Problem Sheet 5

for the lecture "Statistical Physics", Master course "Computational Science", year 2007/08

due date: Tuesday, December 4, 2007

Problem 1 3 points

The "*free volume*" $\widetilde{V}$ of a classic system of N particles in $3D$ is defined as

$$\widetilde{V}^N = \int \exp\left[\beta(\langle U \rangle - U(q_1, ..., q_{3N}))\right] \; dq_1 \; ... \; dq_{3N} \tag{1}$$

where $\beta = 1/(k_B \; T)$, and $U(q_1, ..., q_{3N})$ is the potential energy, and $\langle U \rangle$ is its expected mean value averaged over all possible particle positions.

1. Write the Hamiltonian of the system (suppose only translational degrees of freedom), and calculate the partition function Z.

2. Compute the Helmholtz free energy $A \equiv H \equiv -k_B \; T \; ln(Z)$.

3. Show that the energy of the system is

$$\langle E \rangle = \frac{3N}{2\beta} + \widetilde{V} \tag{2}$$

4. Show that the entropy is given by

$$S = N \; k_B \; \left\{ ln \left[\frac{\widetilde{V}}{N} \; \left(\frac{2 \; \pi \; m \; k_B \; T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\} \tag{3}$$

   [**hint:** remember $A = E - T \; S$]

5. Compare the previous expression with the entropy of an ideal gas. Do you think the name *"free volume"* has some sense? Justify the answer.

6. **Bonus (Optional):** Consider now the particular case of the "*hard sphere*" potential, namely suppose the particles are impenetrable spheres of radius R, i.e., if there is some overlap between spheres ($|q_i - q_j| < 2R$)

$$U(q_1, ..., q_{3N}) = \infty \tag{4}$$

   otherwise

$$U(q_1, ..., q_{3N}) = 0 \tag{5}$$

   show that in this case $\widetilde{V} = V - (N-1) \; b \approx V - N \; b$ where b is the volume of an sphere of radius $2R$. Does this result make some sense?

Problem 2 2.5 points

1. Starting from the thermodynamic expression for the the energy, i.e. $F = U - \tau\sigma$, show that (for a constant number of particles) its differential can be expressed as

$$\mathrm{d}F \;=\; -\sigma\,\mathrm{d}\tau - p\,\mathrm{d}V\;.$$

Remembering that the free energy is a function of the temperature τ and the volume V, i.e. $F(\tau, V)$, take its total differential. Find out by comparison with the differential above, how the the entropy σ and the pressure p can be computed by partial derivatives of F at constant τ and V, respectively.

2. Assume that the canonical partition function of a system is given by the expression

$$Z(\tau, V) \;=\; \mathrm{e}^{\alpha\tau^3 V}\;,$$

where $\alpha > 0$ is a constant. Calculate the free energy, the pressure, the entropy and the internal energy of the system. Any idea as to what this system might be?

Hint: *The total differential of a function $f(x, y)$ which depends on two variables x and y is defined as*

$$\mathrm{d}f(x,y) \;=\; \left.\frac{\partial f}{\partial x}\right|_y \mathrm{d}x + \left.\frac{\partial f}{\partial y}\right|_x \mathrm{d}y\;.$$

Problem 3 1.5 points

The lowest energy level of the oxygen molecule O_2 is threefold degenerate. The next level is doubly degenerate and lies 0.97 eV above the lowest level. Take the lowest level to have energy of 0. Calculate the canonical partition function and the internal energy at 1000 K and at 3000 K.

Hint: $k_\mathrm{B} = 1.38 \times 10^{-23}\frac{\mathrm{J}}{\mathrm{K}}$; $\mathrm{e} = 1.6 \times 10^{-19}\mathrm{C}$.

Problem 4 1.5 points

A system has two non-degenerate energy levels with an energy gap of 0.1 eV $= 1.6 \times 10^{-20}$ J. The lower level has zero energy (call this the ground state). What is the probability of the system being in the upper level if it is in thermal contact with a heat bath at temperature 300 K? At what temperature would that probability be 25% ?

Problem 5 1.5 points

A system has three energy levels of energy 0, $100\,k_\mathrm{B}$K, and $200\,k_\mathrm{B}$K, with degeneracies of 1 , 3 and 5, respectively. Calculate the canonical partition function and the occupation probability for each level. What is the average energy at a temperature of 100 K?