Solutions to home work week 5

1. - The partition function for a single particle can be derived by considering that it is a particles in a box with wavelengths in three dimensions: $\lambda_x = \frac{2L_x}{n_x}$, $\lambda_y = \frac{2L_y}{n_y}$, $\lambda_z = \frac{2L_z}{n_z}$. Using De Broglie relation:

$$p_x = \frac{h}{\lambda_x} = \frac{n_x h}{2L_x} \tag{1}$$

we can "simply" count the number of momentum states in an interval $p + dp$. First, we realise that the momentum space "volume" of one momentum state (with $n_x = n_y = n_z = 1$) is $\frac{h^3}{8V}$. Then the density of momentum states $f(p)$ in the interval $p + dp$ is given by the "momentum-volume" in the positive octant of a sphere with diameter p

$$f(p)dp = \frac{8V}{h^3}\frac{4\pi}{8}p^2 dp = \frac{V}{h^3}4\pi p^2 dp \tag{2}$$

Thus the single-particle partition function

$$\begin{aligned} Z_1 &= \textstyle\int_0^\infty \frac{V}{h^3}4\pi p^2 e^{-\beta\frac{p^2}{2m}}dp \\ &= \frac{V}{h^3}4\pi\frac{2m}{4\beta}\sqrt{\frac{2m\pi}{\beta}} \qquad (3) \\ &= V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \end{aligned}$$

For the many-particle partition function of the mono-atomic ideal gas, we must take into account that the particles are indistinguishable. As discussed in the lecture and in chapter 7 of the book, we achieve this by dividing by $N!$ and take the single particle partition function to the

N^{th} power:

$$Z = \frac{1}{N!} Z_1^N = \frac{V^N}{N!} \left(\frac{2m\pi kT}{h^2} \right)^{\frac{3N}{2}} \tag{4}$$

- The average energy is given by

$$\begin{aligned}
\langle E \rangle &= -\tfrac{\partial}{\partial \beta} \ln Z \\
&= -\tfrac{\partial}{\partial \beta} \left[\ln \tfrac{V^N}{N!} \left(\tfrac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} \right] \\
&= -\tfrac{\partial}{\partial \beta} \left[N \ln V - \ln N! + \tfrac{3}{2} N \ln 2\pi m - \tfrac{3}{2} N \ln h^2 - \tfrac{3}{2} N \ln \beta \right] \\
&= \tfrac{3}{2} NkT
\end{aligned} \tag{5}$$

- Heat capacity for ideal gas is $C_V = \frac{\partial U}{\partial T} = \frac{\partial \langle E \rangle}{\partial T}$. Thus, $\frac{3}{2}Nk$. Clearly the heat capacity should level off to zero near 0 K. This is not the case, so the classical approximation that there is at most one particle in an energy level breaks down. Instead, near 0 K, all particles occupy the ground state energy level!
- For the entropy of the ideal mono-atomic gas we write (equation 2.35):

$$\begin{aligned}
S &= \tfrac{\langle E \rangle}{T} + k \ln Z \\
&= \tfrac{3}{2} Nk + kN \ln V - kN \ln N + kN \\
&\quad + \tfrac{3}{2} N \ln \tfrac{2\pi mk}{h^2} + \tfrac{3}{2} N \ln T
\end{aligned} \tag{6}$$

where we used the Stirling approximation, $\ln N! = N \ln N - N$, which is valid for large N. If T goes to zero, the entropy goes to minus infinity, which is not correct, obviously. At zero K, all particles are in their energetic ground states. There is thus only one microstate, hence the entropy should be zero.

- The Helmholtz free energy is defined as $F = -kT \ln Z$ (chapter 2).
- A relation between pressure and partition function can be obtained from the *fundamental* thermodynamic relation (eq. 4.12), which was derived in the lecture. From it, we derived that $p = -\frac{\partial F}{\partial V}$. Thus, the pressure is given by

$$\begin{aligned} p &= kT\frac{\partial}{\partial V}\ln Z \\ &= kT\frac{\partial}{\partial V}\left[N\ln V - \ln N! + \tfrac{3}{2}N\ln\left(\tfrac{2\pi mkT}{h^2}\right)\right] \qquad (7) \\ &= kT\frac{N}{V} \end{aligned}$$

From this results follows immediately the equation of state of an ideal gas: $pV = NkT$.

2. - To compute the change in entropy when the gas expands, we use macroscopic thermodynamics first. Using the equation of state of the ideal gas and the fact that internal energy does not change for a *reversible* expansion at constant temperature:

$$\begin{aligned} dU &= 0 \\ &= dQ + dw \qquad (8) \\ &= TdS - pdV \end{aligned}$$

we can write

$$\begin{aligned} dS &= \tfrac{p}{T}dV \\ &= \tfrac{kN}{V}dV \end{aligned} \tag{9}$$

To get the entropy change we integrate

$$\begin{aligned} \Delta S &= \textstyle\int_{S_1}^{S_2} dS \\ &= Nk \textstyle\int_{V_1}^{V_2} \tfrac{1}{V}dV \\ &= Nk \ln \tfrac{V_2}{V_1} \end{aligned} \tag{10}$$

If the volume doubles, the result is $\Delta S = Nk \ln 2$

- Both gasses double their volume, so that the total change in entropy is $\Delta S_A + \Delta S_B = (N_A + N_B)k \ln 2$
- If we substitute N_B by N_A in the expression above, we would get $\Delta S = (2N_A)k \ln 2$. However, this cannot be correct, because if we were to put the wall back, we'd have the same situation as before! Thus, the entropy should intuitively *not* increase, but remain the same!
- If we would have started from the partition function instead, we'd have gotten the correct answer. The partition function before removing the wall is

$$\begin{aligned} Z_1 &= Z(N_A, V, T) \times Z(N_A, V, T) \\ &= \tfrac{V^{N_A}}{N_A!} \left(\tfrac{2\pi mkT}{h^2}\right)^{\frac{3}{2}N_A} \times \tfrac{V_A^N}{N_A!} \left(\tfrac{2\pi mkT}{h^2}\right)^{\frac{3}{2}N_A} \\ &= \tfrac{V^{2N_A}}{(N_A!)^2} \left(\tfrac{2\pi mkT}{h^2}\right)^{3N_A} \end{aligned} \tag{11}$$

After removing the wall, the partition function is

$$\begin{aligned}Z_2 &= Z(2N_A, 2V, T) \\ &= \tfrac{(2V)^{2N_A}}{(2N_A)!}\left(\tfrac{2\pi mkT}{h^2}\right)^{3N_A}\end{aligned} \tag{12}$$

The entropy difference is given by

$$\begin{aligned}\Delta S &= S_2 - S_1 \\ &= \tfrac{\langle 2E\rangle}{T} + k\ln Z_2 - 2\tfrac{\langle E\rangle}{T} - k\ln Z_1 \\ &= k\ln\tfrac{Z_2}{Z_1} \\ &= k\ln\tfrac{(2V)^{2N_A}(N_A!)^2}{(V)^{2N_A}(2N_A)!} \\ &= 2N_Ak\ln 2V - 2N_Ak\ln V + 2k\ln N_A! - k\ln(2N_A)! \\ &= 2N_Ak\ln 2 + 2kN_A\ln N_A - 2kN_A - 2N_Ak\ln 2N_a + 2kN_A \\ &= 2N_Ak\ln 2 - 2N_Ak\ln 2 = 0\end{aligned} \tag{13}$$

where we again used the Stirling approximation. Because we took into account the indistinguisibility of the gas particles in the partition function (by dividing through $N!$), the entropy change is zero, as it should be.

3. The partition function of N interacting classical particles can be written as:

$$Z = \frac{1}{h^{3N}N!}\int..\int e^{-\beta\left[\sum_i \frac{p_i^2}{2m_i}+\sum_i\sum_j v(x_i,x_j)\right]}d\mathbf{p}_1d\mathbf{p}_2..d\mathbf{p}_Nd\mathbf{r}_1d\mathbf{r}_2..d\mathbf{r}_N \tag{14}$$

where bold symbols indicate vectors, not magnitudes, *i.e.*:

$$d\mathbf{p}d\mathbf{r} = dp_xdp_ydp_zdxdydz \tag{15}$$

The exponent can be split into momentum dependent and position dependent terms:

$$Z = \frac{1}{h^{3N}N!}\int e^{-\beta\sum_i \frac{p_i^2}{2m_i}}d\mathbf{p}_1d\mathbf{p}_2..d\mathbf{p}_N\times\int e^{-\beta\sum_i\sum_j v(x_i,x_j)}d\mathbf{r}_1d\mathbf{r}_2..d\mathbf{r}_N \tag{16}$$

using that $\int d\mathbf{p} = 4\pi p^2dp$, we can further simplify:

$$Z = \frac{1}{N!}\Pi_i^N\int\frac{4\pi}{h^3}p^2e^{-\beta\frac{p_i^2}{2m_i}}dp_i\times\int e^{-\beta\sum_i\sum_j v(x_i,x_j)}d\mathbf{r}_1d\mathbf{r}_2..d\mathbf{r}_N \tag{17}$$

where the Π_i^N symbol indicates we take the product of N terms, with $1 \leq i \leq N$. Recognizing that the first part is the *translational* partition function of a classical gas with N particles (equations 7.18 - 7.20 in the book, but *without* the V^N term!) we can write:

$$Z = \frac{1}{V^N}Z_1^N\int e^{-\beta\sum_i\sum_j v(x_i,x_j)}d\mathbf{r}_1d\mathbf{r}_2..d\mathbf{r}_N \tag{18}$$

We call the integral over positions the *configurational* partition function Q. Because the translational partition function Z_{tr} can be evaluated analytically, i.e.

$$Z_{\text{tr}} = \frac{1}{N!}Z_1^N = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}N} \tag{19}$$

the major challenge is to evaluate the high-dimensional integral of the configurational partition function.

$$Q = \int \int e^{-\beta \sum_i \sum_j v(x_i, x_j)} d\mathbf{r}_1 d\mathbf{r}_2 .. d\mathbf{r}_N \tag{20}$$

Already for simple pair-wise potentials $v(x_i, x_j)$ it is impossible to compute this integral analytically. Instead, any practical application of statistical mechanics for computing thermodynamic quanties, such as drug binding affinities, reaction free energies, etc., requires (severe) approximations. In the lectures we will discuss two common approaches, namely Metropolis Monte Carlo method and molecular dynamics.