
Statistical Mechanics and Thermodynamics of Simple Systems

Handout 6

Partition function

The partition function, Z , is defined by

$$\boxed{Z = \sum_i e^{-\beta E_i}} \quad (1)$$

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

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

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

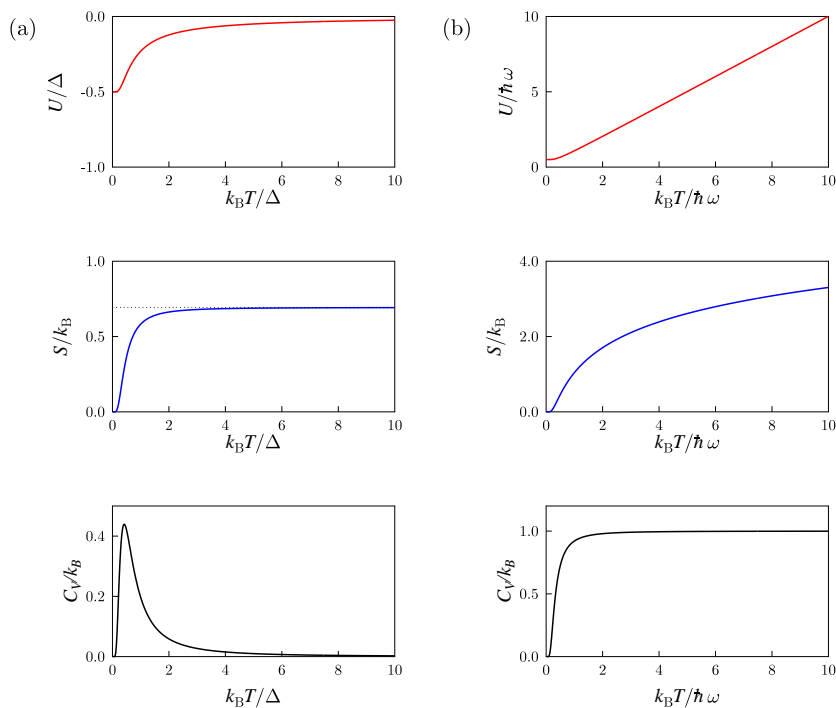
$$Z = \sum_i e^{-\beta E_i} = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} = e^{-\beta\frac{1}{2}\hbar\omega} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}, \quad (3)$$

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	$-\frac{d \ln Z}{d\beta}$
F	$-k_B T \ln Z$
$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{U-F}{T}$	$k_B \ln Z + k_B T \left(\frac{\partial \ln Z}{\partial T}\right)_V$
$p = -\left(\frac{\partial F}{\partial V}\right)_T$	$k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_T$
$H = U + pV$	$k_B T \left[T \left(\frac{\partial \ln Z}{\partial T}\right)_V + V \left(\frac{\partial \ln Z}{\partial V}\right)_T \right]$
$G = F + pV = H - TS$	$k_B T \left[-\ln Z + V \left(\frac{\partial \ln Z}{\partial V}\right)_T \right]$
$C_V = \left(\frac{\partial U}{\partial T}\right)_V$	$k_B T \left[2 \left(\frac{\partial \ln Z}{\partial T}\right)_V + T \left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V \right]$

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

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

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

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

$$Z(N) = Z^N(1). \quad (5)$$

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

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

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

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

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

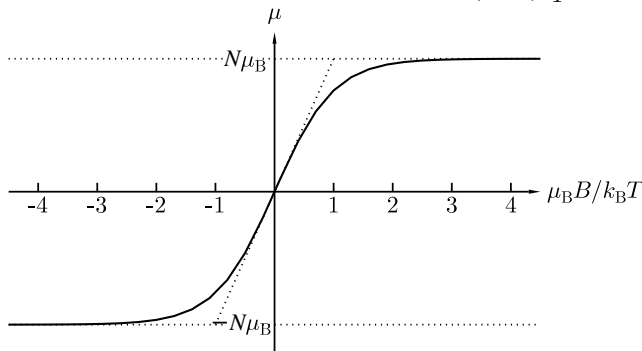
$$Z(N) = Z^N(1) = [2 \cosh(\beta\mu_B B)]^N, \quad (8)$$

and hence F is given by

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

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

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



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

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

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

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

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

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

This yields **Curie's law**:

$$\chi \propto \frac{1}{T}. \quad (14)$$