Time-dependent Non-Equilibrium Molecular Dynamics

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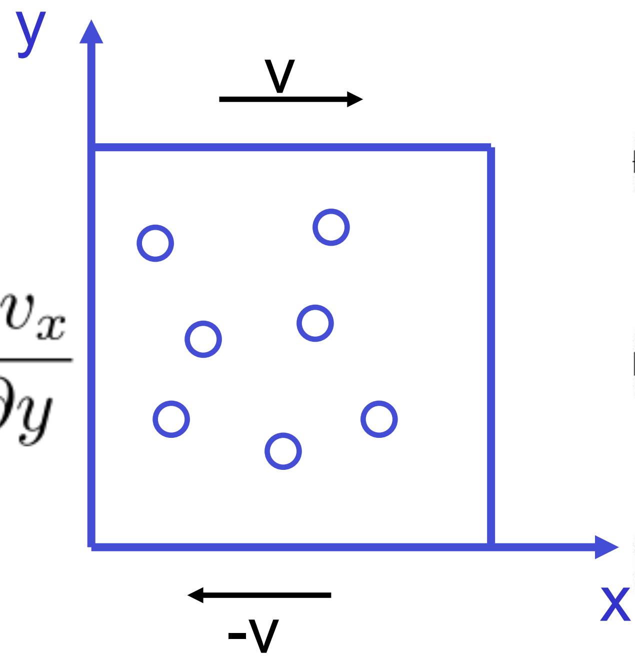
- **t-dependent averages in NEMD (Onsager-Kubo)**
- **sampling an initial condition ensemble by MD**
- **beyond macroscopic Hydrodynamics: Convective cells and relaxation of an interface**

What we mean by Non-Equilibrium

TRANSPORT

SHEAR

$$J_{xy} = \eta \frac{\partial v_x}{\partial y}$$



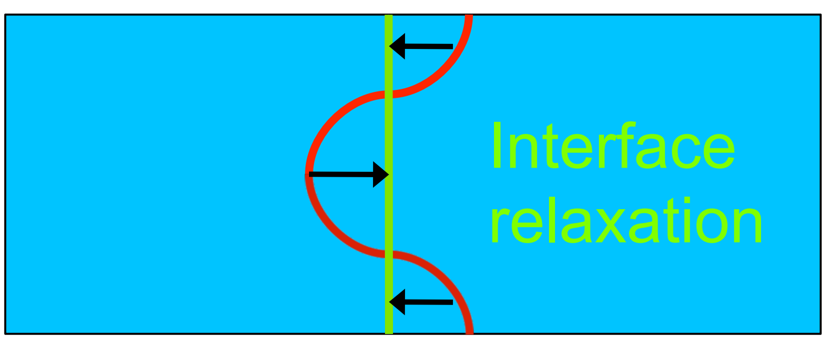
$$\rho(\vec{x},t) = < \hat{\rho}(\vec{x}) >_{ne}$$

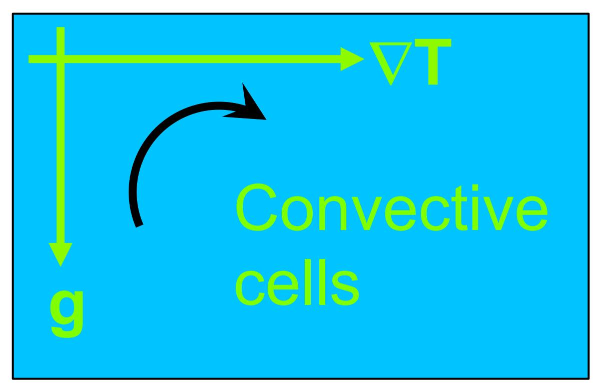
$$\hat{\rho}(\vec{x}) = \sum_i \mu_i \delta(\vec{x} - r_i)$$

$$\vec{v}(\vec{x},t) = \frac{< \vec{\hat{p}}(\vec{x}) >_{ne}}{\rho(\vec{x},t)}$$

$$\vec{\hat{p}}(\vec{x}) = \sum_i \vec{p}_i \delta(\vec{x} - r_i)$$

HYDRODYNAMICS





NEMD (1)

- Assume that a given, time-dependent external local field $\psi(x,t)$ is coupled to our system via a suitable local property

$$A(x|\Gamma) = \sum_{i=1,N} A_i(\Gamma)\delta(r_i - x)$$

- The total Hamiltonian of the system is $\mathcal{H}(\Gamma,t) = \mathcal{H}_0(\Gamma) + \mathcal{H}_p(\Gamma,t)$

$\mathcal{H}_0$ standard equilibrium Hamiltonian

$$\mathcal{H}_P(\Gamma) = -\int dx A(x|\Gamma)\underline{\psi(x,t)}$$

$$= -g\,\chi(t)\sum_i A_i\phi_i \qquad \boxed{\psi(x,t) = g\phi(x)\chi(t)}$$

NEMD (2)

PERTURBED SYSTEM:

- Equations of motion

$$\begin{cases} \dot{r} = \frac{\partial H_0}{\partial p} + \frac{\partial H_p}{\partial p} = \frac{p}{\mu} - g\frac{\partial h_p}{\partial p}\chi(t) \\ \dot{p} = -\frac{\partial H_0}{\partial r} - \frac{\partial H_p}{\partial r} = F + g\frac{\partial h_p}{\partial r}\chi(t) \end{cases}$$

- Liouville equation

$$\frac{\partial m}{\partial t} = iLm = iL_0 m + iL_p m \equiv \{\mathcal{H}_0, m\} + \{\mathcal{H}_p, m\}$$

with $m(\Gamma, t) = S^\dagger m(\Gamma, 0)$

$$S^\dagger(t) = S_0^\dagger(t) + \int_{-\infty}^{t} d\tau S^\dagger(t-\tau) iL_p(\tau) S_0^\dagger(\tau)$$

an observable J of the system evolves with

$$\hat{J}(t) \equiv \hat{J}(\Gamma(t)) = S(t)\hat{J}(\Gamma(0))$$

NEMD (2)

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with $m(\Gamma, t) = S^\dagger m(\Gamma, 0)$

$m_0(\Gamma) = m(\Gamma, 0)$ is a given initial distribution which can be sampled by MD if it comes from a stationary state (in particular but not necessarily an equilibrium one)

Dynamical NEMD [Ciccotti, Jacucci '75]

The time-dependent NE average of a given observable

$$\frac{d\hat{J}}{dt} = -iL\hat{J} \quad , \quad \hat{J}(t) = S(t)\hat{J}$$

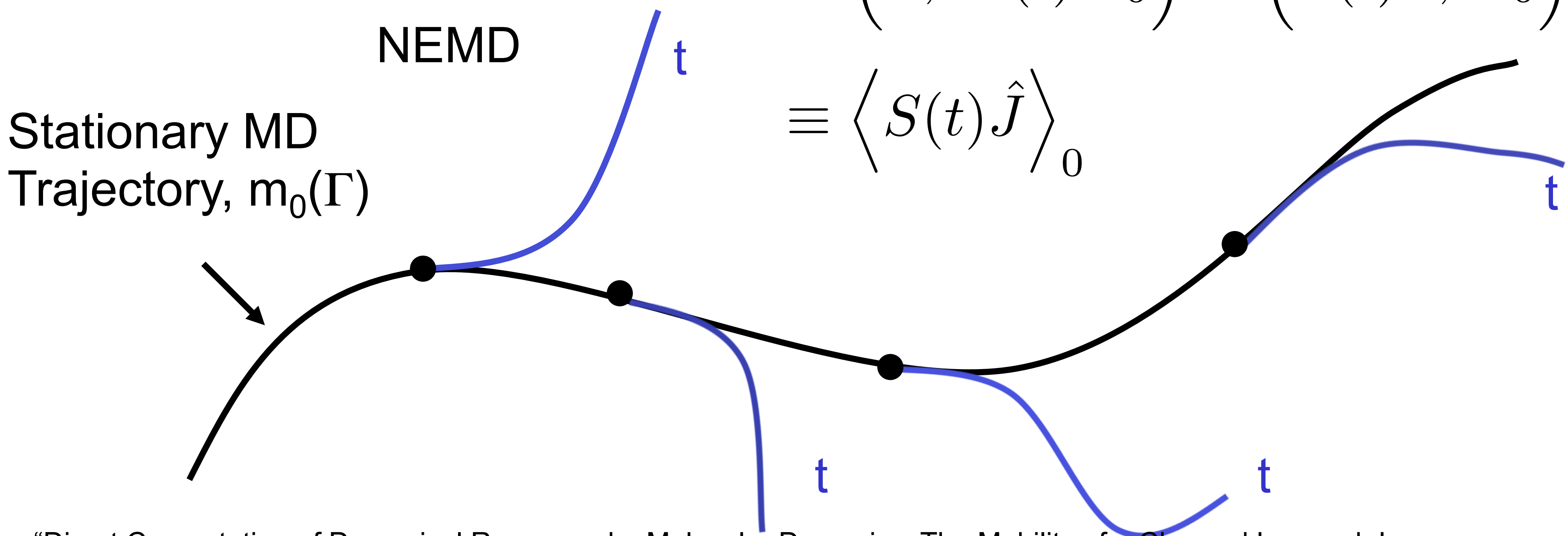
can be obtained as follows

(Onsager-Kubo equation)

$$J(t) = \left\langle \hat{J} \right\rangle_{NE}^{t} = \int d\Gamma \hat{J}(\Gamma) m(\Gamma, t)$$

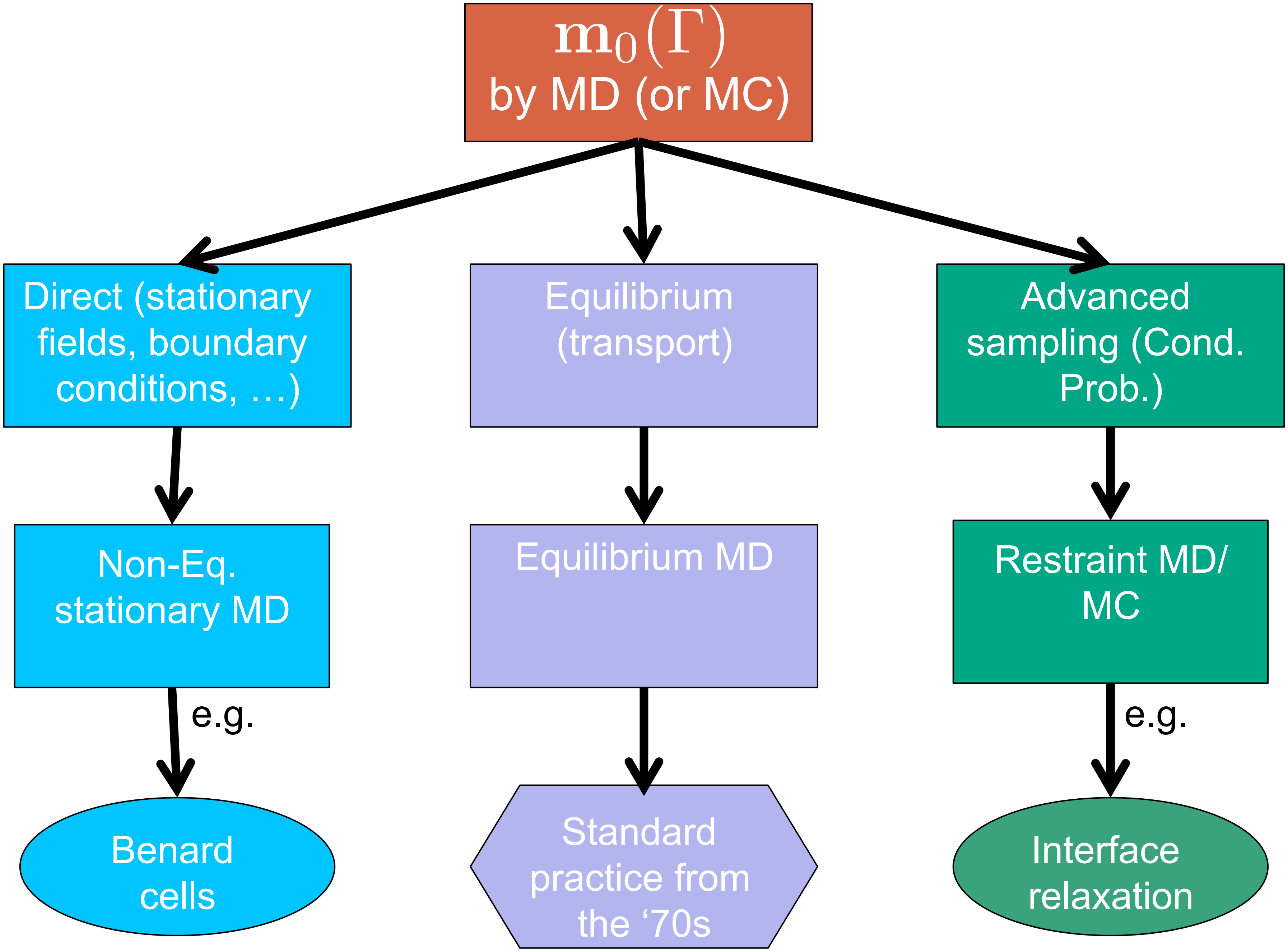
$$\equiv \left(\hat{J}, S^{\dagger}(t) m_0 \right) = \left(S(t)\hat{J}, m_0 \right)$$

$$\equiv \left\langle S(t)\hat{J} \right\rangle_0$$



"Direct Computation of Dynamical Response by Molecular Dynamics: The Mobility of a Charged Lennard-Jones Particle", G. Ciccotti and G. Jacucci, Phys. Rev. Lett. 35 (1975), 789--792

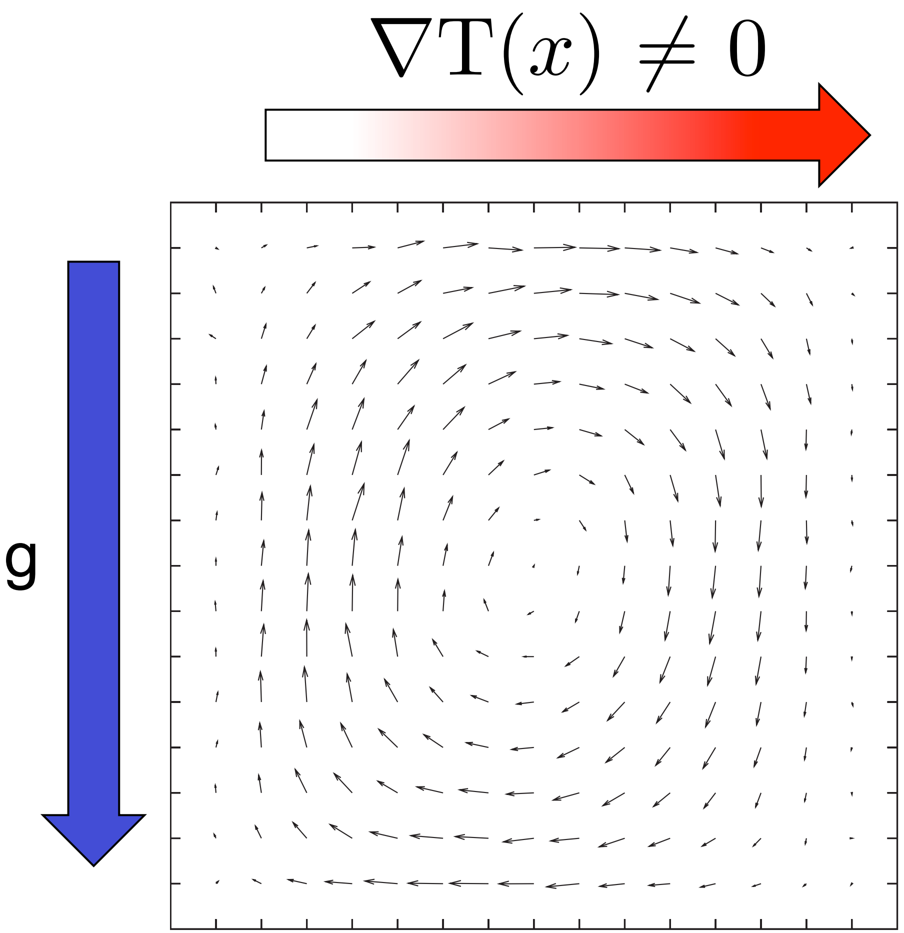
Sampling of the initial distribution



Convection

- Sampling $m_0(\Gamma) = m(\Gamma, t = 0)$: standard stationary Non-Equilibrium MD with $\nabla \mathrm{T}(x) = \mathrm{const.}, g = 0$

- Sampling $J(x, t)$: standard segments of MD, starting at t= 0, with $\nabla \mathrm{T}(x) = \mathrm{const.}$, $g = const.$

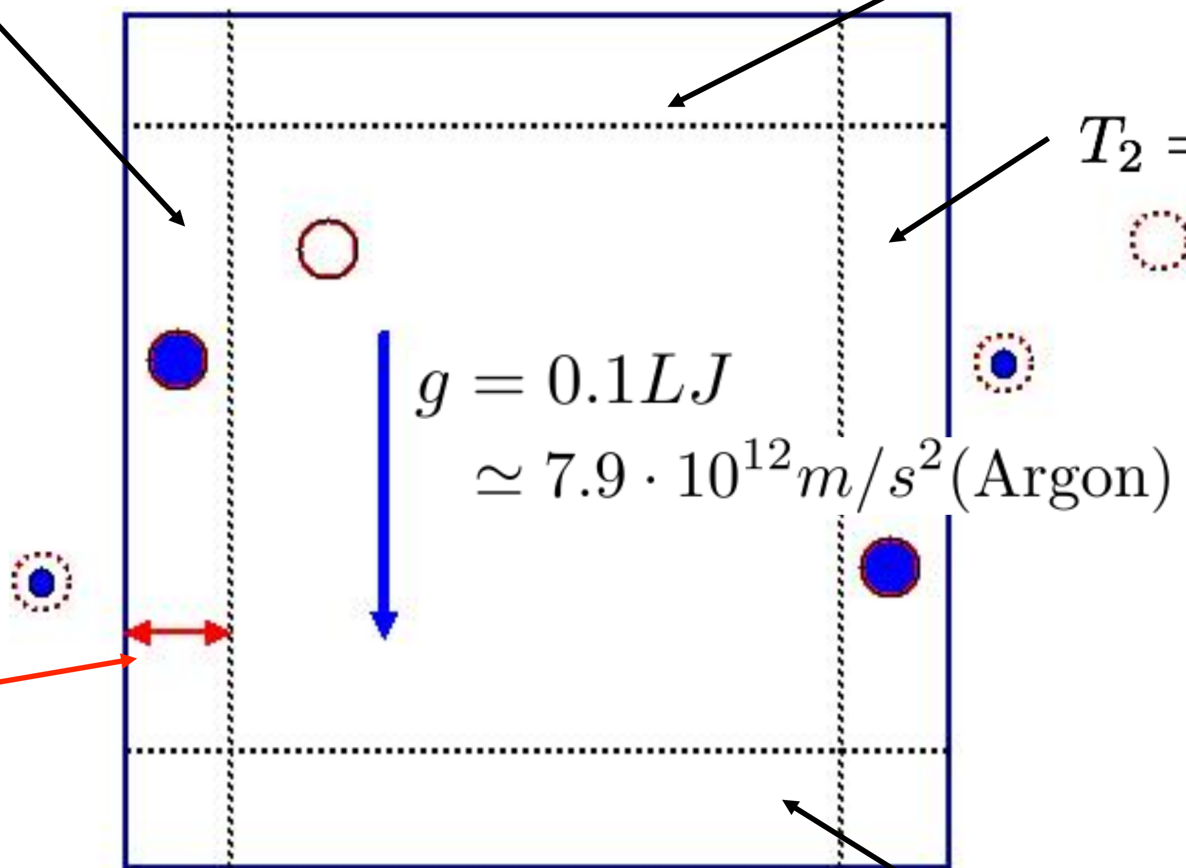


Convection

$T_1 = 1.5$ LJ$\approx 180K$

Confining field $\psi(z)$

$T_2 = 9.9$ LJ$\approx 1196K$



$$g = 0.1LJ$$
$$\simeq 7.9 \cdot 10^{12} m/s^2 (\text{Argon})$$

$l > r_{cut}$ of the potential

$\psi(z)$

$L_{BOX} = 84.9\text{LJ} \approx 289 \overset{o}{A}$ $\quad N_p = 5041$

Averages over 1000 segments

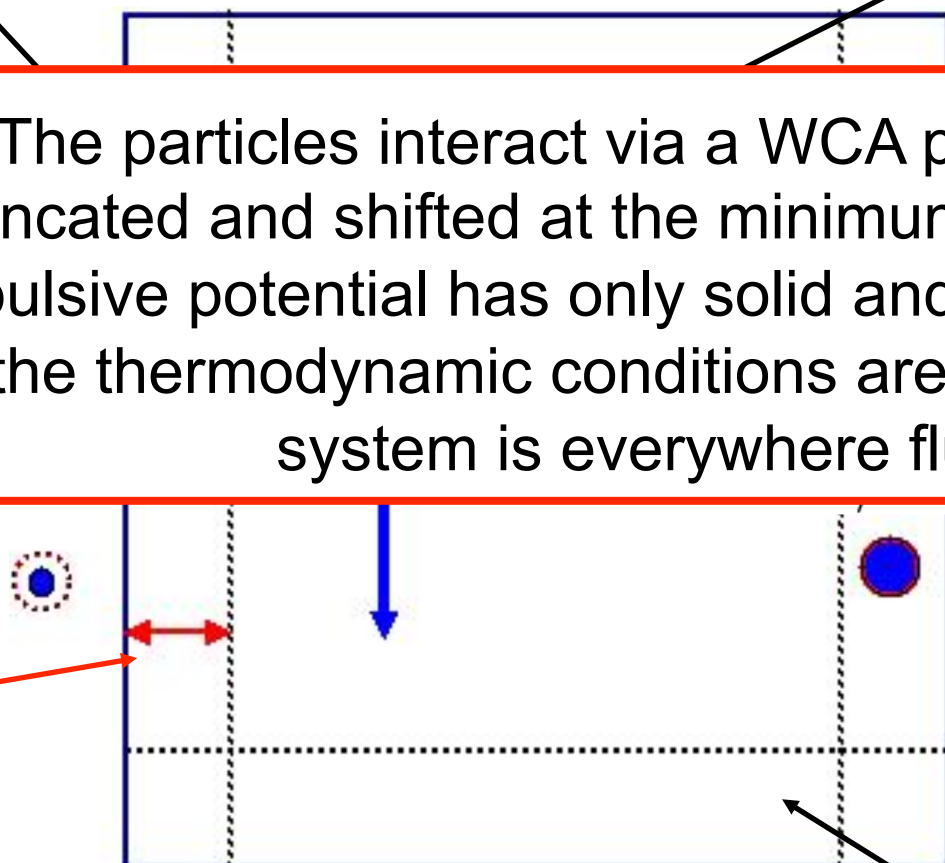
Convection Cells

$T_1 = 1.5 \text{ LJ} \approx 180K$

Confining field $\psi(z)$

$1196K$

The particles interact via a WCA potential (a LJ truncated and shifted at the minimum). A completely repulsive potential has only solid and fluid states and the thermodynamic conditions are such that the system is everywhere fluid.



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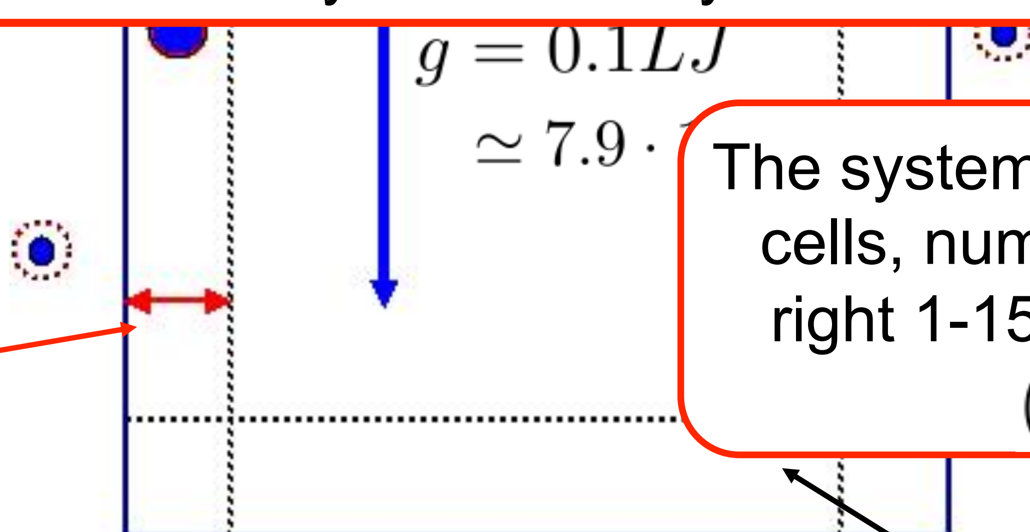

The system is divided in 15*15 cells, numbered from left to right 1-15. A generic cell is (n_x, n_y)

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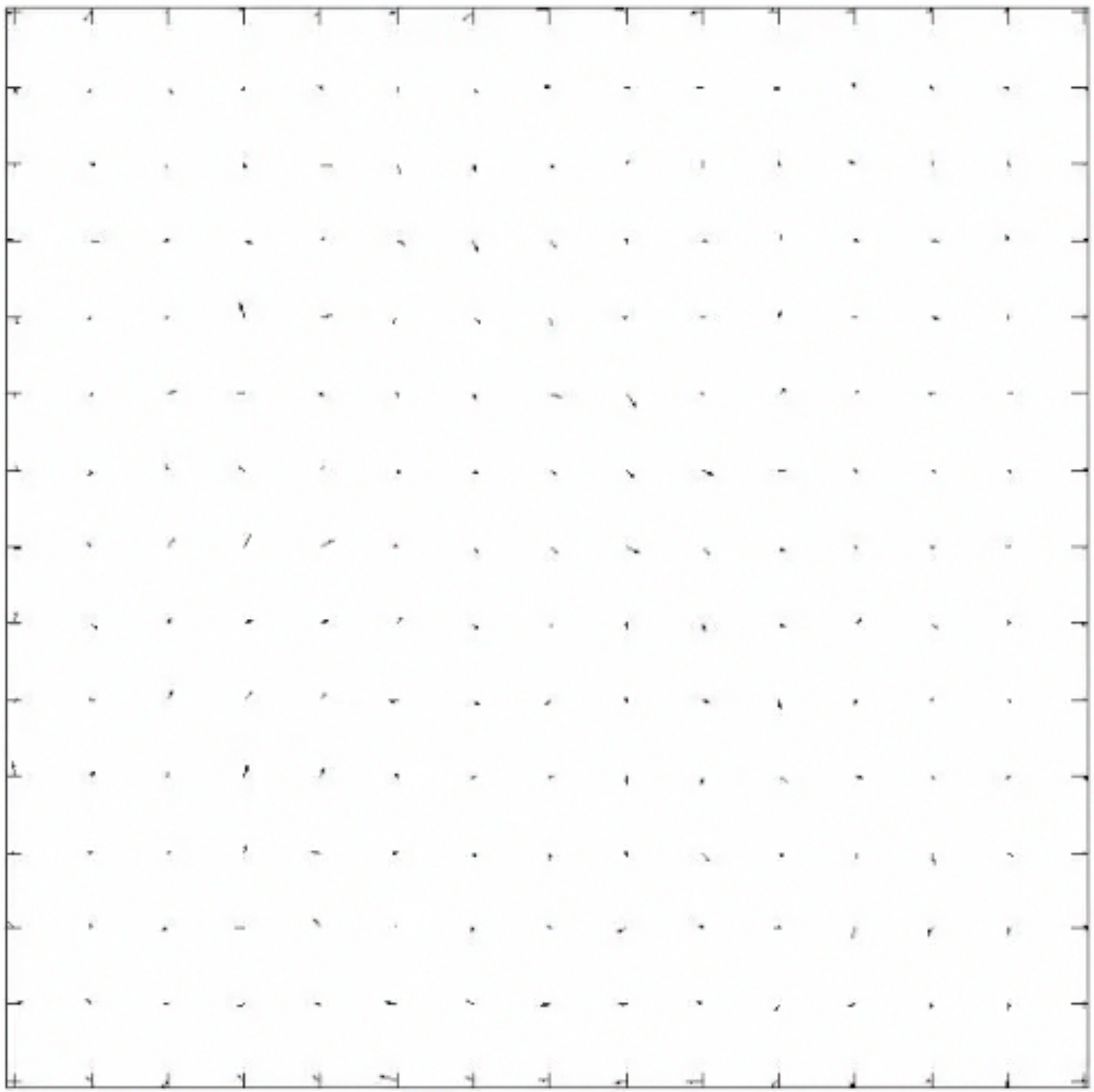
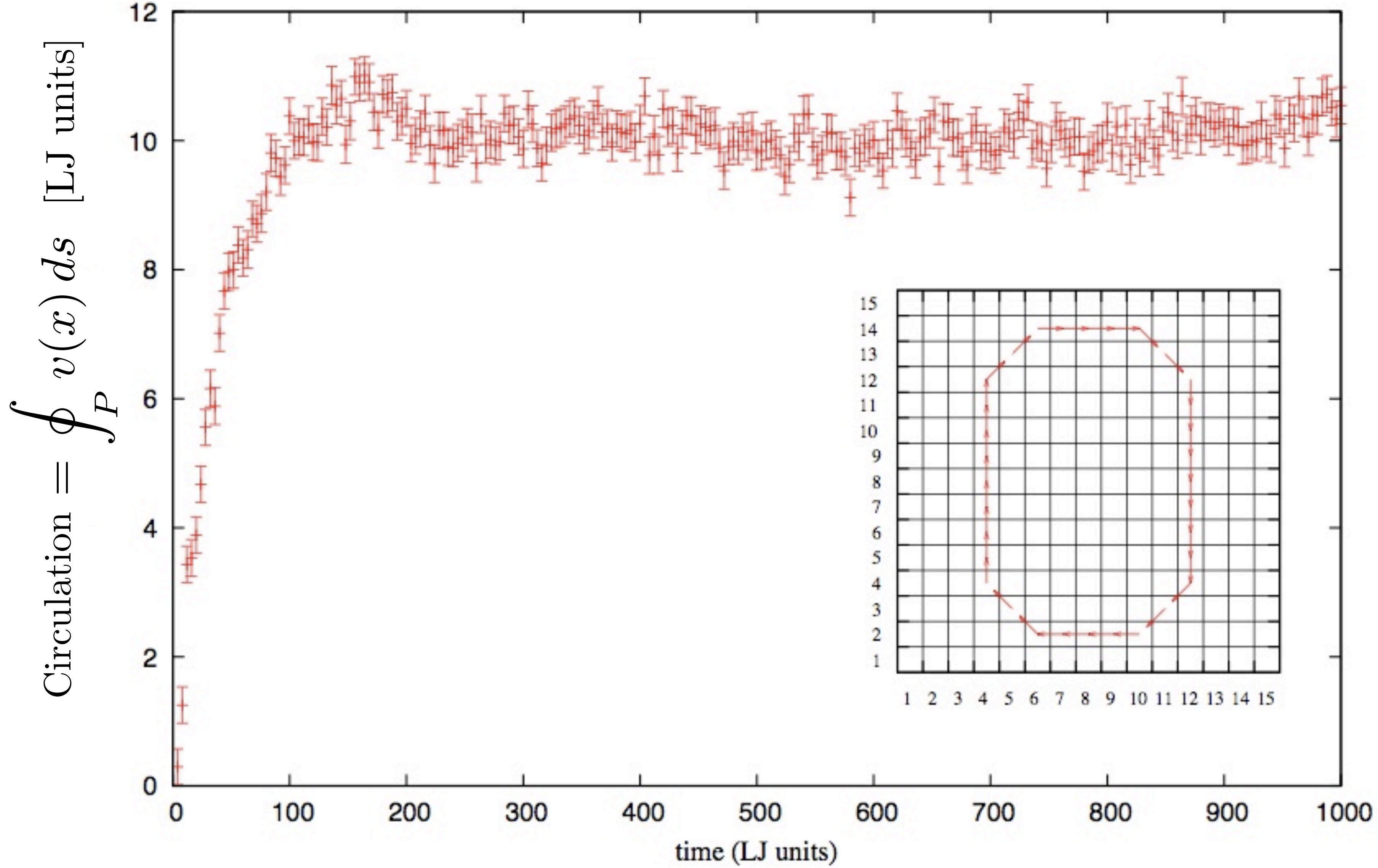
Establishing Convective Cells



Establishing Convective Cells

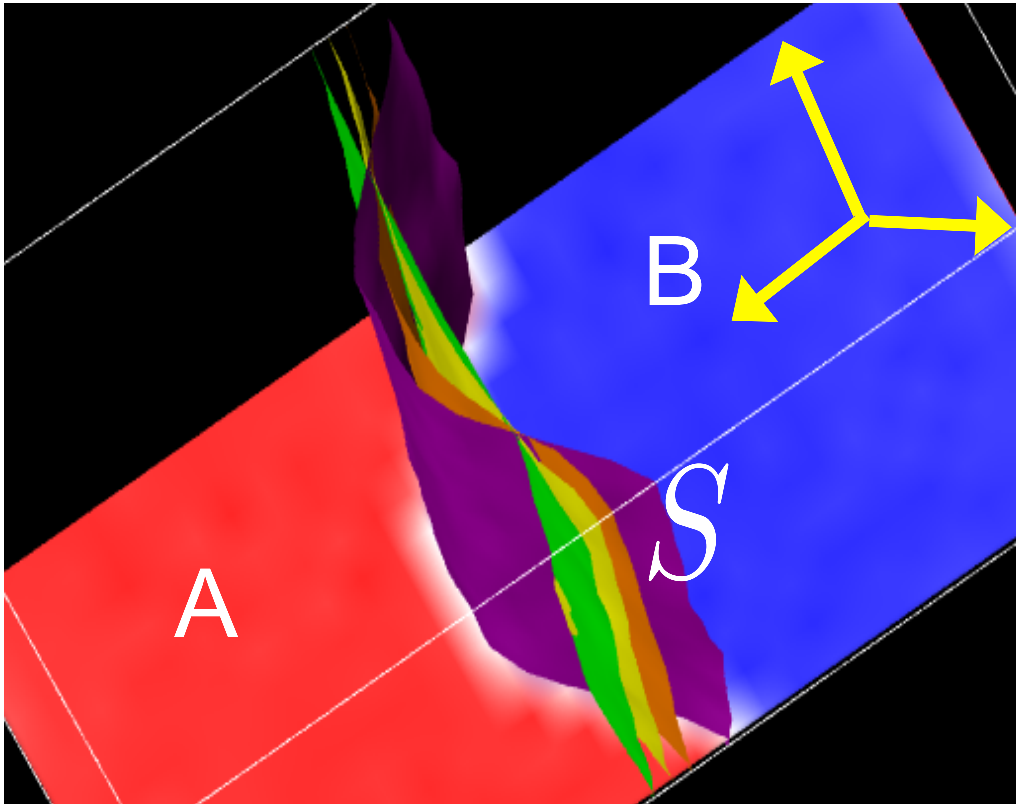
Circulation of the velocity field. The inset shows the path.



Interface Relaxation

- Sampling
  $m_0(\Gamma) = m(\Gamma|\Delta\rho(x) = 0, x \in S)$,
  where $\Delta\rho(x) = \rho^A(x) - \rho^B(x)$:
  restrained MD with $\Delta\rho(x) = 0$
  for $x \in S$ and S a given
  initial interface

- Sampling $J(x,t)$:
  standard segments of MD with
  system Hamiltonian



Hydrodynamics by NEMD

- Field at the grid point $\vec{x}_\beta$ of a discrete decomposition of the simulation box, with the atoms in the phase space point $r,p \equiv (\vec{r}_1,\ldots,\vec{p}_N)$:

$$\hat{O}(\vec{x}_\alpha;\ r,p) = (1/\Omega_\alpha)\int_{\Omega_\alpha} d\vec{x}\sum_{i=1}^{N}\delta\left(\vec{x}-\vec{r}_i\right)O_i(r,p)$$

Where:

- $O_i(r,p) = \mu_i$ for the density
- $O_i(r,p) = p_i$ for the momentum density
- …

Hydrodynamics by NEMD

- The field at time t given initial macroscopic conditions is (Onsager-Kubo)

$$O\left[x,\ t \mid \Delta\rho\left(x_\alpha\right)=0, x_\alpha \in S\right] =$$

$$\int dr^0\, dp^0 m_0\left[r^0, p^0 \mid \Delta\rho\left(x_\alpha\right)=0, x_\alpha \in S\right] \hat{O}\ \left(x;\ r(t), p(t)\right)$$

where

$$m_0\left[r^0, p^0 \mid \Delta\rho(x_\alpha; r^0)=0, x_\alpha \in S\right] = \frac{\exp\left[-\beta H(r^0, p^0)\right] \prod_{x_\alpha \in S} \delta\left(\Delta\rho(x_\alpha; r^0)\right)}{Z * P_{\Delta\hat{\rho}}[\Delta\hat{\rho}(x_\alpha; r^0)=0, x_\alpha \in S]}$$

and $\begin{pmatrix} r(t) \\ p(t) \end{pmatrix} \equiv \begin{pmatrix} r(t;\ r^0, p^0) \\ p(t;\ r^0, p^0) \end{pmatrix}$

unrestrained MD started from a sample of points taken along a restrained MD (next slide)

Conditional Averages by Restrained MD

- $\delta\left(\Delta\rho(x_\alpha;r^0)\right)$ is smoothed by a Gaussian and the sampling of the ensemble at $\Delta\hat{\rho}(\vec{x}_\alpha;r^0)=0$ on the surface S is performed by restrained MD

$$\langle O(\vec{x}_\beta;r(t))\rangle_{cond} = \lim_{k\to\infty} \frac{\left\langle O(\vec{x}_\beta;r(t))\prod_{\vec{x}_\alpha\in S}\exp[-\beta\frac{k}{2}\Delta\hat{\rho}(\vec{x}_\alpha;r^0)^2]\right\rangle_H}{\left\langle\prod_{\vec{x}_\alpha\in S}\exp[-\beta\frac{k}{2}\Delta\hat{\rho}(\vec{x}_\alpha;r^0)^2]\right\rangle_H}$$

$$= \lim_{k\to\infty}\langle O(\vec{x}_\beta;r)\rangle_{H'}$$

where:

$$H'(r,p) = H(r,p) + \frac{k}{2}\sum_{\vec{x}_\alpha\in S}\Delta\hat{\rho}(\vec{x}_\alpha;r)^2$$

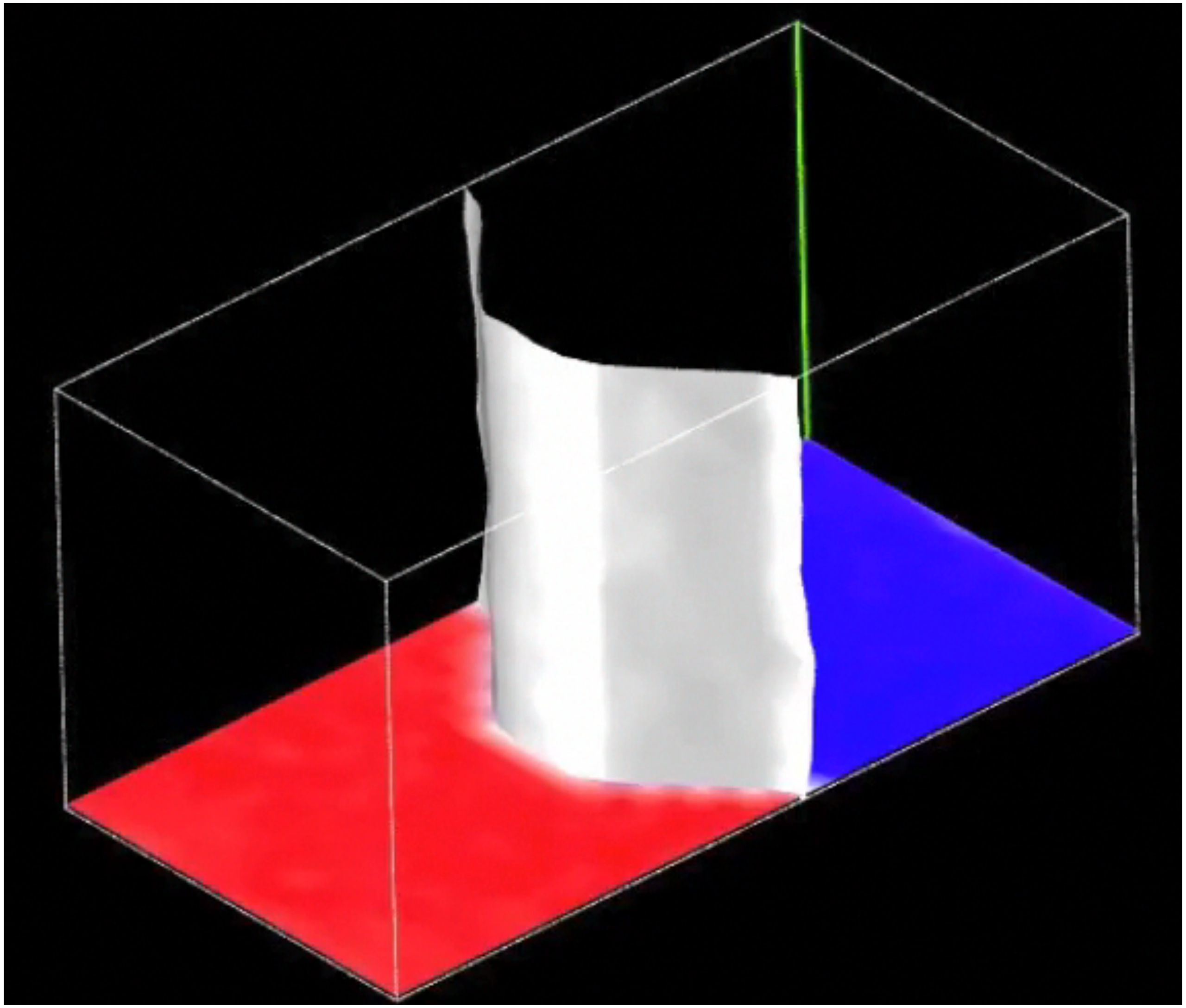
Simulation Details

- 171500 particles: 88889 particles A, 82611 particles B
- Pair potential: $u^{AA}(r) = u^{BB}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$ $u^{AB}(r) = 4\varepsilon\left(\frac{\sigma}{r}\right)^{12}$
- Simulation box: ~(90 x 45 x 45) σ
- Average density: 1.024 particles*σ^3
- Temperature: 1.5 ε/k_b

In the fluid domain of pure L-J

- Simulation time:
  - Restrained MD: 75000 steps
  - Unrestrained MD: 600000 steps
- fields are averaged over (only) 40 unrestrained trajectories (for the moment)

$$\Delta\rho(\vec{x}_\alpha;t) = 0$$



$$v(\vec{x}_{\alpha,\max}) \sim 80\ m/s$$

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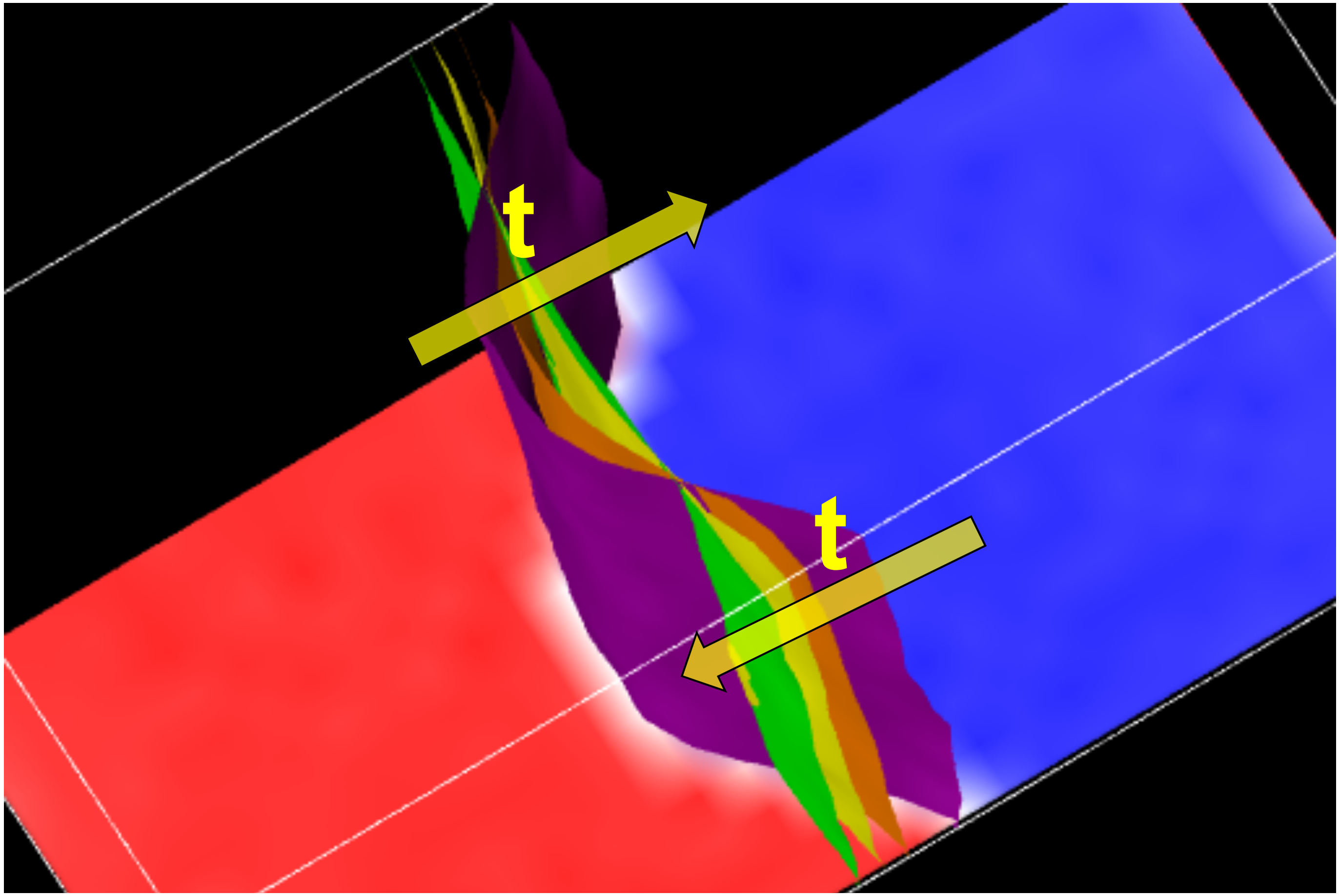

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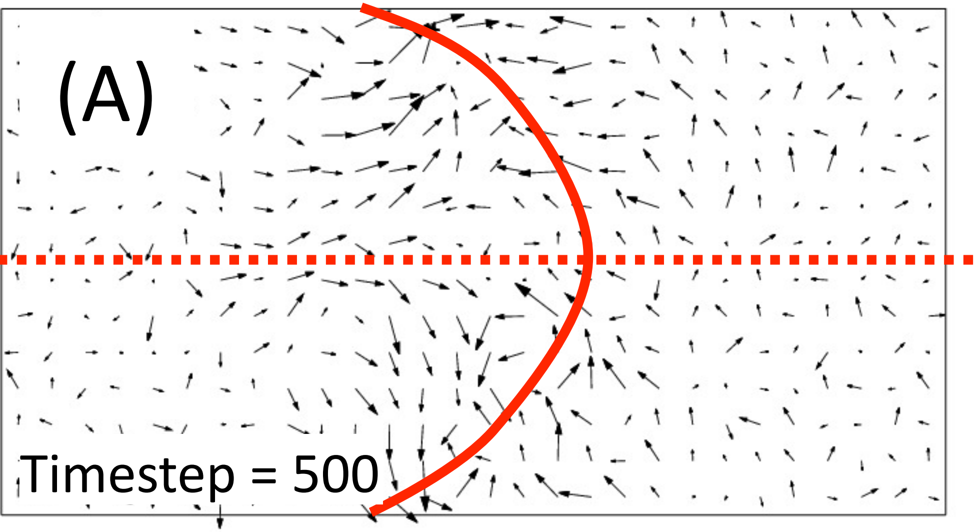
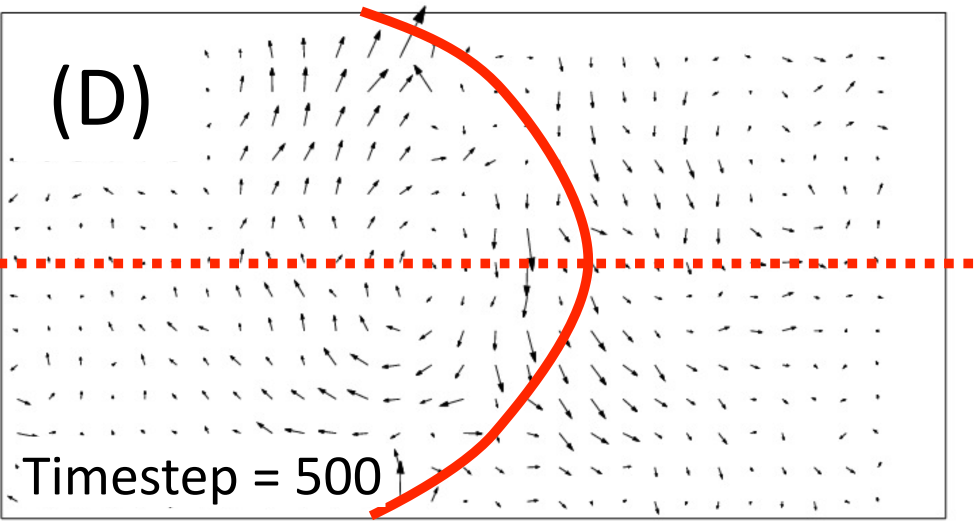
Rigorous non-equilibrium ensemble averages *vs* local time averages



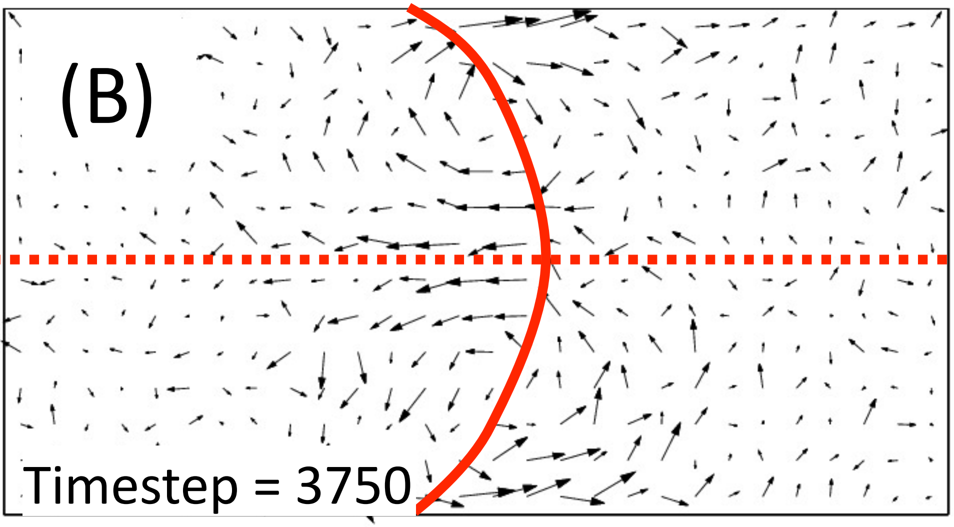
$$\vec{v}(\vec{x},t) = \frac{< \vec{\hat{p}}(\vec{x},t) >_{H'}}{\rho(\vec{x},t)}$$



$$\vec{v}_l(\vec{x},t) = \frac{\frac{1}{2\tau}\int_{t-\tau}^{t+\tau} ds\ \hat{p}(\vec{x},s)}{\frac{1}{2\tau}\int_{t-\tau}^{t+\tau} ds\ \hat{\rho}(\vec{x},s)}$$

- The surface relaxes to the equilibrium by forming initially a two-tail profile of the velocity field that then stabilizes into a double-roll profile
- The velocity field obtained via the local time average technique violates the symmetry of the problem

Rigorous non-equilibrium ensemble averages *vs* local time averages



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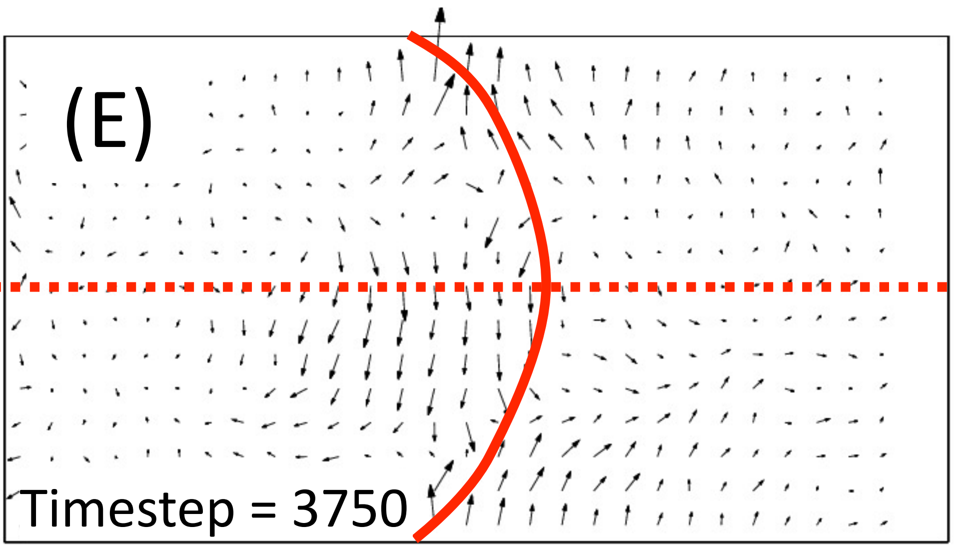

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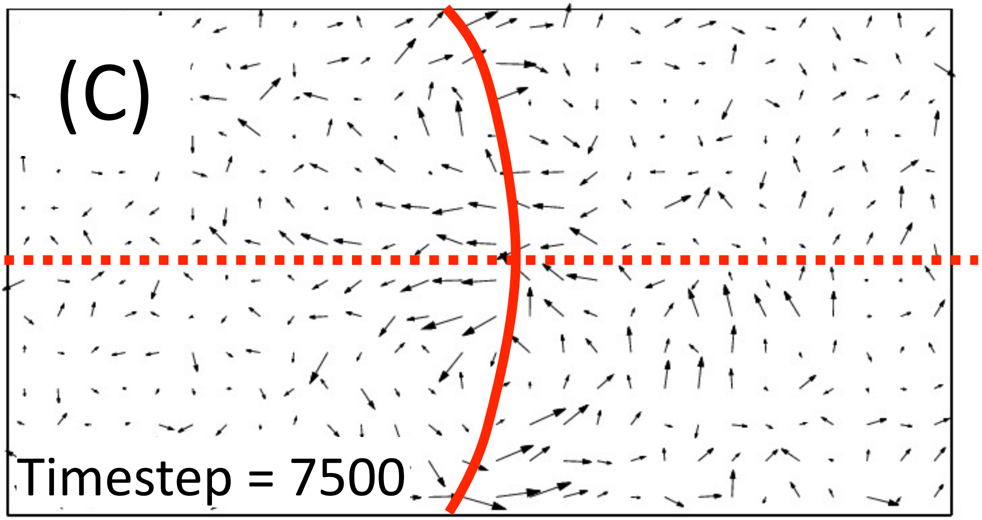

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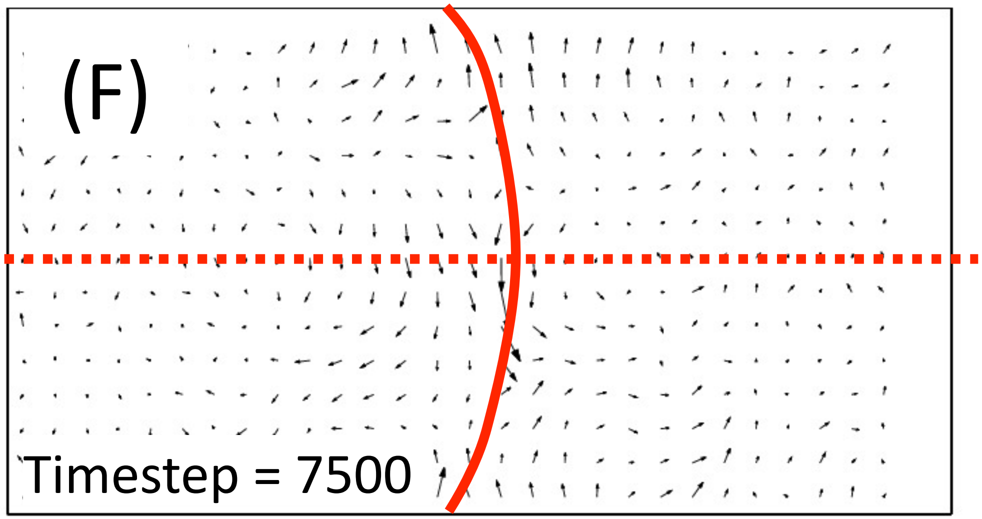

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Conclusions

① It is possible to compute, numerically but, otherwise, rigorously, **time-dependent non-equilibrium responses,** i.e. responses in non-stationary regimes. Local time-averages should be avoided

② Nonequilibrium atomistic dynamics possibly combined with the ability to compute conditional averages (restrained MD) allows to simulate hydrodynamic phenomena *ab initio* (without using phenomenological approximations).

③ **Coupling non-equilibrium non-stationary systems** is a fundamental question of multi-scale approaches

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iit ISTITUTO ITALIANO DI TECNOLOGIA

MARIE CURIE ACTIONS

Computer resources

CINECA

ICHEC Irish Centre for High-End Computing