Example: Paramagnetism

Introduction

• *Idea:* A paramagnetic material is one in which each atom has an intrinsic magnetic dipole moment $\vec{\mu}$; when placed in an external magnetic field $\vec{B}$, the dipole moments align themselves with $\vec{B}$ and enhance it. We want to find the mean magnetization $\bar{M}$ and the susceptibility $\chi = \partial\bar{M}/\partial B|_{T,N}$ as functions of T.

• *Hamiltonian:* For N atoms with magnetic dipole moments μ_i, H is of the form $H_0 - \sum_i \vec{\mu}_i \cdot \vec{B}$, where H_0 is the contribution from phase space degrees of freedom other than the orientation of the μ_i. For example, for fluid particles H_0 might be of the form $\sum_i p_i^2/2m + \sum_{i<j} v(r_{ij})$, while for atoms in a solid lattice it might contain an oscillator-like potential energy; the specific form of this term will not affect our calculation of $\bar{M}$ and χ. Interactions among the μ_i will be considered later, when we discuss ferromagnetism.

Microcanonical Ensemble

• *Quantum system:* For each of the N atoms in the system, the component of the magnetic moment along the direction of the magnetic field can have one of two values $\mu_z = \pm\mu$, with corresponding energies $\epsilon = \mp\mu B$. If $n_\pm$ is the number of atoms with $\mu_z = \pm\mu$ and $n := n_+ - n_-$, then $n_\pm = \frac{1}{2}\,(N \mp n)$ and the total energy of the system is $E_n = -n\mu B$, with $n = -N$, ..., N. The value of E identifies a macrostate, and the multiplicity (number of corresponding microstates) is the number of ways in which $n_\pm$ atoms can be chosen out of N, or

$$\Omega(n) = \binom{N}{n_\pm} = \frac{N!}{[\frac{1}{2}(N+n)]!\,[\frac{1}{2}(N-n)]!}\ .$$

• *Temperature:* The function $\Omega(n)$ has a convex shape, with a maximum at $n = 0$ or $n_+ = n_- = N/2$, so the temperature $k_{\text{B}}T := (\partial \ln\Omega/\partial E)^{-1}$ is negative for $n > 0$. [⋆ How does a system with $T < 0$ behave?]

• *Classical system:* In the classical case, to find the multiplicity we need to calculate the volume $\Omega(E,\Delta)$ of the region of the phase space of N dipoles in which $H(q,p) \in [E, E+\Delta]$, and then calculate $g(E) = \partial\Omega/\partial E$.

Classical Canonical Ensemble

• *Partition function:* Assume again that the system consists of N atoms in a solid lattice, and that the magnetic field is of the form $\vec{B} = B\,\hat{z}$. Integrating over all translational and orientational degrees of freedom,

$$\begin{aligned} Z_B &= \Big(\frac{1}{h^{3N}} \int \mathrm{d}^{3N}r \int \mathrm{d}^{3N}p\, \mathrm{e}^{-\beta H_0}\Big) \oint \mathrm{d}^N\Omega\ \mathrm{e}^{\beta\,\Sigma_i\,\mu_i B\cos\theta_i} \\ &= Z_0 \Big(\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta\,\sin\theta\,\mathrm{e}^{\beta\mu_i B\cos\theta}\Big)^N = (2\pi)^N\,Z_0\,\Big(\frac{2\sinh\beta\mu B}{\beta\mu B}\Big)^N, \end{aligned}$$

where Z_0 is the part of the partition function that does not include the integration over orientations.

• *Magnetization:* From the general relationships, we get for the free energy

$$F = -k_{\text{B}}T\ln Z_B = -k_{\text{B}}T(\ln Z_0 + N\ln 4\pi) - Nk_{\text{B}}T\ln\frac{\sinh\beta\mu B}{\beta\mu B}\ .$$

To find the magnetization and susceptibility, we use the fundamental thermodynamic identity in the form

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N - \vec{M}\cdot\mathrm{d}\vec{B} + ...$$

and, if we define $x := \beta\mu B = \mu B/k_{\text{B}}T$, we get (notice that Z_0 has dropped out of these results; ⋆ plot $\bar{M}$)

$$\bar{M} = -\frac{\partial F}{\partial B}\Big|_{T,V,N} = N\mu\Big(\coth x - \frac{1}{x}\Big)\ , \qquad \chi = \frac{\partial\bar{M}}{\partial B}\Big|_{T,V,N} = N\mu^2\beta\,\Big(\frac{1}{x^2} - \frac{1}{\sinh^2 x}\Big) > 0\ .$$

• *Low and high-temperature limits:* Writing $\coth x$ in terms of $\mathrm{e}^{\pm x}$ we see that as $T \to 0$ all spins are aligned,

$$\bar{M} \sim N\mu\ , \qquad \chi \to 0\ .$$

(However, since the probability distributions for different spins are independent, the correlations between s_i and s_j, $i \neq j$, still vanish.) Near $x = 0$ we can expand $\coth x$ in (Laurent) power series, and we see that as $T \to \infty$, $\bar{M} \sim \frac{1}{2}\,N\mu\,(\beta\mu B) = \frac{1}{2}\,N\beta\mu^2 B \to 0$, as we would expect.
[⋆ Can a paramagnet in a canonical state have $T < 0$?]

• *Reading:* Pathria & Beale, §§ 3.9 and 3.10.

Example: Harmonic Oscillators

• *Classical microcanonical ensemble:* Consider a system of N identical harmonic oscillators, with

$$H(q,p) = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{m\omega^2}{2}\, q_i^2 \right) ,$$

assumed to be oscillating around distinct fixed positions, with mass m and frequency ω. To study the thermodynamics of this system the first step is to calculate its entropy, for which we need to find the volume of the $H(q,p) = E$ hypersurface in phase space. This is similar to the monatomic ideal gas case, but the surface is now topologically a $(6N-1)$-dimensional sphere in $6N$-dimensional phase space.

• *Classical canonical ensemble:* The canonical case is simpler, and we find (for oscillators at fixed locations)

$$Z_{\rm c}^{\rm cm} = \frac{1}{h^N} \prod_{i=1}^{N} \int_{\mathbb{R}} {\rm d}q_i \, {\rm e}^{-\beta K q_i^2/2} \int_{\mathbb{R}} {\rm d}p_i \, {\rm e}^{-\beta p_i^2/2m} = \frac{1}{h^N} \left(\sqrt{\frac{2\pi}{\beta K}} \sqrt{\frac{2\pi m}{\beta}} \right)^N = \frac{1}{(\beta\hbar\omega)^N} \, .$$

Consistently with the equipartition principle, from this one finds that $\bar{E} = N k_{\rm B} T$, and therefore $C = N k_{\rm B}$.

• *Quantum canonical ensemble:* The integral over classical states (phase space) for each oscillator is replaced by a sum over quantum states. Since for each oscillator the eigenstates $|n\rangle$ of the Hamiltonian are discrete, with corresponding eigenvalues $\epsilon_n = (n + \frac{1}{2})\,\hbar\omega$, and the oscillators don't interact, the partition function is

$$Z_{\rm c}^{\rm qm} = \left(\sum_{n=0}^{\infty} {\rm e}^{-\beta\hbar\omega n} \, {\rm e}^{-\beta\hbar\omega/2} \right)^N = \left({\rm e}^{-\beta\hbar\omega/2} \, \frac{1}{1 - {\rm e}^{-\beta\hbar\omega}} \right)^N = \left(\frac{1}{2\sinh(\beta\hbar\omega/2)} \right)^N .$$

In this case, a short calculation gives $\bar{E} = (N\hbar\omega/2)\coth(\beta\hbar\omega/2)$ and $C \propto [1/\sinh(\beta\hbar\omega/2)]^2$.

• *Reading:* Pathria & Beale, §§ 2.4 (classical phase space), 3.8 (canonical), 4.4 (grand canonical), and 5.3C (quantum treatment); Reif, pp 55-56 (classical phase space) and 251-253 (quantum canonical ensemble).

Example: Systems with Discrete Sets of States

• *Idea:* Systems for which the space of states is finite or discrete are motivated by quantum theory, but if the states can be labelled in a simple way we can discuss their thermodynamics simply by calculating Z as a sum over the states, without using the whole quantum formalism.

• *Simple example:* Consider two identical particles, each of which can have one of three values of the single-particle energy $\epsilon_n = n\,\epsilon_0$ (with $n = 0,\ 1,\ 2$), with degeneracies $g_n = 1,\ 2,\ 4$. There are a total of $1+2+4 = 7$ single-particle states $\psi_{(n,m)}$, labeled by $(n,m) = (0,1);\ (1,1),\ (1,2);\ (2,1),\ (2,2),\ (2,3),$ and $(2,4)$.

• *Boltzmann statistics:* Each of the 2 particles can be in any one of 7 states, so the Boltzmann argument used to solve the Gibbs paradox leads to $\Omega_{\rm B} = 7^2/2! = 24.5$ states for the 2-particle system. What went wrong is that we were assuming that all 7^2 pairs of states are double-counted, while in reality the ones in which the two particles are in the same state are not. In the continuum case this is not a problem because those situations are a subset of zero measure of all 2-particle states; in the discrete case it matters.

• *Correct state counting:* If the two particles can be in the same state, the number of 2-particle states is the number of ways of placing the particles in the 7 single-particle states with repetitions, or $\Omega_{\rm BE} = \binom{7}{2} + 7 = 28$. A two-particle state can be written down by indicating which state each particle is in, for example $\psi_{(1,1;2,3)} = \frac{1}{\sqrt{2}}[\psi_{(1,1)} \otimes \psi_{(2,3)} + \psi_{(2,3)} \otimes \psi_{(1,1)}]$ or $\psi_{(1,2;1,2)} = \psi_{(1,2)} \otimes \psi_{(1,2)}$, or simply giving the number of particles in each single-particle state (n,m), for example $|\{N_{(n,m)}\}\rangle = |0;1,0;0,0,1,0\rangle$ or $|0;0,2;0,0,0,0\rangle$, as in Fock space. (If the two particles cannot be in the same state, then we get instead $\Omega_{\rm FD} = \binom{7}{2} = 21$.)

• *Thermal state:* (Bose-Einstein case) The total energy $E = E_1 + E_2$ of the 2-particle system has 5 possible values $E_i = 0,\ \epsilon_0,\ 2\,\epsilon_0,\ 3\,\epsilon_0,\ 4\,\epsilon_0$, with multiplicities $g_i = 1,\ 2,\ 7,\ 8,\ 10$. (As a consistency check, one can verify that $\sum_i g_i = 28$.) For a thermal state at temperature T, the partition function is then the sum

$$Z = \sum\nolimits_{s=1}^{28} {\rm e}^{-\beta E_s} = \sum\nolimits_{i=1}^{5} g_i \, {\rm e}^{-\beta E_i} = 1 + 2\,{\rm e}^{-\beta\epsilon_0} + 7\,{\rm e}^{-2\beta\epsilon_0} + 8\,{\rm e}^{-3\beta\epsilon_0} + 10\,{\rm e}^{-4\beta\epsilon_0} \, .$$