Hybrid Atomistic-Continuum Methods for Dense Liquids

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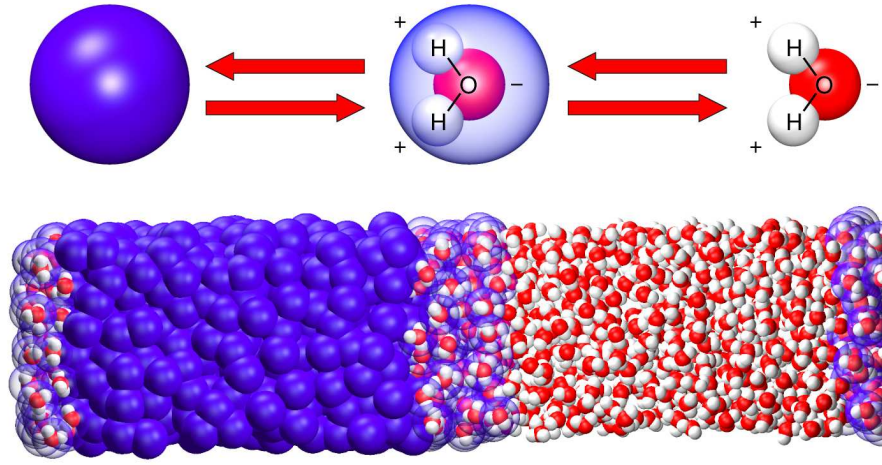
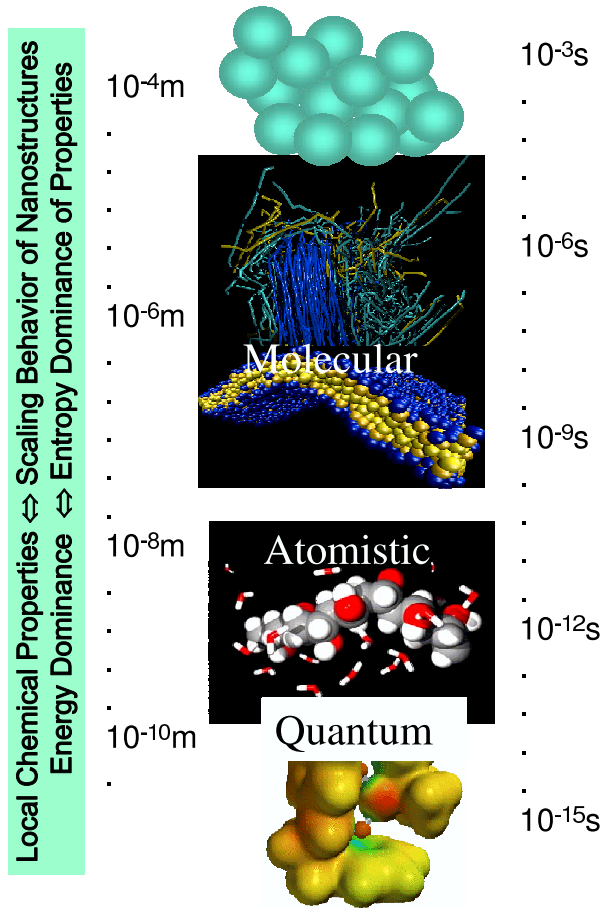
Molecular systems

- **gases**: intermolecular distances are large in comparison with molecular sizes $\longrightarrow$ the intermolecular interactions are negligible
- **hard condensed matter**: strong intermolecular interactions, long-range orientational and positional order
- **molecular liquids and soft matter**: energy-entropy interplay. The free-energy scale: $k_B T$. The relevant properties of the system are determined by the interplay of the various **temporal** and **spatial scales** involved.



Multiscale modeling



MACRO Finite Element Calculations,
Continuum hydrodynamics,
Dissipative Particle Dynamics (DPD)
MD-MC-Lattice Boltzmann

MESO MC statics/dynamics,
MD, NEMD,

MICRO Classical Force Field MD, MC,
Embedded Atomistic-Quantum methods,
Car-Parrinello MD,
Quantum MC,
Quantum Chemical Methods

Praprotnik, Delle Site, Kremer, Annu. Rev. Phys. Chem. **59**, 545 (2008).

Modeling of dense fluids

All-Atom MD simulation:

- allows to study processes at the atomic level of detail
- is often incapable to bridge a gap between a wide range of length and time scales involved in molecular systems

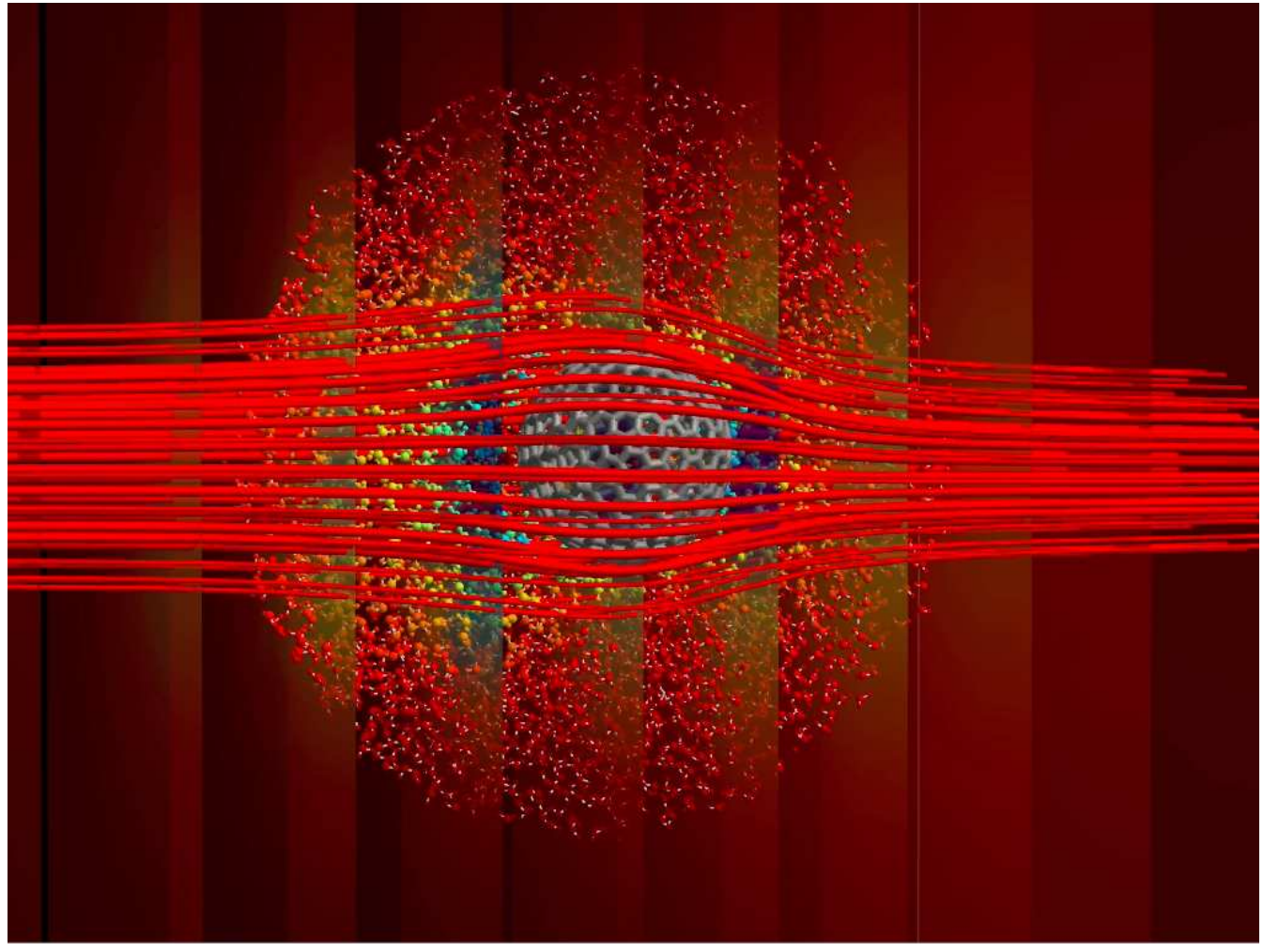
Continuum fluid dynamics (CFD):

- allows to model fluid flows on length scales that are out of scope of MD simulation.
- at lower scales (a few molecular diameters) no-slip boundary condition breaks down and surface to volume effects overcome the inertial effects.

Combining the best from both approaches:

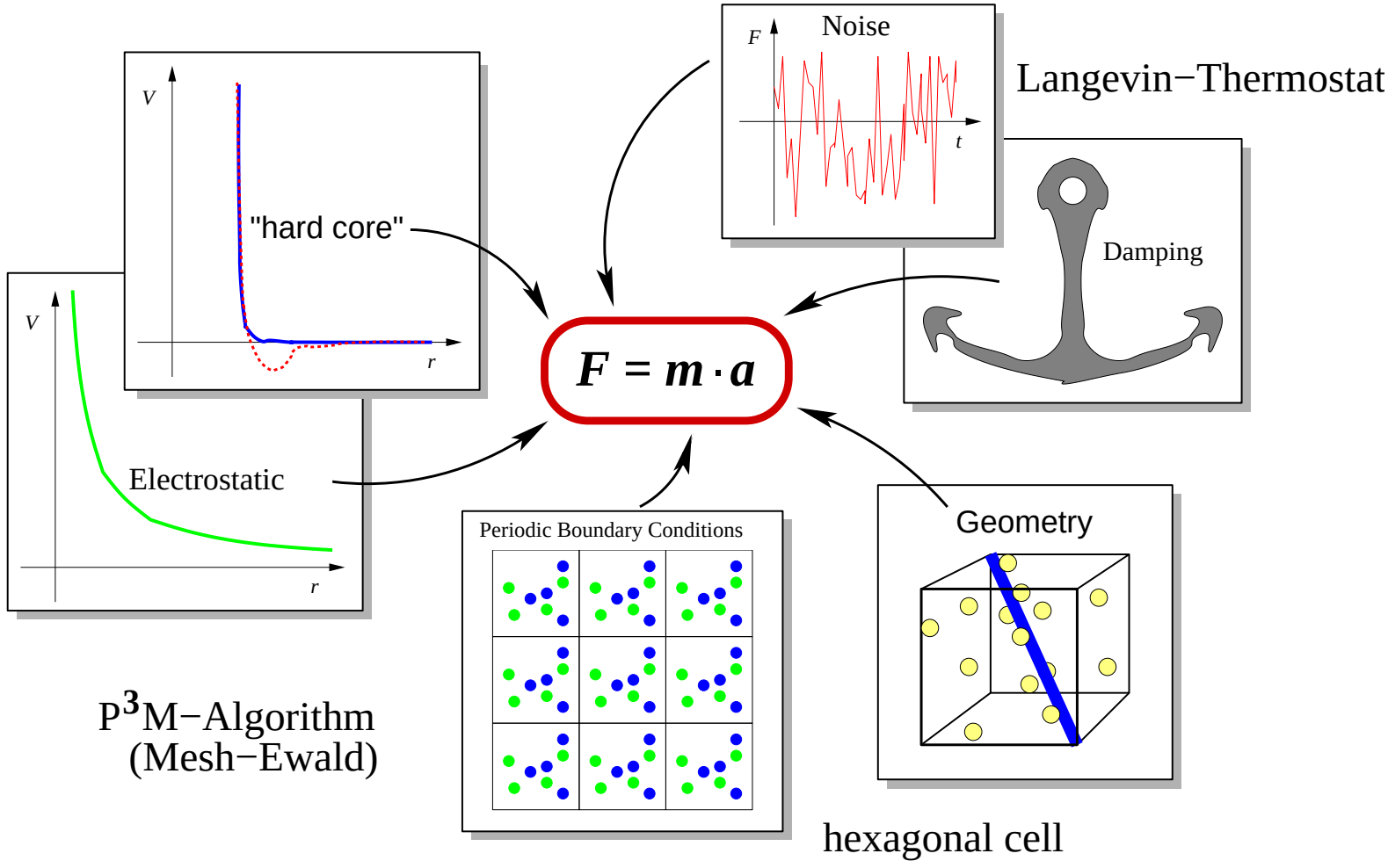
- Hybrid Atomistic-Continuum Methods

Multiscale flow



Kotsalis, Walther, Ding, Praprotnik, Koumoutsakos, submitted.

Molecular Dynamics (MD) simulation



Navier-Stokes equation

Conservation of momentum:

$$\rho(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot \mathbf{\Pi} + \mathbf{f}$$

Stress tensor:

$$\mathbf{\Pi} = -\eta[\nabla \mathbf{u}]^S - \xi \nabla \cdot \mathbf{u}\, \mathbf{I}$$

We consider a Newtonian fluid with dynamic viscosity η and bulk viscosity ξ. The traceless symmetric tensor is defined as $A^S_{\alpha\beta} = (A_{\alpha\beta} + A_{\beta\alpha}) - (2/3)A_{\gamma\gamma}$.

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

Coupling MD and continuum

- **Physical quantities**, i.e., density, momentum, energy, and corresponding fluxes must be **continuous across the interface.**
- **Atomistic** and **continuum** domains provide each other with **boundary conditions.**
- To impose boundary conditions from the **MD to continuum** domain is relatively easy since it involves **temporal and spatial averaging.**
- Imposing the **continuum boundary conditions** on the **particle domain** presents the **major challenge** in hybrid methods.

Hybrid atomistic-continuum schemes

- **state variable (Dirichlet) schemes**
  - **constraint dynamics**: closed systems, unsteady flows
  - **Schwartz alternating method**: steady state, closed systems, good signal-to-noise ratio, iterations required
- **flux-exchange schemes**: open systems, grand canonical ensemble, fluctuating hydrodynamics, unsteady flows, no iterations required

S. T. O'Connell, P. A. Thompson, Phys. Rev. E **52**, R5792 (1995)

N. G. Hadjiconstantinou, A. T. Patera, Int. J. Mod. Phys. **8**, 967 (1997)

T. Werder, J. H. Walther, P. Koumoutsakos, J. Comp. Phys. **205**,373 (2005)

E. G. Flekkoy, G. Wagner, J. Feder, Europhys. Lett. **52**, 271 (2000)

G. De Fabritiis, R. Delgado Buscalioni, P. Coveney, Phys. Rev. Lett **97**, 134501 (2006).

R. Delgado Buscalioni, K. Kremer, M. Praprotnik, J. Chem. Phys. **128**, 114110 (2008)

Continuum fluid dynamics

- **Conservation law** for any conserved fluid variable $\phi(\mathbf{r}, t)$:

$$\partial\phi/\partial t = -\nabla \cdot \mathbf{J}^{\phi}$$

$\mathbf{J}^{\phi}(\mathbf{r}, t)$ is the associated local flux.

  - mass: $\phi = \rho$, $\mathbf{J}^{\phi} = \rho\mathbf{u}$
  - momentum: $\phi = \rho\mathbf{u}$, $\mathbf{J}^{\phi} = \mathbf{J}_p = p\,\mathbf{I} + \rho\mathbf{u}\mathbf{u} + \mathbf{\Pi}$
  - energy: $\phi = \rho\epsilon$, $\mathbf{J}^{\phi} = \rho\epsilon\mathbf{u} + \mathbf{J}_p \cdot \mathbf{u} + q$

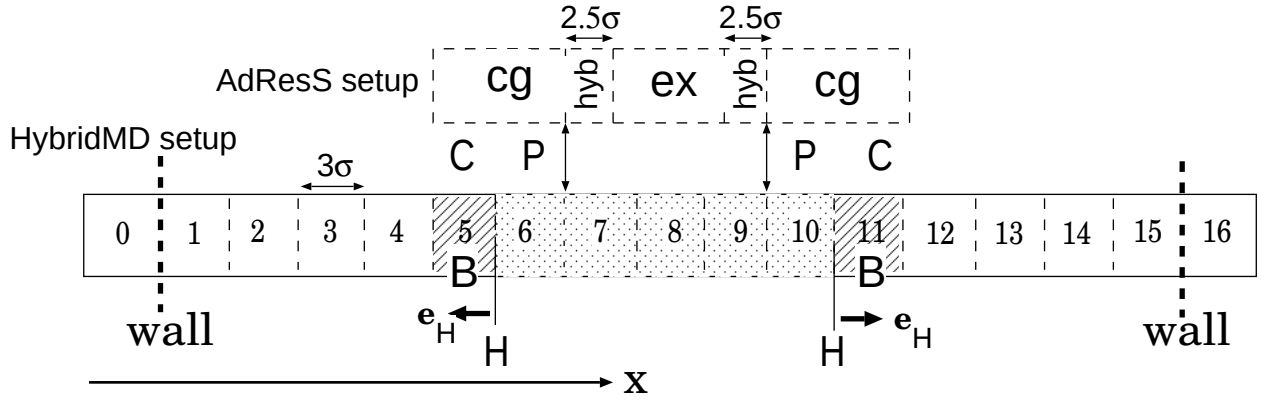
- **Constitutive relations**:
  - Equation of state: $p = p(\rho)$
  - Caloric equation of state: $\epsilon = \epsilon(\rho, T)$
  - Stress tensor: $\mathbf{\Pi} = -\eta[\nabla\mathbf{u}]^S - \xi\nabla \cdot \mathbf{u}\,\mathbf{I}$
  - Conduction heat flux: $q = -k_c\nabla T$

Finite Volume Method

$$\int_{V_C} \partial\phi/\partial t \, dV = -\int_{V_C} \nabla \cdot \mathbf{J}^{\phi} \, dV = -\oint_S \mathbf{J}^{\phi} \cdot dS$$

$$\frac{d\Phi_C}{dt} = -\sum_{f=faces} A_f \mathbf{J}_f^{\phi} \cdot \mathbf{n}_f$$

$\Phi_C = \int_{V_C} \phi(\mathbf{r}, t) d\mathbf{r}^3$. The above eq. is numerically solved by the explicit Euler scheme, where $\mathbf{J}_f^{\phi} = (\mathbf{J}_C^{\phi} + \mathbf{J}_{C+1}^{\phi})/2$.



R. Delgado Buscalioni, K. Kremer, MP, J. Chem. Phys. **128**, 114110 (2008).

Boundary conditions: MD->CFD

- **Mass flux**:

$$\frac{1}{V}\sum_i m_i < \mathbf{v}_i > \cdot\mathbf{n} \longrightarrow \rho\mathbf{u}\cdot\mathbf{n}$$

- **Momentum flux**:

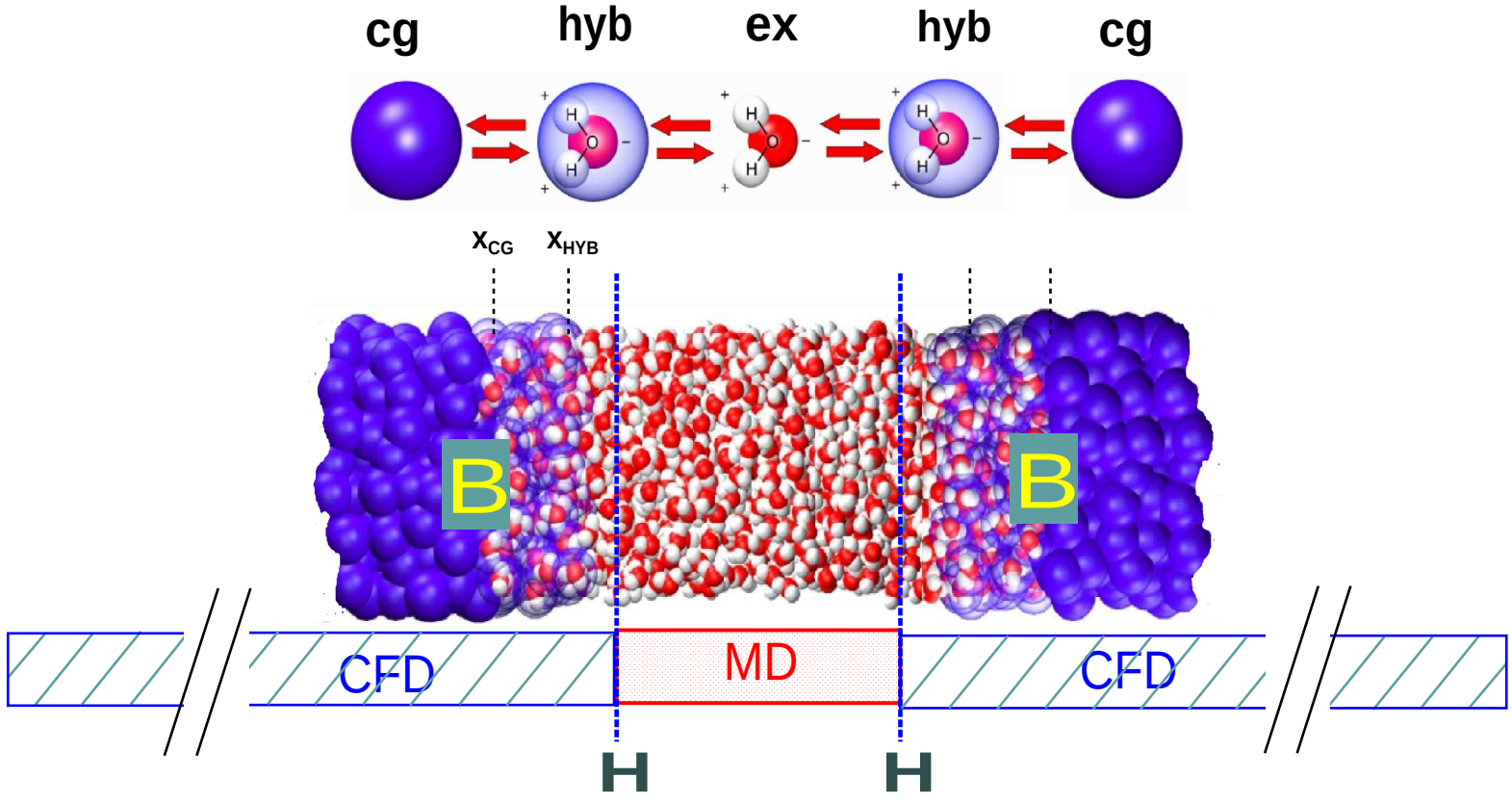
$$\frac{1}{V}\sum_i \left(m_i < \mathbf{v}_i\mathbf{v}_i > + \frac{1}{2}\sum_{j\neq i} < \mathbf{F}_{ij}\mathbf{r}_{ij} > \right) \cdot\mathbf{n} \longrightarrow \mathbf{J}_p\cdot\mathbf{n}$$

- **Energy flux**:

$$\frac{1}{V} < \sum_i m_i\epsilon_i\mathbf{v}_i - \frac{1}{2}\sum_{i\neq j}\mathbf{r}_{ij}\mathbf{v}_{ij}\mathbf{F}_{ij} > \cdot\mathbf{n} \longrightarrow \mathbf{q}\cdot\mathbf{n}$$

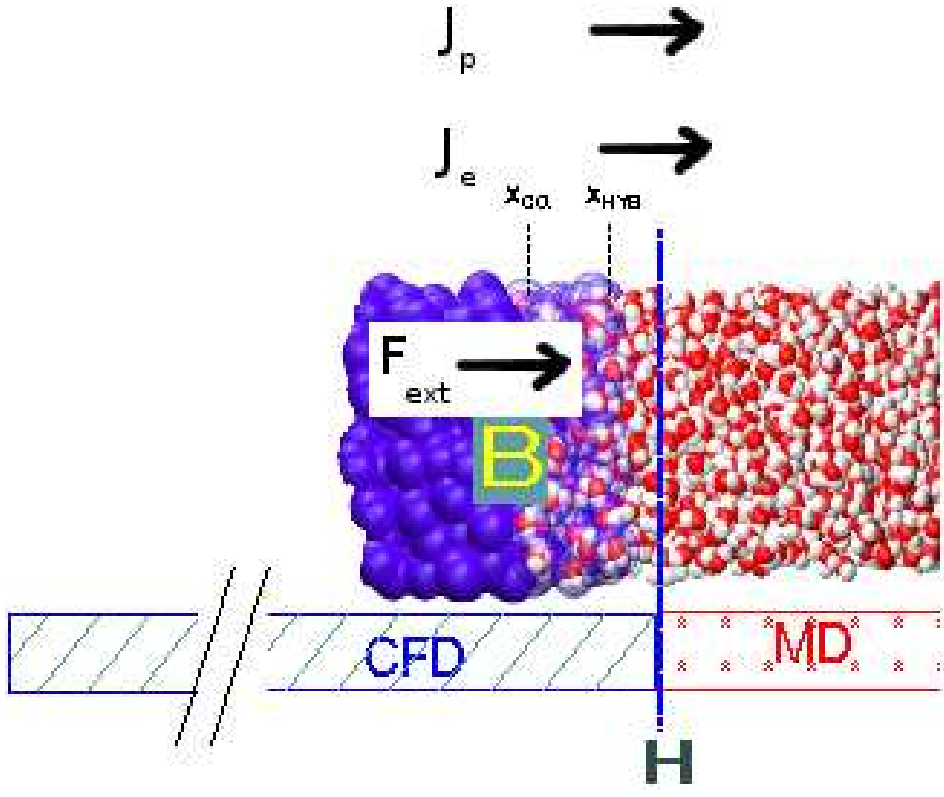
Or using mesoscopic route using constitutive relations.

Buffer



B=buffer (overlap domain) serves to impose fluxes into the particle region.

Flux-exchange coupling



Buffer is a mass and momentum reservoir for the MD domain. It is used to impose the external momentum into MD via $\mathbf{F}^{ext} = \sum_{i \in B} \mathbf{F}_i^{ext}$. Flux at H: $\mathbf{J}_H^{\phi} = (\mathbf{J}_C^{\phi} + \mathbf{J}_P^{\phi})/2$.

Boundary conditions: CFD->MD

Fluxes are imposed onto MD across the hybrid interface H:

- **Momentum**:

$$\mathbf{J}_p \cdot \mathbf{n} A \Delta t = \sum_{i \in B} F_i^{ext} \Delta t + \sum_{i'} \Delta(m_{i'} \mathbf{v}_{i'})$$

- **Energy**:

$$\mathbf{J}_e \cdot \mathbf{n} A \Delta t = \sum_{i \in B} F_i^{ext} \mathbf{v}_i \Delta t + \sum_{i'} \Delta \epsilon_{i'}$$

- **External Force (for momentum);** $g(x_i) = 1$:

$$\mathbf{F}_i^{ext} = g(x_i)\mathbf{F}^{ext} / \sum_{i \in B} g(x_i) = \frac{A}{N_B} \left(\mathbf{J}_p \cdot \mathbf{n} - \frac{\sum_{i'} \Delta(m_{i'} \mathbf{v}_{i'})}{A \Delta t} \right)$$

Flekkoy, Delgado Buscalioni, Coveney, Phys. Rev. E **72**, 026703 (2005).

Velocity of inserted particles

Choices:

- No additional momentum:

$$\mathbf{v}_{i'} = 0$$

- Average velocity of inserted particles is equal to continuum fluid velocity:

$$< \mathbf{v} >= \mathbf{u}$$

- The distribution is for example Maxwellian:

$$(\frac{1}{2}\pi m k_B T)^{3/2} \exp\left(-m(\mathbf{v}-\mathbf{u})^2/2mk_BT\right)$$

Insertion/deletion of molecules

- Controlling the number N_B of molecules in B:

$$\Delta N_B = (\Delta t/\tau_r)(\langle N_B \rangle - N_B)$$

  $\tau_r \sim O(100)$ MD time steps.

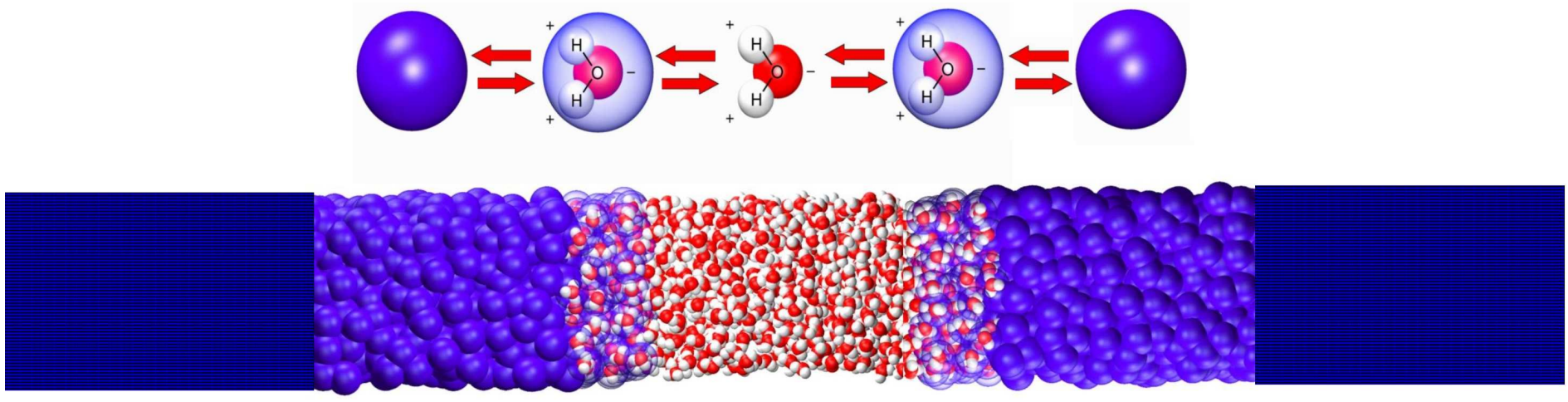
- Delete a molecule if $\Delta N_B < 0$ or when molecule leaves the buffer-end.
- Insert a molecule if $\Delta N_B > 0$ using USHER- Newton-Raphson-like search method on the potential energy surface. A new molecule is inserted at potential energy E_T.

$$\mathbf{r}_{cm}^{n+1} = \mathbf{r}_{cm}^{n} + \frac{\mathbf{F}_{cm}^{n}}{|\mathbf{F}_{cm}^{n}|}\delta r$$

$$\mathbf{r}^{n+1} = \mathcal{R}_{\delta\theta}^{n}\mathbf{r}^{n}$$

Delgado Buscalioni et.al.: J. Chem. Phys **119**, 978 (2003), J. Chem. Phys. **121**, 12139 (2004).

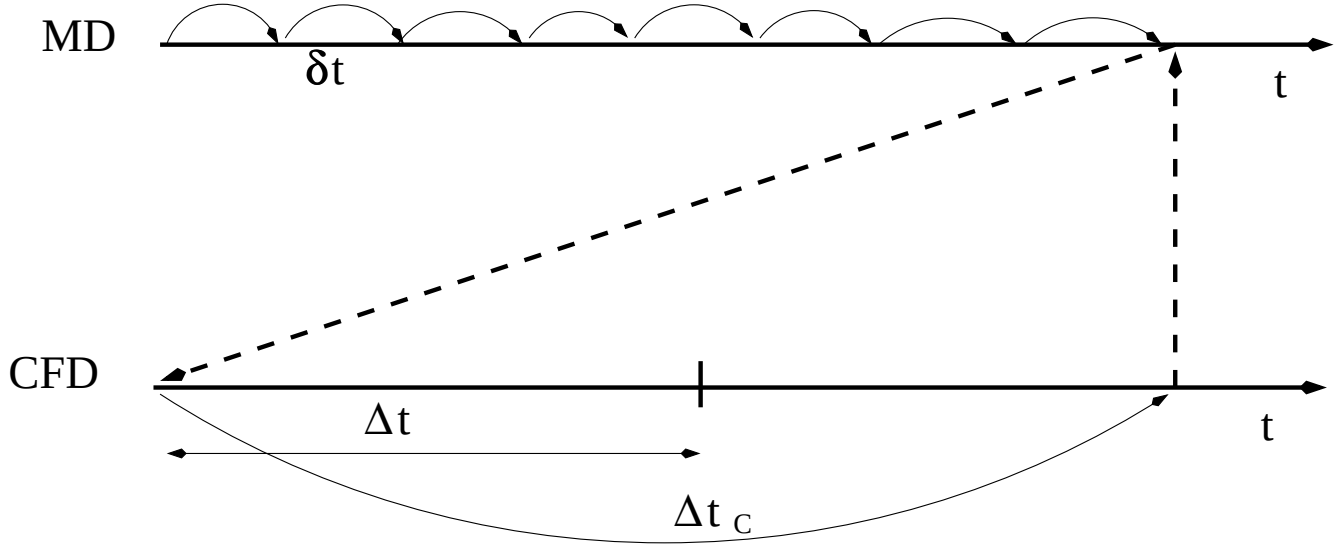
Triple-scale model



- to allow for insertion of larger molecule into a dense liquid
- to allow for grand canonical MD simulation of open molecular systems

R. Delgado Buscalioni, K. Kremer, M. Praprotnik, J. Chem. Phys. **128**, 114110 (2008).
R. Delgado Buscalioni, K. Kremer, M. Praprotnik, arXiv:0908.0397v1 [cond-mat.soft]

Time coupling



coupling time:

$$\Delta t_C = n_{CFD}\Delta t = n_{MD}\delta t$$

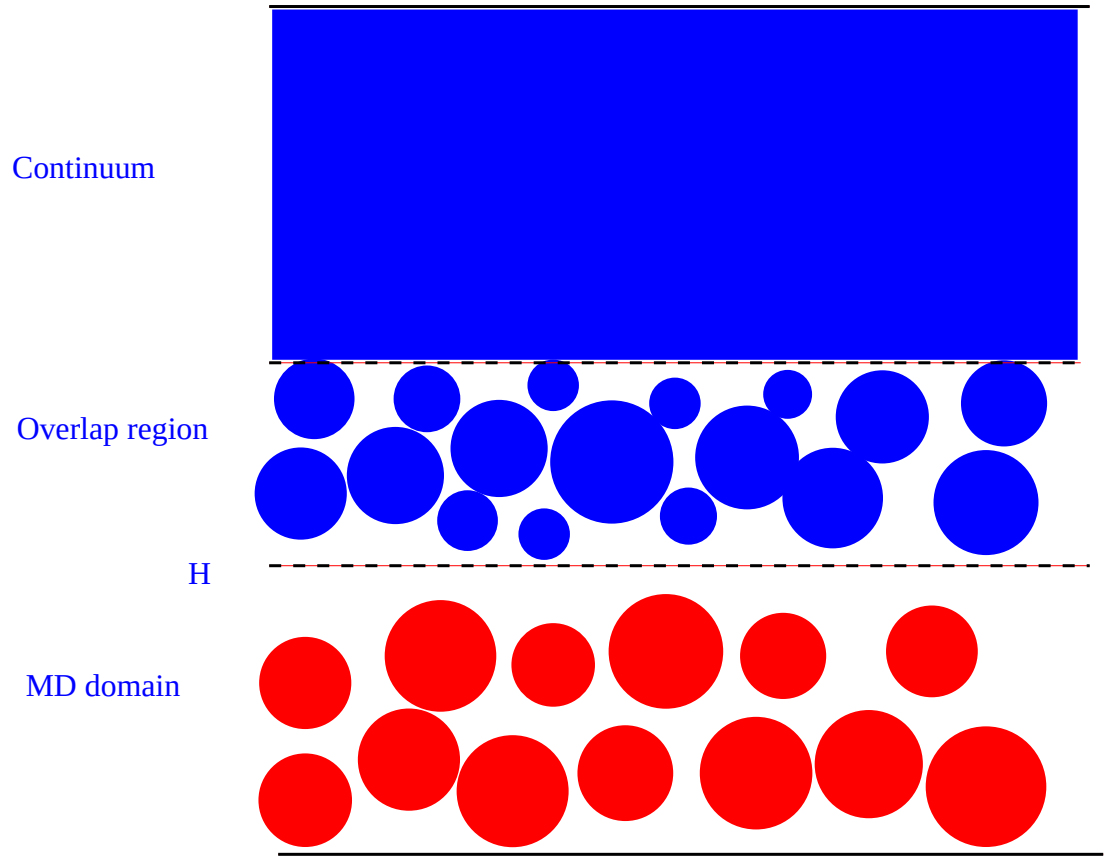
MD decorrelation time:

$$\tau_c \sim 100 fs$$

$$\Delta t = 2\tau_c$$

R. Delgado Buscalioni, G. De Fabritiis, Phys. Rev. E **76**, 036709 (2007).

State variable coupling



In the overlap region both descriptions are valid. However, overlap particles are not part of the system- they serve for communication between the two regimes.

Constraint dynamics method

To impose momentum continuity (Couette flow) the total momentum of the overlapping particles is relaxed to the corresponding continuum fluid element momentum using constraint:

$$\sum_{i=1}^{N} p_i - Mu = 0$$

N is the total number of particles, p_i is the momentum of particle i, u, and M are the velocity and mass of the fluid element, respectively. To terminate the extent of the MD region $F^{ext} = -\alpha p \rho^{-2/3}$ is added to the outer overlap particles.

$$v_i = \frac{p_i}{m} + \xi \left[\frac{M}{Nm} u - \frac{1}{N} \sum_{i=1}^{N} \frac{p_i}{m} \right]$$

$$\frac{\partial p_i}{\partial t} = -\frac{\partial U_{12-6}}{\partial x}$$

S. T. O'Connell, P. A. Thompson, Phys. Rev. E **52**, R5792 (1995)

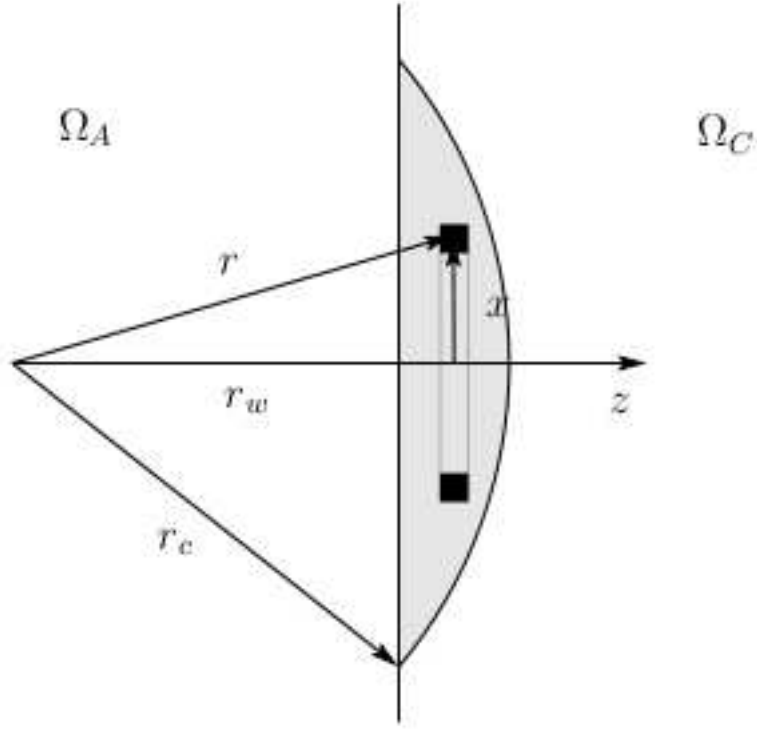
Schwartz alternating method

- Solution of one of the domains provides boundary conditions to the other domain (through the overlap domain) and vice versa.
- This procedure is iterated until both solutions in the overlap domain are matched.
- Requirement: transport conditions of MD and continuum domains must match in the overlap domain.
- Mass transfer across the H is controlled using a virtual particle reservoir.

P. L. Lions, In R. Glowinski ed., First International Symposium on Domain Decomposition Methods for Partial Differential Equations, pp. 1-42, SIAM, 1998.

N. G. Hadjiconstantinou, A. T. Patera, Int. J. Mod. Phys. **8**, 967 (1997)

Effective boundary force+specular wall



T. Werder, J. H. Walther, P. Koumoutsakos, J. Comp. Phys. **205**,373 (2005)

E. M. Kotsalis, J. H. Walther, P. Koumoutsakos, Phys. Rev. E **76**, 0167709 (2007)

Applying pressure to MD domain

$$p = p_K + p_U = k_B T \rho_n + \rho_n \int_0^{r_c} F_m(r)\, dr$$

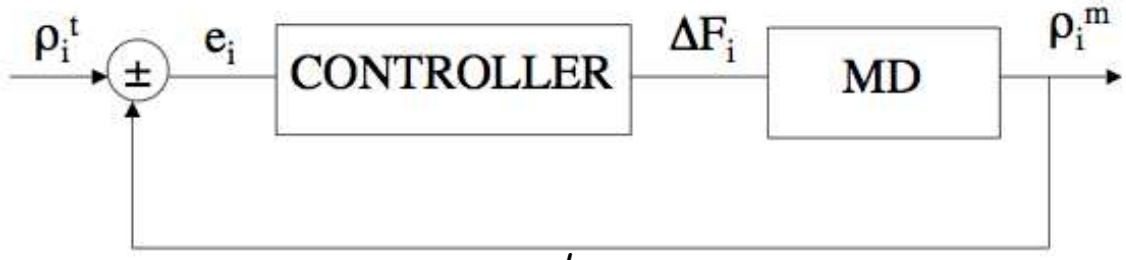
$$F_m(r_w) = -2\pi\rho_n \int_{z=r_w}^{r_c} \int_{x=0}^{\sqrt{r_c^2 - z^2}} g(r) \frac{\partial U_{12-6}(r)}{\partial r} \frac{z}{r} x\, dx dz$$

$$r = \sqrt{x^2 - z^2}$$

T. Werder, J. H. Walther, P. Koumoutsakos, J. Comp. Phys. **205**,373 (2005)

E. M. Kotsalis, J. H. Walther, P. Koumoutsakos, Phys. Rev. E **76**, 0167709 (2007)

Reducing density oscillations



$$e(r_w) = \rho^t - \rho^m(r_w)$$

$$\epsilon(r_w) = \nabla e(r_w) = -\nabla \rho^m(r_w)$$

$$\Delta F_i' = K_p \epsilon_i$$

$$F_i^{new} = F_i^{old} + \Delta F_i = F_i^{old} + 0.25\Delta F_{i-1}' + 0.5\Delta F_i' + 0.25\Delta F_{i+1}'$$

$$E = \sqrt{\frac{1}{N}\sum_{i=1}^{N} e_i^2}$$

E. M. Kotsalis, J. H. Walther, P. Koumoutsakos, Phys. Rev. E **76**, 0167709 (2007)

Other hybrid models

- Using Lattice Boltzmann to solve incompressible Navier Stokes equations:

  A. Dupuis, E. M. Kotsalis, P. Koumoutsakos, Phys. Rev. E **75**, 046704 (2007).

- Total simulation domain is modeled using a continuum solver, where MD computations enter as a local refinement:

  W. Ren, W. E, J. Comp. Phys. **204**, 1 (2005)
  S. Yasuda, R. Yamamoto:, Phys. Fluids **20**, 113101 (2008).

Acknowledgments

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