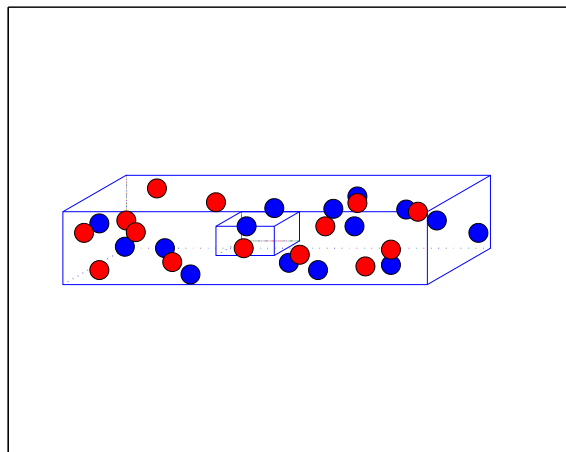


**STATISTICAL MECHANICS
PROBLEMS IN CHANNOLOGY:
A REVIEW**

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Macroscopic Transport Equations

Consider ionic transport in aqueous solution.



Macroscopic Treatment:

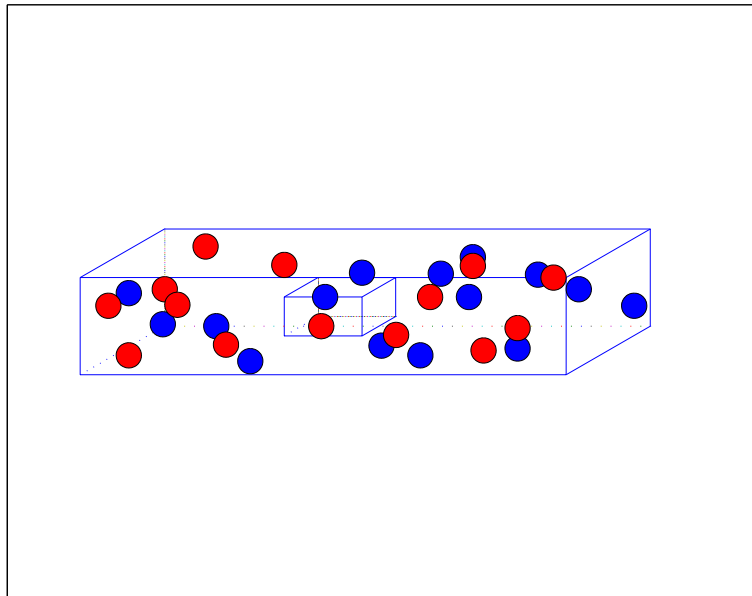
$c_j(\mathbf{x})$ - concentration at \mathbf{x} of species j

$\psi(\mathbf{x})$ - potential of mean field

From macroscopic thermodynamical arguments, the flux J_p of species p is:

$$\mathbf{J}_p(\mathbf{x}) = -D_p \left(\nabla c_p(\mathbf{x}) + c_p(\mathbf{x}) \frac{ez_p}{kT} \nabla \psi(\mathbf{x}) \right)$$

The Nernst-Planck Equation



Conservation laws of mass & momentum:

$$\begin{aligned} 0 &= -\nabla \cdot \mathbf{J}_p(\mathbf{x}) \\ &= \Delta c_p(\mathbf{x}) + \nabla \cdot \left(c_p(\mathbf{x}) \frac{ez_p}{kT} \nabla \psi(\mathbf{x}) \right) \end{aligned}$$

Nernst-Planck / Drift-diffusion equation

The Poisson-Nernst-Planck System

Example: Simple bi-ionic solution (Na^+, Cl^-).

Macroscopic variables are:

$c_p(\mathbf{x}), c_n(\mathbf{x})$ - positive & negative concentrations

$\psi(\mathbf{x})$ - potential of mean field.

Nernst-Planck equations:

$$0 = -\nabla \cdot \mathbf{J}_p(\mathbf{x}) = \Delta c_p(\mathbf{x}) + \nabla \cdot \left(c_p(\mathbf{x}) \frac{e}{kT} \nabla \psi(\mathbf{x}) \right)$$

$$0 = -\nabla \cdot \mathbf{J}_n(\mathbf{x}) = \Delta c_n(\mathbf{x}) - \nabla \cdot \left(c_n(\mathbf{x}) \frac{e}{kT} \nabla \psi(\mathbf{x}) \right)$$

Poisson Equation for potential ψ :

$$\nabla \varepsilon \cdot \nabla \psi(\mathbf{x}) = - \left[c_p(\mathbf{x}) - c_n(\mathbf{x}) + \rho_{\text{fixed}}(\mathbf{x}) \right]$$

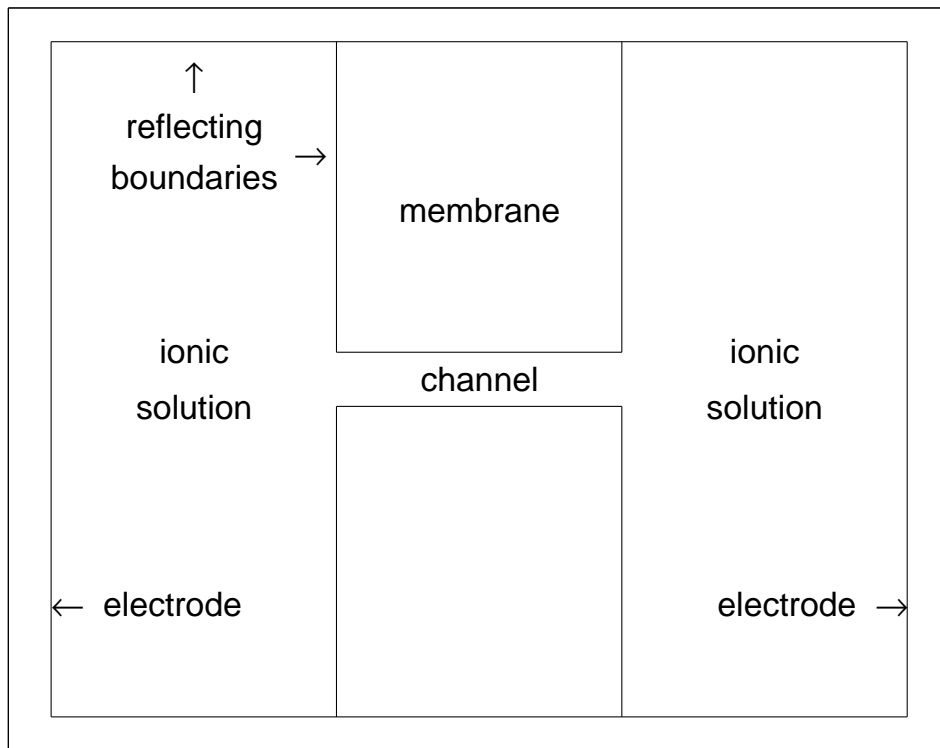
All three equations are non-linearly coupled.

Applications of PNP system

- Semiconductor Device Modeling, electron & hole transport (1950's).
- Transport in Ionic Solution (1900's).
- Ionic Transport through narrow protein channels (1990's).
- Various other transport processes.

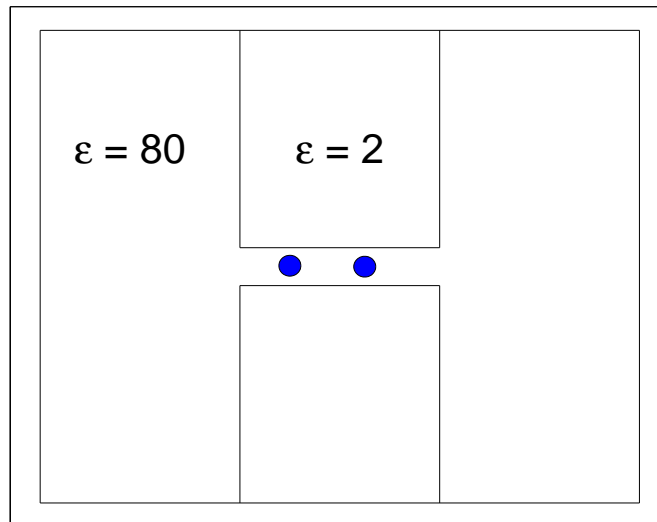
Ionic Transport Through Narrow Channels

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



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

Ionic Transport Through Narrow Channels



- *Single filing phenomena* are due to ion-ion interactions in a narrow channel.
- *Selectivity* - is it related to the finite size of ions?
- *Non-linear phenomena in mixtures and unidirectional currents*, are they due to the finite size of ions?

What is missing PNP?

- There is no derivation from a microscopic model
- There are no finite size ions
- The self energy of an ion near a dielectric interface is ignored
- Water is replaced with dielectric and diffusion coefficients
- There is no difference between ingoing and outgoing fluxes (no unidirectional fluxes)

The PNP hierarchy

- A PNP hierarchy of PDEs was derived by Ebeling *et al.* (see Barthel's book) for the singlet, pair, and higher order densities.
- The point of departure was a $6N$ -dimensional FPE, coupled to Poisson's equations for the electrostatic field, Lennard-Jones forces, and other forces
- The LJ forces account for the finite size of ions. Concentration boundary conditions are imposed on the singlet density.
- The hierarchy is truncated by an extension of the OZE.

What is missing in the PNP hierarchy?

- The hierarchy has to be decoupled at some level, to become finite. This is the *closure problem*, which was partially solved for equilibrium.
- No boundary conditions are known for the pair correlation function and for higher order densities.
- The self energy of an ion near a dielectric interface is still ignored
- Water is still dielectric and diffusion coefficients

What can be resolved with ESM?

Microscopic structure of systems in equilibrium can be described with ESM follows:

Postulate Boltzmann probabilities for configurations:

$$p(\mathbf{r}_1, \dots, \mathbf{r}_N) = \text{Const} \times \exp \left\{ -\frac{U(\mathbf{r}_1, \dots, \mathbf{r}_N)}{k_B T} \right\},$$

where the **energy** of the configuration is

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

In the absence of an external field and in free space, the equilibrium concentration $\rho(\mathbf{x})$ satisfies the BGY equation

$$k_B T \nabla \rho(\mathbf{x}) + \int \rho(\mathbf{y} | \mathbf{x}) \nabla_{\mathbf{x}} U_{1,2}(\mathbf{x} - \mathbf{y}) d\mathbf{y} = 0$$

(by integration).

The BGY equation as a conservation law

The BGY equation can be written as the conservation law

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

with the “boundary condition”

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

In a finite volume Ω the boundary condition

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

defines equilibrium. Once a closure relation (MSA, PY, HNC) is adopted, the pair correlation function (pcf),

$$g(\mathbf{x}, \mathbf{y}) = \frac{\rho(\mathbf{y} | \mathbf{x})}{\rho(\mathbf{y})},$$

can be calculated. It expresses the finite volume of the diffusing particles.

Shape of Pair Correlation Function

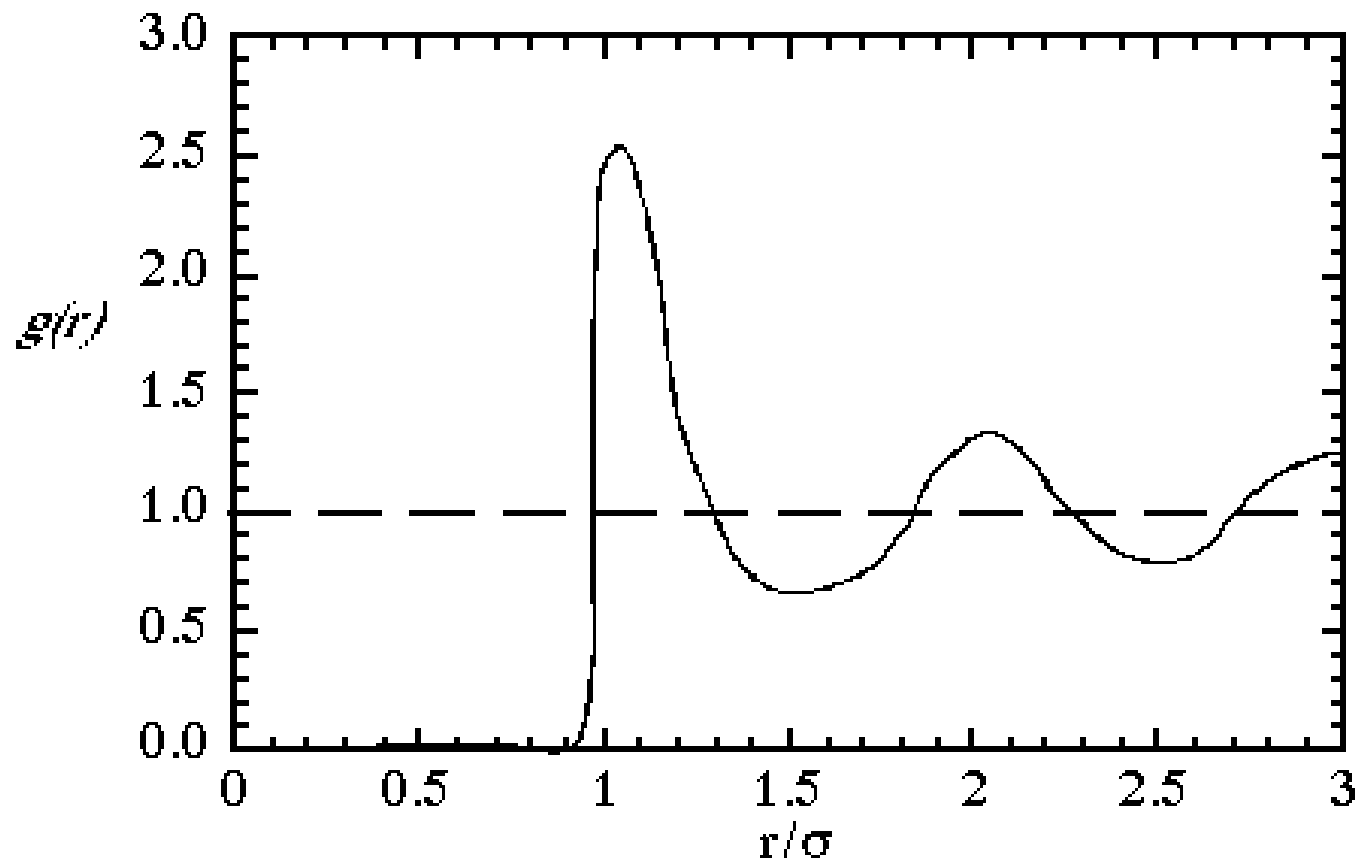


Illustration 3. Qualitative behavior of the radial distribution function in the liquid state.

Non-vanishing flux means non-equilibrium

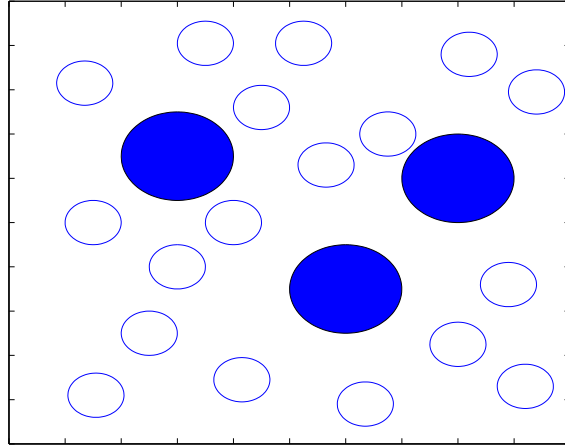
1. A concentration gradient drives the system out of equilibrium.
2. The non-equilibrium pcf is needed for the description of interacting particles diffusing in a finite volume.
3. This description is essential for the description of diffusion of interacting particles in a narrow channel.
4. Diffusion of interacting particles in a finite system, with given boundary conditions, has to be described by a computable set of equations.
for non-equilibrium statistical mechanics in chan-nology.

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.

Dynamics of trajectories



Model: $3N$ memoryless coupled Langevin equations for $h = Ca^{++}, Na^+, Cl^-, \dots$,

$$\ddot{\mathbf{x}}_j^h + \gamma^h(\mathbf{x}_j^h) \dot{\mathbf{x}}_j^h = \frac{\mathbf{f}_j^h(\tilde{\mathbf{x}})}{M^h} + \sqrt{\frac{2\gamma^h(\mathbf{x}_j^h) k_B T}{M^h}} \dot{\mathbf{w}}_j^h,$$

for $j = 1, 2, \dots, N$, where

- $\gamma^h(\mathbf{x}^h)$ = friction coefficient per unit mass
- M^h = effective mass of an ion of species h
- $\mathbf{f}_j^h(\tilde{\mathbf{x}})$ = force on the j -th ion of species h
- $\dot{\mathbf{w}}_j^h$ = i.i.d. standard Gaussian white noises
- $k_B T$ = Thermal energy.

Densities, fluxes, and pdfs

- $c^h(\mathbf{x})$ = time-averaged steady state density of h -ions at \mathbf{x} ,

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

- $p_j^h(\mathbf{x}) = p^h(\mathbf{x})$, $j = 1, \dots, N^h$ = stationary pdf of the j -th h -ion, because all h -ions are indistinguishable,

$$c^h(\mathbf{x}) = N^h p^h(\mathbf{x}).$$

- $p^{h',h''}(\mathbf{y}, \mathbf{z})$ = the joint pdf of h' and h'' -ions.
- $\mathbf{J}^h(\mathbf{x})$ = total flux density of h -ions at \mathbf{x}
- $\mathcal{J}^h(\mathbf{x})$ = flux density of a single h -ion,

$$\mathbf{J}^h(\mathbf{x}) = N^h \mathcal{J}^h(\mathbf{x}).$$

Problem: Find equations for $p^h(\mathbf{x})$, $p^{h',h''}(\mathbf{y}, \mathbf{z})$.

The joint FPE

The stationary pdf of all ions, $p_N(\tilde{\mathbf{x}}, \tilde{\mathbf{v}})$, satisfies the FPE

$$0 = \sum_h \sum_j^{N^h} \mathcal{L}_j^h p_N,$$

where

$$\begin{aligned} \mathcal{L}_j^h = & -\mathbf{v}_j^h \cdot \nabla_{\mathbf{x}_j^h} + \nabla_{\mathbf{v}_j^h} \cdot \left(\gamma^h(\mathbf{x}_j^h) \mathbf{v}_j^h - \frac{\mathbf{f}_j^h(\tilde{\mathbf{x}})}{M^h} \right) \\ & + \frac{\gamma^h(\mathbf{x}_j^h) k_B T}{M^h} \Delta_{\mathbf{v}_j^h}. \end{aligned}$$

The FPE is defined in the region $\tilde{\mathbf{x}} \in \tilde{\Omega}$ and $\tilde{\mathbf{v}} \in \mathbf{R}^{3N}$ in the $6N$ -dimensional phase space.

The FPE as a conservation law

Set

$$\mathbf{J}_{\tilde{\mathbf{v}}^h} = (\mathbf{J}_{\mathbf{v}_1^h}, \dots, \mathbf{J}_{\mathbf{v}_{N^h}^h}), \quad \mathbf{J}_{\tilde{\mathbf{x}}^h} = (\mathbf{J}_{\mathbf{x}_1^h}, \dots, \mathbf{J}_{\mathbf{x}_{N^h}^h}).$$

These are N^h -dimensional flux density vectors in phase space. Their components are the 3D flux densities

$$\begin{aligned} \mathbf{J}_{\mathbf{v}_m^h} = & - \left(\gamma^h(\mathbf{x}_m^h) \mathbf{v}_m^h - \frac{\mathbf{f}_m^h(\tilde{\mathbf{x}})}{M^h} \right) p_N(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}) - \\ & \nabla_{\mathbf{v}_m^h} \frac{\gamma^h(\mathbf{x}_m^h) k_B T}{M^h} p_N(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}), \end{aligned}$$

$$\mathbf{J}_{\mathbf{x}_m^h} = \mathbf{v}_m^h p_N(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}), \quad m = 1, \dots, N^h, \quad \forall h.$$

The FPE can be written as the **flux conservation law**

$$\begin{aligned} 0 &= - \sum_h \left(\nabla_{\tilde{\mathbf{v}}^h}, \nabla_{\tilde{\mathbf{x}}^h} \right) \cdot (\mathbf{J}_{\tilde{\mathbf{v}}^h}, \mathbf{J}_{\tilde{\mathbf{x}}^h}), \\ &= - \sum_h \sum_{j=1}^{N^h} \left(\nabla_{\mathbf{v}_j^h} \cdot \mathbf{J}_{\mathbf{v}_j^h} + \nabla_{\mathbf{x}_j^h} \cdot \mathbf{J}_{\mathbf{x}_j^h} \right). \end{aligned}$$

Boundary conditions

$$\partial\Omega = \partial\Omega_F \cup \partial\Omega_R,$$

- $\partial\Omega_F$ = feedback boundary
- $\partial\Omega_R$ = impermeable (reflecting) boundary

$$\begin{aligned} & \mathbf{J}_{\mathbf{x}_j^h}(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}) \cdot \boldsymbol{\nu}(\mathbf{x}_j^h) \Big|_{\mathbf{x}_j^h \in \partial\Omega_R}, \mathbf{v}_j^h \cdot \boldsymbol{\nu}(\mathbf{x}_j^h) = v = \\ & -\mathbf{J}_{\mathbf{x}_j^h}(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}) \cdot \boldsymbol{\nu}(\mathbf{x}_j^h) \Big|_{\mathbf{x}_j^h \in \partial\Omega_R}, \mathbf{v}_j^h \cdot \boldsymbol{\nu}(\mathbf{x}_j^h) = -v, \end{aligned}$$

On $\partial\Omega_F$, outgoing trajectories are absorbed by the feedback mechanism, and re-injected as incoming trajectories either at the same boundary or at the opposite one.

The problem of boundary conditions: How is the boundary behavior of trajectories expressed as a boundary condition for the joint pdf?

Concentration BCs can be imposed for the singlet density.

The marginal pdfs

The phase space marginals of $p_N(\tilde{\mathbf{x}}, \tilde{\mathbf{v}})$ are

$$p^h(\mathbf{x}_i^h, \mathbf{v}_i^h) = \int_{\tilde{\Omega}_i^h} \times \mathbf{R}^{3N-3} \int p_N(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}) d\tilde{\mathbf{x}}_i^h d\tilde{\mathbf{v}}_i^h$$

$$p^{h,h'}(\mathbf{x}_i^h, \mathbf{v}_i^h, \mathbf{x}_j^{h'}, \mathbf{v}_j^{h'}) =$$

$$\int_{\tilde{\Omega}_{i,j}^{h,h'}} \times \mathbf{R}^{3N-6} \int p_N(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}) d\tilde{\mathbf{x}}_{i,j}^{h,h'} d\tilde{\mathbf{v}}_{i,j}^{h,h'},$$

The configuration space marginal is

$$p^h(\mathbf{x}) = \int_{\mathbf{R}^3} p^h(\mathbf{x}, \mathbf{v}) d\mathbf{v}.$$

The configuratioinal pcf of h and h' ions is

$$p^{h,h'}(\mathbf{x}, \mathbf{y}) =$$

$$\int_{\mathbf{R}^6} \int p^{h,h'}(\mathbf{x}, \mathbf{v}, \mathbf{y}, \mathbf{v}') d\mathbf{v} d\mathbf{v}'.$$

The pair concentration is

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

The connection to the pdf of ESM

Define

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

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

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

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

Other mathematical channel problems

- Derive a PDE description of ions in a narrow channel from a microscopic model
- Derive closure conditions for the PNP hierarchy
- Develop a mathematical theory of small BD and MD simulations: connect channel to continuum, terminate continuum at real or fictitious boundaries.