Addendum to
"Nanoscale Hydrodynamics of Simple Systems"

J.S. Hansen

This addendum is based on some of my own notes that did not make the book and some additional hindsights. Moreover, as I keep working in the field new results relevant for the book theme may be added. I hope this can be a helpful suppliment to the readers.

On the shear waves

In the book the transverse velocity autocorrelation function using Maxwell's viscoelastic model is derived using the linear differential operator $\mathcal{A}$. While this follows the literature and allows for a generalization, it is helpful to show a direct derivation where the operator is not used in an abstract manner.[1]

We start with the momentum balance equation, Eq. (4.3), leaving out the stochastic force term as it will eventualy vanish in the ensemble averaging,

$$\rho_{\text{av}} \frac{\partial \widetilde{\delta u_x}}{\partial t} = -ik_y \widetilde{P}_{yx} \tag{1}$$

implying that

$$\frac{\partial \widetilde{P}_{yx}}{\partial t} = -\frac{\rho_{\text{av}}}{ik_y} \frac{\partial^2 \widetilde{\delta u_x}}{\partial t^2} \, . \tag{2}$$

The symbols are defined in the book. Recall, the Maxwell model reads, Eq. (4.11) in the book,

$$\begin{aligned} ik_y \widetilde{\delta u_x} &= -\frac{1}{\eta_0}\left(1 + \tau_M \frac{\partial}{\partial t}\right) \widetilde{P}_{yx} & (3) \\ &= \frac{\rho_{\text{av}}}{ik_y \eta_0} \frac{\partial \widetilde{\delta u_x}}{\partial t} + \frac{\tau_M \rho_{\text{av}}}{ik_y \eta_0} \frac{\partial^2 \widetilde{\delta u_x}}{\partial t^2} & (4) \end{aligned}$$

[1] Thanks to Solvej for pointing this out.

by the relations Eqs. (1) and (2). Re-arranging we get the desired result

$$\frac{\partial^2 \widetilde{\delta u_x}}{\partial t^2} + \frac{1}{\tau_M}\frac{\partial \widetilde{\delta u_x}}{\partial t} - \frac{\eta_0 k_y^2}{\tau_M \rho_{\mathrm{av}}}\widetilde{\delta u_x} = 0 \ . \tag{5}$$

This is Eq. (4.15) in the book, but again without the stochastic forcing term.

The tricky counter-ion system

Section 6.2 deals with charged systems, and in 6.2.1 and 6.2.2 we investigate the charge density profile near a negatively charged wall, see the geometry in Fig. 6.6. Two different systems are considered, namely, an electrolyte and a counter-ion system. Equation (6.66) proposes a model for the counter-ion density, denoted n_+ as the counter-ion is a cation. As stated in the text, the counter-ion system must fullfill the properties that

$$n_+ \to 0 \ \text{ as } \ z \to \infty \tag{6}$$

since the total charge $Aq\int_0^\infty n_+ \mathrm{d}z$, where A is the wall surface area, cannot diverge. This is in agreement with the surface charge screening effect and furthermore that the electric potential φ has the property

$$\varphi \to 0 \ \text{ as } \ z \to \infty. \tag{7}$$

Equation (6.66) is different from an electrolyte system, Eq. (6.45) composed of both co- and counter-ions which may raise confusion. Here it is shown that Eq. (6.66) can be derived from the chemical potential by re-defining the ion activities for such counter-ion systems.

It is, perhaps, instructive to see the standard case of the electrolyte. The chemical potential of the anions and cations reads

$$\mu_i = \mu_i^o + k_B T \ln(a_i) + q_i\varphi \, , \tag{8}$$

where μ_i^o can be chosen to be the reference chemical potential in bulk (i.e., sufficiently far away from the wall), a_i is the ion activity, and q_i the ion charge. Index i denotes the ion type, + or -. The activity can be given in terms of the density and activity coefficient γ,

$$a_i = \gamma_i \frac{n_i}{n_0} \tag{9}$$

where n_0 is here the density in bulk (this is the same for both anion and cation). In the limit of small electrolyte concentrations $\gamma_i \approx 1$ and, therefore,

$$\mu_i = \mu_i^o + k_B T \ln\left(\frac{n_i}{n_0}\right) + q_i \varphi \,. \tag{10}$$

Notice that in bulk, $z \to \infty$, we have $n_i \to n_0$, and the second term vanishes implying that the electric potential follows Eq. (7) as expected.

In the steady state μ_i is constant, and we have the relation

$$\frac{\partial \varphi}{\partial z} = -\frac{k_B T}{q_i} \frac{\partial}{\partial z} \ln(n_i) \tag{11}$$

Integrating with the limit boundaries

$$\int_{\varphi(z)}^{\varphi(\infty)} \mathrm{d}\varphi = -\frac{k_B T}{q_i} \int_{n_i(z)}^{n_0} \mathrm{d}\ln(n_i) \tag{12}$$

by substitution gives the well-known result for the electrolyte

$$n_i = n_0 e^{-q_i \varphi / k_B T} \,. \tag{13}$$

For a counter-ion system with a negatively charged wall the cation-ion charge is $q_+ = q > 0$. We still have

$$\mu_+ = \mu_+^o + k_B T \ln(a_+) + q\varphi \,, \tag{14}$$

where μ_+^o is the reference potential; here we again use the chemical potential in bulk. Now, recall Eq. (6). This property leaves the definition Eq. (9) invalid. With the choice of reference potential we still must impose that the activity is unity as $z \to \infty$ in the dilute limit. These contraints are fullfilled by defining the activity as

$$a_+ = \gamma_+ \left(\frac{n_+ + n_*}{n_*}\right) \,, \tag{15}$$

where n_* is some non-zero reference density (in the book denoted n_0). Using Eq. (15) the activity is simply understood as an "effective concentration" and the definition is, clearly, not rigorously derived. Continuing, from the steady-state condition we get

$$\frac{\partial \varphi}{\partial z} = -\frac{k_B T}{q_i} \frac{\partial}{\partial z} \ln\left(\frac{n_+ + n_*}{n_*}\right) \,, \tag{16}$$

in the dilute limit. Application of the limiting boundaries

$$\varphi(\infty) = 0 \quad \text{and} \quad n_+(\infty) = 0 \; , \tag{17}$$

and integrating we obtain

$$n_+ = n_*(e^{-q\varphi/k_BT} - 1) \, . \tag{18}$$

This is Eq. (6.66).