

Physics 607
Statistical Physics and Thermodynamics
Professor Valery Pokrovsky

Homework #7

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1 Problem #1

- (1) A single atom (Yb) trapped by a harmonic potential and put into equilibrium with a temperature, T , when an external time-dependent but spatially uniform force, $F(t)$, is turned on at time $t = 0$. For this system we can find the value $\langle e^{-R/T} \rangle$ where R is the work done over the atom during the process by applying the *Jarzynski equality*

$$\langle e^{-\frac{R}{T}} \rangle = e^{-\frac{\Delta F}{T}} \quad (1.1)$$

where ΔF is the change in the free energy from the initial state to the final state. Given that initially the atom was in a harmonic potential we know that the system can be described by the Hamiltonian

$$H_i = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

with energy eigenvalues of

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

after the force has been turned on the Hamiltonian becomes

$$H_f = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 + F(t)x$$

where the energy eigenvalues are shifted such that

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) - \frac{1}{2} \frac{F(t)^2}{m\omega^2}$$

Using this we can calculate the initial free energy through the *Partition Function*

$$Z = \sum_n e^{-\frac{E_n}{T}} \quad (1.2)$$

by

$$F = -T \ln(Z) \quad (1.3)$$

Using equation 1.2 we can calculate the Partition Function initially as

$$\begin{aligned} Z_i &= \sum_{n=0}^{\infty} \exp \left(-\frac{\hbar\omega}{T} (n + 1/2) \right) \\ &= e^{-\hbar\omega/2T} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/T} \right)^n \\ &= \frac{e^{-\hbar\omega/2T}}{1 - e^{-\hbar\omega/T}} \end{aligned}$$

which gives us the initial free energy as

$$F_i = -T \ln(Z_i) = \frac{\hbar\omega}{2} + T \ln \left(1 - e^{-\hbar\omega/T} \right)$$

Repeating for the final state we find that

$$\begin{aligned} Z_f &= \sum_{n=0}^{\infty} \exp \left(-\frac{\hbar\omega}{T} (n + 1/2) + \frac{1}{2m\omega^2} \frac{F(t)^2}{T} \right) \\ &= Z_i e^{F(t)^2/2m\omega^2} \end{aligned}$$

Which implies that the final free energy is

$$F_f = \frac{\hbar\omega}{2} + \ln \left(1 - e^{\hbar\omega/2} \right) - \frac{1}{2} \frac{F(t)^2}{m\omega^2}$$

Therefore we can see the change in energy is related to the force by

$$\Delta F = -\frac{1}{2} \frac{F(t)^2}{m\omega^2}$$

which by equation 1.1 we have

$$\left\langle e^{-\frac{R}{T}} \right\rangle = e^{\frac{F(t)^2}{2m\omega^2 T}}$$

Using this result coupled with the *Crooks Equality*

$$P(-R) = P(R)e^{-\frac{1}{T}(R-\Delta F)} \quad (1.4)$$

we can state that the ration of the distribution functions is

$$\frac{P(-R)}{P(R)} = \exp \left[-\frac{1}{T} \left(R + \frac{1}{2} \frac{F(t)^2}{m\omega^2} \right) \right]$$

- (2) Now rather than turning on an external force we decrease the potential frequency such that $\omega_f < \omega_i$ we note that the final free energy becomes

$$F_f = \frac{\hbar\omega_f}{2} + T \ln \left(1 - e^{-\hbar\omega_f/T} \right)$$

which allows us to calculate ΔF as

$$\begin{aligned} \Delta F &= \frac{\hbar(\omega_f - \omega_i)}{2} + T \ln \left(1 - e^{-\hbar\omega_f/T} \right) - T \ln \left(1 - e^{-\hbar\omega_i/T} \right) \\ &= \frac{\hbar(\omega_f - \omega_i)}{2} + T \ln \left(\frac{1 - e^{-\hbar\omega_f/T}}{1 - e^{-\hbar\omega_i/T}} \right) \end{aligned}$$

Note that for $\omega_f < \omega_i$ the change in free energy is negative like in part (1). We can also see that equation 1.1 becomes

$$\left\langle e^{-\frac{R}{T}} \right\rangle = \frac{e^{-\hbar\omega_f/2T} (1 - e^{-\hbar\omega_f/T})}{e^{-\hbar\omega_i/2T} (1 - e^{-\hbar\omega_i/T})}$$

2 Problem #2

(1) For the given pair interaction potential

$$U(r) = \begin{cases} U_0 & \text{for } r < a \\ 0 & \text{for } r > a \end{cases}$$

we can find the second virial coefficient of the virial expansion given as

$$\frac{p}{T} = \frac{N}{V} + B_2(T) \frac{N^2}{V^2} + B_3(T) \frac{N^3}{V^3} + \dots$$

where the B_j are the virial coefficients. We note that the Hamiltonian with this interaction potential is

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i>j} U(r_{ij})$$

Where r_{ij} is the separation distance given as $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ allowing us to calculate the partition function

$$Z = \frac{1}{N! \lambda^{3N}} \int \prod_{i=1}^N d^3 r_i \exp \left(-\frac{1}{T} \sum_{j<k} U(r_{jk}) \right)$$

where λ is the thermal wavelength defined as

$$\lambda \equiv \sqrt{\frac{2\pi\hbar^2}{mk_B T}}$$

which follows from the ideal case. Now by introducing the *Mayer f function*

$$f(r) = e^{-U(r)/T} - 1$$

where we call $f_{ij} = f(r_{ij})$ which makes the partition function

$$\begin{aligned} Z &= \frac{1}{N! \lambda^{3N}} \int \prod_{i=1}^N d^3 r_i \prod_{j>k} (1 + f_{jk}) \\ &= \frac{1}{N! \lambda^{3N}} \int \prod_{i=1}^N d^3 r_i \prod_{j>k} (1 + f_{jk}) \\ &= \frac{1}{N! \lambda^{3N}} \int \prod_{i=1}^N d^3 r_i \left(1 + \sum_{j>k} f_{jk} + \sum_{j>k, l>m} f_{jk} f_{lm} + \dots \right) \\ &= \frac{V^N}{N! \lambda^{3N}} \left(1 + \frac{N}{2V} \int d^3 r f(r) + \dots \right)^N \\ &= Z_{ideal} \left(1 + \frac{N}{2V} \int d^3 r f(r) + \dots \right)^N \\ &= Z_{ideal} \left(1 + \frac{2\pi N}{V} \int_0^a (e^{-U_0/T} - 1) r^2 dr + \dots \right)^N \\ &= Z_{ideal} \left(1 + \frac{2\pi N a^3}{3V} (e^{-U_0/T} - 1) + \dots \right)^N \end{aligned}$$

Now we can calculate p/T by using the partition function and expanding on N/V

$$\begin{aligned}
\frac{p}{T} &= \frac{\partial \ln(Z)}{\partial V} = \frac{\partial}{\partial V} \left[\ln(Z_{ideal}) + N \ln \left(1 + \frac{2\pi N a^3}{3V} (e^{-U_0/T} - 1) \right) \right] \\
&= \frac{N}{V} + \frac{\partial}{\partial V} \left[N \ln \left(1 + \frac{2\pi N a^3}{3V} (e^{-U_0/T} - 1) \right) \right] \\
&= \frac{N}{V} + \frac{\partial}{\partial V} \left[N \frac{2\pi N a^3}{3V} (e^{-U_0/T} - 1) \right] \\
&= \frac{N}{V} - \frac{2\pi a^3}{3} (e^{-U_0/T} - 1) \left(\frac{N}{V} \right)^2
\end{aligned}$$

So we found the second virial coefficient as

$$B_2 = -\frac{2\pi a^3}{3} (e^{-U_0/T} - 1)$$

note that B_2 is negative which implies that with interactions the pressure is decreased compared to the ideal case.

- (2) In order to calculate the third virial coefficient assuming $|U_0|/T \ll 1$ we note that we have to calculate the higher order cluster integral J_3 . Noting that we calculated

$$J_2 = \frac{4\pi a^3}{3} (e^{-U_0/T} - 1)$$

in part (1). Given that B_3 is related to both J_2 and J_3 by

$$B_3 = J_2^2 - \frac{J_3}{3}$$

all we need to do is calculate

$$J_3 = \int d^3 r_2 d^3 r_3 (f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23} + f_{12} f_{23} f_{23})$$

Noting that the potential is constant we can say that the first three iterations are the same which yields

$$J_3 = 3 \int d^3 r_2 d^3 r_3 f_{12} f_{13} + \int d^3 r_2 d^3 r_3 f_{12} f_{23} f_{23}$$

We can see that the first integral is related the J_2 by

$$\begin{aligned}
J_3 &= 3 \int d^3 r_3 f_{13} \int d^3 r_2 f_{12} \\
&= 3J_2^2
\end{aligned}$$

Note that this term will cancel with the first term in B_3 . So now we calculate the second integral by expanding $f(r)^3$ as

$$f(r)^3 = (e^{-U_0/T} - 1)^3 \approx -\left(\frac{U_0}{T}\right)^3$$

Noting that $f(r)$ is independent of r we get a factor of $(4/3\pi a^3)^2$ from the integration. So it follows that to leading order in U_0/T

$$B_3 \approx -\frac{16\pi^2 a^6}{3} \left(\frac{U_0}{T}\right)^3$$

- (3) Note that in general B_3 is in the form

$$B_3 \approx \frac{16\pi^2 a^6}{3} (e^{U_0/T} - 1)^3$$