PHY 831: Statistical Mechanics
Homework 2

Due September 21st, 2020

1. Show that
$$\left(\frac{\partial E}{\partial N}\right)_{T,V} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V}.$$

$F = E - TS$ (Legendre transformation) $\Rightarrow E = F + TS$

$dF = -p\,dV - S\,dT + \mu\,dN$

so $\left(\frac{\partial E}{\partial N}\right)_{T,V} = \underbrace{\left(\frac{\partial F}{\partial N}\right)_{T,V}}_{\mu} + T\underbrace{\left(\frac{\partial S}{\partial N}\right)_{T,V}}_{} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V}$

$\left(\frac{\partial}{\partial N}\underbrace{\left(\frac{\partial F}{\partial T}\right)_{V,N}}_{S}\right)_{T,V} = -\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial F}{\partial N}\right)_{T,V}}_{\mu}\right)_{N,V} = \left(\partial \mu\right)_{N,V}$

2. Prove the relationship
$$C_P = C_V + TV\frac{\alpha_P^2}{\kappa_T}.$$
Since the isothermal compressibility is always greater than zero for a thermodynamically stable gas, this implies the heat capacity at constant pressure is always greater than the heat capacity at constant volume.

Starting with: $T\,dS = C\,dT$:

$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

$\Rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \quad C_P = T\left(\frac{\partial S}{\partial T}\right)_P$

and with $dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right.\quad P$ we get:

$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T\left(\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right)$

$= \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T dP$

$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$ and with that:

$C_P - C_V = T\left\{\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V\right\} = T\left(\frac{\partial S}{\partial V}\right)_T\underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\alpha_P} = TV\alpha_P\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\substack{\text{M.R.}\\ \left(\frac{\partial P}{\partial T}\right)_V}} = VT\alpha_P\left(\frac{\partial P}{\partial T}\right)_V$

$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$

$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha_P}{\kappa_T} \Rightarrow \boxed{C_P = C_V + TV\frac{\alpha_P^2}{\kappa_T}}$ $\square$

3. Consider N spin-1/2 particles on a lattice (so that the particles are distinguishable) in a state with $N/2+n$ up spins. The Hamiltonian for this system is $H = -\sum_j \sigma_j B$, where $\sigma_j = \pm 1$. This is a simple model for a paramagnetic system.

   (a) Show that the total number of such microstates is

$$\Omega(n) = \frac{N!}{(N/2+n)!(N/2-n)!}.$$

   (I just want you to go through what we did in lecture here.)

Since the particles are distinguishable, there are $N!$ different ways to arrange all particles regardless of their spin.
All particles with spin up/down can change position with any other particle of the same spin without changing the state of the system. Therefore, there are $N_\uparrow! \cdot N_\downarrow!$ permutations of the same system state, and thus we see:

$$\Omega = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{\underbrace{\left(\frac{N}{2}+n\right)}_{N_\uparrow}!\underbrace{\left(\frac{N}{2}-n\right)}_{N_\downarrow}!}$$

   (b) If the total energy of the system is unspecified, the probability of ~~x~~ a particular value of n (which is proportional to the magnetization of the system) is $p(n) = \Omega(n)/2^N$ since there are 2^N possible states of the system. Show that for $N \gg n$, we have

$$p(n) \approx \sqrt{\frac{2}{\pi N}} e^{-2n^2/N}$$

   (hint: use Sterling's formula including factors of $\ln(2\pi N)$.)

$$\ln(n!) = n\ln(n) - n + O(\ln(n))$$

$$n! \sim \sqrt{2\pi n}\left(\frac{n}{e}\right)^n = \sqrt{2\pi n}\, N\, e^{-N}$$

$$u := \frac{2n}{N}$$

With that: $$p(n) = \frac{\Omega(n)}{2^N} = \frac{N!}{2^N\left(\frac{N}{2}+n\right)!\left(\frac{N}{2}-n\right)!} \approx \frac{\cancel{\sqrt{2\pi N}}}{2^N}\cancel{N^N e^{-N}} \frac{\cancel{\exp\left(\frac{N}{2}+N\right)}}{\sqrt{\cancel{\pi N}(1+u)}}\frac{\cancel{\exp\left(\frac{N}{2}-N\right)}}{\sqrt{\pi N(1-u)}}$$

$$\cdot\left(\frac{\cancel{N}}{2}(1+u)\right)^{-\frac{N}{2}(1+u)} \cdot\left(\frac{\cancel{N}}{2}(1-u)\right)^{-N/2(1-u)}$$

$$= \sqrt{\frac{2}{\pi N}}\,(1+u)^{-\frac{N}{2}(1+x)-\frac{1}{2}}\,(1-u)^{-N/2(1-u)-1/2}$$

$$\approx \sqrt{\frac{2}{\pi N}}\exp\left(-\frac{N}{2}\underbrace{(1+u)\ln(1+u)}_{\approx u+\frac{u^2}{2}} - \frac{N}{2}\underbrace{(1-u)\ln(1-u)}_{u-\frac{u^2}{2}}\right)$$

$$\approx \sqrt{\frac{2}{\pi N}}\exp\left(-\frac{Nu^2}{2}\right) = \sqrt{\frac{2}{\pi N}}\exp\left(-\frac{2n^2}{N}\right)$$

(c) Verify that $p(n)$ is normalized.

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

Gaussian PDF

We can easily identify the approximated form of $p(n)$ with the PDF of a Gaussian distribution with $\mu = 0$ and $\sigma = \frac{\sqrt{N}}{2}$, which is obviously normalized!

(d) Use $p(n)$ to calculate $\langle n^2 \rangle$ and $\langle n^4 \rangle$.

Since $\langle n^2 \rangle = \sigma^2$ for a Gaussian, and $\sigma = \frac{\sqrt{N}}{2}$, here: $\langle n^2 \rangle = \frac{N}{4}$!

Generally:

The central absolute moments coincide with plain moments for all even orders, but are nonzero for odd orders. For any non-negative integer p,

$$\mathrm{E}[|X-\mu|^p] = \sigma^p (p-1)!! \cdot \begin{cases} \sqrt{\frac{2}{\pi}} & \text{if } p \text{ is odd} \\ 1 & \text{if } p \text{ is even} \end{cases}$$
$$= \sigma^p \cdot \frac{2^{p/2}\Gamma\left(\frac{p+1}{2}\right)}{\sqrt{\pi}}.$$

Here $n!!$ denotes the double factorial, that is, the product of all numbers from n to 1 that have the same parity as n.

So $\langle n^4 \rangle = E[|n-0|^4] = \left(\frac{\sqrt{N}}{2}\right)^4 3!! = \frac{3N^2}{16}$

(e) Assume that there are two paramagnets, each with N spins, in contact with a total energy of zero. What is the root-mean-square value of n for one of the systems?

Total Energy 0, so we have $N_\uparrow$ and $N_\downarrow$ in total.

So: $\tilde{p}(n) \approx p(n)\,p(-n) \propto \exp(-\frac{4}{N}n^2) \Rightarrow \sigma = \sqrt{\frac{N}{8}} = \sqrt{\langle n^2 \rangle}$

4. Consider two identical particles that cannot occupy the same single-particle state (i.e. fermions), in a 3-level system with single-particle energies 0, ϵ, and 2ϵ.

(a) Find the canonical partition function Z_N.

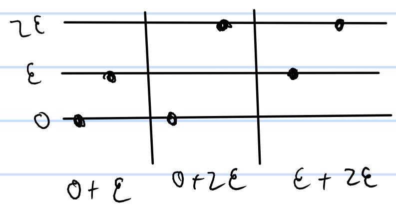
(b) Calculate the average energy. Write down the $T = 0$ and $T = \infty$ limits of the average energy.

(c) Calculate the entropy of the system. Write down the $T = 0$ and $T = \infty$ limits of the average entropy.

(d) Repeat parts (a)-(c), but now assuming that the particles are indistinguishable but can occupy the same state.

(e) Repeat parts (a)-(c), but assume the particles are distinguishable and can occupy the same state.

(a)



$$\Rightarrow Z_N = \exp(-\beta\varepsilon) + \exp(-2\beta\varepsilon) + \exp(-3\beta\varepsilon)$$

(b) $$\langle E \rangle = -\partial_\beta \ln Z_N = \varepsilon \frac{\exp(-\beta\varepsilon) + 2\exp(-2\beta\varepsilon) + 3\exp(-3\beta\varepsilon)}{\exp(-\beta\varepsilon) + \exp(-2\beta\varepsilon) + \exp(-3\beta\varepsilon)}$$

$$\lim_{T\to\infty} \langle E \rangle = \varepsilon \frac{1+2+3}{1+1+1} = 2\varepsilon$$

$$\lim_{T\to 0} \langle E \rangle = \varepsilon \lim_{x\to-\infty} \frac{\exp(x)}{\exp(x)} = \varepsilon$$

(c) $$S = -\left(\frac{\partial F}{\partial T}\right)_V = \beta^2 \left(\frac{\partial F}{\partial \beta}\right)_V = -\beta^2 \partial_\beta \frac{\ln Z_N}{\beta} = \ln Z_N - \frac{\partial_\beta Z_N}{T Z_N} = \ln Z_N + \frac{\langle E \rangle}{T}$$

$$\lim_{T\to\infty} S = \ln(3) + 0 = \ln(3)$$

$$\lim_{T\to 0} S = -\beta\varepsilon + \frac{\varepsilon}{T} = 0$$

(d) Now we have:

Particle 1	0	0	0	ε	ε	2ε
Particle 2	0	ε	2ε	ε	2ε	2ε
Total	0	ε	2ε	2ε	3ε	4ε

$$\Rightarrow Z_N = 1 + \exp(-\beta\varepsilon) + 2\exp(-2\beta\varepsilon) + \exp(-3\beta\varepsilon) + \exp(-4\beta\varepsilon)$$

$$\langle E \rangle = \varepsilon \frac{\exp(-\beta\varepsilon) + 4\exp(-2\beta\varepsilon) + 3\exp(-3\beta\varepsilon) + 4\exp(-4\beta\varepsilon)}{1 + \exp(-\beta\varepsilon) + 2\exp(-2\beta\varepsilon) + \exp(-3\beta\varepsilon) + \exp(-4\beta\varepsilon)}$$

$$\Rightarrow \lim_{T\to\infty} \langle E \rangle = 2\varepsilon \quad \text{and} \quad \lim_{T\to 0} \langle E \rangle = 0$$

Still: $\ln Z_N + \frac{\langle E \rangle}{T}$ (just with new Z_N)

$$\Rightarrow \lim_{T\to\infty} S = \ln(6) \quad \text{and} \quad \lim_{T\to 0} S = 0$$

(e) Now we have:

Particle 1	0	0	0	ε	ε	ε	2ε	2ε	2ε
Particle 2	0	ε	2ε	0	ε	2ε	0	ε	2ε
Total	0	ε	2ε	ε	2ε	3ε	2ε	3ε	4ε

$$\Rightarrow \quad Z_N = 1 + 2\exp(-\beta\varepsilon) + 3\exp(-2\beta\varepsilon) + 2\exp(-3\beta\varepsilon) + \exp(-4\beta\varepsilon)$$

$$\langle E \rangle = \varepsilon \frac{2\exp(-\beta\varepsilon) + 6\exp(-2\beta\varepsilon) + 6\exp(-3\beta\varepsilon) + 4\exp(-4\beta\varepsilon)}{1 + 2\exp(-\beta\varepsilon) + 3\exp(-2\beta\varepsilon) + 2\exp(-3\beta\varepsilon) + \exp(-4\beta\varepsilon)}$$

And S still $\ln Z_N + \frac{\langle E \rangle}{T}$ (just with new Z_N)

So: $\lim_{T\to\infty} \langle E \rangle = 2\varepsilon$, $\lim_{T\to 0} \langle E \rangle = 0$,

$\lim_{T\to\infty} S = \ln 9$, $\lim_{T\to 0} S = 0$.