Freie Universität Berlin
Fachbereich Physik
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Statistical Physics and Thermodynamics (SS 2016)

Problem Sheet 7

Hand in:Thursday, June 9th during the lecture

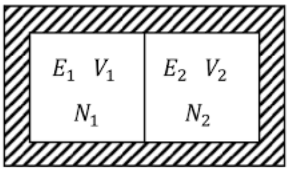
http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre/

1. Gibbs Paradox (7 points)

The equation for the entropy that rises the Gibbs paradox is the following:

$$S_{paradoxical} = k_B \ln \omega(N, V, E) = N k_B \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{\frac{3}{2}} \right] + \frac{3}{2} N k_B$$

Consider a process of mixing two gases by removing the partition between them.



$$\left.\begin{aligned} E &= E_1 + E_2 \\ V &= V_1 + V_2 \\ N &= N_1 + N_2 \end{aligned}\right\} const$$

For simplicity assume:

$$E_1 = E_2 = \frac{E}{2}$$
$$V_1 = V_2 = \frac{V}{2}$$
$$N_1 = N_2 = \frac{N}{2}$$

a) If the two gases are different, explain how do you expect the entropy to change? Calculate the ΔS of the mixing. Is it consistent with your expectations? **(2 points)**

b) If the two gases are similar, explain how do you expect the entropy to change? Calculate the ΔS of the mixing. Is it consistent with your expectations? (This is called the Gibbs paradox) **(2 points)**

Now consider the correct equation for the entropy:

$$S_{correct}(N, V, E) = S_{paradoxical} - k_B N \ln N! = N k_B \ln \left[\frac{V}{N h^3} \left(\frac{4\pi m E}{3N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} N k_B$$

c) Re-calculate the ΔS for part (a) and (b) using the corrected entropy. **(2 points)**

d) How does this change your results? Explain how does it help solving the Gibbs paradox. **(1 point)**

2. Heat Capacity of Diatomic Molecules (6 points)

Consider a molecule that consist of two atoms with mass m_1 and m_2 and separated by distance a. Assume that the molecule behaves like a rigid dumbbell where the Hamiltonian of such molecule is consist of translational and rotational terms:

$$H = H_{trans} + H_{rot}$$

a) The kinetic energy in three dimensions is

$$T = \frac{1}{2}\sum_{i=1}^{2} m_i(\dot{x_i}^2 + \dot{y_i}^2 + \dot{z_i}^2)$$

derive the expression of the kinetic energy in spherical coordinates and show that

$$T_{rot} = \frac{1}{2}I(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta)$$

where I is the moment of inertia. **(2 points)** $\Big($**Hint**: use the relations $\theta_1 = \pi - \theta_2,\ \phi_1 = \pi + \phi_2,\ m_1 r_1 = m_2 r_2,\ a = |r_1| + |r_2|$ $\Big)$

b) Derive the canonical conjugate momenta p_θ and p_ϕ and show that the $H_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}$. **(1 point)** $\Big($**Hint**: use the relations $\mathcal{L}_{rot} = T_{rot} - V = T_{rot},\ H_{rot} = \dot{\theta}p_\theta + \dot{\phi}p_\phi - \mathcal{L}_{rot},\ p_\phi = d\mathcal{L}_{rot}/d\dot{\phi}\quad and \quad p_\theta = d\mathcal{L}_{rot}/d\dot{\theta}$ $\Big)$

c) The rotational partition function of one molecule is defined as

$$Z_{rot} = \frac{1}{(2\pi\hbar)^2}\int d\theta d\phi dp_\theta dp_\phi \exp(-\beta H_{rot})$$

. Calculate the rotational contribution to the heat capacity for a system of N molecules. **(2 points)**

d) The translational Hamiltonian for the center of mass is given by $H_{trans} = \frac{1}{2}\sum_{i=1}^{3}\frac{P_i^2}{m}$ and the

$$Z_{trans} = \frac{1}{(2\pi\hbar)^3}\int dx_1 dx_2 dx_3 dp_1 dp_2 dp_3 \exp(-\beta H_{trans})$$

Calculate the translational contribution to the heat capacity and the total heat capacity for a system of N molecules. **(1 point)**

3. Protein Unfolding: Microcanonical vs Canonical (7 points)

One can simplify the protein structure to N number of building blocks which are linked to one another. Each block can be oriented either upward or downward and has a length of a. (Figure is in the next page)

Now consider the tip of an Atomic Force Microscope (AFM) is attached to one end of the protein and is pulling up the protein with the force $F = \alpha$ where $U = FL$.

a) How many states are there when the protein is unfolded up to length L. Find the entropy in this length. **(2 points)** $\Big($**Hint**: use the relations $N_{up} + N_{down} = N,\ \Delta N a = (N_{up} - N_{down})a = L$ and write down N_{up} and N_{down} in terms of a, L and N. Later on use $\ln(1+x) = x - \frac{1}{2}x^2$ to simplify your expression for the entropy. $\Big)$

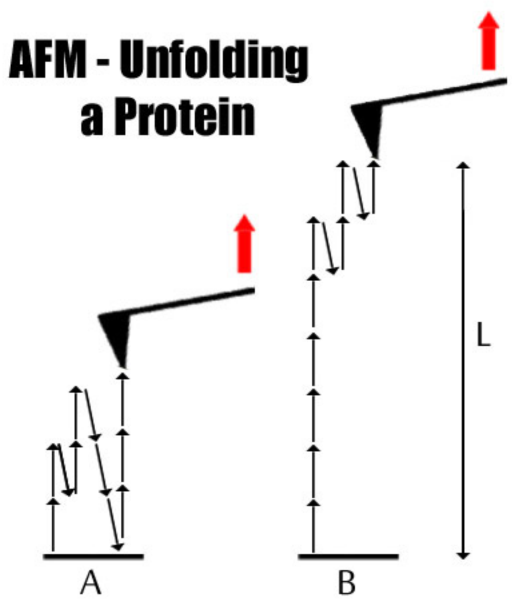
b) Find the temperature of the protein when unfolded to the length L, knowing $\frac{dS}{dU} = \frac{1}{T}$. **(1 point)**

Now consider that no external force is applied and the protein is in contact with a heat reservoir of temperature T.

c) Find the partition function $Z(L)$ and the free energy $F(T, L)$ of the protein. **(2 points)** (**Hint**: Note that for this system $H = 0$ $\Big)$

d) Find the tension of the protein: $\tau = \frac{dF(T,L)}{dL}$. **(1 point)**

e) If we pull the protein from A to B we do work on it, however the internal energy of the protein is always zero in both states, Where does this work go? **(1 point)**



AFM - Unfolding
a Protein
L
A
B