PHY252 PS4 1006940802 April 8^{th} 2022

Q1

a) ϵ : size of energy unit $= \hbar\omega$ in quantum harmonic oscillator.

For one oscillator, the partition function is given by

$$Z = \sum_s e^{-\beta E(s)} \quad , \text{ where } \beta = \frac{1}{kT} .$$

Assuming $E_0 = 0$, the other energy levels are determined by $E_n = \epsilon(n+\frac{1}{2})$ for $n \geq 1$. It doesn't logically make sense for me to assume $E_0 = 0$, so insted I will assume $E_n = \epsilon(n+\frac{1}{2})$ for $n \geq 0$.

The partition function is then

$$Z = \sum_s e^{-\beta\epsilon(n+\frac{1}{2})}$$

$$= \sum_{s=n} e^{-\beta\frac{\epsilon}{2}} \cdot e^{-\beta\epsilon n}$$

$$= e^{-\frac{\beta\epsilon}{2}} \sum_{n=0} e^{-\beta\epsilon n}$$

Apply the summation formula

$$= e^{-\frac{\beta\epsilon}{2}} \left(\frac{1}{1-e^{-\beta\epsilon}}\right)$$

Therefore $\boxed{Z = \frac{e^{-\beta\epsilon/2}}{1-e^{-\beta\epsilon}}}$

b) The average energy can be expressed as $\bar{E} = -\frac{1}{Z}\frac{\partial}{\partial\beta}[Z]$. This is

$$\bar{E} = -\frac{1}{Z}\left[\frac{\partial}{\partial\beta} e^{-\beta\epsilon/2} \cdot (1-e^{-\beta\epsilon})^{-1}\right]$$

$$= -\frac{1}{Z}\left[-\frac{\epsilon}{2} e^{-\beta\epsilon/2} \cdot (1-e^{-\beta\epsilon})^{-1} + e^{-\beta\epsilon/2} \cdot (-1)(1-e^{-\beta\epsilon})^{-2} \cdot (-e^{-\beta\epsilon} \cdot (-\epsilon))\right]$$

$$= -\frac{1}{Z}\left[-\frac{\epsilon}{2} e^{-\beta\epsilon/2} \cdot (1-e^{-\beta\epsilon})^{-1} + \epsilon e^{-\beta\epsilon/2}(1-e^{-\beta\epsilon})^{-2}(-e^{-\beta\epsilon})\right]$$

$$= \frac{\cancel{1-e^{-\beta\epsilon}}}{\cancel{e^{-\beta\epsilon/2}}}\left[+\frac{\epsilon}{2} \cancel{e^{-\beta\epsilon/2}} \cancel{(1-e^{-\beta\epsilon})^{-1}} + \epsilon \cancel{e^{-\beta\epsilon/2}} e^{-\beta\epsilon}(1-e^{-\beta\epsilon})^{\cancel{-2}\,-1}\right]$$

$$= \frac{\epsilon}{2} + \epsilon e^{-\beta\epsilon}(1-e^{-\beta\epsilon})^{-1}$$

$$= \frac{\epsilon}{2} + \epsilon\frac{e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}} \cdot \frac{e^{\beta\epsilon}}{e^{\beta\epsilon}}$$

and therefore

$$\boxed{\bar{E} = \epsilon\left[\frac{1}{2} + \frac{1}{e^{\beta\epsilon}-1}\right]}$$

1c) We can express the total energy of the solid by taking the average energy of each oscillator times N, the number of oscillators.

That is,

$$\boxed{E_{tot} = N\langle E\rangle = N\epsilon\left[\frac{1}{2} + \frac{1}{e^{\beta\epsilon}-1}\right]}$$

1d) The fraction of excited oscillators compared to ground state oscillators is given by $\frac{P(\text{excited})}{P(\text{ground})}$ = difference in energy levels.

Since the probability of finding some state is given by

$$P(s) = \frac{1}{Z}e^{-E(s)/KT},$$ then

$$\frac{P(E_1)}{P(E_0)} = e^{-[E_1 - E_0]/KT}.$$

$$= \exp\left[-\left(\epsilon\cdot\frac{3}{2} - \epsilon\cdot\left(\frac{1}{2}\right)\right)/KT\right]$$

$$= \exp\left[-\epsilon/KT\right].$$

Taking $\epsilon = 2eV$ and $T = 298K \equiv 25°C$, then the fraction of excited states compared to ground state is

$$e^{-\frac{2}{K\cdot 298}} = \exp\left[-\frac{2\,eV}{298\cdot 1.38\times10^{-23}}\right] = \exp\left[-\frac{2\,eV}{298K\cdot 8.617\times10^{-5}\,eV/K}\right]$$

$$\simeq 1.495\times10^{-34}.$$

Therefore $\boxed{\frac{N(\text{excited})}{N(\text{ground})} = 1.5\times10^{-34}}$

Q2 a) 3 distinguishable dipoles:

$\vec{B}_{ext}$ gives a down dipole $E = E_{down} = \alpha$, and an up dipole $E = E_{up} = 0$.

All possible microstates:

	1) All up	2) 1 up, 2 down	3) 2 up, 1 down	4) All down
E:	0	2α	α	3α.

b) The partion function, given

$$Z = \sum_s e^{-E(s)\beta},$$

and summing over all microstates defined by E(s), is then

$$\boxed{Z = 1 + e^{-\alpha\beta} + e^{-2\alpha\beta} + e^{-3\alpha\beta}}$$

c) The average energy of the system is given by

$$\bar{E} = \frac{1}{Z}\sum_s E(s)\, e^{-\beta E(s)}.$$

Taking the partition function from the previous part, we have that

$$\boxed{\bar{E} = \frac{\alpha e^{-\alpha\beta} + 2\alpha e^{-2\alpha\beta} + 3\alpha e^{-3\alpha\beta}}{1 + e^{-\alpha\beta} + e^{-2\alpha\beta} + e^{-3\alpha\beta}}}$$

d) No interation energy with $\vec{B}_{ext}$.

$-\varepsilon$ if parallel, $+\varepsilon$ if antiparallel.

2 macrostates: All parallel, 1 antiparallel

↑↑↑	↑↑↓ ↑↓↑ ↓↑↑	↓↓↓	↑↓↓ ↓↑↓ ↓↓↑
$E = -3\varepsilon$	$E = \varepsilon$	$E = -3\varepsilon$	$E = \varepsilon$.

The partition function is then $Z = e^{3\varepsilon\beta} + e^{-\varepsilon\beta}$.

e) The probability of all 3 dipoles being parallel is equivalent to the probability of finding a microstate in the macrostate of energy $E=-3\varepsilon$. It is given by

$$\mathbb{P}(E=-3\varepsilon) = \frac{e^{3\varepsilon\beta}}{Z} = \frac{e^{3\varepsilon\beta}}{e^{-\varepsilon\beta}+e^{3\varepsilon\beta}}.$$

As a function of temperature, it is

$$\boxed{\mathbb{P}(E=-3\varepsilon\,/\,\text{all parallel}) = \frac{e^{3\varepsilon/KT}}{e^{-\varepsilon/KT}+e^{3\varepsilon/KT}}}.$$

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f) The average energy is again given by

$$\bar{E} = \frac{1}{Z}\sum_s E(s)\,e^{-E(s)\beta}$$

So

$$\boxed{\bar{E} = \frac{-3\varepsilon e^{3\varepsilon/KT}+\varepsilon e^{-\varepsilon/KT}}{e^{3\varepsilon/KT}+e^{-\varepsilon/KT}}}.$$

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Q3 a) The average energy is

$$\bar{E} = \frac{1}{Z} \sum_s E(s)\, e^{-\beta E(s)}$$

$$= \frac{1}{Z} \sum_s \left(-\frac{\partial}{\partial\beta} e^{-\beta E(s)}\right)$$

$$= -\frac{1}{Z} \frac{\partial}{\partial\beta} \sum_s e^{-\beta E(s)}$$ definition of $Z = \sum_s e^{-\beta E(s)}$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial\beta}$$ chain rule

$$= -\frac{\partial}{\partial\beta}[\log Z].$$

Since $\beta = \frac{1}{KT}$, then $d\beta = -\frac{1}{KT^2} dT$

$$\Rightarrow \bar{E} = -\frac{\partial}{-\frac{1}{KT^2}\partial T}[\log Z]$$

$$\boxed{\bar{E} = KT^2 \frac{\partial}{\partial T}[\log Z]}$$ as required.

(b) As before,

$$\overline{E^2} = \frac{1}{Z}\sum_s E(s)^2 e^{-\beta E(s)}$$

$$= \frac{1}{Z}\sum_s \left(\frac{\partial^2}{\partial\beta^2} e^{-\beta E(s)}\right)$$

$$= \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}\sum_s e^{-\beta E(s)}$$ definition of Z.

$$\boxed{\overline{E^2} = +\frac{1}{Z}\frac{\partial^2}{\partial\beta^2} Z}$$

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c) $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. Taking $U = \bar{E}$, we have that

$$= \frac{\partial}{\partial T}\left[KT^2 \frac{\partial}{\partial T}[\log Z]\right] \equiv -\frac{1}{KT^2}\frac{\partial}{\partial\beta}\left[-KT^2 \frac{\partial}{KT^2\partial\beta}[\log Z]\right]$$

$$= \frac{1}{KT^2}\frac{\partial^2}{\partial\beta^2}[\log Z].$$

$$= \frac{1}{KT^2}\left[\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial}{\partial\beta}Z\right)\right]$$

$$= \frac{1}{KT^2}\left[-\frac{1}{Z^2}\frac{\partial^2}{\partial\beta^2}Z + \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}Z\right].$$

$$= \left(\frac{1}{Z} \frac{\partial^2}{\partial \beta^2} [Z] - \left(\frac{1}{Z} \frac{\partial}{\partial \beta} [Z] \right)^2 \right) \cdot \frac{1}{kT^2}$$

$$= \left(\overline{E^2} - \overline{E}^2 \right) \cdot \frac{1}{kT^2}$$

And therefore

$$\boxed{C_V = \frac{\langle E^2 \rangle - \langle E \rangle^2}{kT^2}}$$

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d) Since $\delta E = E - \overline{E}$, then $(\delta E)^2 = E^2 + \overline{E}^2 - 2E\overline{E}$.

Taking this average, since the average is linear, is

$$\overline{(\delta E)^2} = \overline{E^2} + \overline{\overline{E}^2} - \overline{2E\overline{E}}$$
$$= \overline{E^2} + \overline{E}^2 - 2\overline{E}^2$$
$$= \overline{E^2} - \overline{E}^2,$$

which is equivalent to what was found in the previous part. Therefore

$$\boxed{C_V = \frac{\langle (\delta E)^2 \rangle}{kT^2}}.$$

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e) I showed that, in Q3c, that $\frac{\partial^2}{\partial \beta^2} [\log Z] = \langle E^2 \rangle - \langle E \rangle^2$,

but $\overline{E} = -\frac{\partial}{\partial \beta} [\log Z]$ as shown in Q3a, which then implies that

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2}{\partial \beta^2} [\log Z] = -\frac{\partial}{\partial \beta} \left(-\frac{\partial}{\partial \beta} [\log Z] \right)$$

$$= -\frac{\partial}{\partial \beta} [\overline{E}]$$

$$\boxed{= -\frac{\partial}{\partial \beta} [\langle E \rangle]},$$

which is what I wanted to show.

Q4 a) The grand partition function gives

$$\mathcal{Z} = \sum_s \exp\left[-(E(s) - \mu N(s))/kT\right].$$

If the number of particles in each state $N(s) = n$, $n = 0,1,2$ with energy $E(s) = \epsilon n$, then, the probability of a state being occupied by n particles is

$$\mathbb{P}(n) = \frac{1}{\mathcal{Z}} e^{-n(\epsilon-\mu)/kT}.$$

Since each state can only intake 0, 1, or 2 particles, then

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT}.$$

The distribution or average occupancy of a state is the sum

$$\bar{n} = \sum_n n\,\mathbb{P}(n)$$
$$= \frac{1}{\mathcal{Z}} \sum_{n=0}^{2} n e^{-n(\epsilon-\mu)/kT}$$
$$= \frac{1}{\mathcal{Z}}\left[0 + e^{-(\epsilon-\mu)/kT} + 2e^{-2(\epsilon-\mu)/kT}\right].$$

Therefore

$$\boxed{\bar{n} = \frac{e^{-(\epsilon-\mu)/kT} + 2e^{-2(\epsilon-\mu)/kT}}{1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT}}}$$

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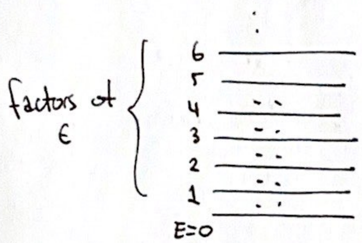
b) When $\epsilon = \mu$, we get in return that

$$\bar{n}(\epsilon=\mu) = \frac{e^0 + 2e^0}{1 + e^0 + e^0} = \frac{3}{3} = 1.$$

For $\epsilon \gg 1$, $e^{-(\epsilon-\mu)/kT}$ is very small, so $\boxed{\bar{n}(\epsilon \gg 1) \approx 0}$

For $\epsilon \ll 1$ and $\mu \gg kT$, then the leading coefficient of the limit is $\frac{2}{1}$, so $\boxed{\bar{n}(\epsilon \ll 1) \approx 2.}$

4c) State defined by energy. Since each state can only hold 2 particles maximum at a time, we can "fill" the states as a "tower"



$$2E_0 + 2E_1 + 2E_2 + 2E_3 + 2E_4 = E_{min}$$

$$2(0) + 2(\epsilon) + 2(2\epsilon) + 2(3\epsilon) + 2(4\epsilon) = E_{min}$$

$$= (2+4+6+8)\,\epsilon$$

$$= 20\epsilon.$$

Since each ϵ is 1eV, then $\boxed{E_{min} = 20 \text{ eV}.}$

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d) With a minimum energy of 20eV and an additional energy of $+5q = 5eV$, then the state is defined by 25eV.

I will assume that the system always uses the 5eV in excess to the ground state.

Since the particles are indistinguishable, the multiplicity Ω is given by the number of ways the particles can arrange themselves given +5eV.

1,1,1,1,1 (5 particles inherit 1 eV each)

2,1,1,1 (4 particles inherit 1 eV and one with another 1eV)

2,2,1

3,1,1 etc, and so on

3,2

4,1

5 (1 particle inherits 5eV in all)

Since there are 7 ways to decompose 5 so that indistinguishable particles inherit different energy amounts, then $\Omega = 7$.

Then $\boxed{S = 1.38 \times 10^{-23} \log 7 \ \frac{J}{K}}$ $(\log \equiv \ln)$

Other Solutions I got: 5, 17, 13, 12, 14. This problem is very confusing.

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Q5

a) As in the textbook, the distribution function is proportional to the probability of a particle having some v, times the number of velocity vectors $\vec{r}$ with $\|\vec{r}\| = v$. That is,

$$D(v) \propto (\mathbb{P} \text{ of having } v) \cdot (\# \text{ of } \vec{r} \text{ with } \|\vec{r}\| = v).$$

The probability is given by $\text{Exp}(-E(s)/kT)$, but $E(s) = \frac{1}{2}mv^2$ (the kinetic energy), and the number of velocity vectors $\vec{r}$ with $\|\vec{r}\| = v$ lies in a two dimensional circle of radius v, which then has surface area $2\pi v$.

Then

$$D(v) = C \cdot 2\pi v \cdot e^{-\frac{mv^2}{2kT}},$$

with $C \in \mathbb{R}$ a constant of proportionality. We proceed by determining C: the probability over all velocities should be equal to 1:

$$\frac{1}{C} = \int_0^\infty dv \cdot 2\pi v \exp\left(-\frac{mv^2}{2kT}\right) \qquad \text{define } a \equiv \frac{m}{2kT}$$

$$= \int_0^\infty dv \cdot 2\pi v \exp(-av^2) \qquad u = -av^2, \quad du = -2av\, dv \Rightarrow dv = -\frac{du}{2av}$$

$$= -\int_0^{-\infty} \frac{du}{2av} \cdot 2\pi v\, e^{u}$$

$$= -\frac{\pi}{a} \cancel{\int_0^{-\infty} du\, e^{u}}^{-1}$$

$$= \frac{\pi}{a}. \qquad \text{Therefore } C = \frac{a}{\pi}, \text{ so the distribution function is}$$

$$D(v) = \frac{a}{\pi} \cdot 2\pi v^2 \cdot \exp(-av^2)$$

$$\Rightarrow \boxed{D(v) = \frac{mv}{kT} \exp\left(-\frac{mv^2}{2kT}\right)}$$

5 b) The most likely velocity vector is $\vec{v} = \vec{0}$, which is because there are just as many molecules in the plane moving with velocity $+\vec{v}$ as there are moving with $-\vec{v}$, so they essentially average to zero.

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c) The most likely speed is given when $D(v)$ reaches a maximum, since the maximum represents a probability peak.

$$\frac{dD(v)}{dv} = \frac{d}{dv}\left[\frac{mv}{kT} e^{-\frac{mv^2}{2kT}}\right]$$

$$0 = \frac{m}{\cancel{kT}} \cancel{e^{-mv^2/2kT}} + \frac{mv}{\cancel{kT}} \cancel{e^{-mv^2/kT \cdot 2}} \left(-\frac{mv}{kT}\right)$$

$$0 = 1 - \frac{mv^2}{kT}$$

$$\Rightarrow \boxed{v = \sqrt{\frac{kT}{m}}}$$ is the most likely speed.