Problem Review Session 6
PHYS 741

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Disclaimer: The problems below are not my own making but are taken from Pathria's Statistical Mechanics (PSM) and past qualifying exams from UNC (Qual).

Practice Problems

1. **(Qual 2011 SM-5)** A long vertical tube with a cross-section area A contains a mixture of n different ideal gases, each with the same number of particles N, but of different masses m_k, $k = 1, \ldots, n$. Find a vertical position of the center of mass of this system in the presence of the Earth's gravity, assuming a constant altitude-independent free fall acceleration g.

2. **(Qual 2012 SM-3)** Consider a classical gas of N identical particles. The energy of the system is given by

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<k} U_{ik}(|\vec{r}_i - \vec{r}_k|).$$

In the dilute (atomic volume $\times N \ll V/N$) and high temperature ($|U| \ll kT$) approximation it can be shown that the partition function can be written as

$$Z(T, V, N) = \frac{1}{N!}\left(\frac{1}{\lambda^3}\right)^N Q_N(V, T) \qquad \text{where} \qquad \lambda = \frac{h}{\sqrt{2\pi m k T}},$$

and the configurational integral $Q_N(V, T)$ is given by

$$Q_N(V, T) = V^N + V^{N-2} \sum_{i<k} \int d^3 r_i \int d^3 r_k (e^{-U_{ik}/kT} - 1).$$

Assume the potential is given by the hard sphere potential

$$U_{ik}(|\vec{r}_i - \vec{r}_k|) = \begin{cases} \infty & |\vec{r}_i - \vec{r}_k| < r_0 \\ 0 & |\vec{r}_i - \vec{r}_k| \geq r_0 \end{cases},$$

where r_0 is the radius of the sphere. Show that the equation of state is given by

$$P\left(V - N\frac{2\pi}{3} r_0^3\right) = NkT.$$

3. **(PSM 4.4)** The probability that a system in the grand canonical ensemble has exactly N particles is given by

$$p(N) = \frac{z^N Q_N(V, T)}{\mathcal{Z}(z, V, T)},$$

where $z = e^{\beta\mu}$ is the fugacity, $Q_N(V, T)$ is the partition function and $\mathcal{Z}(z, V, T)$ is the grand partition function. Verify this statement and show that in the case of a classical, ideal gas the distribution of particles among the members of a grand canonical ensemble is identically a Poisson distribution. Show that

$$\overline{(\Delta N)^2} = kT \left(\frac{\partial \overline{N}}{\partial \mu} \right)_{T,V},$$

where $\overline{N}$ is the average number of particles. Calculate the root mean square fluctuation ΔN for this system from the formula above and from the Poisson distribution, and show that they are the same.

Additional Problem

4. **(PSM 4.7)** Consider a classical system of noninteracting, diatomic molecules enclosed in a box of volume V at temperature T. The Hamiltonian of a single molecule is given by

$$H(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{K}{2}|\vec{r}_1 - \vec{r}_2|^2,$$

where m and K are constants. Study the thermodynamics of this system, including the dependence of the quantity $\langle|\vec{r}_1 - \vec{r}_2|^2\rangle$ on T.

Session 6 Problem 1

Qual 2011 SM-5

The center of mass for the entire mixture is given by

$$z_{CM} = \frac{\sum_{k=1}^{n} z_k m_k}{\sum_{k=1}^{n} m_k}$$

where z_k is the average height of mixture k

Therefore we just need to solve for z_k. This can be done from the canonical ensemble approach, where

$$z_k = \frac{1}{Q_1^k} \int z e^{-\beta(p^2/2m_k + m_k g z)} \frac{d^3q\, d^3p}{h^3}$$

where Q_1^k is the partition function of a single particle w/ mass m_k

$$Q_1^k = \int \frac{d^3p\, d^3q}{h^3} e^{-\beta(p^2/2m_k + m_k g z)}$$

The integrals over momenta space cancel. Additionally integrals over all spatial coordinates besides the z-coordinate will cancel. This leaves us with

$$z_k = \int_0^\infty z e^{-\beta m g z} dz \Big/ \int_0^\infty e^{-\beta m g z} dz$$

If we define $\alpha = \beta m g$ then

$$z_k = -\frac{\partial \ln I_k}{\partial \alpha} \quad \text{w/} \quad I_k \equiv \int_0^\infty e^{-\alpha z} dz = \frac{1}{\alpha}$$

Therefore $z_k = 1/\alpha$ & we can find the center of mass of the mixture

$$z_{CM} = \frac{\sum_{k=1}^{n} \cancel{m_k}/\cancel{m_k}\beta g}{M}$$

$$\boxed{z_{CM} = \frac{n k_B T}{M g}}$$

where $M = \sum_{k=1}^{n} m_k$

Session 6 Problem 2

Qual 2012 SM-3

Essentially for this problem we are calculating the first virial coefficient for a non-ideal weakly-interacting gas that is approximated by a hard-sphere potential.

We can determine the equation of state by recalling that

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad \& \qquad A = -kT \ln Z$$

where Z is the partition function given by the problem. Only the configuration function Q_N depends on V

$$\Rightarrow \frac{P}{kT} = \left(\frac{\partial \ln Q_N}{\partial V}\right)_{N,T} = \frac{1}{Q_N}\left(\frac{\partial Q_N}{\partial V}\right)_{N,T} \qquad (1)$$

So now ... need to evaluate Q_N, which is given by

$$Q_N = V^N + V^{N-2} \sum_{i<k} \int d^3 r_i \int d^3 r_k \left(e^{-\beta U_{ik}} - 1\right)$$

We can simplify this expression by defining the displacement vector $\vec{r}_{ik} = \vec{r}_i - \vec{r}_k$. Note that the Jacobian

$$\frac{\partial \vec{r}_{ik}}{\partial \vec{r}_i} = 1 \quad \Rightarrow \quad \int d^3 r_i \rightarrow \int d^3 r_{ik}$$

$$\Rightarrow Q_N = V^N + V^{N-2} \sum_{i<k} \int d^3 r_k \int d^3 r_{ik} \left[e^{-\beta U_{ik}(r_{ik})} - 1\right]$$

Notice that the integrand only depends on $r_{ik} \equiv |\vec{r}_{ik}|$ therefore we can immediately evaluate the other integral, which just gives us another volume term

$$\Rightarrow Q_N = V^N + V^{N-1} \sum_{i<k} \int d^3 r_{ik} \left(e^{-\beta U_{ik}} - 1\right)$$

Transforming to spherical coordinates, we see that this further simplifies to

$$Q_N = V^N \left[1 + \frac{4\pi}{V} \int_0^\infty d r_{ik} \left(e^{-\beta U_{ik}} - 1\right)\right] r_{ik}^2$$

Considering the form of our potential, the integrand is only non-zero for $r_{ik} < r_0$

$$\Rightarrow Q_N = V^N \left[1 - \frac{4\pi}{V} \sum_{i<k} \int_0^{r_0} dr_{ik} r_{ik}^2 \right]$$

using $e^{-\beta U_{ik}} \to 0$ for $r_{ik} < r_0$, $U_{ik} = \infty$

$$= V^N \left[1 - \frac{4\pi}{V} \sum_{i<k} \left(\frac{r_0^3}{3} \right) \right]$$

Now we just need to evaluate the sum, which is essentially counting the number of two-particle interactions that could occur. We have N particles, so if we choose a particle, there are (N−1) particles it can interact with. If we do this type of pairing then we would count

$N(N-1)$ pairings

But this double counts the interaction between particle 1 & particle 2 by also counting the interaction between particle 2 & particle 1. Therefore we need to divide by 2 to account for double counting. This gives us

$$Q_N = V^N \left[1 - \frac{4\pi r_0^3}{3V} \frac{N(N-1)}{2} \right]$$

$$\simeq V^N \left[1 - \frac{N^2}{V} \frac{2\pi r_0^3}{3} \right]$$ using that $N \gg 1$ so $N-1 \simeq N$

Note that you can also evaluate the sum by rewriting it as

$$\sum_{i<k} = \sum_{k=2}^{N} \sum_{i=1}^{k} (1) = \frac{N(N-1)}{2}$$

Now that we have solved for Q_N, we can take the log according to Eqn. 1

$$\Rightarrow \ln Q_N = N \ln V + \ln\left(1 - \frac{N}{V} \frac{2\pi r_0^3}{3} N \right)$$

As stated by the problem, we are considering the scenario where atomic volume × N ≪ V/N & since atomic volume $\simeq \frac{4\pi}{3} r_0^3$

$$\frac{N}{V}\left(\frac{2\pi r_0^3}{3} N \right) \ll 1$$

Therefore we approximate the log as $\ln\left(1 - \frac{N^2}{V}\frac{2\pi r_0^3}{3}\right) \simeq -\frac{N^2}{V}\frac{2\pi r_0^3}{3}$

Plugging all of our results into Equ 1 we find that

$$\frac{P}{kT} = \frac{N}{V} + \frac{N^2}{V^2}\frac{2\pi r_0^3}{3}$$

Or

$$PV = NkT\left(1 + \frac{N}{V}\frac{2\pi r_0^3}{3}\right)$$

To get this in the form of the problem

$$PV\left(1+\frac{N}{V}\frac{2\pi r_0^3}{3}\right)^{-1} \simeq PV\left(1-\frac{N}{V}\frac{2\pi r_0^3}{3}\right) = NkT$$

$$\Rightarrow \boxed{P\left(V - N\frac{2\pi r_0^3}{3}\right) = NkT}$$

Session 6 Problem 3

Pathria 4.4

We know that for a grand canonical ensemble, the probability of a state having a given energy E_s & number of particles N_r is given by

$$P(N_r, E_s) = \frac{e^{\alpha N_r - \beta E_s}}{\sum_{r,s} e^{\alpha N_r - \beta E_s}} = \frac{z^N e^{-\beta E_s}}{\mathcal{Z}(z,V,T)}$$

$\beta \equiv 1/kT$
$\alpha \equiv \mu\beta$
$\mathcal{Z} \equiv$ grand partition fn

If we just want the probability of a state having N_r particles, then we must sum across all of the energy states

$$P(N) = \frac{\sum_s z^N e^{-\beta E_s}}{\mathcal{Z}(z,V,T)} = \frac{z^N \sum_s e^{-\beta E_s}}{\mathcal{Z}(z,V,T)}$$

$\leftrightarrow$ Sum is just partition function

$$\Rightarrow \boxed{P(N) = \frac{z^N Q_N(V,T)}{\mathcal{Z}(z,V,T)}}$$

We know that for a classical, ideal gas

$$Q_N(V,T) = \frac{1}{N!\,h^{3N}} \int e^{-\beta/2m \sum_{i=1}^{N} p_i^2} \prod_{i=1}^{N} d^3q_i\, d^3p_i$$

$$= \frac{1}{N!}\left[\frac{V}{h^3}(2\pi m kT)^{3/2}\right]^N$$

From this we can solve for the grand partition function

$$\mathcal{Z}(z,V,T) = \sum_{N=0}^{\infty} \frac{1}{N!}\left[\frac{zV}{h^3}(2\pi m kT)^{3/2}\right]^N$$

$$= \sum_{N=0}^{\infty} \frac{\xi^N}{N!}$$

$\xi \equiv zV\lambda^3$; $\lambda = \sqrt{\frac{2\pi m kT}{h^2}}$

just an exponential series

$$= e^{\xi}$$

We can use the grand partition function & partition function to re-express the probability as

$$\boxed{p(N) = \frac{\xi^N}{N!\,e^{\xi}} = \frac{\xi^N e^{-\xi}}{N!}}$$

which is the form of a Poisson distribution.

To find the root mean square fluctuations $\overline{\Delta N}$, recall that

$$\overline{(\Delta N)} = \sqrt{\overline{N^2} - (\overline{N})^2}$$

with

$$\overline{N} = \sum_r N_r\, p(N_r) \qquad \overline{N^2} = \sum_r N_r^2\, p(N_r)$$

or

$$\overline{N} = \frac{\sum_{r,s} N_r e^{-\beta(E_s - \mu N_r)}}{\sum_{r,s} e^{-\beta(E_s-\mu N_r)}} \qquad \overline{N^2} = \frac{\sum_{r,s} N_r^2 e^{-\beta(E_s-\mu N_r)}}{\sum_{r,s} e^{-\beta(E_s-\mu N_r)}}$$

Notice that $\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} = \beta\left(\overline{N^2} - \overline{N}^2\right)$

$$\Rightarrow \overline{(\Delta N)}^2 = kT\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} = kT \sum N \left(\frac{\partial p(N)}{\partial \mu}\right)_{T,V}$$

$$= \sum\left(\frac{N^2}{N!}\frac{d\xi}{dz}\frac{dz}{d\mu} e^{-\xi}\xi^{N-1} - \frac{N}{N!}\xi^N e^{-\xi}\frac{d\xi}{dz}\frac{dz}{d\mu}\right.$$

w/ $\frac{d\xi}{dz} = \frac{\xi}{z}$ $\quad \frac{dz}{d\mu} = \frac{z}{kT}$ $\quad \Rightarrow \frac{d\xi}{d\mu} = \frac{\xi}{kT}$

$$\Rightarrow \overline{(\Delta N)}^2 = kT\left(\frac{\xi}{kT}\right)e^{-\xi}\left(\sum_{N=1}^{\infty}\frac{N}{(N-1)!}\xi^{N-1} - \sum_{N=1}^{\infty}\frac{1}{(N-1)!}\xi^N\right)$$

We can shift the sums by defining $N \to n+1$

$$\Rightarrow \overline{(\Delta N)}^2 = \xi e^{-\xi}\left(\xi\sum_{n=0}^{\infty}\frac{\xi^{n-1}}{(n-1)!} - \xi\sum_{n=0}^{\infty}\frac{\xi^n}{n!} + \sum_{n=0}^{\infty}\frac{\xi^n}{n!}\right)$$

$$= \xi e^{-\xi}\left(\cancel{\xi e^{\xi}} - \cancel{\xi e^{\xi}} + e^{\xi}\right) = \xi$$

$$\Rightarrow \boxed{\overline{\Delta N} = \sqrt{\xi}}$$

Note that the variance of Poisson distribution is also given by $\sigma = \Delta N = \xi$, which matches what we just calculated.