## Aufgabe 9.1 Osmotic pressure

Consider the following experimental arrangement for the measurement of the osmotic pressure:



A semipermeable wall (through which only the solvent can pass) separates the solvent (e.g. water, section 2, left hand side of the figure) from the concentrated solution (e.g. sugar in water, section 1, right hand side of the figure).

Derive again the expression for the osmotic pressure using the Gibbs free energy and the chemical potential. Which is the higher column? Why?

## Aufgabe 9.2 Drying of wet laundry

Imagine to be at the sea on a nice early summer day. The temperature of the air is  $25^{\circ}$ C and the air humidity is 60%. You decide to hang your wet laundry on a clothes line. Why do you expect that after a while the clothes are dry? What happens if the weather get worse and the air humidity rises to 100%?

*Hint:* Consider the different chemical potentials which play a role.

 $(g_{H_2O(g)} = -228.6 \text{ kJ mol}^{-1}, g_{H_2O(l)} = -237.2 \text{ kJ mol}^{-1}, p_{H_2O(g)} = 0.03169 \text{ bar at } T = 25 \text{ °C}$  and  $p = 1 \text{ atm. } p_{H_2O(g)}$  is the maximal vapor pressure at the give temperature and pressure.)



## Aufgabe 9.3 Entropy

In the first weeks of the semester we derived the following formula for the entropy of an ideal gas

$$S = \frac{3}{2}Nk_B \log T + Nk_B \log V + S_0.$$

This expression is false from two points of view:

- a) S is not extensive,
- b) S leads to the Gibbs Paradox.

Show these two issues explicitly and prove that with the substitution  $V \to \frac{V}{N}$  both problems are solved. We will derive the correct formula in the chapter on kinetic theory of gases.

## Aufgabe 9.4 Nucleation \*

Consider a *d*-dimensional elastic membrane (elasticity *C*) in d + 1 dimensions, which can be deformed along the d + 1th "transversal" direction (see figure). This transversal deformation can be described with  $u(\vec{x})$ , where  $\vec{x} \in \mathbb{R}^d$ . The deformation energy is  $\propto (\nabla u)^2$ and the potential for the deformation is made up of a periodic part and of a coupling to a constant external force *F*:

$$V(u) = V_0 (1 - \cos(k_0 u)) - F u$$
.

Then the free energy for the membrane is given by

$$H[u] = \int d^d x \, \left[ \frac{C}{2} (\nabla u)^2 + V(u) \right]$$

- 1. Draw the potential for different values of the external force F? Which possibilities exist for the mobility of the membrane along the transverse direction? Define and determine a critical external force  $F_c$ .
- 2. Let's consider now  $F \ll F_c$  and  $d \ge 2$ . Calculate the approximate energy U(R) of a nucleus with radius R. This is a local deformation of the membrane, which disappears outside R and has the constant value  $u = u_0 = \frac{2\pi}{k_0}$  inside the hypersphere of radius R. Make the assumption that the elastic and potential energy are of the same size for F = 0 and the deformation increases from 0 to  $u_0$  in a small area of width w. Determine the critical radius R, above which the nucleus begins to grow. Why does  $U(R_c)$  correspond to an activation energy, and how does it vary with F?
- 3. With  $V_0 = 0$  the membrane moves according to  $v = F/\eta$ , with a speed v and a friction coefficient  $\eta$ . Determine for our case with periodic potential and temperature T > 0, the drift velocity v as a function of the force F; consider, in particular, the cases  $F \to 0$  and  $F \gg F_c$ .
- 4. In one dimension (elastic line)  $u_{\text{kink}}(x) = \frac{4}{k_0} \arctan(e^{x/w})$  with a constant w is a minimum of the above energy function (free energy equation) for F = 0 which can represent a flank of the nucleus. The energy for a nucleus with radius R and with such two flanks is then

$$U(R) \approx 2E_{\text{kink}}(1 - e^{-R/w}) - Fu_0 R.$$

Calculate the critical radius  $R_c$  and the activation energy. What is different if  $F \to 0$  and what are the consequences for the speed of the line?



FIG. 13. Elastic manifold trapped in a (tilted) washboard potential. Top: One-dimensional elastic string with a finite segment (nucleus) activated to the next valley. The activation energy  $2E_k$  involves the production of two kinks and remains always finite—the string is never in a "glassy" state. Bottom: Two-dimensional elastic surface with a finite nucleus activated to the next valley. The activation energy involves the creation of a one-dimensional (thin) wall, which costs an energy  $2\pi rE_k$ , where r is the radius of the nucleus. If the nucleus is large enough,  $r > r_c$ , it expands and the elastic manifold moves on to the next valley. The critical radius  $r_c$  increases with decreasing driving force F,  $r_c = E_k/u_{\circ}F$ , and the manifold shows glassy behavior with a diverging activation energy at vanishing driving force,  $U(F) = \pi E_k^2/u_{\circ}F$ .

More background on the task in: G. Blatter et al., Rev. Mod. Phys. 66 1125, (1994).