Solutions

PHY 831: Statistical Mechanics
Homework 3

Due Monday Oct 4, 2021

25 pt

1. The 1st Law for a 1-dimensional system (e.g., a stretched wire, spring, polymer, etc.) reads

$$dE = TdS + f dl \,,$$

where f is the external force and dl is the change in length. (Note that the sign of the differential work term differs from the more familiar $-PdV$ because pressure is defined as the outward force on the container.) Let us consider a polymer chain of N links each of length ρ, with each link equally likely to be directed to the right and left.

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(a) We can recycle our previous work on the multiplicity function for a paramagnet $\Omega(N,s)$ to describe this system. Argue that the number of arrangements (i.e., microstates) that give a head-to-tail length of $l = 2|s|\rho$ (i.e., macrostate) is equal to

$$\Omega(N,s) + \Omega(N,-s) = \frac{2N!}{(N/2+s)!(N/2-s)!}$$

10

(b) For $|s| << N$, show that (working in natural units with $k_B = 1$)

$$S = \log\big(2\Omega(N,0)\big) - \frac{l^2}{2N\rho^2} \,.$$

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(c) What is the force f at extension l? This force arises because the polymer wants to coil up (entropy is higher in a coiled configuration than when it's straight.). For instance, if you heat up a rubber band, it contracts.

25 pt

2. Consider a system of N independent quantum harmonic oscillators at constant T with angular frequency ω.

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(a) Compute i) partition function, ii) the average energy, iii) the Helmholtz free energy, and iv) the heat capacity C_V for a single oscillator.

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(b) Now compute the partition function and average energy for a classical oscillator. In what limit does $\langle E\rangle$ become equal to the result from the quantum calculation?

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(c) Show in general that if you have two non-interacting subsystems in thermal equilibrium (i.e., at the same fixed termperature), the partition function factorizes $Z(1+2) = Z(1)Z(2)$.

5 (d) Compute the same quantities as in part a), but now for the system of N oscillators.

25 pt 3. Consider an ideal gas of N identical O_2 molecules, where all molecules have total spin $S = 1$. The gas is in a uniform magnetic field in the z-direction, so the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} - \mu B S_i^z \right).$$

10 (a) Treating the spatial degrees of freedom classically but the spin degrees of freedom as quantized, calculate the partition function $Z(T, N, V, B)$.

5 (b) What are the probabilities for a given molecule to have S_z values of $-1, 0, 1$ at temperature T?

5 (c) Compute the average magnetization per volume $\langle M \rangle / V$, where $M = \mu \sum_i S_i^z$.

5 (d) Compute the zero-field isothermal susceptibility $\chi_T = \frac{\partial \langle M \rangle}{\partial B}\Big|_{B=0}$

25 pt 4. Consider a rod-shaped molecule with moment of inertia I and electric dipole moment μ. In a uniform electric field $\mathcal{E}$ in the z-direction, there will be rotational motion governed by the Hamiltonian

$$\mathcal{H}_{\text{rot}} = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu \mathcal{E} \cos \theta \,.$$

The molecule is connected to a heat bath, so is at constant temperature T.

5 (a) What is the (classical) partition function due to the rotational degrees of freedom?

5 (b) What is the average polarization $P = \langle \mu \cos \theta \rangle$?

5 (c) Compute the zero-field isothermal polarizability $\chi_T = \frac{\partial P}{\partial \mathcal{E}}\Big|_{\mathcal{E}=0}$

10 (d) Compute the average rotational energy and examine the low and high temperature limits.

$\boxed{1.}$

a.) let N_R = # of links to the right
$= \frac{N}{2} + s$

N_L = # of links to the left
$= \frac{N}{2} - s$

head-to-tail length $l = |N_R - N_L| \rho$
$= 2|s|\rho$

$\therefore$ Macro state l is characterized by $|s|$.

In our paramagnet problem, since $E = -2Bs$ we had $s = +|s|$ & $s = -|s|$ as 2 different macrostates. Here however, $s = \pm|s|$ are the <u>same</u>.

$$\boxed{\therefore \Omega_{TOT} = \Omega(N,s) + \Omega(N,-s) = \frac{2N!}{\left(\frac{N}{2}+s\right)!\left(\frac{N}{2}-s\right)!}}$$

b.) $$S = \log \Omega_{TOT} = \log(2N!) - \log\left(\tfrac{N}{2}+s\right)! - \log\left(\tfrac{N}{2}-s\right)!$$
$$\approx 2N\log 2N - 2N - \left(\tfrac{N}{2}+s\right)\log\left(\tfrac{N}{2}+s\right) + \left(\tfrac{N}{2}+s\right) - \left(\tfrac{N}{2}-s\right)\log\left(\tfrac{N}{2}-s\right) + \left(\tfrac{N}{2}-s\right)$$

$$= 2N\log 2N - N - \left(\tfrac{N}{2}+s\right)\log\left(\tfrac{N}{2}+s\right) - \left(\tfrac{N}{2}-s\right)\log\left(\tfrac{N}{2}-s\right)$$

Mathematica .... Taylor expansion for $|S| \ll N$

$$\left(\frac{N}{2}+S\right)\log\left(\frac{N}{2}+S\right) \simeq \frac{N}{2}\log\frac{N}{2} + S\log\frac{N}{2} + S + \frac{S^2}{N}$$

$$\left(\frac{N}{2}-S\right)\log\left(\frac{N}{2}-S\right) = \frac{N}{2}\log\frac{N}{2} - S\log\frac{N}{2} - S + \frac{S^2}{N}$$

$$\Downarrow$$

$$\mathcal{S} = 2N\log 2N - N - N\log\frac{N}{2} - \frac{2S^2}{N}$$

$$* \text{ but } \log[2\Omega(N,0)] = \log 2N! - 2\log\frac{N}{2}!$$

$$\simeq 2N\log 2N - 2N - N\log\frac{N}{2} - N$$

$$= 2N\log 2N - N - N\log\frac{N}{2}$$

$$\therefore \mathcal{S} = \log[2\Omega(N,0)] - \frac{2S^2}{N}$$

but $\ell = 2|S|\rho \quad \therefore \quad |S|^2 = \frac{1}{4}\frac{\ell^2}{\rho^2}$

$$\Rightarrow \boxed{\mathcal{S} = \log[2\Omega(N,0)] - \frac{1}{2N}\frac{\ell^2}{\rho^2}}$$

c.) $dS = \frac{1}{T} dE - \frac{1}{T} f \, d\ell$

$$\therefore \boxed{\frac{f}{T} = -\left.\frac{\partial S}{\partial \ell}\right|_E = +\frac{\ell}{N\rho^2}}$$

$$\boxed{\therefore \; f = \frac{\ell T}{N\rho^2} \quad \text{in } k_B = 1 \text{ units}}$$

$\boxed{2}$

a) $Z_1 = \sum_{n=0}^{\infty} e^{-\beta n \hbar\omega}$

(used $\varepsilon_n = n\hbar\omega$ where I reset the zero of energy to get rid of pesky constant)

$$= \sum_n \left[e^{-\beta\hbar\omega}\right]^n$$

Note: If use $\varepsilon_n = (n+\frac{1}{2})\hbar\omega$

$$Z_1 = \frac{e^{-\frac{\beta}{2}\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{1}{2\sinh\frac{\beta\hbar\omega}{2}}$$

$$\boxed{Z_1 = \frac{1}{1-e^{-\beta\hbar\omega}}}$$

$$\langle E\rangle_1 = \frac{\sum_n \varepsilon_n e^{-\beta\varepsilon_n}}{\sum_n e^{-\beta\varepsilon_n}} = -\frac{\partial}{\partial\beta}\log Z_1$$

$$= -\frac{1}{Z_1}\frac{\partial Z_1}{\partial\beta}$$

$$= -(1-e^{-\beta\hbar\omega})\frac{(-\hbar\omega e^{-\beta\hbar\omega})}{(1-e^{-\beta\hbar\omega})^2}$$

$$= \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$\boxed{\langle E\rangle_1 = \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}}$$

(if use $\varepsilon_n = (n+\frac{1}{2})\hbar\omega$ this picks up extra $\frac{\hbar\omega}{2}$

$$F_1 = -\frac{1}{\beta} \log Z_1$$

$$\boxed{F_1 = k_B T \log\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right)}$$

$$C_{V,1} = \left.\frac{\partial E_1}{\partial T}\right|_V = -k_B \beta^2 \frac{\partial}{\partial \beta} E_1 = -k_B\beta^2 \cdot \hbar\omega \frac{\partial}{\partial\beta}\left(\frac{1}{e^{\beta\hbar\omega} - 1}\right)$$

$$= \frac{k_B \beta^2 (\hbar\omega)^2 \, e^{\beta\hbar\omega}}{(e^{\beta\omega} - 1)^2}$$

$$\boxed{C_V = \frac{k_B (\beta\hbar\omega)^2 \, e^{\beta\hbar\omega}}{(e^{\beta\omega} - 1)^2}}$$

b.) 1 Classical Oscillator

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2$$

$$Z_1 = \frac{1}{2\pi\hbar} \int dp \, e^{-\frac{\beta p^2}{2m}} \times \int dq \, e^{-\frac{\beta m\omega^2}{2} q^2}$$

$$\boxed{Z_1 = \frac{1}{2\pi\hbar} \sqrt{\frac{2\cancel{m}\pi}{\beta}} \cdot \sqrt{\frac{2\pi}{\beta \cancel{m} \omega^2}} = \frac{1}{2\pi} \cdot \frac{2\pi}{\sqrt{\hbar^2\beta^2\omega^2}} = \frac{1}{\hbar\omega\beta}}$$

$$\boxed{\langle E_1 \rangle = \frac{1}{Z_1} \frac{-\partial Z_1}{\partial \beta} = \frac{\hbar\omega}{\hbar\omega\beta^2} = \frac{1}{\beta} = k_B T}$$

c) 2 non-interacting systems

$$\Rightarrow H_{TOT} = H^{①} + H^{②}$$

easiest to do this in phase space

$$Z = \int \frac{d\Gamma_{①}}{\Gamma_0} \int \frac{d\Gamma_{②}}{\Gamma_0} e^{-\beta(H^{①} + H^{②})}$$

where $d\Gamma_{①}$ = phase space differential for system ① etc.

$$= \int \frac{d\Gamma_{①}}{\Gamma_0} e^{-\beta H^{①}} \times \int \frac{d\Gamma_{②}}{\Gamma_0} e^{-\beta H^{②}} = Z(1) \times Z(2)$$

d) Since the N oscillators non-interacting,

$$Z_N = (Z_1)^N \text{ etc.}$$

So F, $\langle E \rangle$, and C_V get scaled by N from the results in part a).

3.

a.) $Z = Z_{\substack{\text{translational}\\ \text{motion}}} \times Z_{\text{spin}}$

$$= \frac{1}{N!}\left(\frac{V}{l_Q}\right)^{3N} \times \left[\sum_{m_s=-1}^{+1} e^{\beta\mu B m_s}\right]^N$$

identical particle ad-hoc correction factor (see L11-12 notes)

from the phase space integral (see class notes)

$$l_Q \equiv \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$$

$$= \frac{1}{N!}\left(\frac{V}{l_Q}\right)^{3N}\left[e^{\beta\mu B} + 1 + e^{-\beta\mu B}\right]^N$$

$$\boxed{Z = \frac{1}{N!}\left[\frac{V}{l_Q^3}\left(e^{\beta\mu B} + 1 + e^{-\beta\mu B}\right)\right]^N}$$

b.) $$\boxed{P_{\text{1-molecule}}(m_s) = \frac{e^{\beta\mu B m_s}}{e^{\beta\mu B} + 1 + e^{-\beta\mu B}} = \frac{e^{\beta\mu B m_s}}{2\cosh\beta\mu B + 1}}$$

c.) $\langle M \rangle = \langle \mu \sum_i S_i^2 \rangle$

$$= \frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial B}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial B} \log Z$$

$$= \frac{1}{\beta} \frac{\partial}{\partial B} \left(\log \left(2\cosh \mu B \beta + 1 \right) \right)$$

mathematica

$$= N\mu \left(\frac{2\sinh \beta\mu B}{2\cosh \beta \mu B + 1} \right)$$

d.) $\chi_T = \frac{\partial}{\partial B} \langle M \rangle \Big|_{B=0}$ = a bunch of awful looking hyperbolic trig functions that fortunately simplify when $B=0$

$$\downarrow$$

$$\boxed{\chi_T = \frac{2}{3} N \beta \mu^2}$$

$\boxed{4.}$

a.) Z_1^{rot}

$$= \frac{1}{(2\pi\hbar)^2} \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dP_\theta \int_{-\infty}^{\infty} dP_\phi \; e^{-\beta\left[\frac{1}{2I}\left(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta}\right) - \mu\mathcal{E}\cos\theta\right]}$$

1st carry out the dP_θ + dP_ϕ integrals

$$= \frac{1}{(2\pi\hbar)^2} \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \; \sqrt{\frac{2\pi I}{\beta}} \cdot \sqrt{\frac{2\pi I \sin^2\theta}{\beta}} \; e^{\beta\mu\mathcal{E}\cos\theta}$$

$$= \frac{1}{(2\pi\hbar)^2} \cdot \frac{2\pi I}{\beta} \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \; \sin\theta \; e^{\beta\mu\mathcal{E}\cos\theta}$$

let $x = \cos\theta$

$dx = -\sin\theta \, d\theta$

$$= \frac{1}{(2\pi\hbar)^2} \cdot \frac{2\pi I}{\beta} \cdot 2\pi \int_{-1}^{1} dx \; e^{\beta\mu\mathcal{E}x}$$

$$\boxed{Z_1^{rot} = \frac{I}{\hbar^2\beta} \cdot \frac{1}{\beta\mu\mathcal{E}} \, 2\sinh\beta\mu\mathcal{E} = \frac{2I}{\hbar^2\beta^2\mu\mathcal{E}} \sinh\beta\mu\mathcal{E}}$$

b.) $P = \langle \mu \cos\theta \rangle$

$$= \frac{1}{\mathcal{E}} \frac{\partial}{\partial \beta} \log Z_1^{rot} \quad \text{(Mathematica...)}$$

$$\boxed{P = \mu \left[\coth(\beta \mu \mathcal{E}) - \frac{1}{\beta \mu \mathcal{E}} \right]}$$

c.) $\chi_T = \left. \frac{\partial P}{\partial \mathcal{E}} \right|_{\mathcal{E}=0} = \beta \mu^2 \left[\frac{1}{(\beta \mu \mathcal{E})^2} - \frac{1}{\sinh^2 \beta \mu \mathcal{E}} \right]$

$$= \beta \mu^2 \left. \left[\frac{\sinh^2 \beta \mu \mathcal{E} - (\beta \mu \mathcal{E})^2}{(\beta \mu \mathcal{E})^2 \sinh^2 \beta \mu \mathcal{E}} \right] \right|_{\mathcal{E}=0}$$

setting $\mathcal{E} = 0$ is indeterminate, so use l'Hopital's rule

$$\boxed{\left. \chi_T \right|_{\mathcal{E}=0} = \frac{1}{3} \frac{\mu^2}{k_B T}}$$

d.) $\langle E^{rot} \rangle = -\frac{\partial}{\partial \beta} \log Z_{rot}$

$$\boxed{= 2k_BT - \mu\mathcal{E} \coth(\beta\mu\mathcal{E})}$$

$\underline{k_BT \gg \mu\mathcal{E}}$: $\boxed{\begin{aligned}\langle E^{rot} \rangle &= 2k_BT - \mu\mathcal{E}\frac{1}{\beta\mu\mathcal{E}} \\ &= k_BT\end{aligned}}$

(in accordance w/ Equipartition)

$\underline{k_BT \ll \mu\mathcal{E}}$: $\langle E^{rot} \rangle \approx -\mu\mathcal{E} + 2k_BT \approx -\mu\mathcal{E}$

(i.e., dominated by the ~~Satur~~ polarization)