

HW 4 Solutions.

1. [Easy review question 1]

Compare the free energy A_p of a system of volume V at T of a classical monatomic ideal gas consisting of $3N$ particles and that A_m of a classical ideal gas mixture consisting of three different monatomic chemical species of N particles each (at T occupying the same volume V).

(1) What is the difference between these free energies? First, guess your answer (with justification).

(2) Do your calculation of A_p and A_m . Does the difference agree with your expectation?

Solution

Since this is an ideal gas, there cannot be any energetic difference. Therefore, the difference must be only the mixing entropy. Thus, A_m is smaller than A_p by $3N \log 3$.

We can almost copy (2.2.3) in the text:

$$Z_p = \left[\frac{en_Q 3V}{3N} \right]^{3N}$$

and

$$Z_m = \left[\frac{en_Q 3V}{N} \right]^{3N}.$$

Therefore,

$$Z_m = Z_p 3^{3N}.$$

That is,

$$A_m = A_p - 3Nk_B T \log 3.$$

Since $A = E - TS$, this implies $S_m - S_p = 3Nk_B \log 3$.

2. [Easy review question 2]

A classical ideal gas consisting of N particles in a volume V has three low lying internal states (non-degenerate) equally separated by energy gap ϵ (i.e., $0, \epsilon$ and 2ϵ). What is the chemical potential of this ideal gas?

Solution

The internal partition function is

$$z_i = (1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon})^N.$$

Therefore,

$$A = A_{ideal} - Nk_B T \log(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}) = Nk_B T \log(n/n_Q) - Nk_B T - Nk_B T \log(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon})$$

Since $N\mu = G = A + PV$,

$$G = Nk_B T \log(n/n_Q) - Nk_B T \log(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon})$$

or

$$\mu = \log(n/n_Q [1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}])$$

What is the general implication? The chemical potential is less than that of the structureless ideal gas. The quantity in $[]$ is the effective number of different chemical species, so

$n/[\dots]$ is the number of particles of each chemical species. That is, the effective number of particles is reduced if there are internal states.

3. [Ensemble equivalence]

We have discussed the constant force ensemble $Y(T, F)$ of a freely jointed polymer chain (The ideal rubber band problem in Section 2.6)

$$Y(T, F) = \int_{-Na}^{Na} Z(T, L) e^{\beta L F} dL,$$

where $Z(T, L)$ is the canonical partition function of the chain with a fixed end-to-end length L . Prove the equivalence of these two descriptions. That is, the (densities of) generalized Gibbs free energy G computed from Y (as $G = -k_B T \log Y$) and that computed from the Helmholtz free energy $A = -k_B T \log Z$ thermodynamically (i.e., by a Legendre transformation: $G = A - LF$) agree in the thermodynamic limit (i.e., in the limit of long polymers). [You can mimic the proof in the notes, but this is much easier, because the integration range is FINITE.]

Solution

From the hint in [] I never expected most of you to compute an explicit example. In any case, we want a general relation that cannot be proved by the study of any concrete model. [Statistical physics is not materials science.]

Simply mimic what is illustrated in Fig. 2.6.1; since you need not worry about infinite integration range, so the hardest part of the microcanonical-canonical equivalence proof is totally ignored. Let L^* be the L that maximizes $Z e^{\beta F L}$. Then, obviously,

$$\int_{L^*-1}^{L^*+1} Z(T, L) e^{\beta L F} dL \leq \int_{-Na}^{Na} Z(T, L) e^{\beta L F} dL \leq 2Na Z(T, L^*) e^{\beta L^* F}.$$

You could replace the leftmost term with $2Z(T, L^*) e^{\beta L^* F}$, so we are done.

If you wish to be a bit more rigorous, we estimate

$$2 \min_{L \in [L^*-1, L^*+1]} Z(T, L) e^{\beta L F} \leq \int_{L^*-1}^{L^*+1} Z(T, L) e^{\beta L F} dL,$$

so taking the log

$$\log \min_{L \in [L^*-1, L^*+1]} Z(T, L) e^{\beta L F} + \log 2 \leq \log Y \leq \log Z(T, L^*) + \beta L^* F + \log(2Na).$$

If the discrepancies are of order $\log N$ or less, we are happy. The second inequality is obviously OK. If the polymer is ideal as discussed we know Z explicitly, so $\log Z$ is extensive, and changing L^* by 1 does not cause any extensive change. Thus we are done. In the general case, first we must demonstrate that $\log Z$ is extensive (for general monomer-monomer interactions). The the rest is the same as the ideal chain case.

4. Suppose there are N noninteracting quantum spins with $S = 1/2$ in a lattice system which has an easy axis in the x -direction:

$$H_0 = -A \sum_{i=1}^N \sigma_{ix},$$

where A is a positive constant, and σ denotes the Pauli operator (i.e., the spin operator is $(\hbar/2)\sigma$). We apply an external magnetic field B in the z -direction, so the interaction Hamiltonian reads

$$H_i = -B \sum_{i=1}^N \sigma_{iz}.$$

(1) Compute

$$Z_1 = \text{Tr} e^{-\beta(H_0 + H_i)}.$$

[Hint: for example, see **27.13** of my Introductory QM notes.]

(2) Compare this with

$$Z_2 = \text{Tr} \{e^{-\beta H_0} e^{-\beta H_i}\}.$$

Is there any macroscopically meaningful difference?

Solution

The formula we need is

$$e^{\boldsymbol{\alpha} \cdot \boldsymbol{\sigma}} = \cosh \alpha + (\boldsymbol{n} \cdot \boldsymbol{\sigma}) \sinh \alpha,$$

where $\boldsymbol{n} = \boldsymbol{\alpha}/\alpha$, the unit direction vector.

$$Z_1 = z_1^N,$$

where

$$z_1 = \text{Tr} e^{\beta(A\sigma_x + B\sigma_z)} = \text{Tr} e^{\boldsymbol{C} \cdot \boldsymbol{\sigma}}$$

with $\boldsymbol{C} = (\beta A, 0, \beta B)$, so in the above formula $\alpha = \beta \sqrt{A^2 + B^2}$, and $\boldsymbol{n} = \boldsymbol{C}/\alpha$. Notice that the trace of the second term vanishes, so

$$z_1 = \text{Tr} \cosh(\beta \sqrt{A^2 + B^2}) = 2 \cosh(\beta \sqrt{A^2 + B^2}).$$

That is,

$$Z_1 = \left[2 \cosh(\beta \sqrt{A^2 + B^2}) \right]^N.$$

To compute Z_2 first we note

$$Z_2 = z_2^N,$$

where

$$z_2 = \text{Tr} e^{\beta A \sigma_x} e^{\beta B \sigma_z}.$$

We can compute

$$\begin{aligned} e^{\beta A \sigma_x} e^{\beta B \sigma_z} &= (\cosh(\beta A) + \sigma_x \sinh(\beta A)) (\cosh(\beta B) + \sigma_z \sinh(\beta B)) \\ &= \cosh(\beta A) \cosh(\beta B) + \dots, \end{aligned}$$

where $\dots$ denotes the traceless terms (notice $\sigma_x \sigma_z = -i\sigma_y$). Therefore,

$$Z_2 = [2 \cosh(\beta A) \cosh(\beta B)]^N.$$

These partition functions come close when the temperature is sufficiently high, but at low temperatures they are quite different.

Thus, we cannot easily study a quantum system with external field based on the study of the system without it.

The following questions can be tricky, so they are extra questions.

(3) What is the partition function $Z(T, M)$ for this system under the condition that the z -component of the magnetization is M (without the B field)?

(4) Is

$$Y(T, B) = \sum_M Z(T, M) e^{+\beta B M}$$

identical to the Z 's above? What is the lesson you learn?

Solution [To outline the idea, I identify σ and the magnetic moment vector, ignoring $\hbar/2$, etc.)

$Z(T, M)$ should be the trace of $e^{\beta A \sum_i \sigma_{xi}}$ over the subspace specified by $S_z = M$, where $S_z = \sum_i \sigma_{zi}$ is the z -component of the total spin angular momentum (I ignore $\hbar/2$). The dimension of this subspace is just $\binom{N}{N_+}$, where $N_{\pm} = (N \pm M)/2$ (as the classical case). This space may be understood to be spanned by $|\pm\rangle \cdots |\pm\rangle$ (where $|\pm\rangle = |1/2, \pm 1/2\rangle$). Therefore,

$$Z(T, M) = \text{Tr}_M e^{-\beta H_0} = \sum \langle \cdots, \pm, \cdots | e^{-\beta H_0} | \cdots, \pm, \cdots \rangle,$$

where $|\cdots, \pm, \cdots\rangle$ is the ket with $N_+ + 1/2$ states. That is

$$\langle \cdots, \pm, \cdots | e^{-\beta H_0} | \cdots, \pm, \cdots \rangle = [\langle + | e^{\beta A \sigma_x} | + \rangle]^{N_+} [\langle - | e^{\beta A \sigma_x} | - \rangle]^{N_-}.$$

We know

$$\langle \pm | e^{\beta A \sigma_x} | \pm \rangle = \cosh(\beta A).$$

Therefore,

$$Z(T, M) = \binom{N}{N_+} \cosh^N(\beta A)$$

Now,

$$Y(T, B) = \sum_M Z(T, M) e^{+\beta B M} = \sum_{N_+} \binom{N}{N_+} \cosh^N(\beta A) e^{+\beta B N_+} e^{+\beta B N_-} = \cosh^N(\beta A) 2^N \cosh^N(\beta B)$$

As expected, we get only the ‘classical version.’

[Legendre-Laplace correspondence fails in QSM]

I said the Legendre-Laplace correspondence so useful in classical statistical mechanics is not always allowed¹. I wish you taste how grave the mismatch is.

¹I emphasize that this is fine for microcanonical, canonical and grand canonical ensembles.