Fluctuating Hydrodynamics and Debye-Hückel-Onsager Theory for Electrolytes

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Electrolyte Solutions

- **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.

FHD for Electrolytes: Momentum

- **Momentum equation** in the Boussinesq (constant density) isothermal approximation for constant dielectric constant ϵ:

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

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

where $\Phi(\mathbf{r}, t)$ is the electrostatic potential and $\boldsymbol{\nabla}\cdot\left(\epsilon \boldsymbol{\nabla}\Phi\right)\boldsymbol{\nabla}\Phi$ is the **Lorentz force**.

- **Stochastic momentum flux** from FHD:

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

- The **electrophoretic** correction to conductivity $\sim \sqrt{c}$ is due to a **coupling of charge and momentum fluctuations**.

FHD for Electrolytes: Mass

- For the **composition equation**, our variables are the mass fractions $w_s = \rho_s/\rho$ 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:

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

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

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

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**.

Poisson equation

- The electric potential $\Phi(\mathbf{r}, t)$ satisfies the **Poisson equation**

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

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

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

- 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 $\delta \mathbf{v}$.

Structure factors

- The **static structure factor matrix** is

$$\mathbf{S} = \left(\begin{array}{c|c} \mathbf{S}_{\mathbf{ww}} & \mathbf{S}_{\mathbf{w}v} \\ \hline \mathbf{S}_{\mathbf{w}v}{}^{*} & S_{vv} \end{array} \right), \tag{3}$$

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:

$$\partial_t \hat{\boldsymbol{\mathcal{U}}} = \boldsymbol{\mathcal{M}} \hat{\boldsymbol{\mathcal{U}}} + \boldsymbol{\mathcal{N}} \hat{\boldsymbol{\mathcal{Z}}}, \tag{6}$$

where $\hat{\boldsymbol{\mathcal{U}}} = (\delta \hat{w}_1, \ldots, \delta \hat{w}_{N_{\mathrm{sp}}}, \delta \hat{v}_x)^T$ and

$$[\boldsymbol{\mathcal{N}} \boldsymbol{\mathcal{N}}^*]_{ii} = \frac{2}{\rho} \begin{cases} k^2 D_i^0 m_i \bar{w}_i & i \leq N_{\mathrm{sp}} \\ k_\perp^2 \nu k_B T & i = N_{\mathrm{sp}} + 1 \end{cases}, \tag{7}$$

with $k_\perp^2 = k^2 - k_x^2 = k^2 \sin^2 \theta$, and θ 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,

$$\boldsymbol{\mathcal{M}} \mathbf{S} + \mathbf{S} \boldsymbol{\mathcal{M}}^* = -\boldsymbol{\mathcal{N}} \boldsymbol{\mathcal{N}}^*. \tag{8}$$

Equilibrium fluctuations

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

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

- At thermodynamic equilibrium $\mathbf{S}^{\mathrm{eq}}_{\mathbf{w}v} = 0$ and $S^{\mathrm{eq}}_{vv} = \sin^2(\theta)k_B T/\rho$ and

$$S^{\mathrm{eq}}_{w_i,w_i} = \frac{1}{\rho}m_i\bar{w}_i - \left(\frac{1}{\epsilon k_B T}\right)\frac{\lambda^2}{1+k^2\lambda^2}\left(m_i z_i\bar{w}_i\right)\left(m_j z_j\bar{w}_j\right). \tag{10}$$

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]

$$\Delta G = \frac{1}{2}\langle \delta q \delta \phi \rangle = \frac{\rho^2}{2\epsilon(2\pi)^3} \int \frac{\mathbf{z}^T \left(\mathbf{S}_{\mathbf{ww}}^{\mathrm{eq}} - \mathrm{Diag}\left\{ m_i \bar{w}_i / \rho \right\} \right) \mathbf{z}}{k^2} \, d\mathbf{k}$$
$$= -\frac{k_B T}{8\pi\lambda^3}.$$

- 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!

Perturbative renormalization of transport coefficients

- 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]:

$$\begin{aligned} \bar{\mathbf{F}}_i = \langle \mathbf{F}_i(\mathbf{w},\mathbf{v}) \rangle &= \mathbf{F}_i(\langle \mathbf{w} \rangle, \langle \mathbf{v} \rangle) + D_i^0 \frac{eV_i}{k_B T} \langle \delta w_i \delta \mathbf{E} \rangle + \langle \delta \mathbf{v} \delta w_i \rangle \\ &\equiv \bar{\mathbf{F}}_i^0 + \bar{\mathbf{F}}_i^{\mathrm{relx}} + \bar{\mathbf{F}}_i^{\mathrm{adv}} \end{aligned} \tag{11}$$

The term $\bar{\mathbf{F}}_i^{\mathrm{relx}}$ is the **relaxation correction** and $\bar{\mathbf{F}}_i^{\mathrm{adv}}$ the **advection correction**.

Perturbative expansion of structure factors

- We can also **expand the linearized FHD equations** in powers of the applied field,

$$\boldsymbol{\mathcal{M}} = \boldsymbol{\mathcal{M}}^{\text{eq}} + \boldsymbol{\mathcal{M}}' + O(\mathcal{X}^2), \tag{12}$$

  where $\boldsymbol{\mathcal{X}}$ is the applied thermodynamic force; $\boldsymbol{\mathcal{M}}^{\text{eq}}$ is $O(\mathcal{X}^0)$ and $\boldsymbol{\mathcal{M}}'$ is $O(\mathcal{X}^1)$.
- Similarly, we can expand the structure factor as $\mathbf{S} = \mathbf{S}^{\text{eq}} + \mathbf{S}' + O(\mathcal{X}^2)$.
- Nonequilibrium fluctuating hydrodynamics makes a **local equilibrium approximation**, which means that the noise covariance matrix $\boldsymbol{\mathcal{N}}\boldsymbol{\mathcal{N}}^*$ is unchanged, giving the linear system

$$\boldsymbol{\mathcal{M}}^{\text{eq}}\mathbf{S}' + \mathbf{S}'(\boldsymbol{\mathcal{M}}^{\text{eq}})^* = -\boldsymbol{\mathcal{M}}'\mathbf{S}^{\text{eq}} - \mathbf{S}^{\text{eq}}(\boldsymbol{\mathcal{M}}')^*. \tag{13}$$

Renormalization of conductivity

- Let's consider an applied electric field $\boldsymbol{\mathcal{X}} \equiv \mathbf{E}_{\text{ext}} = E_{\text{ext}} \mathbf{e}_x$.
- From the **linearized fluctuating PNP** equations in the presence of an applied field one can easily obtain

$$\mathcal{M}' = E_{\text{ext}} \left(\begin{array}{c|c} -\iota \frac{k \cos\theta}{k_B T} \text{Diag}\left(D_i^0 m_i z_i \right) & \mathbf{0} \\ \hline \sin^2(\theta) \mathbf{z}^T & 0 \end{array} \right). \tag{14}$$

- 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:

$$S'_{w_i,v} = \frac{\lambda^2 \sin^2\theta}{1 + \lambda^2 k^2} \frac{m_i \bar{w}_i z_i}{\rho (D_i^0 + \nu)} E_{\text{ext}}. \tag{15}$$

Advective contribution

- The **advective flux correction** comes due to correlations of charge and velocity fluctuations:

$$\bar{\mathbf{F}}_i^{\mathrm{adv}} = \langle \delta \mathbf{v} \delta w_i \rangle = \int_{k=0}^{\pi/(2a_i)} dk \int_{-\pi/2}^{\pi/2} \cos(\theta) d\theta \; S'_{w_i,\mathbf{v}} \tag{16}$$

$$\approx \left(\frac{1}{3\pi a_i} - \frac{1}{6\pi\lambda} \right) \frac{m_i \bar{w}_i z_i}{\eta} \; \mathbf{E}_{\mathrm{ext}} \tag{17}$$

  for Schmidt number $\mathrm{Sc} \gg 1$ 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.

Relaxation contribution

- A similar calculation also gives the **relaxation correction**

$$\bar{\mathbf{F}}_i^{\mathrm{relx}} = \frac{D_i^0 m_i z_i}{k_B T} \langle \delta w_i \delta \mathbf{E} \rangle = -\frac{(2-\sqrt{2}) D_i^0 m_i^2 z_i}{48\pi k_B T \rho \lambda^3} \; \mathbf{E}_{\mathrm{ext}}, \qquad (18)$$

  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**.

Caveats / Future Work

- 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 λ^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.

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