Freie Universität Berlin Hand in before May 4th 2015 until 12:30pm @office 0.3.06 or 0.3.34

Fachbereich Physik
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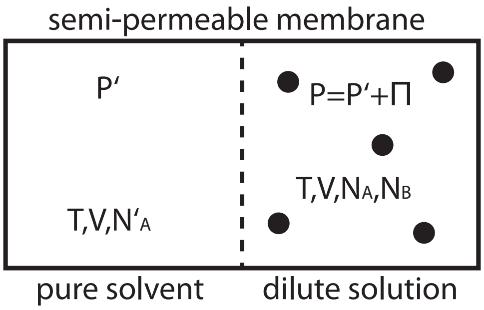
Advanced Statistical Physics II – Problem Sheet 2

Problem 1 – **Osmotic Pressure**



We consider a system, consisting of the solvent A, that is separated from a dilute solution of substance B by a semi-permeable membrane. The membrane is permeable for the solvent meaning the solvent chemical potential μ are identical in both compartments, $\mu_A = \mu'_A$, but it is impermeable to substance B.

Due to the concentration difference a higher pressure arises in the solution. The pressure difference Π is called "osmotic pressure". In the following an expression for the osmotic pressure shall be derived.

a) (1P) We denote the free energies of the left- and right-hand side by $F'(T, V, N'_A)$, $F(T, V, N_A, N_B)$, respectively. Look at the above picture to convince yourself that for $N_A = N'_A$, $N_B = 0$ we have $F(T, V, N_A, 0) = F'(T, V, N'_A)$. Note that the volume of the left and right compartments are the same , and the temperature T is fixed.

b) (3P) Use the Euler theorem for homogeneous functions to show that

$$F'(T, V, N'_A) = -P'V + \mu'_A N'_A, \tag{1}$$

$$F(T, V, N_A, N_B) = -PV + \mu_A N_A + \mu_B N_B. \tag{2}$$

Hint: The Euler theorem for homogeneous functions says that if a differentiable function $f(x_1, ..., x_k)$ is homogeneous of degree m, i.e. if

$$f(\lambda x_1, ..., \lambda x_k) = \lambda^m f(x_1, ..., x_k), \tag{3}$$

then it follows that

$$\frac{\partial f}{\partial x_1} x_1 + ... + \frac{\partial f}{\partial x_k} x_k = mf. \tag{4}$$

(This can easily be proven by taking the derivative with respect to λ on both sides of eq. 3 and then setting $\lambda = 1$.) In thermodynamic language this holds of course only for the extensive variables!

c) (3P) Using your results from the previous parts, derive the following expression for the osmotic pressure:

$$\Pi = P - P' = \phi \frac{\partial f}{\partial \phi}\Big|_C + f(\phi = 0) - f(\phi), \tag{5}$$

with $f = F/V$ the free energy per volume. Here, all quantities are expressed as functions of the concentration fraction of substance B, i.e. $\phi = C_\text{B}/C$ with $C_{\text{A,B}} = N_{\text{A,B}}/V$ and $C = C_\text{A} + C_\text{B}$. Assume the solution density to be constant, i.e. $C'_A = C_A + C_B = C \equiv const.$

d) (2P) Based on eq. 5, derive the van't Hoff law for ideal solutions, that applies for small concentrations ($\phi \to 0$):

$$\Pi \approx C_\text{B} k_B T \tag{6}$$

Hint: The free energy of an ideal gas is approximately given by

$$F(T, V, N_A, N_B) \approx N_A k_B T \left[\ln(\frac{N_A \lambda_A^3}{V}) - 1\right] + N_B k_B T \left[\ln(\frac{N_B \lambda_B^3}{V}) - 1\right],$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength.

e) (1P) Calculate the osmotic pressure of a solution with 0.1, 0.2 and 0.3 mol sugar ($C_{12}H_{22}O_{11}$) per one liter (L) of the solution at $T = 303K$.

Problem 2 – **Fluctuations in the Grand Canonical Ensemble**

The grand canonical potential Ω is expressed as $\Omega(T, V, \mu) = F(T, V, N) - \mu N = -k_B T \ln(\Xi)$, where Ξ is the grand canonical partition function.

a) (2P) Show that the number fluctuation $\langle \Delta N^2 \rangle \equiv \langle N^2 \rangle - \langle N \rangle^2$ can be expressed as

$$\langle \Delta N^2 \rangle = \left(\frac{\partial \langle N \rangle}{\partial(\mu/k_B T)} \right)_{T,V}. \tag{7}$$

b) (2P) Show that in the grand canonical ensemble the energy fluctuation $\langle \Delta E^2 \rangle \equiv \langle E^2 \rangle - \langle E \rangle^2$ can be expressed as

$$\langle \Delta E^2 \rangle = -\left(\frac{\partial \langle E \rangle}{\partial(1/k_B T)} \right)_{z,V}, \tag{8}$$

where $z \equiv e^{\mu/k_B T}$.

c) For non-interacting particles (such as the classical ideal gas), the canonical partition function Z_N reads

$$Z_N = (V f(T))^N / N!, \tag{9}$$

where V is the system volume, and $f(T)$ is a temperature-dependent function.

i) (2P) Show that the grand canonical potential Ω can be expressed as

$$\Omega = -k_B T \gamma, \tag{10}$$

where $\gamma = zV f(T)$.

ii) (2P) Express $\langle \Delta N^2 \rangle$ in terms of γ.

iii) (2P) Show that the energy fluctuation $\langle \Delta E^2 \rangle$ can be expressed as

$$\langle \Delta E^2 \rangle = k_B^2 T^3 \left[2 \left(\frac{\partial \gamma}{\partial T} \right)_{z,V} + T \left(\frac{\partial^2 \gamma}{\partial T^2} \right)_{z,V} \right]. \tag{11}$$