Tutorial: Correlation as Stochasticity

IPAM: Electrochemistry and Stochasticity

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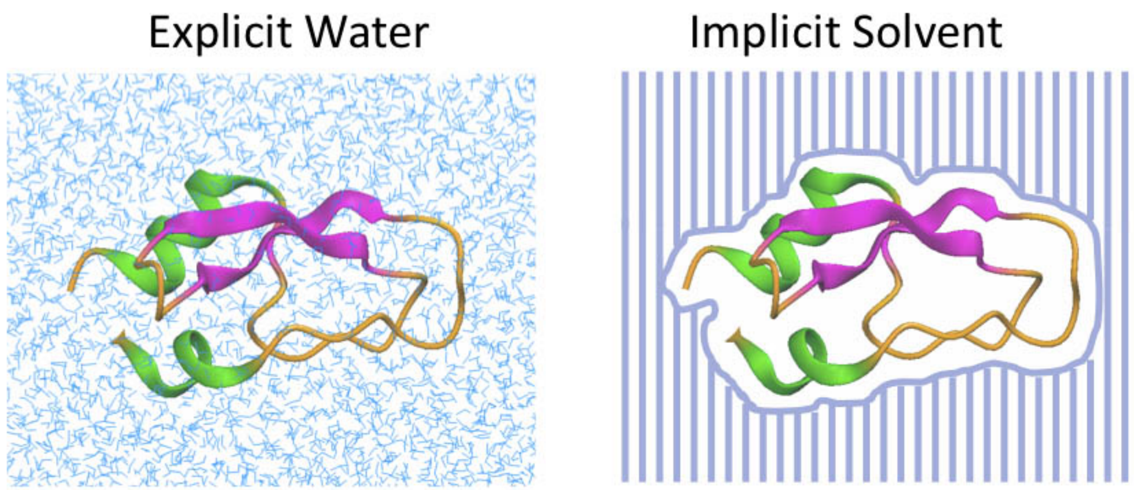
Overview

Electrochemistry: application of voltage to juice rare events.

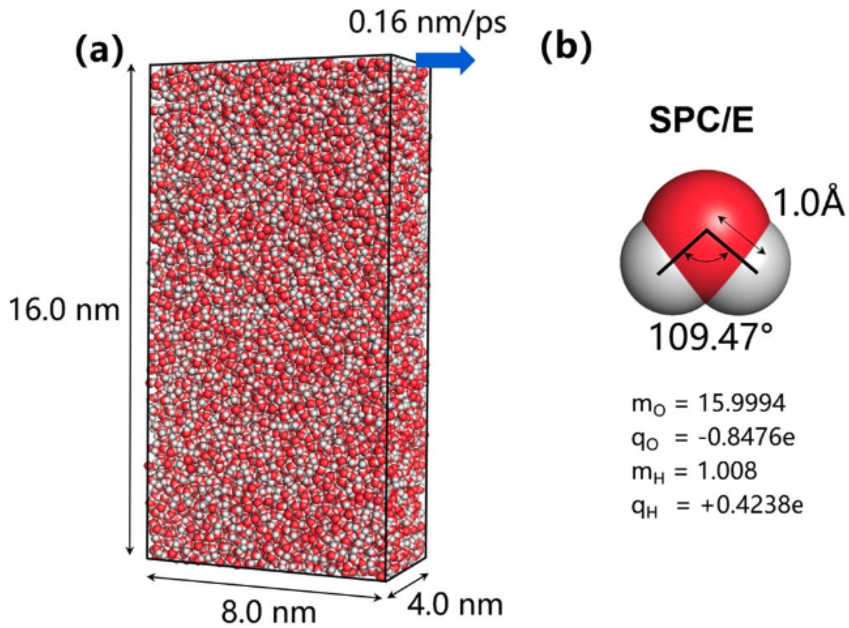
Connect continuum models (implicit water) of electrolyte solutions subject to applied voltage to molecular models that resolve (some) electronic structure through DFT approximations.



Must represent the fluctuations about the mean field that defines the continuum representation.

Requires an understanding of the mechanisms that cause the fluctuations – One sources is **Multiparticle Correlation**. And need a structure inside of which to place the fluctuations.

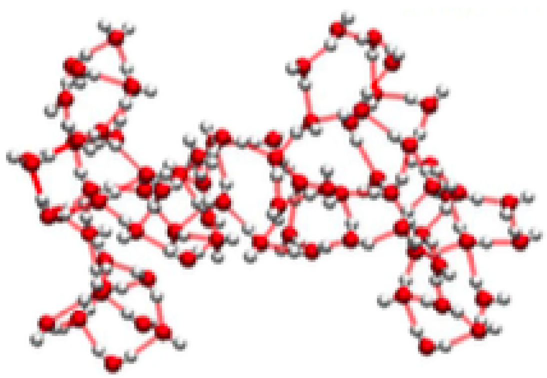
Water forms Networks



Highly polar solvent with tetrahedral shape

Strong dipole moment

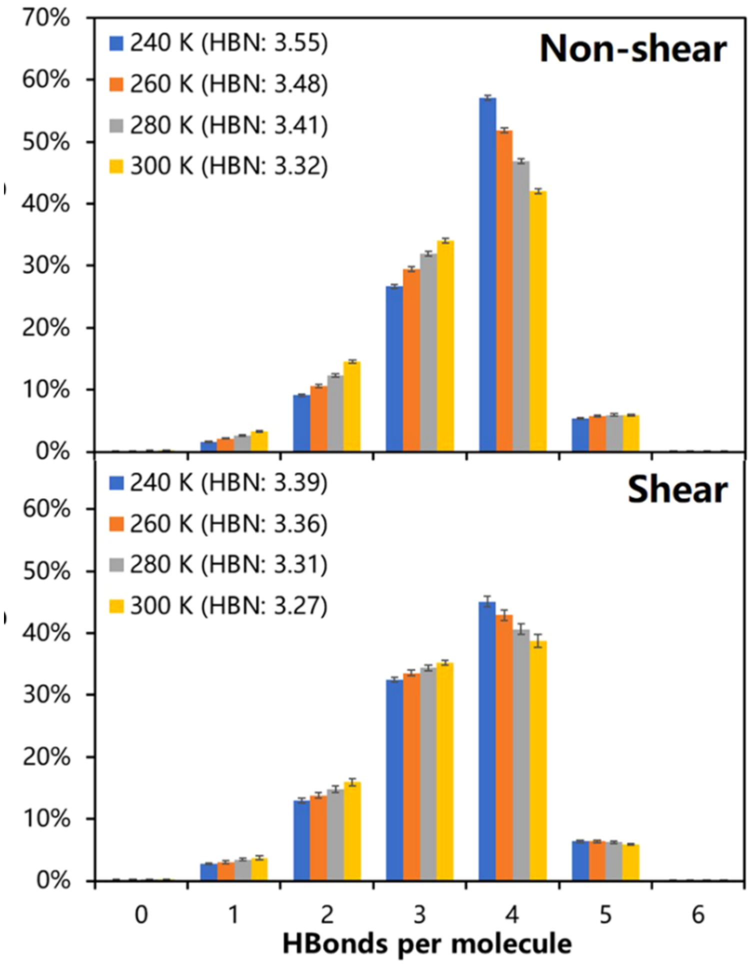
NB: 0.16nm/ps = 357 mph



Forms random networks of hydrogen bonds. Data is from molecular dynamics using distance/angle metrics to infer hydrogen bonding.

Goa, Fang, Ni, Scientific Reports 2021

Water is Exceptional



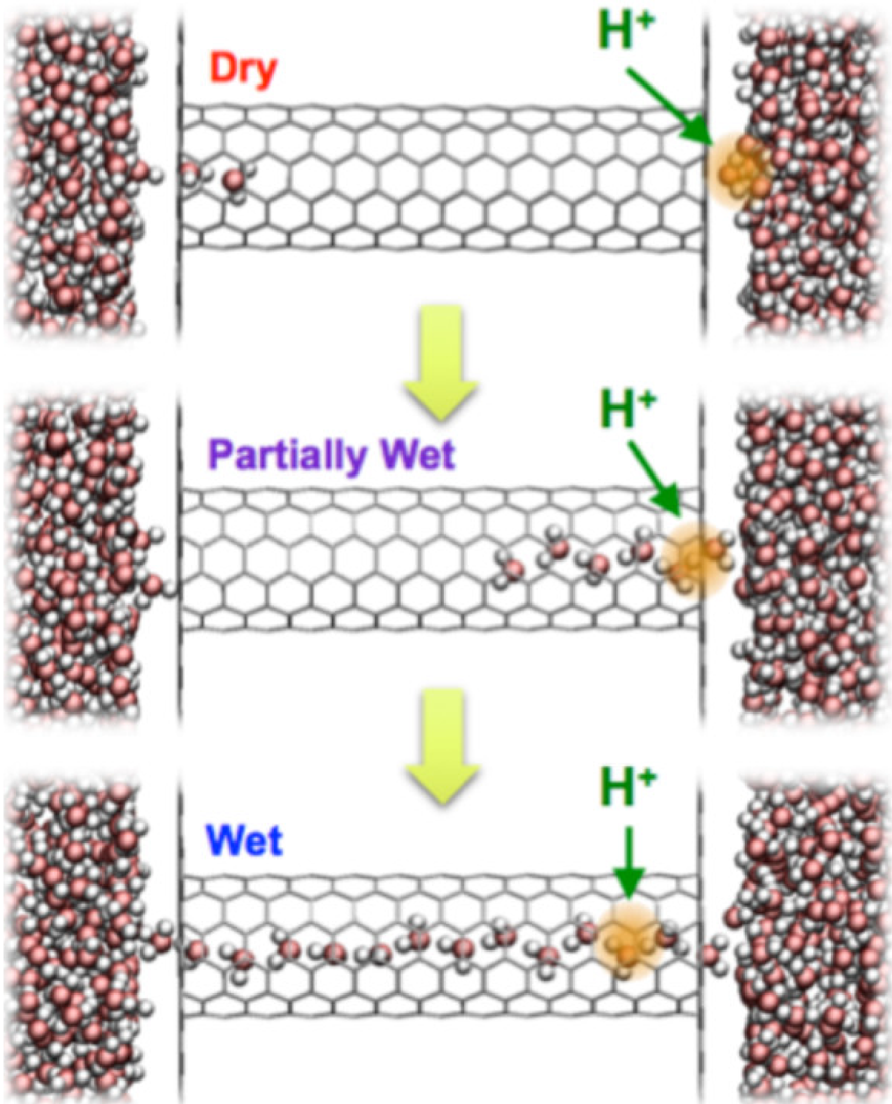
Goa, Fang, Ni, Scientific Reports 2021

Anomalous properties:

+ Density maximum at 4°C,
+ Steep increase in isothermal compressibility and heat capacity upon cooling
+ Non-Arrhenius behavior of viscosity and diffusivity at low pressure

Wide distribution of hydrogen bond statistics, relatively insensitive to temperature or shear.

Frustration and Water Wires



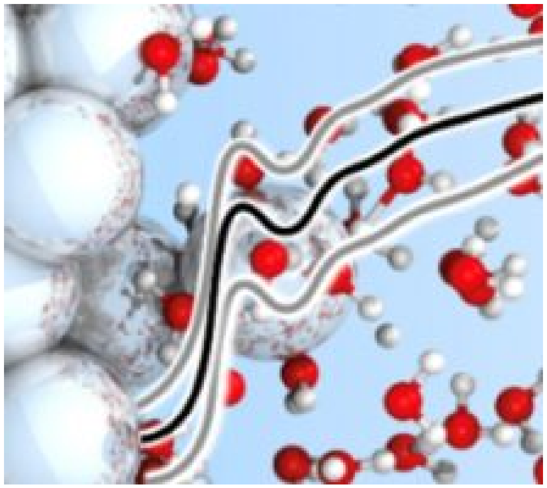
Greg Voth et al, J. Phys. Chem. B 2015

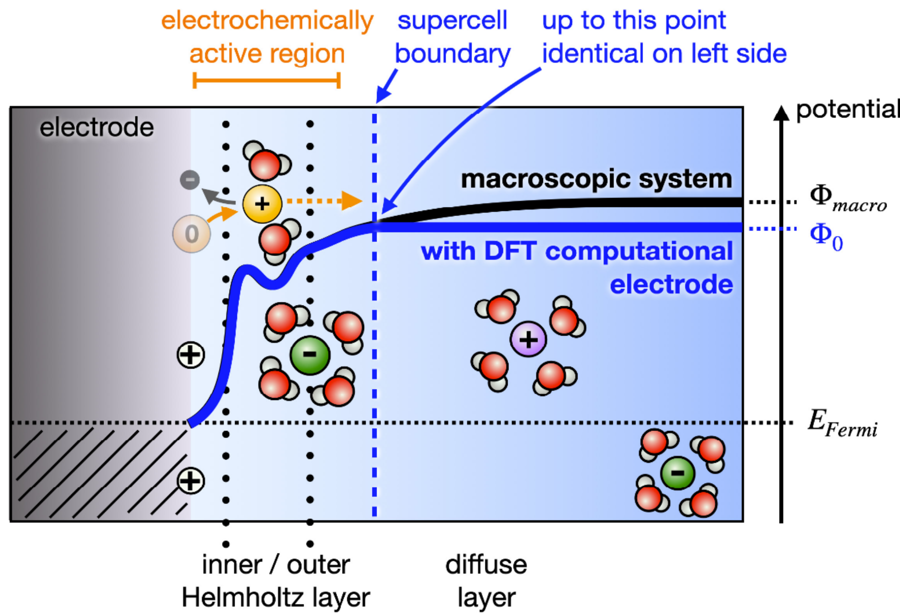
Water molecules induced to form a "water wire" within a narrow hydrophobic cylinder. The wetted cylinder is able to conduct a proton, modeling a proton channel.

Key issue, the anomalously "long-tailed" distribution of hydrogen bond count. Roughly 15% of water molecules have two or fewer hydrogen bonds. These misfits/defects will enter into the hydrophobic tube.

IPAM Fall 2025

Bridging the Gap: Transitioning from Deterministic to Stochastic Interaction Modeling in Electrochemistry





Todorova, Wippermann, Neugebauer,

Exceptionally high energy molecules (eg water) play a significant role in initiating electrochemical reactions.

In supercell computations the transition from explicit water to implicit water at computational electrode must incorporate fluctuations from macroscopic averages.

Tutorial Overview

Present the BBGKY+hydrodynamic framework that connects molecular to continuum models – examine errors of reduction at each step.

Atomistic – Electronic Structure	**Molecular** pair-wise interactions of N particles	**Probabilistic framework**: BBGKY for evolution of particle marginals	**Mean field limit**: uncorrelated dynamics	**Hydrodynamic limit**: average over "microscopic" variables
Electronic DFT	N-particle Hamiltonian ODE	Liouville's equation: Flux law for N-particle probability density and its marginals	Vlasov equation: uncorrelated flow uncouples one-marginal	Integrate out velocity and other microscopic variables.

Hydrodynamic Limit of Correlated BBGKY

Statistical Mechanics approach – notationally terse, significant cognitive jumps.
Probabilist approach – notationally heavy, are there really so many details?
Functional analysis - PDE approach that sits in-between.

N-particle Hamiltonian ODEs

N identical particles at $\bar{X}(t) = \{\bar{x}_i\}_{i=1}^N$ with velocities $\bar{V}(t) = \{\bar{v}_i\}_{i=1}^N$, a two-point potential energy $E : \mathbb{R} \mapsto \mathbb{R}$ and a Hamiltonian

$$H(\bar{X}, \bar{V}) = \overbrace{\frac{1}{N} \sum_{i,j=1}^{N} E(|\bar{x}_i - \bar{x}_j|)}^{\mathcal{E}(\bar{X})} + \sum_{i=1}^{N} \frac{1}{2} \bar{v}_i^2.$$

The N-ODE Hamiltonian flow

$$\frac{d}{dt}\bar{x}_i = \bar{v}_i,$$
$$\frac{d}{dt}\bar{v}_i = \frac{1}{N} \sum_{j=1}^{N} F(\bar{x}_i - \bar{x}_j),$$

where the force F is directed along the straight line between two particles,

$$F(x) = -E'(|x|)\frac{x}{|x|} = -\nabla_x E.$$

Introduce $\bar{z}_i = (\bar{x}_i, \bar{v}_i)^t \in \mathbb{R}^{2d}$ and $\bar{Z} = (\bar{X}, \bar{V})^t$

$$\frac{d\bar{Z}}{dt} = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix} \nabla_Z H(\bar{Z}) = \begin{pmatrix} \bar{V} \\ -\nabla_X \mathcal{E}(\bar{X}) \end{pmatrix}.$$

Probabilistic Interpretation

Let $f_N : \mathbb{R}^{2dN+1} \mapsto \mathbb{R}_+$ be the probability density for the N-particle distribution. For $\bar{\mathrm{Z}}(t)$ a solution of the N-particle ODE and $\Omega \subset \mathbb{R}^{2dN}$, the probability of finding $\bar{\mathrm{Z}}(t) \in \Omega$ is

$$\mathbb{P}(\bar{\mathrm{Z}}(t) \in \Omega) = \int_\Omega f_N(t, z_1, \cdots, z_N) \mathrm{d}z_1 \ldots \mathrm{d}z_N.$$

Given $\bar{\mathrm{Z}} = (\bar{\mathrm{X}}, \bar{\mathrm{V}})$ the empirical measure

$$\mu_N := \frac{1}{N} \sum_{i=1}^{N} \delta_{\bar{z}_i},$$

is a measure on the low dimensional space $\mathbb{R}^{2d}$.

We want to approximate f_N as a (sum of) tensor product of delta functions

$$\otimes_{i=1}^{N} \delta_{\bar{z}_i} = \prod_{i=1}^{N} \delta_{(0,\ldots,0,\bar{z}_i^t,0,\ldots,0)} = \delta_{\bar{\mathrm{Z}}}.$$

The product $f_N \, \mathrm{dZ}$ is a measure on $\mathbb{R}^{2dN}$.

The N-ODE Hamiltonian flow is given by linear projections (moments) of f_N

$$\frac{d}{dt}\bar{x}_i = \int_{\mathbb{R}^{2dN}} v_i f_N(t, \mathrm{Z})\, \mathrm{dZ} = \langle v_i, f_N \rangle_{L^2(\mathbb{R}^{2dN})},$$

$$\frac{d}{dt}\bar{v}_i = \int_{\mathbb{R}^{2dN}} \frac{1}{N} \sum_{j \neq i}^{N} \mathrm{F}(x_i - x_j) f_N(t, \mathrm{Z}) \mathrm{dZ} = \langle \mathrm{F}_i, f_N \rangle_{L^2(\mathbb{R}^{2dN})}.$$

More concretely: If f_N is a tensor product of $\mathbb{R}^{2d}$ delta functions

$$f_N(t, \mathrm{Z}) = \otimes_{i=1}^{N} \delta_{\bar{z}_i(t)},$$

then we recover the N-particle Hamiltonian flow

$$\frac{d}{dt}\bar{x}_i = 1^{2dN-1} \int_{\mathbb{R}^d} v_i \delta_{\bar{v}_i} \mathrm{d}v_i = \bar{v}_i,$$

$$\frac{d}{dt}\bar{v}_i = \frac{1}{N} \sum_{j \neq i}^{N} \int_{\mathbb{R}^{2d}} \mathrm{F}(x_i - x_j) \delta_{\bar{x}_i} \delta_{\bar{x}_j} \mathrm{d}x_i \mathrm{d}x_j,$$

$$= \frac{1}{N} \sum_{j \neq i}^{N} \mathrm{F}(\bar{x}_i - \bar{x}_j) = \mathrm{F}_i(\bar{\mathrm{X}}).$$

Projection of tensor products

Take f_N to be a general tensor product

$$f_N(\mathrm{Z}) = \otimes_{i=1}^N g_i = \prod_{i=1}^N g_i\overbrace{(x_i, v_i)}^{z_i},$$

where each $g_i \geq 0$ has mass one. Then

$$\begin{aligned}
\langle \mathrm{F}_i, f_N \rangle &= \frac{1}{N} \sum_{j \neq i}^N \int_{\mathbb{R}^{2dN}} \mathrm{F}(x_i - x_j) g_1(z_1) \cdots g_N(z_N) \mathrm{d}z_1 \cdots \mathrm{d}z_N, \\
&= \frac{1}{N} \sum_{j \neq i}^N \int_{\mathbb{R}^{2d}} \mathrm{F}(x_i - x_j) \bar{g}_j(x_j) \bar{g}_i(x_i) \mathrm{d}x_j \mathrm{d}x_i, \\
&= \frac{1}{N} \sum_{j \neq i}^N \langle \mathrm{F} * \bar{g}_j, \bar{g}_i \rangle_{L^2}.
\end{aligned}$$

While projection of f_N onto F_i is linear functional, it looks like a sum of quadratic two-particle interactions on the tensor product space.
Moral: tensor product operation is nonlinear (N-linear). Space of N-tensors is highly curved.

An Exercise: Homework

For $f \in L^2(\mathbb{R}^2_+)$ define the quarter-plane radial average map

$$[R(f)](r) := \frac{2}{\pi} \int_0^{\pi/2} f(r\cos\theta, r\sin\theta)\,\mathrm{d}\theta.$$

Show that the map $\mathcal{T} : L^\infty(\mathbb{R}_+) \cap L^1(\mathbb{R}_+) \mapsto L^\infty(\mathbb{R}_+) \cap L^1(\mathbb{R}_+)$ defined by

$$\mathcal{T}(g) = \frac{R(g \otimes g)}{\int_0^\infty R(g \otimes g)\,\mathrm{d}r},$$

is a strict contraction on the mass-one functions with the unique fixed point

$$g(r) = \alpha e^{-r^2},$$

for some $\alpha \in \mathbb{R}$.

The Liouville Equation

The flux of f_N is $\mathcal{J} : \mathcal{C}_c^\infty(\mathbb{R}^{2Nd}) \mapsto [\mathcal{C}_c^\infty(\mathbb{R}^{2Nd})]^{2Nd}$

$$\mathcal{J}(\mathrm{Z}) = (v_1, \ldots, v_N, \mathrm{F}_1, \ldots, \mathrm{F}_N)^t f_N.$$

Even more compactly, define $\mathcal{K} = (\mathrm{K}_1, \ldots \mathrm{K}_N)^t$, with $\mathrm{K}_i = (v_i, \mathrm{F}_i)^t$ so that

$$\mathcal{J} = \mathcal{K} f_N.$$

This generates the conservation law known as the N-particle Liouville Equation

$$\partial_t f_N + \nabla_{\mathrm{Z}} \cdot (\mathcal{K} f_N) = 0.$$

This is a hyperbolic PDE in $\mathbb{R}^{2dN+1}$ variables:

$$\partial_t f_N + \sum_{i=1}^N \nabla_{z_i}(\mathrm{K}_i f_N) = 0,$$

$$\partial_t f_N + \sum_{i=1}^N (v_i \cdot \nabla_{x_i} f_N + \nabla_{v_i} \cdot (\mathrm{F}_i f_N)) = 0,$$

Marginals

Assume that particles are interchangeable – this means f_N is invariant under permutation of its independent variables $f_N(\sigma(\mathrm{Z})) = f_N(\mathrm{Z})$ for any permutation σ of $\{1, \ldots, N\}$.

The j-marginal of f_N, denoted $f_{N,j} : \mathbb{R}^{2dj+1} \mapsto \mathbb{R}$, is the probability distribution of j particles irrespective of the location of the other $N - j$.

$$f_{N,j}(z_1, \ldots z_j) = \int f_N(\mathrm{Z})\, \mathrm{d}z_{j+1} \ldots \mathrm{d}z_N.$$

Correlation is a measure of the difference between the j marginal $f_{N,j}$ and the j-tensor of the one marginal

$$f_{N,1}^{\otimes j} := f_{N,1}(z_1) \cdots f_{N,1}(z_j).$$

If $f_{N,j} = f_{N,1}^{\otimes j}$ for $j = 1, \ldots, N$ then the particle distribution is uncorrelated – the particle positions are independent.

BBGKY: Marginal evolution

Derive an evolution equation for $f_{N,1}$. Write the N-particle Liouville as

$$\partial_t f_N + \sum_{i=1}^{N} \left(v_i \cdot \nabla_{x_i} f_N + \overbrace{\frac{1}{N} \sum_{j \neq i}^{N} \mathrm{F}(x_i - x_j)}^{\mathrm{F}_i(\mathrm{X})} \nabla_{v_i} f_N(\mathrm{Z}) \right) = 0.$$

Multiply the N particle Liouville by $\phi \in \mathcal{C}_c^\infty(\mathbb{R}^{2d})$, $\phi = \phi(z_1)$. When we integrate by parts only the ∇_{z_1} remains:

$$\partial_t \int_{\mathbb{R}^{2dN}} \phi(z_1) f_N(\mathrm{Z})\, \mathrm{dZ} = \int_{\mathbb{R}^{2dN}} \frac{1}{N} \sum_{j=2}^{N} \mathrm{F}(x_1 - x_j) \cdot \nabla_{v_1} \phi(z_1) f_N(\mathrm{Z})\, \mathrm{dZ}.$$

Since the particles are interchangeable switch $z_j \mapsto z_2$, Integrate out irrelevant variables z_j.

$$\partial_t \int_{\mathbb{R}^{2d}} \phi(z_1) f_{N,1}(z_1)\, \mathrm{d}z_1 = \frac{1}{N} \sum_{j=2}^{N} \int_{\mathbb{R}^{4d}} \mathrm{F}(x_1 - x_2) \cdot \nabla_{v_1} \phi(z_1) f_{N,2}(z_1, z_2)\, \mathrm{d}z_1 \mathrm{d}z_2.$$

Since no $\boldsymbol{j}$ on right-hand side, add up the terms

$$\partial_t \int \phi f_{N,1}\, \mathrm{d}z_1 = \frac{N-1}{N} \int \int \mathrm{F}(x_1 - x_2) \cdot \nabla_{v_1} \phi f_{N,2}(z_1, z_2)\, \mathrm{d}z_1 \mathrm{d}z_2,$$

This is the weak formulation (integrate by parts/drop $\mathrm{d}z_1$ integral) of

$$\boxed{\partial_t f_{N,1} + \frac{N-1}{N} \int_{\mathbb{R}^{2d}} \mathrm{F}(x_1 - x_2) \cdot \nabla_{v_1} f_{N,2}\, \mathrm{d}z_2 = 0.}$$

In a more appealing form, if we extend $\mathrm{F}(z) := \mathrm{F}(x)$,

$$\partial_t f_{N,1} + \frac{N-1}{N} \nabla_{v_1} \cdot (\mathrm{F} \circledast_{12} f_{N,2}) = 0.$$

The two-point convolution. If $\mathrm{F} : \mathbb{R}^{2d} \mapsto \mathbb{R}$ and $f : \mathbb{R}^{2dN} \mapsto \mathbb{R}$

$$(\mathrm{F} \circledast_{ij} f)\,(z_i) := \int_{\mathbb{R}^{2(d-1)N}} \mathrm{F}(z_i - z_j) f(\mathrm{Z}) \overbrace{\mathrm{d}z_1 \ldots \mathrm{d}z_N}^{\mathrm{d}z_i \notin}.$$

More generally the j marginal is coupled to the $j+1$st marginal,

$$\partial_t f_{N,j} + \frac{N-j}{N} \sum_{\ell=1}^{j} \nabla_{v_\ell} \cdot \mathrm{F} \circledast_{\ell,j+1} \boxed{f_{N,j+1}} + \frac{1}{N} \sum_{k,\ell=1}^{j} \nabla_{v_\ell} \cdot \mathrm{F} \circledast_{\ell,k} f_{N,j} = 0,$$

Mean Field Reduction

If the Liouville flow is uncorrelated, then $f_{N,j} = f^{\otimes j}$ where $f : \mathbb{R}^{2d} \mapsto \mathbb{R}$. In particular for $j = 2$

$$f_{N,2} = f(z_1)f(z_2)$$

and in the limit as $N \to \infty$ the one-marginal equation

$$\partial_t f_{N,1} + \frac{N-1}{N} \int_{\mathbb{R}^{2d}} \mathrm{F}(x_1 - x_2) \cdot \nabla_{v_1} f_{N,2} \, \mathrm{d}z_2 = 0,$$

reduces to a closed, nonlinear, Vlasov system:

$$\partial_t f + \nabla_v \cdot \left(f \int \mathrm{F}(x - x') f(x', v') \, \mathrm{d}x' \mathrm{d}v' \right) = 0.$$

Writing this as a convolution, and restoring the convective ∇_x terms

$$\partial_t f + v \cdot \nabla_x f + \nabla_v \cdot ((\mathrm{F} * f) f) = 0.$$

This is the mean-field limit.

Rigorous Mean Field Limit

F. Golse : Lecture Notes in Applied Mathematics and Mechanics, Volume 3, Chapter 1, *On the dynamics of large particle systems in the mean field limit. (2016)*

Suppose that

$$\mathrm{F}(x, x') = -\mathrm{F}(x', x),$$
$$|\nabla_z \mathrm{F}| \leq L,$$

Theorem 1.6.3 Let f solve the Vlasov system

$$\partial_t f + v \cdot \nabla_x f + \nabla_v \cdot ((\mathrm{F} * f) f) = 0,$$

with initial data f_0. Let f_N solve the Liouville system

$$\partial_t f_N + \nabla_{\mathrm{Z}} \cdot \mathcal{J}(f_N) = 0,$$

with initial data $f_N(0) = f_0^{\otimes N}$. Then

$$f_{N,j} \rightharpoonup f^{\otimes j}, \quad \text{as} \quad N \to \infty,$$

for $j = 1, \ldots N$.

Morally there exists $C, T > 0$

$$\|f_{N,j} - f^{\otimes j}\|_* \leq \frac{1}{N} e^{Ct}$$

for $t \in [0, T]$.

An Organizing Sub-manifold Result

A more gratifying result would be to establish something like:

Let $N_0 > 1$ be large enough. There exist $\nu, C, \delta > 0$ such that for $N > N_0$ and all initial data that satisfy

$$\|f_N(0) - f_{N,1}^{\otimes N}(0)\| < \delta,$$

the marginals of the solution of the N-particle Liouville equation satisfy the bound

$$\|f_{N,j}(t) - f_{N,1}^{\otimes j}(t)\| \leq C\left(\delta e^{-\nu t} + \frac{1}{N}\right).$$

The one marginal $f_{N,1}$ solves the Vlasov equation up to a residual that satisfies the same error estimate.

Corrections to Mean Field limit

Mitia Duerinckx, Comm. Math Physics **382** (2021).

Bogolyubov corrections to mean field. Assume the mean field limit holds. Assume f_N solve Liouville with tensor product initial data.

Define $h_1 = h_1(z_1)$ and $h_2 = h_2(z_1, z_2)$, via

$$\partial_t h_1 + v \cdot \nabla_x h_1 = \frac{N-1}{N}(\mathrm{F} * h_1) \cdot \nabla_v h_1 + \frac{1}{N}\mathrm{F} * \nabla_v h_2,$$

where

$$\partial_t h_2 + i\mathrm{L}_F h_2 = \mathrm{F} \cdot (\nabla_{v_1} - \nabla_{v_2}) f \otimes f - \\ (\mathrm{F} * f(x_1) \cdot \nabla_{v_1} + \mathrm{F} * f(x_2) \cdot \nabla_{v_2}) f \otimes f,$$

where f solves Vlasov.

Then we have the bound

$$\| f_{N,1} - h_1 \|_* \leq \frac{1}{N^2} e^{Ct}.$$

Mean Field Scaling

Assume the potential $\boldsymbol{E}$ is long range, so

$$\mathrm{F} \sim \frac{1}{|\boldsymbol{r}|^{p}}.$$

With $\boldsymbol{N}$ particles per box of unit volume the separation

$$\ell \sim \left(\frac{1}{N}\right)^{\frac{1}{d}} \implies \mathrm{F} \sim N^{\frac{p}{d}}.$$

Rescale time $\tau = t/N^{\alpha}$ and space $\mathrm{X}' = \mathrm{X}/N^{\beta}$, then $\mathrm{V}' = \mathrm{V}/N^{\beta-\alpha}$

$$\boxed{\partial_{\tau} f_N + V' \cdot \nabla_{\mathrm{X}'} f_N} + N^{\gamma} \nabla_{\mathrm{V}'} \cdot (\mathrm{F} f_N)) = 0,$$

where $\gamma = \beta(p-1) - \alpha$. The uniform density scaling is $\beta = 1/d$. So scaling

$$\alpha = 1 + \beta(p-1)$$

gives a uniform density rescaled force

$$\mathrm{F}' = \frac{1}{N}\mathrm{F}.$$

Hydrodynamic Limits

Motsch and Tadmor J. Stat. Phys. **144** (2011)
For the Vlasov system

$$\boldsymbol{f_t + \nabla_x \cdot (vf) + \nabla_v \cdot ((\mathrm{F} * f)f) = 0,}$$

the particle velocities are ‘microscopic’ variables. Particle positions yield a density which is macroscopic.

$$\boldsymbol{\rho(t,x) = \int_{\mathbb{R}^d} f(t,x,v)\,\mathrm{d}v,}$$
$$\boldsymbol{\rho U(t,x) = \int_{\mathbb{R}^d} f(t,x,v)v\,\mathrm{d}v.}$$

Integrate Vlasov $\times \boldsymbol{1}$ wrt $\mathrm{d}\boldsymbol{v}$

$$\boldsymbol{\rho_t + \nabla_x(\rho U) + \int_{\mathbb{R}^d} \nabla_v((\mathrm{F} * f)f\,\mathrm{d}v = 0,}$$

The last term drops and obtain continuity equation

$$\boxed{\boldsymbol{\rho_t + \nabla_x(\rho U) = 0.}}$$

Multiply Vlasov $\times \boldsymbol{v}$

$$\boldsymbol{\partial_t(vf) + \nabla_x \cdot (fv \otimes v) + v\nabla_v \cdot ((\mathrm{F} * f)f) = 0.}$$

Integrate over velocities

$$\boldsymbol{\partial_t(\rho U) + \nabla_x \cdot \int_{\mathbb{R}^d} f\, v \otimes v \,\mathrm{d}v - \int_{\mathbb{R}^d} (\mathrm{F} * f) f \,\mathrm{d}v = 0.}$$

Define the pressure

$$\begin{aligned}\mathrm{P} &:= \int_{\mathbb{R}^d} \boldsymbol{f\,(v - U) \otimes (v - U)\,\mathrm{d}v},\\ &= \int_{\mathbb{R}^d} \boldsymbol{f\, v \otimes v - f\, U \otimes v - f\, v \otimes U + f U \otimes U \,\mathrm{d}v},\\ &= \int_{\mathbb{R}^d} \boldsymbol{f\, v \otimes v \,\mathrm{d}v - \rho U \otimes U.}\end{aligned}$$

Rewrite convolution term

$$\begin{aligned}\int_{\mathbb{R}^d} \mathrm{F}(\boldsymbol{x - x'}) \boldsymbol{f(x', v') f(x, v) \mathrm{d}x' \mathrm{d}v' \mathrm{d}v} &= \int_{\mathbb{R}^d} \mathrm{F}(\boldsymbol{x - x'}) \boldsymbol{\rho(x') \rho(x) \mathrm{d}x' \mathrm{d}x},\\ &= (\mathrm{F} * \boldsymbol{\rho}) \boldsymbol{\rho},\end{aligned}$$

Obtain an Euler system

$$\begin{aligned}\boldsymbol{(\rho U)_t + \nabla_x \cdot (}\mathrm{P} + \boldsymbol{\rho \overbrace{U \otimes U}^{U \cdot \nabla_x U}) = \rho}\, \mathrm{F} * \boldsymbol{\rho},\\ \boldsymbol{\rho_t + \nabla_x (\rho U) = 0.}\end{aligned}$$

Direct Hydrodynamics from One-Marginal System

A. Diaw and M. Murillo PRE **92** 013107 (2015).

Introduce the two-particle correlation residual

$$h_2(z_1, z_2, t) := f_{N,2} - f_{N,1}^{\otimes 2}$$

The one marginal solves a forced Vlasov system

$$\partial_t f_{N,1} + v_1 \nabla_x f_{N,1} + (F_{\text{ext}} + \mathrm{F} * f_{N,1}) \cdot \nabla_{v_1} f_{N,1} = \int \mathrm{F}(x_1 - x_2) \cdot \nabla_{v_1} h_2 \, \mathrm{d}z_2.$$

Generally would find a closure model

$$h_2(z_1, z_2) := \mathcal{T}(f_{N,1}(z_1))$$

$$\mathcal{T} : H^2(X \times V) \mapsto H^2(X^2 \times V^2).$$

Rather take microstructure moment projections directly

$$\rho = \int_{\mathbb{R}^d} f_{N,1} \, \mathrm{d}v_1,$$

$$\rho U = \int_{\mathbb{R}^d} v_1 f_{N,1} \, \mathrm{d}v_1,$$

$$\mathrm{P}(x, t) = \int_{\mathbb{R}^d} f_1 (v_1 - U) \otimes (v_1 - U) \, \mathrm{d}v_1.$$

Taking moment projections against $\{1, v_1\}$ yields

$$\begin{aligned} \rho_t + \nabla_{x_1} \cdot (\rho U) &= 0, \\ (\rho U)_t + U \cdot \nabla_x U &= -\nabla_x \cdot \mathrm{P} + \rho \mathrm{F}_{\mathrm{ext}} + \mathcal{C}(x_1, t), \end{aligned}$$

where the correlation source term

$$\begin{aligned} \mathcal{C} := 3 &\int_{\mathbb{R}^d} \int_{\mathbb{R}^{2d}} \mathrm{F}(x_1 - x_2) h_2(z_1, z_2) \mathrm{d}v_1 \mathrm{d}z_2, \\ &= 3 \int_{\mathbb{R}^d} \mathrm{F}(x_1 - x_2) \rho_2(x_1, x_2) \mathrm{d}x_2, \\ &= 3\mathrm{F} \circledast_{12} \rho_2, \end{aligned}$$

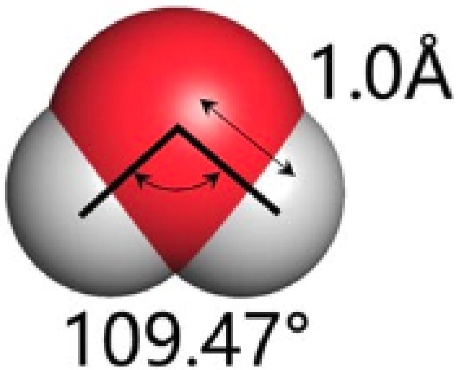
when written in terms of the two-particle density residual

$$\rho_2 := \int h_2 \, \mathrm{d}v_1 \mathrm{d}v_2.$$

Diaw and Murillo examine model closures using DFT and DDFT type ansatz.

Crucially they relate the two particle density to the “correlation function” under a quasi-equilibrium assumption.

Continuum Models from Polar Solvent: Stockmeyer Model



m_O = 15.9994
q_O = -0.8476e
m_H = 1.008
q_H = +0.4238e

Fix a domain $\Omega \subset \mathbb{R}^2$. Consider N interchangeable agents with locations $x_i \in \Omega$ and introduce the dipole charge locations

$$x_i^{\pm} = x_i \pm \frac{\ell}{2} d(\theta)$$

where the dipole angle vector

$$d(\theta) = \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix},$$

controls orientation. The partial charge at $x_i^{\pm}$ is $\pm q$.

The empirical charge density is

$$q_N = q \sum_{i=1}^{N} \left(\delta_{x_i^+} - \delta_{x_i^-} \right).$$

The electric potential solves Poisson's equation

$$\boldsymbol{\varepsilon_0 \Delta \psi = q_N}.$$

If G is the periodic Greens function for the Laplacian on $\boldsymbol{\Omega}$. We make the approximation

$$\mathrm{G}(\boldsymbol{x}-\boldsymbol{x}_i^+) - \mathrm{G}(\boldsymbol{x}-\boldsymbol{x}_i^-) \approx \boldsymbol{\ell}\, \boldsymbol{\nabla}\mathrm{G}(\boldsymbol{x}-\boldsymbol{x}_i)\cdot \boldsymbol{d}(\boldsymbol{\theta}_i),$$

under which the electric potential becomes

$$\boldsymbol{\psi} = \frac{\boldsymbol{q\ell}}{\boldsymbol{\varepsilon_0}} \sum_{i=1}^{N} \boldsymbol{\nabla}_x \mathrm{G}(\boldsymbol{x}-\boldsymbol{x}_i)\cdot \boldsymbol{d}(\boldsymbol{\theta}_i),$$

and the electric potential energy

$$\boldsymbol{\mathcal{E}}_{\mathrm{E}}(\mathrm{X}, \boldsymbol{\Theta}) = \frac{\boldsymbol{q^2\ell^2}}{\boldsymbol{\varepsilon_0}} \sum_{i}^{N} \sum_{j\neq i}^{N} \boldsymbol{d}^t(\boldsymbol{\theta}_j) \boldsymbol{\nabla}_x^2 \mathrm{G}(\boldsymbol{r}_{ij}) \boldsymbol{d}(\boldsymbol{\theta}_i),$$

Here $\boldsymbol{\nabla}^2$ denotes the Hessian operator, ^{t} transposition, and

$$\boldsymbol{r}_{ij} := \boldsymbol{x}_i - \boldsymbol{x}_j$$

is interparticle distance vector.

Caveat: Short Range Forces

Collisions are guided by electronic interactions via a short-range potential $\Phi = \Phi(r, \theta)$ where r is a distance and θ is a relative angle. A simple model, borrowing from collision operators

$$\Phi(r, \theta) = \left(\frac{1}{r^\alpha} - b(\theta) \right) e^{-r^2},$$

which is of Lennard-Jones type in r. The angular dependence should favor mis-alignment, $\theta = \pi$, pushing the location of the minima further out and reduces the depth of the minima, for example

$$b(\theta) = (1 - \cos(\theta))^2/4.$$

The short range collision potential takes the form

$$\mathcal{E}_\Phi := \sum_i^N \sum_{j \neq i}^N \Phi\left(|r_{ij}|, \theta_i - \theta_j\right).$$

Dipolar Molecules the Hamiltonian

We introduce a Hamiltonian of kinetic and potential energies written in terms of position and momentum

$$\mathcal{H}(\mathrm{X}, \Theta, \mathrm{P}, \mathrm{Q}) = \mathcal{U}_{\mathrm{E}}(\mathrm{X}, \Theta) + \mathcal{U}_{\Phi}(\mathrm{X}, \Theta) + \sum_i \left(\frac{|p_i|^2}{2m} + \frac{q_i^2}{2I} \right),$$

where $p_i = v_i m$ is the linear momentum $q_i = I\omega_i$ is its angular momentum, crucially

$$I = m\ell^2/4 \ll m$$

The model is motivated by the approach of

> G. Monet, F. Bresme, A. Kornyshev, H. Berthoumieux, Nonlocal dielectric response of water in nanoconfinement, *Physical Review Letters* **126** 216001 (2021).

Subject to the identification $d(\theta) \sim \mathrm{m}$ (polarization field) and $\nabla\psi \sim \mathrm{D}_0$ (displacement field).

The N-particle Hamiltonian ODE

$$\dot{x}_i = p_i/m = v_i,$$
$$\dot{\theta}_i = q_i/I = \omega_i,$$
$$m\dot{v}_i = -\frac{q^2\ell^2}{\varepsilon_0}\sum_{j\neq i}^{N} d^t(\theta_j)\nabla^3 \mathrm{G}(r_{ij})d(\theta_i) - \sum_{j\neq i}^{N} \partial_r\Phi\left(|r_{ij}|, \theta_i - \theta_j\right) r_{ij},$$
$$I\dot{\omega}_i = -\frac{q^2\ell^2}{\varepsilon_0}\sum_{j\neq i}^{N} d^t(\theta_j)\nabla^2 \mathrm{G}(r_{ij})d^{\perp}(\theta_i) - \sum_{j\neq i}^{N} \partial_\theta\Phi\left(|r_{ij}|, \theta_i - \theta_j\right),$$

Here $\perp$ denotes rotation by $\pi/2$ in particular $\partial_\theta d(\theta) = d^{\perp}(\theta)$.

We record the force fields

$$\mathrm{F}^x(z_i, z_j) := -\frac{q\ell^2}{m\varepsilon_0} d(\theta_i)\nabla_x^3 \mathrm{G}(x_i - x_j)d(\theta_j),$$
$$\mathrm{F}^\theta(z_i, z_j) := -\frac{q^2}{m\varepsilon_0} d(\theta_i)\nabla_x^2 \mathrm{G}(x_i - x_j)d(\theta_j).$$

BBGKY: Marginal Evolution

We drop the short-range terms. The Liouville equation describes the evolution of the scalar probability density $f_N = f_N(t, \mathrm{Z})$, where $\mathrm{Z} = (z_1, \ldots, z_N) \in \mathbb{R}^{6N}$ with $z_i = (x_i, \theta_i, v_i, \omega_i)$. For $\bar{\mathrm{Z}}(t) = (\bar{\mathrm{X}}, \bar{\mathrm{V}}, \bar{\Theta}, \bar{\Omega})$, the probability distribution

$$f_N(t, \bar{\mathrm{Z}}) := \prod_{i=1}^{N} \delta_{\bar{z}_i} = \delta_{\bar{\mathrm{Z}}},$$

leads to the projection formulation of the N-particle Hamiltonian

$$\begin{aligned} \dot{v}_i &= \langle \mathrm{F}_i^x, f_N \rangle_{L^2(\mathbb{R}^{6N})}, \\ \dot{\omega} &= \langle \mathrm{F}_i^\theta, f_N \rangle_{L^2(\mathbb{R}^{6N})}. \end{aligned}$$

where the projection is onto

$$\mathrm{F}_i^x := -\frac{q^2 \ell^2}{m\varepsilon_0} \sum_{j \neq i}^{N} d(\theta_i) \nabla_x^3 \mathrm{G}(x_i - x_j) d(\theta_j),$$

$$\mathrm{F}_i^\theta := -\frac{q^2}{m\varepsilon_0} \sum_{j \neq i}^{N} d(\theta_i) \nabla_x^2 \mathrm{G}(x_i - x_j) d(\theta_j).$$

The evolution of the probability density f_N is governed by a flux

$$\mathcal{J}(f_N) := (\mathrm{V}, \mathrm{F}^x, \Omega, \mathrm{F}^\theta)^t f_N \in \mathbb{R}^{6N},$$

for which the Liouville equation is the conservation law

$$\boldsymbol{\partial_t f_N + \nabla_{\mathrm{Z}} \cdot \mathcal{J}(f_N) = 0,}$$

which in more explicit form is

$$\boldsymbol{\partial_t f_N + \sum_{i=1}^{N} \big(v_i \cdot \nabla_{x_i} f_N + \omega_i \partial_{\theta_i} f_N + \nabla_{v_i} \cdot (\mathrm{F}_i^x f_N) + \partial_{\omega_i} (\mathrm{F}_i^\theta f_N) \big) = 0.}$$

Specifically the one-marginal solves

$$\boldsymbol{\begin{aligned} \partial_t f_{N,1} + v_1 \cdot \nabla_{x_1} f_{N,1} + \omega \partial_\theta f_{N,1} + \\ (N-1) \big(\nabla_{v_1} \cdot (\mathrm{F}^x \circledast_{12} f_{N,2}) + \nabla_{\omega_i} (\mathrm{F}^\theta \circledast_{12} f_{N,2}) \big) = 0. \end{aligned}}$$

Mean Field Rescaling

If we assuming some rescaling of the system parameters

$$\frac{q^2}{m} = \frac{1}{N},$$

with ℓ fixed, then rescale $\mathrm{F}^x \mapsto \frac{1}{N}\bar{\mathrm{F}}^x$ and $\mathrm{F}^\theta \mapsto \frac{1}{N}\bar{\mathrm{F}}^\theta$ then the one-marginal system is better conditioned,

$$\partial_t f_{N,1} + v_1 \cdot \nabla_{x_1} f_{N,1} + \omega \partial_\theta f_{N,1} + \frac{N-1}{N}\Big(\nabla_{v_1} \cdot (\bar{\mathrm{F}}^x \circledast_{12} f_{N,2}) + \nabla_{\omega_i}(\bar{\mathrm{F}}^\theta \circledast_{12} f_{N,2})\Big) = 0.$$

with the formal Vlasov-style mean-field equation

$$f_t + v\nabla_x f + \omega\partial_\theta f + \nabla_v \cdot ((\bar{\mathrm{F}}^x * f)f) + \partial_\omega((\bar{\mathrm{F}}^\theta * f)f) = 0.$$

Continuum Quantities

Identify the microscopic variables $\tilde{\boldsymbol{z}} = (\boldsymbol{v}, \boldsymbol{\theta}, \boldsymbol{\omega})$ and define the local density

$$\boldsymbol{\rho}(\boldsymbol{t}, \boldsymbol{x}) := \int_{\mathbb{R}^4} \boldsymbol{f}(\boldsymbol{t}, \boldsymbol{x}, \tilde{\boldsymbol{z}})\, \mathrm{d}\tilde{\boldsymbol{z}},$$

the density-weighted macroscopic velocity

$$\boldsymbol{\rho}(\boldsymbol{t}, \boldsymbol{x})\boldsymbol{U}(\boldsymbol{t}, \boldsymbol{x}) := \int_{\mathbb{R}^4} \boldsymbol{v}\boldsymbol{f}(\boldsymbol{t}, \boldsymbol{x}, \tilde{\boldsymbol{z}})\, \mathrm{d}\tilde{\boldsymbol{z}},$$

the density-weighted displacement field $\boldsymbol{D}$

$$\boldsymbol{\rho}(\boldsymbol{t}, \boldsymbol{x})\boldsymbol{D}(\boldsymbol{t}, \boldsymbol{x}) := \int_{\mathbb{R}^4} \boldsymbol{d}(\boldsymbol{\theta})\boldsymbol{f}(\boldsymbol{t}, \boldsymbol{x}, \tilde{\boldsymbol{z}})\, \mathrm{d}\tilde{\boldsymbol{z}},$$

and the density-weight macroscopic dipole angular velocity

$$\boldsymbol{\rho}(\boldsymbol{t}, \boldsymbol{x})\boldsymbol{\Omega}(\boldsymbol{t}, \boldsymbol{x}) := \int_{\mathbb{R}^4} \boldsymbol{\omega}\boldsymbol{f}(\boldsymbol{t}, \boldsymbol{x}, \tilde{\boldsymbol{z}})\, \mathrm{d}\tilde{\boldsymbol{z}}.$$

Charge Density Displacement

The charge density $\boldsymbol{\sigma}$ is a conditional probability on position and angle.

Let $\bar{\boldsymbol{f}}$ denote the $(\boldsymbol{v}, \boldsymbol{\omega})$ marginal of $\boldsymbol{f}$,

$$\begin{aligned}\boldsymbol{\sigma}(\boldsymbol{x}) &= \boldsymbol{q} \int_{\mathbb{S}} \bar{\boldsymbol{f}}(\boldsymbol{x} - \frac{\boldsymbol{\ell}}{\mathbf{2}}\boldsymbol{d}(\boldsymbol{\theta}), \boldsymbol{\theta}) - \bar{\boldsymbol{f}}(\boldsymbol{x} + \frac{\boldsymbol{\ell}}{\mathbf{2}}\boldsymbol{d}(\boldsymbol{\theta}), \boldsymbol{\theta})\, \mathrm{d}\boldsymbol{\theta}, \\ &= -\boldsymbol{q}\boldsymbol{\ell} \int_{\mathbb{S}} \boldsymbol{\nabla}_{\boldsymbol{x}} \bar{\boldsymbol{f}} \cdot \boldsymbol{d}(\boldsymbol{\theta})\, \mathrm{d}\boldsymbol{\theta} + \boldsymbol{O}(\boldsymbol{\ell}^2), \\ &= -\boldsymbol{q}\boldsymbol{\ell}\boldsymbol{\nabla}_{\boldsymbol{x}} \cdot (\boldsymbol{\rho}\boldsymbol{D}) + \boldsymbol{O}(\boldsymbol{\ell}^2).\end{aligned}$$

The electric field potential satisfies Poisson's equation

$$\boldsymbol{\varepsilon}_0 \boldsymbol{\Delta}\boldsymbol{\psi} = -\boldsymbol{\sigma} = \boldsymbol{q}\boldsymbol{\ell}\boldsymbol{\nabla}_{\boldsymbol{x}} \cdot (\boldsymbol{\rho}\boldsymbol{D})$$

and hence the induced electric field is proportional to displacement

$$\mathbb{E} := \boldsymbol{\nabla}\boldsymbol{\psi} = \frac{\boldsymbol{q}\boldsymbol{\ell}}{\boldsymbol{\varepsilon}_0}\boldsymbol{\rho}\boldsymbol{D}.$$

The electric field potential energy

$$\boldsymbol{\mathcal{U}}_{\boldsymbol{E}} = \int_{\Omega} \boldsymbol{\varepsilon}_0 |\boldsymbol{\nabla}\boldsymbol{\psi}|^2\, \mathrm{d}\boldsymbol{x} = \frac{\boldsymbol{q}^2\boldsymbol{\ell}^2}{\boldsymbol{\varepsilon}_0} \int_{\Omega} |\boldsymbol{\rho}\boldsymbol{D}|^2\, \mathrm{d}\boldsymbol{x}.$$

Hydrodynamic Limit from Vlasov

The Vlasov hydrodynamic limit is given by the projection of the Vlasov system

$$f_t + v\nabla_x f + \omega\partial_\theta f + \nabla_v \cdot ((\bar{\mathrm{F}}^x * f)f) + \partial_\omega((\bar{\mathrm{F}}^\theta * f)f) = 0,$$

against the functions $\{1, v, d(\theta), \omega\}$ over the microscopic $\tilde{\mathbf{Z}}$ variables.

$$\begin{aligned}
\partial_t \rho + \nabla_x \cdot (\rho U) &= 0,\\
\partial_t(\rho U) + \nabla_x \cdot (\rho U \otimes U + \mathrm{P}^{vv}) &= \frac{\ell^2}{\varepsilon_0}\rho D \left(\nabla_x^3 G * \rho D\right),\\
\partial_t(\rho D) + \nabla_x \cdot \left(\rho D \otimes U + \mathrm{P}^{dv}\right) + &\\
\left(\rho\Omega D + \mathrm{P}^{d\omega}\right)^{\perp} &= 0,\\
\partial_t(\rho\Omega) + \nabla_x \cdot (\rho\Omega U + \mathrm{P}^{\omega v}) &= -\frac{1}{\varepsilon_0}\rho D \left(\nabla_x^2 G * \rho D\right).
\end{aligned}$$

The Four Pressures

The kinetic pressure

$$\mathrm{P}^{vv}(\boldsymbol{t},\boldsymbol{x}) := \int_{\tilde{\mathrm{Z}}} (\boldsymbol{v}-\boldsymbol{U}) \otimes (\boldsymbol{v}-\boldsymbol{U}) \boldsymbol{f}(\boldsymbol{t},\boldsymbol{x},\tilde{\mathrm{Z}})\, \mathrm{d}\tilde{\mathrm{Z}},$$

the $\boldsymbol{dv}$-pressure

$$\mathrm{P}^{dv}(\boldsymbol{t},\boldsymbol{x}) := \int_{\tilde{\mathrm{Z}}} (\boldsymbol{d}(\boldsymbol{\theta})-\boldsymbol{D}) \otimes (\boldsymbol{v}-\boldsymbol{U}) \boldsymbol{f}(\boldsymbol{t},\boldsymbol{x},\tilde{\mathrm{Z}})\, \mathrm{d}\tilde{\mathrm{Z}},$$

the $\boldsymbol{d\omega}$-pressure

$$\mathrm{P}^{d\omega}(\boldsymbol{t},\boldsymbol{x}) := \int_{\tilde{\mathrm{Z}}} (\boldsymbol{\omega}-\boldsymbol{\Omega})(\boldsymbol{d}-\boldsymbol{D}) \boldsymbol{f}\, \mathrm{d}\tilde{\mathrm{Z}},$$

and the $\boldsymbol{\omega v}$-Pressure

$$\mathrm{P}^{\omega v} = \int_{\tilde{\mathrm{Z}}} (\boldsymbol{\omega}-\boldsymbol{\Omega})(\boldsymbol{v}-\boldsymbol{U}) \boldsymbol{f}(\boldsymbol{t},\boldsymbol{x},\tilde{\mathrm{Z}})\, \mathrm{d}\tilde{\mathrm{Z}}.$$

The pressure terms can not be (trivially) expressed in terms of the four moments considered here, in some sense they represent forces that drive the system onto the lower dimensional hydrodynamic (macroscopic) system.

Derivation of Right-Hand Sides

The right-hand side of the $\boldsymbol{U}$-equation

$$\begin{aligned}
\mathrm{S}^{x}(\boldsymbol{x};\boldsymbol{\rho},\boldsymbol{D}) &= -\frac{\ell^2}{\varepsilon_0}\int\int \boldsymbol{\nabla}_x^3 \mathrm{G}(\boldsymbol{x}-\boldsymbol{x}')\boldsymbol{d}(\boldsymbol{\theta}')\boldsymbol{f}(\boldsymbol{t},\boldsymbol{X}')\,\mathrm{d}\boldsymbol{X}'\cdot\boldsymbol{d}(\boldsymbol{\theta})\boldsymbol{f}(\boldsymbol{t},\tilde{\mathrm{Z}})\,\mathrm{d}\tilde{\mathrm{Z}},\\
&= -\frac{\ell^2}{\varepsilon_0}\int\int \boldsymbol{\nabla}_x^3 \mathrm{G}(\boldsymbol{x}-\boldsymbol{x}')\boldsymbol{\rho}(\boldsymbol{x}')\boldsymbol{D}(\boldsymbol{x}')\boldsymbol{\rho}(\boldsymbol{x})\boldsymbol{D}(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}',\\
&= -\frac{\ell^2}{\varepsilon_0}\boldsymbol{\rho}\boldsymbol{D}\left(\boldsymbol{\nabla}_x^3 \boldsymbol{G} * \boldsymbol{\rho}\boldsymbol{D}\right).
\end{aligned}$$

The form of the $\boldsymbol{dw}$-pressure arises from integration by parts and the relation $\boldsymbol{\partial_\theta d(\theta) = -d^\perp(\theta)}$,

$$\begin{aligned}
\int_{\tilde{\mathrm{Z}}} \boldsymbol{\omega}\boldsymbol{\partial_\theta f}\,\boldsymbol{d}(\boldsymbol{\theta})\,\mathrm{d}\tilde{\mathrm{Z}} &= \int_{\tilde{\mathrm{Z}}} \boldsymbol{\omega}\boldsymbol{d}^\perp(\boldsymbol{\theta})\boldsymbol{f}\,\mathrm{d}\tilde{\mathrm{Z}},\\
&= \int_{\tilde{\mathrm{Z}}} (\boldsymbol{\omega}-\boldsymbol{\Omega})(\boldsymbol{d}-\boldsymbol{D})^\perp \boldsymbol{f}\mathrm{d}\tilde{\mathrm{Z}} + \boldsymbol{\rho}\boldsymbol{\Omega}\boldsymbol{D}^\perp.
\end{aligned}$$

The right-hand side of the $\boldsymbol{\Omega}$ equation, denoted $\boldsymbol{S^\theta}$, follows a similar rational.

Hydrodynamic Limit of First Marginal

The first-marginal system couples $f_1 := f_{N,1}(z_1)$ to $f_2 := f_{N,2}(z_1, z_2)$. Collect the position and velocity variables $\mathrm{X} = (x, \theta)$ and $\mathrm{V} = (v, \omega)$ we have

$$\partial_t f_1 + \mathrm{V}_1 \cdot \nabla_{\mathrm{X}_1} f_1 = -\frac{d(\theta_1)}{\varepsilon_0} \int_{\mathbb{R}^6} \nabla_x^2 G(x_1 - x_2) d(\theta_2) \nabla_{\omega_1} f_2 \mathrm{d} z_2 - \frac{\ell^2 d(\theta_1)}{\varepsilon_0} \int_{\mathbb{R}^6} \nabla_x^3 G(x_1 - x_2) d(\theta_2) \nabla_{v_1} f_2 \mathrm{d} z_2 .$$

Introducing the second marginal residual

$$h_2(\mathrm{Z}_1, \mathrm{Z}_2) = f_2(\mathrm{Z}_1, \mathrm{Z}_2) - \overbrace{f_1(Z_1) f_1(Z_2)}^{f_1^{\otimes 2}},$$

yields a Vlasov system "perturbed" by correlation

$$\partial_t f_1 + V_1 \cdot \nabla_{X_1} f_1 + \nabla_{V_1} \cdot (\mathbb{F}(f_1) f_1) = \mathcal{C}(h_2),$$

where the correlation term

$$\mathcal{C}(h_2) = -\frac{\ell^2}{\varepsilon_0} d(\theta_1) \int \nabla_x^3 G(x_1 - x_2) d(\theta_2) \nabla_{v_1} h_2 \, \mathrm{dZ}_2 - \frac{1}{\varepsilon_0} d(\theta_1) \int \nabla_x^2 G(x_1 - x_2) d(\theta_2) \nabla_{\omega_1} h_2 \, \mathrm{dZ}_2 .$$

Hydrodynamic First Marginal

Take the moment projections against $\{1, v_1, \theta_1, \omega_1\}$ yields the same system given by the Vlasov but subject to additional, stochastic terms arising from the second marginal residual.

$$\partial_t \rho + \nabla_x \cdot (\rho U) = 0,$$

$$\partial_t(\rho U) + \nabla_x \cdot (\rho U \otimes U + \mathrm{P}^{vv}) = -\frac{\ell^2}{\varepsilon_0}\Big(\rho D \left(\nabla_x^3 G * \rho D\right) + \nabla_x^3 \mathrm{G}\circledast_{12} : D_2\Big),$$

$$\partial_t(\rho D) + \nabla_x \cdot \left(\rho D \otimes U + \mathrm{P}^{dv}\right) + \left(\rho \Omega D + \mathrm{P}^{d\omega}\right)^{\perp} = 0,$$

$$\partial_t(\rho \Omega) + \nabla_x \cdot (\rho \Omega U + \mathrm{P}^{\omega v}) = -\frac{1}{\varepsilon_0}\Big(\rho D \left(\nabla_x^2 G * \rho D\right) + \nabla_x^2 \mathrm{G}\circledast_{12} : D_2\Big).$$

where the two-marginal residual matrix displacment $D_2 : \mathbb{R}^4 \mapsto \mathbb{R}^{2\times 2}$,

$$D_2(x_1, x_2) := \int_{\mathbb{R}^8} d(\theta_1) \otimes d(\theta_2) \boxed{\boxed{h_2(x_1, x_2, \tilde{z}_1, \tilde{z}_2)}} \, \mathrm{d}\tilde{z}_1 \mathrm{d}\tilde{z}_2.$$

Follow-up Ideas: 1) Limiting Cases

Take $\ell \ll 1$, drop the source terms in U equation. Take $U = 0$ and ρ constant in time and space. Combine the displacement and the Ω equations

$$\partial_t^2 D - \Omega^2 D + \frac{D^\perp}{\varepsilon_0} \left(\rho D (\nabla_x^2 G * (\rho D)) + \nabla_x^2 G \circledast_{12} D_2 \right) = 0.$$

Follow up Ideas 2) AC Impedance

Introduce a fixed macroscopic charge density $Q(x)$ into the electrostatic equation

$$\varepsilon_0 \Delta \psi = -q\ell \nabla_x \cdot (\rho D) + \cos(\omega t) Q(x).$$

Take spatially-fixed charge Q comprised of two sheets charges of opposite sign in a periodic box. Recover a macroscopic-hydrodynamic system with electric potential ψ_{eff} satisfying Poisson's equation

$$\nabla \cdot (\varepsilon_{\text{eff}}(\omega) \nabla \psi_{\text{eff}}) = Q,$$

with $\varepsilon_{\text{eff}} \in \mathbb{R}^{2\times 2}$.

Examine convergence to the hydrodynamic limit perhaps under assumption some version of a strong alignment limit, shadowing approach of [10, 8].

- Use DFT style ideas to develop closed 'self-consistent' expression for $h_2 = h_2(f_1)$.
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