TKJ4215 Statistisk termodynamikk i kjemi og biologi
Eksamen 30.05.2011, 09.00-13.00

Norges Teknisk-Naturvitenskapelige Universitet
Hjelpemiddelkode A. (Alle trykte og håndskrevne hjelpemidler tillatt. Alle kalkulatorer tillatt.)
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NB: Oppgavene teller ikke like mye. Totalt er 100 poeng fordelt på tre oppgaver. Se parantes etter oppgavenummer for antall poeng per deloppgave.

English

Exercise 1 (10,10,15)

a) Regard a set of energy levels with energies,

$$\varepsilon_m = m\varepsilon, \quad \varepsilon > 0, \quad m = 0, 1, 2, \ldots, \infty$$

What does the Boltzmann distribution law (at constant temperature and at equilibrium) tell us about the relative population $\frac{n_i}{n_j}$ of the energy levels i and j for large and small ε, respectively?

b) Also, discuss the relative population at two limiting cases: $T \rightarrow 0$ and $T \rightarrow \infty$. Explain how this is consistent with our interpretation of entropy.

c) Most real-life systems are like in case (a), an infinitely number of excited states are available. However, an inventive nano scientist manages to synthesize a molecule with only ten states,

$$\varepsilon_m = m\varepsilon, \quad \varepsilon > 0, \quad m = 0, 1, 2, \ldots, 9$$

For N molecules, the internal energy, U, is

$$U = \sum_i n_i \varepsilon_i \qquad \sum_i n_i = N$$

Discuss how the entropy as a function of the internal energy, $S(U)$, behaves both for this case and for the case in (a) with an infinite number of excited states.

[Hint: Look at $U = 0$, $U = 9N\varepsilon$, and a value of U somewhere in between and make a rough estimate of the order of magnitude of $S(U)$]

Exercise 2 (10,10)

a) Give the partition function for an ideal gas with N indistinguishable molecules. Regard three types of systems: argon atoms, water molecules and butane (C_4H_{10}) molecules. Discuss the relative importance of the various contributions to the molecular partition function by comparing the three types of systems. The electronic ground state is not degenerate for any of of the systems. Which approximations do we do when we regard a gas as being ideal?

b) If we would like to calculate the pressure, p, from the partition function discussed in (a), which information is required about the molecules and about the system, respectively, to do the actual calculation?

Exercise 3 (15,15,15)

Consider a two-dimensional lattice (surface) where each point on the lattice is occupied with an in-plane electric dipole moment, $\vec{\mu} = (\mu_x, \mu_y)$. In our model, the dipole moment can point only in four different directions: north, south, west and east, as indicated in the figure.
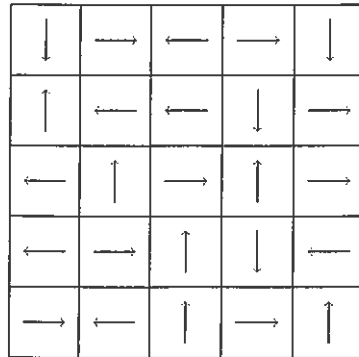

Each dipole moment interacts only with its nearest neighbours, ($z = 4$). The interaction energy between two dipole moments $\vec{\mu}_1$ and $\vec{\mu}_2$ are given according to,

$$V_{12} = -\frac{3 \left(\vec{\mu}_1 \cdot \vec{R}_{12} \right) \left(\vec{\mu}_2 \cdot \vec{R}_{12} \right) - (\vec{\mu}_1 \cdot \vec{\mu}_2) R_{12}^2}{R_{12}^5}$$

where $\vec{R}_{12}$ is the distance vector (R_x, R_y) between two dipole moments so that $R_{12} = |\vec{R}_{12}|$ and R_{12} is the distance.

a) Consider a model where the orientation of each dipole moment is random (and not correlated with the orientation of the neighbouring dipole moment). For N dipole moments, what is the internal energy, U? What is the total dipole moment of the system? What is the Helmholtz free energy, F, at a given temperature, T? Ignore boarder effects, i.e. assume that each of the N dipole moments has a coordination number of $z = 4$.

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b) Let us apply an external field $\vec{E} = (E, 0)$ so that the system becomes completely ordered, see figure.
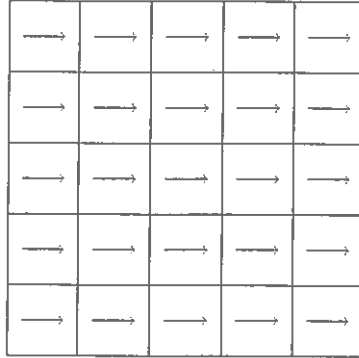
The interaction energy between a dipole moment, $\vec{\mu}_i$, and the external electric field is

$$V_E = -\vec{\mu}_i \cdot \vec{E}$$

In which direction will the dipole moments point to get a favourable energy? What is the internal energy, U, in this case? What is the free energy, F?

c) Let us now consider the process of going from a random phase as discussed in (a) to an ordered phase in an electric field as discussed in (b). What is the free energy difference, ΔF? What is the condition for that the random phase is stable at a field $\vec{E}$ and at a field $\vec{E} = 0$? Explain if it is possible to impose a phase transition by applying an external electric field to the system. What happens if the temperature is increased? What happens if the volume is decreased?