Adaptive Resolution Simulation of Liquid Water

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Adaptive resolution simulation

- **Motivation:**
  - to treat in a simulation only as many degrees of freedom (DOFs) as absolutely necessary for the problem considered.
- **Method:** *AdResS (Adaptive Resolution Scheme)*
  - allows for an dynamical switching between the atomistic and mesoscopic levels of detail $\Longrightarrow$ 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, i.e., liquid water at ambient conditions.

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

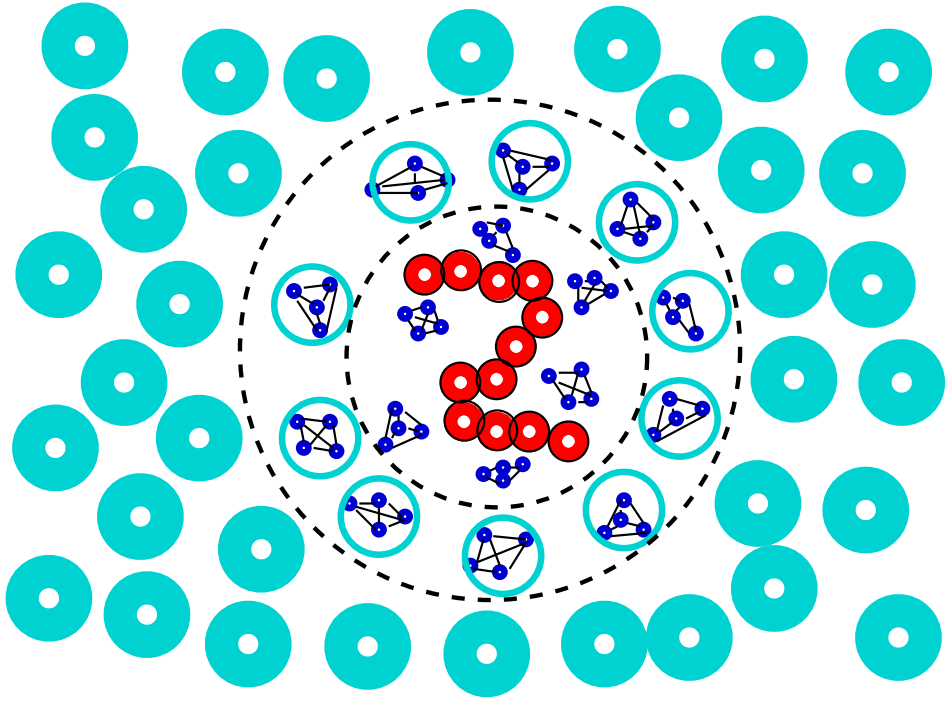
Mesoscopic MD simulation:

- reduces the number of DOFs by retaining only those that are relevant for the property of interest $\Longrightarrow$ 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

Macromolecule in solvent

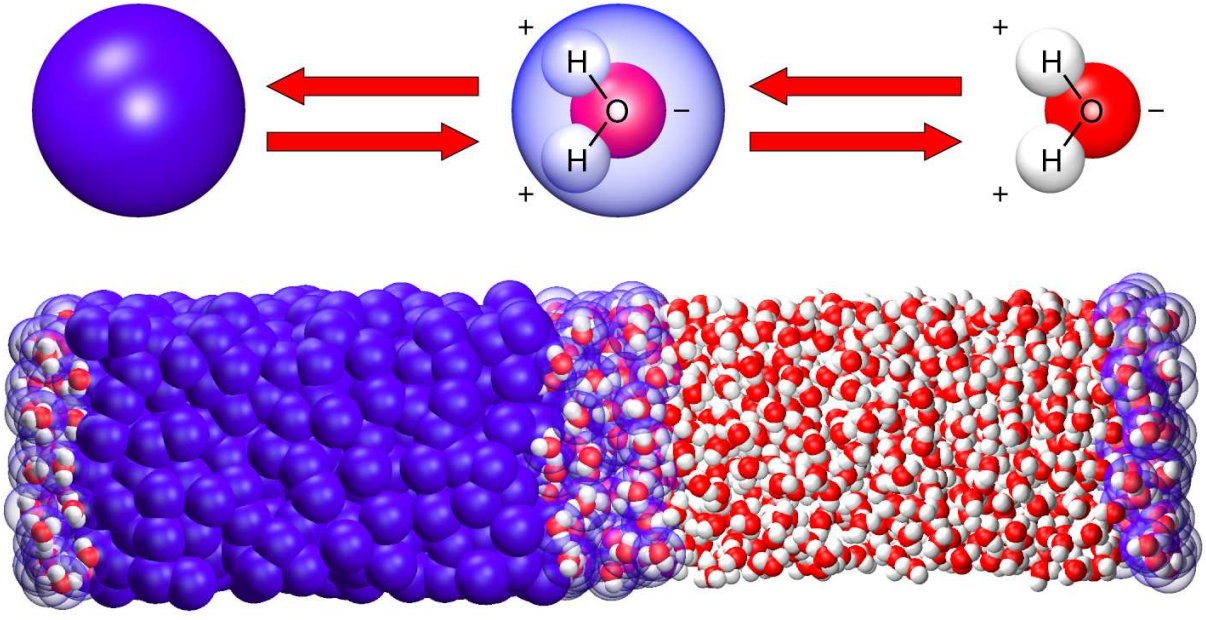


MP, L. Delle Site, K. Kremer, J. Chem. Phys. **123**, 224106 (2005).

MP, L. Delle Site, K. Kremer, Phys. Rev. E **73**, 066701 (2006).

MP, L. Delle Site, K. Kremer, J. Chem. Phys. **126**, 134902 (2007).

Hybrid atomistic/mesoscopic model

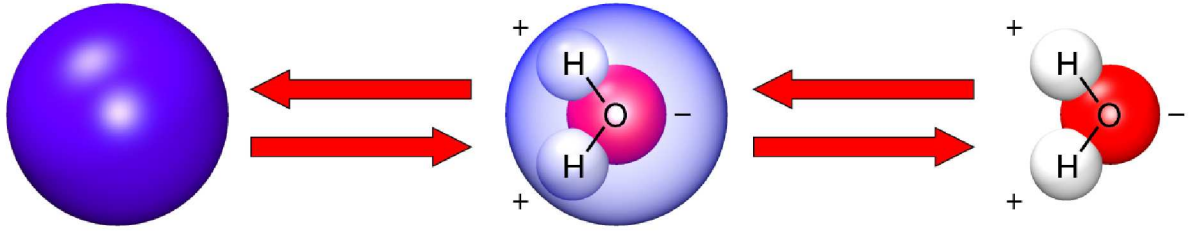


The simulation speed-up is $\sim 17 - 20$ compared to atomistic simulations.

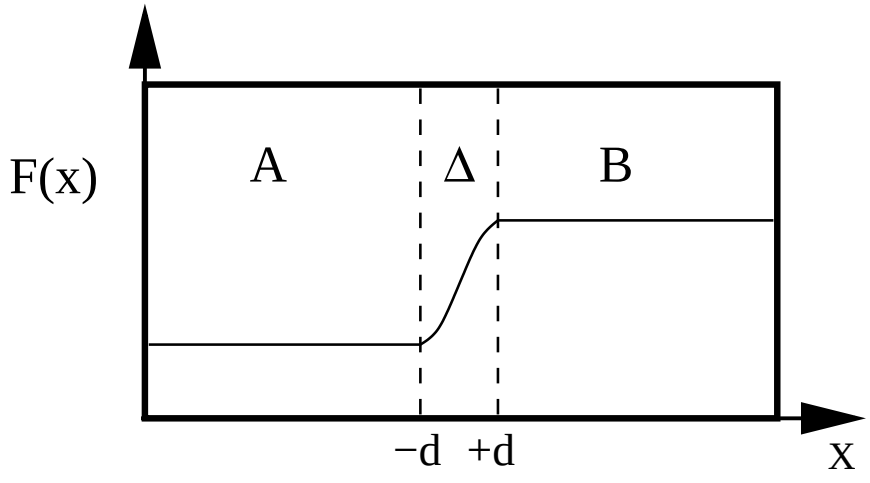
MP, S. Matysiak, L. Delle Site, K. Kremer, C. Clementi, J. Phys.: Condens. Matter, **19**, 292201, 2007.

Number of molecular degrees of freedom

- An all-atom rigid TIP3P water molecule has a defined spatial orientation and 6 DOFs:
  - 3 translational
  - 3 rotational
- One particle mesoscopic molecule has no defined spatial orientation and only 3 translational DOFs.
- Changing the degrees of freedom on the fly:

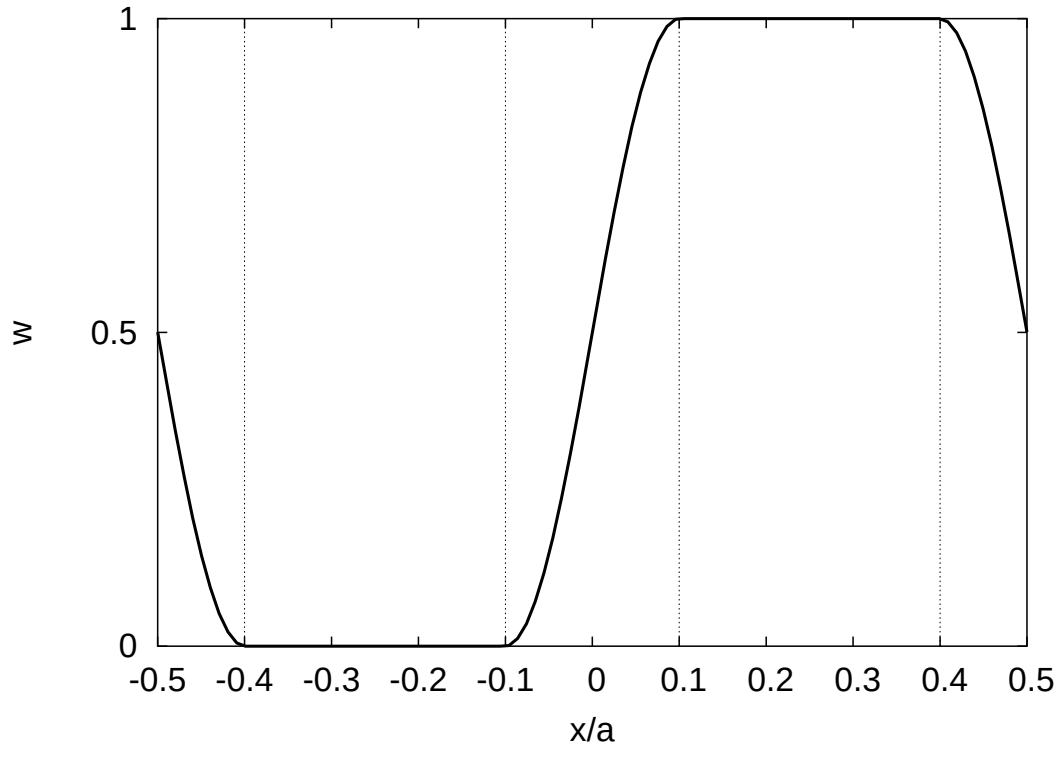


Transition region



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

Weighting function = order parameter



- The switching procedure implies that in the transition regime, where $0 < w(x) < 1$, we deal with fractional DOFs, i.e., by switching on/off a DOF we continuously change **the dimensionality of the phase space.**

Hybrid method 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:

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

where

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

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

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

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!

Langevin thermostat

Equation of motion for the i-th particle:

$$m_i \frac{d^2\mathbf{r_i}}{dt^2} = \mathbf{F}_i - m_i\Gamma\frac{d\mathbf{r}_i}{dt} + \mathbf{W}_i(t).$$

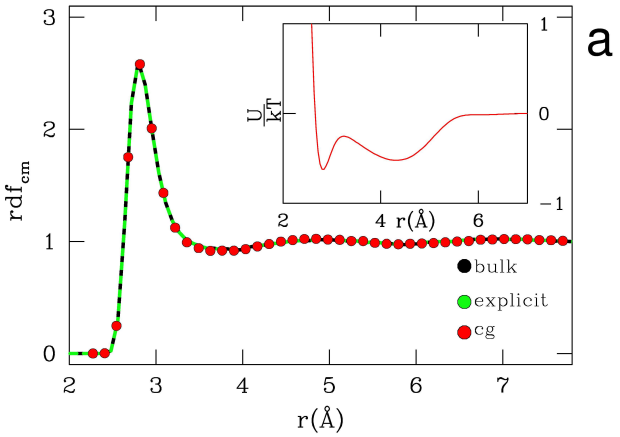
Fluctuation-dissipation theorem:

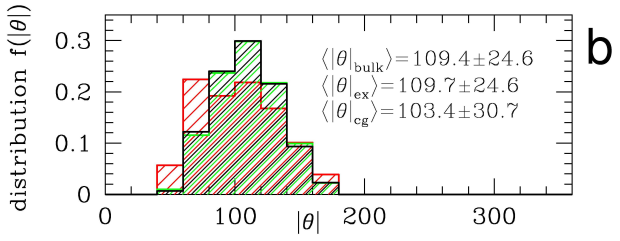
$$< \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') >= \delta_{ij}\delta(t-t')6\sqrt{m_i m_j}k_B T\Gamma.$$

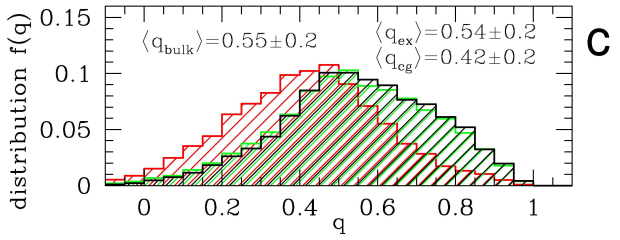
Reaction Field method:

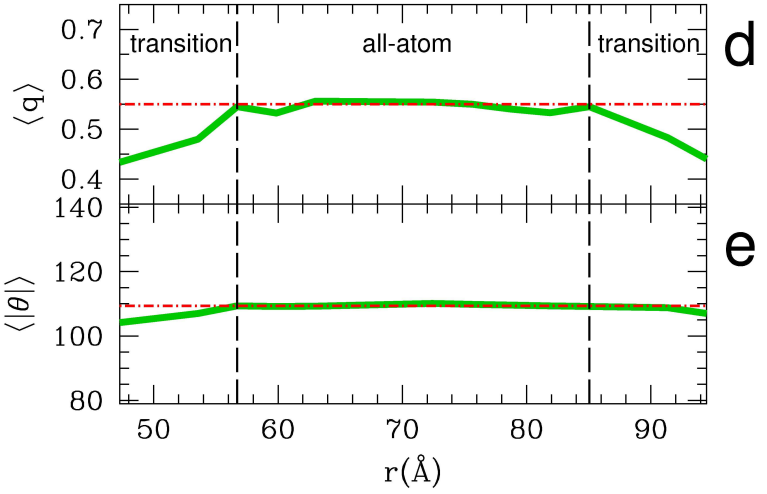
$$\mathbf{F}^{atom}_{C_{i_\alpha j_\beta}}(\mathbf{r}_{i_\alpha j_\beta}) = \frac{e_{i_\alpha}e_{j_\beta}}{4\pi\epsilon_0}\left[\frac{1}{r^3_{i_\alpha j_\beta}} - \frac{1}{R_c^3}\frac{2(\epsilon_{RF}-1)}{1+2\epsilon_{RF}}\right]\mathbf{r}_{i_\alpha j_\beta}.$$

Static properties



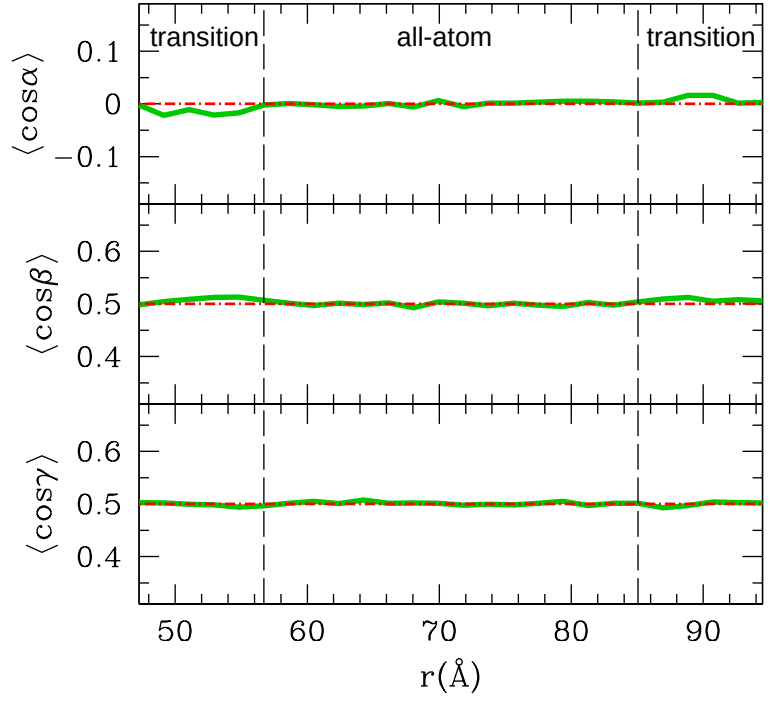






$$q = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(cos\psi_{jk} + \frac{1}{3}\right)^2$$

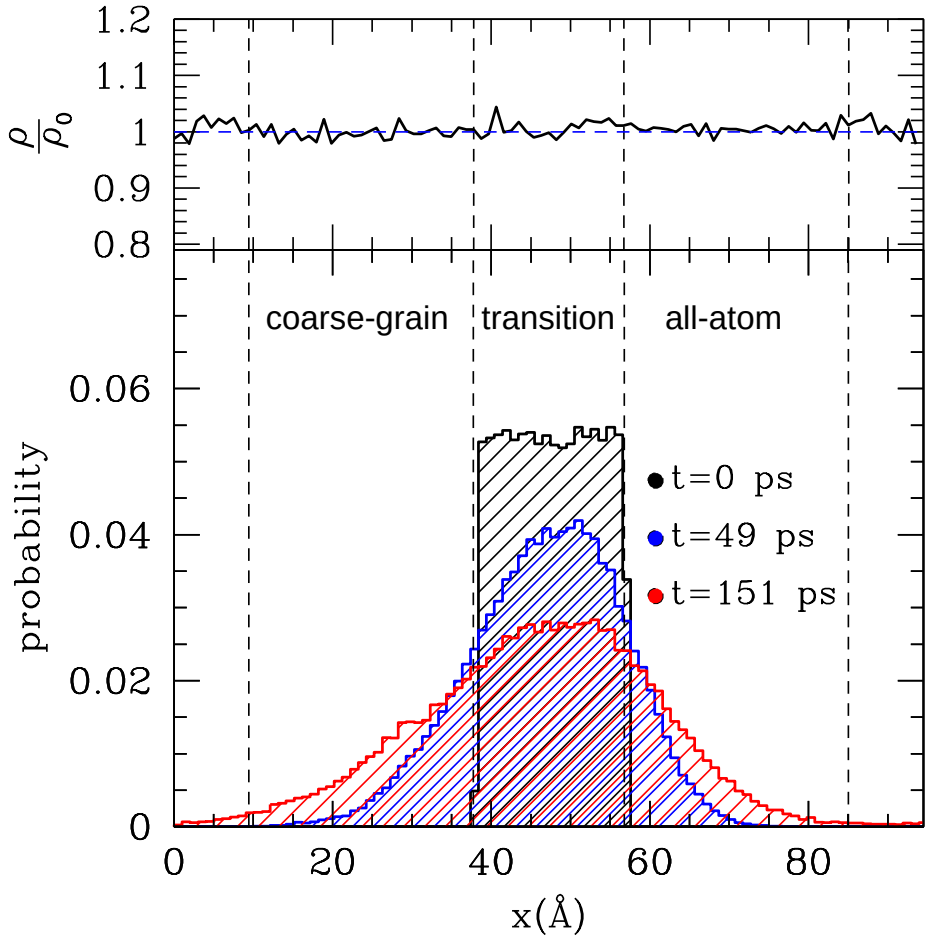
Interface effect of the cg water



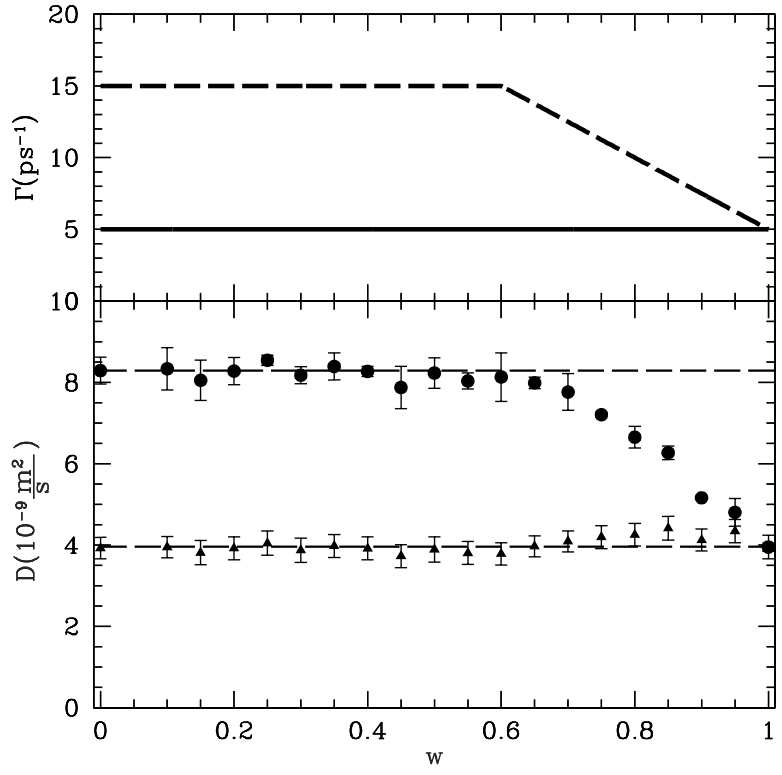
The transition regime neutralizes the interface effect of the *c*g water $\Longrightarrow$

the structure of water in the explicit regime is the same as in the bulk.

Diffusion across the transition regime I.



Diffusion coefficient across the simulation box



S. Matysiak, C. Clementi, MP, K. Kremer, L. Delle Site, J. Chem. Phys, in press.

Position dependent Langevin thermostat

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

$$m_i dv_i/dt = F_i - m_i\Gamma(x)v_i + R_i(x,t) \tag{1}$$

where $R_i(x,t)$ is:

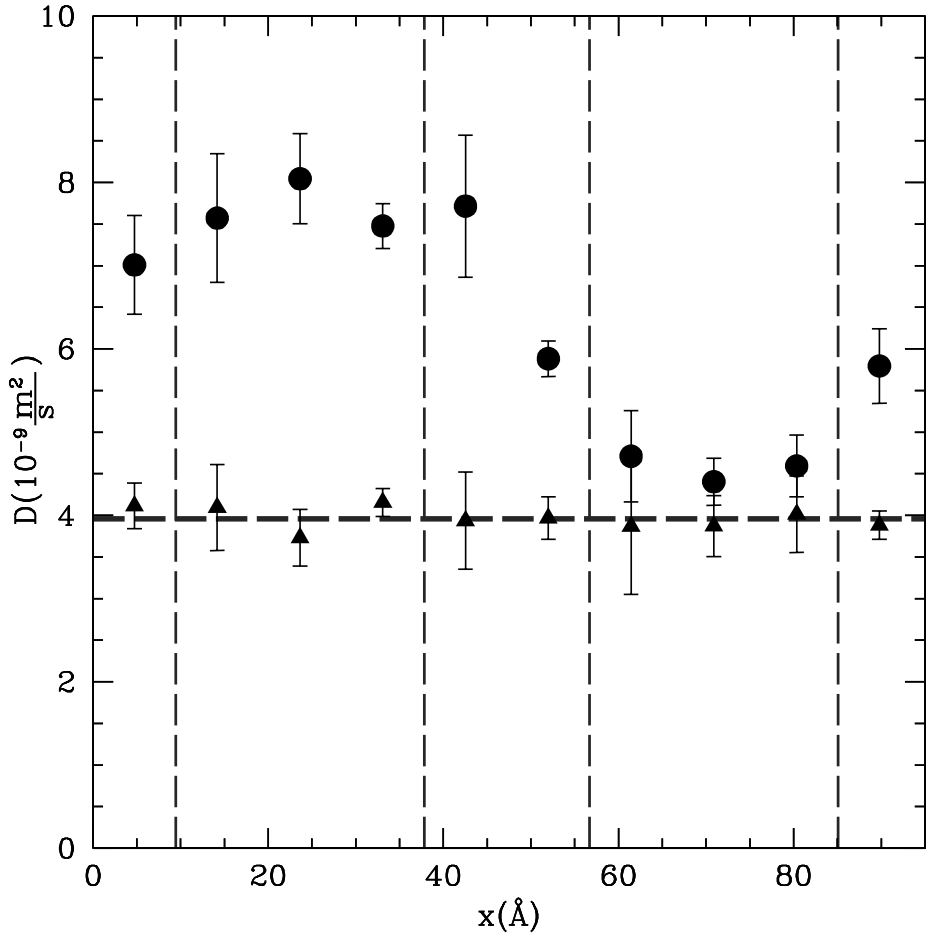
$$\langle R_i(x,t)\rangle = 0, \tag{2}$$

$$\langle R_i(x,t_1)R_j(x,t_2)\rangle = 2\Gamma(x)m_i kT\delta(t_1-t_2)\delta_{ij} \tag{3}$$

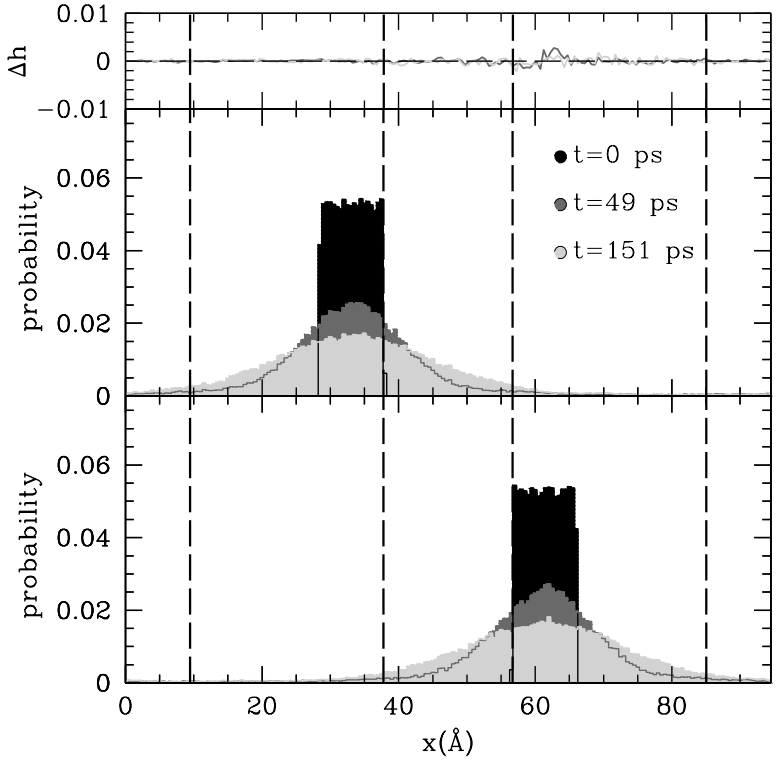
$$\Gamma(x) = \begin{cases} \Gamma_{cg} & \text{if } x \leq 0.6 \\ \alpha x + \beta & \text{if } 0.6 < x \leq 1.0 \end{cases} \tag{4}$$

This choice provides a simple interpolation between the two limit values of $\Gamma(0.6) = \Gamma(0) = \Gamma_{cg} = 15ps^{-1}$ and $\Gamma(1) = \Gamma_{all-atom} = 5ps^{-1}$. The parameters α and β are $-25ps^{-1}$ and $30ps^{-1}$, respectively.

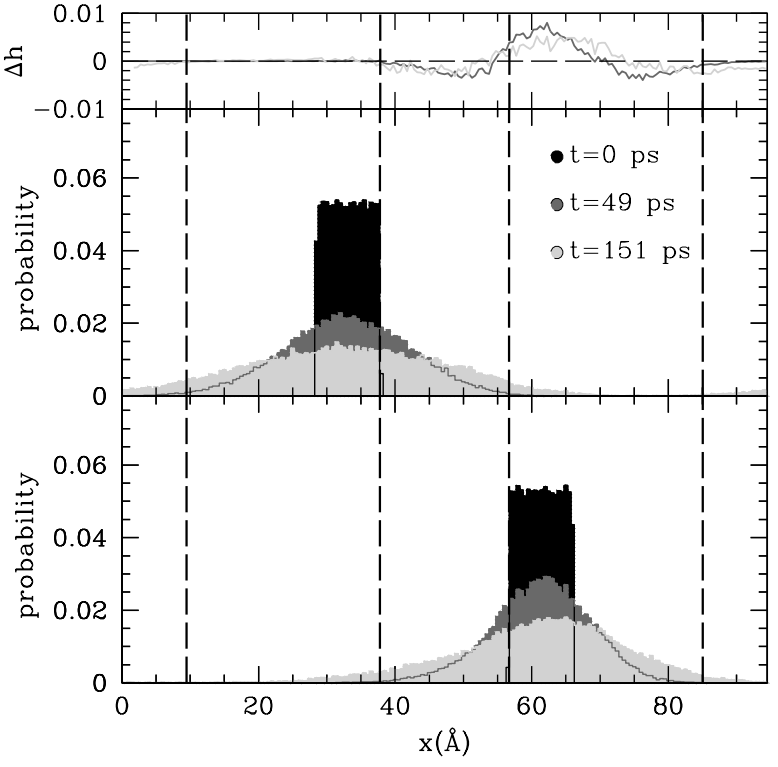
Diffusion coefficient in the hybrid system



Diffusion coefficient across the simulation box II.

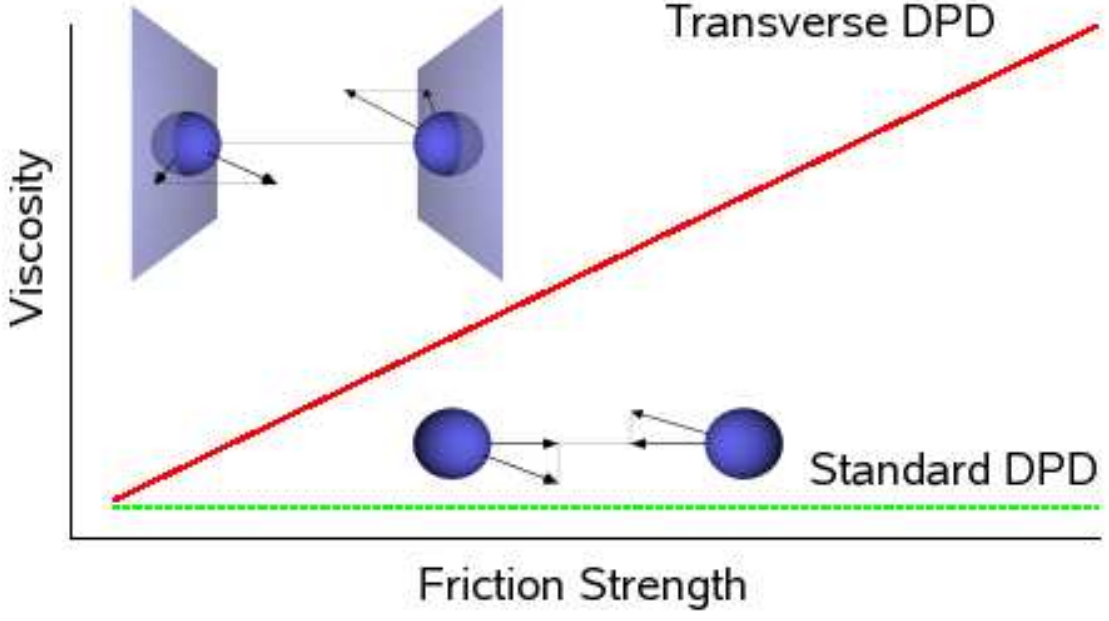


(c) Position dependent thermostat



(d) Regular thermostat

Transverse DPD thermostat



Christoph Junghans, MP, Kurt Kremer, Soft Matter, 2008, DOI:10.1039/b713568h.

Conclusions

Adaptive Resolution MD simulation:

- Changing resolution is formally equivalent to a phase transition $\longrightarrow$ 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.
- AdResS was applied to MD simulations of a liquid water at standard conditions.
- The simulation speed-up for liquid water is $\sim 17 - 20$ compared to atomistic simulations.

Future work:

- Application to different soft matter systems and molecular liquids.