

Worksheet 2: Statistical Mechanics and Molecular Dynamics

April Cooper, Patrick Kreissl und Sebastian Weber

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University of Stuttgart

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1 Statistical Mechanics

1.1 Task 1

First we had to consider a system A consisting of two subsystems A_1 and A_2 with the related numbers of configurations $\Omega_1 = 10^{20}$ and $\Omega_2 = 10^{22}$.

The number of configurations available to the combined system is $\Omega = \Omega_1 \cdot \Omega_2 = 10^{42}$.

As the entropy is defined as $S = \ln(\Omega)k_B$ the entropies are:

$$S_1 = k_B \ln(\Omega_1) = k_B \ln(10^{20}), S_2 = k_B \ln(\Omega_2) = k_B \ln(10^{22}), S = k_B \ln(\Omega) = k_B \ln(10^{42}).$$

Then were asked to give the factor by which the number of available configurations increases in a system with given initial V_1, T, p_1 if V_1 was expanded isothermal by 0.001%.

With the help of the first law of thermodynamics it follows that for $T = \text{const}$ it is:

$dS = \frac{p}{T}dV$, which leads with the ideal gas equation to

$$\begin{aligned} \Delta S &= \int_{V_1}^{V_2} \frac{k_B N}{V} dV \\ &= k_B N \ln \left(\frac{V_2}{V_1} \right) \\ &= 10^{-7} k_B N \end{aligned} \tag{1}$$

If you consider now the definition of S: $\Delta S = \ln(\hat{\Delta}\Omega)k_B$ you get with equation (1):

$$\hat{\Delta}\Omega = \exp\left(\frac{\Delta S}{k_B}\right) = \exp(10^{-7}N) = \frac{\Omega_2}{\Omega_1}$$

Finally we were asked to give the factor by which the number of available configurations increases in a system with given initial N, V, T_1 when an energy of 150 kJ is added to the system at constant Volume.

Analogous to the task before it can be derived that $\Delta S = c_v N \ln \left(\frac{T_2}{T_1} \right)$. Using again that the factor by which the number of configurations is given by $\hat{\Delta}\Omega = \exp\left(\frac{S}{k_B}\right)$ it follows that:

$$\hat{\Delta}\Omega = \exp\left(\frac{c_v N \ln\left(\frac{T_2}{T_1}\right)}{k_B}\right) = \exp\left(\frac{c_v N}{k_B}\right) \frac{T_2}{T_1}$$

Using that $T_2 = \frac{\Delta Q}{c_v N} + T_1$ and plugging in the given values leads finally to:

$$\hat{\Delta}\Omega = \exp\left(\frac{2c_v}{k_B}\right) \left(\frac{78}{300c_v} - 1\right) = \frac{\Omega_2}{\Omega_1}$$

1.2 Task 2 - Thermodynamic Variables in the Canonical Ensemble

Given the Helmholtz free energy F we were asked to derive expressions for U, p, S . Using the Maxwell relations it follows:

$$S = -\frac{\partial F}{\partial T} = \ln(Q(N, V, T))k_B + \frac{k_B T}{Q(N, V, T)} \frac{\partial Q(N, V, T)}{\partial T}$$

$$p = -\frac{\partial F}{\partial V} = \frac{1}{\beta Q(N, V, T)} \frac{\partial Q(N, V, T)}{\partial V}$$

The derivation of the equation for U is as follows:

It is known from statistical mechanics that $Q(N, V, T) = \frac{1}{h^{3N} N!} \int d\Gamma \exp(-\beta H)$. The thermodynamic properties of the system can be obtained by $Q(N, V, T) = \exp(-\beta F(N, V, T))$. To justify this identification we show first that F is extensive and then that $F = U - TS$, where $U = \langle H \rangle$.

That F is extensive can be derived directly from $Q(N, V, T) = \frac{1}{h^{3N} N!} \int d\Gamma \exp(-\beta H)$. When the system is split up into two systems with a very weak correlation, then is Q a product of two factors. To show the second equivalence we rewrite $F = U - TS$ to $U = \langle H \rangle = A - T \left(\frac{\partial A}{\partial T} \right)$. To show this we divide the two expressions of Q that we stated before and therefore get:

$$\frac{1}{h^{3N} N!} \int d\Gamma \exp(\beta(F - H)) = 1$$

Deriving both sides by β leads to:

$$\frac{1}{h^{3N} N!} \int d\Gamma \exp(\beta(F - H)) (F - H + \beta \left(\frac{\partial F}{\partial \beta} \right)) = 0$$

This is equivalent to $F - U - T \left(\frac{\partial F}{\partial T} \right)$, wherefore it is: $U = F + TS$.

1.3 Task 3 - Ideal Gas

Given the partition function $Q(N, V, T)$ we had to derive expressions for the free Helmholtz energy $F(N, V, T)$ and the pressure $p(N, V, T)$.

As we know from task 2 it is $F = -\frac{\ln(Q(N, V, T))}{\beta}$. Plugging in the $Q(N, V, T)$ given on the sheet and using the hint leads to:

$$\begin{aligned} F &= -\frac{\ln(Q(N, V, T))}{\beta} \\ &= -k_B T \ln \left(\frac{V^N}{\lambda^{3N} N!} \right) \\ &= -k_B T (N \ln(V) - N \ln(\lambda^3) - \ln(N!)) \\ &= -k_B T N (\ln(V) - \ln(\lambda^3) - \ln(N) + 1) \\ &= k_B T N \left(\ln \left(\frac{N \lambda^3}{V} \right) - 1 \right) \end{aligned} \quad (2)$$

Applying the Maxwell relation $\frac{-\partial F}{\partial V} = p$ on equation (1) it follows:

$$\begin{aligned} p &= \frac{-\partial F}{\partial V} \\ &= \frac{-\partial k_B T N \left(\ln \left(\frac{N \lambda^3}{V} \right) - 1 \right)}{\partial V} \\ &= \frac{k_B T N}{V} \end{aligned} \tag{3}$$

As it is obvious equation(3) leads to the ideal gas law : $pV = Nk_B T$.

2 Molecular Dynamics: Lennard-Jones Fluid

2.1 Implementation of the Lennard Jones Potential

The Lennard Jones Potential is $V_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right)$