Physics 127a: Class Notes

Lecture 7: Canonical Ensemble – Simple Examples

The canonical partition function provides the standard route to calculating the thermodynamic properties of macroscopic systems—one of the important tasks of statistical mechanics

$$\text{Hamiltonian} \rightarrow Q_N = \sum_j e^{-\beta E_j} \rightarrow \text{free energy } A(T, V, N) \rightarrow \text{etc.} \tag{1}$$

A number of simple examples illustrate this type of calculation, and provide useful physical insight into the behavior of more realistic systems. The following are simple because they are a collection of noninteracting objects, which makes the enumeration of states easy.

Harmonic Oscillators

Classical The Hamiltonian for one oscillator in one space dimension is

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{2}$$

with m the mass of the particle and ω_0 the frequency of the oscillator. The partition function for *one* oscillator is

$$Q_1 = \int_{-\infty}^{\infty} \exp\left[-\beta\left(\frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right)\right]\frac{dx\,dp}{h}. \tag{3}$$

The integrations over the Gaussian functions are precisely as in the ideal gas, so that

$$Q_1 = \frac{1}{h}\left(\frac{2\pi m}{\beta}\right)^{1/2}\left(\frac{2\pi}{\beta m\omega_0^2}\right)^{1/2} = \frac{kT}{\hbar\omega_0}, \tag{4}$$

introducing $\hbar = h/2\pi$ for convenience.

For N independent oscillators

$$Q_N = (Q_1)^N = \left(\frac{kT}{\hbar\omega_0}\right)^N \tag{5}$$

and then

$$A = NkT \ln\left(\frac{\hbar\omega_0}{kT}\right), \tag{6}$$

$$U = NkT, \tag{7}$$

$$S = Nk\left[\ln\left(\frac{kT}{\hbar\omega_0}\right) + 1\right], \tag{8}$$

$$\mu = kT \ln\left(\frac{\hbar\omega_0}{kT}\right). \tag{9}$$

Equation (7) is an example of the general *equipartition theorem*: each coordinate or momentum appearing as a quadratic term in the Hamiltonian (e.g. $p^2/2m$, $Kx^2/2$) contributes $\frac{1}{2}kT$ to the average energy in the classical limit. The proof is an obvious generalization of the integrations done in Eq. (4)—see *Pathria* §3.7 for a more formal proof.

For oscillators in 3 space dimensions, replace N by $3N$ in the above expressions.

Quantum The quantum calculation is very easy in this case. The energy levels of a single, one dimensional harmonic oscillator are

$$E_j = (j + \tfrac{1}{2})\hbar\omega_0 \tag{10}$$

so that

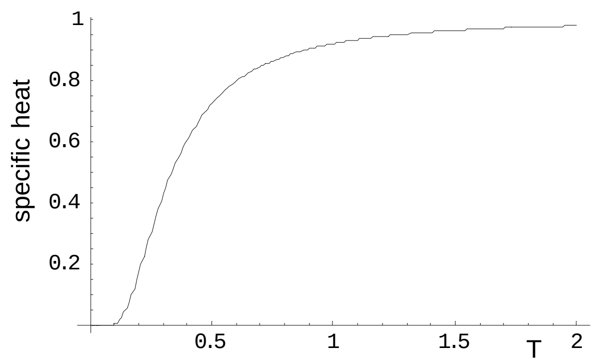
$$Q_1 = \sum_j e^{-\beta(j+1/2)\hbar\omega_0} \tag{11}$$

$$= \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}} = \frac{1}{2\sinh(\beta\hbar\omega_0/2)}. \tag{12}$$

For N one dimensional oscillators $Q_N = (Q_1)^N$ from which the thermodynamic behavior follows

$$A = NkT \ln[2\sinh(\beta\hbar\omega_0/2)] = N\left[\frac{1}{2}\hbar\omega_0 + kT\ln\left(1 - e^{-\beta\hbar\omega_0}\right)\right], \tag{13}$$

$$U = \frac{1}{2}N\hbar\omega_0\coth(\beta\hbar\omega_0/2) = N\hbar\omega_0\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_0} - 1}\right]. \tag{14}$$



Specific heat of N one dimensional harmonic oscillators scaled to Nk as a function of temperature (scaled to $\hbar\omega_0/k$).

It is interesting to focus on the specific heat

$$C = \frac{\partial U}{\partial T} = Nk(\beta\hbar\omega_0)^2\frac{e^{\beta\hbar\omega_0}}{\left(e^{\beta\hbar\omega_0} - 1\right)^2}. \tag{15}$$

For $T \to \infty$, $\beta \to 0$ and the exponentials can be expanded, and we find the classical, equipartition result $C = Nk$. For any finite temperature the specific heat is reduced *below* the classical result, and for low temperatures $kT \ll \hbar\omega_0$ the exponentials are large and $C \simeq Nk(\hbar\omega_0/kT)^2 e^{-\hbar\omega_0/kT}$ so that the specific heat is exponentially small. The results are plotted above. These results, with $N \to 3N$, are the *Einstein model* for the specific heat of the phonons in a solid.

Paramagnetism

Consider N magnetic moments μ in an applied magnetic field B. There is competition between the magnetic energy of size μB which tends to align the moments along the field, and the thermal fluctuations.

Classical vector spins The Hamiltonian is

$$H = -\sum_{i=1}^{N} \vec{\mu} \cdot \vec{B} = -\mu B \sum_{i}^{N} \cos\theta_i \tag{16}$$

taking the field $\vec{B}$ to be in the z direction and θ_i is the polar angle of the ith moment. This gives the partition function $Q_N = (Q_1)^N$ with

$$Q_1 = \int d\Omega\, e^{\beta\mu B \cos\theta} \tag{17}$$

with

$$\int d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \tag{18}$$

the integral over all angles.

The average z magnetic moment is $\langle M_z \rangle = N \langle \mu_z \rangle$

$$\langle \mu_z \rangle = \frac{\int d\Omega\, \mu \cos\theta\, e^{\beta\mu B \cos\theta}}{\int d\Omega\, e^{\beta\mu B \cos\theta}} = kT \frac{\partial \ln Q_1}{\partial B}. \tag{19}$$

The one-moment partition function is easily evaluated

$$Q_1 = 2\pi \int_{-1}^{1} d(\cos\theta) e^{\beta\mu B \cos\theta} = 4\pi \frac{\sinh(\beta\mu B)}{\beta\mu B}, \tag{20}$$

so that

$$\langle \mu_z \rangle = \mu\, L(\beta\mu B), \tag{21}$$

with L the *Langevin function*

$$L(x) = \coth x - \frac{1}{x}. \tag{22}$$

Note that $L(x \to \infty) \to 1$, and for small x

$$L(x) \simeq \frac{x}{3} - \frac{x^3}{45} + \cdots . \tag{23}$$

For large temperatures or small fields (small $\beta\mu B$)

$$\langle M_z \rangle \simeq \frac{N\mu^2 B}{3kT}. \tag{24}$$

The linear increase with a small applied field is known as the magnetic susceptibility $\chi = \partial \langle M_z \rangle / \partial B|_{B\to 0}$, so that

$$\chi = \frac{N\mu^2}{3kT}. \tag{25}$$

This T^{-1} susceptibility is known as a *Curie susceptibility*.

Ising model This might correspond to a quantum spin-$\frac{1}{2}$($S = \frac{1}{2}$) system in which each spin has only two possible orientations, or a classical spin with strong, uniaxial, crystalline anisotropy. The Hamiltonian is

$$H = -\sum_i \mu_i B \tag{26}$$

with $\mu_i = \pm\mu$ the magnetic moment of the ith spin. We assume there is no interaction *between* different spins.

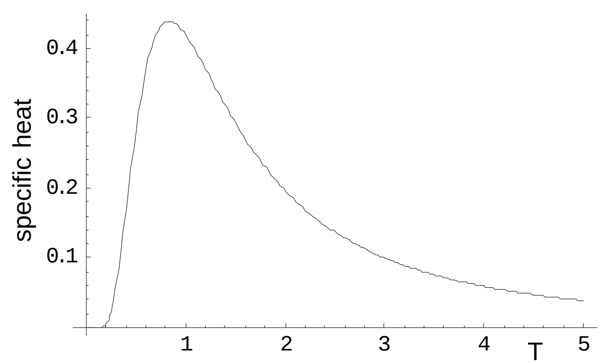
There are only two states for a single spin so the calculation Q_1 is very easy

$$Q_1 = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\mu B/kT). \tag{27}$$

Since the spins are non-interacting $Q_N = (Q_1)^N$, and so

$$A(N,T) = -NkT \ln\left[2\cosh(\mu B/kT)\right], \tag{28}$$

$$U = -N\mu B\ \tanh(\mu B/kT). \tag{29}$$

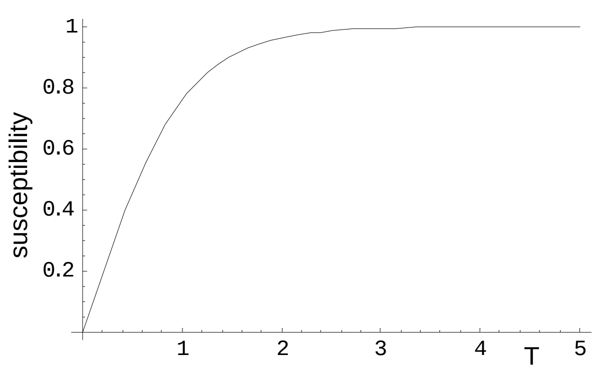


Specific heat scaled to Nk as a function of temperature scaled to $\mu B/k$ for N moments μ in a field B.

The specific heat is

$$C = Nk\left(\frac{\mu B}{kT}\right)^2 \frac{1}{\cosh^2\left(\frac{\mu B}{kT}\right)} \tag{30}$$

which is plotted in the figure. The specific heat is proportional to T^{-2} at high temperatures and exponentially small at low temperatures. In between is a peak at $kT \simeq \mu B$ known as a Schottky anomaly. Since we can also understand the specific heat as $C = T\partial S/\partial T$, we identify the anomaly with the decrease in entropy as the moments become ordered along the field.



Magnetization scaled to $N\mu$ as a function of temperature scaled to $\mu B/k$ for N spin-$\frac{1}{2}$ objects.

We are also interested in the average magnetic moment

$$\langle M_z \rangle = \frac{\sum_i \mu_i e^{-\beta\mu_i B}}{\sum_i e^{-\beta\mu_i B}}. \tag{31}$$

Just as in calculating the average energy we see this is conveniently written

$$\langle M_z \rangle = kT \frac{\partial}{\partial B} \ln Q_N = -\frac{\partial A}{\partial B} \tag{32}$$

(with partials at constant N, T). This gives

$$\langle M_z \rangle = N\mu \tanh\left(\frac{\mu B}{kT}\right). \tag{33}$$

At *large* field or *low* temperature we get saturation $\langle M_z \rangle \simeq N\mu$, whereas at *small* fields or *high* temperature the behavior is linear in the field $\langle M_z \rangle \simeq N\mu^2 B/kT$. The susceptibility is

$$\chi = \frac{N\mu^2}{kT}. \tag{34}$$

again of Curie form.

Pathria §3.9 studies the case of arbitrary S quantum spins.