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 $\rho(P,Q)$ 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
Quantum systems with many particles have wavefunctions that are functions of all the positions of all the particles (or, in momentum space, all the momenta of all the particles).

So, for example, if \(|V\rangle\) is a vertically polarized photon, and \(|H\rangle\) is a horizontally polarized photon, then the superposition \((1/\sqrt{2})(|V\rangle + |H\rangle)\) is a diagonally polarized photon, while the unpolarized photon is a mixture of half \(|V\rangle\) and half \(|H\rangle\), described by the density matrix \(\frac{1}{2}(|V\rangle\langle V| + |H\rangle\langle H|)\). The superposition is in both states, the mixture is in perhaps one or perhaps the other (see Exercise 7.6).

already has probability densities; even for systems in a definite state \(\Psi(Q)\) the probability is spread among different configurations \(\Psi(Q)|\Psi(Q)\rangle |^2\) (or momenta \(\Psi(P)|\Psi(P)\rangle |^2\)). 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 \(\Psi_n(Q)\). 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 \(A\). In a particular state \(\Psi_n\), the quantum expectation is

\[ \langle A\rangle_{\text{pure}} = \int \Psi_n^*(Q) A \Psi_n(Q) d^3NQ. \]  \hspace{1cm} (7.1)

So, in the ensemble the expectation is

\[ \langle A\rangle = \sum_n p_n \int \Psi_n^*(Q) A \Psi_n(Q) d^3NQ. \]  \hspace{1cm} (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 \(\Psi_n\) 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 \(\exp(-\beta(E_n - N_n\mu))/\Xi\) (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 \(\Psi_n\), 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 \(\Psi_n\). Instead, we will write the ensemble average (eqn 7.2) in terms of \(A\) and an operator \(\rho\), 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\(^3\)

\[ \langle A\rangle = \sum_n p_n \langle \Psi_n | A | \Psi_n \rangle. \]  \hspace{1cm} (7.3)

Pick any complete orthonormal basis \(\Phi_\alpha\). Then the identity operator is

\[ 1 = \sum_\alpha |\Phi_\alpha\rangle \langle \Phi_\alpha|. \]  \hspace{1cm} (7.4)
and, substituting the identity (eqn 7.4) into eqn 7.3 we find

\[
\begin{align*}
\langle A \rangle &= \sum_n p_n \langle \Psi_n | \left( \sum_\alpha | \Phi_\alpha \rangle \langle \Phi_\alpha | \right) A | \Psi_n \rangle \\
&= \sum_n p_n \sum_\alpha \langle \Phi_\alpha | A | \Psi_n \rangle \langle \Psi_n | \Phi_\alpha \rangle \\
&= \sum_\alpha \langle \Phi_\alpha | A | \left( \sum_n p_n | \Psi_n \rangle \langle \Psi_n | \right) | \Phi_\alpha \rangle \\
&= \text{Tr}(A \rho), \quad (7.5)
\end{align*}
\]

where

\[
\rho = \left( \sum_n p_n | \Psi_n \rangle \langle \Psi_n | \right) \quad (7.6)
\]

is the \textit{density matrix}.

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 \( \Phi \), has \( \rho_{\text{pure}} = | \Phi \rangle \langle \Phi | \). In the position basis \( | Q \rangle \), this pure-state density matrix has matrix elements

\[
\rho_{\text{pure}}(Q, Q') = \langle Q | \rho_{\text{pure}} | Q' \rangle = \Phi^\dagger(Q') \Phi(Q).
\]

Thus in particular we can reconstruct 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:

\[
\rho_{\text{pure}}^2 = | \Phi \rangle \langle \Phi | \Phi \rangle \langle \Phi | = | \Phi \rangle \langle \Phi | = \rho_{\text{pure}}.
\]

**Normalization.** The trace of a pure-state density matrix \( \text{Tr}\rho_{\text{pure}} = 1 \), since we can pick an orthonormal basis with our wavefunction \( \Phi \) 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:

\[
\text{Tr} \rho = \text{Tr} \left( \sum_n p_n | \Psi_n \rangle \langle \Psi_n | \right) = \sum_n p_n \text{Tr} \left( | \Psi_n \rangle \langle \Psi_n | \right) = \sum_n p_n = 1. \quad (7.8)
\]

**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 \( \rho_{\text{canon}} \) is diagonal in the energy basis:

\[
\rho_{\text{canon}} = \frac{\sum_n \exp(-\beta E_n) | E_n \rangle \langle E_n |}{Z} \quad (7.9)
\]

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

\[
f(\rho) = \begin{pmatrix} f(\rho_{11}) & 0 & \ldots \\ 0 & f(\rho_{22}) & \ldots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (7.10)
\]

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

\[\text{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 \( \text{Tr}(M) = \sum_\alpha | \Phi_\alpha \rangle \langle M | \Phi_\alpha \rangle \).} \]

\[\text{In particular, since \( \Phi \) is normalized \( \Phi^\dagger(Q') \Phi(Q) = 1 \), and thus \( \Phi(Q) = \frac{\rho(Q, Q')}{\sqrt{\int dQ' | \rho(Q, Q') |^2} \}} \]

\[\text{up to the single phase \( \Phi(Q) = \Phi^\star(Q) \) for any point \( Q' \).} \]

\[\text{Notice that the states \( \Psi_n \) in a general mixture need not be eigenstates or even orthogonal.} \]

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

\[\text{At the end, change back to the original basis. This procedure also defines \( \log M \) (eqn 7.14).} \]
by the trace
\[ Z = \sum_n \exp(-\beta E_n) = \sum_n \langle E_n | \exp(-\beta \mathcal{H}) | E_n \rangle = \text{Tr}(\exp(-\beta \mathcal{H})). \] (7.11)

Second, the numerator
\[ \sum_n |E_n\rangle \exp(-\beta E_n) \langle E_n| = \sum_n |E_n\rangle \exp(-\beta \mathcal{H}) \langle E_n| = \exp(-\beta \mathcal{H}), \] since \( \mathcal{H} \) (and thus \( \exp(-\beta \mathcal{H}) \)) is diagonal in the energy basis. Hence
\[ \rho_{\text{canon}} = \frac{\exp(-\beta \mathcal{H})}{\text{Tr}(\exp(-\beta \mathcal{H}))}. \] (7.13)

**Entropy.** The entropy for a general density matrix will be
\[ S = -k_B \text{Tr}(\rho \log \rho). \] (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: \(^8\)
\[ \frac{\partial \rho}{\partial t} = \sum_n p_n \left( \frac{\partial |\Psi_n\rangle}{\partial t} \langle \Psi_n| + |\Psi_n\rangle \frac{\partial \langle \Psi_n|}{\partial t} \right). \] (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 \( \Psi_n^* (Q) \):
\[ \frac{\partial \Psi_n^*}{\partial t} = \left( \frac{\partial \Psi_n}{\partial t} \right)^* = i\hbar^{-1} \mathcal{H} \Psi_n, \] (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)

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

\[^8\] The \( p_n \) are the probability that one started in the state \( \Psi_n \), and thus manifestly do not change with time.

\[^9\] 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.