PHY 831: Statistical Mechanics
Homework 2

Due September 21st, 2020

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

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.

3. Consider N spin $1/2$ particles 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
   $$\Omega(n) = \frac{N!}{(N/2+n)!(N/2-n)!}.$$

   (b) If the total energy of the system is unspecified, the probability of a 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 $\ln(2\pi N)$.)

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

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

   (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?

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.

1) $$\left(\frac{\partial E}{\partial N}\right)_{T,V} = \underbrace{\left(\frac{\partial F}{\partial N}\right)_{T,V}}_{=\,\mu} + T\left(\frac{\partial S}{\partial N}\right)_{T,V} \qquad \text{and} \qquad \frac{\partial^2 F}{\partial T \partial N} = -\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{N,V}$$

$$\Rightarrow \left(\frac{\partial E}{\partial N}\right)_{T,V} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{N,V}$$

2) $$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} = \overbrace{T\left(\frac{\partial S}{\partial T}\right)_{V,N}}^{C_V} + T\left(\frac{\partial S}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

also $$\left(\frac{\partial S}{\partial V}\right)_{T} = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial P}{\partial T}\right)_{V,N} = -\left(\frac{\partial P}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

$$C_P = C_V - T\underbrace{\left(\frac{\partial P}{\partial V}\right)_{T,N}}_{=\,-(V\kappa_T)^{-1}}\underbrace{\left(\frac{\partial V}{\partial T}\right)^2_{P,N}}_{=\,V\alpha_P}$$

$$= C_V + TV\frac{\alpha_P^2}{\kappa_T}$$

3) a) $N!$ ways to choose ordering of spins if first $N/2 + n$ spins are up and the rest are down.

This over counts by a factor $N_\uparrow!\, N_\downarrow!$ since the $\left\{\begin{matrix}\text{down}\\ \text{up}\end{matrix}\right\}$ spins can be re-ordered to give the same state.

$$N_\uparrow = \frac{N}{2} + n \qquad N_\downarrow = \frac{N}{2} - n$$

$$\Rightarrow \quad \Omega(n) = \frac{N!}{\left(\frac{N}{2}+n\right)!\left(\frac{N}{2}-n\right)!}$$

b) $$p(n) \simeq \frac{\sqrt{2\pi N}}{2^N} \cancel{N^N} \cancel{e^{-N}} \frac{1}{\sqrt{\pi N(1+x)}} \frac{1}{\sqrt{\pi N(1-x)}} \cancel{e^{\frac{N}{2}(1+x)}} \cancel{e^{\frac{N}{2}(1-x)}}$$

$$\boxed{x = \frac{2n}{N}}$$

$$\times \left[\frac{N}{2}(1+x)\right]^{-\frac{N}{2}(1+x)} \left[\frac{N}{2}(1-x)\right]^{-N/2(1-x)}$$

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

$$\simeq \sqrt{\frac{2}{\pi N}} \exp\left[-\frac{N}{2}(1+x)\log(1+x) - \frac{N}{2}(1-x)\log(1-x)\right]$$

$$(1+x)\log(1+x) \simeq x + \frac{x^2}{2}$$

$$\simeq \sqrt{\frac{2}{\pi N}} \exp\left[-\frac{N}{2}x^2\right] = \sqrt{\frac{2}{\pi N}} \exp\left[-\frac{2}{N}n^2\right]$$

c) just a gaussian with mean $= 0$ $\quad \sigma = \frac{\sqrt{N}}{2}$

d) $\langle n^2 \rangle = \frac{N}{4} \qquad \langle n^4 \rangle = \frac{3N^2}{16}$

e) $$p(n) \propto \Omega_1(n)\,\Omega_2(-n)$$
$$\propto p_1(n)\,p_2(-n) \propto \exp\left[-\frac{4}{N}n^2\right]$$

$$\Rightarrow \sqrt{\langle n^2 \rangle} = \sigma = \sqrt{\frac{N}{8}}$$

4) a) allowed levels: $0+\varepsilon,\ 0+2\varepsilon,\ \varepsilon+2\varepsilon$

$$\Rightarrow \quad Z_N = e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}$$

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

$$\langle E\rangle(T\to\infty) = \varepsilon\,\frac{6}{3} = 2\varepsilon$$

$$\langle E\rangle(T\to 0) = \varepsilon$$

c) $$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = \beta^2\left(\frac{\partial F}{\partial \beta}\right)_{N,V} = -\beta^2\,\partial_\beta\,\beta^{-1}\ln Z_N$$

$$= \ln Z_N - \frac{\partial_\beta Z_N}{T Z_N} = \ln Z_N + \frac{\langle E\rangle}{T}$$

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

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

d) allowed states: $0+0,\ 0+\varepsilon,\ 0+2\varepsilon,\ \varepsilon+\varepsilon,\ \varepsilon+2\varepsilon,\ 2\varepsilon+2\varepsilon$

$$Z_N = 1 + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}$$

$$\langle E\rangle = \varepsilon\,\frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + 3e^{-3\beta\varepsilon} + 4e^{-4\beta\varepsilon}}{Z_N}$$

$$\langle E\rangle(T\to\infty) = 2\varepsilon \qquad \langle E\rangle(T\to 0) = 0$$

$$S(T\to\infty) = \ln(6) \qquad S(T\to 0) = 0$$

e) allowed states:

Particle 1	Particle 2	
0	0	$= 0$
0	1	$= \varepsilon$
0	2	$= 2\varepsilon$
1	0	$= \varepsilon$
1	1	$= 2\varepsilon$
1	2	$= 3\varepsilon$
2	0	$= 2\varepsilon$
2	1	$= 3\varepsilon$
2	2	$= 4\varepsilon$

$$Z_N = 1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}$$

$$\langle E\rangle(T\to 0) = 0 \qquad \langle E\rangle(T\to\infty) = 2\varepsilon$$

$$S(T\to 0) = 0 \qquad S(T\to\infty) = \ln 9$$