Quantum statistical mechanics

Quantum statistical mechanics governs most of solid-state physics (metals, semiconductors, and glasses) and parts of molecular physics and astrophysics (white dwarfs, neutron stars). It spawned the origin of quantum mechanics (Planck's theory of the black-body spectrum) and provides the framework for our understanding of other exotic quantum phenomena (Bose condensation, superfluids, and superconductors). Applications of quantum statistical mechanics are significant components of courses in these various subjects. We condense our treatment of this important subject into this one chapter in order to avoid overlap with other physics and chemistry courses, and also in order to keep our treatment otherwise accessible to those uninitiated into the quantum mysteries.

In this chapter, we assume the reader has some background in quantum mechanics. We will proceed from the abstract to the concrete, through a series of simplifications. We begin (Section 7.1) by introducing *mixed states* for quantum ensembles, and the advanced topic of *density matrices* (for non-equilibrium quantum systems which are not mixtures of energy eigenstates). We illustrate mixed states in Section 7.2 by solving the finite-temperature quantum harmonic oscillator. We discuss the statistical mechanics of identical particles (Section 7.3). We then make the vast simplification of presuming that the particles are non-interacting (Section 7.4), which leads us to the Bose–Einstein and Fermi distributions for the filling of single-particle eigenstates. We contrast Bose, Fermi, and Maxwell–Boltzmann statistics in Section 7.5. We illustrate how amazingly useful the non-interacting particle picture is for quantum systems by solving the classic problems of black-body radiation and Bose condensation (Section 7.6), and for the behavior of metals (Section 7.7).

7.1 Mixed states and density matrices

Classical statistical ensembles are probability distributions $\rho(\mathbb{P}, \mathbb{Q})$ in phase space. How do we generalize them to quantum mechanics? Two problems immediately arise. First, the Heisenberg uncertainty principle tells us that one cannot specify both position and momentum for a quantum system at the same time. The states of our quantum system will not be points in phase space. Second, quantum mechanics

already has probability densities; even for systems in a definite state[1] $\Psi(\mathbb{Q})$ the probability is spread among different configurations $|\Psi(\mathbb{Q})|^2$ (or momenta $|\widetilde{\Psi}(\mathbb{P})|^2$). In statistical mechanics, we need to introduce a second level of probability, to discuss an ensemble that has probabilities p_n of being in a variety of quantum states $\Psi_n(\mathbb{Q})$. Ensembles in quantum mechanics are called *mixed states*; they are not superpositions of different wavefunctions, but incoherent mixtures.[2]

Suppose we want to compute the ensemble expectation of an operator $\mathbf{A}$. In a particular state Ψ_n, the quantum expectation is

$$\langle \mathbf{A} \rangle_{\text{pure}} = \int \Psi_n^*(\mathbb{Q}) \mathbf{A} \Psi_n(\mathbb{Q}) \, \mathrm{d}^{3N}\mathbb{Q}. \tag{7.1}$$

So, in the ensemble the expectation is

$$\langle \mathbf{A} \rangle = \sum_n p_n \int \Psi_n^*(\mathbb{Q}) \mathbf{A} \Psi_n(\mathbb{Q}) \, \mathrm{d}^{3N}\mathbb{Q}. \tag{7.2}$$

Except for selected exercises, for the rest of the book we will use mixtures of states (eqn 7.2). Indeed, for all of the equilibrium ensembles, the Ψ_n may be taken to be the energy eigenstates, and the p_n either a constant in a small energy range (for the microcanonical ensemble), or $\exp(-\beta E_n)/Z$ (for the canonical ensemble), or $\exp\left(-\beta(E_n - N_n\mu)\right)/\Xi$ (for the grand canonical ensemble). For most practical purposes you may stop reading this section here, and proceed to the quantum harmonic oscillator.

7.1.1 Advanced topic: density matrices.

What do we gain from going beyond mixed states? First, there are lots of systems that cannot be described as mixtures of energy eigenstates. (For example, any such mixed state will have time independent properties.) Second, although one can define a general, time-dependent ensemble in terms of more general bases Ψ_n, it is useful to be able to transform between a variety of bases. Indeed, superfluids and superconductors show an exotic *off-diagonal long-range order* when looked at in position space (Exercise 9.8). Third, we will see that the proper generalization of Liouville's theorem demands the more elegant, operator-based approach.

Our goal is to avoid carrying around the particular states Ψ_n. Instead, we will write the ensemble average (eqn 7.2) in terms of $\mathbf{A}$ and an operator $\boldsymbol{\rho}$, the *density matrix*. For this section, it is convenient to use Dirac's bra-ket notation, in which the mixed-state ensemble average can be written[3]

$$\langle \mathbf{A} \rangle = \sum_n p_n \langle \Psi_n | \mathbf{A} | \Psi_n \rangle. \tag{7.3}$$

Pick any complete orthonormal basis Φ_α. Then the identity operator is

$$\mathbf{1} = \sum_\alpha |\Phi_\alpha\rangle\langle\Phi_\alpha| \tag{7.4}$$

and, substituting the identity (eqn 7.4) into eqn 7.3 we find

$$
\begin{aligned}
\langle \mathbf{A} \rangle &= \sum_n p_n \langle \Psi_n | \left(\sum_\alpha |\Phi_\alpha\rangle\langle\Phi_\alpha| \right) \mathbf{A} |\Psi_n\rangle \\
&= \sum_n p_n \sum_\alpha \langle \Phi_\alpha | \mathbf{A}\Psi_n \rangle \langle \Psi_n | \Phi_\alpha \rangle \\
&= \sum_\alpha \langle \Phi_\alpha \mathbf{A} | \left(\sum_n p_n |\Psi_n\rangle\langle\Psi_n| \right) |\Phi_\alpha\rangle \\
&= \text{Tr}(\mathbf{A}\boldsymbol{\rho}),
\end{aligned}
\tag{7.5}
$$

where[4]

$$
\boldsymbol{\rho} = \left(\sum_n p_n |\Psi_n\rangle\langle\Psi_n| \right)
\tag{7.6}
$$

is the *density matrix*.

[4]The trace of a matrix is the sum of its diagonal elements, and is independent of what basis you write it in. The same is true of operators; we are summing the diagonal elements $\text{Tr}(M) = \sum_\alpha \langle \Phi_\alpha | M | \Phi_\alpha \rangle$.

There are several properties we can now deduce about the density matrix.

Sufficiency. In quantum mechanics, all measurement processes involve expectation values of operators. Our density matrix therefore suffices to embody everything we need to know about our quantum system.

Pure states. A pure state, with a definite wavefunction Φ, has $\boldsymbol{\rho}_{\text{pure}} = |\Phi\rangle\langle\Phi|$. In the position basis $|\mathbb{Q}\rangle$, this pure-state density matrix has matrix elements $\boldsymbol{\rho}_{\text{pure}}(\mathbb{Q}, \mathbb{Q}') = \langle\mathbb{Q}|\boldsymbol{\rho}_{\text{pure}}|\mathbb{Q}'\rangle = \Phi^*(\mathbb{Q}')\Phi(\mathbb{Q})$. Thus in particular we can reconstruct[5] the wavefunction from a pure-state density matrix, up to an overall physically unmeasurable phase. Since our wavefunction is normalized $\langle\Phi|\Phi\rangle = 1$, we note also that the square of the density matrix for a pure state equals itself: $\boldsymbol{\rho}_{\text{pure}}^2 = |\Phi\rangle\langle\Phi||\Phi\rangle\langle\Phi| = |\Phi\rangle\langle\Phi| = \boldsymbol{\rho}_{\text{pure}}$.

[5]In particular, since Φ is normalized $|\Phi^*(\mathbb{Q}')|^2 = \int d\mathbb{Q} \, |\rho(\mathbb{Q}, \mathbb{Q}')|^2$ and thus

$$
\Phi(\mathbb{Q}) = \frac{\rho(\mathbb{Q}, \mathbb{Q}')}{\sqrt{\int d\widetilde{\mathbb{Q}} \, |\rho(\widetilde{\mathbb{Q}}, \mathbb{Q}')|^2}}
\tag{7.7}
$$

up to the single phase $\phi^*(\mathbb{Q}')$ for any point $\mathbb{Q}'$.

Normalization. The trace of a pure-state density matrix $\text{Tr}\boldsymbol{\rho}_{\text{pure}} = 1$, since we can pick an orthonormal basis with our wavefunction Φ as the first basis element, making the first term in the trace sum one and the others zero. The trace of a general density matrix is hence also one, since it is a probability distribution of pure-state density matrices:

$$
\text{Tr}\boldsymbol{\rho} = \text{Tr}\left(\sum_n p_n |\Psi_n\rangle\langle\Psi_n| \right) = \sum_n p_n \text{Tr}\left(|\Psi_n\rangle\langle\Psi_n|\right) = \sum_n p_n = 1.
\tag{7.8}
$$

[6]Notice that the states Ψ_n in a general mixture need not be eigenstates or even orthogonal.

Canonical distribution. The canonical distribution is a mixture of the energy eigenstates $|E_n\rangle$ with Boltzmann weights $\exp(-\beta E_n)$. Hence the density matrix $\boldsymbol{\rho}_{\text{canon}}$ is diagonal in the energy basis:[6]

$$
\boldsymbol{\rho}_{\text{canon}} = \sum_n \frac{\exp(-\beta E_n)}{Z} |E_n\rangle\langle E_n|.
\tag{7.9}
$$

[7]What is the exponential of a matrix M? We can define it in terms of a power series, $\exp(M) = \mathbf{1} + M + M^2/2! + M^3/3! + \ldots$, but it is usually easier to change basis to diagonalize M. In that basis, any function $f(M)$ is given by

$$
f(\boldsymbol{\rho}) = \begin{pmatrix} f(\boldsymbol{\rho}_{11}) & 0 & 0 & \ldots \\ 0 & f(\boldsymbol{\rho}_{22}) & 0 & \ldots \\ \ldots & & & \end{pmatrix}.
\tag{7.10}
$$

At the end, change back to the original basis. This procedure also defines $\log M$ (eqn 7.14).

We can write the canonical density matrix in a basis-independent form using the Hamiltonian operator $\mathcal{H}$. First, the partition function is given[7]

by the trace

$$Z = \sum_n \exp(-\beta E_n) = \sum_n \langle E_n | \exp(-\beta \mathcal{H}) | E_n \rangle = \text{Tr}\left(\exp(-\beta \mathcal{H})\right).$$
(7.11)

Second, the numerator

$$\sum_n |E_n\rangle \exp(-\beta E_n)\langle E_n| = \sum_n |E_n\rangle \exp(-\beta \mathcal{H})\langle E_n| = \exp(-\beta \mathcal{H}),$$
(7.12)

since $\mathcal{H}$ (and thus $\exp(-\beta \mathcal{H})$) is diagonal in the energy basis. Hence

$$\boldsymbol{\rho}_{\text{canon}} = \frac{\exp(-\beta \mathcal{H})}{\text{Tr}\left(\exp(-\beta \mathcal{H})\right)}.$$
(7.13)

Entropy. The entropy for a general density matrix will be

$$S = -k_B \text{Tr}\left(\boldsymbol{\rho} \log \boldsymbol{\rho}\right).$$
(7.14)

Time evolution for the density matrix. The time evolution for the density matrix is determined by the time evolution of the pure states composing it:[8]

[8]The p_n are the probability that one *started* in the state Ψ_n, and thus manifestly do not change with time.

$$\frac{\partial \boldsymbol{\rho}}{\partial t} = \sum_n p_n \left(\frac{\partial |\Psi_n\rangle}{\partial t}\langle \Psi_n| + |\Psi_n\rangle\frac{\partial \langle \Psi_n|}{\partial t} \right).$$
(7.15)

Now, the time evolution of the 'ket' wavefunction $|\Psi_n\rangle$ is given by operating on it with the Hamiltonian:

$$\frac{\partial |\Psi_n\rangle}{\partial t} = \frac{1}{i\hbar}\mathcal{H}|\Psi_n\rangle,$$
(7.16)

and the time evolution of the 'bra' wavefunction $\langle \Psi_n|$ is given by the time evolution of $\Psi_n^*(\mathbb{Q})$:

$$\frac{\partial \Psi_n^*}{\partial t} = \left(\frac{\partial \Psi_n}{\partial t} \right)^* = \left(\frac{1}{i\hbar}\mathcal{H}\Psi_n \right)^* = -\frac{1}{i\hbar}\mathcal{H}\Psi_n^*,$$
(7.17)

so since $\mathcal{H}$ is Hermitian, we have

$$\frac{\partial \langle \Psi_n|}{\partial t} = -\frac{1}{i\hbar}\langle \Psi_n|\mathcal{H}.$$
(7.18)

[9]The *commutator* of two matrices $[A, B] = AB - BA$. Notice that eqn 7.19 is *minus* the formula one uses for the time evolution of operators in the Heisenberg representation.

Hence[9]

$$\frac{\partial \boldsymbol{\rho}}{\partial t} = \sum_n p_n \frac{1}{i\hbar}\Big(\mathcal{H}|\Psi_n\rangle\langle \Psi_n| - |\Psi_n\rangle\langle \Psi_n|\mathcal{H}\Big) = \frac{1}{i\hbar}\left(\mathcal{H}\boldsymbol{\rho} - \boldsymbol{\rho}\mathcal{H}\right)$$

$$= \frac{1}{i\hbar}[\mathcal{H}, \boldsymbol{\rho}].$$
(7.19)

Quantum Liouville theorem. This time evolution law 7.19 is the quantum version of Liouville's theorem. We can see this by using the

equations of motion 4.1, $\dot{q}_\alpha = \partial\mathcal{H}/\partial p_\alpha$, and $\dot{p}_\alpha = -\partial\mathcal{H}/\partial q_\alpha$ and the definition of Poisson brackets

$$\{A, B\}_P = \sum_\alpha \frac{\partial A}{\partial q_\alpha}\frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha}\frac{\partial B}{\partial q_\alpha} \tag{7.20}$$

to rewrite Liouville's theorem that the total time derivative is zero (eqn 4.7) into a statement about the partial time derivative:

$$\begin{aligned}
0 = \frac{\mathrm{d}\rho}{\mathrm{d}t} &= \frac{\partial\rho}{\partial t} + \sum_\alpha \frac{\partial\rho}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial\rho}{\partial p_\alpha}\dot{p}_\alpha \\
&= \frac{\partial\rho}{\partial t} + \sum_\alpha \left(\frac{\partial\rho}{\partial q_\alpha}\frac{\partial\mathcal{H}}{\partial p_\alpha} - \frac{\partial\rho}{\partial p_\alpha}\frac{\partial\mathcal{H}}{\partial q_\alpha}\right),
\end{aligned} \tag{7.21}$$

so

$$\frac{\partial\rho}{\partial t} = \{\mathcal{H}, \boldsymbol{\rho}\}_P. \tag{7.22}$$

Using the classical↔quantum correspondence between the Poisson brackets and the commutator $\{\ \}_P \leftrightarrow (1/i\hbar)[\ ]$ the time evolution law 7.19 is precisely the analogue of Liouville's theorem 7.22.

Quantum Liouville and statistical mechanics. The classical version of Liouville's equation is far more compelling an argument for statistical mechanics than is the quantum version. The classical theorem, you remember, states that $\mathrm{d}\rho/\mathrm{d}t = 0$; the density following a point on the trajectory is constant, hence any time-independent density must have ρ constant along the trajectories. If the trajectory covers the energy surface (ergodicity), then the probability density has to be constant on the energy surface, justifying the microcanonical ensemble.

For an isolated quantum system, this argument breaks down. The condition that an equilibrium state must be time independent is not very stringent. Indeed, $\partial\boldsymbol{\rho}/\partial t = [\mathcal{H}, \boldsymbol{\rho}] = 0$ for any mixture of many-body energy eigenstates. In principle, isolated quantum systems are very non-ergodic, and one must couple them to the outside world to induce transitions between the many-body eigenstates needed for equilibration.[10]

[10]This may seem less of a concern when one realizes just how peculiar a many-body eigenstate of a large system really is. Consider an atom in an excited state contained in a large box. We normally think of the atom as being in an energy eigenstate, which decays after some time into a ground state atom plus some photons. Clearly, the atom was only in an approximate eigenstate (or it would not decay); it is in a *resonance* that is an eigenstate if we ignore the coupling to the electromagnetic field. The true many-body eigenstates of the system are weird delicate superpositions of states with photons being absorbed by the atom and the atom emitting photons, carefully crafted to produce a stationary state. When one starts including more atoms and other interactions, the true many-body eigenstates are usually pretty useless (apart from the ground state and the lowest excitations). Tiny interactions with the outside world disrupt these many-body eigenstates, and usually lead efficiently to equilibrium.
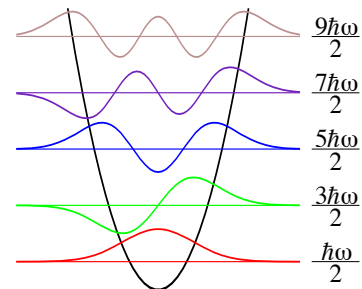
7.2 Quantum harmonic oscillator

The harmonic oscillator is a great example of how statistical mechanics works in quantum systems. Consider an oscillator of frequency ω. The energy eigenvalues are $E_n = (n + \frac{1}{2})\hbar\omega$ (Fig. 7.1). Hence its partition function is a geometric series $\sum x^n$, which we can sum to $1/(1-x)$:

$$\begin{aligned}
Z_{\mathrm{qho}} &= \sum_{n=0}^{\infty} \mathrm{e}^{-\beta E_n} = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega(n+1/2)} \\
&= \mathrm{e}^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty}\left(\mathrm{e}^{-\beta\hbar\omega}\right)^n = \mathrm{e}^{-\beta\hbar\omega/2}\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega}} \\
&= \frac{1}{\mathrm{e}^{\beta\hbar\omega/2} - \mathrm{e}^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}.
\end{aligned} \tag{7.23}$$

Fig. 7.1 The quantum states of the harmonic oscillator are at equally-spaced energies.
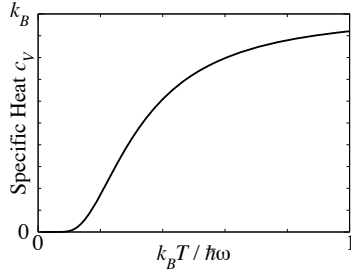
Fig. 7.2 The specific heat for the quantum harmonic oscillator.

The average energy is

$$\langle E \rangle_{\text{qho}} = -\frac{\partial \log Z_{\text{qho}}}{\partial \beta} = \frac{\partial}{\partial \beta}\left[\frac{1}{2}\beta\hbar\omega + \log\left(1 - e^{-\beta\hbar\omega}\right)\right]$$
$$= \hbar\omega\left(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}\right) = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right), \qquad (7.24)$$

which corresponds to an average excitation level

$$\langle n \rangle_{\text{qho}} = \frac{1}{e^{\beta\hbar\omega} - 1}. \qquad (7.25)$$

The specific heat is thus

$$c_V = \frac{\partial E}{\partial T} = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\hbar\omega/k_B T}}{\left(1 - e^{-\hbar\omega/k_B T}\right)^2} \qquad (7.26)$$

(Fig. 7.2). At high temperatures, $e^{-\hbar\omega/k_B T} \approx 1 - \hbar\omega/k_B T$, so $c_V \to k_B$ as we found for the classical harmonic oscillator (and as given by the equipartition theorem). At low temperatures, $e^{-\hbar\omega/k_B T}$ becomes exponentially small, so the specific heat goes rapidly to zero as the energy asymptotes to the zero-point energy $\frac{1}{2}\hbar\omega$. More specifically, there is an energy gap[11] $\hbar\omega$ to the first excitation, so the probability of having any excitation of the system is suppressed by a factor of $e^{-\hbar\omega/k_B T}$.

7.3   Bose and Fermi statistics

In quantum mechanics, identical particles are not just hard to tell apart—their quantum wavefunctions must be the same, up to an overall phase change,[12] when the coordinates are swapped (see Fig. 7.3). In particular, for bosons[13] the wavefunction is unchanged under a swap, so

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi(\mathbf{r}_2, \mathbf{r}_1, \ldots, \mathbf{r}_N) = \Psi(\mathbf{r}_{P_1}, \mathbf{r}_{P_2}, \ldots, \mathbf{r}_{P_N}) \quad (7.27)$$

for any permutation P of the integers $1, \ldots, N$. For fermions[14]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \ldots, \mathbf{r}_N) = \sigma(P)\,\Psi(\mathbf{r}_{P_1}, \mathbf{r}_{P_2}, \ldots, \mathbf{r}_{P_N}),$$
$$(7.28)$$

where $\sigma(P)$ is the sign of the permutation P.[15]

The eigenstates for systems of identical fermions and bosons are a subset of the eigenstates of distinguishable particles with the same Hamiltonian:

$$\mathcal{H}\Psi_n = E_n\Psi_n; \qquad (7.29)$$

in particular, they are given by the distinguishable eigenstates which obey the proper symmetry properties under permutations. A non-symmetric eigenstate Φ with energy E may be symmetrized to form a Bose eigenstate by summing over all possible permutations P:

$$\Psi_{\text{sym}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = (\text{normalization})\sum_P \Phi(\mathbf{r}_{P_1}, \mathbf{r}_{P_2}, \ldots, \mathbf{r}_{P_N}) \quad (7.30)$$

or antisymmetrized to form a fermion eigenstate

$$\Psi_{\mathrm{asym}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = (\text{normalization}) \sum_P \sigma(P) \Phi(\mathbf{r}_{P_1}, \mathbf{r}_{P_2}, \ldots, \mathbf{r}_{P_N})$$

(7.31)

if the symmetrization or antisymmetrization does not make the sum zero. These remain eigenstates of energy E, because they are combinations of eigenstates of energy E.

Quantum statistical mechanics for identical particles is given by restricting the ensembles to sum over symmetric wavefunctions for bosons or antisymmetric wavefunctions for fermions. So, for example, the partition function for the canonical ensemble is still

$$Z = \mathrm{Tr}\left(\mathrm{e}^{-\beta H}\right) = \sum_n \mathrm{e}^{-\beta E_n},$$

(7.32)

but now the trace is over a complete set of many-body symmetric (or antisymmetric) states, and the sum is over the symmetric (or antisymmetric) many-body energy eigenstates.

7.4   Non-interacting bosons and fermions

Many-body quantum statistical mechanics is hard. We now make a huge approximation: we will assume our quantum particles do not interact with one another. Just as for the classical ideal gas, this will make our calculations straightforward.

The non-interacting Hamiltonian is a sum of single-particle quantum Hamiltonians H:

$$\mathcal{H}^{\mathrm{NI}} = \sum_{j=1}^N H(\mathbf{p}_j, \mathbf{r}_j) = \sum_{j=1}^N \frac{\hbar^2}{2m} \nabla_j^2 + V(\mathbf{r}_j).$$

(7.33)

Let ψ_k be the single-particle eigenstates of H, then

$$H\psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}).$$

(7.34)

For distinguishable particles, the many-body eigenstates can be written as a product of orthonormal single-particle eigenstates:

$$\Psi_{\mathrm{dist}}^{\mathrm{NI}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \prod_{j=1}^N \psi_{k_j}(\mathbf{r}_j),$$

(7.35)

where particle j is in the single-particle eigenstate k_j. The eigenstates for non-interacting bosons are given by symmetrizing over the coordinates r_j:

$$\Psi_{\mathrm{boson}}^{\mathrm{NI}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = (\text{normalization}) \sum_P \prod_{j=1}^N \psi_{k_j}(\mathbf{r}_{P_j}),$$

(7.36)
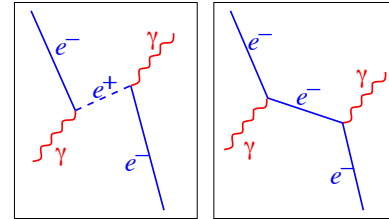
Fig. 7.3 Feynman diagram: identical particles. In quantum mechanics, two electrons (or two atoms of the same isotope) are fundamentally identical. We can illustrate this with a peek at an advanced topic mixing quantum field theory and relativity. Here is a scattering event of a photon off an electron, viewed in two reference frames; time is vertical, a spatial coordinate is horizontal. On the left we see two 'different' electrons, one which is created along with an anti-electron or positron e^+, and the other which later annihilates the positron. On the right we see the same event viewed in a different reference frame; here there is only one electron, which scatters two photons. (The electron is *virtual*, moving faster than light, between the collisions; this is allowed in intermediate states for quantum transitions.) The two electrons on the left are not only indistinguishable, they are the *same particle*! The antiparticle is also the electron, traveling backward in time.

and naturally the fermion eigenstates are given by antisymmetrizing over all $N!$ possible permutations, and renormalizing to one,[16]

$$\Psi^{\text{NI}}_{\text{fermion}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}}\sum_P \sigma(P)\prod_{j=1}^N \psi_{k_j}(\mathbf{r}_{P_j}).$$

(7.38)

Let us consider two particles in orthonormal single-particle energy eigenstates ψ_k and ψ_ℓ. If the particles are distinguishable, there are two eigenstates $\psi_k(\mathbf{r_1})\psi_\ell(\mathbf{r_2})$ and $\psi_k(\mathbf{r_2})\psi_\ell(\mathbf{r_1})$. If the particles are bosons, the eigenstate is $(1/\sqrt{2})\,(\psi_k(\mathbf{r_1})\psi_\ell(\mathbf{r_2}) + \psi_k(\mathbf{r_2})\psi_\ell(\mathbf{r_1}))$. If the particles are fermions, the eigenstate is $(1/\sqrt{2})\,(\psi_k(\mathbf{r_1})\psi_\ell(\mathbf{r_2}) - \psi_k(\mathbf{r_2})\psi_\ell(\mathbf{r_1}))$.

What if the particles are in the same single-particle eigenstate ψ_ℓ? For bosons, the eigenstate $\psi_\ell(\mathbf{r_1})\psi_\ell(\mathbf{r_2})$ is already symmetric and normalized.[17] For fermions, antisymmetrizing a state where both particles are in the same state gives zero: $\psi_\ell(\mathbf{r_1})\psi_\ell(\mathbf{r_2}) - \psi_\ell(\mathbf{r_2})\psi_\ell(\mathbf{r_1}) = 0$. This is the Pauli exclusion principle: you cannot have two fermions in the same quantum state.[18]

How do we do statistical mechanics for non-interacting fermions and bosons? Here it is most convenient to use the grand canonical ensemble (Section 6.3); in this ensemble we can treat each eigenstate as being populated independently from the other eigenstates, exchanging particles directly with the external bath (analogous to Fig. 6.2). The grand partition function hence factors:

$$\Xi^{\text{NI}} = \prod_k \Xi_k.$$

(7.39)

The grand canonical ensemble thus allows us to separately solve the case of non-interacting particles one eigenstate at a time.

Bosons. For bosons, all fillings n_k are allowed. Each particle in eigenstate ψ_k contributes energy ε_k and chemical potential $-\mu$, so

Fig. 7.4 **Bose–Einstein, Maxwell–Boltzmann, and Fermi–Dirac** distributions, $\langle n \rangle(\varepsilon)$. Occupation number for single-particle eigenstates as a function of energy ε away from the chemical potential μ. The Bose–Einstein distribution diverges as μ approaches ε; the Fermi–Dirac distribution saturates at one as μ gets small.

$$\Xi^{\text{boson}}_k = \sum_{n_k=0}^{\infty} e^{-\beta(\varepsilon_k - \mu)n_k} = \sum_{n_k=0}^{\infty}\left(e^{-\beta(\varepsilon_k - \mu)}\right)^{n_k} = \frac{1}{1 - e^{-\beta(\varepsilon_k - \mu)}}$$

(7.40)

and the boson grand partition function is

$$\Xi^{\text{NI}}_{\text{boson}} = \prod_k \frac{1}{1 - e^{-\beta(\varepsilon_k - \mu)}}.$$

(7.41)

The grand free energy ($\Phi = -k_B T \log \Xi$, eqn 6.36) is a sum of single-state grand free energies:

$$\Phi^{\text{NI}}_{\text{boson}} = \sum_k \Phi^{\text{boson}}_k = \sum_k k_B T \log\left(1 - e^{-\beta(\varepsilon_k - \mu)}\right).$$

(7.42)

Because the filling of different states is independent, we can find out the expected number of particles in state ψ_k. From eqn 6.38,

$$\langle n_k \rangle = -\frac{\partial \Phi^{\text{boson}}_k}{\partial \mu} = -k_B T \frac{-\beta e^{-\beta(\varepsilon_k - \mu)}}{1 - e^{-\beta(\varepsilon_k - \mu)}} = \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1}.$$
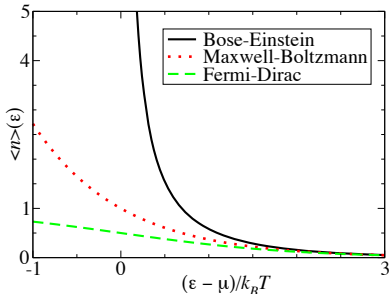
(7.43)

This is called the *Bose–Einstein* distribution (Fig. 7.4)

$$\langle n \rangle_{\text{BE}} = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}. \tag{7.44}$$

The Bose–Einstein distribution describes the filling of single-particle eigenstates by non-interacting bosons. For states with low occupancies, where $\langle n \rangle \ll 1$, $\langle n \rangle_{\text{BE}} \approx e^{-\beta(\varepsilon-\mu)}$, and the boson populations correspond to what we would guess naively from the Boltzmann distribution.[19] The condition for low occupancies is $\varepsilon_k - \mu \gg k_B T$, which usually arises at high temperatures[20] (where the particles are distributed among a larger number of states). Notice also that $\langle n \rangle_{\text{BE}} \to \infty$ as $\mu \to \varepsilon_k$ since the denominator vanishes (and becomes negative for $\mu > \varepsilon_k$); systems of non-interacting bosons always have μ less than or equal to the lowest of the single-particle energy eigenvalues.[21]

Notice that the average excitation $\langle n \rangle_{\text{qho}}$ of the quantum harmonic oscillator (eqn 7.25) is given by the Bose–Einstein distribution (eqn 7.44) with $\mu = 0$. We will use this in Exercise 7.2 to argue that one can treat excitations inside harmonic oscillators (vibrations) as particles obeying Bose statistics (phonons).

Fermions. For fermions, only $n_k = 0$ and $n_k = 1$ are allowed. The single-state fermion grand partition function is

$$\Xi_k^{\text{fermion}} = \sum_{n_k=0}^{1} e^{-\beta(\varepsilon_k-\mu)n_k} = 1 + e^{-\beta(\varepsilon_k-\mu)}, \tag{7.45}$$

so the total fermion grand partition function is

$$\Xi_{\text{fermion}}^{\text{NI}} = \prod_k \left(1 + e^{-\beta(\varepsilon_k-\mu)} \right). \tag{7.46}$$

For summing over only two states, it is hardly worthwhile to work through the grand free energy to calculate the expected number of particles in a state:

$$\langle n_k \rangle = \frac{\sum_{n_k=0}^{1} n_k \exp(-\beta(\varepsilon_k-\mu)n_k)}{\sum_{n_k=0}^{1} \exp(-\beta(\varepsilon_k-\mu)n_k)} = \frac{e^{-\beta(\varepsilon_k-\mu)}}{1 + e^{-\beta(\varepsilon_k-\mu)}} = \frac{1}{e^{\beta(\varepsilon_k-\mu)} + 1}, \tag{7.47}$$

leading us to the *Fermi–Dirac* distribution

$$f(\varepsilon) = \langle n \rangle_{\text{FD}} = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}, \tag{7.48}$$

where $f(\varepsilon)$ is also known as the Fermi function (Fig. 7.5). Again, when the mean occupancy of state ψ_k is low, it is approximately given by the Boltzmann probability distribution, $e^{-\beta(\varepsilon-\mu)}$. Here the chemical potential can be either greater than or less than any given eigenenergy ε_k. Indeed, at low temperatures the chemical potential μ separates filled states $\varepsilon_k < \mu$ from empty states $\varepsilon_k > \mu$; only states within roughly $k_B T$ of μ are partially filled.

[19] We will derive this from Maxwell–Boltzmann statistics in Section 7.5.

[20] This may seem at odds with the formula, but as T gets large μ gets large and negative even faster. This happens (at fixed total number of particles) because more states at high temperatures are available for occupation, so the pressure μ needed to keep them filled decreases.

[21] Chemical potential is like a pressure pushing atoms into the system. When the river level gets up to the height of the fields, your farm gets flooded.
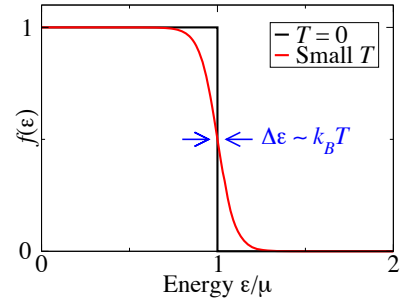

Fig. 7.5 The Fermi distribution $f(\varepsilon)$ of eqn 7.48. At low temperatures, states below μ are occupied, states above μ are unoccupied, and states within around $k_B T$ of μ are partially occupied.

[22]Just in case you have not heard, neutrinos are quite elusive. A lead wall that can stop half of the neutrinos would be light-years thick.

[23]Landau's insight was to describe interacting systems of fermions (e.g., electrons) at temperatures low compared to the Fermi energy by starting from the non-interacting Fermi gas and slowly 'turning on' the interaction. (The Fermi energy $\varepsilon_F = \mu(T = 0)$, see Section 7.7.) Excited states of the non-interacting gas are electrons excited into states above the Fermi energy, leaving holes behind. They evolve in two ways when the interactions are turned on. First, the excited electrons and holes push and pull on the surrounding electron gas, creating a *screening cloud* that *dresses* the bare excitations into *quasiparticles*. Second, these quasiparticles develop lifetimes; they are no longer eigenstates, but *resonances*. Quasiparticles are useful descriptions so long as the interactions can be turned on slowly enough for the screening cloud to form but fast enough so that the quasiparticles have not yet decayed; this occurs for electrons and holes near the Fermi energy, which have long lifetimes because they can only decay into energy states even closer to the Fermi energy [9, p. 345]. Later workers fleshed out Landau's ideas into a systematic perturbative calculation, where the quasiparticles are poles in a quantum Green's function (see Exercise 10.9 for a classical example of how this works). More recently, researchers have found a renormalization-group interpretation of Landau's argument, whose coarse-graining operation removes states far from the Fermi energy, and which flows to an effective non-interacting Fermi gas (see Chapter 12 and Exercise 12.8).

The chemical potential μ is playing a large role in these calculations. How do you determine it? You normally know the expected number of particles N, and must vary μ until you reach that value. Hence μ directly plays the role of a particle pressure from the outside world, which is varied until the system is correctly filled.

The amazing utility of non-interacting bosons and fermions. The classical ideal gas is a great illustration of statistical mechanics, and does a good job of describing many gases, but nobody would suggest that it captures the main features of solids and liquids. The non-interacting approximation in quantum mechanics turns out to be far more powerful, for quite subtle reasons.

For bosons, the non-interacting approximation is quite accurate in three important cases: photons, phonons, and the dilute Bose gas. In Section 7.6 we will study two fundamental problems involving non-interacting bosons: black-body radiation and Bose condensation. The behavior of superconductors and superfluids shares some common features with that of the Bose gas.

For fermions, the non-interacting approximation would rarely seem to be useful. Electrons are charged, and the electromagnetic repulsion between the electrons in an atom, molecule, or material is always a major contribution to the energy. Neutrons interact via the strong interaction, so nuclei and neutron stars are also poor candidates for a non-interacting theory. Neutrinos are hard to pack into a box.[22] There are experiments on cold, dilute gases of fermion atoms, but non-interacting fermions would seem a model with few applications.

The truth is that the non-interacting Fermi gas describes all of these systems (atoms, metals, insulators, nuclei, and neutron stars) remarkably well. Interacting Fermi systems under most common circumstances behave very much like collections of non-interacting fermions in a modified potential. The approximation is so powerful that in most circumstances we ignore the interactions; whenever we talk about exciting a '1S electron' in an oxygen atom, or an 'electron–hole' pair in a semiconductor, we are using this effective non-interacting electron approximation. The explanation for this amazing fact is called Landau Fermi-liquid theory.[23]

7.5 Maxwell–Boltzmann 'quantum' statistics

In classical statistical mechanics, we treated indistinguishable particles as distinguishable ones, except that we divided the phase-space volume, (or the partition function, in the canonical ensemble) by a factor of N!:

$$\Omega_N^{\mathrm{MB}} = \frac{1}{N!}\Omega_N^{\mathrm{dist}},$$
$$Z_N^{\mathrm{MB}} = \frac{1}{N!}Z_N^{\mathrm{dist}}. \tag{7.49}$$

This was important to get the entropy to be extensive (Section 5.2.1). This approximation is also sometimes used in quantum statistical mechanics, although we should emphasize that it does not describe either bosons, fermions, or any physical system. These bogus particles are said to obey *Maxwell–Boltzmann* statistics.[24]

What is the canonical partition function for the case of N non-interacting distinguishable quantum particles? If the partition function for one particle is

$$Z_1 = \sum_k e^{-\beta \varepsilon_k} \tag{7.50}$$

then the partition function for N non-interacting, distinguishable (but otherwise similar) particles is

$$Z_N^{\text{NI,dist}} = \sum_{k_1, k_2, \ldots, k_n} e^{-\beta(\varepsilon_{k_1} + \varepsilon_{k_2} + \cdots + \varepsilon_{k_N})} = \prod_{j=1}^{N} \left(\sum_{k_j} e^{-\beta \varepsilon_{k_j}} \right) = Z_1^{N}. \tag{7.51}$$

So, the Maxwell–Boltzmann partition function for non-interacting particles is

$$Z_N^{\text{NI,MB}} = Z_1^{N}/N!. \tag{7.52}$$

Let us illustrate the relation between these three distributions by considering the canonical ensemble of two non-interacting particles in three possible states of energies ε_1, ε_2, and ε_3. The Maxwell–Boltzmann partition function for such a system would be

$$\begin{aligned} Z_2^{\text{NI,MB}} &= \frac{1}{2!} \left(e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2} + e^{-\beta \varepsilon_3} \right)^2 \\ &= \frac{1}{2} e^{-2\beta \varepsilon_1} + \frac{1}{2} e^{-2\beta \varepsilon_2} + \frac{1}{2} e^{-2\beta \varepsilon_3} \\ &\quad + e^{-\beta(\varepsilon_1 + \varepsilon_2)} + e^{-\beta(\varepsilon_1 + \varepsilon_3)} + e^{-\beta(\varepsilon_2 + \varepsilon_3)}. \end{aligned} \tag{7.53}$$

The $1/N!$ fixes the weights of the singly-occupied states[25] nicely; each has weight one in the Maxwell–Boltzmann partition function. But the doubly-occupied states, where both particles have the same wavefunction, have an unintuitive suppression by $\frac{1}{2}$ in the sum.

There are basically two ways to fix this. One is to stop discriminating against multiply-occupied states, and to treat them all democratically. This gives us non-interacting bosons:

$$Z_2^{\text{NI,boson}} = e^{-2\beta \varepsilon_1} + e^{-2\beta \varepsilon_2} + e^{-2\beta \varepsilon_3} + e^{-\beta(\varepsilon_1 + \varepsilon_2)} + e^{-\beta(\varepsilon_1 + \varepsilon_3)} + e^{-\beta(\varepsilon_2 + \varepsilon_3)}. \tag{7.54}$$

The other way is to 'squelch' multiple occupancy altogether. This leads to fermions:

$$Z_2^{\text{NI,fermion}} = e^{-\beta(\varepsilon_1 + \varepsilon_2)} + e^{-\beta(\varepsilon_1 + \varepsilon_3)} + e^{-\beta(\varepsilon_2 + \varepsilon_3)}. \tag{7.55}$$

Thus the Maxwell–Boltzmann distribution treats multiple occupancy of states in an unphysical compromise between democratic bosons and exclusive fermions.

[24]Sometimes it is said that distinguishable particles obey Maxwell–Boltzmann statistics. Many properties are independent of the $N!$ in the denominator of eqn 7.49, such as the occupancy $\langle n \rangle$ of non-interacting single-particle eigenstates (eqn 7.60). But this factor does matter for other properties, like the entropy of mixing and the Helmholtz free energy, so we reserve the term Maxwell–Boltzmann for undistinguished particles (Section 3.5).

[25]More precisely, we mean those many-body states where the single-particle states are all singly occupied or vacant.

Here we have been comparing the different distributions within the canonical ensemble. What about the grand canonical ensemble, which we actually use for calculations?[26] The grand partition function for Maxwell–Boltzmann statistics is

$$\Xi^{\mathrm{NI,MB}} = \sum_M Z_M^{\mathrm{NI,MB}}\, \mathrm{e}^{M\beta\mu} = \sum_M \frac{1}{M!}\left(\sum_k \mathrm{e}^{-\beta\varepsilon_k}\right)^M \mathrm{e}^{M\beta\mu}$$

$$= \sum_M \frac{1}{M!}\left(\sum_k \mathrm{e}^{-\beta(\varepsilon_k-\mu)}\right)^M = \exp\left(\sum_k \mathrm{e}^{-\beta(\varepsilon_k-\mu)}\right)$$

$$= \prod_k \exp\left(\mathrm{e}^{-\beta(\varepsilon_k-\mu)}\right). \tag{7.56}$$

The grand free energy is

$$\Phi^{\mathrm{NI,MB}} = -k_B T \log \Xi^{\mathrm{NI,MB}} = \sum_k \Phi_k, \tag{7.57}$$

with the single-particle grand free energy

$$\Phi_k = -k_B T \mathrm{e}^{-\beta(\varepsilon_k-\mu)}. \tag{7.58}$$

[27]It is amusing to note that non-interacting particles fill single-particle energy states according to the same law

$$\langle n\rangle = \frac{1}{\mathrm{e}^{\beta(\varepsilon-\mu)}+c}, \tag{7.59}$$

with $c = -1$ for bosons, $c = 1$ for fermions, and $c = 0$ for Maxwell–Boltzmann statistics.

Finally, the expected[27] number of particles in a single-particle eigenstate with energy ε is

$$\langle n\rangle_{\mathrm{MB}} = -\frac{\partial\Phi}{\partial\mu} = \mathrm{e}^{-\beta(\varepsilon-\mu)}. \tag{7.60}$$

This is precisely the Boltzmann factor for filling the state that we expect for non-interacting distinguishable particles; the indistinguishability factor $N!$ does not alter the filling of the non-interacting single-particle states.
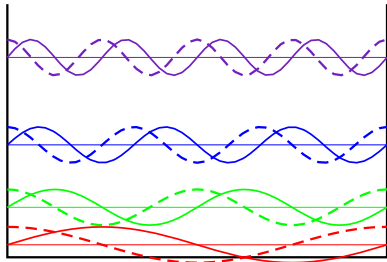
Fig. 7.6 Particle in a box. The quantum states of a particle in a one-dimensional box with periodic boundary conditions are sine and cosine waves ψ_n with n wavelengths in the box, $k_n = 2\pi n/L$. With a real box (zero boundary conditions at the walls) one would have only sine waves, but at half the spacing between wavevectors $k_n = \pi n/L$, giving the same net density of states.

[28]That is, the value of ψ at the walls need not be zero (as for an infinite square well), but rather must agree on opposite sides, so $\psi(0,y,z) \equiv \psi(L,y,z)$, $\psi(x,0,z) \equiv \psi(x,L,z)$, and $\psi(x,y,0) \equiv \psi(x,y,L)$. Periodic boundary conditions are not usually seen in experiments, but are much more natural to compute with, and the results are unchanged for large systems.

7.6 Black-body radiation and Bose condensation

7.6.1 Free particles in a box

For this section and the next section on fermions, we shall simplify even further. We consider particles which are not only non-interacting and identical, but are also *free*. That is, they are subject to no external potential, apart from being confined in a box of volume $L^3 = V$ with *periodic boundary conditions*.[28] The single-particle quantum eigenstates of such a system are products of sine and cosine waves along the three directions—for example, for any three non-negative integers n_i,

$$\psi = \left(\frac{2}{L}\right)^{3/2} \cos\left(\frac{2\pi n_1}{L}x\right)\cos\left(\frac{2\pi n_2}{L}y\right)\cos\left(\frac{2\pi n_3}{L}z\right). \tag{7.61}$$

There are eight such states with the same energy, substituting sine for cosine in all possible combinations along the three directions. These are

more conveniently organized if we use the complex exponential instead of sine and cosine:

$$\psi_{\mathbf{k}} = (1/L)^{3/2} \exp(i\mathbf{k} \cdot \mathbf{r}), \tag{7.62}$$

with $\mathbf{k} = (2\pi/L)(n_1, n_2, n_3)$ and the n_i can now be any integer.[29] The allowed single-particle eigenstates form a regular square grid in the space of wavevectors k, with an average density $(L/2\pi)^3$ per unit volume of k-space:

$$\text{density of plane waves in } \mathbf{k}\text{-space} = V/8\pi^3. \tag{7.63}$$

For a large box volume V, the grid is extremely fine, and one can use a continuum approximation that the number of states falling into a **k**-space region is given by its volume times the density (eqn 7.63).[30]

7.6.2 Black-body radiation

Our first application is to electromagnetic radiation. Electromagnetic radiation has plane-wave modes similar to eqn 7.62. Each plane wave travels at the speed of light c, so its frequency is $\omega_k = c|\mathbf{k}|$. There are two modes per wavevector $\mathbf{k}$, one for each polarization. When one quantizes the electromagnetic field, each mode becomes a quantum harmonic oscillator.

Before quantum mechanics, people could not understand the equilibration of electromagnetic radiation. The equipartition theorem predicted that if you could come to equilibrium, each mode would have $k_B T$ of energy. Since there are immensely more wavevectors in the ultraviolet and X-ray ranges than in the infra-red and visible,[31] opening your oven door would theoretically give you a sun-tan or worse (the so-called *ultraviolet catastrophe*). Experiments saw a spectrum which looked compatible with this prediction for small frequencies, but was (fortunately) cut off at high frequencies.

Let us calculate the equilibrium energy distribution inside our box at temperature T. The number of single-particle plane-wave eigenstates $g(\omega)\,d\omega$ in a small range $d\omega$ is[32]

$$g(\omega)\,d\omega = (4\pi k^2)\left(\frac{d|\mathbf{k}|}{d\omega}d\omega\right)\left(\frac{2V}{(2\pi)^3}\right), \tag{7.64}$$

where the first term is the surface area of the sphere of radius k, the second term is the thickness of the spherical shell for a small $d\omega$, and the last is the density of single-particle plane-wave eigenstate wavevectors times two (because there are two photon polarizations per wavevector). Knowing $\mathbf{k}^2 = \omega^2/c^2$ and $d|\mathbf{k}|/d\omega = 1/c$, we find the density of plane-wave eigenstates per unit frequency:

$$g(\omega) = \frac{V\omega^2}{\pi^2 c^3}. \tag{7.65}$$

Now, the number of photons is not fixed; they can be created or destroyed, so their chemical potential μ is zero.[33] Their energy $\varepsilon_k = \hbar\omega_k$. Finally, they are to an excellent approximation identical, non-interacting
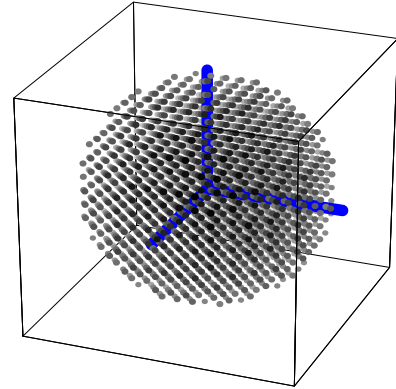
Fig. 7.7 k-sphere. The allowed **k**-space points for periodic boundary conditions form a regular grid. The points of equal energy lie on a sphere.

[29]The eight degenerate states are now given by the choices of sign for the three integers.

[30]Basically, the continuum limit works because the shape of the box (which affects the arrangements of the allowed **k** vectors) is irrelevant to the physics so long as the box is large. For the same reason, the energy of the single-particle eigenstates is independent of direction; it will be proportional to $|\mathbf{k}|$ for massless photons, and proportional to $\mathbf{k}^2$ for massive bosons and electrons (Fig. 7.7). This makes the calculations in the following sections tractable.

[31]There are a thousand times more wavevectors with $|k| < 10k_0$ than for $|k| < k_0$. The optical frequencies and wavevectors span roughly a factor of two (an octave for sound), so there are eight times as many optical modes as there are radio and infra-red modes.

[32]We are going to be sloppy and use $g(\omega)$ as eigenstates per unit frequency for photons, and later we will use $g(\varepsilon)$ as single-particle eigenstates per unit energy. Be warned: $g_\omega(\omega)\,d\omega = g_\varepsilon(\hbar\omega)\,d\,\hbar\omega$, so $g_\omega = \hbar g_\varepsilon$.

[33]See Exercise 7.2 to derive this from the quantum harmonic oscillator.

Fig. 7.8 The Planck black-body radiation power spectrum, with the Rayleigh–Jeans approximation, valid for low frequency ω.

[34]Why is this called *black-body* radiation? A black surface absorbs all radiation at all frequencies. In equilibrium, the energy it absorbs at a given frequency must equal the energy it emits, otherwise it would push the system out of equilibrium. (This is called *detailed balance*, Section 8.2.) Hence, ignoring the small surface cooling due to radiation, a black body emits a thermal distribution of photons (see Exercise 7.7).
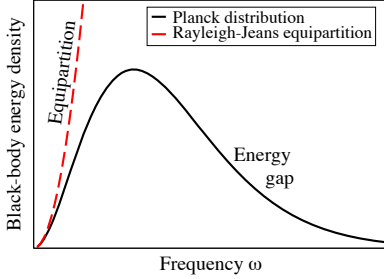
bosons, so the number of photons per eigenstate with frequency ω is $\langle n \rangle = 1/(e^{\hbar\omega/k_BT} - 1)$. This gives us a number of photons:

$$(\# \text{ of photons}) \, d\omega = \frac{g(\omega)}{e^{\hbar\omega/k_BT} - 1} \, d\omega \qquad (7.66)$$

and an electromagnetic (photon) energy per unit volume $u(\omega)$ given by

$$
\begin{aligned}
V u(\omega) \, d\omega &= \frac{\hbar\omega g(\omega)}{e^{\hbar\omega/k_BT} - 1} \, d\omega \\
&= \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3 \, d\omega}{e^{\hbar\omega/k_BT} - 1}
\end{aligned}
\qquad (7.67)
$$

(Fig. 7.8). This is Planck's famous formula for black-body radiation.[34] At low frequencies, we can approximate $e^{\hbar\omega/k_BT} - 1 \approx \hbar\omega/k_BT$, yielding the Rayleigh–Jeans formula

$$
\begin{aligned}
V u_{\mathrm{RJ}}(\omega) \, d\omega &= V \left(\frac{k_BT}{\pi^2 c^3} \right) \omega^2 \, d\omega \\
&= k_BT g(\omega),
\end{aligned}
\qquad (7.68)
$$

just as one would expect from equipartition: k_BT per classical harmonic oscillator.

For modes with frequencies high compared to $k_BT/\hbar$, equipartition no longer holds. The energy gap $\hbar\omega$, just as for the low-temperature specific heat from Section 7.2, leads to an excitation probability that is suppressed by the exponential Boltzmann factor $e^{-\hbar\omega/k_BT}$ (eqn 7.67, approximating $1/(e^{\hbar\omega/k_BT} - 1) \approx e^{-\hbar\omega/k_BT}$). Planck's discovery that quantizing the energy averted the ultraviolet catastrophe was the origin of quantum mechanics, and led to his name being given to $\hbar$.

7.6.3 Bose condensation

How does our calculation change when the non-interacting free bosons cannot be created and destroyed? Let us assume that our bosons are spinless, have mass m, and are non-relativistic, so their energy is $\varepsilon = p^2/2m = -\hbar^2\nabla^2/2m$. If we put them in our box with periodic boundary conditions, we can make the same continuum approximation to the density of states as we did in the case of black-body radiation. In eqn 7.63, the number of plane-wave eigenstates per unit volume in $\mathbf{k}$-space is $V/8\pi^3$, so the density in momentum space $\mathbf{p} = \hbar\mathbf{k}$ is $V/(2\pi\hbar)^3$. For our massive particles $d\varepsilon/d|\mathbf{p}| = |\mathbf{p}|/m = \sqrt{2\varepsilon/m}$, so the number of plane-wave eigenstates in a small range of energy $d\varepsilon$ is

$$
\begin{aligned}
g(\varepsilon) \, d\varepsilon &= (4\pi p^2) \left(\frac{d|\mathbf{p}|}{d\varepsilon} \, d\varepsilon \right) \left(\frac{V}{(2\pi\hbar)^3} \right) \\
&= (4\pi(2m\varepsilon)) \left(\sqrt{\frac{m}{2\varepsilon}} \, d\varepsilon \right) \left(\frac{V}{(2\pi\hbar)^3} \right) \\
&= \frac{V m^{3/2}}{\sqrt{2}\pi^2\hbar^3} \sqrt{\varepsilon} \, d\varepsilon,
\end{aligned}
\qquad (7.69)
$$

where the first term is the surface area of the sphere in **p**-space, the second is the thickness of the spherical shell, and the third is the density of plane-wave eigenstates per unit volume in **p**-space.

Now we fill each of these single-particle plane-wave eigenstates with an expected number given by the Bose–Einstein distribution at chemical potential μ, $1/(e^{(\varepsilon-\mu)/k_BT}-1)$. The total number of particles N is then given by

$$N(\mu) = \int_0^\infty \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/k_BT}-1}\,d\varepsilon. \qquad (7.70)$$

We must vary μ in this equation to give us the correct number of particles N. For bosons, as noted in Section 7.4, μ cannot be larger than the lowest single-particle eigenenergy (here $\varepsilon_0 = 0$), so μ will always be negative. For larger numbers of particles we raise μ up from below, forcing more particles into each of the single-particle states. There is a limit, however, to how hard we can push; when $\mu = 0$ the ground state gets a diverging number of particles.

For free bosons in three dimensions, the integral for $N(\mu = 0)$ converges to a finite value.[35] Thus the largest number of particles $N^{\text{cont}}_{\text{max}}$ we can fit into our box within our continuum approximation for the density of states is the value of eqn 7.70 at $\mu = 0$:

$$\begin{aligned}
N^{\text{cont}}_{\text{max}} &= \int \frac{g(\varepsilon)}{e^{\varepsilon/k_BT}-1}\,d\varepsilon \\
&= \frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty d\varepsilon\, \frac{\sqrt{\varepsilon}}{e^{\varepsilon/k_BT}-1} \\
&= V\left(\frac{\sqrt{2\pi mk_BT}}{h}\right)^3 \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{z}}{e^z-1}\,dz \\
&= \left(\frac{V}{\lambda^3}\right)\zeta(3/2). \qquad (7.71)
\end{aligned}$$

Here ζ is the Riemann zeta function,[36] with $\zeta(\tfrac{3}{2}) \approx 2.612$ and $\lambda = h/\sqrt{2\pi mk_BT}$ is again the thermal de Broglie wavelength (eqn 3.59). Something new has to happen at a critical density:

$$\frac{N^{\text{cont}}_{\text{max}}}{V} = \frac{\zeta(3/2)}{\lambda^3} = \frac{2.612\ \text{particles}}{\text{deBroglie volume}}. \qquad (7.72)$$

This has an elegant interpretation: the quantum statistics of the particles begin to dominate the behavior when they are within around a thermal de Broglie wavelength of one another.

What happens when we try to cram more particles in? Our approximation of the distribution of eigenstates as a continuum breaks down. Figure 7.9 shows a schematic illustration of the first few single-particle eigenvalues. When the distance between μ and the bottom level ε_0 becomes significantly smaller than the distance between the bottom and the next level ε_1, the continuum approximation (which approximates the filling of ε_0 using an integral half-way to ε_1) becomes qualitatively wrong. The low-energy states, viewed as a continuum, cannot accommodate the extra bosons. Instead, the lowest state absorbs all the extra particles

[35] At $\mu = 0$, the denominator of the integrand in eqn 7.70 is approximately ε/k_BT for small ε, but the numerator goes as $\sqrt{\varepsilon}$, so the integral converges at the lower end: $\int_0^X \varepsilon^{-1/2} \sim (\tfrac{1}{2}\varepsilon^{1/2})|_0^X = \sqrt{X}/2$.

[36] The Riemann ζ function $\zeta(s) = [1/(s-1)!]\int_0^\infty z^{s-1}/(e^z-1)\,dz$ is famous for many reasons. It is related to the distribution of prime numbers. It is the subject of the famous unproven *Riemann hypothesis*, that its zeros in the complex plane, apart from those at the negative even integers, all have real part equal to $\tfrac{1}{2}$.
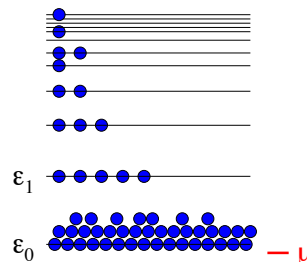

Fig. 7.9 Bose condensation. The chemical potential μ is here so close to the ground state energy ε_0 that the continuum approximation to the density of states breaks down. The ground state is macroscopically occupied (that is, filled by a non-zero fraction of the total number of particles N).

added to the system beyond $N_{\max}^{\text{cont}}$.[37] This is called *Bose–Einstein condensation.*

Usually we do not add particles at fixed temperature, instead we lower the temperature at fixed density N/V. Bose condensation then occurs at temperature

$$k_B T_c^{\text{BEC}} = \frac{h^2}{2\pi m} \left(\frac{N}{V \zeta(3/2)} \right)^{2/3}. \tag{7.73}$$

Bose condensation was first accomplished experimentally in 1995 (see Exercise 7.14).

Bose condensation has also long been considered the underlying principle behind superfluidity. Liquid He^4 undergoes an unusual transition at about $2.176\,\text{K}$ to a state without viscosity; it will swirl round a circular tube for as long as your refrigeration lasts. The quantitative study of the superfluid transition involves the interactions between the helium atoms, and uses the scaling methods that we will introduce in Chapter 12. But it is interesting to note that the Bose condensation temperature for liquid He^4 (with $m = 6.65 \times 10^{-24}\,\text{g}$ and volume per particle $V/N = 27.6\,\text{cm/mole}$) is $3.13\,\text{K}$—quite close to the superfluid transition temperature.

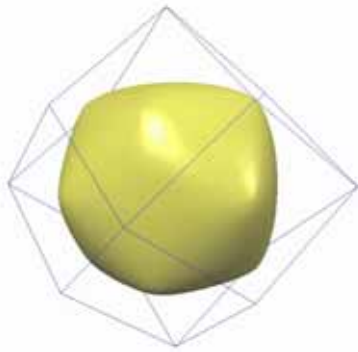## 7.7 Metals and the Fermi gas

Fig. 7.10 The Fermi surface for lithium, from [29]. The Fermi energy for lithium is $4.74\,\text{eV}$, with one conduction electron outside a helium closed shell. As for most metals, the Fermi energy in lithium is much larger than k_B times its melting point ($4.74\,\text{eV} = 55\,000\,\text{K}$, melting point $453\,\text{K}$). Hence it is well described by this $T = 0$ Fermi surface, slightly smeared by the Fermi function (Fig. 7.5).

We claimed in Section 7.4 that many systems of strongly-interacting fermions (metals, neutron stars, nuclei) are surprisingly well described by a model of non-interacting fermions. Let us solve for the properties of N *free* non-interacting fermions in a box.

Let our particles be non-relativistic and have spin $1/2$. The single-particle eigenstates are the same as those for bosons except that there are two states (spin up, spin down) per plane wave. Hence the density of states is given by twice that of eqn 7.69:

$$g(\varepsilon) = \frac{\sqrt{2} V m^{3/2}}{\pi^2 \hbar^3} \sqrt{\varepsilon}. \tag{7.74}$$

[38]Equation 7.77 has an illuminating derivation in **k**-space, where we fill all states with $|\mathbf{k}| < k_F$. Here the Fermi wavevector k_F has energy equal to the Fermi energy, $\hbar k_F^2/2m = p_F^2/2m = \varepsilon_F$, and hence $k_F = \sqrt{2\varepsilon_F m}/\hbar$. The resulting sphere of occupied states at $T = 0$ is called the *Fermi sphere.* The number of fermions inside the Fermi sphere is thus the **k**-space volume of the Fermi sphere times the **k**-space density of states,

$$N = \left((4/3)\pi k_F{}^3\right)\left(\frac{2V}{(2\pi)^3}\right) = \frac{k_F{}^3}{3\pi^2} V, \tag{7.76}$$

equivalent to eqn 7.77.

The number of fermions at chemical potential μ is given by integrating $g(\varepsilon)$ times the expected number of fermions in a state of energy ε, given by the Fermi function $f(\varepsilon)$ of eqn 7.48:

$$N(\mu) = \int_0^\infty g(\varepsilon) f(\varepsilon)\, \mathrm{d}\varepsilon = \int_0^\infty \frac{g(\varepsilon)}{\mathrm{e}^{(\varepsilon - \mu)/k_B T} + 1}\, \mathrm{d}\varepsilon. \tag{7.75}$$

What chemical potential will give us N fermions? At non-zero temperature, one must do a self-consistent calculation, but at $T = 0$ one can find N by counting the number of states below μ. In the zero-temperature limit (Fig. 7.5) the Fermi function is a step function $f(\varepsilon) = \Theta(\mu - \varepsilon)$; all states below μ are filled, and all states above μ are empty. The zero-temperature value of the chemical potential is called the *Fermi energy* ε_F. We can find the number of fermions by integrating up to $\mu = \varepsilon_F$:[38]

$$N = \int_0^{\varepsilon_F} g(\varepsilon)\,\mathrm{d}\varepsilon = \frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}V \int_0^{\varepsilon_F} \sqrt{\varepsilon}\,\mathrm{d}\varepsilon = \frac{(2\varepsilon_F m)^{3/2}}{3\pi^2\hbar^3}V. \qquad (7.77)$$

We mentioned earlier that the independent fermion approximation was startlingly useful even though the interactions are not small. Ignoring the Coulomb repulsion between electrons in a metal, or the strong interaction between neutrons in a neutron star, gives an excellent description of their actual behavior. However, our calculation above also assumed that the electrons are free particles, experiencing no external potential. This approximation is not particularly accurate in general; the interactions with the atomic nuclei are important, and is primarily what makes one material different from another. In particular, the atoms in a crystal will form a periodic potential for the electrons.[39] One can show that the single-particle eigenstates in a periodic potential are periodic functions times $\exp(i\mathbf{k}\cdot\mathbf{r})$, with exactly the same wavevectors $\mathbf{k}$ as in the free fermion case. The filling of the Fermi surface in $\mathbf{k}$-space is changed only insofar as the energies of these single-particle states are no longer isotropic. Some metals (particularly the alkali metals, like lithium in Fig. 7.10) have roughly spherical Fermi surfaces; many (see Fig. 7.11 for aluminum) are quite intricate, with several pieces to them [9, chapters 9–11].
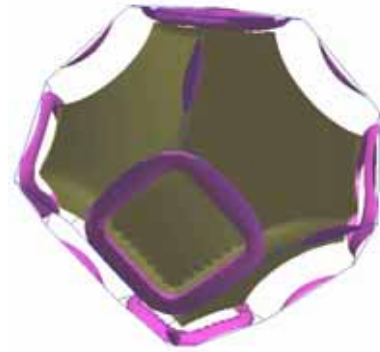

Fig. 7.11 The Fermi surface for aluminum, also from [29]. Aluminum has a Fermi energy of 11.7 eV, with three conduction electrons outside a Ne closed shell.

[39]Rather than using the Coulomb potential for the nucleus, a better approximation is given by incorporating the effects of the *inner shell* electrons into the periodic potential, and filling the Fermi sea with the remaining *conduction* electrons.

Exercises

We start with two exercises on the different types of identical particle statistics: *Ensembles and quantum statistics* and *Phonons and photons are bosons*. We then use quantum mechanics to set the scale of classical statistical mechanics in *Phase-space units and the zero of entropy*, and ask again *Does entropy increase in quantum systems?* In *Photon density matrices* and *Spin density matrix* we give elementary examples of this advanced topic.

Quantum statistical mechanics is the foundation of many fields. We start with three examples from optics: *Light emission and absorption*, *Einstein's A and B*, and *Bosons are gregarious: superfluids and lasers*. We provide three prototypical calculations in condensed-matter physics: *Crystal defects*, *Phonons on a string*, and *Fermions in semiconductors*. We provide two exercises on Bose condensation: *Bose condensation in a band* and *Bose condensation: the experiment*. Finally, we introduce two primary applications to astrophysics: *The photon-dominated Universe* and *White dwarfs, neutron stars, and black holes*.

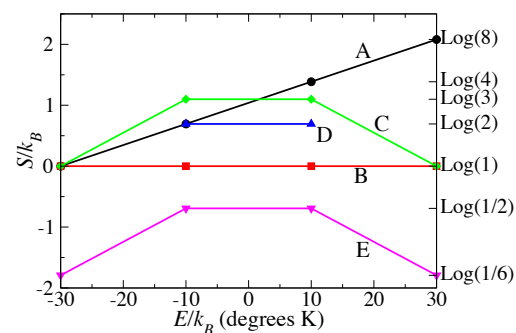(7.1) **Ensembles and quantum statistics.** (Quantum) ③

Fig. 7.12 Microcanonical three particles.

A system has two single-particle eigenfunctions, with energies (measured in degrees Kelvin) $E_0/k_B = -10$ and $E_2/k_B = 10$. Experiments are performed by adding three non-interacting particles to these two states, either identical spin-1/2 fermions, identical spin-

less bosons, distinguishable particles, or spinless identical particles obeying Maxwell–Boltzmann statistics. Please make a table for this exercise, giving your answers for the four cases (Fermi, Bose, Distinguishable, and Maxwell–Boltzmann) for each of the three parts. Substantive calculations may be needed.

(a) *The system is first held at constant energy. In Fig. 7.12 which curve represents the entropy of the fermions as a function of the energy? Bosons? Distinguishable particles? Maxwell–Boltzmann particles?*
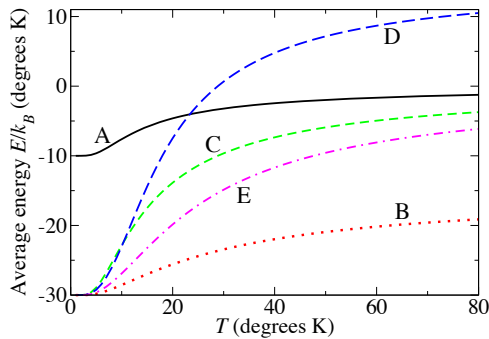

Fig. 7.13 Canonical three particles.

(b) *The system is now held at constant temperature. In Fig. 7.13 which curve represents the mean energy of the fermions as a function of temperature? Bosons? Distinguishable particles? Maxwell–Boltzmann particles?*
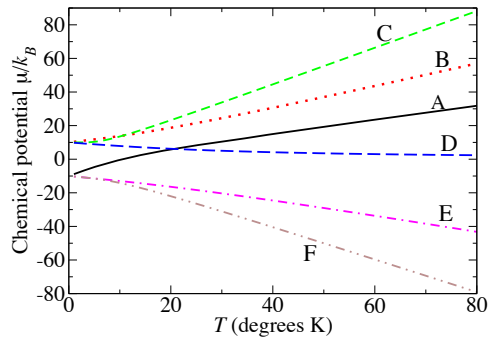

Fig. 7.14 Grand canonical three particles.

(c) *The system is now held at constant temperature, with chemical potential set to hold the average number of particles equal to three. In Fig. 7.14, which curve represents the chemical potential of the fermions as a function of temperature? Bosons? Distinguishable? Maxwell–Boltzmann?*

(7.2) **Phonons and photons are bosons.** (Quantum) ③

Phonons and photons are the elementary, harmonic excitations of the elastic and electromagnetic fields. We have seen in Exercise 7.11 that phonons are decoupled harmonic oscillators, with a distribution of frequencies ω. A similar analysis shows that the Hamiltonian of the electromagnetic field can be decomposed into harmonic normal modes called photons.

This exercise will explain why we think of phonons and photons as particles, instead of excitations of harmonic modes.

(a) *Show that the canonical partition function for a quantum harmonic oscillator of frequency ω is the same as the grand canonical partition function for bosons multiply filling a single state with energy $\hbar\omega$, with $\mu = 0$ (apart from a shift in the arbitrary zero of the total energy of the system).*

The Boltzmann filling of a harmonic oscillator is therefore the same as the Bose–Einstein filling of bosons into a single quantum state, except for an extra shift in the energy of $\hbar\omega/2$. This extra shift is called the *zero-point energy*. The excitations within the harmonic oscillator are thus often considered as particles with Bose statistics: the nth excitation is n bosons occupying the oscillator's quantum state.

This particle analogy becomes even more compelling for systems like phonons and photons where there are many harmonic oscillator states labeled by a wavevector k (see Exercise 7.11). Real, massive Bose particles like He^4 in free space have single-particle quantum eigenstates with a dispersion relation[40] $\varepsilon_k = \hbar^2 k^2/2m$. Phonons and photons have one harmonic oscillator for every k, with an excitation energy $\varepsilon_k = \hbar\omega_k$. If we treat them, as in part (a), as bosons filling these as single-particle states we find that they are completely analogous to ordinary massive particles. (Photons even have the dispersion relation of a massless boson. If we take the mass to zero of a relativistic particle, $\varepsilon = \sqrt{m^2c^4 - \mathbf{p}^2 c^2} \to |\mathbf{p}|c = \hbar c|\mathbf{k}|$.)

[40]The *dispersion relation* is the relationship between energy and wavevector, here ε_k.

(b) *Do phonons or photons Bose condense at low temperatures? Can you see why not? Can you think of a non-equilibrium Bose condensation of photons, where a macroscopic occupation of a single frequency and momentum state occurs?*

(7.3) **Phase-space units and the zero of entropy.** (Quantum) ③

In classical mechanics, the entropy $S = k_B \log \Omega$ goes to minus infinity as the temperature is lowered to zero. In quantum mechanics the entropy per particle goes to zero,[41] because states are quantized and the ground state is the only one populated. This is Nernst's theorem, the third law of thermodynamics.

The classical phase-space shell volume $\Omega(E) \, \delta E$ (eqn 3.5) has units of $((\text{momentum}) \times (\text{distance}))^{3N}$. It is a little perverse to take the logarithm of a quantity with units. The natural candidate with these dimensions is Planck's constant h^{3N}; if we measure phase-space volume in units of h per dimension, $\Omega(E) \, \delta E$ will be dimensionless. Of course, the correct dimension could be a constant times h, like $\hbar$...

(a) *Arbitrary zero of the classical entropy. Show that the width of the energy shell δE in the definition of $\Omega(E)$ does not change the microcanonical entropy per particle $S/N = k_B \log(\Omega(E))/N$ in a large system. Show that the choice of units in phase space does change the classical entropy per particle.*

We want to choose the units of classical phase-space volume so that the entropy agrees with the quantum entropy at high temperatures. How many quantum eigenstates per unit volume of classical phase space should we expect at high energies? We will fix these units by matching the quantum result to the classical one for a particular system, and then check it using a second system. Let us start with a free particle.

(b) *Phase-space density of states for a particle in a one-dimensional box. Show, or note, that the quantum momentum-space density of states for a free quantum particle in a one-dimensional box of length L with periodic boundary conditions is L/h. Draw a picture of the classical phase space of this box (p, x), and draw a rectangle of length*

L for each quantum eigenstate. Is the phase-space area per eigenstate equal to h, as we assumed in Section 3.5?

This works also for N particles in a three-dimensional box.

(c) *Phase-space density of states for N particles in a box. Show that the density of states for N free particles in a cubical box of volume V with periodic boundary conditions is V^N/h^{3N}, and hence that the phase-space volume per state is h^{3N}.*

Let us see if this choice of units[42] also works for the harmonic oscillator.

(d) *Phase-space density of states for a harmonic oscillator. Consider a harmonic oscillator with Hamiltonian $\mathcal{H} = p^2/2m + \frac{1}{2}m\omega^2 q^2$. Draw a picture of the energy surface with energy E, and find the volume (area) of phase space enclosed. (Hint: The area of an ellipse is $\pi r_1 r_2$ where r_1 and r_2 are the largest and smallest radii, corresponding to the major and minor axes.) What is the volume per energy state, the volume between E_n and E_{n+1}, for the eigenenergies $E_n = (n + \frac{1}{2})\hbar\omega$?*

(7.4) **Does entropy increase in quantum systems?** (Mathematics, Quantum) ③

We saw in Exercise 5.7 that in classical Hamiltonian systems the non-equilibrium entropy $S_{\text{nonequil}} = -k_B \int \rho \log \rho$ is constant in a classical mechanical Hamiltonian system. Here you will show that in the microscopic evolution of an isolated quantum system, the entropy is also time independent, even for general, time-dependent density matrices $\rho(t)$.

Using the evolution law (eqn 7.19) $\partial\rho/\partial t = [\mathcal{H}, \rho]/(i\hbar)$, prove that $S = \text{Tr}(\boldsymbol{\rho} \log \boldsymbol{\rho})$ is time independent, where $\boldsymbol{\rho}$ is any density matrix. (Hint: Show that $\text{Tr}(\mathbf{ABC}) = \text{Tr}(\mathbf{CAB})$ for any matrices $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$. Also you should know that an operator $\mathbf{M}$ commutes with any function $f(\mathbf{M})$.)

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[41] If the ground state is degenerate, the entropy does not go to zero, but it typically stays finite as the number of particles N gets big, so for large N the entropy per particle goes to zero.

[42] You show here that ideal gases should calculate entropy using phase-space units with $h = 1$. To argue this directly for interacting systems usually involves semiclassical quantization [70, chapter 48, p. 170] or path integrals [39]. But it must be true. We could imagine measuring the entropy difference between the interacting system and an ideal gas, by slowly and reversibly turning off the interactions between the particles, measuring the entropy flow into or out of the system. Thus, setting the zero of entropy for the ideal gas sets it for all systems.

(7.5) **Photon density matrices.**   (Quantum) ③
Write the density matrix for a vertically polarized photon $|V\rangle$ in the basis where $|V\rangle = \binom{1}{0}$ and a horizontal photon $|H\rangle = \binom{0}{1}$. Write the density matrix for a diagonally polarized photon, $(1/\sqrt{2}, 1/\sqrt{2})$, and the density matrix for unpolarized light (note 2 on p. 136). Calculate $\mathrm{Tr}(\boldsymbol{\rho})$, $\mathrm{Tr}(\boldsymbol{\rho}^2)$, *and* $S = -k_B\mathrm{Tr}(\boldsymbol{\rho}\log\boldsymbol{\rho})$. *Interpret the values of the three traces physically.* (Hint: One is a check for pure states, one is a measure of information, and one is a normalization.)

(7.6) **Spin density matrix.**[43]   (Quantum) ③
Let the Hamiltonian for a spin be

$$\mathcal{H} = -\frac{\hbar}{2}\mathbf{B}\cdot\vec{\sigma}, \tag{7.78}$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the three Pauli spin matrices, and $\mathbf{B}$ may be interpreted as a magnetic field, in units where the gyromagnetic ratio is unity. Remember that $\sigma_i\sigma_j - \sigma_j\sigma_i = 2\mathrm{i}\epsilon_{ijk}\sigma_k$. Show that any 2×2 density matrix may be written in the form

$$\boldsymbol{\rho} = \frac{1}{2}(\mathbf{1} + \mathbf{p}\cdot\vec{\sigma}). \tag{7.79}$$

Show that the equations of motion for the density matrix $\mathrm{i}\hbar\partial\boldsymbol{\rho}/\partial t = [\mathcal{H}, \boldsymbol{\rho}]$ can be written as $\mathrm{d}\mathbf{p}/\mathrm{d}t = -\mathbf{B}\times\mathbf{p}$.

(7.7) **Light emission and absorption.**   (Quantum) ②
The experiment that Planck was studying did not directly measure the energy density per unit frequency (eqn 7.67) inside a box. It measured the energy radiating out of a small hole, of area A. Let us assume the hole is on the upper face of the cavity, perpendicular to the z axis.
What is the photon distribution just inside the boundary of the hole? Few photons come into the hole from the outside, so the distribution is depleted for those photons with $v_z < 0$. However, the photons with $v_z > 0$ to an excellent approximation should be unaffected by the hole—since they were emitted from far distant walls of the cavity, where the existence of the hole is a negligible perturbation. So, presuming the relevant photons just inside the hole are distributed in the same way as in the box as a whole (eqn 7.67), how many leave in a time $\mathrm{d}t$?
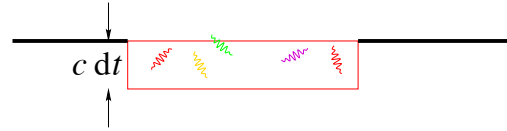

Fig. 7.15 Photon emission from a hole. The photons leaving a cavity in a time $\mathrm{d}t$ are those within $v_z\,\mathrm{d}t$ of the hole.

As one can see geometrically (Fig. 7.15), those photons within $v_z\,\mathrm{d}t$ of the boundary will escape in time $\mathrm{d}t$. The vertical velocity $v_z = c\cos(\theta)$, where θ is the photon velocity angle with respect to the vertical. The Planck distribution is isotropic, so the probability that a photon will be moving at an angle θ is the perimeter of the θ circle on the sphere divided by the area of the sphere, $2\pi\sin(\theta)\,\mathrm{d}\theta/(4\pi) = \frac{1}{2}\sin(\theta)\,\mathrm{d}\theta$.
(a) *Show that the probability density*[44] *$\rho(v_z)$ for a particular photon to have velocity v_z is independent of v_z in the range $(-c, c)$, and thus is $1/2c$.* (Hint: $\rho(v_z)\,\Delta v_z = \rho(\theta)\,\Delta\theta$.)
An upper bound on the energy emitted from a hole of area A is given by the energy in the box as a whole (eq. 7.67) times the fraction $Ac\,\mathrm{d}t/V$ of the volume within $c\,\mathrm{d}t$ of the hole.
(b) *Show that the actual energy emitted is $1/4$ of this upper bound.* (Hint: You will need to integrate $\int_0^c \rho(v_z)v_z\,\mathrm{d}v_z$.)
Hence the power per unit area emitted from the small hole in equilibrium is

$$P_{\text{black}}(\omega, T) = \left(\frac{c}{4}\right)\frac{\hbar}{\pi^2 c^3}\frac{\omega^3\,\mathrm{d}\omega}{\mathrm{e}^{\hbar\omega/k_B T} - 1}. \tag{7.80}$$

Why is this called black-body radiation? Certainly a small hole in a large (cold) cavity looks black—any light entering the hole bounces around inside until it is absorbed by the walls. Suppose we placed a black object—a material that absorbed radiation at all frequencies and angles—capping the hole. This object would absorb radiation from the cavity, rising in temperature until it came to equilibrium with the cavity—emitting just as much radiation as it absorbs. Thus the overall power per unit area emitted by our black object in equilibrium at a given temperature must equal that of the hole. This must also be true if we place a selective filter

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[43] Adapted from exam question by Bert Halperin, Harvard University, 1976.
[44] We are being sloppy again, using the same name ρ for the probability densities per unit velocity and per unit angle.

between the hole and our black body, passing through only particular types of photons. Thus the emission and absorption of our black body must agree with the hole for every photon mode individually, an example of the *principle of detailed balance* we will discuss in more detail in Section 8.2.

How much power per unit area $P_{\text{colored}}(\omega, T)$ is emitted in equilibrium at temperature T by a red or maroon body? A white body? A mirror? These objects are different in the fraction of incident light they absorb at different frequencies and angles $a(\omega, \theta)$. We can again use the principle of detailed balance, by placing our colored object next to a black body and matching the power emitted and absorbed for each angle and frequency:

$$P_{\text{colored}}(\omega, T, \theta) = P_{\text{black}}(\omega, T)a(\omega, \theta). \quad (7.81)$$

Finally, we should calculate $Q_{\text{tot}}(T)$, the total power per unit area emitted from a black body at temperature T, by integrating eqn 7.80 over frequency.

(c) *Using the fact that $\int_0^\infty x^3/(e^x - 1)\, dx = \pi^4/15$, show that*

$$Q_{\text{tot}}(T) = \int_0^\infty P_{\text{black}}(\omega, T)\, d\omega = \sigma T^4 \quad (7.82)$$

and give a formula for the Stefan–Boltzmann *constant σ.* ($\sigma = 5.67 \times 10^{-5}\,\text{erg cm}^{-2}\,\text{K}^{-4}\,\text{s}^{-1}$; use this to check your answer.)

(7.8) **Einstein's A and B.**   (Quantum, Optics, Mathematics) ③
Einstein used statistical mechanics to deduce basic truths about the interaction of light with matter very early in the development of quantum mechanics. In particular, he established that *stimulated emission* was demanded for statistical mechanical consistency, and found formulæ determining the relative rates of absorption, spontaneous emission, and stimulated emission. (See Feynman [41, I.42–5].)
Consider a system consisting of non-interacting atoms weakly coupled to photons (electromagnetic radiation), in equilibrium at temperature $k_B T = 1/\beta$. The atoms have two energy eigenstates E_1 and E_2 with average populations N_1 and N_2; the relative population is given as usual

by the Boltzmann distribution

$$\left\langle \frac{N_2}{N_1} \right\rangle = e^{-\beta(E_2 - E_1)}. \quad (7.83)$$

The energy density in the electromagnetic field is given by the Planck distribution (eqn 7.67):

$$u(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}. \quad (7.84)$$

An atom in the ground state will absorb electromagnetic energy from the photons at a rate that is proportional to the energy density $u(\omega)$ at the excitation energy $\hbar\omega = E_2 - E_1$. Let us define this absorption rate per atom to be $2\pi B u(\omega)$.[45] An atom in the excited state E_2, with no electromagnetic stimulation, will decay into the ground state with a rate A, emitting a photon. Einstein noted that neither A nor B should depend upon temperature.

Einstein argued that using just these two rates would lead to an inconsistency.

(a) *Compute the long-time average ratio N_2/N_1 assuming only absorption and spontaneous emission. Even in the limit of weak coupling (small A and B), show that this equation is incompatible with the statistical distributions 7.83 and 7.84.* (Hint: Write a formula for dN_1/dt, and set it equal to zero. Is the resulting B/A temperature independent?)

Einstein fixed this by introducing stimulated emission. Roughly speaking, an atom experiencing an oscillating electromagnetic field is more likely to emit photons into that mode. Einstein found that the stimulated emission rate had to be a constant $2\pi B'$ times the energy density $u(\omega)$.

(b) *Write the equation for dN_1/dt, including absorption (a negative term) and spontaneous and stimulated emission from the population N_2. Assuming equilibrium, use this equation and eqns 7.83 and 7.84 to solve for B, and B' in terms of A.*   These are generally termed the Einstein A and B coefficients.

Let us express the stimulated emission rate in terms of the number of excited photons per mode (see Exercise 7.9(a) for an alternative derivation).

(c) *Show that the rate of decay of excited atoms $A + 2\pi B' u(\omega)$ is enhanced by a factor of $\langle n \rangle + 1$*

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[45]The literature uses $u_{\text{cycles}}(f)$ where $f = \omega/2\pi$ is in cycles per second, and has no factor of 2π. Since $u_{\text{cycles}}(f)\, df = u(\omega)\, d\omega$, the absorption rate $B u_{\text{cycles}}(f) = B u(\omega)\, d\omega/df = 2\pi B u(\omega)$.

over the zero temperature rate, where $\langle n \rangle$ is the expected number of photons in a mode at frequency $\hbar\omega = E_2 - E_1$.

(7.9) **Bosons are gregarious: superfluids and lasers.** (Quantum, Optics, Atomic physics) ③
Adding a particle to a Bose condensate. Suppose we have a non-interacting system of bosonic atoms in a box with single-particle eigenstates ψ_n. Suppose the system begins in a Bose-condensed state with all N bosons in a state ψ_0, so

$$\Psi_N^{[0]}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \psi_0(\mathbf{r}_1) \cdots \psi_0(\mathbf{r}_N). \quad (7.85)$$

Suppose a new particle is gently injected into the system, into an equal superposition of the M lowest single-particle states.[46] That is, if it were injected into an empty box, it would start in state

$$\phi(\mathbf{r}_{N+1}) = \frac{1}{\sqrt{M}}\big(\psi_0(\mathbf{r}_{N+1}) + \psi_1(\mathbf{r}_{N+1})$$
$$+ \ldots + \psi_{M-1}(\mathbf{r}_{N+1})\big). \quad (7.86)$$

The state $\Phi(\mathbf{r}_1, \ldots \mathbf{r}_{N+1})$ after the particle is inserted into the non-interacting Bose condensate is given by symmetrizing the product function $\Psi_N^{[0]}(\mathbf{r}_1, \ldots, \mathbf{r}_N)\phi(\mathbf{r}_{N+1})$ (eqn 7.30).
(a) *Calculate the symmetrized initial state of the system with the injected particle. Show that the ratio of the probability that the new boson enters the ground state (ψ_0) is enhanced over that of its entering an empty state (ψ_m for $0 < m < M$) by a factor $N + 1$. (Hint: First do it for $N = 1$.)*
So, if a macroscopic number of bosons are in one single-particle eigenstate, a new particle will be much more likely to add itself to this state than to any of the microscopically populated states. Notice that nothing in your analysis depended on ψ_0 being the lowest energy state. If we started with a macroscopic number of particles in a single-particle state with wavevector $\mathbf{k}$ (that is, a superfluid with a supercurrent in direction $\mathbf{k}$), new added particles, or particles scattered by inhomogeneities, will preferentially enter into that state. This is an alternative approach to understanding the persistence of supercurrents,

complementary to the topological approach (Exercise 9.7).
Adding a photon to a laser beam. This 'chummy' behavior between bosons is also the principle behind lasers.[47] A laser has N photons in a particular mode. An atom in an excited state emits a photon. The photon it emits will prefer to join the laser beam than to go off into one of its other available modes by a factor $N+1$. Here the N represents *stimulated emission*, where the existing electromagnetic field pulls out the energy from the excited atom, and the $+1$ represents *spontaneous emission* which occurs even in the absence of existing photons.
Imagine a single atom in a state with excitation energy energy E and decay rate Γ, in a cubical box of volume V with periodic boundary conditions for the photons. By the energy-time uncertainty principle, $\langle \Delta E \, \Delta t \rangle \geq \hbar/2$, the energy of the atom will be uncertain by an amount $\Delta E \propto \hbar\Gamma$. Assume for simplicity that, in a cubical box without pre-existing photons, the atom would decay at an equal rate into any mode in the range $E - \hbar\Gamma/2 < \hbar\omega < E + \hbar\Gamma/2$.
(b) *Assuming a large box and a small decay rate Γ, find a formula for the number of modes M per unit volume V competing for the photon emitted from our atom. Evaluate your formula for a laser with wavelength $\lambda = 619\,\text{nm}$ and the linewidth $\Gamma = 10^4\,\text{rad/s}$. (Hint: Use the density of states, eqn 7.65.)*
Assume the laser is already in operation, so there are N photons in the volume V of the lasing material, all in one plane-wave state (a *single-mode laser*).
(c) *Using your result from part (a), give a formula for the number of photons per unit volume N/V there must be in the lasing mode for the atom to have 50% likelihood of emitting into that mode.*
The main task in setting up a laser is providing a population of excited atoms. Amplification can occur if there is a *population inversion*, where the number of excited atoms is larger than the number of atoms in the lower energy state (definitely a non-equilibrium condition). This is made possible by *pumping* atoms into the excited state by

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[46]For free particles in a cubical box of volume V, injecting a particle at the origin $\phi(\mathbf{r}) = \delta(\mathbf{r})$ would be a superposition of *all* plane-wave states of equal weight, $\delta(\mathbf{r}) = (1/V)\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}}$. (In second-quantized notation, $a^\dagger(\mathbf{x} = 0) = (1/V)\sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger$.) We 'gently' add a particle at the origin by restricting this sum to low-energy states. This is how quantum tunneling into condensed states (say, in Josephson junctions or scanning tunneling microscopes) is usually modeled.
[47]Laser is an acronym for 'light amplification by the stimulated emission of radiation'.

using one or two other single-particle eigenstates.

(7.10) **Crystal defects.** (Quantum, Condensed matter) ②

A defect in a crystal has one on-center configuration with energy zero, and M off-center configurations with energy ϵ, with no significant quantum tunneling between the states. The Hamiltonian can be approximated by the $(M+1) \times (M+1)$ matrix

$$\mathcal{H} = \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 0 & \epsilon & 0 & \cdots \\ 0 & 0 & \epsilon & \cdots \end{pmatrix}. \qquad (7.87)$$

There are N defects in the crystal, which can be assumed stuck in position (and hence distinguishable) and assumed not to interact with one another.
Write the canonical partition function $Z(T)$, the mean energy $E(T)$, the fluctuations in the energy, the entropy $S(T)$, and the specific heat $C(T)$ as a function of temperature. Plot the specific heat per defect $C(T)/N$ for $M = 6$; set the unit of energy equal to ϵ and $k_B = 1$ for your plot. Derive a simple relation between M and the change in entropy between zero and infinite temperature. Check this relation using your formula for $S(T)$.
The bump in the specific heat for a two-state system is called a *Schottky anomaly*.

(7.11) **Phonons on a string.** (Quantum, Condensed matter) ③

A continuum string of length L with mass per unit length μ under tension τ has a vertical, transverse displacement $u(x,t)$. The kinetic energy density is $(\mu/2)(\partial u/\partial t)^2$ and the potential energy density is $(\tau/2)(\partial u/\partial x)^2$. The string has fixed boundary conditions at $x = 0$ and $x = L$.
Write the kinetic energy and the potential energy in new variables, changing from $u(x,t)$ to normal modes $q_k(t)$ with $u(x,t) = \sum_n q_{k_n}(t) \sin(k_n x)$, $k_n = n\pi/L$. Show in these variables that the system is a sum of decoupled harmonic oscillators. Calculate the density of normal modes per unit frequency $g(\omega)$ for a long string L. Calculate the specific heat of the string $c(T)$ per unit length in the limit $L \to \infty$, treating the oscillators quantum mechanically. What is the specific heat of the classical string?

Almost the same calculation, in three dimensions, gives the low-temperature specific heat of crystals.

(7.12) **Semiconductors.** (Quantum, Condensed matter) ③

Let us consider a caricature model of a doped semiconductor [9, chapter 28]. Consider a crystal of phosphorous-doped silicon, with $N - M$ atoms of silicon and M atoms of phosphorous. Each silicon atom contributes one electron to the system, and has two states at energies $\pm\Delta/2$, where $\Delta = 1.16\,\text{eV}$ is the energy gap. Each phosphorous atom contributes *two* electrons and two states, one at $-\Delta/2$ and the other at $\Delta/2 - \epsilon$, where $\epsilon = 0.044\,\text{eV}$ is much smaller than the gap.[48] (Our model ignores the quantum mechanical hopping between atoms that broadens the levels at $\pm\Delta/2$ into the conduction band and the valence band. It also ignores spin and chemistry; each silicon really contributes four electrons and four levels, and each phosphorous five electrons and four levels.) To summarize, our system has $N + M$ spinless electrons (maximum of one electron per state), N valence band states at energy $-\Delta/2$, M impurity band states at energy $\Delta/2 - \epsilon$, and $N - M$ conduction band states at energy $\Delta/2$.

(a) *Derive a formula for the number of electrons as a function of temperature T and chemical potential μ for the energy levels of our system.*

(b) *What is the limiting occupation probability for the states as $T \to \infty$, where entropy is maximized and all states are equally likely? Using this, find a formula for $\mu(T)$ valid at large T, not involving Δ or ϵ.*

(c) *Draw an energy level diagram showing the filled and empty states at $T = 0$. Find a formula for $\mu(T)$ in the low-temperature limit $T \to 0$, not involving the variable T.* (Hint: Balance the number of holes in the impurity band with the number of electrons in the conduction band. Why can you ignore the valence band?)

(d) *In a one centimeter cubed sample, there are $M = 10^{16}$ phosphorous atoms; silicon has about $N = 5 \times 10^{22}$ atoms per cubic centimeter. Find μ at room temperature $(1/40\,\text{eV})$ from the formula you derived in part (a). (Probably trying various μ is easiest; set up a program on your calculator*

[48]The phosphorous atom is neutral when both of its states are filled; the upper state can be thought of as an electron bound to a phosphorous positive ion. The energy shift ϵ represents the Coulomb attraction of the electron to the phosphorous ion; it is small because the dielectric constant is large semiconductor [9, chapter 28].

or computer.) At this temperature, what fraction of the phosphorous atoms are ionized (have their upper energy state empty)? What is the density of holes (empty states at energy $-\Delta/2$)?

Phosphorous is an *electron donor*, and our sample is doped n-type, since the dominant carriers are electrons; p-type semiconductors are doped with holes.

(7.13) **Bose condensation in a band.** (Atomic physics, Quantum) ②

The density of single-particle eigenstates $g(E)$ of a system of non-interacting bosons forms a band; the eigenenergies are confined to a range $E_{\min} < E < E_{\max}$, so $g(E)$ is non-zero in this range and zero otherwise. The system is filled with a finite density of bosons. Which of the following is necessary for the system to undergo Bose condensation at low temperatures?

(a) $g(E)/(e^{\beta(E-E_{\min})}+1)$ *is finite as* $E \to E_{\min}^{-}$.
(b) $g(E)/(e^{\beta(E-E_{\min})} - 1)$ *is finite as* $E \to E_{\min}^{-}$.
(c) $E_{\min} \geq 0$.
(d) $\int_{E_{\min}}^{E} g(E')/(E' - E_{\min})\,\mathrm{d}E'$ *is a convergent integral at the lower limit* $E_{\min}$.
(e) *Bose condensation cannot occur in a system whose states are confined to an energy band.*

(7.14) **Bose condensation: the experiment.** (Quantum, Atomic physics) ④

Anderson, Ensher, Matthews, Wieman and Cornell in 1995 were able to get a dilute gas of rubidium-87 atoms to Bose condense [4].

(a) *Is rubidium-87 (37 protons and electrons, 50 neutrons) a boson or a fermion?*

(b) *At their quoted maximum number density of* $2.5 \times 10^{12}/\mathrm{cm}^3$, *at what temperature* T_c^{predict} *do you expect the onset of Bose condensation in free space? They claim that they found Bose condensation starting at a temperature of* $T_c^{\mathrm{measured}} = 170\,\mathrm{nK}$. *Is that above or below your estimate?* (Useful constants: $h = 6.6262 \times 10^{-27}\,\mathrm{erg\,s}$, $m_n \sim m_p = 1.6726 \times 10^{-24}\,\mathrm{g}$, $k_B = 1.3807 \times 10^{-16}\,\mathrm{erg/K}$.)

The trap had an effective potential energy that was harmonic in the three directions, but anisotropic with cylindrical symmetry. The frequency along the cylindrical axis was $f_0 = 120\,\mathrm{Hz}$ so $\omega_0 \sim 750\,\mathrm{Hz}$, and the two other frequencies were smaller by a factor of $\sqrt{8}$: $\omega_1 \sim 265\,\mathrm{Hz}$. The Bose condensation was observed by abruptly removing the trap potential,[49] and

letting the gas atoms spread out; the spreading cloud was imaged 60 ms later by shining a laser on them and using a CCD to image the shadow.
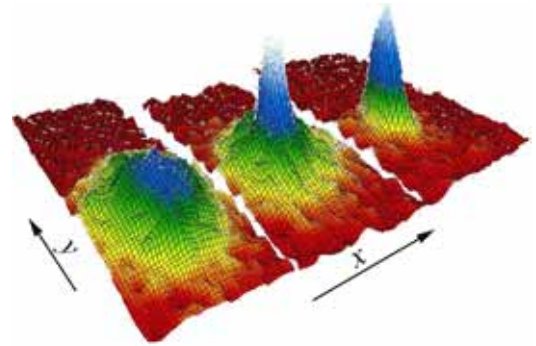

Fig. 7.16 Bose–Einstein condensation at 400, 200, and 50 nano-Kelvin. The pictures are spatial distributions 60 ms after the potential is removed; the field of view of each image is $200\,\mu\mathrm{m} \times 270\,\mu\mathrm{m}$. The left picture is roughly spherically symmetric, and is taken before Bose condensation; the middle has an elliptical Bose condensate superimposed on the spherical thermal background; the right picture is nearly pure condensate. From [4]. Thanks to the Physics 2000 team for permission to reprint this figure.

For your convenience, the ground state of a particle of mass m in a one-dimensional harmonic oscillator with frequency ω is $\psi_0(x) = (m\omega/\pi\hbar)^{1/4}\,e^{-m\omega x^2/2\hbar}$, and the momentum-space wavefunction is $\tilde{\psi}_0(p) = (1/(\pi m\hbar\omega))^{1/4}\,e^{-p^2/2m\hbar\omega}$. In this 3D problem the solution is a product of the corresponding Gaussians along the three axes.

(c) *Will the momentum distribution be broader along the high-frequency axis (ω_0) or one of the low-frequency axes (ω_1)? Assume that you may ignore the small width in the initial position distribution, and that the positions in Fig. 7.16 reflect the velocity distribution times the time elapsed. Which axis, x or y in Fig. 7.16, corresponds to the high-frequency cylinder axis? What anisotropy does one expect in the momentum distribution at high temperatures (classical statistical mechanics)?*

Their Bose condensation is not in free space; the atoms are in a harmonic oscillator potential. In the calculation in free space, we approximated

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[49] Actually, they first slowly reduced it by a factor of 75 and then abruptly reduced it from there; let us ignore that complication.

the quantum states as a continuum density of states $g(E)$. That is only sensible if $k_B T$ is large compared to the level spacing near the ground state.

(d) *Compare $\hbar\omega$ to $k_B T$ at the Bose condensation point T_c^{measured} in their experiment. ($\hbar = 1.05459 \times 10^{-27}\,\text{erg s}$; $k_B = 1.3807 \times 10^{-16}\,\text{erg/K}$.)*

For bosons in a one-dimensional harmonic oscillator of frequency ω_0, it is clear that $g(E) = 1/(\hbar\omega_0)$; the number of states in a small range ΔE is the number of $\hbar\omega_0$s it contains.

(e) *Compute the density of single-particle eigenstates*

$$g(E) = \int_0^\infty \mathrm{d}\varepsilon_1\,\mathrm{d}\varepsilon_2\,\mathrm{d}\varepsilon_3\,g_1(\varepsilon_1)g_2(\varepsilon_2)g_3(\varepsilon_3)$$
$$\times\,\delta\left(E - (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)\right) \quad (7.88)$$

for a three-dimensional harmonic oscillator, with one frequency ω_0 and two of frequency ω_1. Show that it is equal to $1/\delta E$ times the number of states in $\vec{\varepsilon}$-space between energies E and $E + \delta E$. Is the thickness of this triangular slab equal to δE?

Their experiment has $N = 2 \times 10^4$ atoms in the trap as it condenses.

(f) *By working in analogy with the calculation in free space, find the maximum number of atoms that can occupy the three-dimensional harmonic oscillator potential in part (e) without Bose condensation at temperature T. (You will want to know $\int_0^\infty z^2/(\mathrm{e}^z - 1)\,\mathrm{d}z = 2\,\zeta(3) = 2.40411$.) According to your calculation, at what temperature T_c^{HO} should the real experimental trap have Bose condensed?*

(7.15) **The photon-dominated Universe.**[50] (Astrophysics) ③

The Universe is currently not in equilibrium. However, in the microwave frequency range it is filled with radiation that is precisely described by a Planck distribution at $2.725 \pm 0.001\,\text{K}$ (Fig. 7.17).

The microwave background radiation is a window back to the *decoupling time*, about $380\,000$ years after the Big Bang,[51] when the temperature dropped low enough for the protons and electrons to combine into hydrogen atoms. Light does not travel far in ionized gases; it accelerates

the charges and scatters from them. Hence, before this time, our Universe was very close to an equilibrium soup of electrons, nuclei, and photons.[52] The neutral atoms after this time were transparent enough that almost all of the photons traveled for the next 13 billion years directly into our detectors.

These photons in the meantime have greatly increased in wavelength. This is due to the subsequent expansion of the Universe. The initial Planck distribution of photons changed both because of the Doppler effect (a red-shift because the distant gas that emitted the photon appears to be moving away from us) and because the photons are diluted into a larger volume. The Doppler shift both reduces the photon energy and squeezes the overall frequency range of the photons (increasing the number of photons per unit frequency).
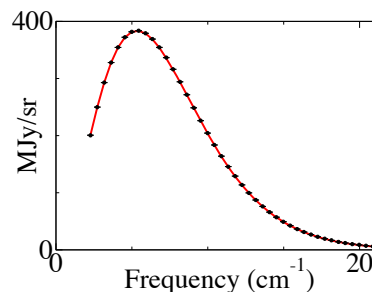

Fig. 7.17 Planck microwave background radiation, as measured by the COBE satellite [42]. The units on the axes are those used in the original paper: inverse centimeters instead of frequency (related by the speed of light) on the horizontal axis and Mega-Janskys/steridian for the vertical axis (1 MegaJansky $= 10^{-20}\,\text{W}\,\text{m}^{-2}\,\text{Hz}^{-1}$). The curve is the Planck distribution at $2.725\,\text{K}$.

One might ask why the current microwave background radiation is thermal (Fig. 7.17), and why it is at such a low temperature . . .

(a) *If the side of the box L and the wavelengths of the photons in the box are all increased by a factor f, what frequency ω' will result from a photon with initial frequency ω? If the original density of photons is $n(\omega)$, what is the density of photons $n'(\omega')$ after the expansion? Show that*

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[50]This exercise was developed with the help of Dale Fixsen and Eanna Flanagan.

[51]Numbers quoted were reasonable estimates when the exercise was written. See also [143] for a history of the early Universe.

[52]The neutrinos fell out of equilibrium somewhat earlier.

Planck's form for the number of photons per unit frequency per unit volume

$$\frac{\omega^2}{\pi^2 c^3 (e^{\hbar \omega / k_B T} - 1)} \qquad (7.89)$$

(from eqn 7.66) is preserved, except for a shift in temperature. What is the new temperature T', in terms of the original temperature T and the expansion factor f?

This is as expected; an adiabatic expansion leaves the system in equilibrium, but at a different temperature.

(b) *How many microwave background photons are there per cubic centimeter? How does this compare to the average atomic density in the Universe ($n_{matter} \sim 2.5 \times 10^{-7}$ atoms/cm^3)? (Note $\int_0^\infty x^2/(e^x - 1) \, dx = 2\zeta(3) \approx 2.404$. Useful constants: $\hbar = 1.05 \times 10^{-27}$ erg s, $c = 3 \times 10^{10}$ cm/s, and $k_B = 1.38 \times 10^{-16}$ erg/K.)*

Cosmologists refer to the current Universe as *photon dominated*, because there are currently many more photons than atoms.

We can also roughly estimate the relative contributions of photons and atoms to other properties of the Universe.

(c) *Calculate formulæ for the entropy S, the internal energy E, and the pressure P for the photon gas in a volume V and temperature T. For simplicity, write them in terms of the Stefan–Boltzmann constant[53] $\sigma = \pi^2 k_B^4/60\hbar^3 c^2$. Ignore the zero-point energy in the photon modes[54] (which otherwise would make the energy and pressure infinite, even at zero temperature).*

(Hint: You will want to use the grand free energy Φ for the photons. For your information, $\int_0^\infty x^3/(e^x - 1) \, dx = \pi^4/15 = -3 \int_0^\infty x^2 \log(1 - e^{-x}) \, dx$, where the last integral can be integrated by parts to get the first integral.)

(d) *Calculate formulæ for the entropy, mass-energy[55] density, and pressure for an ideal gas of hydrogen atoms at density n_{matter} and the same volume and temperature. Can we ignore quantum mechanics for the atomic gas? Assemble your results from parts (c) and (d) into a table comparing photons to atoms, with four columns giving the two analytical formulæ and*

then numerical values for $V = 1$ cm^3, the current microwave background temperature, and the current atom density. Which are dominated by photons? By atoms? (Hint: You will want to use the Helmholtz free energy A for the atoms. More useful constants: $\sigma = 5.67 \times 10^{-5}$ erg cm^{-2} K^{-4} s^{-1}, and $m_H \approx m_p = 1.673 \times 10^{-24}$ g.)

Before the decoupling time, the coupled light-and-matter soup satisfied a wave eqn [60]:

$$\rho \frac{\partial^2 \Theta}{\partial t^2} = B\nabla^2\theta. \qquad (7.90)$$

Here Θ represents the local temperature fluctuation $\Delta T/T$. The constant ρ is the sum of three contributions: the matter density, the photon energy density E/V divided by c^2, and a contribution P/c^2 due to the photon pressure P (this comes in as a component in the stress-energy tensor in general relativity).

(e) *Show that the sum of the two photon contributions to the mass density is proportional to $E/(c^2V)$. What is the constant of proportionality?*

The constant B in our wave eqn 7.90 is the bulk modulus: $B = -V(\partial P/\partial V)|_S$.[56] At decoupling, the dominant contribution to the pressure (and to B) comes from the photon gas.

(f) *Write P as a function of S and V (eliminating T and E), and calculate B for the photon gas. Show that it is proportional to the photon energy density E/V. What is the constant of proportionality?*

Let R be the ratio of ρ_{matter} to the sum of the photon contributions to ρ from part (e).

(g) *What is the speed of sound in the Universe before decoupling, as a function of R and c?* (Hint: Compare with eqn 10.78 in Exercise 10.1 as a check for your answer to parts (e)–(g).)

Exercise 10.1 and the ripples-in-fluids animation at [137] show how this wave equation explains much of the observed fluctuations in the microwave background radiation.

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[53]The Stefan–Boltzmann law says that a black body radiates power σT^4 per unit area, where σ is the Stefan–Boltzmann constant; see Exercise 7.7.

[54]Treat them as bosons (eqn 7.42) with $\mu = 0$ rather than as harmonic oscillators (eqn 7.23).

[55]That is, be sure to include the mc^2 for the hydrogen atoms into their contribution to the energy density.

[56]The fact that one must compress adiabatically (constant S) and not isothermally (constant T) is subtle but important (Isaac Newton got it wrong). Sound waves happen too fast for the temperature to equilibrate. Indeed, we can assume at reasonably long wavelengths that there is no heat transport (hence we may use the adiabatic modulus). All this is true both for air and for early-Universe photon gasses.

(7.16) **White dwarfs, neutron stars, and black holes.** (Astrophysics, Quantum) ③

As the energy sources in large stars are consumed, and the temperature approaches zero, the final state is determined by the competition between gravity and the chemical or nuclear energy needed to compress the material.

A simplified model of ordinary stellar matter is a Fermi sea of non-interacting electrons, with enough nuclei to balance the charge. Let us model a white dwarf (or black dwarf, since we assume zero temperature) as a uniform density of He^4 nuclei and a compensating uniform density of electrons. Assume Newtonian gravity. Assume the chemical energy is given solely by the energy of a gas of non-interacting electrons (filling the levels to the Fermi energy).

(a) *Assuming non-relativistic electrons, calculate the energy of a sphere with N zero-temperature non-interacting electrons and radius R.*[57] *Calculate the Newtonian gravitational energy of a sphere of He^4 nuclei of equal and opposite charge density. At what radius is the total energy minimized?*

A more detailed version of this model was studied by Chandrasekhar and others as a model for white dwarf stars. Useful numbers: $m_p = 1.6726 \times 10^{-24}$ g, $m_n = 1.6749 \times 10^{-24}$ g, $m_e = 9.1095 \times 10^{-28}$ g, $\hbar = 1.05459 \times 10^{-27}$ erg s, $G = 6.672 \times 10^{-8}$ cm^3/(g s^2), $1\,\mathrm{eV} = 1.60219 \times 10^{-12}$ erg, $k_B = 1.3807 \times 10^{-16}$ erg/K, and $c = 3 \times 10^{10}$ cm/s.

(b) *Using the non-relativistic model in part (a), calculate the Fermi energy of the electrons in a white dwarf star of the mass of the Sun, 2×10^{33} g, assuming that it is composed of helium.*
(i) *Compare it to a typical chemical binding energy of an atom. Are we justified in ignoring the electron–electron and electron–nuclear interactions (i.e., chemistry)?* (ii) *Compare it to the temperature inside the star, say 10^7 K. Are we justified in assuming that the electron gas is degenerate (roughly zero temperature)?* (iii) *Compare it to the mass of the electron. Are we roughly justified in using a non-relativistic theory?* (iv) *Compare it to the mass difference between a proton and a neutron.*

The electrons in large white dwarf stars are relativistic. This leads to an energy which grows more slowly with radius, and eventually to an upper bound on their mass.

(c) *Assuming extremely relativistic electrons with $\varepsilon = pc$, calculate the energy of a sphere of non-interacting electrons. Notice that this energy cannot balance against the gravitational energy of the nuclei except for a special value of the mass, M_0. Calculate M_0. How does your M_0 compare with the mass of the Sun, above?*

A star with mass larger than M_0 continues to shrink as it cools. The electrons (see (iv) in part (b) above) combine with the protons, staying at a constant density as the star shrinks into a ball of almost pure neutrons (a *neutron star*, often forming a *pulsar* because of trapped magnetic flux). Recent speculations [107] suggest that the 'neutronium' will further transform into a kind of quark soup with many strange quarks, forming a transparent insulating material.

For an even higher mass, the Fermi repulsion between quarks cannot survive the gravitational pressure (the quarks become relativistic), and the star collapses into a black hole. At these masses, general relativity is important, going beyond the purview of this text. But the basic competition, between degeneracy pressure and gravity, is the same.

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[57]You may assume that the single-particle eigenstates have the same energies and **k**-space density in a sphere of volume V as they do for a cube of volume V; just like fixed versus periodic boundary conditions, the boundary does not matter to bulk properties.