Solutions Problem Set 5

1)

a) Recall, to go from the microcanonical ensemble at fixed E to the canonical ensemble at fixed T we took a Laplace transform of the microcanonical partition function $\Omega(E)$.

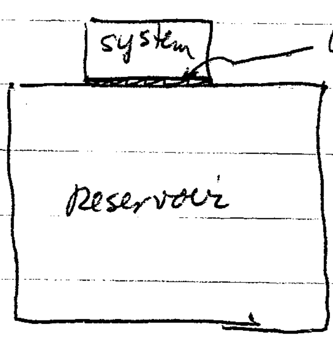
$$Q_N = \int_0^\infty \frac{dE}{\Delta E}\, e^{-\beta E}\, \Omega(E)$$

What is in the exponential is $\frac{E}{k_B T}$, where $\frac{1}{T}$ is the conjugate variable to E in the entropy formulation. So to go from the canonical to the constant pressure ensemble, we take a Laplace transform of Q_N from V to its conjugate variable $\frac{P}{T}$

$$\boxed{Z(T,P,N) = \int_0^\infty \frac{dV}{\Delta V}\, e^{-\beta P V}\, Q_N(T,V)}$$

where ΔV is an arbitrary unit of volume taken so that Z is dimensionless.

We could derive the above by methods similar to those used to derive the canonical ensemble from the microcanonical ensemble. Consider our system in contact with a thermal and volume reservoir



wall conducts heat and can slide so that system and reservoir may exchange volume.

If E, V are ~~tot~~ energy and volume of the system, and total energy E_T and total volume V_T are fixed,

then the energy of the reservoir is $E_T - E$
and the volume of the reservoir is $V_T - V$

The number of states of the total system, in which the system of interest ~~has~~ has energy E and volume V is

$$\Omega(E,V)\,\Omega_R(E_T - E, V_T - V)$$

$$= \Omega(E,V)\, e^{\frac{S_R(E_T - E, V_T - V)}{k_B}}$$

expand $S_R(E_T - E, V_T - V) \simeq S_R(E_T, V_T)$

$$+ \left(\frac{\partial S_R}{\partial E}\right)_V (-E) + \left(\frac{\partial S_R}{\partial V}\right)_E (-V)$$

$$= S_R(E_T, V_T) - \frac{1}{T} E - \frac{p}{T} V$$

so the probability for the system of interest to have energy E and volume V is

$$P(E,V) \propto \Omega(E,V)\,\Omega_R(E_T - E, V_T - V)$$
$$\propto \Omega(E,V)\, e^{-(E+pV)/k_B T}$$

The partition function is just the normalizing constant for this probability density

$$Z(T,p) = \int \frac{dE}{\Delta} \int \frac{dV}{\Delta V}\, \Omega(E,V)\, e^{-\beta E}\, e^{-\beta p V}$$

Rearranging we get:

$$Z(T,p) = \int_0^\infty \frac{dV}{\Delta V} e^{-\beta p V} \int_0^\infty \frac{dE}{\Delta} \Omega(E,V) e^{-\beta E}$$

$$= \int_0^\infty \frac{dV}{\Delta V} e^{-\beta p V} Q_N(E,V)$$

b) $G(T,p,N) = -k_B T \ln Z(T,p,N)$

In the ensemble with fluctuating volume, the average volume is given by

$$\langle V \rangle = \int dV \; V \; P(V)$$

where the probability density to have volume V is just

$$P(V) = \frac{e^{-\beta p V} Q_N(T,V)}{\Delta V \; Z(T,p,N)}$$

so $$\langle V \rangle = \frac{\int \frac{dV}{\Delta V} V e^{-\beta p V} Q_N(T,V)}{Z(T,p,N)}$$

Now compare this to

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = -\frac{k_B T}{Z}\left(\frac{\partial Z}{\partial p}\right)_{T,N}$$

$$= \frac{-k_B T}{Z} \int \frac{dV}{\Delta V} (-\beta V) e^{-\beta p V} Q_N(T,V)$$

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = \frac{1}{Z}\int \frac{dV}{\Delta V}\, V e^{-\beta p V} Q_N(T,V)$$

so $\left(\frac{\partial G}{\partial p}\right)_{T,N} = \langle V \rangle$ which is what we expect from classical thermodynami

c) Isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial V^2}\right)_{T,N} \quad \text{since } V = \left(\frac{\partial G}{\partial p}\right.$$

evaluate $\left(\frac{\partial^2 G}{\partial V^2}\right)_{T,N}$ using $G = -k_B T \ln Z$

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = \frac{-k_B T}{Z}\left(\frac{\partial Z}{\partial p}\right)_{T,N} = \langle V \rangle$$

$$\Rightarrow \left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} = \frac{-k_B T}{Z}\left(\frac{\partial^2 Z}{\partial p^2}\right)_{T,N} + \frac{k_B T}{Z^2}\left(\frac{\partial Z}{\partial p}\right)^2_{T,N}$$

$$= \frac{-k_B T}{Z}\left(\frac{\partial^2 Z}{\partial p^2}\right)_{T,N} + \frac{1}{k_B T}\langle V \rangle^2$$

Now
$$\frac{1}{Z}\frac{\partial^2 Z}{\partial p^2} = \frac{1}{Z}\int \frac{dV}{\Delta V}\left(\frac{\partial^2}{\partial p^2} e^{-\beta p V}\right) Q_N$$

$$= \frac{1}{Z}\int \frac{dV}{\Delta V}(-\beta V)^2 e^{-\beta p V} Q_N$$

$$= \int dV\, (-\beta V)^2 P(V)$$

$$= \frac{1}{(k_B T)^2}\langle V^2 \rangle$$

So $\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,V} = -\frac{1}{k_BT}\langle V^2\rangle + \frac{1}{k_BT}\langle V\rangle^2$

$$\boxed{\kappa_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial V^2}\right)_{T,V} = \frac{\langle V^2\rangle - \langle V\rangle^2}{k_BT\,V}}$$

So $k_BTV\kappa_T = \langle V^2\rangle - \langle V\rangle^2$ is the variance of the fluctuations in volume.

Since κ_T and T are intensive quantities, the above implies that $\langle V^2\rangle - \langle V\rangle^2 \propto V$

So the relative fluctuation in V

$$\frac{\sqrt{\langle V^2\rangle - \langle V\rangle^2}}{V} \sim \frac{\sqrt{V}}{V} \sim \frac{1}{\sqrt{V}} \to 0$$

as $V \to \infty$

d) For the ideal gas $Q_N(T,V) = \frac{Q_1^N}{N!} = \frac{V^N}{N!\lambda^{3N}}$

where $\lambda = \sqrt{\frac{h^2}{2\pi m k_BT}}$ is the thermal wavelength

So $\quad Z(T,p,N) = \int \frac{dV}{\Delta V} \, e^{-\beta p V} \, \frac{V^N}{N! \, \lambda^{3N}}$

we need the following integral

$\int_0^\infty dV \, e^{-\beta p V} \, V^N$ integrate by parts

$$= \left[\frac{V^N e^{-\beta p V}}{-\beta p} \right]_0^\infty + \int_0^\infty dV \, \frac{e^{-\beta p V}}{\beta p} \, N \, V^{N-1}$$

first term vanish when evaluate at the limits, so

$$\int_0^\infty dV \, e^{-\beta p V} \, V^N = \frac{N}{\beta p} \int dV \, e^{-\beta p V} \, V^{N-1}$$

$$= \frac{N(N-1)}{(\beta p)^2} \int dV \, e^{-\beta p V} \, V^{N-2}$$

$$= \frac{N!}{(\beta p)^N} \int_0^\infty dV \, e^{-\beta p V}$$

$$= \frac{N!}{(\beta p)^N} \left[\frac{e^{-\beta p V}}{-\beta p} \right]_0^\infty$$

$$= \frac{N!}{(\beta p)^{N+1}}$$

So

$$Z = \frac{1}{\Delta V \, N! \, \lambda^{3N}} \, \frac{N!}{(\beta p)^{N+1}} = \left(\frac{k_B T}{p} \right)^{N+1} \frac{1}{\lambda^{3N} \, \Delta V}$$

$$\boxed{Z(T,p,N) = \left(\frac{k_B T}{p} \right)^{N+1} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \frac{1}{\Delta V}}$$

$$G(T,p,N) = -k_B T \ln Z(T,p,N)$$

$$= -k_B T \ln \left\{ \left(\frac{k_B T}{p}\right)^{N+1} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \frac{1}{\Delta V} \right\}$$

$$= -k_B T N \ln \left[\frac{k_B T}{p} \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \right]$$

$$- k_B T \ln \left[\frac{k_B T}{p \, \Delta V} \right]$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N}$$

We can write G as

$$G = -k_B T \left[\ln\left(T^{\frac{5N}{2}+1}\right) + \text{const} \right]$$

where "const" depends on p and N but not on T

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = -k_B \left[\ln\left(T^{\frac{5N}{2}+1}\right) + \text{const} \right]$$

$$- k_B T \left(\frac{5N}{2}+1\right) \frac{1}{T}$$

$$= -\left(\frac{5N}{2}+1\right) k_B \ln T + \text{const}'$$

indep of T

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} = -\left(\frac{5N}{2}+1\right) k_B \frac{1}{T}$$

So finally

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}$$

$$= T\left(\frac{5N}{2}+1\right)k_B\frac{1}{T}$$

$$C_p = \left(\frac{5}{2}N+1\right)k_B$$

$$\boxed{C_p \simeq \frac{5}{2}Nk_B}$$ in limit N is large

this is the expected result for the ideal gas.

2)

$$\mathcal{H}^{(1)} = \frac{|\vec{p}|^2}{2m} + \frac{1}{2} m \omega_0^2 |\vec{r}|^2$$

a) Since there are 3 quadratic momentum degrees of freedom, and 3 spatial quadratic degrees of freedom for <u>each</u> particle, the equipartition theorem gives for the average energy

$$\boxed{\langle E \rangle = 6N\left(\tfrac{1}{2} k_B T\right) = 3N k_B T}$$

b) The probability for a single particle to be found with momentum $\vec{p}$ at position $\vec{r}$ is just given by the Boltzmann factor

$$P \propto e^{-\beta \mathcal{H}^{(1)}[\vec{r}, \vec{p}]}$$

since particles are non-interacting

Integrating over momentum $\vec{p}$, the probability to find the particle at position $\vec{r}$ is

$$P(\vec{r}) \propto e^{-\beta\left(\frac{1}{2} m \omega_0^2 |\vec{r}|^2\right)}$$

The density of particles at $\vec{r}$ is just proportional to the probability to find one particle at $\vec{r}$. Hence

$$n(\vec{r}) = C e^{-m\omega_0^2 r^2/2k_BT}$$

where C is determined by the normalization condition

$$N = \int d^3r \; n(\vec{r}) = 4\pi C \int_0^\infty dr \, r^2 e^{-m\omega_0^2 r^2/2k_BT}$$

where the 4π comes from integrating over the direction of $\vec{r}$ ie

$$\int d^3r = \int_0^{2\pi} d\varphi \int_0^{\theta} d\theta \sin\theta \int_0^\infty dr \, r^2$$

$$= 4\pi \int_0^\infty dr \, r^2$$

To do the integral, make a substitution of variables

$$x = \sqrt{\frac{m\omega_0^2}{k_BT}} \; r$$

$$\Rightarrow \quad N = 4\pi C \left(\frac{k_BT}{m\omega_0^2}\right)^{3/2} \int_0^\infty dx \; x^2 e^{-x^2/2}$$

you can now either look up the integral or remember from the properties of the Normal probability distribution (Gaussian with $\sigma = 1$)

$$\int_{-\infty}^{\infty} dx \; x^2 \frac{e^{-x^2/2}}{\sqrt{2\pi}} = 1$$

so $\int_0^\infty dx\, x^2 e^{-x^2/2} = \frac{1}{2}\int_{-\infty}^{\infty} dx\, x^2 e^{-x^2/2} = \frac{1}{2}\sqrt{2\pi} = \sqrt{\frac{\pi}{2}}$

So

$$N = 4\pi C \left(\frac{k_B T}{m\omega_0^2}\right)^{3/2} \sqrt{\frac{\pi}{2}}$$

$$C = \frac{N}{4\pi}\sqrt{\frac{2}{\pi}}\left(\frac{m\omega_0^2}{k_B T}\right)^{3/2}$$

$$\boxed{n(\vec{r}) = \frac{N}{4\pi}\sqrt{\frac{2}{\pi}}\left(\frac{m\omega_0^2}{k_B T}\right)^{3/2} e^{-m\omega_0^2 r^2/2k_B T}}$$

density has a Gaussian shape with decay length $l = \sqrt{\frac{k_B T}{m\omega_0^2}}$, ie

$$n(\vec{r}) \propto \frac{1}{l^3} e^{-r^2/2l^2}$$

The smaller T, the closer the distribution stays to the origin

c) $\langle r \rangle = \int d^3r\, |\vec{r}|\, p(\vec{r})$

prob to have a particle at $\vec{r}$

$$p(\vec{r}) = \frac{n(\vec{r})}{N} = \frac{1}{4\pi}\sqrt{\frac{2}{\pi}}\frac{1}{l^3} e^{-r^2/2l^2}$$

with l defined as above

$$\langle r \rangle = 4\pi \int_0^\infty dr\, r^2\, r\, \frac{1}{4\pi}\sqrt{\frac{2}{\pi}}\frac{1}{l^3} e^{-r^2/2l^2}$$

$$\langle r \rangle = \sqrt{\frac{2}{\pi}} \frac{1}{\ell^3} \int_0^\infty dr \, r^3 \, e^{-r^2/2\ell^2}$$

change variables of integration to $x = r/\ell$

$$\langle r \rangle = \sqrt{\frac{2}{\pi}} \, \ell \underbrace{\int_0^\infty dx \, x^3 \, e^{-x^2/2}}_{=2}$$

$= 2$ look up or otherwise evaluate

$$\boxed{\langle r \rangle = 2\sqrt{\frac{2}{\pi}} \, \ell = 2\sqrt{\frac{2}{\pi}} \sqrt{\frac{k_B T}{m\omega_0^2}} = \sqrt{\frac{8 k_B T}{\pi m \omega_0^2}}}$$

d) To find the pressure $p(r)$ at radial distance r from origin, consider an imaginary box of volume ΔV centered at position $\vec{r}$ in the gas. The length of the box should be small compared to ℓ so that the density $n(\vec{r})$ can be taken as approximately constant throughout the box, but ΔV should be large enough that it contain many particles $\Delta N \approx \Delta V \, n(\vec{r})$.

Consider a box of ΔV about the point $\vec{r}$.
If ΔV is small on the length scale $l = \sqrt{\frac{k_B T}{m\omega_0^2}}$

then the number of particles in the box is

$$\Delta N = n(\vec{r})\,\Delta V \qquad \text{with } n(\vec{r}) \text{ as in part (b)}$$

the one particle partition function for the particles in ΔV is

$$Q_1 = \frac{1}{h^3}\int_{-\infty}^{\infty} d^3p \int_{\Delta V} d^3r \; e^{-\beta\left[\frac{|\vec{p}|^2}{2m} + \frac{1}{2}m\omega_0^2|\vec{r}|^2\right]}$$

$$= \frac{(2\pi m k_B T)^{3/2}}{h^3} \underbrace{e^{-\frac{\beta m\omega_0^2 r^2}{2}}\,\Delta V}_{\text{approx integrand as constant over the small region of integration } \Delta V}$$

The partition function for the ΔN particles in the box is then

$$Q_{\Delta N}(T, \Delta V) = \frac{1}{(\Delta N)!}\,Q_1^{\Delta N}$$

and $$A = -k_B T \ln Q_{\Delta N} = -k_B T\left[\Delta N \ln Q_1 - \ln(\Delta N)!\right]$$

The pressure in the box is then

$$p = -\left(\frac{\partial A}{\partial \Delta V}\right)_{T, \Delta N}$$

The only ΔV dependence of A is from the term $-k_B T \, \Delta N \ln Q_1$

$$\ln Q_1 = \ln \Delta V + (\text{stuff independent of } \Delta N)$$

$$\Rightarrow \quad p = k_B T \, \Delta N \frac{\partial}{\partial \Delta V} \ln \Delta V$$

$$p = k_B T \frac{\Delta N}{\Delta V}$$

now use $\Delta N = \Delta V \, n(\vec{r})$ and we get

$$\boxed{p = n(\vec{r}) \, k_B T}$$

ideal gas law holds locally!

$$\boxed{p(\vec{r}) = \frac{N k_B T}{4\pi} \sqrt{\frac{2}{\pi}} \left(\frac{m \omega_0^2}{k_B T} \right)^{3/2} e^{-m\omega_0^2 r^2 / 2 k_B T}}$$

pressure decreases as $p \sim \frac{1}{\ell^3} e^{-r^2/2\ell^2}$

as r increases

3)

we know $\sum_i P_i E_i = \langle E \rangle$

and we know $\sum_i P_i N_i = \langle N \rangle$

we want to maximize $S = -k_B \sum_i P_i \ln P_i$

subject to the above constraints, as well

as $\sum_i P_i = 1$

So we want to use Lagrange multipliers and maximize

$$\tilde{S} \equiv S + \lambda k_B \sum_j P_j - \beta k_B \sum_j P_j E_j + \alpha k_B \sum_i P_j N_j$$

$$0 = \frac{\partial \tilde{S}}{\partial p_i} = \frac{\partial}{\partial p_i} \left\{ -k_B \sum_j \left[P_j \ln P_j - \lambda P_j + \beta P_j E_j - \alpha P_j N_j \right] \right\}$$

$$\Rightarrow 0 = 1 + \ln P_i - \lambda + \beta E_i - \alpha N_i$$

$$\Rightarrow \ln P_i = \lambda - \beta E_i + \alpha N_i - 1$$

$$P_i = e^{\lambda - 1} e^{-\beta E_i + \alpha N_i}$$

If we define $\alpha = \beta\mu$ then we have

$$P_i = e^{\lambda - 1} \, e^{-\beta(E_i - \mu N_i)}$$

$$\sum_i P_i = e^{\lambda-1} \sum_i e^{-\beta(E_i - \mu N_i)} = 1$$

$$\Rightarrow \quad e^{\lambda - 1} = \frac{1}{\sum_i e^{-\beta(E_i - \mu N_i)}}$$

So
$$\boxed{P_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\sum_j e^{-\beta(E_j - \mu N_j)}}}$$

This is just the probability distribution of the grand canonical ensemble, if we interpret $\beta = \frac{1}{k_B T}$ and μ is the chemical potential.

β and μ are determined by the conditions

$$\sum_i P_i E_i = \langle E \rangle \quad \text{and} \quad \sum_i P_i N_i = \langle N \rangle$$

$$\frac{\sum_i e^{-\beta(E_i - \mu N_i)} E_i}{\sum_j e^{-\beta(E_j - \mu N_j)}} = \langle E \rangle \quad \text{and} \quad \frac{\sum_i e^{-\beta(E_i - \mu N_i)} N_i}{\sum_j e^{-\beta(E_j - \mu N_j)}} = \langle N \rangle$$