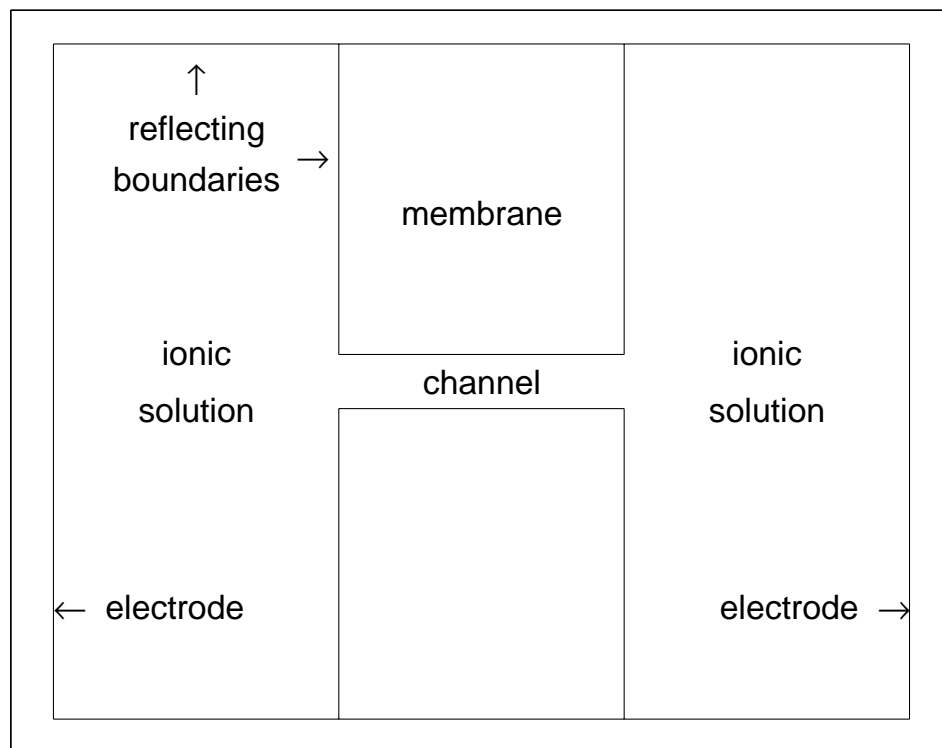# Derivation of averaged equations for ionic flow through confined systems

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Ionic Transport Through Narrow Channels

Ionic permeation through an open protein channel of a lipid membrane.

Mathematically: Diffusion through a narrow and long "(charged) hole" in a wall.

Microscopic Structure and Equilibrium Statistical Physics

Postulate of EST: The probability measure in con¯guration space is Boltzmann's distribution,

$$p(\boldsymbol{r}_1, ... \boldsymbol{r}_N) = Z_N^{-1} \exp\left\{-\frac{U(\boldsymbol{r}_1, ..., \boldsymbol{r}_N)}{k_B T}\right\},$$

where the energy of the configuration is

$$U(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) = \sum_{i \neq j} U_{1,2}(\boldsymbol{r}_i - \boldsymbol{r}_j) + \sum_i \varphi(\boldsymbol{r}_i).$$

In the absence of an external field and in free space, the equilibrium concentration in $\boldsymbol{R}^3$,

$$\rho(\boldsymbol{x}) = N \int_{\boldsymbol{R}^3} p(\boldsymbol{x}, \boldsymbol{r}_2 ... \boldsymbol{r}_N) \, d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N,$$

satisfies the BGY equation

$$k_B T \nabla \rho(\boldsymbol{x}) + \int_{\boldsymbol{R}^3} \rho(\boldsymbol{y} \,|\, \boldsymbol{x}) \nabla_{\boldsymbol{x}} U_{1,2}(\boldsymbol{x} - \boldsymbol{y}) \, d\boldsymbol{y}$$

$$\equiv -\boldsymbol{J}(\boldsymbol{x}) = 0.$$

The BGY equation as a conservation law

The BGY equation can be written as the conservation law

$$\nabla \cdot \boldsymbol{J}(\boldsymbol{x}) = 0$$

with the "boundary condition"

$$\boldsymbol{J}(\infty) = 0.$$

In a finite volume Ω the boundary condition

$$\boldsymbol{J}(\boldsymbol{x}) \cdot \boldsymbol{\nu}(\boldsymbol{x})|_{x \in \partial\Omega} = 0$$

defines equilibrium. A concentration gradient on the boundary drives the system out of equilibrium. This is the point of departure for non-equilibrium theory.

What replaces the Boltzmann distribution in non-equilibrium?

- Boltzmann's distribution "counts" (i.e., assigns probabilities) to configurations.

- There are no configurations in non–equilibrium, due to flux.

- What should replace configurations?

- How do you count it?

Answer: Replace Boltzmann's probability measure on particle configurations with a probability measure on particle trajectories.

The FPSE for the singlet pdf

The following equation has been derived in Barthel's book: for $h =$ Na$^+$, Cl$^-$, ...,

$$0 = \nabla_x \cdot J^h(x) =$$

$$-\nabla_x \cdot \left(\frac{\bar{f}^h(x)}{M^h \gamma^h(x)} p^h(x) - \frac{k_B T}{M^h \gamma^h(x)} \nabla_x\, p^h(x) \right),$$

where

$$\bar{f}^h(x) = \int_{\tilde{\Omega}} f^h(\tilde{x}) p_{N-1}(\tilde{x}_i^h \mid x_i^h = x)\, d\tilde{x}_i^h ..$$

The relations

$$c^h(x) \;=\; N^h p^h(x)$$

$$c^{h,h'}(x, y) \;=\; N^h N^{h'} p^{h,h'}(x, y).$$

convert the FPSE to the NPE for the singlet and pair ionic densities. These equations, however, depend on the yet undetermined average forces, but are otherwise exact.

What is missing?

The FPSEs are defined in the finite domain $x \in \Omega$ and $y \in \Omega$. Boundary conditions for $p^h(x)$ and $p^{h,h'}(x, y)$ have to be imposed for $x \in \partial\Omega$ and $y \in \Omega$ and $y \in \partial\Omega$ and $x \in \Omega$. Once these boundary conditions are specified, the pair correlation function $p^{h,h'}(x, y)$ is completely determined, provided the forces $\bar{f}^k_m(x, y)$ are known.

Boundary conditions for the joint pdf of N diffusers: Two exactly solvable problems

1. **Equilibrium= vanishing flux**

The equilibrium case, as far as boundary conditions are concerned, is trivial and un-instructive. However, it can be used as a benchmark, because non-equilibrium results have to reduce to equilibrium results in the limit of vanishing flux.

2. **A system of independent (non-interacting) ions diffusing in an external potential $V(x)$ between two fixed concentrations**

This case gives the key insight into boundary conditions.

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1. Dependent di®users in equilibrium

A assume that the total potential of the system
is given by

$$U_N(\tilde{x}) = \sum_{1 \leq i < j \leq N} U(|x_i - x_j|).$$

and that the friction is state-independent. The
Langevin equations are

$$\ddot{x}_i + \gamma \dot{x}_i + \frac{1}{M^h} \nabla_{x_i^h} U_N(\tilde{x}) = \sqrt{2\varepsilon}\, \dot{w}_i^h,$$

for $i = 1, 2, \ldots, N$,

where

$$\varepsilon^h = \frac{\gamma k_B T}{M^h}.$$

The equilibrium solution of the FPSE

The FPSE is

$$0 = \sum_i \nabla_i \cdot \left[\frac{1}{M\gamma} \nabla_i U_N(\tilde{\boldsymbol{x}}) p_N(\tilde{\boldsymbol{x}}) + \frac{k_B T}{M\gamma} \nabla_i p_N(\tilde{\boldsymbol{x}}) \right]$$

$$= -\sum_{j=1}^{N} \nabla \boldsymbol{x}_j \cdot \boldsymbol{J}_j(\tilde{\boldsymbol{x}}).$$

The equilibrium condition of vanishing flux is

$$\boldsymbol{J}_j(\tilde{\boldsymbol{x}}) = 0, \quad \text{for all } j,$$

and the solution of the FPSE in this case is

$$p_N(\tilde{\boldsymbol{x}}) = \frac{e^{-U_N(\tilde{\boldsymbol{x}})/k_B T}}{Z_N},$$

where Z_N is the configurational partition function of equilibrium statistical mechanics. This recovers the Boltzmann distribution of equilibrium theory.

2. Independent di®users

Consider a system of independent (non-interacting, i.e., uncharged) particles diffusing in an external potential $V(\boldsymbol{x})$ between two fixed concentrations. The potential is

$$U_N(\tilde{\boldsymbol{x}}) = \sum_{j=1}^{N} V(\boldsymbol{x}_j).$$

Statistical independence means that the joint pdf is the product of the pdfs of the individual ions. Therefore, the solution of the FPSE in the $3N$-dimensional configuration space is

$$p_N(\tilde{\boldsymbol{x}}) = \prod_{j=1}^{N} p(\boldsymbol{x}_j),$$

where $p(\boldsymbol{x}_j)$, the probability density of the j-th ion, is the solution of the 3-dimensional FPSE

$$0 = \nabla_{\boldsymbol{x}_j} \cdot \frac{1}{M\gamma}[\nabla_{\boldsymbol{x}_j} V(\boldsymbol{x}_j) p(\boldsymbol{x}_j) + k_B T \nabla_{\boldsymbol{x}_j} p(\boldsymbol{x}_j)]$$

$$= -\nabla_{\boldsymbol{x}_j} \cdot \mathcal{J}_j(\boldsymbol{x}_j)$$

Boundary conditions

The $3N$-dimensional flux vanishes on reflect-
ing boundaries, and singlet concentrations are
given on the other boundaries. This condition
determines the singlet flux density $\mathcal{J}^1(\boldsymbol{x})$ on
$\partial\Omega$ and this flux will be assumed known hence-
forward. Denote

- $\partial\Omega_r =$ reflecting boundaries
- $\partial\Omega_F =$ feedback boundary, where fixed con-
centrations are maintained

The boundary concentrations determine the
boundary fluxes for all j,

$$\mathcal{J}_j(\boldsymbol{x}_j) \cdot \boldsymbol{\nu}(\boldsymbol{x}_j) = 0 \quad \text{for } \boldsymbol{x}_j \in \partial\Omega_r$$

$$\mathcal{J}_j(\boldsymbol{x}_j) \cdot \boldsymbol{\nu}(\boldsymbol{x}_j) = \mathcal{J}^1(\boldsymbol{x}_j) \cdot \boldsymbol{\nu}(\boldsymbol{x}_j) \quad \text{for } \boldsymbol{x}_j \in \partial\Omega_F.$$

Note that the concentrations have to be nor-
malized so that

$$\int_\Omega p(\boldsymbol{x}_j)\,d\boldsymbol{x}_j = 1, \quad \forall j.$$

Boundary °uxes of independent di®users

Since

$$p_N(\tilde{\boldsymbol{x}}) = \prod_{j=1}^{N} p(\boldsymbol{x}_j),$$

we obtain

$$\boldsymbol{J}_j(\tilde{\boldsymbol{x}}) = \mathcal{J}^1(\boldsymbol{x}_j) \prod_{i \neq j} p(\boldsymbol{x}_i) = \mathcal{J}^1(\boldsymbol{x}_j) p_{N-1}(\tilde{\boldsymbol{x}}_j)$$

$$= \mathcal{J}^1(\boldsymbol{x}_j) p_{N-1}(\tilde{\boldsymbol{x}}_j \,|\, \boldsymbol{x}_j).$$

The last equality expresses the independence of $\boldsymbol{x}_j$ of the remaining $\tilde{\boldsymbol{x}}_j$. This conditioning anticipates the case of dependent ions. It expresses the boundary behavior of ions when the boundaries are put anywhere in the bath, where average concentrations and potentials are fixed.

Boundary °uxes of independent di®users (continued)

The relation

$$\boldsymbol{J}_j(\tilde{\boldsymbol{x}}) = \mathcal{J}^1(\boldsymbol{x}_j) p_{N-1}(\tilde{\boldsymbol{x}}_j \,|\, \boldsymbol{x}_j),$$

with

$$\boldsymbol{x}_j \in \partial\Omega, \quad \tilde{\boldsymbol{x}}_j \in \tilde{\Omega}_j,$$

is the connection between the j-th component of the boundary flux of $p_N(\tilde{\boldsymbol{x}})$ and the singlet boundary flux. When $\mathcal{J}^1(\boldsymbol{x})$ is known, this boundary condition means that the feedback mechanism removes and inserts ions into the system at the boundary, depending on the configuration of ions inside the domain, with fixed flux density that maintains the boundary concentrations.

Boundary conditions for $p_N(\tilde{x})$ of dependent di®users

With the above interpretation in mind, we adopt the relation

$$\boldsymbol{J}_j(\tilde{\boldsymbol{x}}) \cdot \boldsymbol{\nu}(\boldsymbol{x}_j) = \mathcal{J}^1(\boldsymbol{x}_j) \cdot \boldsymbol{\nu}(\boldsymbol{x}_j) p_{N-1}(\tilde{\boldsymbol{x}}_j \,|\, \boldsymbol{x}_j)$$

$$\text{for } \boldsymbol{x}_j \in \partial\Omega, \quad \tilde{\boldsymbol{x}}_j \in \tilde{\Omega}_j$$

as the boundary condition for the joint pdf $p_N(\tilde{\boldsymbol{x}})$. This is the connection between the j-th component of the $3N$-dimensional flux, and the 3-dimensional singlet flux of the j-th ion on the boundary. It can also be written as

$$-k_B T \frac{\partial \log p_N(\tilde{\boldsymbol{x}})}{\partial \boldsymbol{\nu}(\boldsymbol{x}_i)} - \frac{\partial U(\tilde{\boldsymbol{x}})}{\partial \boldsymbol{\nu}(\boldsymbol{x}_i)} =$$

$$M\gamma \mathcal{J}^1(\boldsymbol{x}_i) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i) \frac{p_{N-1}(\tilde{\boldsymbol{x}}_i \,|\, \boldsymbol{x}_i)}{p_N(\tilde{\boldsymbol{x}})} =$$

$$M\gamma \frac{\mathcal{J}^1(\boldsymbol{x}_i) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i)}{p(\boldsymbol{x}_i)} \quad \text{for } \boldsymbol{x}_i \in \partial\Omega, \ \tilde{\boldsymbol{x}}_i \in \tilde{\Omega}_i.$$

Boundary conditions for lower dimensional densities of dependent di®users

Integration of the boundary condition over the domain with respect to any number of coordinates gives the boundary conditions

$$\boldsymbol{J}_i^h(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_k) \cdot \boldsymbol{\nu}_i(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_k) =$$

$$\mathcal{J}^{1,h}(\boldsymbol{x}_i) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i) p(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_k \,|\, \boldsymbol{x}_i)$$

for $\boldsymbol{x}_i \in \partial\Omega, \boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_k \in \Omega, \ (i > k).$

Boundary conditions for lower dimensional densities of dependent di®users (continued)

The boundary condition is equivalent to the boundary condition

$$
-k_B T \frac{\partial \log p_k^h(x_1, x_2, \ldots, x_k)}{\partial \nu_i(x_1, x_2, \ldots, x_k)}
$$

$$
+\bar{f}_i^h(x_1, x_2, \ldots, x_k) \cdot \nu_i(x_1, x_2, \ldots, x_k) =
$$

$$
M\gamma \frac{\mathcal{J}^{1,h}(x_i) \cdot \nu(x_i)}{p(x_i)},
$$

for $x_i \in \partial\Omega$, $x_1, x_2, \ldots, x_k \in \Omega$, $(i > k)$. The force $\bar{f}_i^h(x_1, x_2, \ldots, x_k)$ acts on the (i, h) ion at the boundary point x_i, given the coordinates of the first k ions, $(x_1, x_2, \ldots, x_k)$.

Boundary conditions for the pair density of dependent di®users

In particular,

$$\boldsymbol{J}_i^{h|h'}(\boldsymbol{x}_i \mid \boldsymbol{x}_j) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i) = \mathcal{J}^h(\boldsymbol{x}_i) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i) p^{h'|h}(\boldsymbol{x}_j \mid \boldsymbol{x}_i)$$

for $\boldsymbol{x}_i \in \partial\Omega, \ \boldsymbol{x}_j \in \Omega,$

or equivalently,

$$-k_B T \frac{\partial}{\partial \boldsymbol{\nu}(\boldsymbol{x}_i)} \log p^{h,h'}(\boldsymbol{x}_i, \boldsymbol{x}_j)$$

$$+\bar{\boldsymbol{f}}_i^{h|h'}(\boldsymbol{x}_i, \boldsymbol{x}_j) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i)$$

$$= M^h \gamma^h \mathcal{J}^h(\boldsymbol{x}_i) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i) \frac{p^{h'|h}(\boldsymbol{x}_j \mid \boldsymbol{x}_i)}{p^{h,h'}(\boldsymbol{x}_i, \boldsymbol{x}_j)}$$

$$= M^h \gamma^h \frac{\mathcal{J}^h(\boldsymbol{x}_i) \cdot \boldsymbol{\nu}(\boldsymbol{x}_i)}{p^h(\boldsymbol{x}_i)} \quad \text{for } \boldsymbol{x}_i \in \partial\Omega, \ \boldsymbol{x}_j \in \Omega.$$

Interpretation

In the general case the single ion flux $\mathcal{J}^h(\boldsymbol{x})$ is not known on the boundary, due to the unknown forces $\bar{\boldsymbol{f}}_i(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_k)$, for all combinations of species. Thus the boundary conditions couple the equation and boundary conditions for $p^{h,h'}(\boldsymbol{x}, \boldsymbol{y})$ to those of $p^h(\boldsymbol{x})$, and the same is true for all $p^{h_1, \ldots, h_k}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_k)$ of all combinations of species. The probability flux density components $\boldsymbol{J}^{h|h'}(\boldsymbol{x} \,|\, \boldsymbol{y}) \cdot \boldsymbol{\nu}(\boldsymbol{x})$ for $\boldsymbol{x} \in \partial\Omega$, $\boldsymbol{y} \in \Omega$, of the six-dimensional flux of $p^{h,h'}(\boldsymbol{x}, \boldsymbol{y})$ are the three-dimensional "normal components" of the boundary flux.

The case of $p^h(x) = 0$

If $p^h(x) = 0$ for $x \in \partial\Omega$, the boundary condition for $p^{h,h'}(x,y)$ at $x \in \partial\Omega$, $y \in \Omega$ is

$$p^{h,h'}(x,y) = 0 \quad \text{for } x \in \partial\Omega, \ y \in \Omega.$$

because

$$p^{h,h'}(x,y) \leq p^h(x) \quad \text{for all } x, y \in \Omega.$$

With these boundary conditions, the FPSEs for all $p^h(x)$ and $p^{h,h'}(x,y)$ are coupled through the single ion fluxes $\mathcal{J}^h(x)$ and the forces. The concentration and flux boundary conditions determine the single ion density and the joint pdfs, provided the forces are known. However, the forces are unknown (see analysis below).

The connection to the correlation functions of statistical mechanics

The average concentration of the h-species in the bath is defined as

$$\rho^h = \frac{1}{|\Omega|} \int_\Omega c^h(\boldsymbol{x}) \, d\boldsymbol{x},$$

where $|\Omega|$ is the volume of Ω. Thus

$$c^h(\boldsymbol{x}) = N^h p^h(\boldsymbol{x}) = \rho^h g^h(\boldsymbol{x}).$$

The function $g^h(\boldsymbol{x})$ is the non-equilibrium generalization of the singlet correlation function of equilibrium statistical physics. It is related to $p^h(\boldsymbol{x})$ by

$$g^h(\boldsymbol{x}) = |\Omega| p^h(\boldsymbol{x}).$$

Thus

$$\int_\Omega p^h(\boldsymbol{x}) \, d\boldsymbol{x} = 1, \quad \int_\Omega g^h(\boldsymbol{x}) \, d\boldsymbol{x} = |\Omega|,$$

$$\int_\Omega c^h(\boldsymbol{x}) \, d\boldsymbol{x} = N^h.$$

The connection to the correlation functions of statistical mechanics (continued)

Similarly, we define another non-dimensional function,

$$c^{h,h'}(\boldsymbol{x}, \boldsymbol{y}) = c^h(\boldsymbol{x})c^{h'}(\boldsymbol{y})g^{h,h'}(\boldsymbol{x}, \boldsymbol{y}).$$

The function $g^{h,h'}(\boldsymbol{x}, \boldsymbol{y})$ is the non-equilibrium generalization of the equilibrium pair correlation function. We have the relations

$$c^{h,h'}(\boldsymbol{x}, \boldsymbol{y}) = N^h N^{h'} p^{h,h'}(\boldsymbol{x}, \boldsymbol{y}),$$

$$g^{h,h'}(\boldsymbol{x}, \boldsymbol{y}) = \frac{p^{h,h'}(\boldsymbol{x}, \boldsymbol{y})}{p^h(\boldsymbol{x})p^{h'}(\boldsymbol{y})}.$$

The forces

We assume that the forces acting on a ion in the bath are an external force $\boldsymbol{E}(\boldsymbol{x})$, due to an external field (e.g., a gravitational force or hydrodynamical drag), electrostatic interaction force, and a Lennard-Jones force, due to the presence of all other ions in the bath. The former is independent of the configuration of the ions, and depends on the location of the ion in the bath. The interaction force depends on the configuration of all bath ions.

The Lennard-Jones interactions

Denote
- $LJ^h(x) =$LJ force on an h-ion at x
- $LJ^{h,h'}(|y-x|) =$LJ force between h and h' ions, located at x and y, respectively.

Its direction is along $x-y$. This implies that

$$\int_\Omega LJ^{h,h'}(|y-x|)\,dy = 0$$

for x sufficiently far from the boundary. The total LJ force on an h ion at x is the average

$$\overline{LJ}^h(x) = \sum_{h'} \int_\Omega LJ^{h,h'}(|y-x|)N^{h'}p^{h'|h}(y\mid x)\,dy.$$

This is the LJ component of the hereto unknown force in the FPSE.

Di®usion of LJ ions

In the absence of all forces other than LJ, the conditional density $p^{h'|h}(y \mid x)$ is a function of the distance $|y - x|$ and the integral vanishes, due to radial symmetry. The total LJ force on an h ion at x, given an h' ion at y, is

$$\overline{LJ}^{h|h'}(x \mid y) = LJ^{h,h'}(|y - x|) +$$

$$\sum_{h''} \int_{\Omega} LJ^{h,h''}(|x - z|) N^{h''} p^{h''|h',h}(z \mid x, y)\, dz.$$

In this case $\bar{f}_x^{h|h'}(x \mid y) = \overline{LJ}^{h|h'}(x \mid y)$. Similarly,

$$\overline{LJ}^{h''|h',h}(z \mid xy) =$$

$$LJ^{h'',h'}(|z - y|) + LJ^{h'',h}(|z - x|) +$$

$$\sum_{h'''} \int LJ^{h''',h''}(|w - z|) \times$$

$$N^{h'''} p^{h'''|h'',h',h}(w \mid z, y, x)\, dw,$$

and so on.

All equations are coupled

The FPSE for the singlet density $p^h(x)$, is coupled to that for the pair density $p^{h,h'}(x, y)$, through the force term $\bar{f}^h(x)$ and the relation of the boundary conditions. Similarly, the FPSE for the pair density is coupled to all higher order correlation functions through the force terms. A **closure relation** is needed.

The electrostatic forces

Set
- $\rho_{perm}(\boldsymbol{x}) =$ permanent charge density
- $z^h =$ valence of h ions.
- $\phi(\boldsymbol{x}) =$ electrostatic potential
- $\boldsymbol{f}_i^h =$ electrostatic force the (i, h) ion at $\boldsymbol{x}_i^h$

The potential is the solution of Poisson's equation

$$\nabla \cdot \varepsilon(\boldsymbol{x}) \nabla \phi(\boldsymbol{x}) =$$

$$-\frac{1}{\varepsilon_0} \left[\rho_{perm}(\boldsymbol{x}) + \sum_h \sum_{j=1}^{N^h} z^h \delta(\boldsymbol{x} - \boldsymbol{x}_j^h) \right],$$

with boundary conditions at electrodes and the standard continuity conditions at dielectric interfaces. The force is given by

$$\boldsymbol{f}_i^h = -ez^h \nabla_{\boldsymbol{x}} \left(\phi(\boldsymbol{x}) - \frac{1}{4\pi\varepsilon_0 \varepsilon(\boldsymbol{x}_i^h)} \frac{1}{|\boldsymbol{x} - \boldsymbol{x}_i^h|} \right) \Bigg|_{\boldsymbol{x} = \boldsymbol{x}_i^h}.$$

The last term on the right hand side removes the singularity of the potential $\phi(\boldsymbol{x})$ at the location of the ion.

The composition of $f_i^h(\tilde{x})$

We decomposed the force into

$$f_i^h(\tilde{x}) = f_i^h(\tilde{x}, P) + f_D^h(x_i^h),$$

where
- $f_i^h(\tilde{x}, P)$ =the force exerted by all other ions in the solution, the permanent charge, the charges on the electrodes that maintain a fixed applied voltage, and the surface charges induced by these ions
- $f_D^h(x_i^h)$ =a self induced force produced by the surface charges induced at the dielectric interfaces by the ion at x_i^h.

If there are no dielectric interfaces, this induced force is zero. Note that this force component is proportional to the **square** of the ion's charge, regardless of its sign. For example, it is equal for monovalent anions and cations alike.

Calculation of the components

$$\boldsymbol{f}_i^h(\tilde{\boldsymbol{x}}, P) = -z^h e \nabla_{\boldsymbol{x}} \, \phi_i^h(\boldsymbol{x}, \tilde{\boldsymbol{x}}_i^h)|_{\boldsymbol{x}=\boldsymbol{x}_i^h},$$

where

$$\nabla_{\boldsymbol{x}} \cdot \varepsilon(\boldsymbol{x}) \nabla_{\boldsymbol{x}} \phi_i^h(\boldsymbol{x}, \tilde{\boldsymbol{x}}_i^h) =$$

$$-\frac{e}{\varepsilon_0}[\rho_{perm}(\boldsymbol{x}) + z^h \sum_{(j,h')\neq(i,h)} \delta\left(\boldsymbol{x} - \boldsymbol{x}_j^{h'}\right)],$$

(same BCs, the (i, h) ion is removed).

$$\boldsymbol{f}_D^h\left(\boldsymbol{x}_i^h\right) = -z^h e \times$$

$$\nabla_{\boldsymbol{x}} \left(\phi_D(\boldsymbol{x}, \boldsymbol{x}_i^h) - \frac{1}{4\pi\varepsilon(\boldsymbol{x}_i^h)\varepsilon_0} \frac{e}{|\boldsymbol{x} - \boldsymbol{x}_i^h|} \right) \Bigg|_{\boldsymbol{x}=\boldsymbol{x}_i^h},$$

where

$$\nabla_{\boldsymbol{x}} \cdot \varepsilon(\boldsymbol{x}) \nabla_{\boldsymbol{x}} \phi_D(\boldsymbol{x}, \boldsymbol{y}) = -\frac{e}{\varepsilon_0} \delta(\boldsymbol{x} - \boldsymbol{y}),$$

with homogeneous BCs at the electrodes.

The averaged forces 1

The averaged forces $\bar{\boldsymbol{f}}^h(\boldsymbol{x})$ and $\bar{\boldsymbol{f}}_{\boldsymbol{x}}^{h|h'}(\boldsymbol{x}\,|\,\boldsymbol{y})$ consist of LJ forces, as described above, and electrostatic forces. The electrostatic component of the force $\bar{\boldsymbol{f}}^h(\boldsymbol{x})$, denoted $\bar{\boldsymbol{f}}_E^h(\boldsymbol{x})$, is given by

$$\bar{\boldsymbol{f}}_E^h(\boldsymbol{x}) = -z^h e \nabla_{\boldsymbol{y}} \bar{\phi}^h(\boldsymbol{y}\,|\,\boldsymbol{x})|_{\boldsymbol{y}=\boldsymbol{x}} + \boldsymbol{f}_D^h(\boldsymbol{x})$$

with averaged mean field potentials $\bar{\phi}^h(\boldsymbol{z}\,|\,\boldsymbol{x})$ that satisfy the Poisson equations

$$\nabla_{\boldsymbol{y}} \cdot \left[\varepsilon(\boldsymbol{y}) \nabla_{\boldsymbol{y}} \bar{\phi}^h(\boldsymbol{y}\,|\,\boldsymbol{x}) \right] =$$

$$-\frac{e}{\varepsilon_0} \left[\rho_{perm}(\boldsymbol{y}) + \sum_{h'} z^{h'} e c^{h'|h}(\boldsymbol{y}\,|\,\boldsymbol{x}) \right],$$

with the applied voltage conditions on the electrodes. The Poisson equation for the averaged potential is obtained by averaging the Poisson equation with the point charges.

The averaged forces 2

The electrostatic force acting on an h ion at x, given an h' ion at y, can be written as

$$\boldsymbol{f}_{\boldsymbol{x}}^{h|h'}(\boldsymbol{x} \,|\, \boldsymbol{y}) = f_D^h(\boldsymbol{x}) - z^h e \nabla \boldsymbol{x} \phi_{perm}(\boldsymbol{x})$$

$$-z^h e \nabla \boldsymbol{x} \bar{\phi}^{h'}(\boldsymbol{x} \,|\, \boldsymbol{y}) - z^h e \nabla \boldsymbol{z} \bar{\phi}^{h,h'}(\boldsymbol{z} \,|\, \boldsymbol{x}, \boldsymbol{y}) \,|_{\boldsymbol{z}=\boldsymbol{x}} \,,$$

where
- $f_D^h(\boldsymbol{x}) =$ is the self force
- $\phi_{perm}(\boldsymbol{x}) =$ potential of permanent charge and applied voltage
- $\bar{\phi}^{h'}(\boldsymbol{x} \,|\, \boldsymbol{y}) =$ potential at x of all other ions, given a point charge $z^{h'} e$ at y (0 BCs).
- $\bar{\phi}^{h,h'}(\boldsymbol{z} \,|\, \boldsymbol{x}, \boldsymbol{y}) =$ potential at z of all other ions, given an h ion at x and an h' ion at y (0 BCs). It satisfies

$$\nabla \boldsymbol{z} \cdot \varepsilon(\boldsymbol{z}) \nabla \boldsymbol{z} \phi^{h,h'}(\boldsymbol{z} \,|\, \boldsymbol{x}, \boldsymbol{y}) =$$

$$-\frac{e}{\varepsilon_0} \left[\rho_{perm}(\boldsymbol{z}) + \sum_{h''} z^{h''} e c^{h,h'}(\boldsymbol{z} \,|\, \boldsymbol{x}, \boldsymbol{y})) \right],$$

and so on.

Closure relations

A closure relation, that expresses a higher order correlation function in terms of lower order correlation functions renders the FPSEs finitely solvable. A closure at level 2 is a relationship of type

$$p(x, y) = \mathcal{F}\left[p(x), p(y)\right],$$

where $\mathcal{F}$ is an operator, renders the first FPSE solvable. However, such a closure does not recover the results of equilibrium theory for the pair function. A closure relations at level 3 is

$$p\left(x, y, z,\right) =$$
$$\mathcal{F}\left[p(x, z), p(y, z), p(x, y), p\left(x\right), p\left(y\right), p\left(z\right)\right].$$

Closure relations (continued)

The simple multiplicative closure relation

$$p(x, y, z) = \frac{p(x, y)p(x, z)p(z, y)}{p(x)p(y)p(z)}$$

is also known to be insufficient, but a multiplicative closure at level 4 gives satisfactory results in equilibrium. Multiplicative closure relations have probabilistic interpretation and sufficient conditions can be found for their validity. This analysis will be done elsewhere.

An iterative scheme for solving any closure relation, together with the boundary value problem for the FPSEs, where the fluxes are given as above, begins with a guess, $p_{(0)}^{h,h'}(x, y)$, for the pair correlation function $p^{h,h'}(x, y)$. This defines the direct correlation force by a numerical inversion scheme, the mean force $\bar{f}_x^{h,h'}(x, y)$, and the flux in the FPSE. Now, the boundary value problem for the level 2 FPSE defines the next iteration, $p_{(1)}^{h,h'}(x, y)$, and so on, until the scheme converges.

The PNP system revisited

The approximation $c_{i|j}(\boldsymbol{y}|\boldsymbol{x}) = c_i(\boldsymbol{y})$ closes the system.

Result: Closed PNP system with unconditional variables, with additional dielectric self force term

$$-e\nabla_{\boldsymbol{y}} \cdot \left(\phi_{ch}(\boldsymbol{x}) - \frac{e}{4\pi\varepsilon\varepsilon_0|\boldsymbol{y} - \boldsymbol{x}|}\right)\bigg|_{\boldsymbol{y}=\boldsymbol{x}}$$

This term is present only near dielectric interfaces. Without this term, the standard PNP system is recovered.

Conclusion: This approximation neglects all finite size effects and discrete charge effects. Therefore PNP is not valid in narrow channels or near dielectric interfaces.

Summary

Main Results: 1. Derivation of continuum equations for ion transport, from molecular model. The result is a conditional PNP Hierarchy, which contains finite size & ion-ion electrostatic effects.

Conclusion: Standard PNP is valid only in bulk. Not valid in confined geometries or near interfaces.

2. C-PNP Hierarchy is the non-equilibrium generalization of the well known BBGKY Hierarchy of equilibrium statistical physics.

With the C-PNP equations and a closure relation, we can study the microscopic structure of non-equilibrium systems.
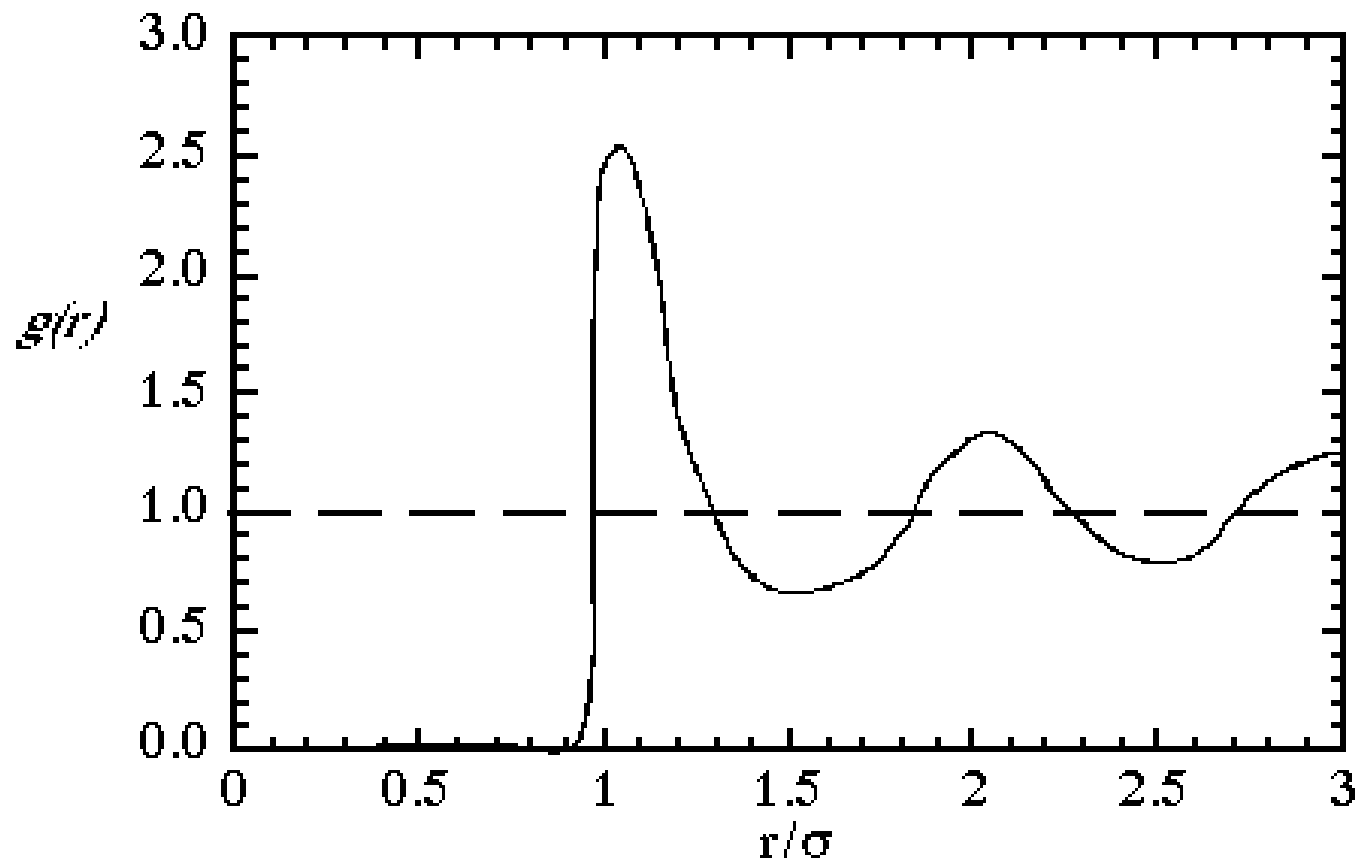
Shape of Pair Correlation Function

Illustration 3. Qualitative behavior of the radial distribution function in the liquid state.

Open Mathematical Problems & Further Research

Needed:

- Derivation of non-equilibrium closure relations

- Derivation of boundary conditions for conditional and higher order densities.

- Criteria for a good closure / Error Analysis for a given closure ?

Open Problems:

- Computational Problems.
- Connection of small simulations to surrounding continuum.
- Non-Equilibrium simulations with flux ??