7.2.
  - First law of thermodynamics, Eq. (4.44).
- **Statistical-Equilibrium Ensembles**
  - Summary table - Sec. 4.2.2 .
  - General form of distribution function, Sec. 4.4.2 and Eqs. (4.21) and (4.23).
  - Canonical, Sec. 4.4.1 and Eq. (4.19); Grand Canonical, Secs. 4.4.2 and 4.8 and Eq. (4.24c); Gibbs, Sec. 4.4.2 and Eq. (4.24b); Microcanonical, Sec. 4.5.
  - Grand potential and grand partition function, and their use to deduce thermodynamic properties of a system, Sec. 4.8 and Ex. 4.6.
  - For a single-particle quantum state (mode):
    - For fermions: Fermi-Dirac distribution, Eqs. (4.26).
    - For bosons: Bose-Einstein distribution, Eqs. (4.27) and Bose-Einstein condensate, Sec. 4.10.
    - For classical particles: Boltzmann distribution, Eq. (4.28).

Bibliography

Anderson, M.H, Ensher, J.R., Matthews, M.R., Weiman C.E. and Cornell, E.A. 1995. *Science*, **269**, 198.

Cornell, E. 1996. *J. Res. Natl. Inst. Stand. Technol.* **101**, 419.

Cohen-Tannoudji, C. , Diu, B., and Laloë, F. 1977. *Quantum Mechanics*, New York: Wiley

Dalfovo, F., Giorgini, S., Pitaevski, L.P., and Stringari, S. 1999. *Reviews of Modern Physics*, **71**, 463–512.

Einstein, A. 1925. *Sitzungsber. K. Preuss. Akad. Wiss., Phys. Math. Kl.*, **3**, 18.

Ensher, J.R., Jin, D.S., Mathews, M.R., Wieman, C.E., and Cornell, E.A. 1996. *Physical Review Letters*, **77**, 4984.

Feynman, R. P. 1972. *Statistical Mechanics*,Reading: Benjamin-Cummings

Frautschi, Steven, 1982. *Entropy in an expanding universe*, Science 217, 593–599.

V.P. Frolov and D.N. Page. 1993. *Phys. Rev. Lett.* bf 71, 2902.

Goldstein, Herbert, 1980. *Classical Mechanics. (Second Edition)*, New York: Addison Wesley

Goldstein, Herbert, Poole, Charles, and Safko, John, 2002. *Classical Mechanics. (Third Edition)*, New York: Addison Wesley

Goodstein, D. L., 1985. *States of Matter*, New York: Dover Publications

Hawking, Stephen W. 1976. *Particle creation by black holes*, Communications in Mathematical Physics, 43, 199–220.

Hawking, S. W. 1989. *Entropy decrease in contracting universe*

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

Landauer, R. 1961. “Irreversibility and Heat Generation in the Computing Process,” *IBM J. Research and Development*, **3**, 183.

Landauer, R. 1991. “Information is Physical,” *Physics Today*, May 1991, p. 23.

Lewin, L. 1981. *Polylogarithms and Associated Functions.* North Holland.

Lifshitz, E. M. & Pitaevskii, L. P. 1980. *Statistical Physics. Part 1 (Third Edition)*,Oxford: Pergamon.

Lynden-Bell, D. 1967,*Monthly Notices of the Royal Astronomical Society*, 136, 101.

Mathews, Jon & Walker, Robert L. 1964. *Mathematical Methods of Physics*, New York: Benjamin.

Ogorodnikov, K. F. 1965. *Dynamics of Stellar Systems*, Oxford: Pergamon.

Pathria, R. K. 1972. *Statistical Mechanics*, Oxford: Pergamon.

Penrose, R. 1989. *The Emperor's New Mind*, Oxford: Oxford University Press.

Reichl, L. E. 1980. *A Modern Course in Statistical Physics*, London: Arnold.

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

Riedi, P.C. 1988. *Thermal Physics*Oxford: Oxford Science Publications.

Shannon, C.E. 1948. "A mathematical theory of communication" *The Bell System Technical Journal*, **27**, 379; available at http:XXXXXX.

ter Haar, D. 1955. "Foundations of Statistical Mechanics," *Reviews of Modern Physics*, **27**, 289.

Thornton, Stephen T. and Marion, Jerry B. 2004. *Classical Dynamics of Particles and Systems*, Brooks/Cole, Belmont California.

Thorne, Kip S., Price, Richard H., & Macdonald, Douglas M., 1986. *Black Holes: The Membrane Paradigm*, New Haven: Yale University Press.

Tolman, R. C. 1938. *The Principles of Statistical Mechanics*, Oxford: Oxford University Press.

Wald, R.M. 1994. *Quantum Field Theory in Curved Spacetime and Black Hole Thermodynamics*, Chicago: University of Chicago Press.

Wald, R.M. 2001. *Living Rev. Relativity* **4**, 6. URL http://www.livingreviews.org/lrr-2001-6 .

Zipf, G. K. 1935. *Psycho-Biology of Languages*, Houghton-Mifflan.

Zurek, W. and Thorne, K.S. 1986. *Phys. Rev. Lett.* **24**, 2171.