











Systems: closed and semi-closed

Systems play the same role in statistical mechanics 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,

SEMICLOSED SYSTEMS

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, τ_{int} , are short compared with the external timescales, τ_{ext} , on which they exchange energy, entropy, particles, and so forth, 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 $\tau_{im}/\tau_{ext}\ll 1$; in this sense, it is a variant of a two-lengthscale expansion (Box 3.3).

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

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Hamiltonian dynamics for closed systems 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 (see, e.g., Marion and Thornton, 1995; Landau and Lifshitz, 1976; Goldstein, Poole, and Safko, 2002). The system's classical state is described by generalized coordinates $\mathbf{q} \equiv \{q_i\}$ and generalized momenta $\mathbf{p} \equiv \{p_i\}$, where the index j runs from 1 to W = (the system's number of degrees of freedom). The evolution of q, p is governed by Hamilton's equations dp_j dq j ðН ðН (4.1)dt ∂p_j dt ∂qj 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.

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 the same number of degrees of freedom, W; are governed by hamiltonians with the same functional forms $H(\mathbf{q}, \mathbf{p})$; and have the same volume V and total internal energy E (or \mathcal{E} , including rest masses). 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. 4.5), it then is called *microcanonical*; see Table 4.1.

	Microcanonical (const. NVE) Canonical (const. NVT) Grand Canonical (const. µVT)
TABLE 4.1: Statistical-	equilibrium ensembles used in this chapter
TABLE 4.1: Statistical- Ensemble	equilibrium ensembles used in this chapter Quantities exchanged with surroundings
TABLE 4.1: Statistical- Ensemble Microcanonical	equilibrium ensembles used in this chapter Quantities exchanged with surroundings Nothing
TABLE 4.1: Statistical- Ensemble Microcanonical Canonical	equilibrium ensembles used in this chapter Quantities exchanged with surroundings Nothing Energy E
TABLE 4.1: Statistical- Ensemble Microcanonical Canonical Gibbs	equilibrium ensembles used in this chapter Quantities exchanged with surroundings Nothing Energy E Energy E and volume V



Distribution function

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

$$\mathcal{N}_{\text{states}}(W, \mathbf{q}, \mathbf{p}) = \frac{dN_{\text{states}}}{dW_{q}dW_{p}} \equiv \frac{dN_{\text{states}}}{d\Gamma_{W}}.$$
 (4.5)

Here we have used

$$d^{W}q \equiv dq_{1}dq_{2}\cdots dq_{W}, \quad d^{W}p \equiv dp_{1}dp_{2}\cdots dp_{W}, \quad d\Gamma_{W} \equiv d^{W}q \ d^{W}p. \tag{4.6}$$

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

$$\sum_{n} \rho_{n} = \sum_{W} \int \rho \mathcal{N}_{\text{states}} d\Gamma_{W} = 1.$$
(4.7)

GEOMETRICAL VIEWPOINT

Equations (4.4)-(4.7) require some discussion. Just as the events and 4-momenta 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 $\{q, p\} \equiv$ $\{q_1, q_2, \ldots, q_W, p_1, p_2, \ldots, p_W\}$ are the coordinates of that phase-space location. When one makes a canonical transformation from one set of generalized coordinates and momenta to another (Ex. 4.1), the qs and ps change, but the geometric location in phase space does not. Moreover, just as the individual spatial and momentum volumes dV_x and dV_p occupied by a set of relativistic particles in kinetic theory are frame dependent, but their product $dV_x dV_p$ is frame-independent [cf. Eqs. (3.7a)–(3.7c)], 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 (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 $N_{\text{states}} = dN_{\text{states}}/d\Gamma_W$ and the statistical mechanical distribution function $\rho(t; W, q, p)$, like their kinetic-theory counterparts, are geometric, coordinateindependent quantities: they are unchanged by a canonical transformation. See Ex. 4.1 and references cited there.

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DENSITY OF STATES

Classical thermodynamics was one of the crowning achievements of nineteenthcentury 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. 3, was how to count the number of states available to a system. As we saw in Chap. 3, the number density of quantum mechanical states in the 6-dimensional, single-particle phase space of kinetic theory is (ignoring particle spin) $\mathcal{N}_{\text{states}} = 1/h^3$, where *h* is Planck's constant. Generalizing to the 2*W*-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.

When the laws of

quantum mechanics were developed, it became clear that all identical particles are indistinguishable, so having particle 1 at location A in phase space and an identical particle 2 at location B must be counted as the same state as particle 1 at B and particle 2 at A. Correspondingly, if we attribute half the quantum state to the classical phase-space location {1 at A, 2 at B} and the other half to {1 at B, 2 at A}, then the classical number density of states per unit volume of phase space must be reduced by a factor of 2—and more generally by some *multiplicity factor* M. In general, therefore, we can write the actual number density of states in phase space as

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

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

$$\boxed{\sum_{n} \rho_{n} \equiv \sum_{W} \int \rho \mathcal{N}_{\text{states}} d\Gamma_{W} = \sum_{W} \int \rho \frac{d\Gamma_{W}}{\mathcal{M}h^{W}} = 1.}$$
(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	
hat $\mathcal{M} = N!$. If we include the effects of quantum mechanical spin (and the spin states	
an be regarded as degenerate), then there are g_s [Eq. (3.16)] more states present in	
he phase space of each particle than we thought, so an individual state's multiplicity	
$\mathcal A$ (the number of different phase-space locations to be attributed to the state) is	
educed to	

 $\mathcal{M} = \frac{N!}{g_s^N}$ for a system of N identical particles with spin s.

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

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ENSEMBLE AVERAGE

Each system in an ensemble is endowed with a total energy that is equal to its hamiltonian, $E = H(\mathbf{q}, \mathbf{p})$ [or relativistically, $\mathcal{E} = H(\mathbf{q}, \mathbf{p})$]. 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 *E* over all systems in the ensemble:

$$\langle E \rangle = \sum_{n} \rho_{n} E_{n} = \sum_{W} \int \rho E \mathcal{N}_{states} d\Gamma_{W} = \sum_{W} \int \rho E \frac{d\Gamma_{W}}{\mathcal{M}h^{W}}.$$
 (4.10a)

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

$$\langle A \rangle = \sum_{n} \rho_n A_n. \tag{4.10b}$$

Our probabilistic distribution function $\rho_n = \rho(t; \mathbf{W}, \mathbf{q}, \mathbf{p})$ 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). 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* $\hat{\rho}$ becomes our classical probabilistic distribution function $\rho(t, W, \mathbf{q}, \mathbf{p})$; see Box 4.2 for some details.

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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. (4.15), thereby converting it into the statistical mechanical version of the Boltzmann transport equation:

$$\left(\frac{d\rho}{dt}\right)_{\substack{\text{moving with a}\\\text{fiducial system}}} = \left(\frac{d\rho}{dt}\right)_{\text{interactions}}.$$
(4.16)

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

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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:

 $\rho_{\text{canonical}} = C \exp(-\mathcal{E}/k_B T), \quad \rho_{\text{canonical}} = C' \exp(-E/k_B T) \text{ nonrelativistically.}$

Here $\mathcal{E}(\mathbf{q},\mathbf{p})$ is the energy of a system at location $\{\mathbf{q},\mathbf{p}\}$ in phase space, k_B is Boltzmann's constant, T is the temperature of the heat bath, and C is whatever normalization constant is required to guarantee that $\sum_n \rho_n = 1$. The nonrelativistic expression is obtained by removing all the particle rest masses from the total energy \mathcal{E} and then taking the low-temperature, low-thermal-velocities limit.

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(4.20)





Henceforth (except in Sec. 4.10.2, when discussing black-hole atmospheres), we restrict our baths always to be at rest in our chosen reference frame and to be nonrotating 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 **P** and angular momentum **J** (if momentum and angular momentum are not exchanged with the bath), or it can involve no explicit dependence on **P** and **J** (if momentum and angular momentum are exchanged with the bath; cf. Eq. (4.22) 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 the canonical one [Eq. (4.20)]:

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

where (obviously) the constants C and C' are related by

$$C' = C \exp\left[-\sum_{I} N_{I} m_{I} / k_{B} T\right]$$

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(4.25a)

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SINGLE-PARTICLE QUANTUM STATES (MODES)

As an important example, let each system be a single-particle quantum state of some field. These quantum states can exchange particles (quanta) with one another. 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) $\eta = 1/(e^{(\mathcal{E}-\tilde{\mu})/(k_BT)} - 1)$, which we used in our kinetic-theory studies in the last chapter [Eqs. (3.22a), (3.22b)]. Our derivation of these mean occumation numbers will

Choose one specific mode 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 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 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 for mode S are states in which S contains a finite number n of particles (quanta). Denote by \mathcal{E}_S the energy of one particle residing in mode S. Then the mode's total energy when it is in the state $|n\rangle$ (when it contains n quanta) is $\mathcal{E}_n = n\mathcal{E}_S$. [For a freely traveling, relativistic electron mode, $\mathcal{E}_S = \sqrt{m^2 + p^2}$, Eq. (1.40), where p is the mode's momentum, $p_e = jh/L$ for some integer j and similarly for p_y and p_z ; for a phonon mode with angular eigenfrequency of vibration ω , $\mathcal{E}_g = \hbar\omega$.] 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. (4.25c)]

$$\rho_n = C \exp\left(\frac{-\mathcal{E}_n + \tilde{\mu}n}{k_B T}\right) = C \exp\left(\frac{n(\tilde{\mu} - \mathcal{E}_S)}{k_B T}\right), \quad (4.26)$$

where $\tilde{\mu}$ and T are the chemical potential and temperature of the bath of other modes, with which the mode S interacts.⁸







BOSON MODES: BOSE-EINSTEIN DISTRIBUTION

Suppose that S is a boson mode (i.e., its particles have integral spin), so it can contain any nonnegative number of quanta; that is, *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 (4.26), resulting in

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

From this grand canonical distribution we can deduce the mean number of bosons in mode S:

$$\eta_{\mathcal{S}} \equiv \langle n \rangle = \sum_{n=1}^{\infty} n\rho_n = \frac{1}{\exp[(\mathcal{E}_{\mathcal{S}} - \tilde{\mu})/(k_B T)] - 1} = \frac{1}{\exp[(E_{\mathcal{S}} - \mu)/(k_B T)] - 1},$$
(4.28b)

in accord with Eq. (3.22b). As for fermions, this *Bose-Einstein mean occupation num*ber and underlying grand canonical distribution (4.28a) are valid generally, and not solely for the freely moving bosons of Chap. 3.

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

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

In Sec. 4.9 we explore an important modern application of the Bose-Einstein mean occupation number (4.28b): *Bose-Einstein condensation* of bosonic atoms in a magnetic trap.



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4.4.4 Equipartition Theorem for Quadratic, Classical Degrees of Freedom

As a second example of statistical equilibrium distribution functions, we derive the classical equipartition theorem using statistical methods.

classical equipartition theorem using statistical methods. To motivate this theorem, consider a diatomic molecule of nitrogen, N_2 . To a good approximation, its energy (its hamiltonian) can be written as

$$E = \frac{p_x^2}{2M} + \frac{p_y^2}{2M} + \frac{p_z^2}{2M} + \frac{P_\ell^2}{2M_\ell} + \frac{1}{2}M_\ell\,\omega_v^2\,\ell^2 + \frac{J_x^2}{2I} + \frac{J_y^2}{2I}.$$
 (4.3)

Here *M* is the molecule's mass; p_x , p_y , and p_z are the components of its translational momentum; and the first three terms are the molecule's kinetic energy of translation. The next two terms are the molecule's longitudinal vibration energy, with ℓ the change of the molecule's length (change of the separation of its two nuclei) from equilibrium, P_ℓ the generalized momentum conjugate to that length change, ω_v , the vibration frequency, and M_ℓ the generalized mass associated with that vibration. The last two terms are the molecule's energy of end-over-end rotation, with J_x and J_y the components of angular momentum associated with this two-dimensional rotator and I its moment of inertia.

Notice that every term in this hamiltonian is quadratic in a generalized coordinate or generalized momentum! Moreover, each of these coordinates and momenta appears only in its single quadratic term and nowhere else, and the density of states is independent of the value of that coordinate or momentum. We refer to such a coordinate or momentum as a *quadratic degree of freedom*. In some cases (e.g., the vibrations and rotations but not the translations), the en-

In some cases (e.g., the vibrations and rotations but not the translations), the energy $E_{\xi} = \alpha \xi^2$ of a quadratic degree of freedom ξ is quantized, with some energy separation e_0 between the ground state and first excited state (and with energy separations to higher states that are $\lesssim e_0$). If (and only if) the thermal energy $k_B T$ is significantly larger than e_0 , then the quadratic degree of freedom ξ will be excited far above its ground state and will behave classically. The equipartition theorem applies only at these high temperatures. For diatomic nitrogen, the rotational degrees of freedom J_x and J_y have $e_0 \sim 10^{-4}$ eV and $e_0/k_B \sim 1$ K, so temperatures big compared

to 1 K are required for J_x and J_y to behave classically. By contrast, the vibrational degrees of freedom ℓ and P_ℓ have $\varepsilon_0 \sim 0.1$ eV and $\varepsilon_0/k_B \sim 1,000$ K, so temperatures of a few thousand Kelvins are required for them to behave classically. Above $\sim 10^4$ K, the hamiltonian (4.30) fails: electrons around the nuclei are driven into excited states, and the molecule breaks apart (dissociates into two free atoms of nitrogen).

(4.28a)

(4.29)

The equipartition theorem holds for any classical, quadratic degree of freedom [i.e., at temperatures somewhat higher than $T_{o} = e_o/(k_BT)$]. We derive this theorem using the canonical distribution (4.25a). We write the molecules total energy as $E = \alpha \zeta^2 + E'$, where E' does not involve ζ . Then the mean energy associated with ζ is

$$\langle E_{\xi} \rangle = \frac{\int \alpha \xi^2 \ e^{-\beta(\alpha \xi^2 + E')} d\xi \ d(\text{other degrees of freedom})}{\int \ e^{-\beta(\alpha \xi^2 + E')} d\xi \ d(\text{other degrees of freedom})}. \tag{4.31}$$

Here the exponential is that of the canonical distribution function (4.25a), the denominator is the normalizing factor, and we have set $\beta \equiv 1/(k_BT)$. Because ξ does not appear in the portion E' of the energy, its integral separates out from the others in both numerator and denominator, and the integrals over E' in numerator and denominator cancel. Rewriting $\int \alpha \xi^2 \exp(-\beta \alpha \xi^2) d\xi$ as $-d/d\beta [\int \exp(-\beta \alpha \xi^2) d\xi]$, Eq. (4.31) becomes

$$\langle E_{\xi} \rangle = -\frac{d}{d\beta} \ln \left[\int \exp(-\beta \alpha \xi^2) d\xi \right]$$

= $-\frac{d}{d\beta} \ln \left[\frac{1}{\sqrt{\beta \alpha}} \int du e^{-u^2} du \right] = \frac{1}{2\beta} = \frac{1}{2} k_B T.$ (4.32)

Therefore, in statistical equilibrium, the mean energy associated with any classical, quadratic degree of freedom is $\frac{1}{2}k_BT$. This is the equipartition theorem. Note that the factor $\frac{1}{2}$ follows from the quadratic nature of the degrees of freedom.

For our diatomic molecule, at room temperature there are three translational and two rotational classical, quadratic degrees of freedom $(p_x, p_x, p_x), p_x, J_x, J_y)$, so the mean total energy of the molecule is $\frac{5}{2}k_BT$. At a temperature of several thousand Kelvins, the two vibrational degrees of freedom, ℓ and P_ℓ , become classical and the molecule's mean total energy is $\frac{1}{2}k_BT$. Above $\sim 10^6$ K the molecule dissociates, and its two parts (the two nitrogen atoms) have only translational quadratic degrees of freedom, so the mean energy per atom is $\frac{3}{2}k_BT$.

Translational, rotational and vibrational degrees of freedom

Motion	Structure	Degrees of freedom	Average energy
Translation	All	3	$\frac{3}{2}kT$
	Linear	2	kT
Rotation	Non-linear	3	$\frac{3}{2}kT$
Vibration	Linear	3N - (3 + 2) = 3N - 5	$2(3N-5)\frac{1}{2}kT$
	Non-linear	3N - (3 + 3) = 3N - 6	$2(3N-6)\frac{\overline{1}}{2}kT$
Total	Linear	3 <i>N</i>	$\left(3N-\frac{5}{2}\right)kT$
	Non-linear	3N	3(N-1)kT



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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 sakes, 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 $\{q, p\}$ 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 on a timescale $\tau_{\rm ext}$, then the time between snapshots should be $\Delta t \gg \tau_{\rm axt}$, and its snapshots will be canonically distributed; 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 average¹⁰ of any function of the system's location in phase space is equal to the statistical-equilibrium ensemble average:

$$\bar{A} \equiv \lim_{T \to \infty} \frac{1}{T} \int_{-T/2}^{+T/2} A(\mathbf{q}(t), \mathbf{p}(t)) = \langle A \rangle \equiv \sum_{n} A_{n} \rho_{n}.$$

(4.33)

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 .







Paradox ? 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. It still creates controversy (see, e.g., Hawking and Penrose, 2010; Penrose, 1999). 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?



As time passes each system evolves under the action of the systems' common hamiltonian. As depicted in Fig. 4.2b, this evolution distorts the occupied region of phase space; but Liouville's theorem dictates that the occupied region's volume remain unchanged and, correspondingly, that the ensemble's entropy remains unchanged.

$$S = -k_B \int (\rho \ln \rho) \mathcal{N}_{\text{states}} d\Gamma = k_B \ln(\mathcal{N}_{\text{states}} \Delta \Gamma)$$

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 —and in the process the entropy is supposed to increase.

Coarsening

Figure 4.2b,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. 4.2b), 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 (or ceases to be able to keep 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. 4.2c). More typically, the physicist will perform a coarsegrained smearing out on some given, constant scale at all times. 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 (though often a practical necessity) to perform coarse-grain averaging that causes entropy to increase and causes the ensemble to evolve into statistical equilibrium.

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Discarding correlations

When one reexamines these issues in quantum mechanical language, one discovers that the entropy increase is caused by the physicist's 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 toward 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 example, see Box 4.3 and Ex. 4.9.



4.10 Statistical Mechanics in the Presence of Gravity

Systems with significant gravity behave quite differently in terms of their statistical mechanics than do 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, resulting in 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 state some things without derivation. This is necessary in part because many of the phenomena we describe rely for their justification on general relativity (Part VII) and/or quantum field theory in curved spacetime (see, e.g., Parker and Toms, 2009).

Galaxies as closed systems of non-interacting stars



 $\tau_{\rm int} \sim 2R/v \sim 10^8$ yr.

4.10.1 Galaxies 12

A galaxy is dominated by a roughly spherical distribution of dark matter (believed to comprise elementary particles with negligible collision cross section) with radius $R_D \sim 3 \times 10^{11}$ m and mass $M_D \sim 10^{12}$ kg. The dark matter and roughly $N \sim 10^{11}$ stars, each with fiducial mass $m \sim 10^{30}$ kg, move in a common gravitational potential well. (As we discuss in Chap. 28, the ratio of regular, or baryonic, matter to dark matter is roughly 1:5 by mass.) The baryons (stars plus gas) are mostly contained within a radius $R \sim 3 \times 10^{30}$ m. The characteristic speed of the dark matter and the stars and gas is $\nu \sim (GM_D/R_D)^{1/2} \sim (GNm/R)^{1/2} \sim 200 \, {\rm km} \, {\rm s}^{-1}$. For the moment, focus on the stars, with total mass M = Nm, ignoring the dark matter and gas, whose presence does not change our conclusions.

Age of galaxy 0^{10} yr. Galaxies have distant encounters with their neighbors on timescales that can be smaller than their ages but still much longer than τ_{ini} ; in this sense, they can be thought of as semiclosed systems weakly coupled to their environments. In this subsection, we 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 parameter¹⁵ is smaller than $\sim Gm/v^2 \sim R/N$, are also negligibly rare except, sometimes, near the center of a galaxy (which we ignore until the last paragraph of this subsection). We can therefore regard each of the galaxy's stars as moving in a gravitational potential determined by the smoothed-out mass of the dark matter and all the other stars, and can use Hamiltonian dynamics to describe their motions.

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Littopy of a galaxy	
Probability density of N stars	Are galaxies at equilibrium ?
Imagine that we have an ensemble of such galaxies, all with the same number of stars <i>N</i> , the same mass <i>M</i> , and the same energy <i>E</i> (in a tiny range δE). 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 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 ~ $R^3(mv)^3$, the density of single-particle quantum states (modes) in each star's phase space is $1/h^3$, the number of available modes is the product of these, ~ $(Rmv/h)^3$, and the probability of the star occupying the chosen mode, or any other mode, is the reciprocal of this product, ~ $(h/(Rmv))^3$. The probability of the galaxy occupying a state in its phase space is the produbilities for each of its <i>N</i> stars [Eq. (4.18c)]:	Are real galaxies in statistical equilibrium? To gain insight into this question, we estimate the entropy of a galaxy in our ensemble and 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 intropy. Ignoring the (negligible) correlations among stars, the entropy computed by integating $p \mid n \rho$ over the galaxy's full $6N$ -dimensional phase space is just N times the entropy associated with a single star, which is $S \sim Nk_B \ln(\Delta \Gamma/h^3)$ [Eqs. (4.37) and (4.8a)], where $\Delta \Gamma$ is the phase-space volume over which the star wanders in its regoldc, hamiltonian-induced motion (i.e., the phase space volume available to the star). We express this entropy in terms of the galaxy's total mass M and its total nonrelativistic energy $E \sim -GM^2/(2R)$ as follows. Since the characteristic stellar speed is $v \sim (GM/R)^{1/2}$, the volume of phase space over which the star wanders is $\Delta \Gamma \sim (mv)^3 R^3 \sim (GMm^2 R)^{3/2} \sim (-G^2 M^3 m^2/(2E))^{3/2}$, and the entropy is therefore $S_{\text{Galaxy}} \sim (M/n)k_B \ln(\Delta \Gamma/h^3) \sim (3M/(2m))k_B \ln(-G^2 M^3 m^2/(2Eh^2))$. (4.58)

The galaxy entropy increases

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 orbital radius r arbitrarily large. By this thought experiment, we discover that galaxies cannot be in a state of maximum entropy at fixed E and M; they therefore cannot be in a true state of statistical equilibrium.¹⁶ (One might wonder whether there is entropy associated with the galaxy's gravitational field, some of which is due to the stars, 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 gravitational field equation, by the stars' spatial distribution.)



4.10.2 Black Holes 12

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 Ω_H as the hole's horizon. This remarkable conclusion, due to Stephen Hawking (1976), William Unruh (1976), and Paul Davies (1977), is discussed pedagogically in books by Thorne, Price, and MacDonald (1986) and Frolov and Zelnikov (2011), and more rigorously in a book by Wald (1994). 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 nearly zero angular momentum) do they have any hope of escaping. The few that do escape make up a tiny trickle of Hawking radiation (Hawking, 1975) that will ultimately cause the black hole to evaporate, unless it grows more rapidly due to infall of material from the external universe (which it will unless the black hole is far less massive than the Sun).

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In discussing the distribution function for the hole's thermalized, rotating atmosphere, one must take account of the fact that the locally measured energy of a particle decreases as it climbs out of the hole's gravitational field (Ex. 26.4). 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}_{∞} . This \mathcal{E}_{∞} 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 blackbody cavity. Into each upgoing mode (single-particle quantum state) *a* of any and every quantum field that can exist in Nature, it deposits particles that are thermalized with (redshifted) temperature T_H , vanishing chemical potential, and angular velocity Ω_H . As a result, the mode's distribution function—which is the 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 with 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

$$\rho_a = C \, \exp\left[\frac{-\mathcal{E}_{a\,\infty} + \mathbf{\Omega}_H \cdot \mathbf{j}_a}{k_B T_H}\right] \tag{4.59}$$

The temperature T_H and angular velocity Ω_H , like all properties of a black hole, are determined completely by the hole's spin angular momentum J_H and its mass M_H . To within factors of order unity, they have magnitudes [Ex. 26.16 and Eq. (26.77)]

$$T_{H} \sim \frac{\hbar}{8\pi k_{B} G M_{H}/c^{3}} \sim \frac{6 \times 10^{-8} \,\mathrm{K}}{M_{H}/M_{\odot}}, \quad \Omega_{H} \sim \frac{J_{H}}{M_{H} (2 G M_{H}/c^{2})^{2}}. \tag{4.60}$$

For a very slowly rotating hole the "~" becomes an "=" in both equations. 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 conceivably have been formed in the big bang) is T_H high enough to be physically interesting.

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First law of thermodynamics & BH Entropy

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 some developed in the next chapter, one can argue that the atmosphere's equilibrium distribution (4.59) implies the following form for the first law (where we set c = 1):

 $dM_{H} = T_{H}dS_{H} + \Omega_{H} \cdot d\mathbf{J}_{H}$ (4.61)

[cf. Eq. (26.92)]. Here dM_H is the change of the hole's mass due to the accretion (with each infalling particle contributing its \mathcal{E}_{∞} to dM_H), dJ_H is the change of the hole's spin angular momentum due to the accretion (with each infalling particle contributing its j), and dS_H is the increase of the black hole's entropy. Because this first law can be deduced using the techniques of statistical mechanics

Increases this first have can be deduced using the textinglate of statistical interimitation of the sentropy increases has the standard statistical mechanical origin and interpretation: if N_{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 dJ_H), then $dS_H = k_B \log N_{states}$ [cf. Eq. (4.35)]. 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 dJ_H . Correspondingly, we can regard the hole's total entropy as k_B times the logarithm of the number of ways is not that. That number of ways is normous, and correspondingly, the hole's

entropy is enormous. This analysis, when carried out in full detail (Zurek and Thorne, 1985), reveals that the entropy is [Eq. (26.93)]

$$S_H = k_B \frac{A_H}{4L_P^2} \sim 1 \times 10^{77} k_B \left(\frac{M_H}{M_\odot}\right)^2,$$
 (4.62)

where $A_H\sim 4\pi (2GM_H/c^2)$ is the surface area of the hole's horizon, and $L_P=\sqrt{G\hbar/c^3}=1.616\times 10^{-33}\,{\rm cm}$ is the Planck length—a result first proposed by Bekenstein (1972) and first proved by Hawking (1975).

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 that fall inward through the horizon cannot get back out. From the perspective of quantum field theory, the horizon produces the thermal behavior. From that of statistical mechanics, the horizon 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.¹⁷









More on Black Hole Thermodynamics & SM (D. Wallace)

In this article, and its sequel, I want to lay out as carefully and thoroughly as I can the theoretical evidence for BHT. It is written with the zeal of the convert: I began this project sharing at least some of the outsiders' scepticism, and became persuaded that the evidence is enormously strong both that black holes are thermodynamical systems in the fullest sense of the word, and that their thermodynamic behaviour has a statistical-mechanical underpinning in quantum gravity (and, as a consequence, that black hole evaporation is a unitary process not different in kind from the cooling of other hot systems, and that it involves no fundamental loss of information).

Black hole thermodynamics (BHT) is perhaps the most striking and unexpected development in the theoretical physics of the last forty years. It combines the three main areas of 'fundamental' theoretical physics — quantum theory, general relativity, and thermal physics — and it offers a conceptual testing ground for quantum gravity that might be the nearest that field has to experimental evidence. Yet BHT itself relies almost entirely on theoretical arguments, and its most celebrated result — Hawking's argument that black holes emit radiation — has no direct empirical support and little prospect of getting any. So to outsiders — to physicists in other disciplines, or to philosophers of science — the community's confidence in BHT can seem surprising, or even suspicious. Can

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4.10.3 The Universe 12

Observations and theory agree that the universe, when far younger than 1 s old, settled into a very hot, highly thermalized state. All particles except gravitons were in statistical equilibrium at a common, declining temperature, until the dark matter and the neutrinos dropped out of equilibrium and (like the gravitons) became thermodynamically isolated.

During this early relativistic era, the equations of relativistic cosmology imply (as discussed in Sec. 28.4.1) that the temperature *T* of the universe at age *t* satisfied $T/T_P \sim (t/t_P)^{-1/2}$. Here $T_P \equiv [\hbar c^5/(Gk_B^2)]^{1/2} \sim 10^{32}$ K is the Planck temperature, and $t_P = (\hbar G/c^5)^{1/2} \sim 10^{-43}$ s is the Planck time. (This approximate T/T_P relationship can be justified on dimensional grounds.) Now the region that was in causal contact at time *t* (i.e., that was contained within a mutual cosmological horizon) had a volume $\sim (ct)^3$, and thermodynamic considerations imply that the number of relativistic particles that were in causal contact at time *t* was $N \sim (k_B T t/\hbar)^3 \sim (t/t_P)^{3/2}$. (This remains roughly true today when *N* has grown to $\sim 10^{91}$, essentially all in microwave background photons.) The associated entropy was then $S \sim Nk_B$ (cf. Sec. 4.8).

Although this seems like an enormous entropy, gravity can do even better. The most efficient way to create entropy, as described in Sec. 4.10.2, is to form massive black holes. Suppose that out of all the relativistic particle mass within the horizon, $M \sim Nk_BT/c^2$, a fraction f has collapsed into black holes of mass M_H . Then, with the aid of Sec. 4.10.2, we estimate that the associated entropy is $S_H \sim f(M_H/M)(t/t_P)^{1/2}S$. If we use the observation that every galaxy has a central black hole with mass in the $\sim 10^6$ – 10^9 solar mass range, we find that $f \sim 10^{-4}$ and $S_H \sim 10^{11}S$ today!

Now it might be claimed that massive black holes are thermodynamically isolated from the rest of the universe because they will take so long to evaporate. That may be so as a practical matter, but more modest gravitational condensations that create stars and starlight can produce large local departures from thermodynamic equilibrium, accompanied by (indeed, driven by) a net increase of entropy and can produce the conditions necessary for life to develop.



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

It is believed that galaxies formed when slight overdensities in the dark matter and gas (presumably irregular in shape) stopped expanding and began to contract under their mutual gravitational attraction. Much of the gas was quickly converted into stars. The dark-matter particles and the stars had very little random motion at this stage relative to their random motions today, $v \sim 200 \text{ km s}^{-1}$. Correspondingly, although their physical volume \mathcal{V}_x was initially only moderately larger than today, their momentum-space volume \mathcal{V}_p was far smaller than it is today. Translated into the language of an ensemble of N such galaxies, the initial coordinate-space volume $\int d^{3N}x \sim \mathcal{V}_x^N$ occupied by each of the ensemble's galaxies was moderately larger than it is today, while its momentum-space volume $\int d^{3N}p \sim \mathcal{V}_p{}^N$ was far smaller. The phase-space volume $\mathcal{V}_x^N \mathcal{V}_p^N$ 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 contraction, which requires 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

$$\frac{dE}{dt} = \frac{\partial H}{\partial t} = m \frac{\partial \Phi}{\partial t}.$$
(4.66)

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The largest changes of energy occurred when the galaxy was contracting dynamically (collapsing), so the potential changed significantly on the timescale it took stars to cross the galaxy, $\tau_{int} \sim 2R/v$. 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, the particles and newly formed stars could be thought of as following highly perturbed radial orbits. The orbits of nearby stars were somewhat similar, though not identical. Therefore small elements of occupied phase space became highly contorted as the particles and stars moved along their phase-space paths.

Let us make a simple model of this process by assuming the individual particles and stars initially populate a fraction $f \ll 1$ of the final occupied phase-space volume V_{final} . After one dynamical timescale $\tau_{int} \sim R/v$, this small volume $f V_{\text{final}}$ is (presumably) deformed into a convoluted surface that folds back on itself once or twice like dough being kneaded by a baker, while still occupying the same volume $f V_{\text{final}}$. After *n* dynamical timescales, there are $\sim 2^n$ such folds (cf. Fig. 4.2b 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. We expect that 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 approximately equal to $-\log_2 10^{-3} \tau_{int} \sim 10 \tau_{int} \sim 10^9$ yr, which is 10 times shorter than the present age of galaxies. Therefore it need not be a surprise that the galaxy we know best, our own Milky Way, exhibits little obvious vestigial trace of its initial high-density (low phase-space-volume) distribution function.20

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6 is {101}, 7 is {110}, 8 is {111}, etc.). If $N_{\text{states}} = 4$, 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 $N_{\text{states}} = 8$, the number of binary digits needed is 3, so our measurement gives us 3 bits of information. In general, we need $\log_2 N_{\text{states}}$ binary digits to distinguish the states from one another, so the amount of information gained in measuring the system's state is the base-2 logarithm of the number of states the system could have been in:

$$I = \log_2 N_{\text{states}} = (1/\ln 2) \ln N_{\text{states}} = 1.4427 \ln N_{\text{states}}.$$
 (4.67a)

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

$$I = S/(k_B \ln 2).$$
 (4.67b)

The measurement reduces the system's entropy from $S = k_B \ln N_{\text{states}}$ 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.





If there are only two possible symbols, we have one bit per symbol in our message. If there are four possible (equally likely) symbols, we have two bits per symbol, and so forth.

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 $p_A \simeq 0.07$, while the letter "Z" occurs with the much smaller frequency $p_Z \simeq 0.001$. All English messages, of character length $L \gg N = 27$, constructed by a typical English speaker, will have these frequencies of occurrence for "A" and "Z". Any purported message with frequencies for "A" and "Z" differing substantially from 0.07 and 0.001 will 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 $\log_2 27$.

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A straightforward generalization of this argument (Ex. 4.17) shows that, when one constructs messages with very large length $L \gg N$ from a pool of N symbols that occur with frequencies p_1, p_2, \ldots, p_N , the minimum number of bits required to distinguish all the allowed messages from one another (i.e., the amount of information in each message) is

$$I = L \sum_{n=1}^{N} -p_n \log_2 p_n;$$
(4.70)

so the average information per symbol in the message is

$$\bar{I} = \sum_{n=1}^{N} -p_n \log_2 p_n = (1/\ln 2) \sum_{n=1}^{N} -p_n \ln p_n.$$
(4.71)

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MEMORY AND ENTROPY

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 $\Delta S = Lk_B \ln 2$ and correspondingly, one increases the thermal energy (heat) of the memory and environment by at least $\Delta Q = T \Delta S = Lk_B T \ln 2$ (Ex. 4.21).

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Bibliographic Note

Statistical mechanics has inspired a variety of readable and innovative texts. The classic treatment is Tolman (1938). Classic elementary texts are Kittel (2004) and Kittel and Kroemer (1980). Among more modern approaches that deal in much greater depth with the topics covered in this chapter are Lifshitz and Pitaevskii (1980), Chandler (1987), Sethna (2006), Kardar (2007), Reif (2008), Reichl (2009), and Pathria and Beale (2011). The Landau-Lifshitz textbooks (including Lifshitz and Pitaevskii, 1980) are generally excellent after one has already learned the subject at a more elementary level. 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 (2002). Readable, elementary introductions to information theory are Raisbeck (1963) and Pierce (2012); an advanced text is McEliece (2002).

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