Aston University
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hybrid MD/HD modelling

Modelling liquid solutions at atomistic and continuum representation at the same time: hybrid MD/hydrodynamics implementation of two dimensional water model

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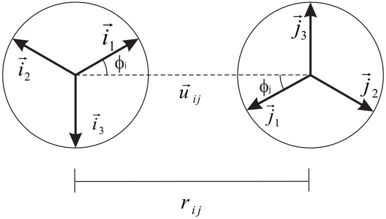
Introduction

The talk's plan:

I. Mercedes-Benz water
II. Hybrid MD/HD framework

Mercedes-Benz water



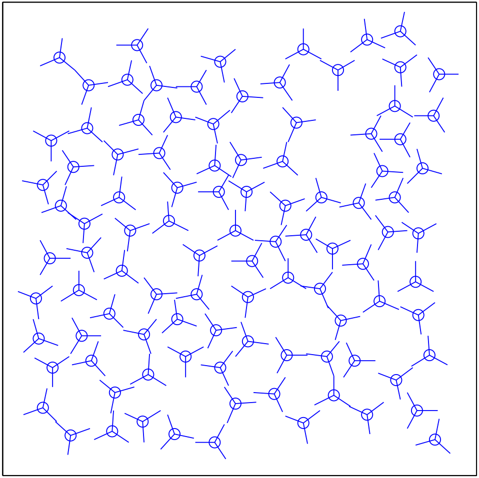
$$\Phi = \Phi_{LJ} + \Phi_{HB},$$

where Φ_{LJ} is the Lennard-Jonnes potential, Φ_{HB} is the explicit hydrogen bonding term:

$$\Phi_{HB} = \epsilon_{HB} \cdot G(r_{ij} - r_{HB}) \sum_{ij}^{N} G(\vec{i}_k \cdot \vec{u}_{ij} - 1) G(\vec{j}_l \cdot \vec{u}_{ij} + 1),$$

G is the Gaussian function $G(x) = e^{\frac{-x^2}{2\sigma^2}}$.

MB water snapshot



MB water thermodynamics

The thermodynamic properties are expressed through K, $\frac{\partial \Phi}{\partial A}$ only:
temperature: $T = \frac{2}{3N}\langle K \rangle$,
pressure: $P = \rho\, k_B T - \left\langle \frac{\partial \Phi}{\partial A} \right\rangle$,
isochoric heat capacity

$$\frac{C_V}{N k_B} = \left(\frac{2}{3} \langle K \rangle \langle K^{-1} \rangle + N(1 - \langle K \rangle \langle K^{-1} \rangle) \right)^{-1}.$$

$$K = \sum_{i=1}^{N} \frac{m \vec{v}_i^2}{2} + \frac{I \omega_i^2}{2},$$

where I is the moment of inertia, $\vec{v}_i$ and ω_i are the translational and angle velocities.

$$\frac{d\Phi}{dA} = \frac{1}{2A} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} dx \frac{d\Phi_{ij}}{dx} + dy \frac{d\Phi_{ij}}{dy}.$$

MB water thermodynamics

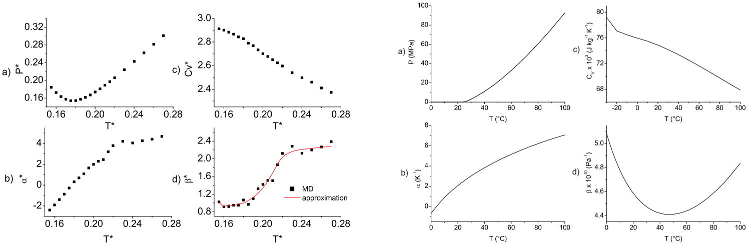


Figure : Isothermal compressibility β^*, pressure P^*, isochoric heat capacity C_V^*, isothermal expansion coefficient α^*.

MB water structure

$$g_r^{(2)}(r) = \frac{2V}{N^2}\left\langle \sum_{i<j} \delta(r - |\vec{u}_{ij}|) \right\rangle,$$

$$g_\phi^{(2)}(r) = \frac{1}{Z_{ij}}\left\langle \sum_{i<j} z_{ij}\delta(r - |\vec{u}_{ij}|) \right\rangle,$$

$$z_{ij} = \sum_{k=1}^{3}\sum_{l=1}^{3} G(\vec{i}_k \cdot \vec{u}_{ij} - 1)G(\vec{j}_l \cdot \vec{u}_{ij} + 1),$$

$$Z_{ij} = \int_0^\infty \left\langle \sum_{i<j} z_{ij}\delta(r - |\vec{u}_{ij}|) \right\rangle dr,$$

where N is the number of molecules in the corresponding solvation shell, Z_{ij} is the normalization factor.

MB water structure

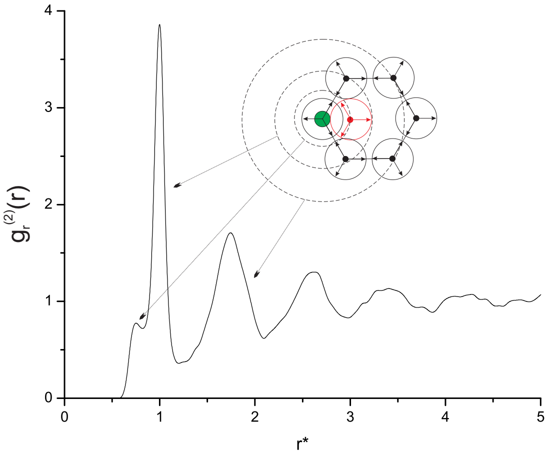


Figure : Radial distribution function. The reference molecule is shown in green. The 'interstitial' water is red.

MB water structure

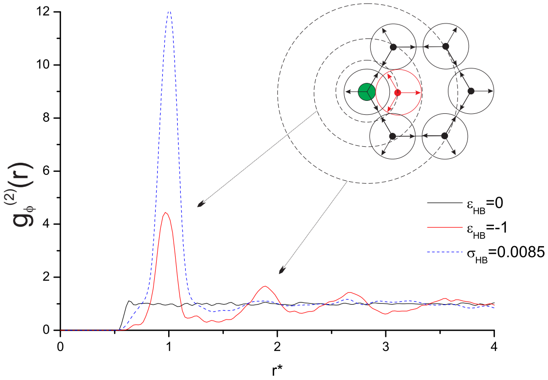
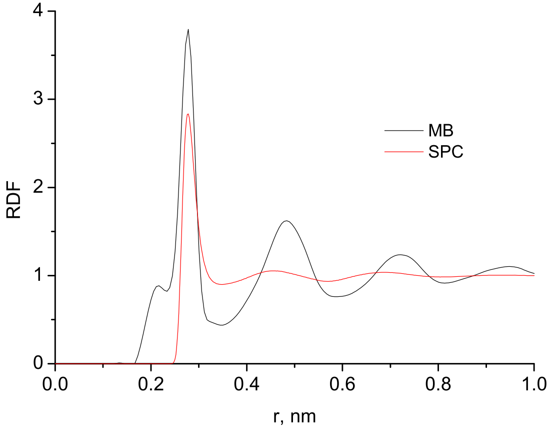


Figure : Orientation contribution as a function of distance.

MB water structure



MB water dynamics

The velocity autocorrelation function:

$$f_v(\tau) = \langle \vec{v}(t) \cdot \vec{v}(t+\tau) \rangle \,,$$

where $\vec{v}(t)$ and $\vec{v}(t+\tau)$ are translational velocities at time moments t and $t+\tau$.
The rotation velocity autocorrelation function:

$$f_\omega(\tau) = \langle \omega(t) \cdot \omega(t+\tau) \rangle \,,$$

where $\omega(t) = \frac{\partial \phi}{\partial t}$ is rotational velocity.

MB water dynamics

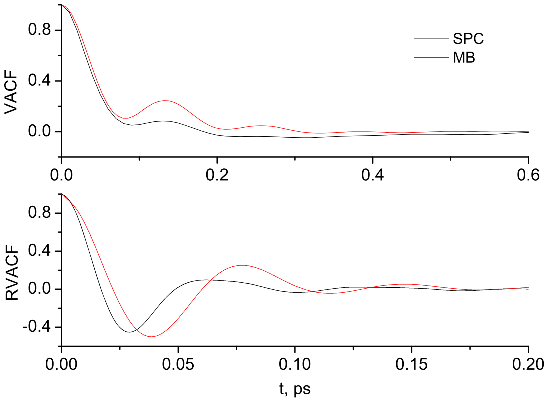


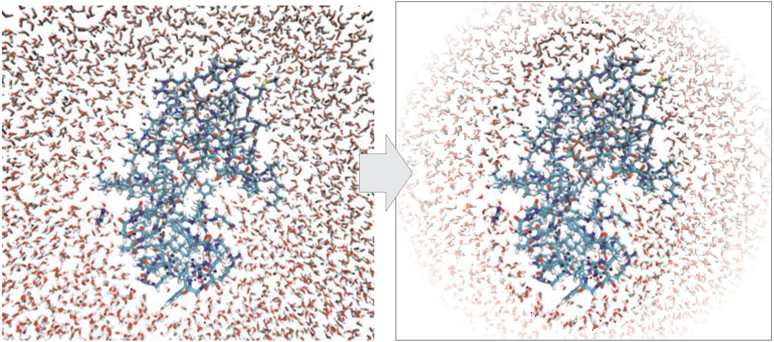
Figure : Velocity autocorrelation functions for MB and SPC models.

MB water summary

- Two dimensional water qualitatively and sometimes quantitatively represents the properties of real water.
- Molecular dynamics of the model works well and reproduces the results of Monte Carlo.
- The usefulness of the model: N^2 dependence on system size, easy visualisation.

Hybrid MD/HD: motivation

Motivation: true *multiscaling*



Hybrid MD/HD: hydrodynamics

Continuous representation (hydrodynamics)

- All started with macroscopic thermodynamical quantities: the properties of the system **as a whole**, the largest possible scale.
- Describing the system at smaller scales: the properties become **fields** changing in **time**:

$$\rho(\mathbf{x}, t), \mathbf{u}(\mathbf{x}, t), T(\mathbf{x}, t).$$

- $\mathbf{x}$ is the Euclidean 3D space.
- The equations of motion are the FD equations.
- The solution is the values of the fields at each location in space at every instant of time: $\rho(\mathbf{x}, t), \mathbf{u}(\mathbf{x}, t), T(\mathbf{x}, t)$.

Hybrid MD/HD: atomistic

Atomistic representation

- The variables are the positions and momenta of the point masses, the atoms:

$$\{\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N\}$$

- The space is the $6N$-dimentional phase space.
- The atoms interact through empirically (in MD) defined Hamiltonian $H(\mathbf{q}, \mathbf{p})$
- The equations of motion describing $\mathbf{q}(t), \mathbf{p}(t)$ are the Hamilton equations

$$\frac{\mathrm{d}q_i(t)}{\mathrm{d}t} = \frac{\partial H(\mathbf{q}, \mathbf{p})}{\partial p_i}, \frac{\mathrm{d}p_i(t)}{\mathrm{d}t} = -\frac{\partial H(\mathbf{q}, \mathbf{p})}{\partial q_i}.$$

- The solution is the molecular trajectory: the values of the coordinates and momenta at every moment of time:

$$\mathbf{q}(t), \mathbf{p}(t).$$

Connecting the representations

Calculating the continuous density:

$$\rho_q(\mathbf{q};\mathbf{x},t) = \sum_{j=1}^{N} m\delta(\mathbf{q}_i(t) - \mathbf{x})$$

It is a *function of the molecular coordinates* (phase space variable), which also parametrically depends on $\mathbf{x}$ and t.

Connecting the representations

How the measurement is done: a probe of spatial dimensionality $\Delta\mathbf{x}$ is placed at the point $\mathbf{x}$ for a period of time Δt at time t.

The 'true' (measured) value of $\rho(\mathbf{x}, t)$ is obtained by overaging $\rho_q(\mathbf{q}; \mathbf{x}, t)$ over $\Delta\mathbf{x}$ and Δt.

$$\rho(\mathbf{x}, t) = \langle \rho_q(\mathbf{q}; \mathbf{x}, t) \rangle_{\Delta\mathbf{x}, \Delta t}$$

Connecting the representations

Mathematically $\rho(\mathbf{x}, t)$ is a *functional*: for every point in space $\mathbf{x}$ and moment t it associates a *number* (the value of the density) for the given *function* $\mathbf{q}(t)$ (on the interval $[t, t + \Delta t]$).
Ergodic hypothesis: such functional can be constructed by introducing a function $F(\mathbf{q}, \mathbf{p})$ which has the property

$$\rho(\mathbf{x}, t) = \int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\rho_q(\mathbf{q}; \mathbf{x}, t)F(\mathbf{q}, \mathbf{p}).$$

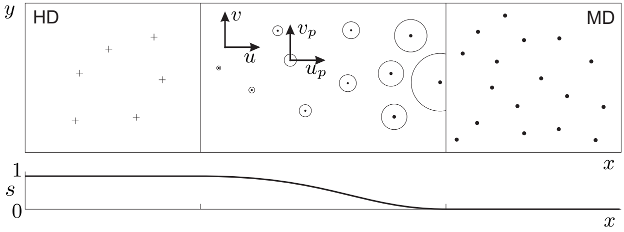
This function should satisfy normalisation condition.
It is the **phase space distribution function**.
It has a meaning of probability.

Connecting the representations

This is MD→HD transformation.

HD→MD - ???

Connecting the representations



- The end domains HD and MD are described by purely hydrodynamic and purely Newtonian equations of motion respectively.
- In the hybrid domain the fluid consists of two “phases”:
  - HD phase is a continuum water with volume fraction $s = \frac{V_1}{V}$,
  - MD phase is a phase that incorporates atoms, its volume fraction is $(1 - s)$.
- The parameter $s = s(x)$ is the function of space coordinates, such that $s = 1$ in the HD domain, $s = 0$ in the MD domain.

Mass conservation

For HD phase:

$$\frac{\partial}{\partial t}(s\rho) + \frac{\partial}{\partial x_i}(u_i s\rho) = J,$$

For MD phase:

$$\frac{\partial}{\partial t}\left((1-s)\sum_{p=1,N(t)} \rho_p\right) + \frac{\partial}{\partial x_i}\left((1-s)\sum_{p=1,N(t)} \rho_p u_{ip}\right) = -J,$$

where $\rho_p = m_p/V$ is the density of MD particles and J is the birth/death rate due to the coupling between the phases.

Modified MD equations

MD velocities are constrained to HD phase in the $s \to 1$ limit:

$$\frac{dx_{ip}}{dt} = u_{ip} + s(u_i - u_{ip}) + s(1-s)\alpha \frac{\partial}{\partial x_i}\left(\tilde{\rho} - \sum_{p=1,N(t)} \rho_p\right) / \rho_p / N(t),$$

where $\tilde{\rho} = s\rho + (1-s)\sum_{p=1,N(t)} \rho_p$.

The source J

From the modified MD the source J can be found:

$$J = s\frac{\partial}{\partial t}\sum_{p=1,N(t)}\rho_p + \frac{\partial}{\partial x_i}\left(su_i\sum_{p=1,N(t)}\rho_p\right) + \frac{\partial}{\partial x_i}\left(s(1-s)\alpha\frac{\partial}{\partial x_i}\left(\tilde{\rho} - \sum_{p=1,N(t)}\rho_p\right)\right),$$

where $\tilde{\rho} = s\rho + (1-s)\sum_{p=1,N(t)}\rho_p$.

$\tilde{\rho}$ is diffused towards $\sum_{p=1,N(t)}\rho_p$:

$$\frac{D}{Dt}\left(\tilde{\rho} - \sum_{p=1,N(t)}\rho_p\right) = \frac{\partial}{\partial x_i}\left(s(1-s)\alpha\frac{\partial}{\partial x_i}\left(\tilde{\rho} - \sum_{p=1,N(t)}\rho_p\right)\right).$$

Conservation of momentum

For HD phase:

$$\frac{\partial}{\partial t}(s u_i \rho) + \frac{\partial}{\partial x_j}(u_j u_i s \rho) = sF_i + J_2,$$

where J_2 is the HD-MD interaction force and F_i is the hydrodynamic force, calculated from Landau-Lifshitz fluctuating hydrodynamics model:

$$\begin{aligned} F_i &= -\frac{\partial T_{ij}^{FH}}{\partial x_i} \\ T_{ij}^{FH} &= T_{ij} + \tilde{T}_{ij} \\ T_{ij} &= \left(p - \xi \frac{\partial}{\partial x_\alpha} u_\alpha\right)\delta_{ij} - \nu\left(\frac{\partial}{\partial x_i} u_j + \frac{\partial}{\partial x_j} u_i - 2D^{-1}\frac{\partial}{\partial x_\alpha} u_\alpha \delta_{ij}\right) \end{aligned}$$

where D is the problem dimension, p is pressure, ξ, ν are the (macro) viscosity coefficients, $\tilde{T}_{ij}$ is a random Gaussian matrix with zero mean and correlations depending on the viscosities and $k_B T$.

Conservation of momentum

For MD phase:

$$\frac{\partial}{\partial t}\left((1-s)\sum_{p=1,N(t)} u_{i,p}\rho_p\right) + \frac{\partial}{\partial x_j}\left((1-s)\sum_{p=1,N(t)} \rho_p u_{i,p} u_{j,p}\right) = (1-s)\sum_{p=1,N(t)} F_{i,p} - J_2$$

Modified MD equation for the force

Similarly to the modified equation for MD velocities:

$$\frac{du_{jp}}{dt} = (1-s)F_{jp}/\rho_p + sF_j/\rho_p/N(t)$$
$$+ \frac{\partial}{\partial x_i}\left(s(1-s)\alpha \sum_{p=1,N(t)} u_{jp}/N(t)\frac{\partial}{\partial x_i}\left(\tilde{\rho} - \sum_{p=1,N(t)} \rho_p\right)\right)\frac{1}{\rho_p N}$$
$$- \frac{\partial}{\partial x_i}\left(s(1-s)\beta\frac{\partial}{\partial x_i}\left(\tilde{u}_j\tilde{\rho} - \sum_{p=1,N(t)} u_{jp}\rho_p\right)\right)/\rho_p/N(t),$$

where $\tilde{\rho} = s\rho + (1-s)\sum_{p=1,N(t)}\rho_p$,
$\tilde{u}_j = \left[s\rho u_j + (1-s)\sum_{p=1,N(t)}\rho_p u_{jp}\right]/\tilde{\rho}$.

The source J_2

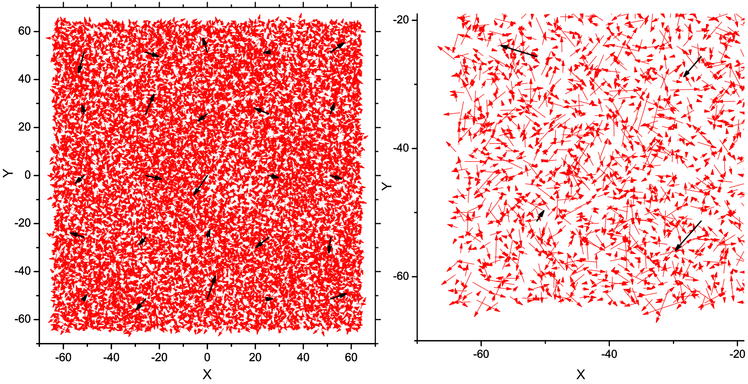
$$J_2 = s\frac{\partial}{\partial t}\sum_{p=1,N(t)}\rho_p u_{jp} + \frac{\partial}{\partial x_i}\left(s u_i \sum_{p=1,N(t)}\rho_p u_{jp}\right) - sF_j +$$
$$\frac{\partial}{\partial x_i}\left(s(1-s)\beta\frac{\partial}{\partial x_i}\left(\tilde{u}_j\tilde{\rho} - \sum_{p=1,N(t)} u_{jp}\rho_p\right)\right),$$

where $\tilde{\rho} = s\rho + (1-s)\sum_{p=1,N(t)}\rho_p$,
$\tilde{u}_j = \left[s\rho u_j + (1-s)\sum_{p=1,N(t)}\rho_p u_{jp}\right]/\tilde{\rho}$.
$\tilde{u}_j\tilde{\rho}$ is diffused towards $\sum_{p=1,N(t)} u_{jp}\rho_p$:

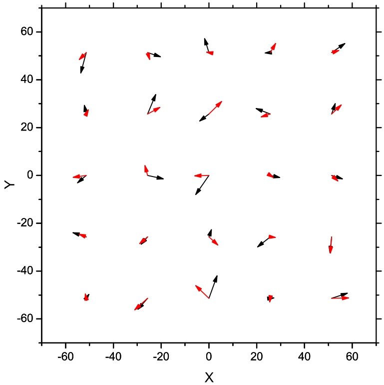
$$\frac{D}{Dt}\left(\tilde{u}_j\tilde{\rho} - \sum_{p=1,N(t)} u_{jp}\rho_p\right) =$$
$$\frac{\partial}{\partial x_i}\left(s(1-s)\beta\frac{\partial}{\partial x_i}\left(\tilde{u}_j\tilde{\rho} - \sum_{p=1,N(t)} u_{jp}\rho_p\right)\right).$$

Results

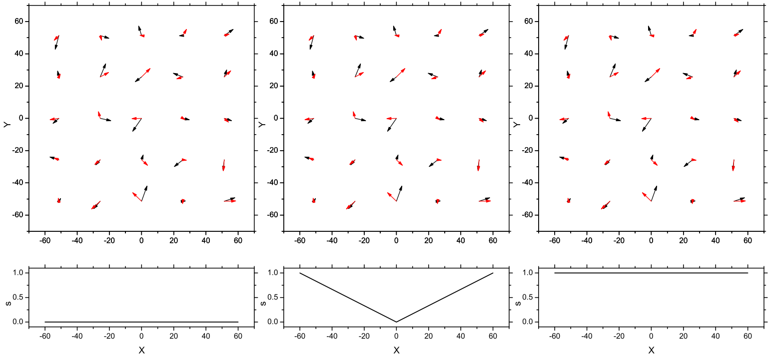
Preliminary results for 2D Lennard-Jones liquid:



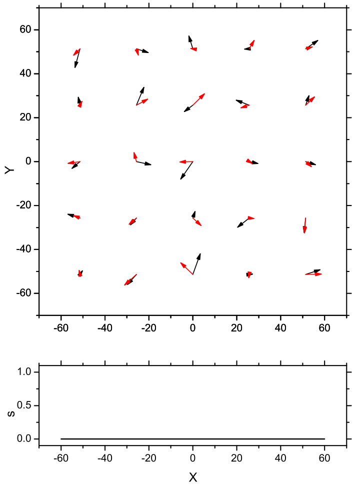
Results



Results



Results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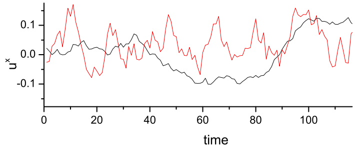
0.1
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-0.1
u^x
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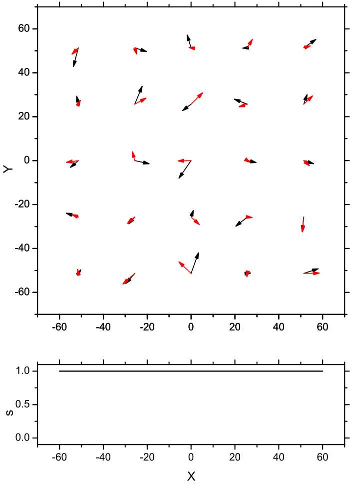
time

Results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-60 -40 -20 0 20 40 60
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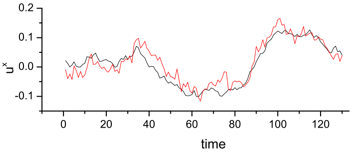
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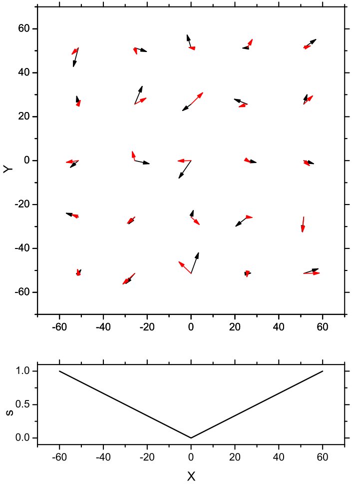
-0.1
u^x
0 20 40 60 80 100 120
time

Results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X
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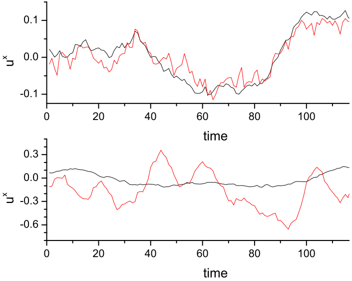
u^x
time
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0.0
-0.1
0.3
-0.3
-0.6
0
20
40
60
80
100

Conclusions

- Atomistic and continuum representations of liquid can be connected seamlessly and consistently in space and time.
- The domains of each representations can be defined arbitrarily in space and time.
- The conceptual novelty: studying the properties of different representations at the same space and time scale.
- The advantage in applications: very substantial saving on computation at the HD domain without loosing the atomistic details of the core.
- Outlook: multiple scales.

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