Statistical Mechanics and Thermodynamics of Simple Systems

Handout 8

Partition function

The partition function, Z, is defined by

$$\boxed{Z = \sum_i \mathrm{e}^{-\beta E_i}} \tag{1}$$

where the sum is over all states of the system (each one labelled by i).

(a) The two-level system: Let the energy of a system be either $-\Delta/2$ or $\Delta/2$. Then

$$Z = \mathrm{e}^{\beta\Delta/2} + \mathrm{e}^{-\beta\Delta/2} = 2\cosh\left(\frac{\beta\Delta}{2}\right). \tag{2}$$

(b) The simple harmonic oscillator: The energy of the system is $(n+\frac{1}{2})\hbar\omega$ where $n = 0, 1, 2, \ldots$, and hence

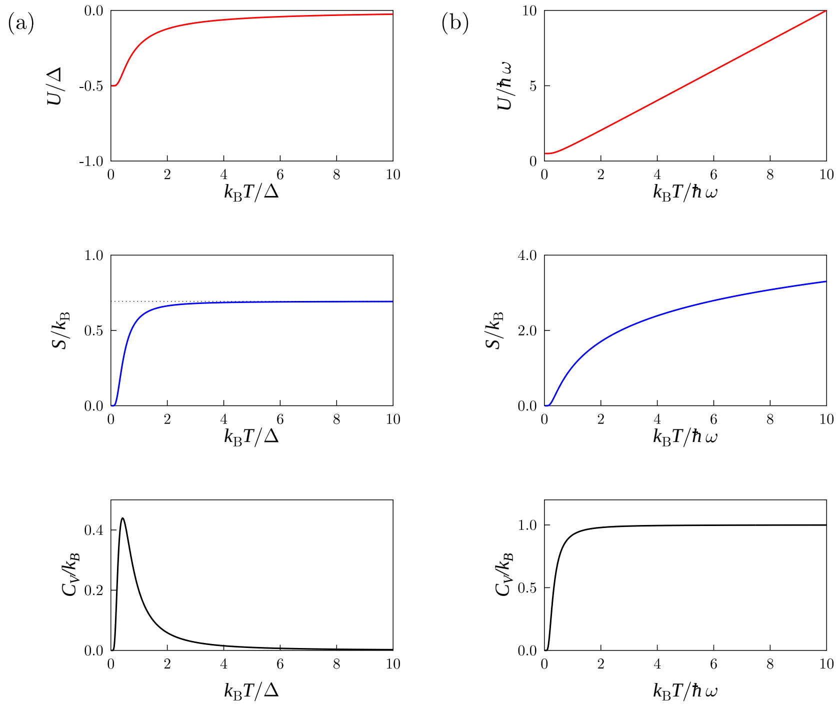
$$Z = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta(n+\frac{1}{2})\hbar\omega} = \mathrm{e}^{-\beta\frac{1}{2}\hbar\omega}\sum_{n=0}^{\infty}\mathrm{e}^{-n\beta\hbar\omega} = \frac{\mathrm{e}^{-\frac{1}{2}\beta\hbar\omega}}{1-\mathrm{e}^{-\beta\hbar\omega}}, \tag{3}$$

Using the partition function to obtain functions of state

The table below lists the thermodynamic quantities derived from the partition function Z.

	Function of state	Statistical mechanical expression
U		$-\dfrac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$
F		$-k_\mathrm{B}T\ln Z$
S	$= -\left(\frac{\partial F}{\partial T}\right)_V = \frac{U-F}{T}$	$k_\mathrm{B}\ln Z + k_\mathrm{B}T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V$
p	$= -\left(\frac{\partial F}{\partial V}\right)_T$	$k_\mathrm{B}T\left(\dfrac{\partial \ln Z}{\partial V}\right)_T$
H	$= U + pV$	$k_\mathrm{B}T\left[T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
G	$= F + pV = H - TS$	$k_\mathrm{B}T\left[-\ln Z + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
C_V	$= \left(\frac{\partial U}{\partial T}\right)_V$	$k_\mathrm{B}T\left[2\left(\dfrac{\partial \ln Z}{\partial T}\right)_V + T\left(\dfrac{\partial^2 \ln Z}{\partial T^2}\right)_V\right]$

You probably only need to remember the first two; the others can be quickly worked out.



The internal energy U, the entropy S and the heat capacity C_V for (a) the two-state system (with energy levels $\pm\Delta/2$) and (b) the simple harmonic oscillator with angular frequency ω.

Combining partition functions

Suppose the energy contains two independent contributions a and b with energy levels E_i^a and E_j^b, respectively, then

$$\begin{aligned} Z &= \sum_i \sum_j \mathrm{e}^{-\beta(E_i^a + E_j^b)} \\ &= Z_a Z_b, \end{aligned} \tag{4}$$

i.e. the product of the partition functions for the a and b systems. The generalization to more independent contributions is obvious: $Z = Z_a Z_b Z_c \ldots$.

Following from this, if $Z(1)$ is the partition function for one system, then the partition function for an assembly of N *distinguishable* systems each having exactly the same set of energy levels (e.g. N localized harmonic oscillators, all with the same frequency) is

$$Z(N) = Z^N(1). \tag{5}$$

If the N systems are *indistinguishable* (e.g. an ideal gas of identical atoms or molecules) then

$$Z(N) = \frac{Z^N(1)}{N!}. \tag{6}$$

Example: the spin–$\frac{1}{2}$ paramagnet

In quantum mechanics, a particle with spin angular momentum equal to $\frac{1}{2}$, placed in a magnetic field B along the z direction, can exist in one of two eigenstates:

- $|\uparrow\rangle$, with angular momentum parallel to the B field, and hence magnetic moment along z equal to $-\mu_B$ (costing an energy $+\mu_B B$).
- $|\downarrow\rangle$, with angular momentum antiparallel to the B field, and hence magnetic moment along z equal to $+\mu_B$ (costing an energy $-\mu_B B$).

Here $\mu_B = e\hbar/2m$ is the **Bohr magneton** and we have used the fact that energy$= -\boldsymbol{\mu}\cdot\mathbf{B}$, and also that for a negatively charged particle (the electron) the angular momentum is antiparallel to the magnetic moment.

Therefore, one spin$-\frac{1}{2}$ particle behaves like a two-state system, with the two states having energies $E = \pm\mu_B B$, and the single-particle partition function is simply

$$Z(1) = \mathrm{e}^{\beta\mu_B B} + \mathrm{e}^{-\beta\mu_B B} = 2\cosh(\beta\mu_B B). \tag{7}$$

A spin$-\frac{1}{2}$ **paramagnet** is an assembly of N such particles which are assumed to be *non-interacting*, i.e. each particle is independent and "does its own thing".

The N-particle partition function, treating the spin$-\frac{1}{2}$ particles as distinguishable, is given by

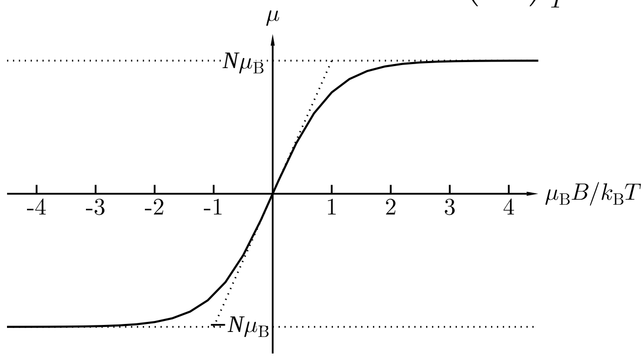
$$Z(N) = Z^N(1) = [2\cosh(\beta\mu_B B)]^N, \tag{8}$$

and hence F is given by

$$F = -k_B T \ln Z(N) = -Nk_B T \ln[2\cosh(\beta\mu_B B)]. \tag{9}$$

We can work out the total magnetic moment μ of the paramagnet by computing

$$\mu = -\left(\frac{\partial F}{\partial B}\right)_T = N\mu_B \tanh(\beta\mu_B B). \tag{10}$$



The behaviour of μ, given by eqn (10), is shown in the figure on the left.

The magnetization M is the magnetic moment per unit volume, so

$$M = \frac{\mu}{V} = \frac{N\mu_B}{V}\tanh(\beta\mu_B B). \tag{11}$$

The **magnetic susceptibility** χ is defined by $M = \chi H$ where H is a small applied field, or more formally $\chi = \left(\frac{\partial M}{\partial H}\right)_T$. The use of a scalar χ assumes the material is isotropic. When $\beta\mu_B B \ll 1$ we can use $\tanh x \approx x$ for $x \ll 1$ to find that

$$M \approx \frac{N\mu_B^2 B}{V k_B T}. \tag{12}$$

By definition, $B = \mu_0(H + M) = \mu_0(1+\chi)H$ for a paramagnet. For a weakly magnetic material (like a paramagnet) $\chi \ll 1$, and therefore

$$\chi \approx \frac{\mu_0 M}{B} = \frac{N\mu_0\mu_B^2}{V k_B T}. \tag{13}$$

This yields **Curie's law:**

$$\chi \propto \frac{1}{T}. \tag{14}$$

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