

Addendum to "Nanoscale Hydrodynamics of Simple Systems"

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This addendum is based on some of my own notes that did not make the book and some additional hind-sights. I hope this can be a helpful supplement 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 eventually vanish in the ensemble averaging,

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

implying that

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

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

$$ik_y \widetilde{\delta u_x} = -\frac{1}{\eta_0} \left(1 + \tau_M \frac{\partial}{\partial t} \right) \widetilde{P}_{yx} \quad (3)$$

$$= \frac{\rho_{\text{av}}}{ik_y \eta_0} \frac{\partial \widetilde{\delta u_x}}{\partial t} + \frac{\tau_M \rho_{\text{av}}}{ik_y \eta_0} \frac{\partial^2 \widetilde{\delta u_x}}{\partial t^2} \quad (4)$$

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

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

¹Thanks to Solvej for recommending this

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

The de Gennes order parameter

Equation (5.27) defines the de Gennes order parameter

$$S = \frac{1}{2}(3\langle \cos^2(\theta) \rangle - 1), \quad (6)$$

where θ is the angle between the characteristic molecular vector and the wall normal vector. (Not "the wall" as stated in the text - see erratum.) S has the properties

1. $S = -1/2$: the molecular vectors are (mostly) parallel to the wall
2. $S = 1$: the molecular vectors are (mostly) normal to the wall
3. $S = 0$: the molecular vectors are uniformly oriented.

We here prove the last property in two dimensions; the other properties can be found from same ideas. In two dimensions, we let the molecular vector coordinate be given by (x, z) , and the z -axis is the normal to the wall (as used in the book). Let the molecular vector length, l_m be fixed; then the vector x -coordinate is found simply using $x = \sqrt{l_m^2 - z^2}$, such that $z^2 \leq l_m^2$ and $x \geq 0$. The uniformity pertains to the vector coordinates and (not the angle). Then, the probability density function for the z vector coordinate is

$$f(z) = \frac{1}{2l_m} 1_A(z), \quad (7)$$

where 1_A is the indicator function on the domain

$$A = \{z \in \mathbf{R} : -l_m \leq z \leq l_m\}.$$

The angle between the wall normal and the molecular vector is then $\cos(\theta) = z/l_m$ or $\theta = \cos^{-1}(z/l)$, where $0 \leq \theta \leq \pi$. Since the inverse cosine function is monotonically decreasing, we find the probability density for θ (which is worth listing as well)

$$\begin{aligned} g(\theta) &= f(l_m \cos(\theta)) \left| \frac{d}{d\theta} l_m \cos(\theta) \right| \\ &= \frac{1}{2} \sin(\theta) \end{aligned} \quad (8)$$

So the angle is sine-distributed. We are not after the angle distribution, but the distribution of $\cos^2 \theta$. Since we have the distribution for θ we can simply continue from here; let $w = \cos^2 \theta$ ($0 \leq w \leq 1$) for brevity. Then $\theta = \cos^{-1}(\sqrt{w})$ and

$$\begin{aligned} h(w) &= f(\cos^{-1}(\sqrt{w})) \left| \frac{d}{dw} \cos^{-1}(\sqrt{w}) \right| \\ &= \frac{1}{2\sqrt{w}}. \end{aligned} \quad (9)$$

The expected value (or expectation value) of w is

$$\langle \cos^2 \theta \rangle = \langle w \rangle = \frac{1}{2} \int_0^1 \sqrt{w} dw = \frac{1}{3} \quad (10)$$

Substitution into Eq. (6) we get the desired result $S = 0$.

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 system 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 fulfill that

$$n_+ \rightarrow 0 \text{ as } z \rightarrow \infty \quad (11)$$

since the total charge $Aq \int_0^\infty n_+ dz$, where A is the wall surface area, cannot diverge. This is in agreement with the surface charge screening effect. Since the density converges to zero as $z \rightarrow \infty$, we can choose the reference point to be at infinite, hence, the electric potential φ fulfills

$$\varphi \rightarrow 0 \text{ as } z \rightarrow \infty. \quad (12)$$

See Griffith's book *Introduction to Electrodynamics*, Chapter 2. I final note here, the choice of reference potential is not unique, of course, and e.g. Israelachvili chooses this differently.

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 counter-ion systems.

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

$$\mu_i = \mu_i^o + k_B T \ln(a_i) + q_i \varphi, \quad (13)$$

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 ,

$$a_i = \gamma_i \frac{n_i}{n_0} \quad (14)$$

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,

$$\mu_i = \mu_i^o + k_B T \ln\left(\frac{n_i}{n_0}\right) + q_i \varphi. \quad (15)$$

Notice that in bulk, $z \rightarrow \infty$, we have $n_i \rightarrow n_0$, and the second term vanishes implying that the electric potential follows Eq. (12) as expected.

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

$$\frac{\partial \varphi}{\partial z} = -\frac{k_B T}{q_i} \frac{\partial}{\partial z} \ln(n_i) \quad (16)$$

Integrating with the limit boundaries

$$\int_{\varphi(z)}^{\varphi(\infty)} d\varphi = -\frac{k_B T}{q_i} \int_{n_i(z)}^{n_0} d \ln(n_i) \quad (17)$$

by substitution gives the well-known result for the electrolyte

$$n_i = n_0 e^{-q_i \varphi / k_B T}. \quad (18)$$

For a counter-ion system with a negatively charged wall the cation-ion charge is $q_+ = q > 0$. Recall that the definition of the chemical potential is the partial derivative of the system free energy with respect to n_+ , thus, sufficiently far away from the wall we have $\mu_+ = 0$ due to Eq. (11). This property also leaves the definition of the activity Eq.(14) invalid. We have

$$\mu_+ = k_B T \ln(a_+) + q \varphi, \quad (19)$$

We now define the activity by

$$a_+ = \gamma_+ \left(\frac{n_+ + n_*}{n_*} \right), \quad (20)$$

where n_* is some non-zero reference density (in the book denoted n_0). Using Eq. (20) the activity is simply understood as an "effective concentration" and the definition is, clearly, not rigorously derived. The activity coefficient is dependent of the reference concentration, but we still have the property that $\gamma_+ \rightarrow 1$ as $n_+ \rightarrow 0$. Hence, continuing from the steady-state condition we get

$$\frac{\partial \varphi}{\partial z} = -\frac{k_B T}{q_i} \frac{\partial}{\partial z} \ln \left(\frac{n_+ + n_*}{n_*} \right), \quad (21)$$

in the dilute limit. Application of the limiting boundaries

$$\varphi(\infty) = 0 \quad \text{and} \quad n_+(\infty) = 0, \quad (22)$$

and integrating we obtain

$$n_+ = n_* (e^{-q\varphi/k_B T} - 1). \quad (23)$$

This is Eq. (6.66).