Solutions to home work week 7

1. - The particles interact with each other through harmonic potentials. You can consider the $3N$ generalized coordinates q_i the *normal modes* of our $3N$-dimensional systems. In general normal modes are linear combinations of atomic displacements (i.e $x_j \rightarrow x_j + \Delta_j$) and are independent to third order in the potential. The Hamiltonian of such systems is

   $$H = \sum_i^{3N} \frac{p_i^2}{2m_i} + \sum_i^{3N} \frac{1}{2} k_i q_i^2 \tag{1}$$

   The partition function for this system is

   $$\begin{aligned} Z &= \tfrac{1}{N! h^{3N}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} .. \int_{-\infty}^{\infty} e^{-\beta \sum_i^{3N} \frac{p_i^2}{2m_i}} dp_1 dp_2 .. dp_{3N} \\ & \quad \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} .. \int_{-\infty}^{\infty} e^{-\beta \sum_{i=1}^{3N} \frac{1}{2} k_i q_i^2} dq_1 dq_2 .. dq_{3N} \\ &= \tfrac{1}{N! h^{3N}} \Pi_{i=1}^{3N} \left[\int_{-\infty}^{\infty} e^{-\beta \frac{p_i^2}{2m_i}} dp_i \right] \times \Pi_{i=1}^{3N} \left[\int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} k_i q_i^2} dq_i \right] \end{aligned} \tag{2}$$

   Note that here we do not use the usual trick for the (non-generalized) Cartesian momenta: $dp_x dp_y dp_z = 4\pi p^2 dp$, but we integrate over all $3N$ dp_i independent (generalized) momenta instead. Both integrals can be solved analytically with the help of equation A.31 on page 322 of the book:

   $$Z = \frac{1}{N! h^{3N}} \Pi_{i=1}^{3N} \sqrt{\frac{2\pi m_i}{\beta}} \times \Pi_{i=1}^{3N} \sqrt{\frac{2\pi}{\beta k_i}} \tag{3}$$

The average energy $\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z$:

$$\begin{aligned}
\langle E\rangle &= -\tfrac{\partial}{\partial\beta}\left[-\ln N! - 3N\ln h\right] \\
&\quad -\tfrac{\partial}{\partial\beta}\left[\tfrac{1}{2}\textstyle\sum_{i=1}^{3N}\ln[2\pi m_i] - \tfrac{1}{2}\sum_{i=1}^{3N}\ln\beta\right] \\
&\quad -\tfrac{\partial}{\partial\beta}\left[\tfrac{1}{2}\textstyle\sum_{i=1}^{3N}\ln[\tfrac{2\pi}{k_i}] - \tfrac{1}{2}\sum_{i=1}^{3N}\ln\beta\right] \qquad (4) \\
&= \tfrac{1}{2}\textstyle\sum_{i=1}^{3N}\tfrac{1}{\beta} + \tfrac{1}{2}\sum_{i=1}^{3N}\tfrac{1}{\beta} \\
&= \tfrac{3}{2}NkT + \tfrac{3}{2}NKT \\
&= kT
\end{aligned}$$

- The potential energy and kinetic energy are the first and second term in the previous expression, but we will derive them formally here. The expectation value of the kinetic energy is given as the sum of the probabilities of particle i having kinetic energy $p_i^2/2m_i$. Since that probability is the Boltzmann factor divided by the partition function, we have:

$$\langle E_{\text{kin}}\rangle = \sum_{i=1}^{3N}\frac{\int \frac{p_i^2}{2m_i}e^{-\beta\frac{p_i^2}{2m_i}}\,dp_i}{\int e^{-\beta\frac{p_i^2}{2m_i}}\,dp_i} \qquad (5)$$

  where we divided the integrals over the momenta of all other particles $j \neq i$ and the integrals over the generalized coordinates of all particles, including i. Both nominator and denominator can be evaluated analytically with the help of equation A.31:

$$\begin{aligned}
\langle E_{\text{kin}}\rangle &= \textstyle\sum_{i=1}^{3N} \frac{\frac{1}{2m_i}\frac{1}{2}2m_ikT\sqrt{2\pi m_ikT}}{\sqrt{2\pi m_ikT}} \\
&= \textstyle\sum_{i=1}^{3N} \frac{1}{2}kT \\
&= \tfrac{3}{2}NkT
\end{aligned} \tag{6}$$

- The potential energy is obtained as:

$$\langle E_{\text{pot}}\rangle = \sum_{i=1}^{3N} \frac{\int \frac{1}{2}k_iq_i^2 e^{-\beta\frac{1}{2}k_iq_i^2}\,dq_i}{\int e^{-\beta\frac{1}{2}k_iq_i^2}\,dp_i} \tag{7}$$

where we again divided by the integrals of the other generalized momenta ($i \neq j$ and the integrals of all momenta. This can also be worked out analytically.

$$\begin{aligned}
\langle E_{\text{pot}}\rangle &= \textstyle\sum_{i=1}^{3N} \frac{\frac{1}{2}k_i\frac{2kT}{2k_i}\sqrt{\frac{2\pi kT}{k_i}}}{\sqrt{\frac{2\pi kT}{k_i}}} \\
&= \textstyle\sum_{i=1}^{3N} \frac{1}{2}kT \\
&= \tfrac{3}{2}NkT
\end{aligned} \tag{8}$$

Thus, on average, the is $\frac{1}{2}kT$ of energy per harmonic degree of freedom. This is the equipartition theorem.

2. The reaction A → B was discussed in the lecture, but it is always a good exercise to repeat the steps. We assume that the molecules behave as a perfect classical gas, both in state A and B. Thus, if there are N_A molecules in state

A and N_B molecules in state B, the free energy is

$$F = -kT \ln[Z] = -kT \ln[Z_A \times Z_B] \tag{9}$$

with

$$Z_A = \frac{V^{N_A}}{N_A!} \left(\frac{2\pi m_A kT}{h^2} \right)^{\frac{3}{2}N_A} (Z_A^{\text{int}})^{N_A} \tag{10}$$

and

$$Z_B = \frac{V^{N_B}}{N_B!} \left(\frac{2\pi m_B kT}{h^2} \right)^{\frac{3}{2}N_B} (Z_B^{\text{int}})^{N_B} \tag{11}$$

Converting an small amount of A into B, we have for the change in free energy

$$\frac{dF}{dN_A} dN_A = -kT \frac{d}{dN_A} \ln Z dN_A \tag{12}$$

Because the total number of molecules remains constant

$$dN_A + dN_B = 0 \tag{13}$$

so that

$$\frac{dN_B}{dN_A} = -1 \tag{14}$$

and

$$\begin{aligned} \frac{dF}{dN_A} &= \frac{\partial F}{\partial N_A} + \frac{\partial F}{\partial N_B}\frac{dN_B}{dN_A} \\ &= \frac{\partial F}{\partial N_A} - \frac{\partial F}{\partial N_B} \end{aligned} \tag{15}$$

We can thus re-write the expression for the derivative in total free energy as:

$$
\begin{aligned}
\tfrac{dF}{dN_A} &= -kT\tfrac{\partial}{\partial N_A}\left[N_A \ln V - N_A \ln N_A + N_A + N_A \ln\left[\left(\tfrac{2\pi m_A kT}{h^2}\right)^{\frac{2}{3}} Z_A^{\text{int}}\right]\right] \\
&\quad +kT\tfrac{\partial}{\partial N_B}\left[N_B \ln V - N_B \ln N_B + N_B + N_B \ln\left[\left(\tfrac{2\pi m_B kT}{h^2}\right)^{\frac{2}{3}} Z_B^{\text{int}}\right]\right] \\
&= -kT\left[\ln V - \ln N_A + \ln\left[\left(\tfrac{2\pi m_A kT}{h^2}\right)^{\frac{2}{3}} Z_A^{\text{int}}\right]\right] \\
&\quad -kT\left[-\ln V + \ln N_B - \ln\left[\left(\tfrac{2\pi m_B kT}{h^2}\right)^{\frac{2}{3}} Z_B^{\text{int}})\right]\right] \\
&= -kT\left[\ln\tfrac{[B]}{[A]} - \ln\tfrac{Z_1 Z_A^{\text{int}}/V}{Z_1 Z_B^{\text{int}}/V}\right]
\end{aligned}
\qquad (16)
$$

where $[A] = \frac{N_A}{V}$ and Z_1 the partition function of a *single* ideal gas molecule: $Z_1 = V(\frac{2\pi mkT}{h^2})^{\frac{3}{2}}$. If we call $f_A^0 = Z_1 Z_A^{\text{int}}/V$ and $-kT\ln f_A^0$ the standard 'chemical potential' per molecule, so that when multiplied by Avogadro's number, we get μ_A^0, the standard chemical potential of A, we can rewrite the derivative of the free energy as

$$\frac{\partial F}{\partial N_A} = -kT\ln\frac{[B]}{[A]} - f_B + f_A \qquad (17)$$

In equilibrium, nothing changes anymore, so that $\frac{\partial F}{\partial N_A} = 0$. Thus,

$$f_B - f_A = -kT\ln\frac{[B]}{[A]} \qquad (18)$$

Or, after multiplication with Avogadro's number

$$\Delta F^0 = \mu_B^0 - \mu_A^0 = -RT\ln\frac{[B]}{[A]} \qquad (19)$$