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Advanced Statistical Physics (WS11/12)
Problem sheet 6

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Problem 1: Poisson-Boltzmann Equation

Consider a system of equally charged particles of elementary charge e and particle density $\rho(\mathbf{r})$ in an external potential $V(\mathbf{r})$. The Helmholtz free energy can be approximated by the functional:

$$\beta F[\rho] = \int \mathrm{d}^3 r\, \rho(\mathbf{r})[\log(\rho(\mathbf{r})\Lambda^3) - 1] + \beta \int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) + \frac{1}{2}\lambda_B \int \mathrm{d}^3 r\, \mathrm{d}^3 r'\, \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Show that by the minimisation $\delta F[\rho]/\delta\rho(\mathbf{r}) - \mu = 0$ (with constant chemical potential μ) one can obtain the Poisson-Boltzmann equation:

$$\rho(\mathbf{r}) = \rho_0 \exp\left(-\beta\, V(\mathbf{r}) - \lambda_B \int \mathrm{d}^3 r'\, \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\right),$$

where Λ is the thermal wavelength and $\lambda_B = \beta\, e^2/(4\pi\epsilon_0)$ the so-called Bjerrum length.

What physical quantity is represented by the second term in of the exponent? Express the PB equation by this quantity instead of the density.

Problem 2: Ideal Magnet

Consider a system of N non-interacting, classical, magnetic spins in a magnetic field h at temperature T with the Hamiltonian

$H = -\sum_{j=1}^{N} m_j h$, where $m_j = \pm 1$.

a) Calculate the canonical partition function and use it to derive the free energy $F(h, T)$.

b) Determine the entropy S and the average value of the total magnetic momentum $M = \sum_j \langle m_j \rangle$.

c) Calculate the internal energy U of the system and give an equation of state to connect T, h and M.

Problem 3: Absorbing Surface

Discuss an absorbing surface with N active sites. Each site can absorb one gas molecule. The surface is in contact with a gas of chemical potential μ at pressure P and temperature T. Assume that the energy of an absorbed molecule is reduced by $\epsilon_0 > 0$ compared to the energy of a free molecule.

a) Calculate the grand canonical partition function.

b) Calculate the average coverage Θ, which is the ratio of the number of absorbed molecules and the number of surfaces sites N.

Hint: You can use $(1+x)^N = \sum_k N! x^k / [k!(N-k)!]$ in part a)

Problem 4: Tonks Gas

N stiff rods of length a are being positioned on a line within the length L (cf. figure). The rod's motion is one dimensional. The interaction between two rods $V(x_1, x_2)$ is given by:

$$V(x_1, x_2) = \begin{cases} \infty & \text{for } |x_1 - x_2| < a, \\ 0 & \text{otherwise,} \end{cases}$$

where x_i is the position of the center of the ith rod.

Calculate the canonical partition function Z_N, the Helmholtz free energy F, the internal energy U and the pressure $P = -\left(\frac{\partial F}{\partial L}\right)_{N,T}$ of the system.

Control: Solution for Z_N:

$$Z_N = \frac{1}{N!}\left(\sqrt{\frac{2\,\pi\, m\, k_B\, T}{h^2}}(L - N\,a)\right)^N$$