## 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  $\chi = \partial \bar{M} / \partial B|_{TN}$  as functions of T.

• Hamiltonian: For N atoms with magnetic dipole moments  $\mu_i$ , 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  $\mu_i$ . 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  $\overline{M}$ and  $\chi$ . Interactions among the  $\mu_i$  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  $n_{+}$  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  $k_{\rm B}T := (\partial \ln \Omega / \partial E)^{-1}$  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,

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

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

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

To find the magnetization and susceptibility, we use the fundamental thermodynamic identity in the form  $dF = -S dT - p dV + \mu dN - \vec{M} \cdot d\vec{B} + \dots$ 

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

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

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

 $\bar{M} \sim N \mu \; , \qquad \chi \to 0 \; . \label{eq:main_state}$ 

(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  $T \to \infty$ ,  $\overline{M} \sim \frac{1}{2} N \mu \left(\beta \mu B\right) = \frac{1}{2} N \beta \mu^2 B \to 0$ , as we would expect. [\* Can a paramagnet in a canonical state have T < 0?]

• Reading: Kennett, § 1.3.1 (quantum microcanonical state); 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  $\omega$ . 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 (2N - 1)-dimensional sphere in 2N-dimensional phase space.

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

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

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

• 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

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

A short calculation then gives  $\bar{E} = (N\hbar\omega/2) \coth(\beta\hbar\omega/2)$  and  $C \propto [1/\sinh(\beta\hbar\omega/2)]^2$ .  $[T \to 0 \text{ limit?}]$ 

• Reading: Kennett, § 4.4.3 (classical); Pathria & Beale, §§ 2.4 (phase space), 3.8 (canonical), 4.4 (grand canonical), and 5.3C (quantum); Reif, pp 55-56 (classical phase space) and 251-253 (quantum, canonical).

#### 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. This will lead to an important observation.

• 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<sup>2</sup> 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

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