

Advanced Statistical Physics II – Problem Sheet 7

Problem 1 – Electroosmotic flow: Application of Onsager relations

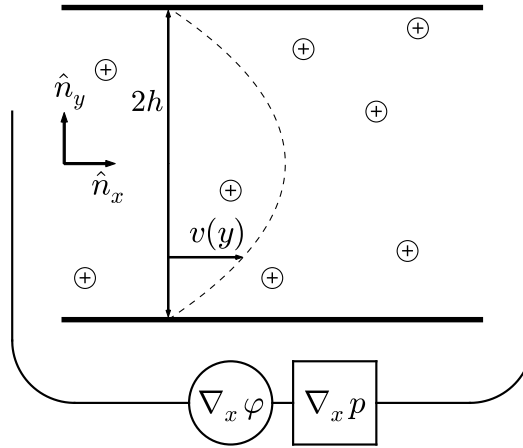


Figure 1: Free expansion of an ideal gas.

Consider an electrolyte solution (with charge density ρ^c and conductivity σ (per unit length in \hat{n}_z -direction)) that are both constant in space and time between two plates that are infinitely long in \hat{n}_z -direction but that have a finite length in \hat{n}_x -direction. The charge between the plates precisely neutralizes the charge on the plates. The stress tensor of the solution is given as

$$\sigma_{ij} = -\delta_{ij}p + \eta(\nabla_i v_j + \nabla_j v_i), \quad (1)$$

where η is the viscosity. We apply constant pressure- and voltage-gradients $\nabla_x p$, $\nabla_x \varphi$ between the left and right end of the plates, which act as driving forces for average volume and electric current flows $J_x^v \equiv J^v$, $J_x^e \equiv J^e$ (both flows are per unit length in \hat{n}_z -direction). Assuming reservoirs to source and drain the flows on the left and right side of the plates, we expect there to be a steady-state flow profile between the plates after some time.

The Onsager reciprocal relations say that the matrix L in

$$\begin{pmatrix} J^v \\ J^e \end{pmatrix} = \begin{pmatrix} L_{vv} & L_{ve} \\ L_{ev} & L_{ee} \end{pmatrix} \begin{pmatrix} -\nabla_x p \\ -\nabla_x \varphi \end{pmatrix}, \quad (2)$$

is symmetric. The goal of this exercise is to explicitly calculate the matrix elements for our setup and verify that the calculated L is indeed symmetric, i.e. $L_{12} = L_{21}$.

a) Assuming a steady-state flow profile that has a nonvanishing velocity only in the x-direction, i.e. $\vec{v}(\vec{r}, t) = v(y)\hat{n}_x$ with no slip boundary conditions (i.e. $v(-h) = v(h) = 0$), solve the momentum balance equation for our electrolyte solution between the plates.

Hint: The result you should get is

$$v(y) = \frac{h^2}{2\eta} (-\nabla_x p - \rho^c \nabla_x \varphi) \left[1 - \left(\frac{y}{h} \right)^2 \right]. \quad (3)$$

b) Average your result from a) over the channel height to calculate the average volume flow J^v . Express your result as a linear combination of the thermodynamic driving forces $-\nabla_x p, -\nabla_x \varphi$.

c) Write down the average electric current density J^e and write it as a linear combination of the thermodynamic driving forces $\nabla_x p, \nabla_x \varphi$.

Hint: Assume the contributions to the electric current to consist of i) a background current that follows Ohm's law $\vec{J} = \sigma \vec{E}$ and ii) excess charges that move with a velocity given by the fluid velocity profile $v(y)$.

d) Use your results from b) and c) to write down the matrix L . Does your L fulfill the Onsager reciprocal relations?

Remark: The effect that an electric field in the neighborhood of charged surfaces creates a flow is called electro-osmosis, it can be intuitively understood since the electric field acts on the mobile charge carriers in the fluid while the charged plates are held fixed by external forces. It is a universal phenomenon since all surfaces acquire surface charges when in contact with water. It is used in practical applications to pump fluids in micro and nano fluidic devices and is very useful since no moving parts are involved. In the opposite process, the electrostatic potential created by a pressure gradient is called the streaming potential and is used in applications for conversion from mechanical energy into electric energy. Convince yourself why the efficiencies of these conversion processes is typically quite low, but they are nevertheless extremely useful in applications where efficiency is not the main purpose.

Problem 2 – Thermal conduction and diffusion - minimum entropy production and stability

Our goal in this problem is to show that the entropy production is minimal and stable for a system under the influence of diffusion and a heat flux. We assume a system with constant pressure p in a fixed volume V at a temperature $T(\mathbf{x}, t)$. Further we have two kind of particles with concentration $c_1(\mathbf{x}, t)$ and $c_2(\mathbf{x}, t)$ and chemical potential $\mu_1(\mathbf{x}, t)$ and $\mu_2(\mathbf{x}, t)$ with $c_1 + c_2 = c = const$. We have the following balance equations given

$$\rho \frac{\partial c_1}{\partial t} = -\nabla \mathbf{J}_1 \quad (4)$$

$$\rho \frac{\partial c_2}{\partial t} = -\nabla \mathbf{J}_2 \quad (5)$$

$$\rho \frac{\partial u}{\partial t} = -\nabla \mathbf{J}_q \quad (6)$$

$$\rho \frac{\partial s}{\partial t} = -\nabla \mathbf{J}_s + \sigma \quad (7)$$

a) Derive the following expression for the entropy balance equation

$$\rho \frac{\partial s}{\partial t} = -\nabla \left(\frac{1}{T} [\mathbf{J}_q - (\mu_1 - \mu_2) \mathbf{J}_1] \right) + \mathbf{J}_q \cdot \nabla \frac{1}{T} - \mathbf{J}_1 \cdot \nabla \frac{\mu_1 - \mu_2}{T} \quad (8)$$

And explain where the term $\mu_1 - \mu_2$ comes from and why we only need to focus on the concentration flow \mathbf{J}_1 .

Hint: Use the fundamental equation and remember that the entire concentration is constant. ($c_1 + c_2 = c = const.$)

b) From Eq. (8) we can read off the entropy flux

$$\mathbf{J}_s = \frac{1}{T} [\mathbf{J}_q - (\mu_1 - \mu_2) \mathbf{J}_1] \quad (9)$$

and the entropy production

$$\sigma = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \mathbf{J}_1 \cdot \nabla \frac{\mu_1 - \mu_2}{T} \quad (10)$$

The phenomenological equations written as linear relations for the heat flux and diffusion flux are

$$\mathbf{J}_q = L_{qq} \nabla \frac{1}{T} - L_{q1} \nabla \frac{\mu_1 - \mu_2}{T} \quad (11)$$

$$\mathbf{J}_1 = L_{1q} \nabla \frac{1}{T} - L_{11} \nabla \frac{\mu_1 - \mu_2}{T} \quad (12)$$

Write down the total entropy production

$$P = \int \sigma dV \quad (13)$$

i) Derive the equation

$$2L_{qq} \Delta \frac{1}{T} - (L_{q1} + L_{1q}) \Delta \frac{\mu_1 - \mu_2}{T} = 0 \quad (14)$$

for variations of $\delta(\frac{1}{T})$.

ii) Derive the equation

$$(L_{q1} + L_{1q}) \Delta \frac{1}{T} - 2L_{11} \Delta \frac{\mu_1 - \mu_2}{T} = 0 \quad (15)$$

for variations of $\delta(\frac{\mu_1 - \mu_2}{T})$, where $\Delta = \nabla \cdot \nabla$.

Hint: Recall that the state of minimum entropy production follows from the condition

$$\delta P = 0. \quad (16)$$

c) Now you are able to show, together with the Onsager relations, that

$$\frac{\partial c_1}{\partial t} = 0 \quad (17)$$

$$\frac{\partial u}{\partial t} = 0 \quad (18)$$

Use these two equations to show that $\frac{\partial T}{\partial t} = 0$ follows. Thus the minimum entropy production is a stationary state.

Hint: Assume that $u = u(c_1, c_2, t, T)$.

d) The next step is to show that the stationary state is stable

$$\frac{\partial P}{\partial t} \leq 0. \quad (19)$$

Derive the following expression

$$\frac{\partial P}{\partial t} = -2 \int dV \left\{ \nabla \mathbf{J}_q \frac{\partial}{\partial t} \frac{1}{T} - \nabla \mathbf{J}_1 \frac{\partial}{\partial t} \frac{\mu_1 - \mu_2}{T} \right\} \quad (20)$$

Hint: Use your result from Eq. (13) and derive it with respect to t . Then partial integration will help you eventually.

e) Introduce the enthalpy $h (= u + pv)$ and derive the following three equations

$$\rho \frac{\partial h}{\partial t} = -\nabla \mathbf{J}_q \quad (21)$$

$$\frac{\partial h}{\partial t} = c_p \frac{\partial T}{\partial t} + (\mu_1 - \mu_2) \frac{\partial c_1}{\partial t} \quad (22)$$

$$\frac{\partial}{\partial t} \frac{\mu_1 - \mu_2}{T} = -\frac{\mu_1 - \mu_2}{T^2} \frac{\partial T}{\partial t} + \frac{1}{T} \frac{\partial \mu_1 - \mu_2}{\partial c_1} \frac{\partial c_1}{\partial t} \quad (23)$$

Hint: Assume $h = h(c_1, c_2, t, T)$

f) Finally use the results from e) and put them in Eq. (20) to derive the following equation

$$\frac{\partial P}{\partial t} = -2 \int dV \frac{\rho}{T} \left\{ \frac{c_p}{T} \left(\frac{\partial T}{\partial t} \right)^2 + \frac{\partial(\mu_1 - \mu_2)}{\partial c_1} \left(\frac{\partial c_1}{\partial t} \right)^2 \right\} \leq 0. \quad (24)$$

and explain why the two terms inside the integrand are positive.

Hint: Recall that the Gibbs free energy is convex in c_1 : $\frac{\partial^2 G}{\partial c_1^2} \geq 0$.