Problem Set 10
Statistical Mechanics
summer 2024

Prof. Dr. R. Hentschke
TA: Lena Tarrach (F12.19)
Bergische Uni Wuppertal

Problem 27: 1D Ising model

Consider the partition function of the one-dimensional (1D) Ising model, i.e. a linear chain of N spins

$$Q_N = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \ldots \sum_{s_N=\pm 1} \exp[\frac{J}{T}(s_1 s_2 + s_2 s_3 + \ldots + s_{N-1} s_N)] \, .$$

(a) Show that

$$Q_{N+1} = 2\cosh(J/T) Q_N \, .$$

(4 points)

(b) Based on the result in (a) you can immediately write down Q_N. Use the relation

$$\frac{1}{N}\langle E \rangle = \frac{1}{N} \frac{\partial}{\partial(-1/T)} \ln Q_N$$

to calculate the energy per spin as function of the coupling strength J and the temperartur T. Sketch the energy per spin vs T.

(3 points)

Problem 28: *mean field*-theory for a system of electric dipoles

The Hamiltonian of an electric dipole $\vec{p}$ is given by $H = -\vec{p} \cdot \vec{E}_{loc}$. We assume that the local electric field $\vec{E}_{loc}$ at the position of the dipole is the result of the average dipole moment at this position, i.e. $\vec{E}_{loc} = K\langle \vec{p} \rangle$. The quantity K is a positive contant and $\vec{E}_{loc}$ is oriented parallel to the z-axis, i.e. $\vec{E}_{loc} = Kp\ (0, 0, \langle \cos\theta \rangle)$.

Obtain an equation for $\langle \cos\theta \rangle$. Note that the average dipole moment is given by $\langle \vec{p} \rangle = (0, 0, \langle p_z \rangle) = p(0, 0, \langle \cos\theta \rangle)$. Show graphically that, depending on temperature, only the solution $\langle \cos\theta \rangle = 0$, i.e. $\langle \vec{p} \rangle = 0$, exists or that there are two additional solutions $\langle \cos\theta \rangle \neq 0$ bzw. $\langle \vec{p} \rangle \neq 0$. Specify the critical temperature $T_c = T_c(K, p)$ at which this cross-over happens.

(4 points)

Problem 29: One-dimensional electron gas

The energy per electron $\langle E\rangle/N$ in a one-dimensional electron gas at $T = 0$ is given by

$$\frac{\langle E\rangle}{N} = \frac{1}{3}\epsilon_F \ ,$$

where $\epsilon_F = \hbar^2 k_F^2/(2m_e)$ is the Fermi energy and k_F is the magnitude of the Fermi wave vector. Derive an expression describing the compressibility $\kappa = -V^{-1}(\partial P/\partial V)^{-1}$ of the electron gas, where P is the pressure and V is the (one-dimensional) volume.

Hint: Remember the important formula from TD relating the free energy F to the internal energy $E = \langle E\rangle$ and the entropy ($T = 0$!).

(4 points)

Problem 30: Adsorption from the gas phase

In problem 23 you had shown that the chemical potential of molecules adsorbed on a surface is given by

$$\mu_s = k_B T \ln \frac{\theta}{(1-\theta)q_s(T)} \ ,$$

where $\theta = N/N_o$ is the coverage (dt.: Bedeckung) and $q_s(T)$ is the molecular partition function on the surface.

Now assume that the surface is in chemical equilibrium with an ideal gas of the same molecules, i.e. $\mu_s = \mu_g$, where μ_g is the chemical potential of the ideal gas. Derive an equation for $\theta(T, P)$, where P is the pressure in the gas, and plot $\theta(T, P)$ vs. P in the range from 10^{-4} bar to 10^3 bar (use a log-scale) for three temperatures, i.e. $T = 100$ K, 200 K and 300 K.

Hints: (i) Consider point-like molecules, i.e. the molecules do not posses internal degrees of freedom. (ii) $q_s(T) = \exp[-\beta\epsilon]q_{s,vib}(T)$, where $q_{s,vib}$ is the partition function of a three-dimensional classical oscillator with the Hamiltonian $H = p^2/(2m) + m\omega^2 q^2/2$. Here p is the momentum, q is the position, m is the mass, and $m\omega^2$ is the force constant of the oscillator. Use the adsorption energy $\epsilon = -13.5$ kJ/mol and the force constant $m\omega^2 = 1.3 \cdot 10^{21}$

kJ/(m^2 mol) [1]. This means that the adsorbed molecules are in a surface potential which allows them to vibrate like classically excited oscillators. Note that the form of $q_s(T)$ is analogous to the partition function of a small molecule, which was the product of various factors, e.g. the electronic factor, the vibrational partition function, etc.

Remark: In this example we allow monolayer coverage only.

(6 points)

[1] These numbers are taken from the Anwendungsbeispiel V.2 starting on page 217 in https://constanze.materials.uni-wuppertal.de/fileadmin/physik/theochemphysik/Skripten/MolModell.pdf, where I discuss the adsorption of methane on graphite. Specifically, ϵ corresponds to $u_s^{(o)}$ in Eq. (V.20) and $2m\omega^2$ is $u_s^{(2)}$ in the same equation.