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 $\Omega_1 = 10^{2}0$ and $\Omega_2 = 10^{2}2$.
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 = const it is:
$dS = \frac{p}{T}dV$, which leads with the ideal gas equation to

$$\Delta S = \int_{V1}^{V2} \frac{k_B N}{V}dV$$
$$= k_B N ln\left(\frac{V_2}{V_1}\right)$$
$$= 10^{-7}k_B N \tag{1}$$

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

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

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.

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 fist 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 corelation, 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:

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

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

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

As it is obvious equation(2) leads to the ideal gas law : $pV = Nk_B T$.