Fluctuating Hydrodynamics and Debye-Hückel-Onsager Theory for Electrolytes

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Thermal fluctuations play a key role at mesoscopic systems and, as I will demonstrate, can affect macroscopic observables.

Primarily interested in the case when fluctuations are weak, i.e., lots of molecules are involved, but fluctuations still make a difference: fluctuating hydrodynamics (FHD).

Electrolyte solutions are important for batteries, ion-selective membranes, biology, etc.

Here we study the bulk transport coefficients of a binary electrolyte using the fluctuating Poisson-Nernst-Planck equations: conductivity and collective diffusion coefficient. Originally studied using other methods by Debye-Hückel-Onsager (DHO theory) a long time ago, a lot of it forgotten and never picked up by chemical engineers, probably in part because of complexity.
Momentum equation in the Boussinesq (constant density) isothermal approximation for constant dielectric constant $\epsilon$:

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \pi = -\nabla \cdot (\rho \mathbf{vv}^T) + \nabla \cdot (\eta \ddot{\mathbf{v}} + \Sigma) + \nabla \cdot (\epsilon \nabla \Phi) \nabla \Phi,$$

$$\nabla \cdot \mathbf{v} = 0,$$

where $\Phi (r, t)$ is the electrostatic potential and $\nabla \cdot (\epsilon \nabla \Phi) \nabla \Phi$ is the Lorentz force.

**Stochastic momentum flux** from FHD:

$$\Sigma = \sqrt{\eta k_B T} \left[ \mathbf{Z}^{\text{mom}} + (\mathbf{Z}^{\text{mom}})^T \right].$$

The **electrophoretic** correction to conductivity $\sim \sqrt{c}$ is due to a coupling of charge and momentum fluctuations.
For the **composition equation**, our variables are the mass fractions \( w_s = \frac{\rho_s}{\rho} \) since \( \rho = \rho_0 \) is constant.

The mass density \( \rho_s = w_s \rho \) of species \( s \) for a mixture of \( N_S \) species satisfies a fluctuating advection-diffusion equation:

\[
\frac{\partial (\rho w_s)}{\partial t} = -\nabla \cdot (\rho w_s \mathbf{v}) - \nabla \cdot \mathbf{F}_s,
\]

The **dissipative and stochastic diffusive mass fluxes** for a dilute species are,

\[
\mathbf{F}_s \approx -\rho D_s^0 \left( \nabla w_s + \frac{m_s w_s z_s}{k_B T} \nabla \Phi \right) + \sqrt{2 \rho m_s w_s D_s^0} \mathbf{Z}^\text{mass}_s,
\]

where \( m_s \) is the molecular mass and the charge per unit mass is \( z_s \), and \( D_s^0 \) is the **bare** self-diffusion coefficient at infinite dilution.
The electric potential $\Phi(r, t)$ satisfies the **Poisson equation**

$$- \nabla \cdot (\epsilon \nabla \Phi) = \rho \sum_{s=1}^{N_s} w_s z_s. \quad (1)$$

A key mesoscopic length is the **Debye length**

$$\lambda_D \approx \left( \frac{\epsilon k_B T}{\sum_{s=1}^{N_s} \rho w_s m_s z_s^2} \right)^{1/2}. \quad (2)$$

From now on we consider a **non-equilibrium steady state** under the action of an applied concentration gradient or electric field.

The fluctuations of the composition from the average $\bar{w}_s = \langle w_s \rangle$ are $\delta w_s = w_s - \bar{w}_s$, and the fluctuations of the fluid velocity are $\delta \mathbf{v}$. 

**Poisson equation**
Structure factors

- The **static structure factor matrix** is

  \[
  S = \begin{pmatrix}
  S_{ww} & S_{wv} \\
  S_{wv}^* & S_{vv}
  \end{pmatrix},
  \tag{3}
  \]

  where each element is a cross correlation in Fourier space,

  \[
  S_{fg}(\mathbf{k}) = \langle \delta \hat{f}(\mathbf{k}) \delta \hat{g}(\mathbf{k})^* \rangle
  \tag{4}
  \]

  where \( \hat{f}(\mathbf{k}) \) is the Fourier transform of \( f(\mathbf{r}) \) and star denotes conjugate transpose.

- By Plancherel’s theorem,

  \[
  \langle (\delta f)(\delta g)^* \rangle = \frac{1}{(2\pi)^3} \int d\mathbf{k} \ S_{fg}(\mathbf{k}).
  \tag{5}
  \]

- Macroscopic gradient applied in the \( x \)-direction so only \( v_x \) is retained in the structure factors.
Linearized FHD

- The FHD equations can be linearized around the macroscopic steady state and Fourier transformed to obtain for each wavenumber an Ornstein-Uhlenbeck process:

\[ \partial_t \hat{\mathbf{u}} = \mathbf{M} \hat{\mathbf{u}} + \mathbf{N} \hat{\mathbf{z}}, \]  

(6)

where \( \hat{\mathbf{u}} = (\delta \hat{w}_1, \ldots, \delta \hat{w}_{N_{sp}}, \delta \hat{v}_x)^T \) and

\[ [\mathbf{N} \mathbf{N}^*]_{ii} = \frac{2}{\rho} \left\{ \begin{array}{ll}
k^2 D_i^0 m_i \bar{w}_i & i \leq N_{sp} \\
k^2 \nu k_B T & i = N_{sp} + 1
\end{array} \right., \]  

(7)

with \( k^2 = k^2 - k^2_x = k^2 \sin^2 \theta \), and \( \theta \) is the angle between \( \mathbf{k} \) and the \( x \) axis.

- Structure factor is the solution of the continuous Lyapunov equation and easy to obtain using computer algebra,

\[ \mathbf{M} \mathbf{S} + \mathbf{S} \mathbf{M}^* = -\mathbf{N} \mathbf{N}^*. \]  

(8)
The fluctuations in the electric field can be expressed in terms of species fluctuations $(\iota = \sqrt{-1})$,

$$
\delta \hat{E} = -\iota k \delta \phi = -\frac{\iota k}{\epsilon k^2} \delta \hat{q} = -\rho \frac{\iota k}{\epsilon k^2} \sum_i z_i \delta \hat{w}_i. \quad (9)
$$

At thermodynamic equilibrium $S_{\text{wv}}^{\text{eq}} = 0$ and $S_{\text{vv}}^{\text{eq}} = \sin^2(\theta) k_B T / \rho$ and

$$
S_{\text{wi},\text{wi}}^{\text{eq}} = \frac{1}{\rho} m_i \bar{w}_i - \left( \frac{1}{\epsilon k_B T} \right) \frac{\lambda^2}{1 + k^2 \lambda^2} (m_i z_i \bar{w}_i)(m_j z_j \bar{w}_j). \quad (10)
$$
Renormalization of free energy

- It is well-known that the colligative properties (e.g., vapor pressure, freezing point) of electrolyte solutions depend on their ionic strength.
- Ionic interactions renormalize the Gibbs free energy by [1]

\[
\Delta G = \frac{1}{2} \langle \delta q \delta \phi \rangle = \frac{\rho^2}{2\epsilon(2\pi)^3} \int \frac{z^T (S_{ww}^{eq} - \text{Diag} \{ m_i \bar{w}_i / \rho \}) z}{k^2} dk \\
= -\frac{k_B T}{8\pi \lambda^3}.
\]

- This result leads directly to the limiting law of Debye and Hückel for point ions and shows an experimentally measurable effect of mesoscopic thermal charge fluctuations.
- It is important to note that a broad range of wavenumbers contributes to the integral over \( k \), not just microscopic scales!
In perturbative (one-loop) renormalization theory we expand to quadratic order in fluctuations and then use the solution of the linearized FHD equations to obtain the quadratic terms.

This has been applied to many situations and is not rigorous but is simple to execute and leads to computable predictions of nonlinear (quadratic) FHD.

Here we expand the fluxes of the ions (giving the electric current) to quadratic order in the fluctuations [2, 3]:

\[
\bar{F}_i = \langle F_i(w, v) \rangle = F_i(\langle w \rangle, \langle v \rangle) + D_i^0 \frac{eV_i}{k_B T} \langle \delta w_i \delta E \rangle + \langle \delta v \delta w_i \rangle
\]

\[
\equiv \bar{F}_i^0 + \bar{F}_i^{\text{relx}} + \bar{F}_i^{\text{adv}}
\]  

(11)

The term \(\bar{F}_i^{\text{relx}}\) is the relaxation correction and \(\bar{F}_i^{\text{adv}}\) the advection correction.
We can also expand the linearized FHD equations in powers of the applied field,

\[ \mathcal{M} = \mathcal{M}^{\text{eq}} + \mathcal{M}' + O(\mathcal{X}^2), \]

where \( \mathcal{X} \) is the applied thermodynamic force; \( \mathcal{M}^{\text{eq}} \) is \( O(\mathcal{X}^0) \) and \( \mathcal{M}' \) is \( O(\mathcal{X}^1) \).

Similarly, we can expand the structure factor as

\[ S = S^{\text{eq}} + S' + O(\mathcal{X}^2). \]

Nonequilibrium fluctuating hydrodynamics makes a local equilibrium approximation, which means that the noise covariance matrix \( \mathcal{N}_N^* \) is unchanged, giving the linear system

\[ \mathcal{M}^{\text{eq}}S' + S'(\mathcal{M}^{\text{eq}})^* = -\mathcal{M}'S^{\text{eq}} - S^{\text{eq}}(\mathcal{M}')^*. \]
Let’s consider an applied electric field $\mathbf{\chi} \equiv \mathbf{E}_{\text{ext}} = E_{\text{ext}} \mathbf{e}_x$.

From the linearized fluctuating PNP equations in the presence of an applied field one can easily obtain

$$\mathcal{M}' = E_{\text{ext}} \left( -\frac{\lambda^2}{k_B T} \frac{k \cos \theta}{\sin^2(\theta)} \text{Diag} \left( \frac{D_i^0 m_i z_i}{\rho(D_i^0 + \nu)} \right) \mathbf{1} \right).$$

(14)

The conductivity gets renormalized by the fluctuations by two pieces: a relaxation and an advective contribution.

The **advective flux correction** is due to the **non-equilibrium** contribution to the structure factor:

$$S'_{w_i,\nu} = \lambda^2 \frac{\sin^2 \theta}{1 + \lambda^2 k^2} \frac{m_i \bar{v}_i z_i}{\rho(D_i^0 + \nu)} E_{\text{ext}}.$$  

(15)
The **advective flux correction** comes due to correlations of charge and velocity fluctuations:

\[
\vec{F}_{\text{adv}}^i = \langle \delta v \delta w_i \rangle = \int_{k=0}^{\pi/(2a_i)} dk \int_{-\pi/2}^{\pi/2} \cos(\theta) d\theta \ S'_{w_i,v}
\]

\[
\approx \left( \frac{1}{3\pi a_i} - \frac{1}{6\pi \lambda} \right) \frac{m_i \bar{w}_i z_i}{\eta} \ E_{\text{ext}}
\]

for Schmidt number \( Sc \gg 1 \) and \( \lambda \gg a \) (dilute solution).

The first piece \( \sim 1/a_i \) comes from the **renormalized Stokes-Einstein relationship**

\[
D_s = D_s^0 + \frac{k_B T}{6\pi a_i \eta}.
\]

The second piece \( \sim 1/\lambda \) is called the **electrophoretic correction** and is \( \sim \sqrt{c} \); it was first obtained by Onsager and Fuoss by much more complicated means.
A similar calculation also gives the relaxation correction

$$\mathbf{F}_{relx}^i = \frac{D^0_i m_i z_i}{k_B T} \langle \delta w_i \delta \mathbf{E} \rangle = -\frac{(2 - \sqrt{2}) D^0_i m_i^2 z_i}{48 \pi k_B T \rho \lambda^3} \mathbf{E}_{ext},$$

which is in exact agreement with the result obtained by Onsager and Fuoss.

- **Fluctuating hydrodynamics is a powerful modeling tool at mesoscopic scales**, as demonstrated here by the calculation of the thermodynamic and transport corrections for electrolytes.
- The (fluctuating) **PNP equations** need to be corrected to order square root in the ionic strength, and are thus valid only for very dilute solutions.
In the analytical perturbative approach followed here, all corrections to the linearized fluctuating PNP equations appear additively, not multiplicatively as they should; to compute those we need **nonlinear computational FHD**.

The theoretical calculation here only works for rather dilute electrolytes. For realistic conditions we have $\lambda \sim a$ and we cannot really separate microscopic and electrostatic effects.

There are also too few ions per $\lambda^3$ volume, so we **need to treat ions as particles** using Brownian HydroDynamics – WIP.

At length scales $\gg \lambda$ the solution is **electroneutral** [4] but near boundaries it is not, so one needs to couple these two descriptions.

