Molecular Dynamics: an outlook

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Molecular Dynamics: an outlook

- Where from MD simulations?
- What is MD?
- MD(or, for that, MC) as Equilibrium Statistical Mechanics
- A challenging case: Rare Events and Free Energies
- MD as Non-Equilibrium StatMech (➔ multiscale etc)
- Hydrodynamics from an atomistic viewpoint

if time permits

- Holonomic constraints and *Blue Moon*

Where from MD simulations?

The fundamental law

In principle, the behavior of a piece of matter in ordinary conditions comes out of *t*-dependent Schroedinger Equation and QStatMech with

[Relativistic Quantum Field Theory not needed for that!]

$$\mathcal{H}(r, R; p, P) = K_N(P) + \underbrace{K_e(p) + \underset{\text{Coulomb}}{\underline{V(r, R)}}}_{H_e(r, p|R)}$$

$$\boxed{i\hbar\frac{\partial\widetilde{\Psi}(r, R, t)}{\partial t} = \mathcal{H}\widetilde{\Psi}(r, R, t) \;\Leftrightarrow\; \mathcal{H}\Psi_n = E_n\Psi_n}$$

Not Soluble by Brute Force

Born-Oppenheimer approximation

since $m_N \gg m_e$

$$H_e(r,p\,|R)\Phi_s(r\,|R) = E_s(R)\Phi_s(r\,|R)$$

and $|\nabla_R \Phi_s| \ll |\nabla_r \Phi_s|$

$$\boxed{\Psi(r,R;t) = \sum_s \chi_s(R;t)\Phi_s(r|R) \simeq \chi_0(R;t)\Phi_0(r|R)}$$

i.e. the (often valid) **adiabatic approximation**

where

Where from MD simulations?

$\chi_0(R;t)$ is given by

$$\boxed{\begin{aligned} \imath\hbar\frac{\partial}{\partial t}\chi_0(R;t) &= \mathcal{H}_N(R,P)\chi_0(R;t) \\ &\equiv \left[K_N(P) + E_0(R)\right]\chi_0(R;t) \end{aligned}}$$

the strict adiabatic approximation (no electronic jumps allowed)

the dynamics of the nuclei, apparently independent from the electrons, is driven by $E_0(R)$ as interaction potential (a mean field, modelizable, no more Coulomb!)

Where from MD simulations?

when

- nuclei are heavy enough
- temperature is high enough so that

$$\Lambda = \frac{h}{\sqrt{m_N k_B T}} << \text{internuclear} \quad r$$

Dynamics, no more quantum, is Newton:

$$\boxed{m_N \ddot{R} = -\nabla E_0(R)}$$

Where from MD simulations?

to sum up:

- a classical system of particles interacting via an *effective* interaction potential, E_0

- E_0 can be obtained *ab initio (AIMD)* or by some suitable fitting procedure➔phenomenological model, e.g. with a Pairwise Additive Potential, $V(R) = \sum_{i<j} v(R_{ij})$

- if PAP, the equations of motion are numerically integrable for a number of particles finite but large enough to study, by statistical approach, the thermal properties of matter

Equilibrium (classical) Statistical Mechanics (1)

- a closed system evolving in time under time-independent forces will reach a STATIONARY state

- the microscopic properties are ‘irrelevant’ while the statistical (or macroscopic) are stable and interesting (THERMODYNAMICS).

They can be computed by time or ensemble averages:

Equilibrium (classical) Statistical Mechanics (2)

$$O = \overline{\hat{O}(R,P)} \equiv \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt\, \hat{O}(R(t), P(t))$$

$$= \frac{1}{\mathcal{N}} \sum_{i=1}^{\mathcal{N}} \hat{O}\left(R(ih), P(ih)\right) = \sum_{l \in \text{visited states}} \left[\frac{n_l}{\mathcal{N}}\right] \hat{O}_l$$

$$\simeq \int dR dP\, \rho(R,P) \hat{O}(R,P) = \langle \hat{O}(R,P) \rangle$$

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Equilibrium (classical) Statistical Mechanics (3)

$$
\begin{aligned}
O = \overbrace{\boxed{\overline{\hat{O}(R,P)}}}^{\text{Boltzmann}} &\equiv \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} dt\,\overbrace{\boxed{\hat{O}(R(t),P(t))}}^{\text{Observable}} \\
&= \frac{1}{\mathcal{N}}\sum_{i=1}^{\mathcal{N}}\hat{O}\left(R(ih),P(ih)\right) = \sum_{l\in\text{visited states}} \underbrace{\boxed{\left[\frac{n_l}{\mathcal{N}}\right]}}_{\nu_l\text{ probability of state } l}\hat{O}_l \\
&\simeq \int dRdP\,\underbrace{\boxed{\rho(R,P)}}_{\text{Ensemble or probability density}}\hat{O}(R,P) = \underbrace{\boxed{\langle O\rangle}}_{\text{Gibbs}}
\end{aligned}
$$

- ◆ properties coming from an observable ➔ mechanical (e.g., pressure)
- ◆ properties coming from n_l or ρ , i.e. probability ➔ thermal (e.g., free energy)

(BO originated) Classical Stat. Mech. Model

Theoretically:

- $N\,(\to\infty)$ atoms / molecules $\Longleftrightarrow$ point particles (p.p.), $(r_1,\ldots,r_N)$ / connected sets of p.p., $(\{r_1\}\ldots\{r_N\})$

Interactions between p.p., $V_N\left(\{r_1\}\ldots\{r_N\}\right)$

- Boundary Conditions (compulsory, no BC’s no equilibrium)
- Initial Conditions (necessary to start although irrelevant for macroscopic behavior. However, they can be a headache!)
- Evolution laws: Newton equations and Laplace deterministic dream, $\{r(t;r_0,p_0),p(t;r_0,p_0)\}_{t\in(0,\tau\to\infty)}$

What is MD?

Computationally:

$$N \sim 32 \div 10^6\ (10^9), \quad n = \frac{N}{V}$$

Boundary Conditions : Periodic (PBC)

for thermodynamic
limit: min(S/V) effect

Initial Conditions: positions, regular lattice; velocities, maxwellian

V_N : *simple* pairwise additive $\left(\sum_{i<j} v_{ij};\ \mathcal{O}(N^2)\right)$; short range (MIC)

extensions: ➔ long range (Coulomb) by Ewald sums

➔ n-body potentials $\mathcal{O}(N^n)$ but glue potential

$$V_N(\alpha) \text{ with } \alpha = \sum_{i<j} \varphi_{ij} \ldots$$

➔ stiff intramolecular potentials:

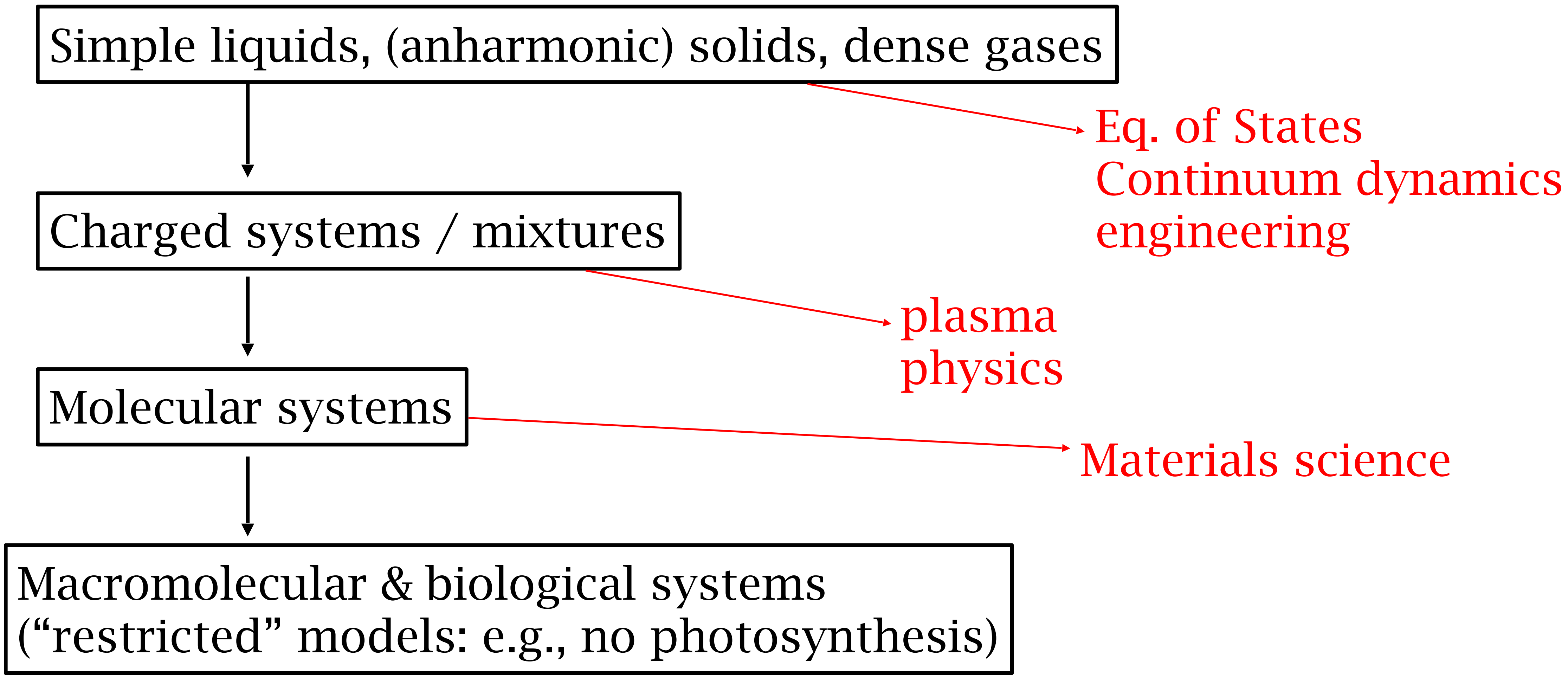
Constraints: $\sigma(r) = 0;\ m\ddot{r} = F - \lambda\nabla\sigma$: SHAKE
Multiple Time-Step (Martyna,Tuckerman, Berne) : RESPA

Integration Algorithms: robust, time reversible, symplectic
e.g. velocity Verlet

Various ensembles (thermostats, barostats …):
extended variables simulations (Andersen, Nosé, Hoover,…

APPLICATIONS

What can be done?



Simple liquids, (anharmonic) solids, dense gases

1956

Eq. of States
Continuum dynamics
engineering

Charged systems / mixtures

plasma
physics

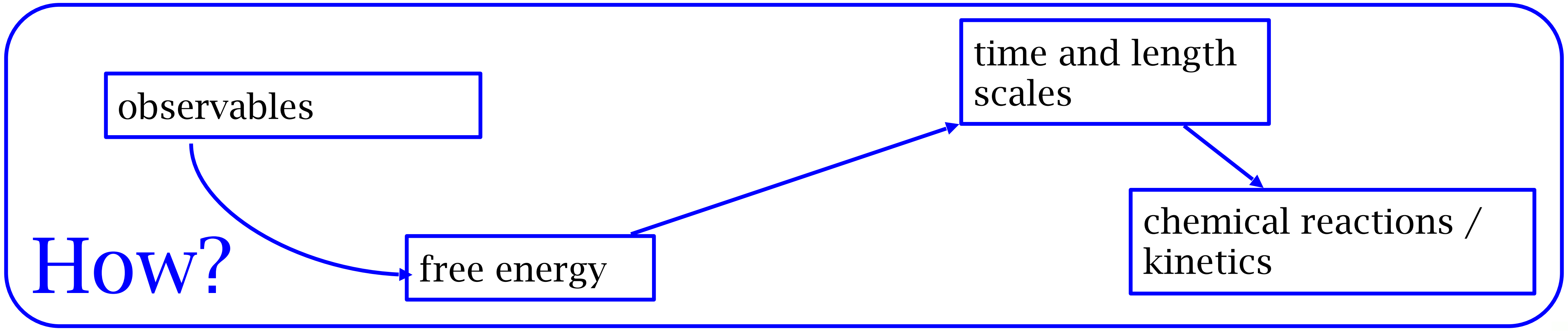
Molecular systems

1971

Materials science

Macromolecular & biological systems
("restricted" models: e.g., no photosynthesis)

1976



How?

observables

free energy

time and length scales

chemical reactions / kinetics

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Free energies for rare events

Probabilistic interpretation of the thermal properties

- Entropy (Boltzmann)

$$S(E) = k_B ln\Sigma(E) \equiv -k_B ln\frac{1}{\Sigma(E)} = -k_B lnP_E(\Gamma)$$

- Similarly in general ensembles

$$F(\cdots) = -k_B T ln \mathcal{Z}(\cdots) \approx k_B T ln[f(\Gamma)]$$

where $f(\Gamma)$ is the probability density function of the given ensemble

Mechanical vs thermal properties

Mechanical property

$$\mathcal{O} = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt\,\hat{\mathcal{O}}(\Gamma(t)) = \sum_s P_s\mathcal{O}_s =$$

Thermal property

$$= \int d\Gamma \underbrace{\begin{pmatrix}\exp[-\beta S(E)]\\ 0\end{pmatrix}}_{\frac{\delta(H(\Gamma)-E)}{\int d\Gamma\,\delta(H(\Gamma)-E)}} \hat{\mathcal{O}}(\Gamma) =$$

$$= \int d\mathcal{O}^*\mathcal{O}^*\left\{\int d\Gamma\,\delta(\hat{\mathcal{O}}(\Gamma)-\mathcal{O}^*)\frac{\delta(H(\Gamma)-E)}{\int\delta(H(\Gamma)-E)}\right\} =$$

$$= \int d\mathcal{O}^*\mathcal{O}^*P_{\hat{\mathcal{O}}}(\mathcal{O}^*)$$

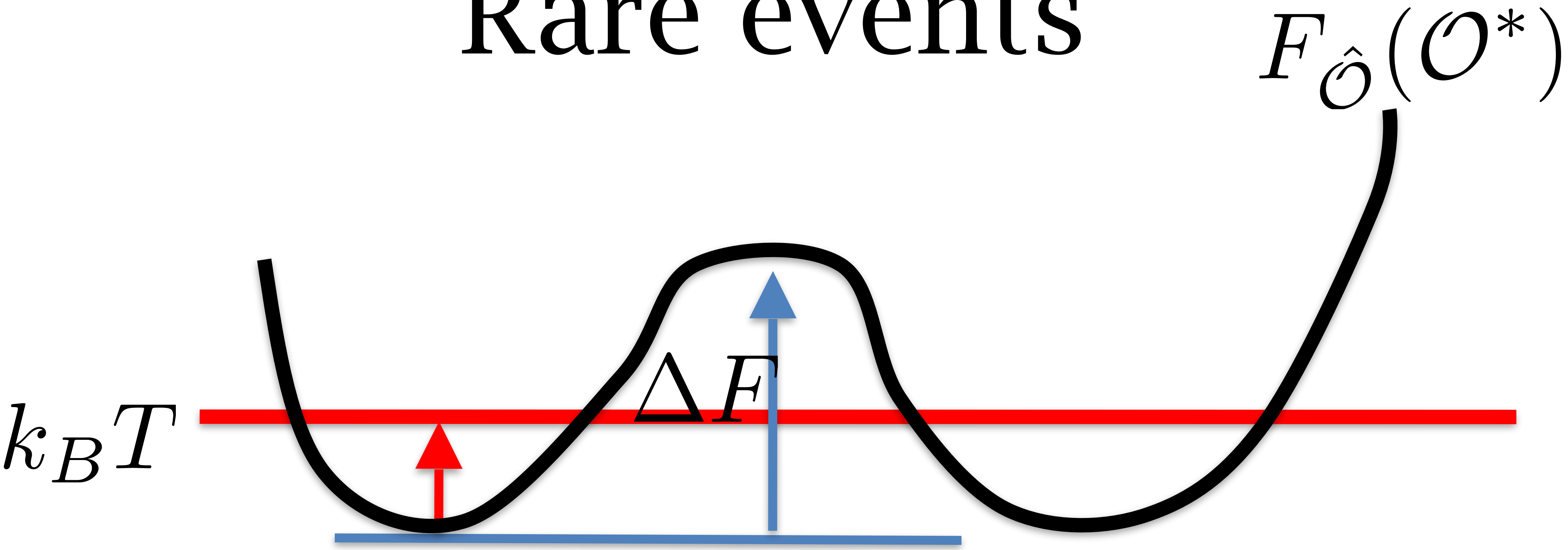
Free energy of collective variables

- Given a collective variable (i.e. a function of the configuration space) $\hat{\mathcal{O}}(x)$, the free energy associated with its probability density function is

$$-\frac{F_{\hat{\mathcal{O}}}(\mathcal{O}^*)}{T} = k_B ln P_{\hat{\mathcal{O}}}(\mathcal{O}^*) =$$

$$k_B \ln \frac{\int d\Gamma f(\Gamma)\delta(\hat{\mathcal{O}}(x)-\mathcal{O}^*)}{\mathcal{Z}}$$

Rare events



$$\tau \propto \exp\left[\frac{\Delta F}{k_BT}\right]$$

- If $\Delta F >> k_BT$ then $\tau >> t_{max}$

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TA-MD/MC (Temperature Accelerated Molecular Dynamics/Monte Carlo)

Accelerating the sampling of the collective coordinates so as to sample $P_{\hat{\mathcal{O}}}(\mathcal{O}^*)$, including the low probability regions

- Extended (adiabatically separated) molecular dynamics
  - atomic degrees of freedom (x)
  - Extra degrees of freedom connected to the collective variables (z)
  - Coupling potential term between x and z: $\frac{k}{2}\left(\mathcal{O}(x) - z\right)^2$

$$\begin{cases} m\ddot{x} = -\nabla V(x) - k(\hat{\mathcal{O}}(x) - z)\nabla\hat{\mathcal{O}}(x) + thermo(T) \\ \mu\ddot{z} = -k(z - \hat{\mathcal{O}}(x)) + thermo(\bar{T}) \end{cases}$$

L. Maragliano and E. Vanden-Eijnden, Chem. Phys. Lett. 426 (2006), 168

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TAMD: adiabaticity

- x are much faster than z

→ z moves according to the effective force

$$-\frac{1}{\tau}\int dt k(z-\mathcal{O}(x(t))) \overset{E.H.}{=} -\frac{\int dx\ \ k(z-\mathcal{O}(x))\exp\left[-\beta\left(V(x)+\frac{k}{2}(z-\mathcal{O}(x))^2\right)\right]}{\int dx\ \ k\exp\left[-\beta\left(V(x)+\frac{k}{2}(z-\mathcal{O}(x))^2\right)\right]}$$

(we have assumed that, apart for the z , the remaining degrees of freedom of the system are ergodic)

TAMD: the strong coupling limit

- Interpretation of the effective force as mean force

$$-\frac{\int dx\ k(z-\mathcal{O}(x))\exp\left[-\beta\left(V(x)+\frac{k}{2}(z-\mathcal{O}(x))^2\right)\right]/\mathcal{Z}}{\mathcal{Z}_k(z)/\mathcal{Z}}$$

$k \to \infty$

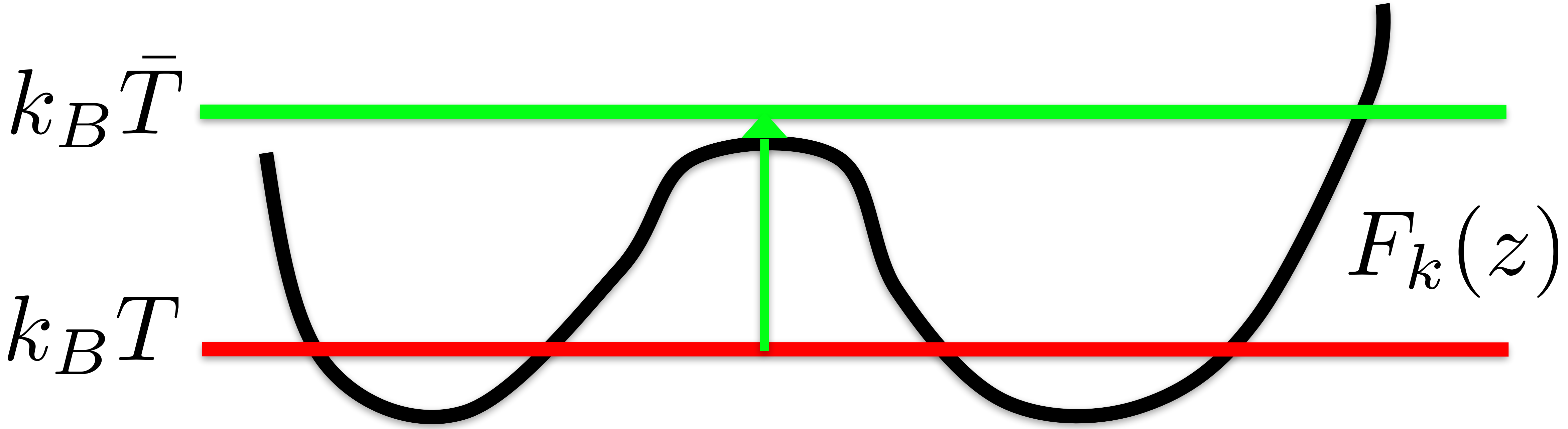
$\exp[-\beta\frac{k}{2}(\mathcal{O}-z)^2] \to \delta(\mathcal{O}-z)$

$$-\int dx \quad k(\mathcal{O}(x)-z)\frac{P(x,z)}{P(z)}$$

$$\frac{d}{dz}\beta^{-1}\ln\frac{\mathcal{Z}_k(z)}{\mathcal{Z}} \xrightarrow[k\to\infty]{} \frac{d}{dz}\beta^{-1}\ln\frac{\mathcal{Z}(z)}{\mathcal{Z}}$$

TAMD: collective variable at high temperature

$$\bar{T} >> T$$



$$\tau \propto \exp\left[\frac{\Delta F_k}{k_B\bar{T}}\right] \qquad \tau \approx t_{max}$$

Suitable interpolation algorithms (e.g. Single Sweep) can be used to reconstruct from these data the free energy surface

TAMC:
the problem of non-analytical Collective Variables

- In TAMD nuclei evolve under the action of:

$$-\nabla V(x) - k(\mathcal{O}(x) - z)\nabla \mathcal{O}(x)$$

- TAMD (but also Metadynamics, Adiabatic Dynamics, …) can be used only if the collective variable is an explicit-analytic function of the atomic positions
- In TAMC nuclei are evolved by MC instead than by MD according to the accelerated probability density function while the z 's are still evolved by MD.
  The adiabaticity conditions are easy to generalise so that we have a more powerful tool

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Where is TAMC extension important?

- Classical cases
  - Nucleation
  - Rigorous collective variable to localize vacancies in solids
- Quantum cases: let the observable be the quantum average then $\mathcal{O}(x) =< \psi(r;x)|\hat{\mathcal{O}}(r,x)|\psi(r;x) >$

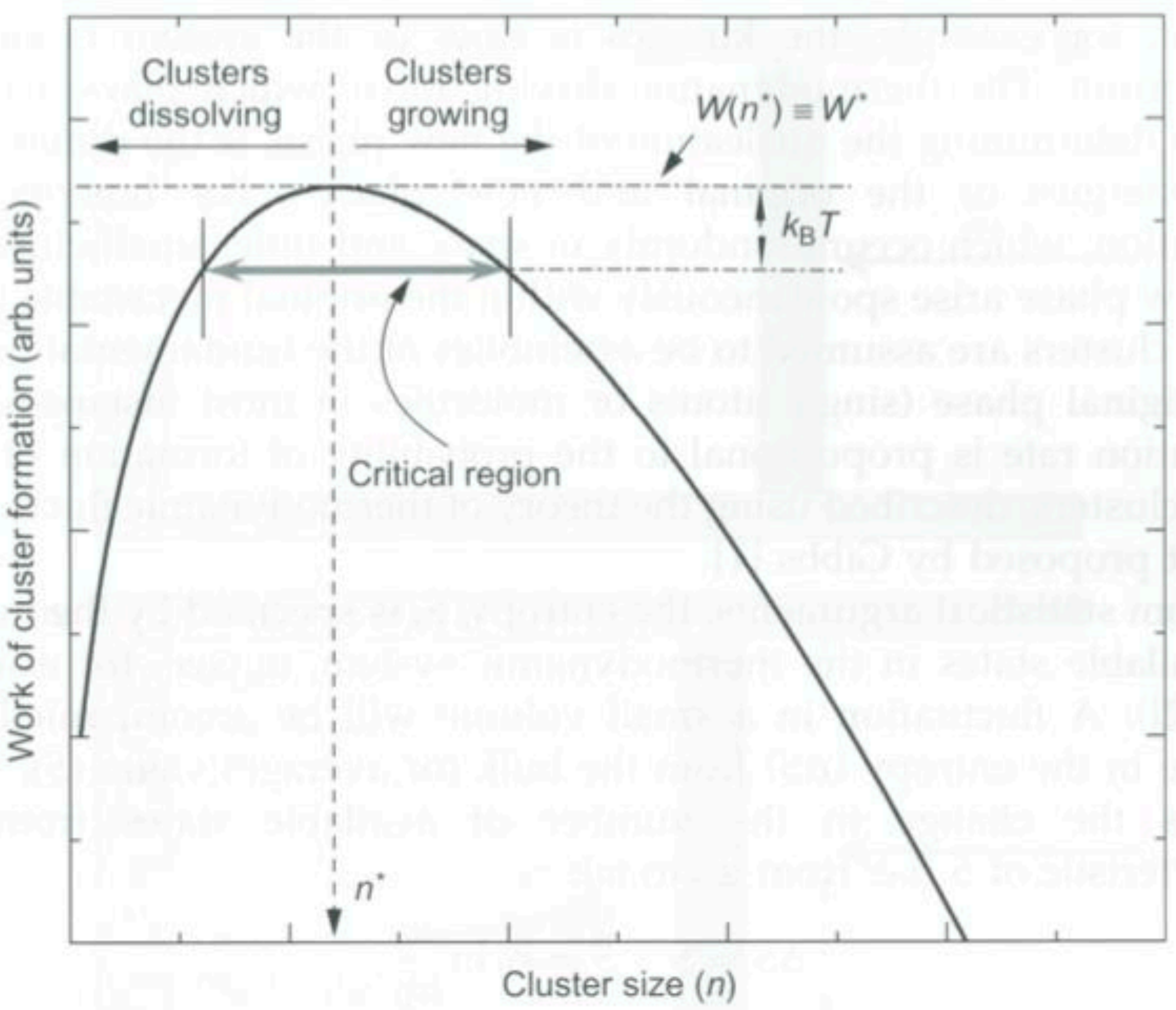
$$\begin{aligned}\nabla\mathcal{O}(x) =& < \nabla\psi(r;x)|\hat{\mathcal{O}}(r,x)|\psi(r;x) > \\ &+ < \psi(r;x)|\hat{\mathcal{O}}(r,x)|\nabla\psi(r;x) > \\ &+ < \psi(r;x)|\nabla\hat{\mathcal{O}}(r,x)|\psi(r;x) >\end{aligned}$$

therefore for TAMD, and similar techniques, we need $\nabla\psi(r;x)$

TAMC: application to the nucleation of a moderately undercooled L-J liquid

Targets

- Get the free energy as a function of the number of atoms of a given crystalline nucleus
- Critical size of the nucleus
- Mechanism of growth of the nucleus (hopefully)



Typical free energy as function of the number of atoms in the crystalline nucleus

Collective variable for nucleation

- Nucleus Size (NS): $\bar{\mathcal{N}}(x)$
  - Number of atoms in the largest cluster of (i) connected, (ii) crystal-like atoms

    (i) Two atoms with $x_{ij} \leq 1.4\,\sigma$ are connected when their q_{6m} are almost parallel[1]

$$\frac{\left|\sum_{m=-6}^{6} q(i)_{lm} q(j)_{lm}\right|}{\left|q(i)_{lm}\right| \left|q(j)_{lm}\right|} \geq 0.5$$

    (ii) Crystal-like atoms: atoms with 7 or more connected atoms[1]

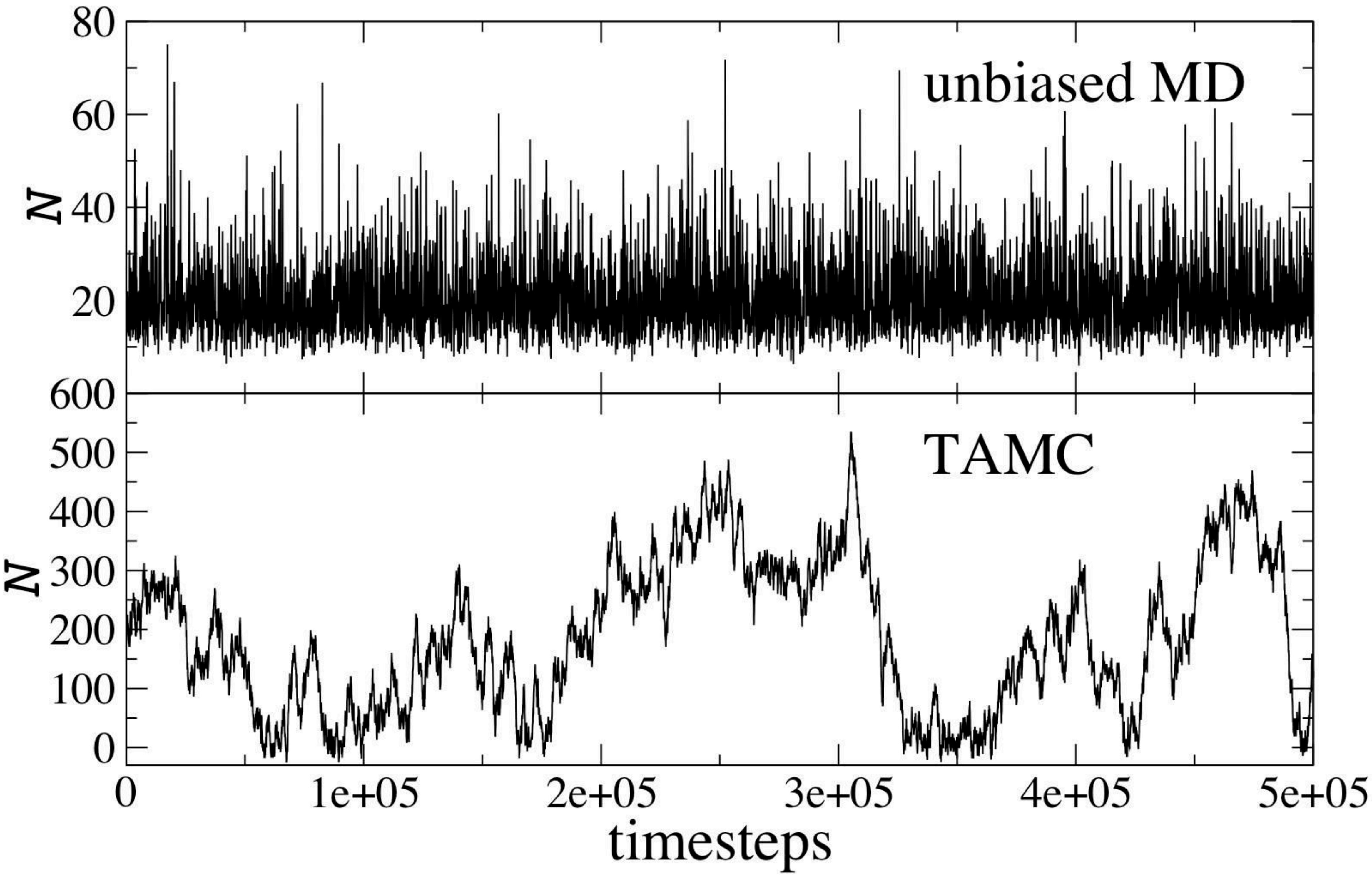
- To identify the largest cluster one has to use methods of graph theory (e.g. the “Deep First search” which we used)

↓

The NS is mathematically well defined but non analytical

1) P. R. ten Wolde, M. J. Ruiz-Montero and D. Frenkel, J. Chem. Phys. 104 (1996) 9932

Results: timeline MD vs TAMC



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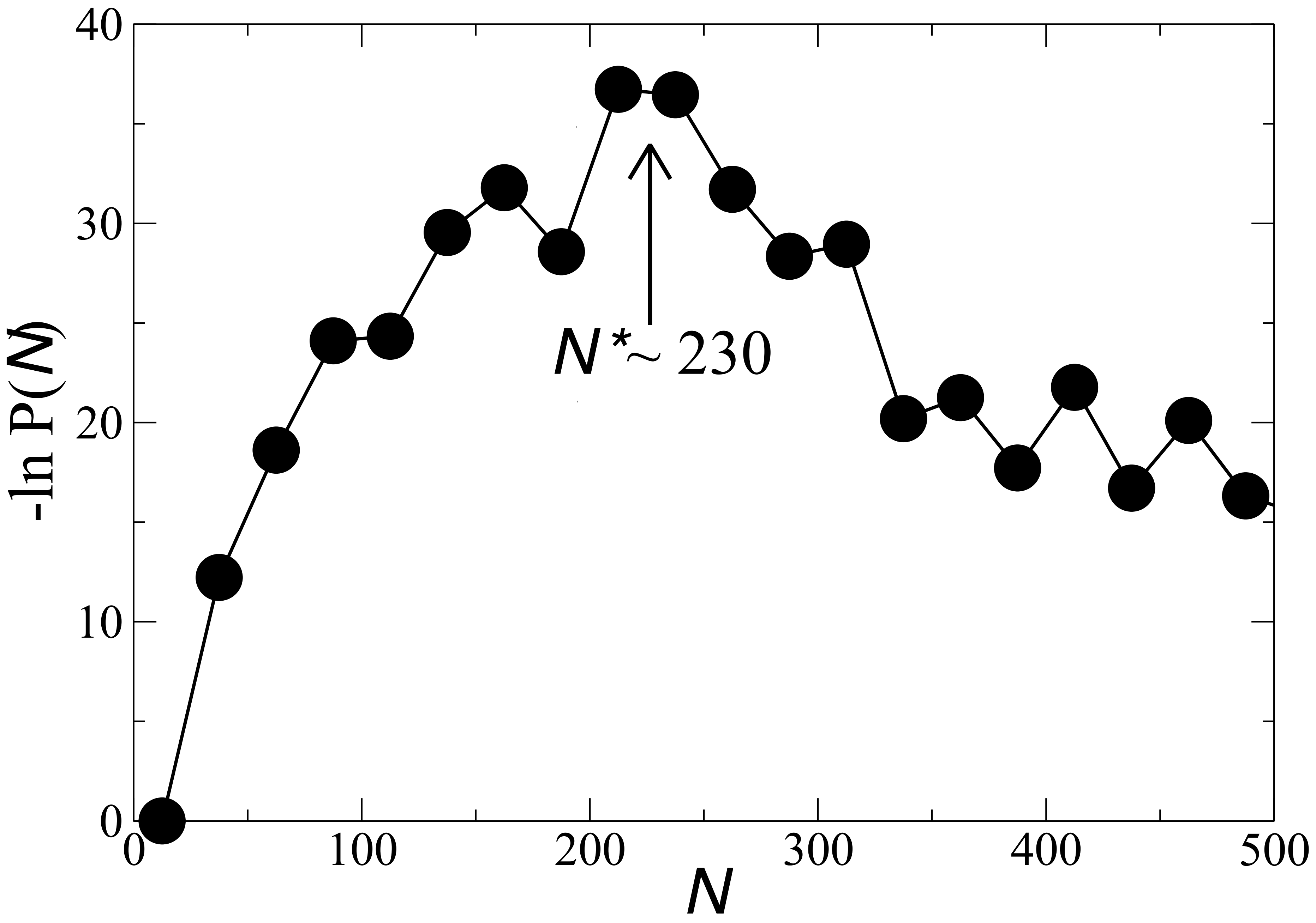
Results: free energy vs $\mathcal{N}(x)$



G. Ciccotti and S. Meloni, *"Temperature Accelerated Monte Carlo (TAMC): a method for sampling the free energy surface of non-analytical collective coordinates"* PCCP, 13, 5952 (2011)

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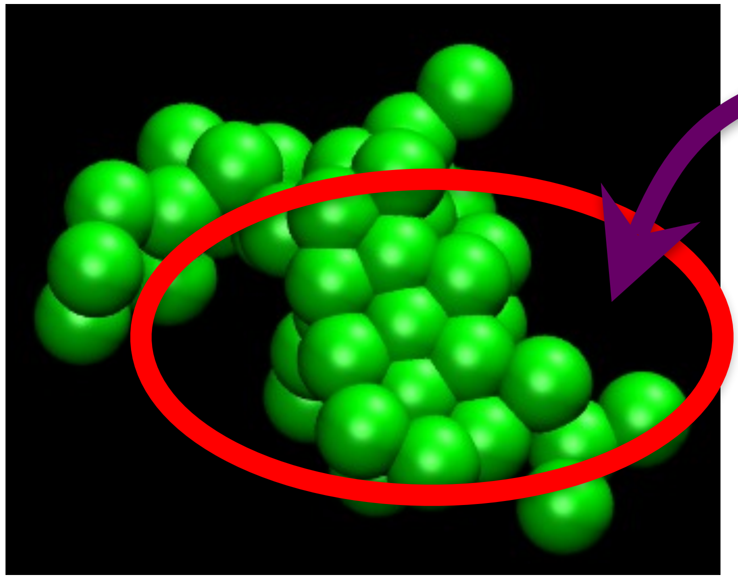
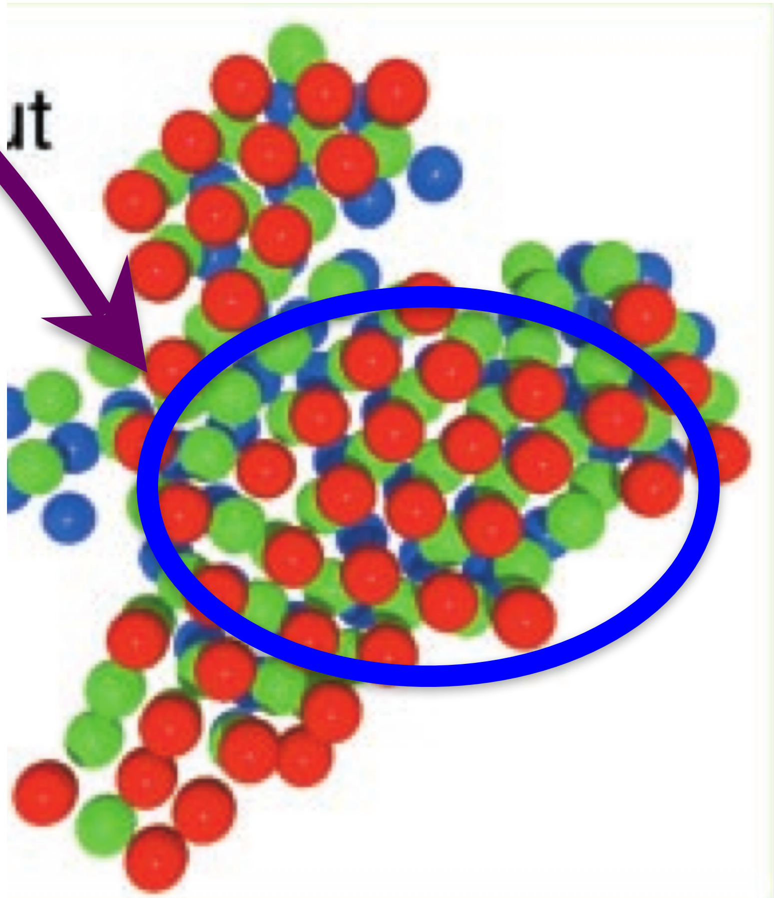
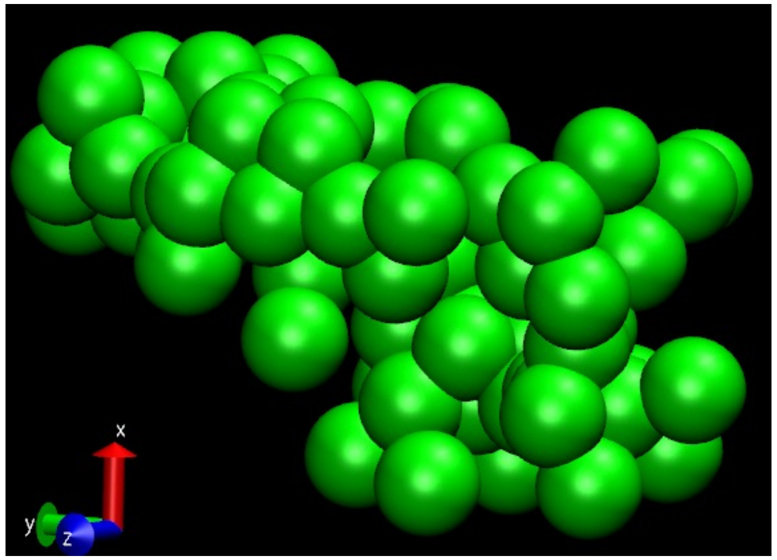
Results: nucleus configurations



3-layers thick cut through a post-critical nucleus in our simulations



3-layers thick cut through a post-critical nucleus of colloids (by 3D imaging[1])



an under-critical nucleus in our simulations

[1] U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, D. A. Weitz, *Science* 292 (2001), 258

Non-Equilibrium MD (Dynamical-NEMD)

Hydrodynamic limit of $F_k(t)$

In books, after the derivation of the Navier-Stokes Eq.s (i.e. conservation laws (exact) + constitutive relations & local equilibrium hypothesis (phenomenological and approximate)) we are given

$n_k(t) = f(k, t)$ - i.e an explicit form for $n_k(t)$

Then, is said, multiplying by $n_{-k}(0)$ and taking an "ensemble average", we get

$$F_k(t) = 1/N << n_k(t) n_{-k}(0) >>$$

BUT $n_k(t)$ is a macroscopic quantity, there is no ensemble over which to average. What kind of average is $\langle\langle \cdots \rangle\rangle$?

Hydrodynamic limit of $F_k(t)$

The question is: what is the meaning of the macroscopic $n_k(t)$ in Stat. Mech. and within the given approximations? Well,

$$n_k(t) = \langle \hat{n}_k\left(\Gamma(t)\right) \left| \hat{n}_{-k}(\Gamma) = n_{-k}(0) \right\rangle$$

i.e. is a standard **conditional average over a suitable ensemble**.

Multiplying by the condition and averaging over its probability distribution $P_{\hat{n}_{-k}}\left(n_{-k}(0)\right)$ we get the $F_k(t)$: puzzle solved!

The question of this talk is: can we compute hydrodynamic fields, included $n_k(t)$, by some rigorous D-NEMD approach?

Relation between microscopic and macroscopic fields

How is defined the microscopic field $\hat{O}(\vec{x},\Gamma)$ associated to the macroscopic field $O(\vec{x},t)$?

$$\hat{O}(\vec{x},\Gamma) = \sum_{i=1}^{N} \hat{\mathcal{O}}_i(\Gamma)\delta(\vec{x}-\vec{r}_i)$$

is the microscopic property associated to the field, $\mathcal{O}_i(\Gamma)$

e.g. : $n(\vec{x},t) \rightarrow \hat{\mathcal{O}}_i(\Gamma) = m_i$, $\vec{p}(\vec{x},t) \rightarrow \hat{\mathcal{O}}_i(\Gamma) = \vec{p}_i$, …

The macroscopic field $O(\vec{x},t)$ is related to the corresponding microscopic field via a suitable average, conditional to the values of a set of scalar/field observables at *t=0*, ($\hat{C}(\vec{x},\Gamma) = C(\vec{x},t=0)$) :

$$O(\vec{x},t) = \langle \hat{O}(\vec{x},\Gamma(t)) \rangle_{cond}$$

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Dynamic NEMD [Ciccotti, Jacucci ‘75]

Compute the time-dependent NE average of a given observable

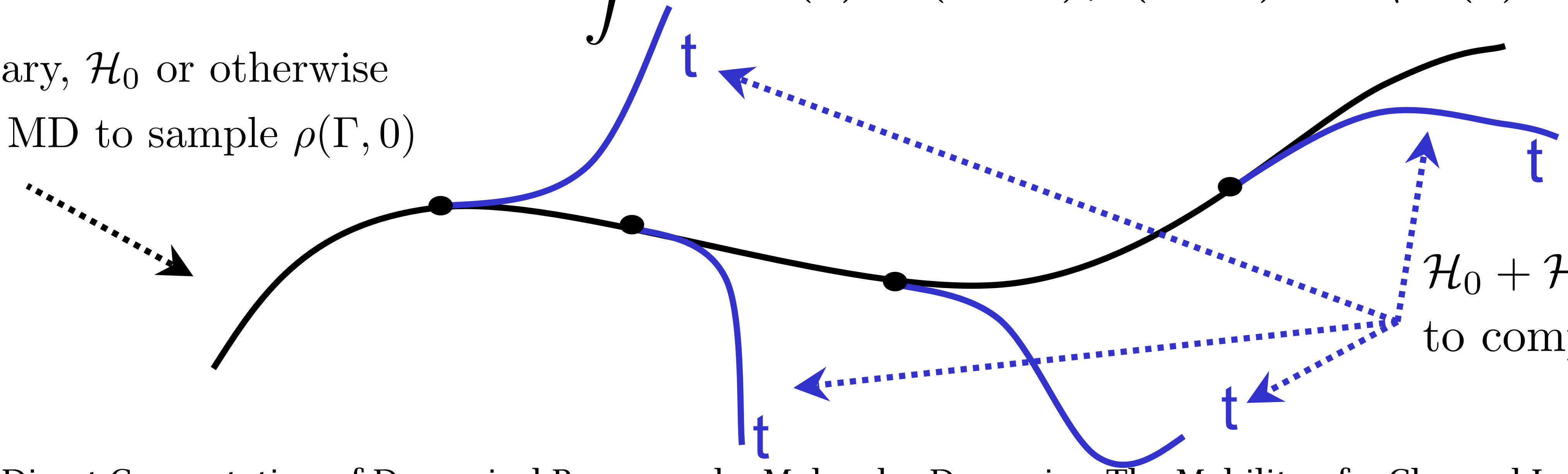
$$\frac{d\hat{O}}{dt} = -iL\hat{O}, \;\; \hat{O}(\vec{x},t) = S(t)\hat{O}(\vec{x},0) \qquad iL = \{\mathcal{H}_0, \cdot\} + \{\mathcal{H}_p(t), \cdot\}$$

$$\frac{\partial\rho}{\partial t} = \imath L\rho\,, \quad \rho(\Gamma,t) = S^\dagger(t)\rho(\Gamma,0)$$

Use the <u>Onsager-Kubo equation</u>:

$$O(\vec{x},t) =< \hat{O}(\vec{x},\Gamma) >_t= \int d\Gamma\hat{O}(\vec{x},\Gamma)\rho(\Gamma,t) \equiv \int d\Gamma\hat{O}(\vec{x},\Gamma)S^\dagger(t)\rho(\Gamma,0)$$

$$= \int d\Gamma S(t)\hat{O}(\vec{x},\Gamma)\rho(\Gamma,0) \equiv \langle S(t)\hat{O}(\vec{x},\Gamma)\rangle_0$$



Stationary, $\mathcal{H}_0$ or otherwise driven, MD to sample $\rho(\Gamma,0)$

$\mathcal{H}_0 + \mathcal{H}_p$ driven MD to compute $S(t)\hat{O}(\vec{x},\Gamma)$

“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

Conditional (initial) probability density function

$$\rho(\Gamma,0) = \rho\left(\Gamma \middle| \hat{C}(\vec{x},\Gamma) = C(\vec{x},0)\right)$$

$$= \frac{\exp[-\beta H(\Gamma)] \prod_{\vec{x}} \delta\left(\hat{C}(\vec{x},\Gamma) - C(\vec{x},0)\right)}{\mathcal{Z} P_{\hat{C}(\vec{x})}(C(\vec{x},0))}$$

$\prod_{\vec{x}}$ indicates that the Dirac delta $\delta\left(\hat{C}(\vec{x},\Gamma) - C(\vec{x},0)\right)$ is valid over the entire ordinary space; $\mathcal{Z}$ is the partition function and $P_{\hat{C}(\vec{x})}(C(\vec{x},0))$ denotes the probability to observe a value of the microscopic field $\hat{C}(\vec{x},\Gamma)$ equal to $C(\vec{x},0)$.

In practice, in simulations the fields are computed over a discretization of the ordinary space $\{\vec{x}_\alpha\}_{\alpha=1,M}$ and the $\delta(\vec{x}-\vec{r}_i)$ in their definition are mollified (e.g. replaced by gaussians) such that the field changes smoothly when particles move from one “cell” to another

Conditional averages by restrained MD

- The sampling of the conditional ensemble can be performed by restrained MD

$$< \hat{O}(\vec{x}_\beta, \Gamma(t)) >_{cond} = \lim_{k \to \infty} \frac{\left\langle \hat{O}(\vec{x}_\beta, \Gamma(t)) \prod_{\vec{x}_\alpha} \exp\left[-\beta k/2 \left(\hat{C}(\vec{x}_\alpha, \Gamma) - C(\vec{x}_\alpha) \right)^2 \right] \right\rangle_H}{\left\langle \prod_{\vec{x}_\alpha} \exp\left[-\beta k/2 \left(\hat{C}(\vec{x}_\alpha, \Gamma) - C(\vec{x}_\alpha) \right)^2 \right] \right\rangle_H}$$

where:

$$= \lim_{k \to \infty} < \hat{O}(\vec{x}_\beta, \Gamma(t)) >_{H'}$$

$$H'(\Gamma) = H(\Gamma) + \sum_{\vec{x}_\alpha} k/2 \left(\hat{C}(\vec{x}_\alpha, \Gamma) - C(\vec{x}_\alpha) \right)^2$$

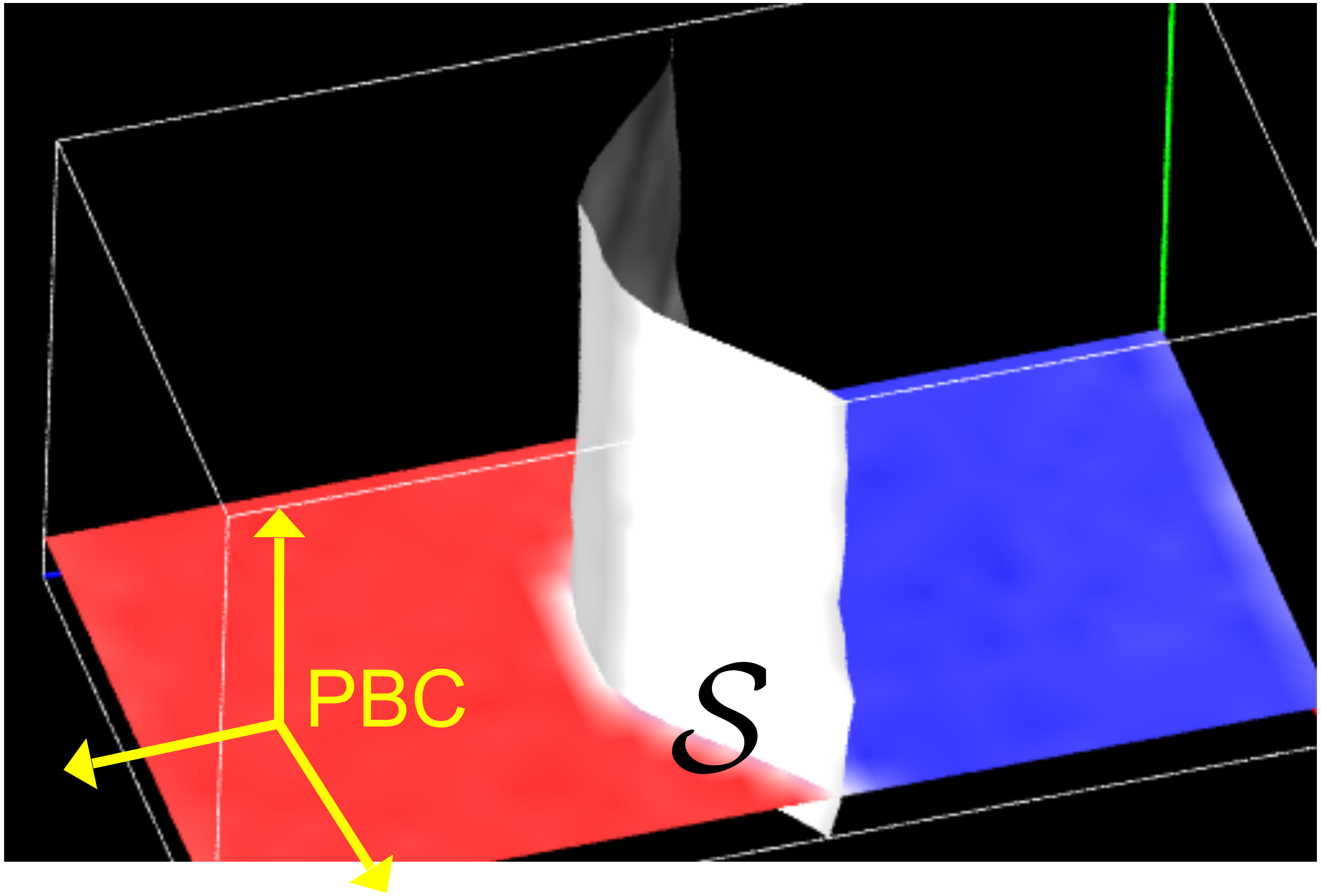
Simulation Details

- 171500 particles: 88889 particles A, 82611 particles B
- Pair potential: $u^{AA}(r) = u^{BB}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad u^{AB}(r) = 4\varepsilon\left(\frac{\sigma}{r}\right)^{12}$
- Simulation box: ~(90σ x 45σ x 45σ)
- Average density: 1.024 particles x σ^3
- Temperature: 1.5 ε/k_b
- Simulation time:
  - Restrained MD: 75000 steps
  - Unrestrained MD: 600000 steps
- fields are averaged over (only) 40 unrestrained trajectories

In the fluid domain of pure L-J

Hydrodynamic evolution of an interface by restrained- and NE-MD

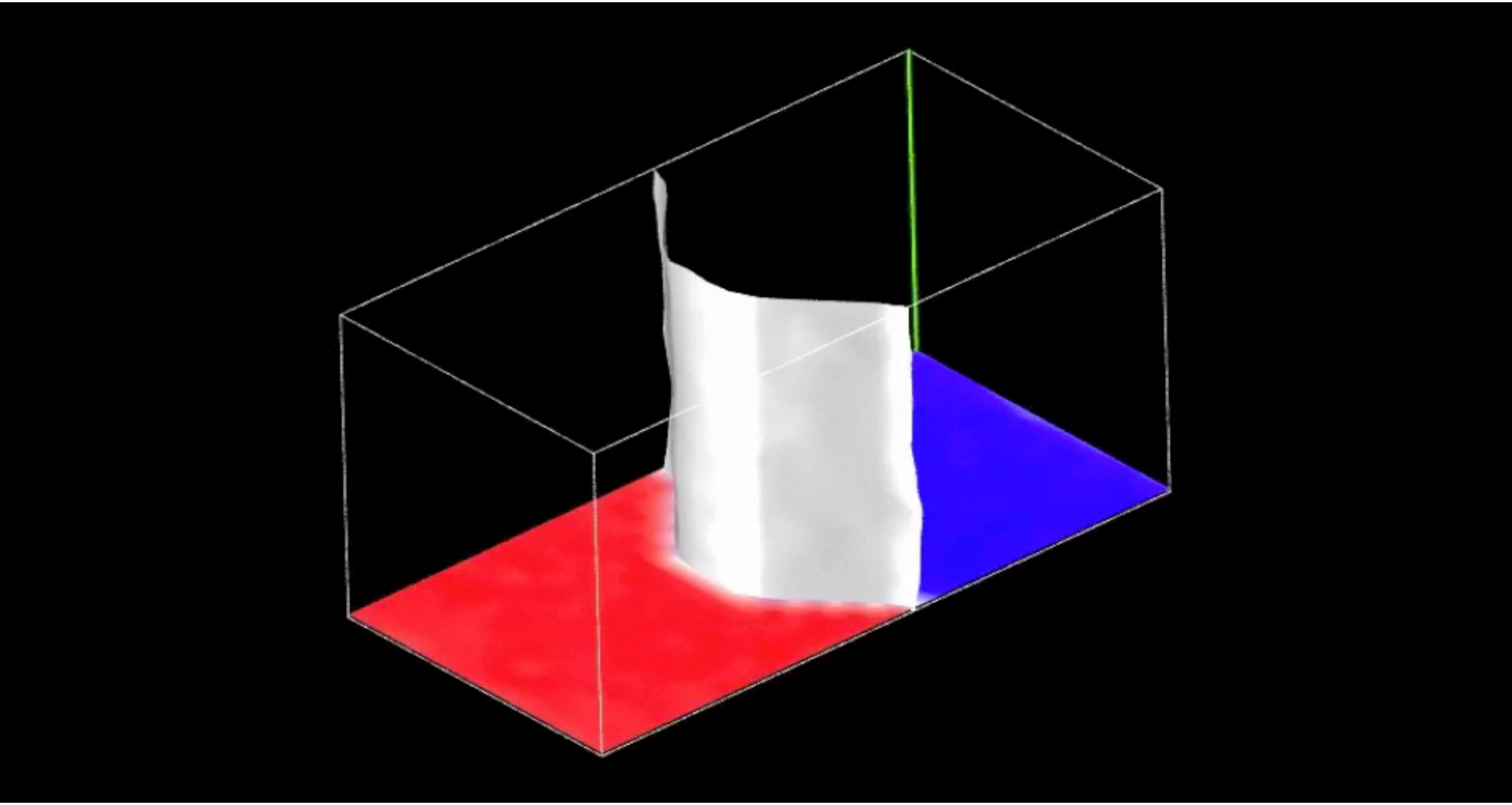
$$\Delta n(\vec{x}_\alpha, \Gamma) = n^A(\vec{x}_\alpha, \Gamma) - n^B(\vec{x}_\alpha, \Gamma) = 0\,, \qquad \vec{x}_\alpha \in S$$



"Hydrodynamics from statistical mechanics: combined dynamical-NEMD and conditional sampling to relax an interface between two immiscible liquids.", S. Orlandini, S. Meloni, G. Ciccotti, Phys. Chem. Chem. Phys. 13, 13177 (2011)

Hydrodynamics from Dynamical Non-Equilibrium Molecular Dynamics

$$\Delta n(\vec{x}_\alpha, t) = 0$$



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

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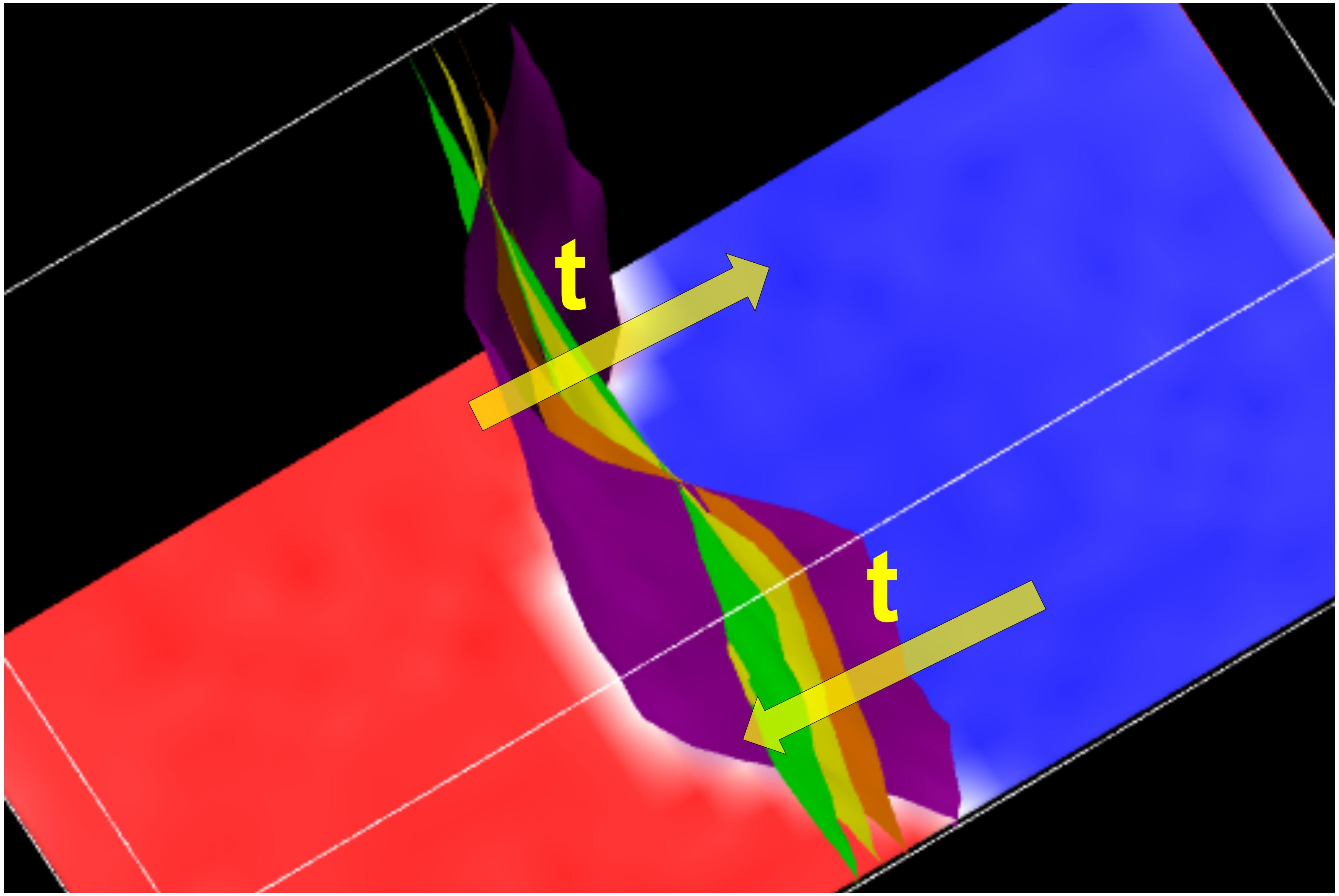
Hydrodynamics from Dynamical Non-Equilibrium Molecular Dynamics

$$\Delta n(\vec{x}_\alpha, t) = 0$$



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

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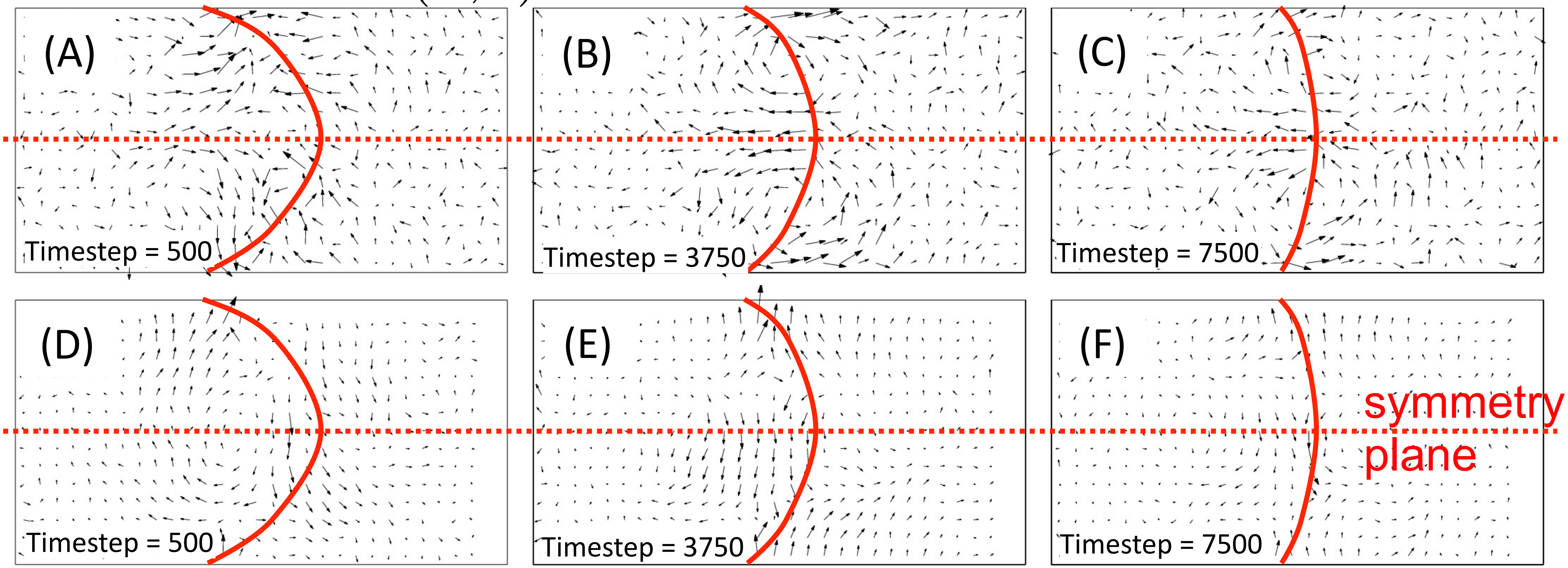
Rigorous non-equilibrium ensemble averages vs local time averages (1)

$$\vec{v}(\vec{x},t) = \frac{\langle \hat{\vec{p}}(\vec{x},t)\rangle_{H'}}{n(\vec{x},t)}$$

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



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

The velocity field obtained via the local time average technique violates the symmetry of the problem

Conclusions

① Molecular Dynamics Simulations (MS) are a regular chapter of Theoretical Physics BUT they are amenable to real applications both for the analysis of experiments and for engineering

② New algorithms have been, and continue to be, introduced to circumvent practical limitations of the MS, i.e. problems which cannot be solved by brute force. A good example has been TAMD/ TAMC

③ Also NonEquilibrium situations can be confronted by a proper use of Onsager-Kubo relationship. This opens the way to represent directly transport but also to atomistic simulations (without constitutive hypotheses) of hydrodynamical phenomena.

Dynamical systems with (holonomic) constraints

$$\mathcal{L}\left(\{\mathbf{r},\dot{\mathbf{r}}\}\right) = \frac{1}{2}\sum_{i,\alpha} m_{i\alpha}\dot{\mathbf{r}}_{i\alpha}^{2} - \mathcal{U}\left(\{\mathbf{r}\}\right) \qquad \begin{cases} i = 1, N & \textit{\# molecules} \\ \alpha = 1, n_i & \textit{\# atoms in molecule } i \end{cases}$$

$$\textit{plus} \qquad \sigma_k\left(\{\mathbf{r}\}\right) = 0\,, \qquad k = 1, f \quad \textit{\# constraints}$$

$$\text{e.g.} \qquad \sigma\left(\{\mathbf{r}\}\right) = \left(\mathbf{r}_{i\alpha} - \mathbf{r}_{i\beta}\right)^2 - d_{i,\alpha\beta}^2 = 0$$

To keep the trajectories satisfying the constraints $\left(\, \sigma\left(\{\mathbf{r}(t)\}\right) = 0\,, \quad \forall t \,\right)$

we must have also $\left(\, \dot{\sigma} = \dot{\mathbf{r}} \cdot \nabla_r \sigma\left(\{\mathbf{r}(t)\}\right) = 0\,, \quad \forall t \,\right)$

Moreover, if the constraint forces do not do work (i.e. conserve energy)

$$\dot{\mathbf{r}} \cdot \mathcal{G}\left(\{\mathbf{r}\}\right) = 0\,, \qquad \mathcal{G}_{i\alpha} = -\sum_{k=1}^{f} \lambda_k \nabla_{i\alpha}\sigma_k \equiv -\lambda \cdot \nabla_{i\alpha}\sigma$$

where the intensity λ of the constraint force has to be determined

SHAKE (1)

By differentiating two times the constraint relations σ's we find

$$\ddot{\sigma}_k = \ddot{\mathbf{r}} \cdot \nabla_r \sigma_k + (\dot{\mathbf{r}}\dot{\mathbf{r}}) \cdot (\nabla_r \nabla_r)\, \sigma_k = 0 \qquad (*)$$

and from $\dfrac{d}{dt}\dfrac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}} - \dfrac{\partial \mathcal{L}}{\partial \mathbf{r}} = \mathcal{G}$ i.e. $m\ddot{\mathbf{r}} = \mathbf{F} - \lambda \cdot (\nabla_r \sigma)$ $(**)$

$$\ddot{\sigma} = \frac{1}{m}\left(\mathbf{F} - (\lambda \nabla_r) \cdot \sigma\right) \cdot \nabla_r \sigma + (\dot{\mathbf{r}}\dot{\mathbf{r}} \cdot \nabla_r \nabla_r)\, \sigma = 0 \qquad (***)$$

from which the <u>useless</u> solution of the linear system $(***)$

$$\lambda = \mathcal{Z}^{-1}\left[(\mathbf{F} \cdot \nabla_r)\, \sigma + (\dot{\mathbf{r}}\dot{\mathbf{r}} \cdot \nabla_r \nabla_r)\, \sigma\right], \qquad \mathcal{Z}_{k\ell} = \nabla_r \sigma_k \cdot \nabla_r \sigma_\ell$$

due to the problem of the algorithmic error, destroying the model.

SHAKE (2)

E.g.

$$\mathbf{r}(t+h) = \mathbf{r}(t) + h\dot{\mathbf{r}} + \frac{h^2}{2m}\left[\mathbf{F}(t) + \mathcal{G}(t)\right] + \mathcal{O}(h^3) \qquad (+)$$

$\mathcal{G}(t)$ exact at all timesteps will destroy in time the conservation of constraints

Instead, exploiting the "freedom" to choose the λ to satisfy the constraints one can write the set of equations

$$\sigma_k\left(\{\mathbf{r}(t+h)\}\right) = 0\,, \qquad k = 1, \ldots, f \qquad (++)$$

where, plugging e.g. (+) in (++) one gets λ values which satisfy exactly the constraints at timestep *(t+h)* without increasing the algorithmic error

(++) can be solved by any efficient algorithm.
E.g. the Newton-Raphson method

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SMwC (1)

Statistical Mechanics of systems with constraints in cartesian coordinates

In analytical mechanics, in presence of constraints

$$\mathbf{r} \longrightarrow \mathbf{r}(\mathbf{q}) \qquad \mathbf{r} : 3N \, ; \mathbf{q} : 3N - f$$

$$\dot{\mathbf{r}} = \dot{\mathbf{q}} \cdot \nabla_q \mathbf{r}$$

$$\mathcal{L}'\left(\mathbf{r}, \dot{\mathbf{r}}\right) \longrightarrow \mathcal{L}'\left(\mathbf{q}, \dot{\mathbf{q}}\right) \quad \Longrightarrow \quad \mathcal{H}\left(\mathbf{q}, \mathbf{p}^q\right) \quad \left(\mathbf{p}^q = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{q}}}\right)$$

and, for Statistical Mechanics

$$\mathcal{Q} = \int d\mathbf{q} d\mathbf{p}^q e^{-\beta \mathcal{H}(\mathbf{q}, \mathbf{p}^q)}$$

NOW: instead of assuming the constraints satisfied, let us take the constraint functions as ***f*** generalized coordinates. THEN

$$\mathbf{r} \longleftrightarrow \left((\mathbf{q},\, \sigma) \equiv \mathbf{u}\right) \qquad \mathbf{p}^r \longleftrightarrow \left(\mathbf{p}^u \equiv (\mathbf{p}^q,\, \mathbf{p}^\sigma)\right)$$ with $\mathbf{p}^u = \mathbf{M}\dot{\mathbf{u}}$

The constrained system will be obtained putting back $\sigma(\mathbf{r}) = 0 \,, \quad \dot{\sigma}(\mathbf{r}, \dot{\mathbf{r}}) = 0$

SMwC (2)

Considering that

$$\mathcal{L}(\mathbf{r},\dot{\mathbf{r}}) = \mathcal{K}(\dot{\mathbf{r}}) - \mathcal{V}(\mathbf{r}) = \mathcal{L}(\mathbf{u},\dot{\mathbf{u}}) = \frac{1}{2}\dot{\mathbf{u}}^T\mathbf{M}\dot{\mathbf{u}} - \mathcal{V}'(\mathbf{u})$$

$$\mathbf{p}^u = \begin{pmatrix} \mathbf{p}^q \\ \mathbf{p}^\sigma \end{pmatrix} = \frac{\partial \mathcal{L}'}{\partial \dot{\mathbf{u}}} = \mathbf{M}\dot{\mathbf{u}} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^T & \Gamma \end{pmatrix} \begin{pmatrix} \dot{\mathbf{q}} \\ \dot{\sigma} \end{pmatrix}$$

i.e. $\dot{\mathbf{u}} = \begin{pmatrix} \dot{\mathbf{q}} \\ \dot{\sigma} \end{pmatrix} = \mathbf{M}^{-1}\mathbf{p}^u = \begin{pmatrix} \Delta & \mathbf{E} \\ \mathbf{E}^T & \mathbf{Z} \end{pmatrix} \begin{pmatrix} \mathbf{p}^q \\ \mathbf{p}^\sigma \end{pmatrix}$

we have that $\dot{\sigma} = 0$

corresponds to $\dot{\sigma} = \mathbf{E}^T\mathbf{p}^q + \mathbf{Z}\mathbf{p}^\sigma = 0$

i.e. to $\mathbf{p}^\sigma$ not zero, for $\dot{\sigma} = 0$, but equal to $\tilde{\mathbf{p}}^\sigma = \tilde{\mathbf{Z}}^{-1}\tilde{\mathbf{E}}^T\mathbf{p}^q$

and $\mathbf{p}^\sigma + \tilde{\mathbf{p}}^\sigma = \tilde{\mathbf{Z}}^{-1}\dot{\sigma}$

SMwC (3)

Now our result is at hand, since

$$\mathcal{L}'(\mathbf{u}, \dot{\mathbf{u}}) \longleftrightarrow \mathcal{H}'(\mathbf{p}^u, \mathbf{u})$$

$$\mathcal{H}_c(\mathbf{p}^q, \mathbf{q}) = \mathcal{H}'(\mathbf{p}^q, \mathbf{p}^\sigma = \mathbf{Z}^{-1}\mathbf{E}^T\mathbf{p}^q \, , \, \mathbf{q}, \sigma = 0)$$

so

$$\mathcal{Q} = \int d\mathbf{q} d\mathbf{p}^q e^{-\beta\mathcal{H}_c} = \int d\mathbf{u} d\mathbf{p}^u e^{-\beta\mathcal{H}'(\mathbf{p}^u, \mathbf{u})} \delta\left(\sigma\right) \delta\left(\mathbf{p}^\sigma - \tilde{\mathbf{p}}^\sigma\right)$$

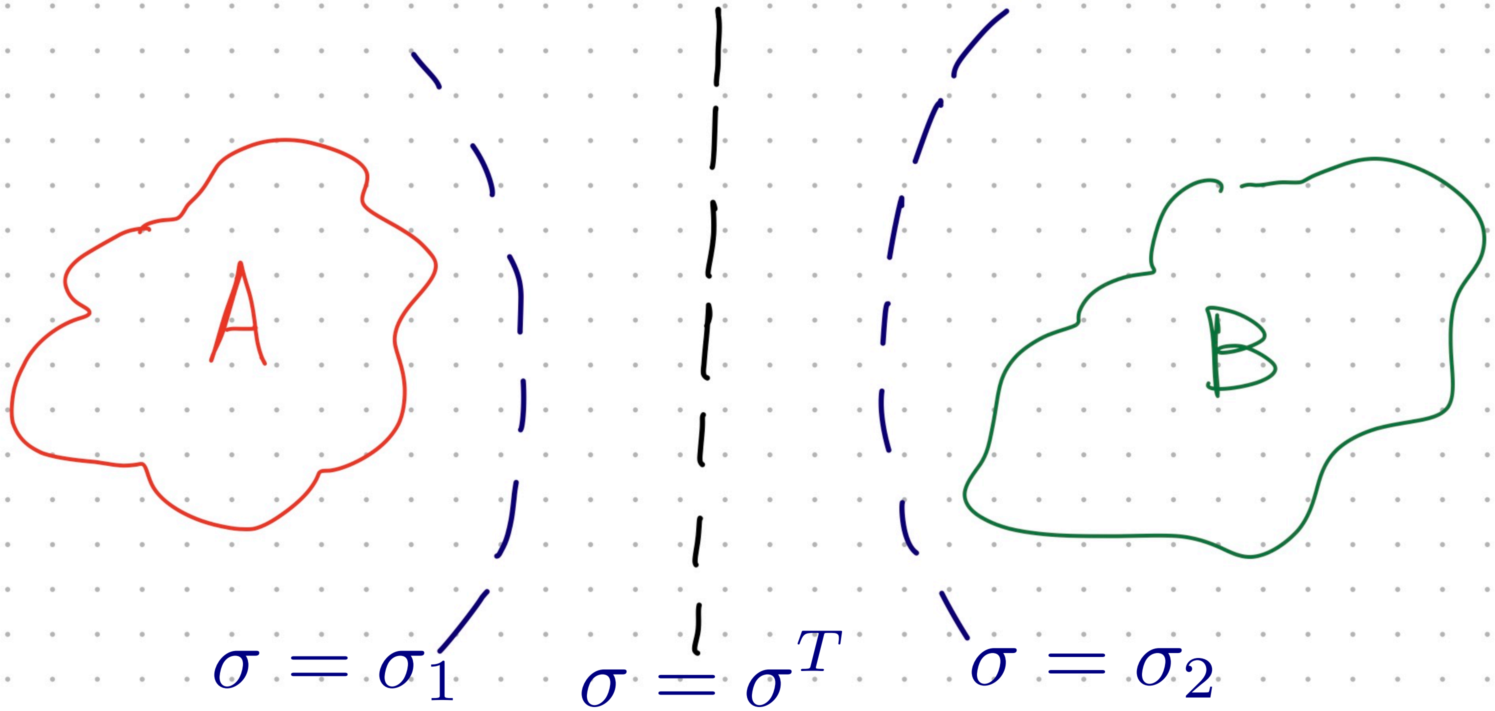
$$= \int d\mathbf{r} d\mathbf{p}^r e^{-\beta\mathcal{H}(\mathbf{p}^r, \mathbf{r})} \delta\left(\sigma(\mathbf{r})\right) \delta\left(\mathbf{Z}^{-1}\dot{\sigma}(\mathbf{r}, \mathbf{p}^r)\right)$$

where $d\mathbf{u} d\mathbf{p}^u = d\mathbf{r} d\mathbf{p}^r$ since the transformation is canonical and the Jacobian is = 1

Moreover $\varrho(\mathbf{r}, \mathbf{p}^r) = \frac{1}{\mathcal{Q}} e^{-\beta\mathcal{H}(\mathbf{p}^r, \mathbf{r})} \delta\left(\sigma(\mathbf{r})\right) \delta\left(\mathbf{Z}^{-1}\dot{\sigma}(\mathbf{r}, \mathbf{p}^r)\right)$

ASBM (1)

Accelerated (*but rigorous*) Sampling: *Blue Moon Ensemble*



We assume a metastability in configurational space and the existence of at least one configurational function (also often improperly called a *reaction coordinate*) such that its values going from **A** to **B** grow monotonically from σ_A to $\sigma_B > \sigma_A$ and can then be used to characterise the STATE of the system at and between the two metastable states. The system spends the majority of its time in **A** or **B** and very little in between. The transitional region has almost zero probability to be visited and **MD** is unable to sample the full space

ASBM (2)

We would like to know $\mathcal{P}_\sigma(\sigma')$ for all possible values (probable and improbable) of σ'.

1. using $\sigma(\{\mathbf{r}\})$ as a constraint we can sample by MD any chosen region

2. By knowing the probability in presence of a constraint (as shown before) we can demonstrate that

   $$\frac{d\ln\mathcal{P}_\Xi(\xi')}{d\xi'} \propto \langle \mathbf{F}_{\xi'}\rangle_{cond} = \frac{\langle corr\,\mathbf{F}_{\xi'}\rangle_{constrained}}{\langle corr\rangle_{constrained}} \tag{$\times$}$$

   where the second term is virtually impossible to sample while the third is obtained with full statistics.

3. the integral of (✕) [THERMODYNAMICAL INTEGRATION] provides a direct measure of the strength of the metastability