

Simulacije z uporabo metode AdResS: sklopitev atomistične in grobozrnote resolucije

Matej Praprotnik

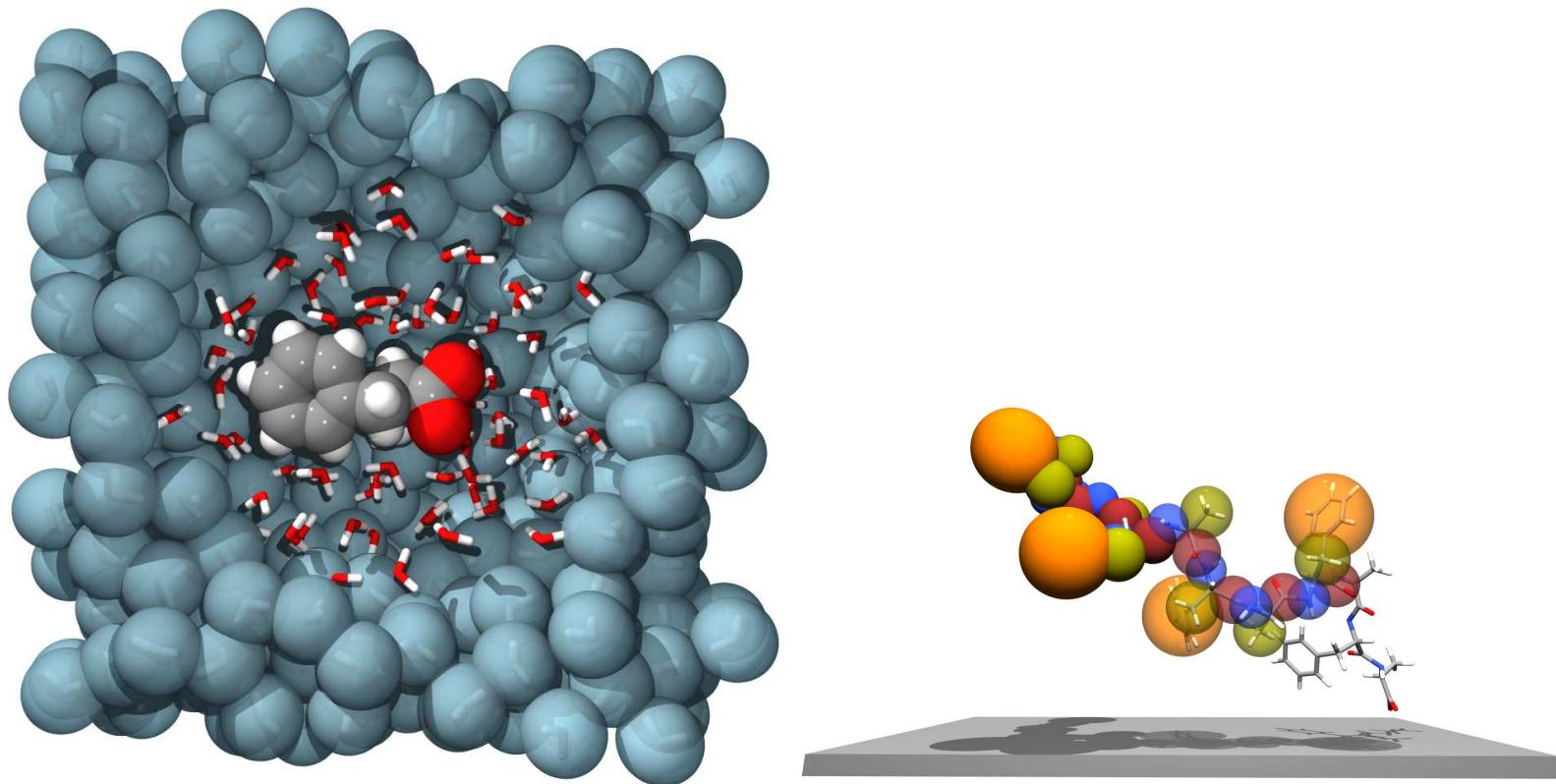
praprot@cmm.ki.si

Laboratorij za Molekularno Modeliranje

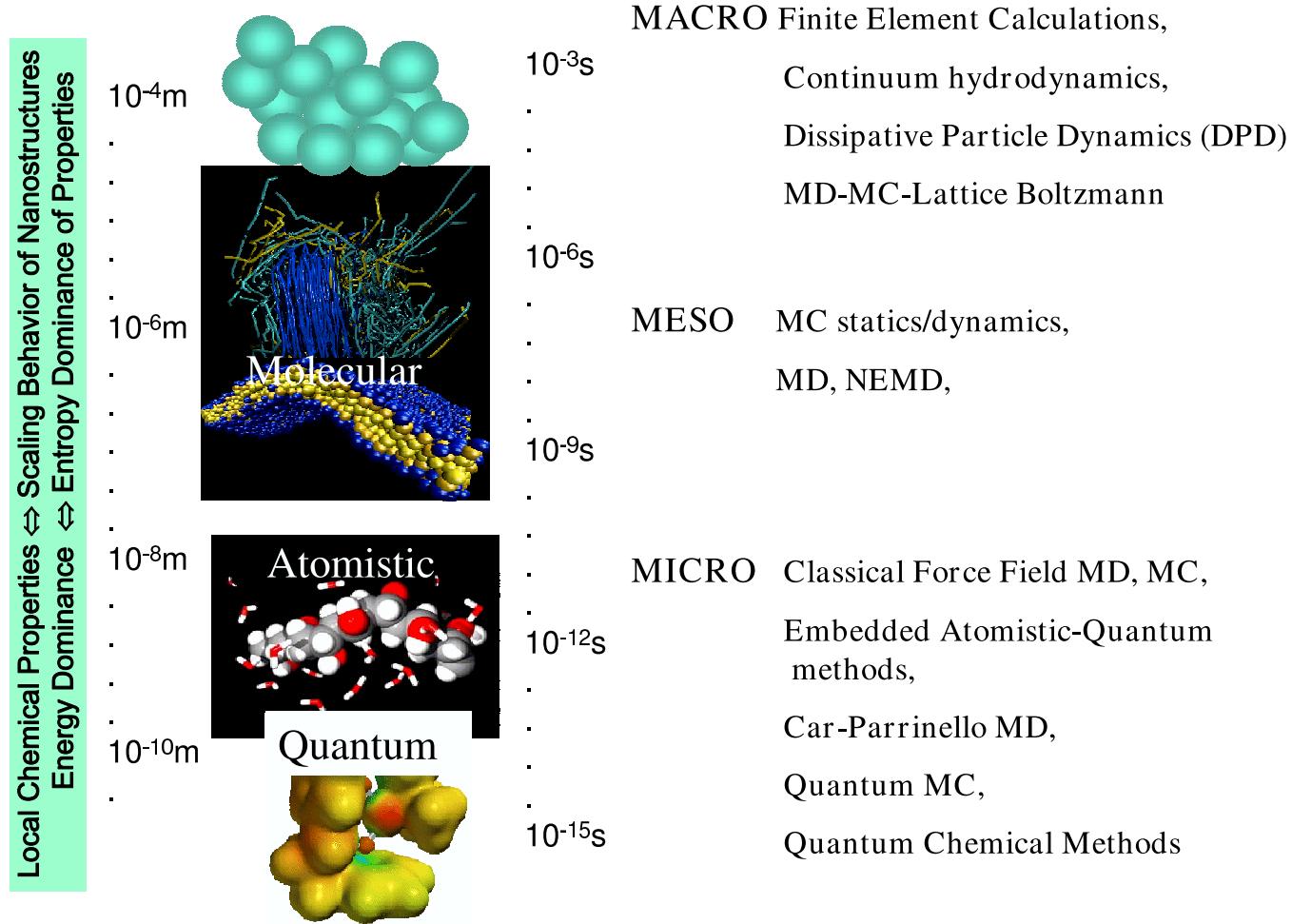
Kemijski inštitut

Ljubljana

Multiscale Phenomena



Multiscale Modeling



Adaptive Resolution Simulation

● Motivation:

- to simplify the model to the largest extent possible while keeping all the necessary details where this is required.

● Method: *AdResS (Adaptive Resolution Scheme)*

- allows for an dynamical switching between the atomistic and mesoscopic levels of detail \Rightarrow on-the-fly changing of the number of DOFs
- tailor-made for molecular systems where spatially localized domains with the required atomistic resolution exchange particles with the remainder of the system sufficiently described on the mesoscopic scale.

● Results:

- accurately reproduces the statistical properties of the reference all-atom system.

MD Simulation

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

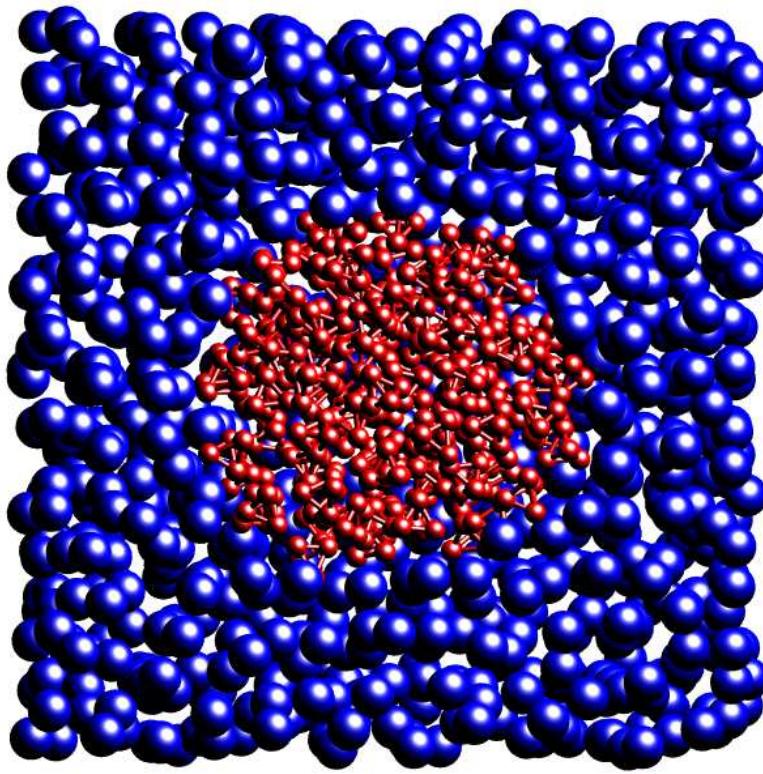
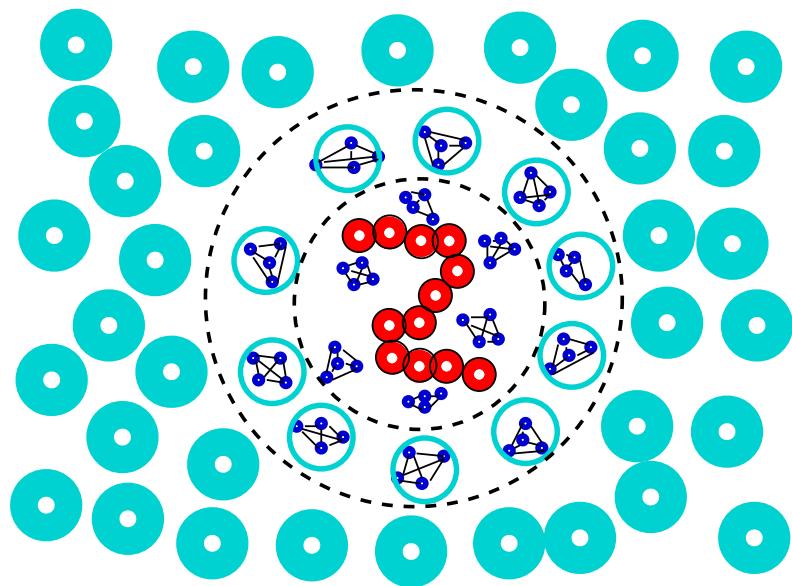
Mesoscopic MD simulation:

- reduces the number of DOFs by retaining only those that are relevant for the property of interest \Rightarrow longer length and time scales can be reached
- specific chemical details are usually lost in the coarse-graining procedure

Combining the best from both approaches:

- Hybrid Adaptive MD Schemes

Hybrid Atomistic/Mesoscopic Liquid

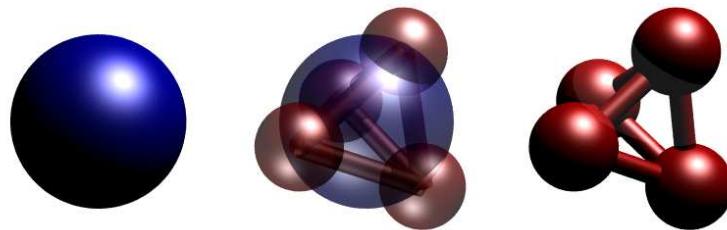


M. Praprotnik, L. Delle Site, K. Kremer, J. Chem. Phys. 126, 134902 (2007).

M. Praprotnik, L. Delle Site, K. Kremer, Phys. Rev. E 73, 066701 (2006).

Changing Number of DOFs

- A tetrahedral molecule has a defined spatial orientation and $3N = 12$ DOFs:
 - 3 translational
 - 3 rotational
 - $3N - 6 = 6$ vibrational
- One particle mesoscopic molecule has no defined spatial orientation and only 3 translational DOFs.



M. Praprotnik, L. Delle Site, K. Kremer, J. Chem. Phys. **123**, 224106 (2005).

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

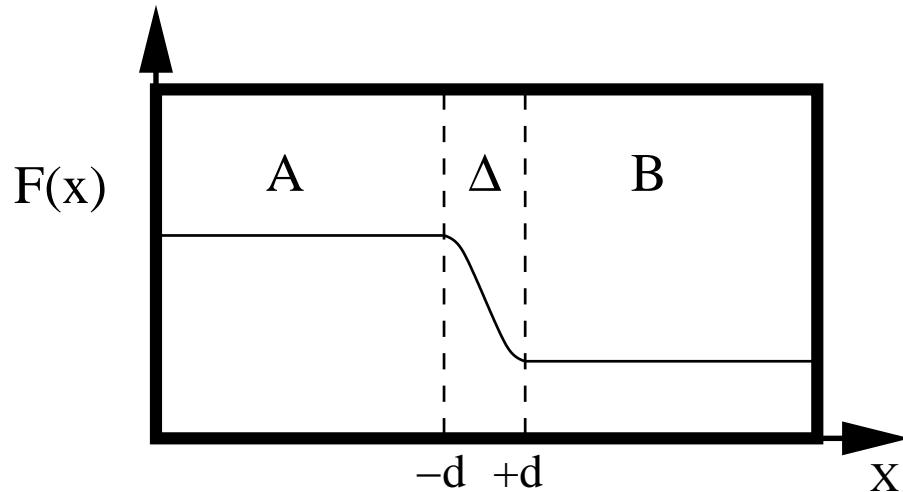
Geometrically Induced Phase Transition

In thermodynamical equilibrium, boundary conditions analogous to two-phase coexistence must be satisfied:

$$\mu_{ex} = \mu_{cg}, \quad p_{ex} = p_{cg}, \quad T_{ex} = T_{cg}.$$

The rotational and vibrational parts of the free energy can be viewed as the latent heat, which is supplied or taken by the thermostat, at this transition.

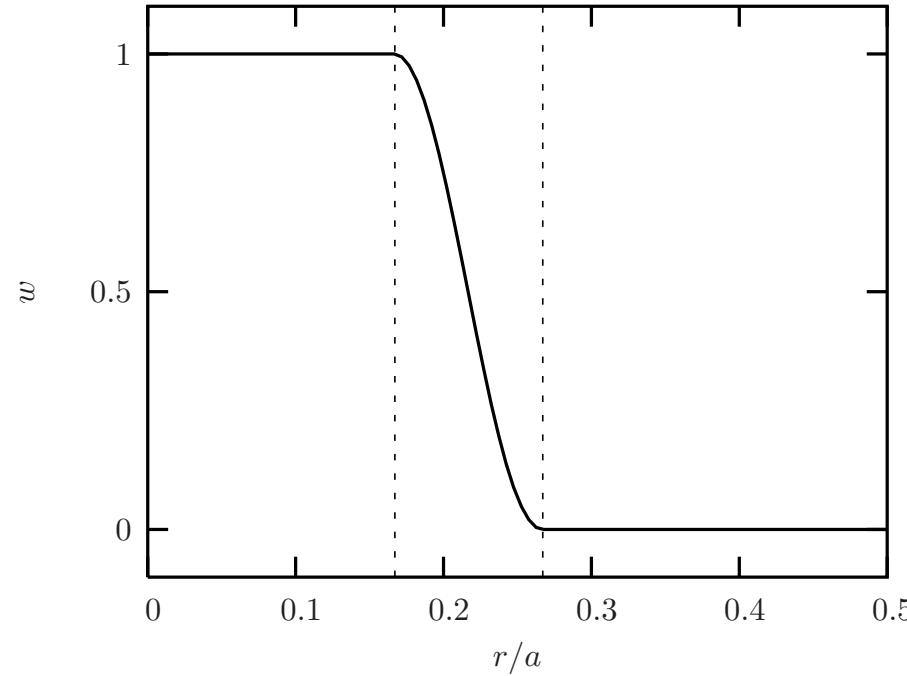
Free Energy Density Profile



- Molecules in A and B are **physically identical** but differently represented.
- The number of DOFs is $n = n(x)$ with: $n_A = \text{const}_A$; $n_B = \text{const}_B$; and $n_\Delta = n(x)$
- The system is in equilibrium which implies:
 $\lim_{x \rightarrow d^-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \rightarrow d^+} \frac{\partial F_B(x)}{\partial x} = 0 \implies$
 $\lim_{x \rightarrow d^-} \frac{\partial n_A(x)}{\partial x} = \lim_{x \rightarrow d^+} \frac{\partial n_B(x)}{\partial x} = 0$

$\partial F_A / \partial N_A = \mu_A$ and $\partial F_B / \partial N_B + \phi = \mu_B$, where ϕ is the latent heat per molecule.

Weighting Function = Order Parameter



- The values $w = 1$ and $w = 0$ correspond to the atomistic and coarse-grained regions, respectively, while the values $0 < w < 1$ correspond to the transition (*hyb*) regime.

M. Praprotnik, L. Delle Site, K. Kremer, J. Chem. Phys. 123, 224106 (2005).

Latent Heat

For a generic switchable degree of freedom p the kinetic energy contribution to the free energy per particle is:

$$A_p = -kT \log \left[\int e^{-\beta p^2} d^w p \right] = \mu_p^{kin}(w) \quad (1)$$

and thus the total contribution of the entire set of switchable degrees of freedom (assuming that they decouple) is:

$$\mu^{kin}(w) = \sum_{DOF} \mu_p^{kin}(w). \quad (2)$$

and the component to the latent heat $\phi(x)^{kin} = \mu_A^{kin} - \mu^{kin}(w)$. The analitical solution of Eq.1 is:

$$\mu_p^{kin}(w) \sim C k T \left(\frac{w}{2} \right) \log(T) \quad (3)$$

where C is a constant, k the Boltzmann constant, and T is the temperature. The latent heat must be supplied/removed by a **local thermostat**.

S. Poblete, M. Praprotnik, K. Kremer,L. Delle Site, J. Chem. Phys. 132, 114101 (2010).

Equipartition Theorem

- For the fractional quadratic DOF Θ with the weight $w = \alpha$ we can write the **partition function** as:

$$\begin{aligned}\exp(-\beta F_\alpha) &= C \int \exp(-\beta f(\alpha)p_\Theta^2/2) dV_\alpha = \\ &= 2C \int_0^\infty \exp(-\beta f(\alpha)p_\Theta^2/2) |p_\Theta|^{\alpha-1} \frac{dp_\Theta}{\Gamma(\alpha)} = \\ &= \frac{2^{\alpha/2} C \Gamma(\alpha/2)}{\Gamma(\alpha)} f(\alpha)^{-\alpha/2} \beta^{-\alpha/2} \sim \beta^{-\alpha/2}.\end{aligned}$$

- $\langle K_\alpha \rangle = \frac{d(\beta F_\alpha)}{d\beta} = \frac{\alpha}{2\beta} = \frac{\alpha k_B T}{2}$.
- In equilibrium $T_A = T_B = T_\Delta = T$ and thus: $n_\alpha \sim \alpha$.

M. Praprotnik, K. Kremer, L. Delle Site, Phys. Rev. E 75, 017701 (2007).

AdResS

AdResS consists of two main steps:

1. Derive the effective pair potential U^{cm} between coarse-grained molecules on the basis of the reference all-atom system.
2. Couple the atomistic and mesoscopic scales:

$$\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}_{\alpha\beta}^{atom} + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}_{\alpha\beta}^{cm},$$

where

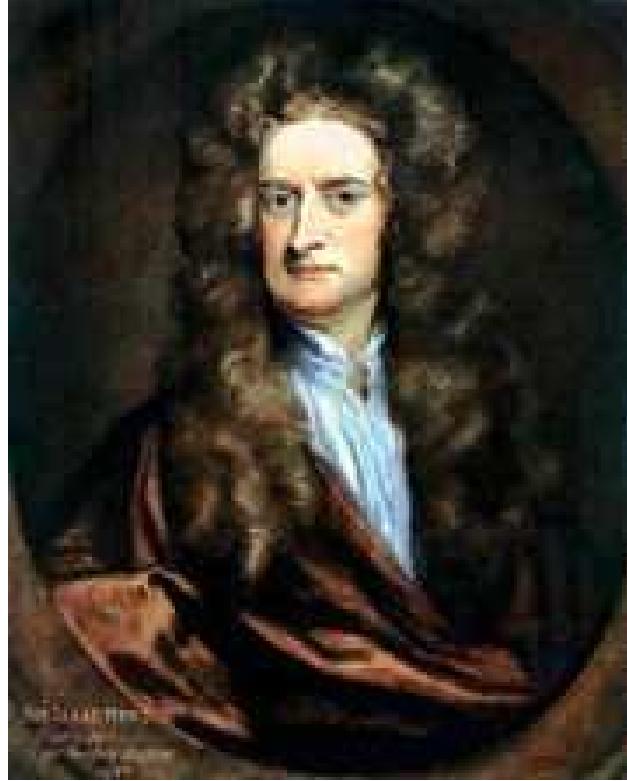
$$\mathbf{F}_{\alpha\beta}^{atom} = \sum_{i\alpha,j\beta} \mathbf{F}_{i\alpha j\beta}^{atom}$$

is the sum of all pair interactions between explicit atoms of molecules α and β and

$$\begin{aligned}\mathbf{F}_{i\alpha j\beta}^{atom} &= -\frac{\partial U^{atom}}{\partial \mathbf{r}_{i\alpha j\beta}}, \\ \mathbf{F}_{\alpha\beta}^{cm} &= -\frac{\partial U^{cm}}{\partial \mathbf{R}_{\alpha\beta}}.\end{aligned}$$

M. Praprotnik, L. Delle Site, K. Kremer, J. Chem. Phys. 123, 224106 (2005).

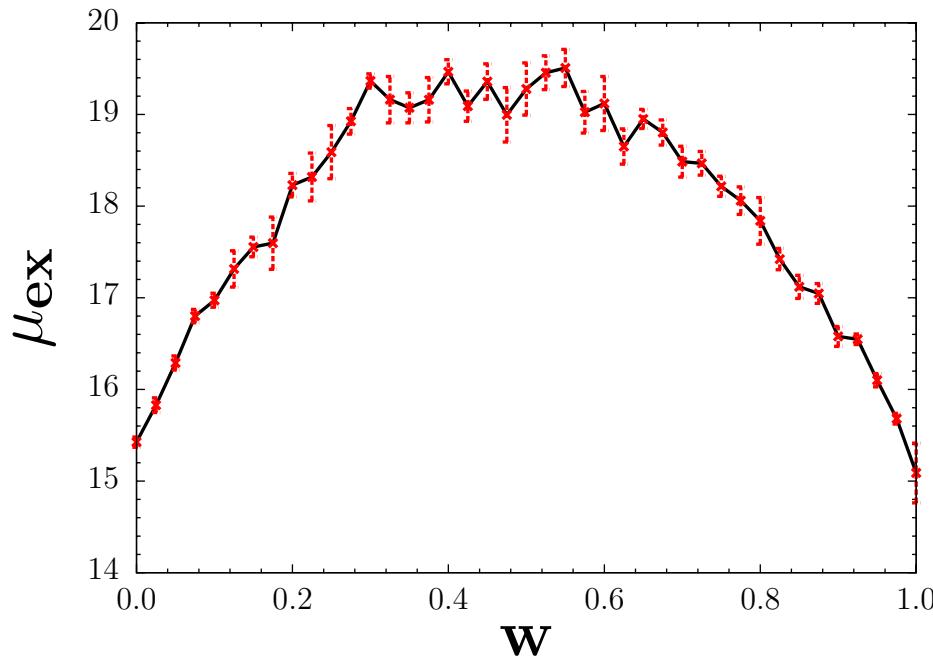
May the Force be with you



One must interpolate the **forces** and not the interaction potentials
if the **Newton's Third Law** is to be satisfied!

M. Praprotnik, K. Kremer, L. Delle Site, J. Phys. A: Math. Theor. **40**, F281, 2007.

Generalized AdResS



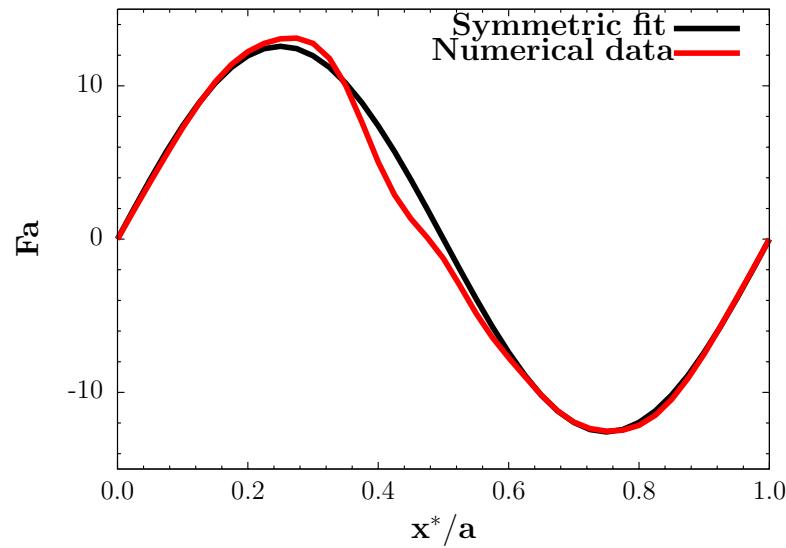
$$\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}_{\alpha\beta}^A + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}_{\alpha\beta}^B - \mathbf{F}^{TD}$$

where

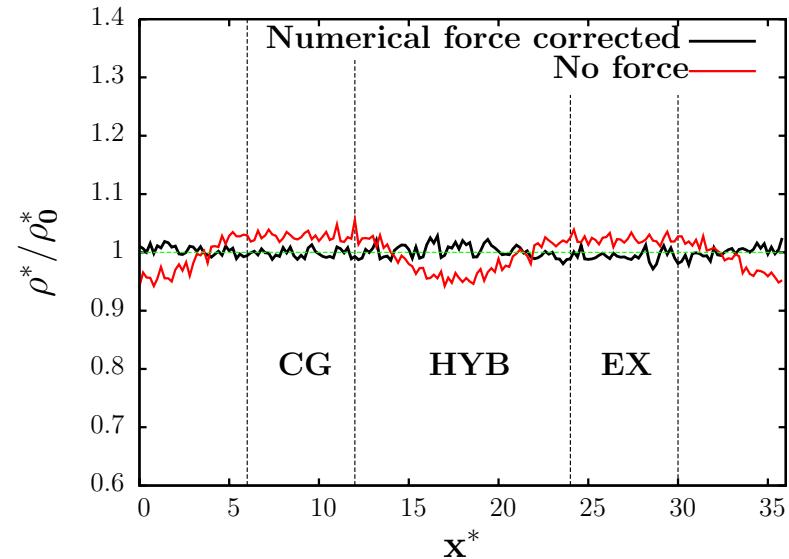
$$F_x^{TD} = -\frac{\partial \mu^{exc}}{\partial x}$$

S. Poblete, M. Praprotnik, K. Kremer, L. Delle Site, J. Chem. Phys. **132**, 114101 (2010).

Thermodynamic Force

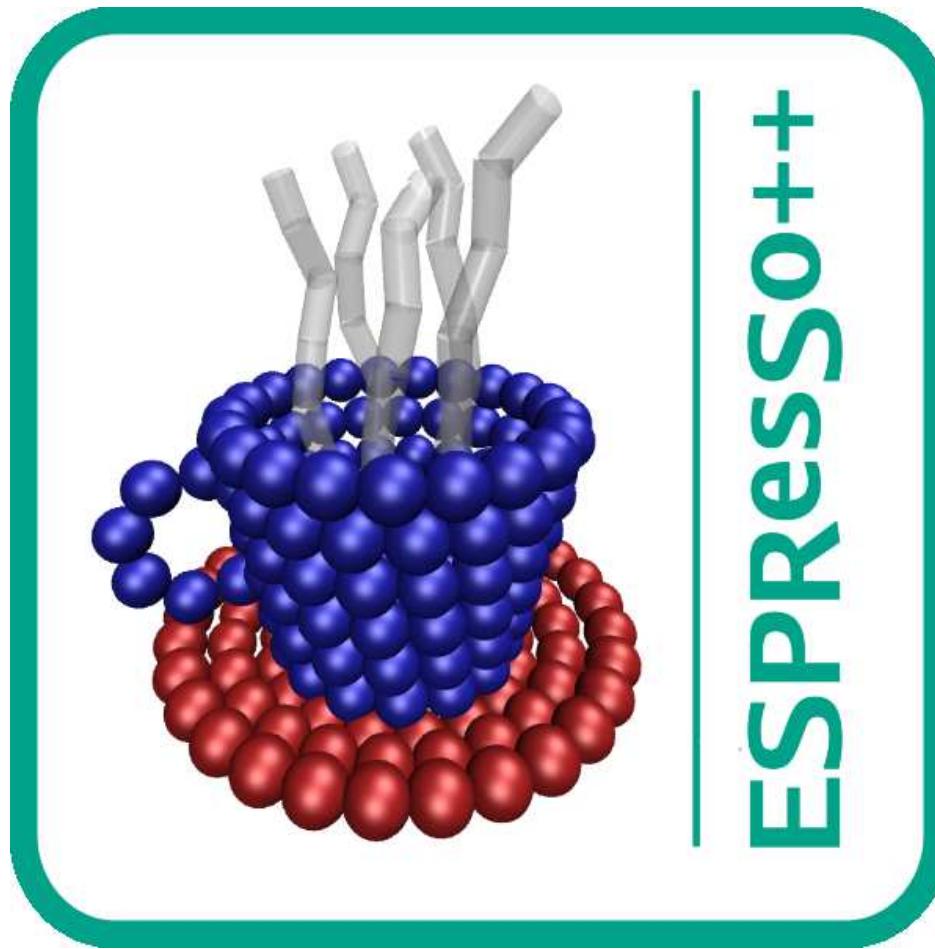


(e) thermodynamic force



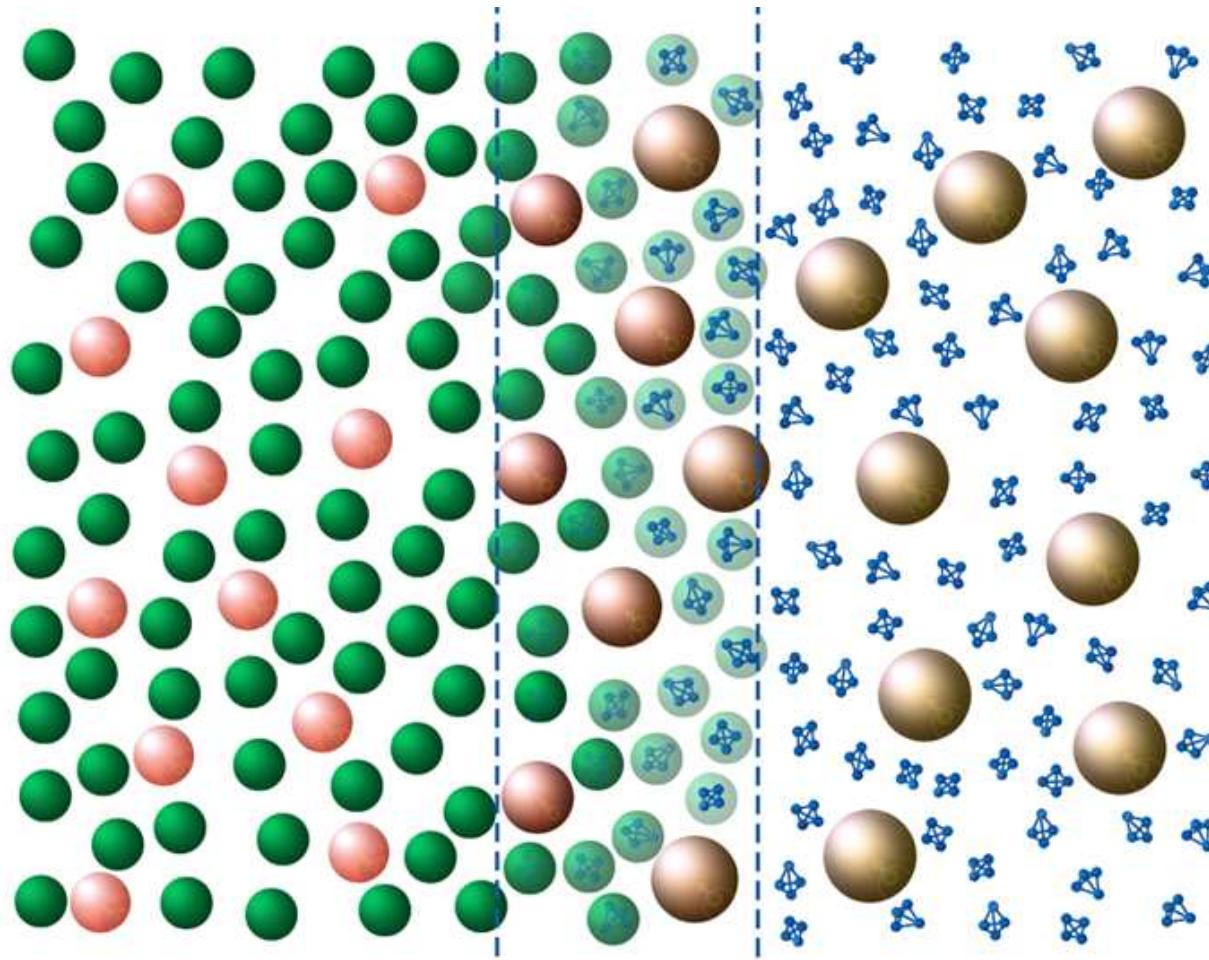
(f) density across the simulation box

ESPResSo++



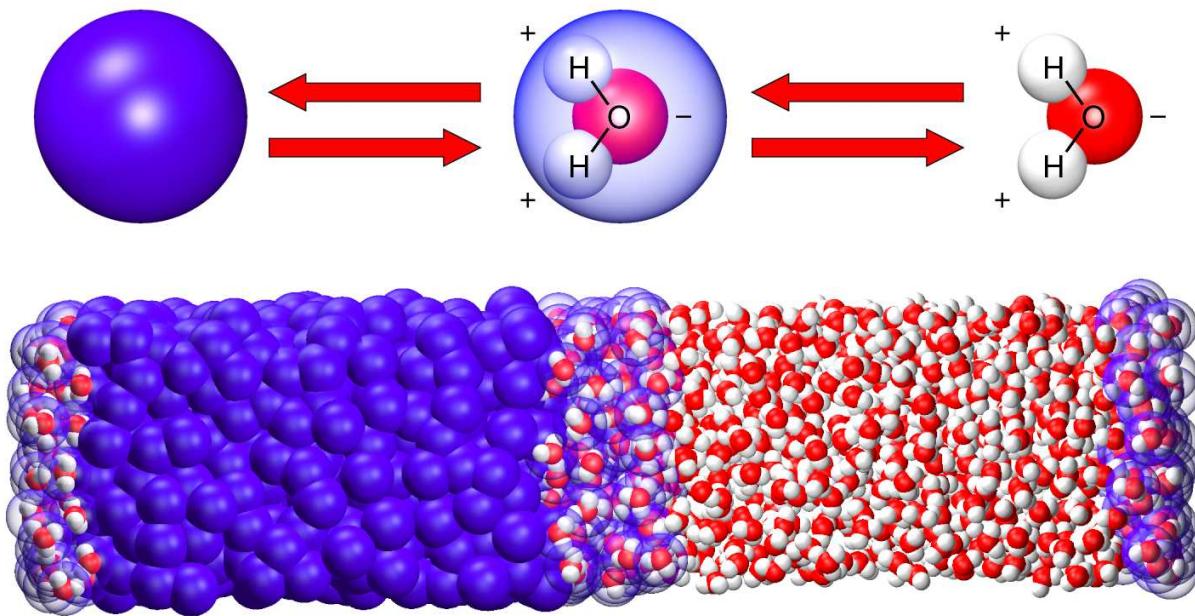
<https://www.espresso-pp.de/>

Mixture



S. Poblete, M. Praprotnik, K. Kremer,L. Delle Site, J. Chem. Phys. 132, 114101 (2010).

Liquid Water



- M. Praprotnik, S. Matysiak, L. Delle Site, K. Kremer, C. Clementi, J. Phys.: Condens. Matter **19**, 292201 (2007).
- S. Matysiak, C. Clementi, M. Praprotnik, K. Kremer, L. Delle Site, J. Chem. Phys. **128**, 024503 (2008).

Mapping of Structural Properties

In the limit $\rho = 0$:

$$U^{eff}(r) = F(r) = -k_B T \ln g(r).$$

For systems with $\rho > 0$ the above relation is used as an initial approximation in the iteration scheme, i.e, **Iterative Boltzmann inversion**:

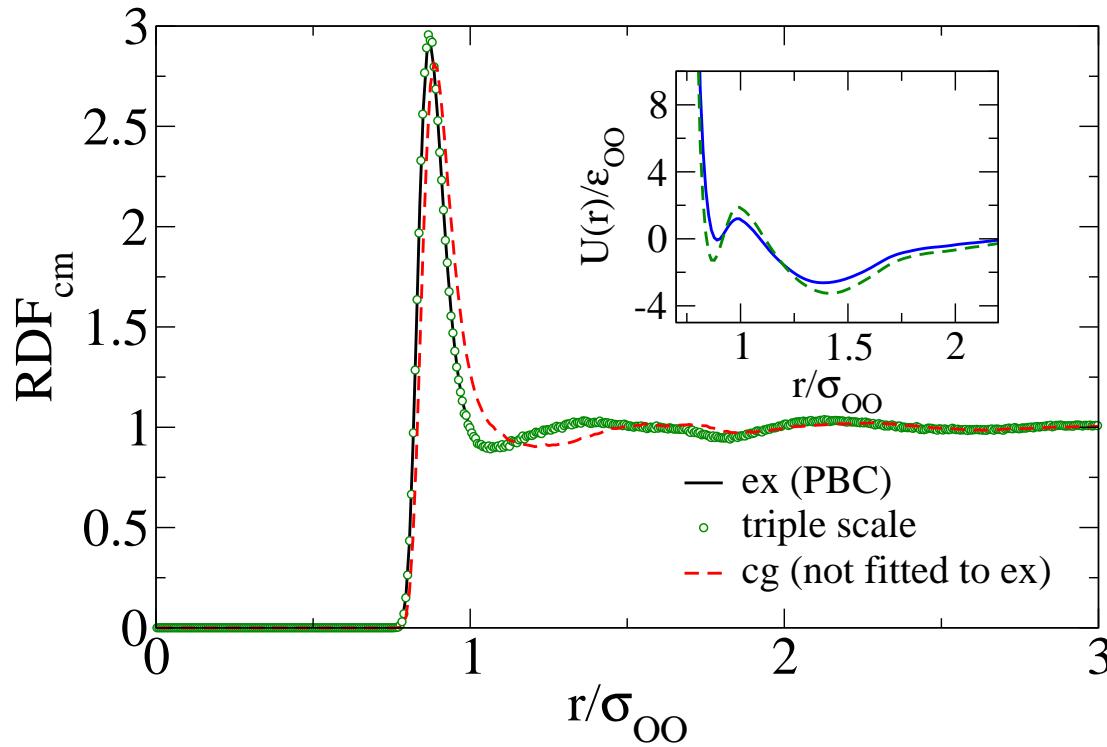
$$U_{i+1}^{eff}(r) = U_i^{eff}(r) + k_B T \ln \frac{g_i(r)}{g_{target}(r)}$$

Ramp pressure correction:

$$\Delta U_{lin} = A(1 - \frac{r}{r_{cut}}).$$

D. Reith, M. Pütz, F. Müller-Plathe, J. Comput. Chem., **24**, 1624, (2003).

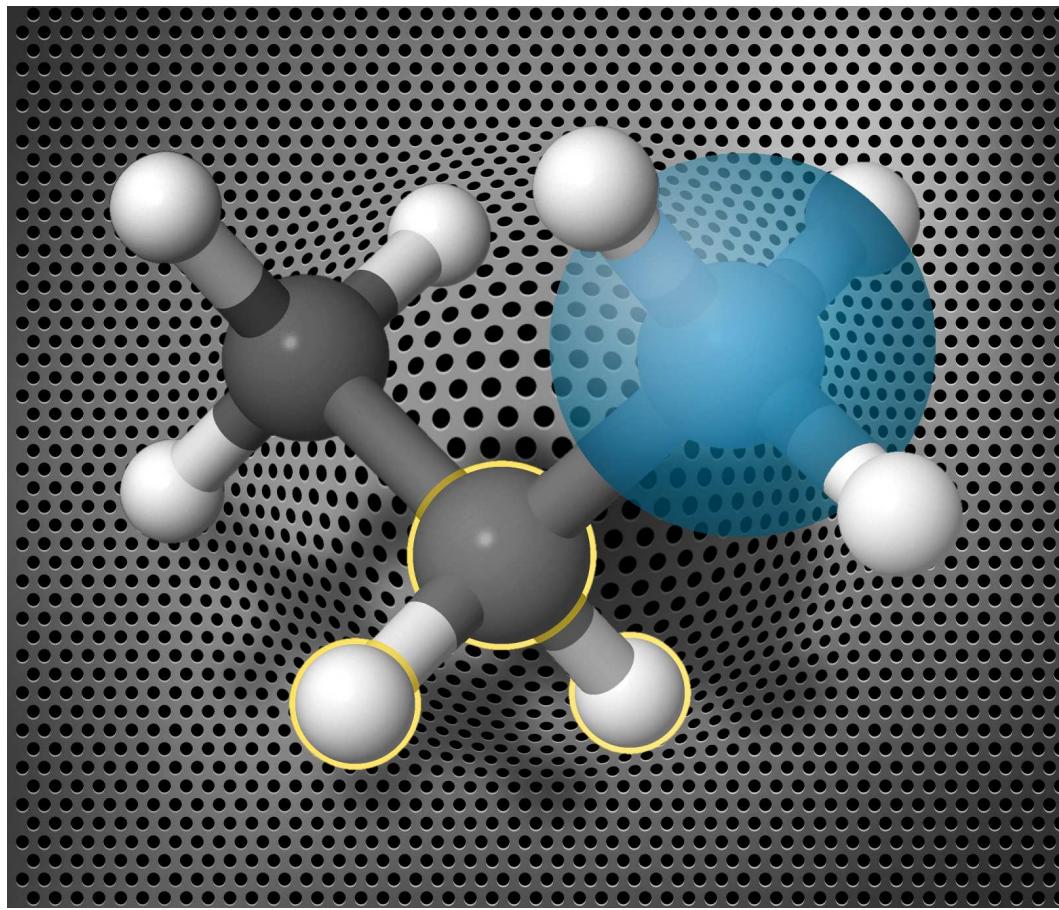
Coarse-Grained Model



- Center-of-mass RDF of the flexible TIP3P water model and the effective potential.

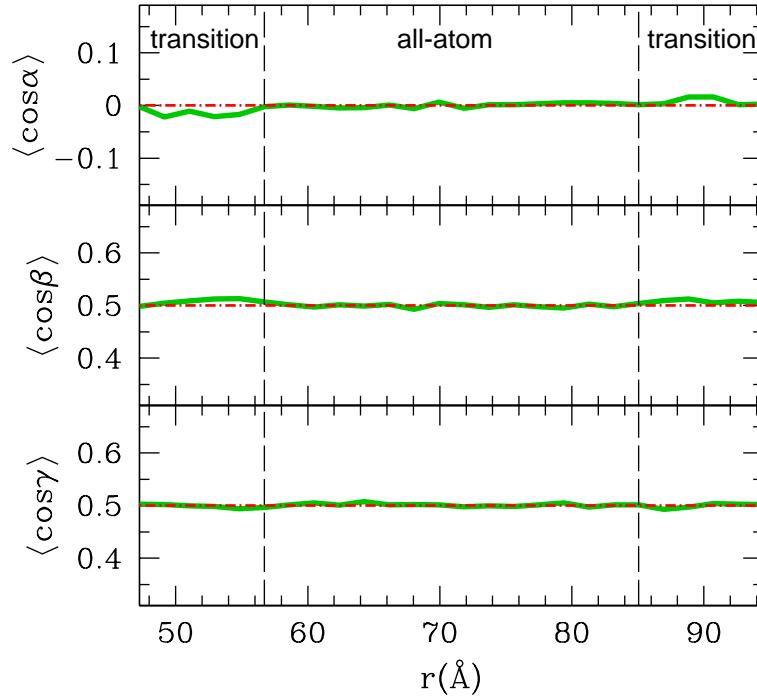
R. Delgado Buscalioni, K. Kremer, M. Praprotnik, J. Chem. Phys. 131, 244107, (2009).

STOCK (<http://stock.cmm.ki.si>)



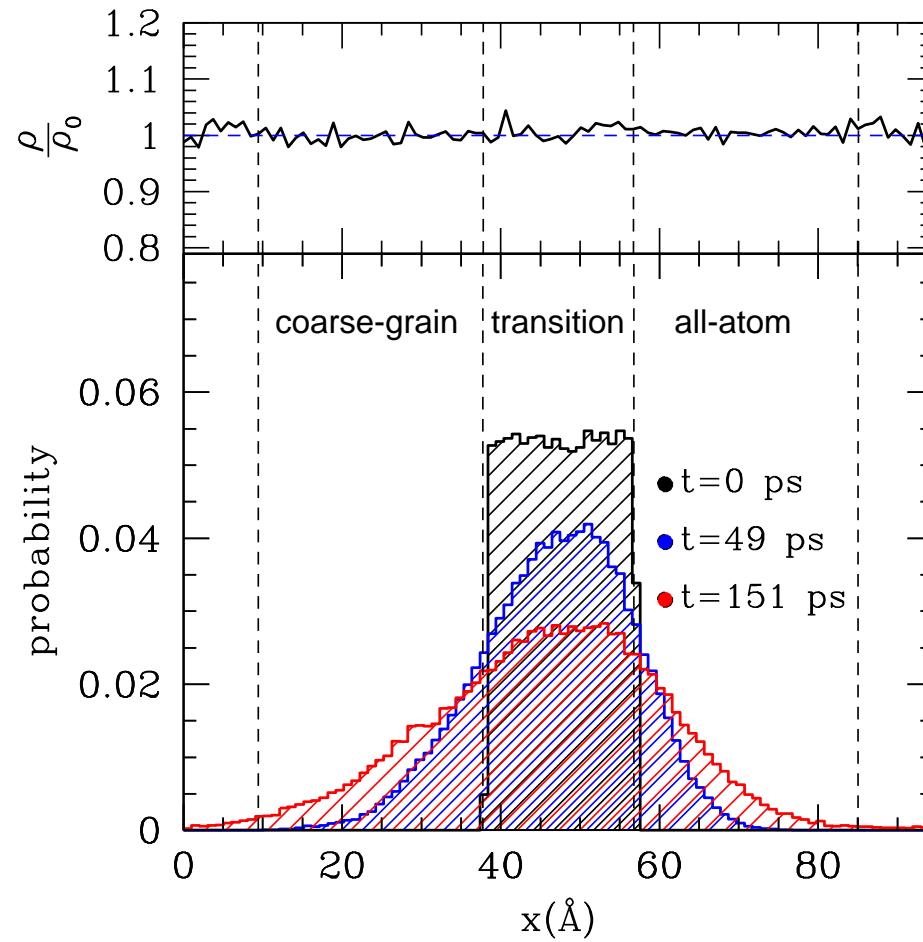
S. Bevc, C. Junghans, M. Praprotnik, J. Comput. Chem., DOI: 10.1002/jcc.23806, (2015).

Interface Effect of the CG Water

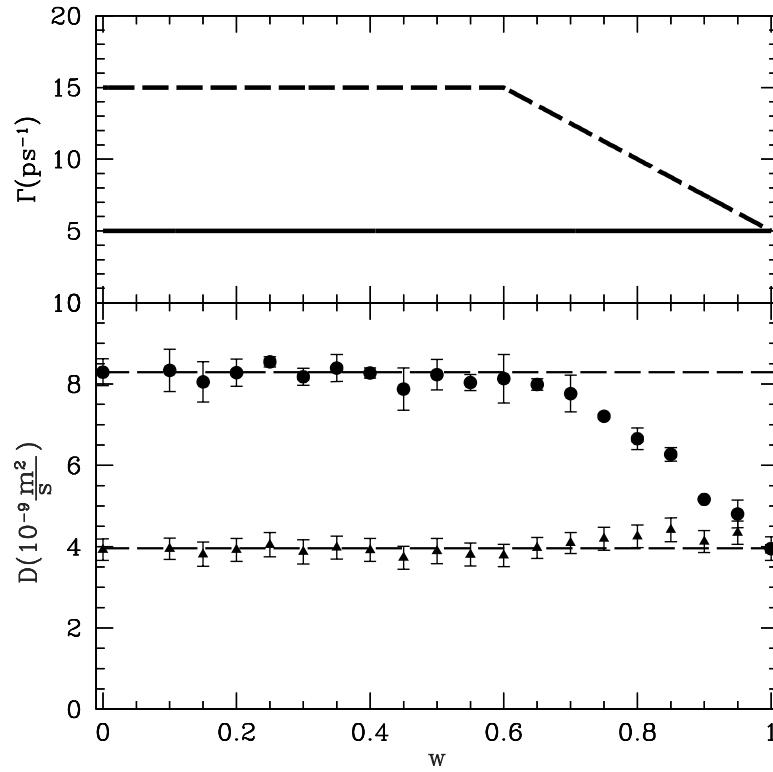


The transition regime neutralizes the interface effect of the cg water \Rightarrow
the structure of water in the explicit regime is the same as in the bulk.

Mapping of Dynamical Properties



Diffusion coefficient



S. Matysiak, C. Clementi, M. Praprotnik, K. Kremer, L. Delle Site, J. Chem. Phys 128, 024503, 2008.

Position Dependent Langevin Thermostat

The Langevin equation with a position dependent coefficient $\Gamma(x)$ can be written as:

$$m_i dv_i / dt = F_i - m_i \Gamma(x) v_i + R_i(x, t) \quad (4)$$

where $R_i(x, t)$ is:

$$\langle R_i(x, t) \rangle = 0, \quad (5)$$

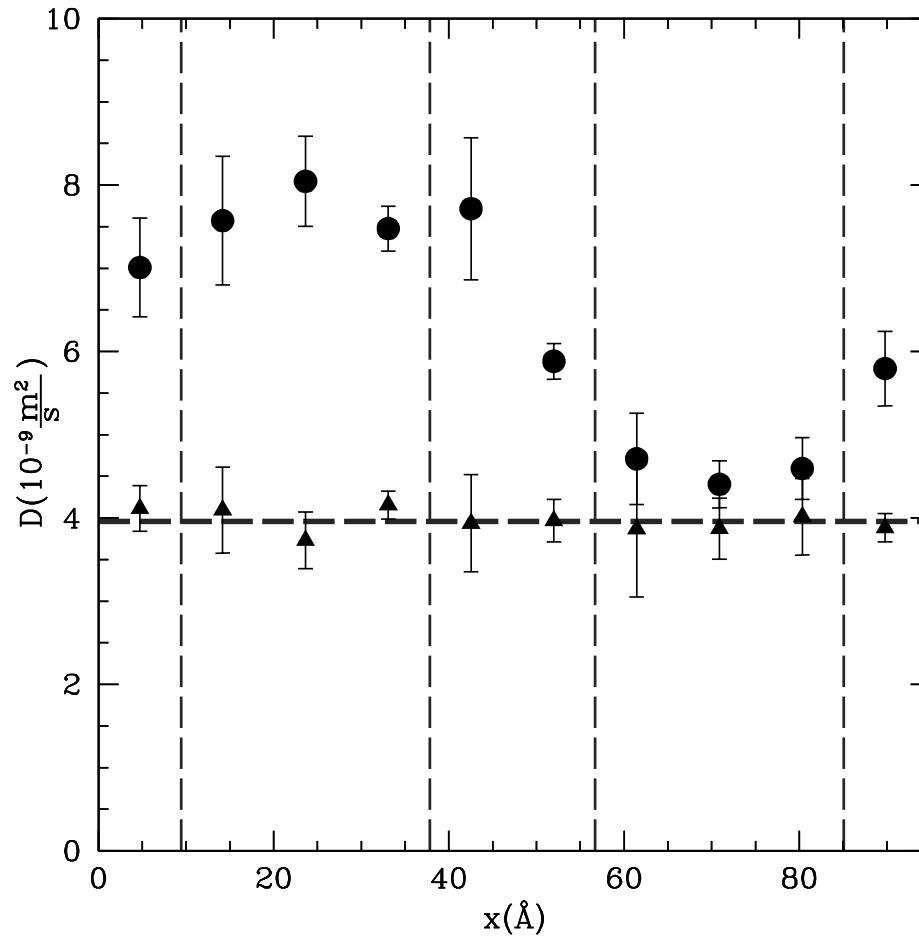
$$\langle R_i(x, t_1) R_j(x, t_2) \rangle = 2\Gamma(x) m_i kT \delta(t_1 - t_2) \delta_{ij} \quad (6)$$

$$\Gamma(w) = \begin{cases} \Gamma_{cg} & \text{if } w \leq 0.6 \\ \alpha w + \beta & \text{if } 0.6 < w \leq 1.0 \end{cases} \quad (7)$$

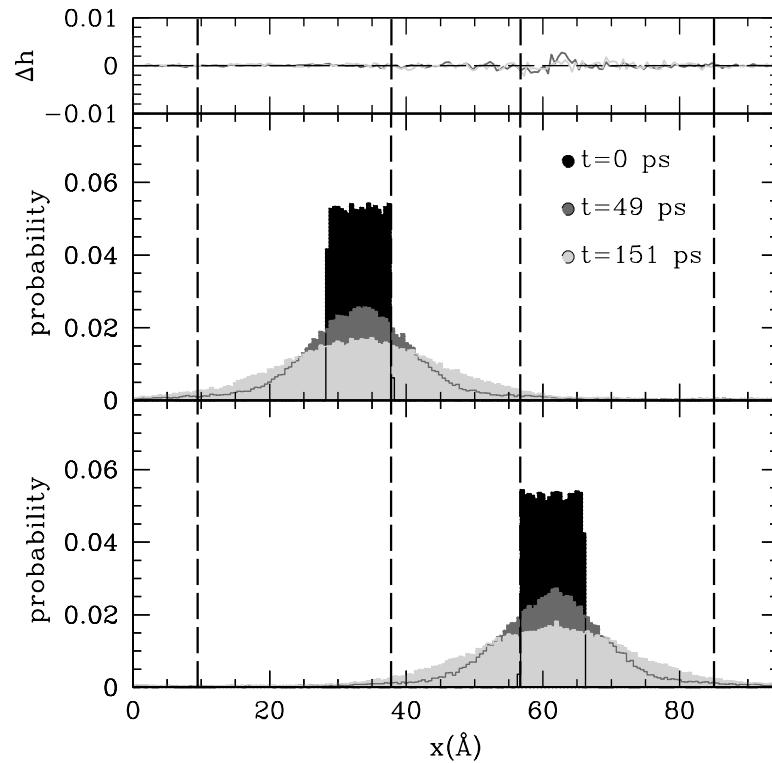
This choice provides a simple interpolation between the two limit values of

$\Gamma(0.6) = \Gamma(0) = \Gamma_{cg} = 15 \text{ ps}^{-1}$ and $\Gamma(1) = \Gamma_{all-atom} = 5 \text{ ps}^{-1}$. The parameters α and β are -25 ps^{-1} and 30 ps^{-1} , respectively.

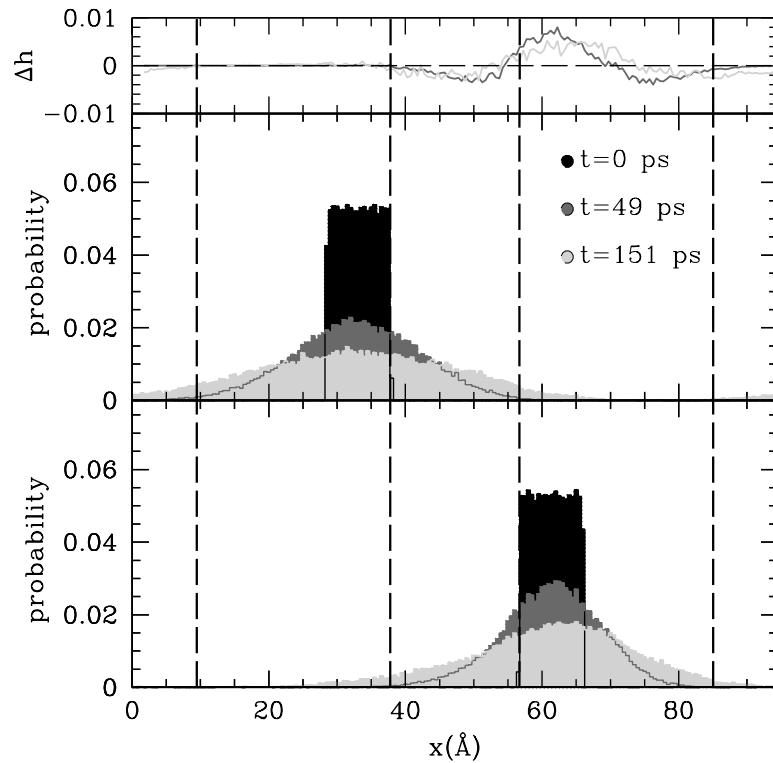
Diffusion in the Hybrid System



Diffusion Across the Transition Regime

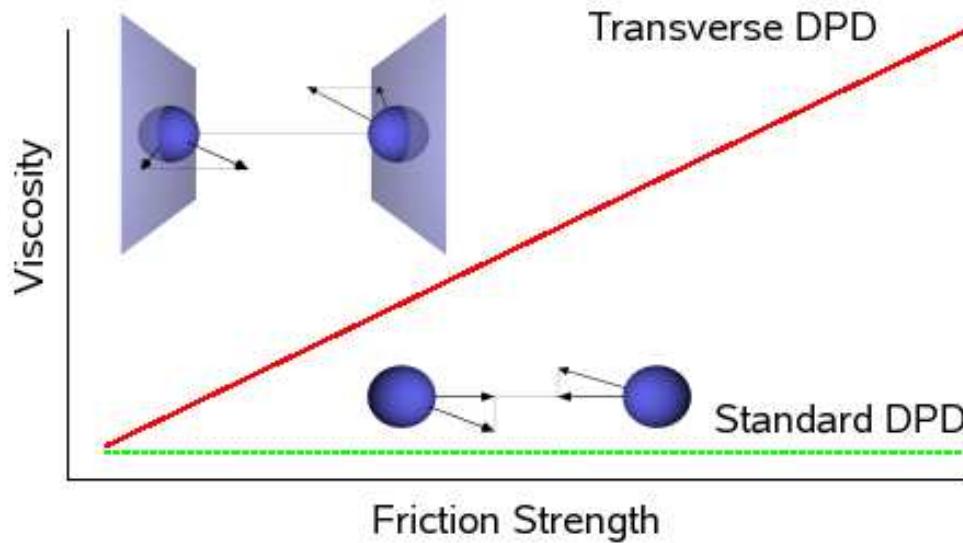


(g) Position dependent thermostat



(h) Regular thermostat

Transverse DPD Thermostat



- The variation of the **dissipative particle dynamics (DPD)** thermostat includes the damping of the **perpendicular** components of the relative velocity, yet keeping the advantages of conserving **Galilei invariance** and within our error bar also **hydrodynamics**. It allows for **controlling transport properties** of molecular fluids.

C. Junghans, M. Praprotnik, K. Kremer, Soft Matter 4, 156 (2008).

Transverse DPD Thermostat II

$$\dot{\vec{p}}_i = \vec{F}_i^C + \vec{F}_i^D + \vec{F}_i^R ,$$

$$\vec{F}_{ij}^D = -\zeta w^D(r_{ij}) \overleftrightarrow{P}_{ij}(\vec{r}_{ij}) \vec{v}_{ij}$$

$$\vec{F}_{ij}^R = \sigma w^R(r_{ij}) \overleftrightarrow{P}_{ij}(\vec{r}_{ij}) \vec{\theta}_{ij} ,$$

$\overleftrightarrow{P}_{ij}(\vec{r}_{ij})$ is a projection operator

$$\overleftrightarrow{P} = \overleftrightarrow{P}^T = \overleftrightarrow{P}^2,$$

which is symmetric in the particle indices ($\overleftrightarrow{P}_{ij} = \overleftrightarrow{P}_{ji}$).

The noise vector $\vec{\theta}_{ij}$

$$\langle \vec{\theta}_{ij}(t) \otimes \vec{\theta}_{kl}(t') \rangle = 2 \overleftrightarrow{I} (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \delta(t - t') ,$$

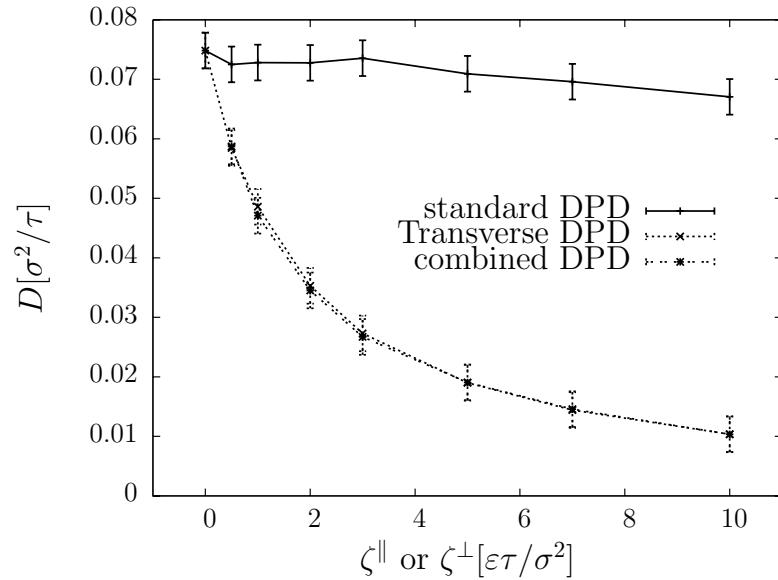
is antisymmetric in the particle indices ($\vec{\theta}_{ij} = -\vec{\theta}_{ji}$).

If we choose the projector along the interatomic axis between particle i and j

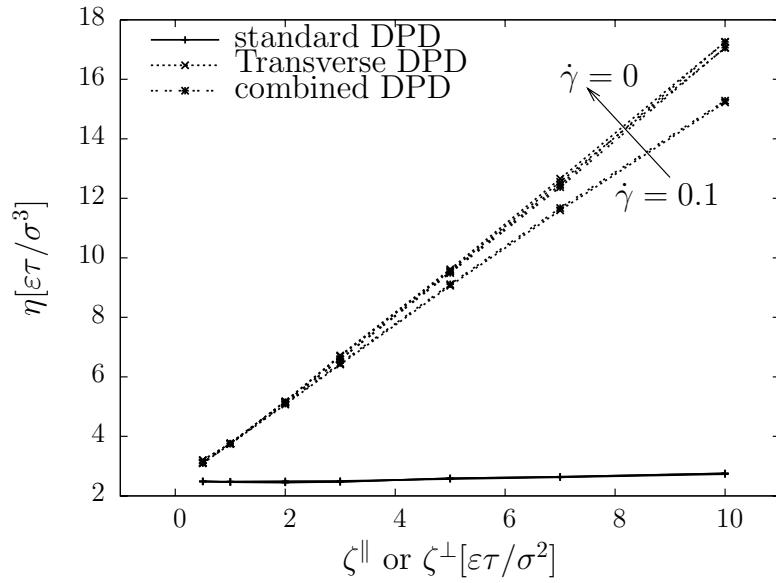
$\overleftrightarrow{P}_{ij}(\vec{r}_{ij}) = \hat{r}_{ij} \otimes \hat{r}_{ij}$ we retain the standard DPD thermostat.

$\overleftrightarrow{P}_{ij}(\vec{r}_{ij}) = \overleftrightarrow{I} - \hat{r}_{ij} \otimes \hat{r}_{ij}$ yields the Transverse DPD thermostat.

Tuning Transport Coefficients



(i) Diffusion constant



(j) Shear viscosity

Conclusions

● Adaptive Resolution MD simulation:

- Changing resolution is formally equivalent to a phase transition → latent heat.
- For a smooth variation of the resolution we introduce a transition regime.
- The temperature in the transition region can be obtained by extending the equipartition theorem to non-integer dimensions.

● Hybrid method AdResS:

- Allows for a dynamical switching of the spatial resolution.
- We treat only as many DOFs as absolutely necessary for the problem considered.
- Structural properties of the cg model are mapped to the atomistic one via the effective potential derivation using standard methods.
- The scheme is robust against the details of the cg model.
- Transport coefficients of the cg model are tuned to the atomistic ones using the Transverse DPD thermostat.
- AdResS was so far applied to MD simulations of a simple tetrahedral liquid, a macromolecule in an explicit solvent, liquid water at standard conditions, and a binary mixture.

Acknowledgments

Kurt Kremer, Max Planck Institute for Polymer Research, Mainz, Germany

Luigi Delle Site, Max Planck Institute for Polymer Research, Mainz, Germany