



Adaptive Resolution Simulation of Molecular Liquids

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Outline



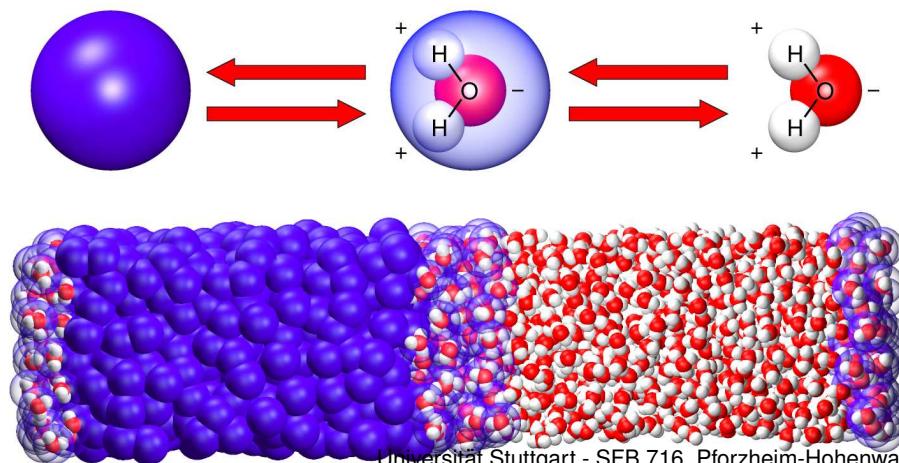
- ⑥ **Introduction:** molecular liquids and soft matter, length- and time-scales, multiscale modeling
- ⑥ **Hybrid Adaptive Resolution Scheme (AdResS):** linking atomic and mesoscopic length-scales
- ⑥ **Triple-scale AdResS-HybridMD method:** coupling particle-based and continuum descriptions of a liquid



Molecular systems



- ⑥ **gases**: intermolecular distances are large in comparison with molecular sizes
→ the intermolecular interactions are negligible
- ⑥ **hard condensed matter**: strong intermolecular interactions, long-range orientational and positional order
- ⑥ **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.



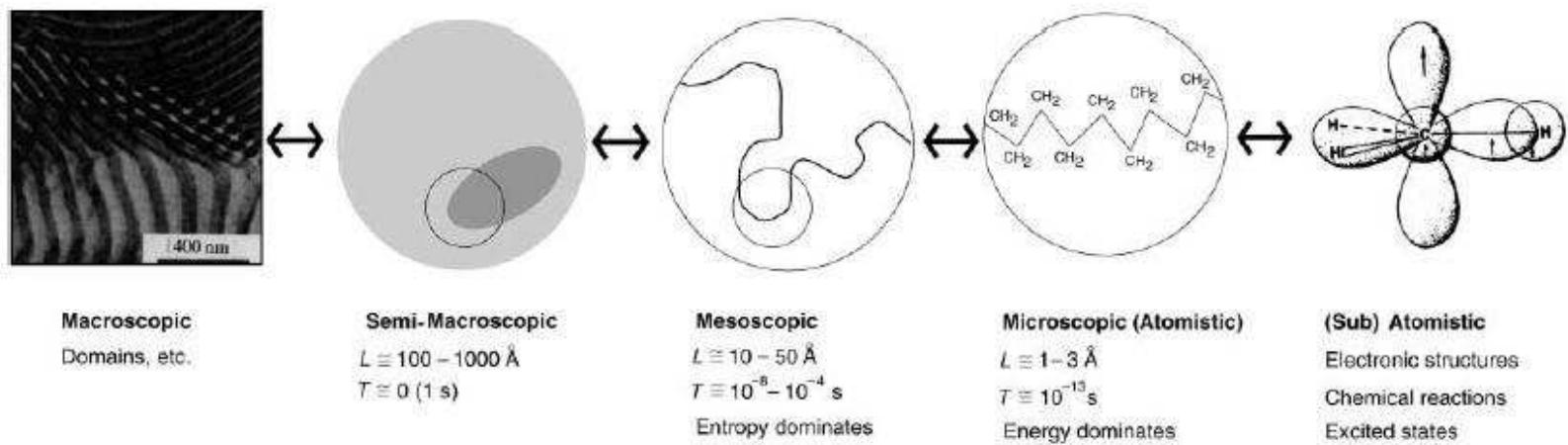


Length-scales



Wide range of characteristic length-scales:

- ⌚ bond length: $\sim 0.1\text{nm}$
- ⌚ persistence length of polymers: $\sim 1\text{nm}$
- ⌚ radius of gyration: $\sim 10\text{nm}$
- ⌚ macroscopic domains' size: $\sim 1\mu\text{m}$

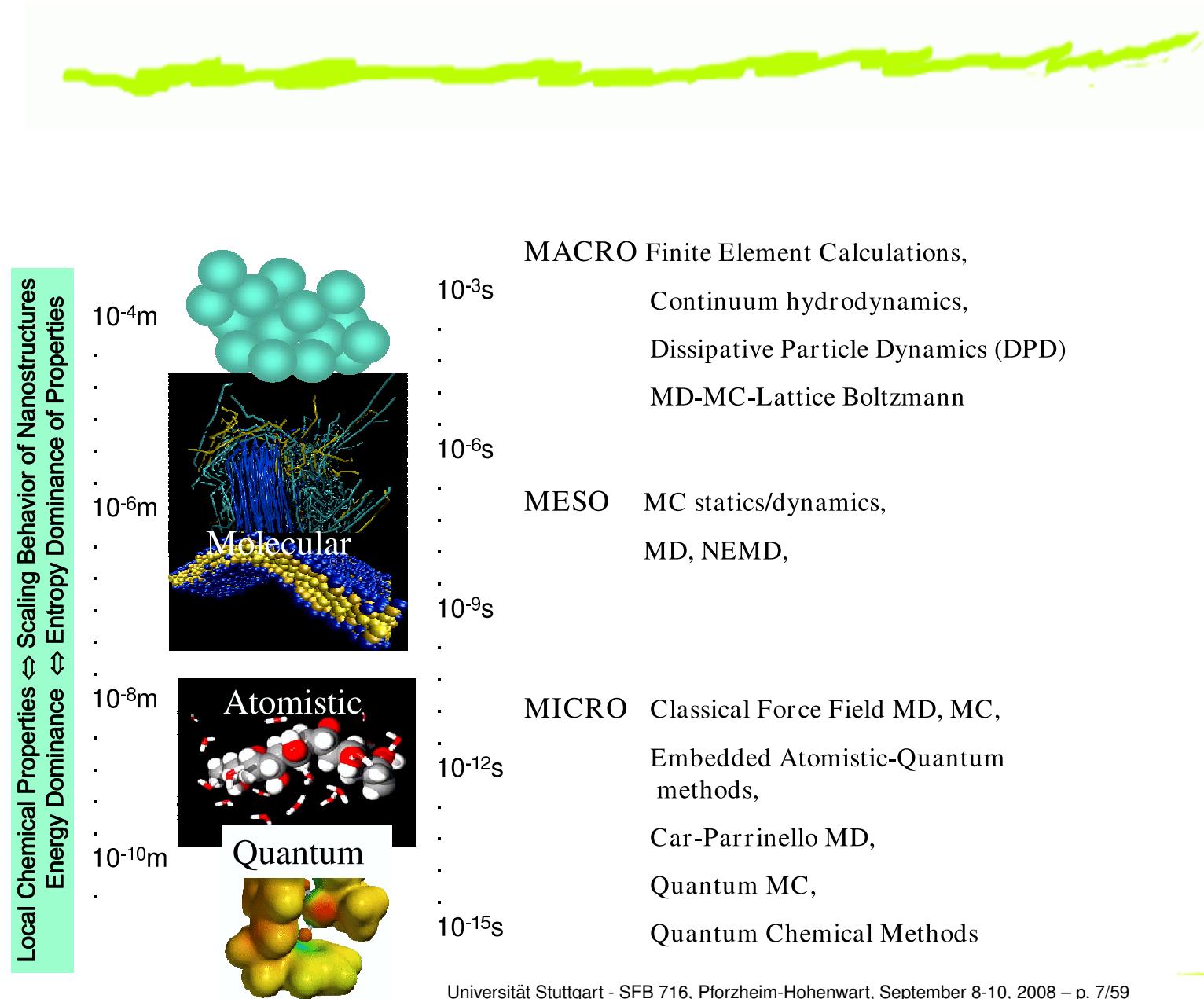


Wide range of characteristic time-scales:

- ⌚ covalent bond vibrations: $\sim 10 \cdot 10^{-15} s$
- ⌚ angle bending: $\sim 20 \cdot 10^{-15} s$
- ⌚ atom dynamics governed by torsional and van der Waals interactions:
 $\sim 40 \cdot 10^{-15} s$
- ⌚ atom dynamics governed by long-range Coulomb interactions: $\sim 10^{-12} s$
- ⌚ relaxation times of macromolecular segments: $10^{-12} - 10^{-9} s$
- ⌚ maximal macromolecular relaxation times: $\sim 1 s$



Multiscale modeling





Adaptive resolution simulation



⑥ Motivation:

- △ to treat in a simulation only as many degrees of freedom (DOFs) as absolutely necessary for the problem considered.

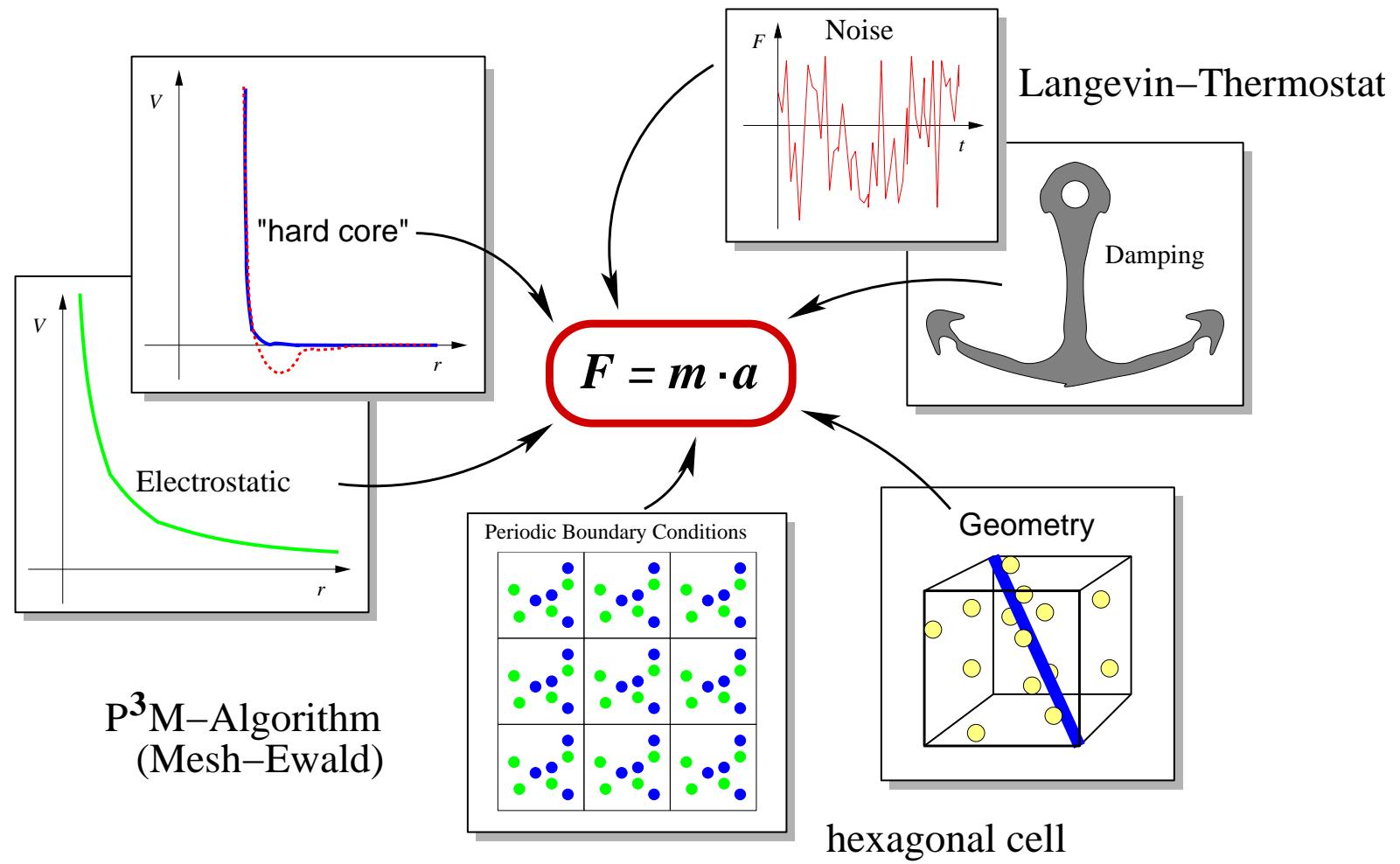
⑥ Method: *AdResS (Adaptive Resolution Scheme)*

- △ 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 required atomistic resolution exchange particles with the remainder of the system sufficiently described on the mesoscopic scale.

⑥ Results:

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

Molecular Dynamics (MD) simulation





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:

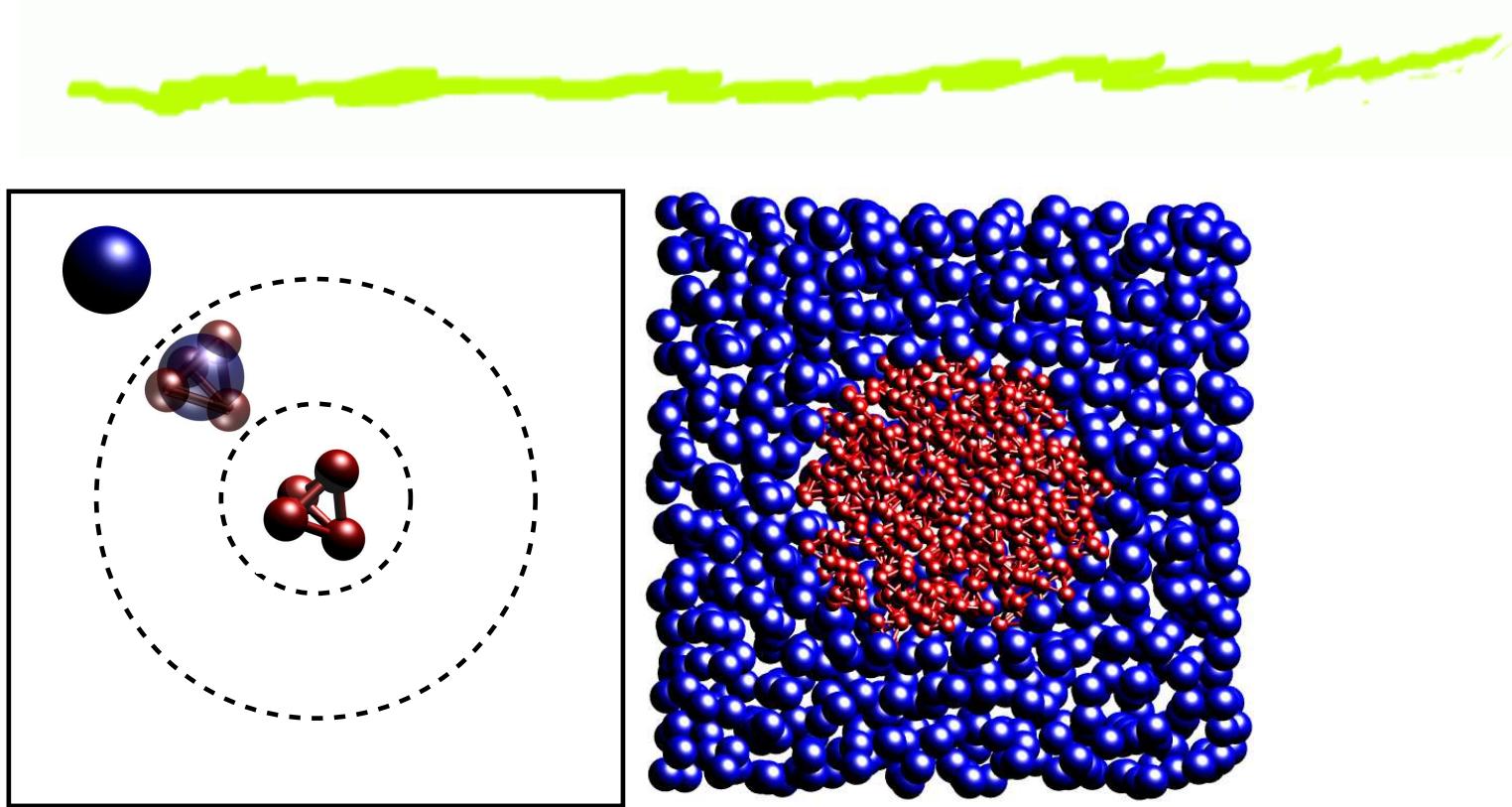
- ⌚ reduces the number of DOFs by retaining only those that are relevant for the property of interest \Rightarrow longer length and time scales can be reached
- ⌚ specific chemical details are usually lost in the coarse-graining procedure

Combining the best from both approaches:

- ⌚ Hybrid Adaptive MD Schemes



Hybrid atomistic/mesoscopic liquid



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

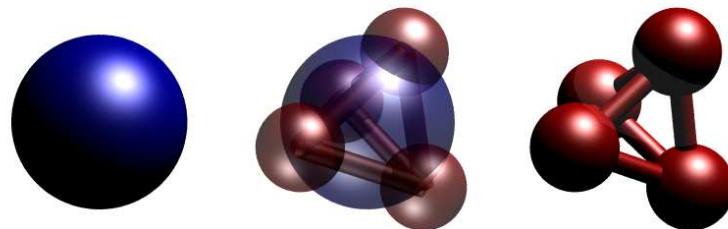
MP, L. Delle Site, K. Kremer, Phys. Rev. E **73**, 066701, 2006.



Changing number of degrees of freedom



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



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

MP, L. Delle Site, K. Kremer, Annu. Rev. Phys. Chem. **59**, 545, 2008.



Geometrically induced phase transition

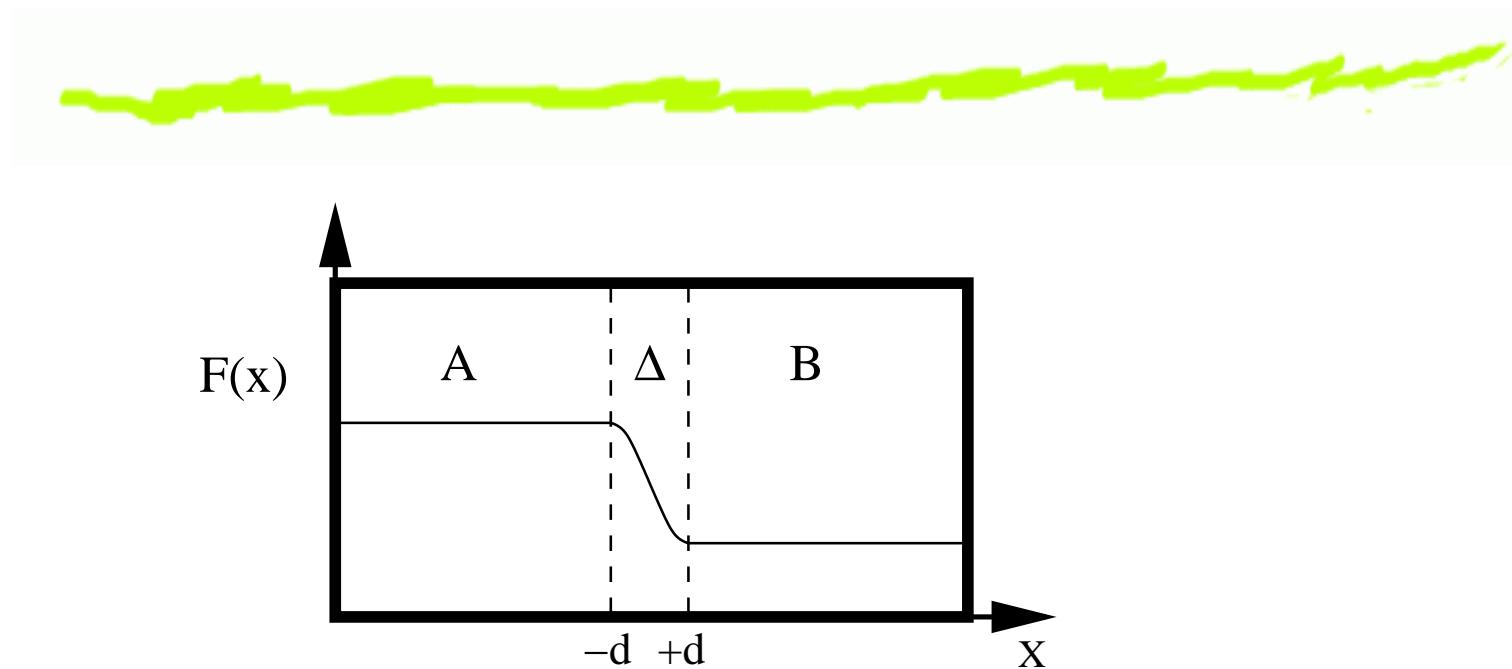


In thermodynamical equilibrium, boundary conditions analogous to two-phase coexistence must be satisfied:

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

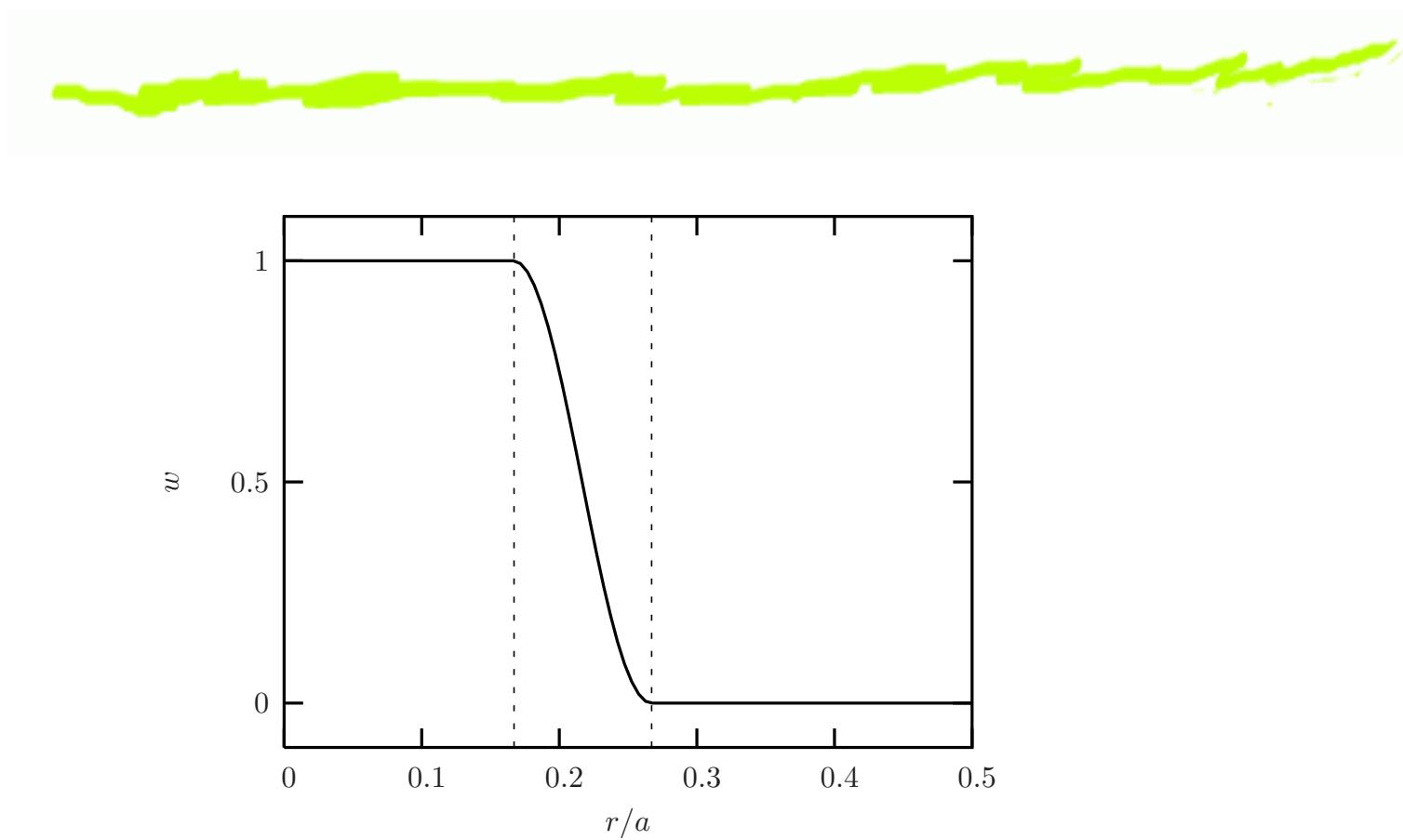
The rotational and vibrational parts of the free energy can be viewed as the latent heat, which is supplied or taken by the thermostat, at this transition.

Transition region



- ⑥ Molecules in A and B are **physically identical** but **differently represented**.
- ⑥ The number of DOFs is $n = n(x)$ with: $n_A = \text{const}_A$; $n_B = \text{const}_B$; and $n_\Delta = n(x)$
- ⑥ The system is in equilibrium which implies:
 $\lim_{x \rightarrow d^-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \rightarrow d^+} \frac{\partial F_B(x)}{\partial x} = 0 \implies$
 $\lim_{x \rightarrow d^-} \frac{\partial n_A(x)}{\partial x} = \lim_{x \rightarrow d^+} \frac{\partial n_B(x)}{\partial x} = 0$

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.



AdResS: Linking atomic and mesoscopic length-scales



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

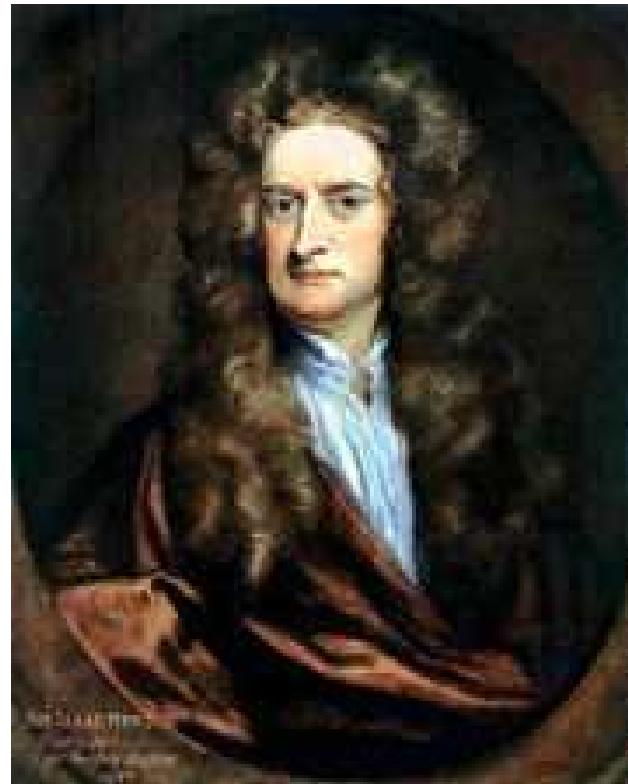
$$\mathbf{F}_{\alpha\beta}^{atom} = \sum_{i\alpha,j\beta} \mathbf{F}_{i\alpha j\beta}^{atom}$$

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

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



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!

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



Continuous change of the phase space dimensionality



- ⑥ 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**.
- ⑥ To properly describe this situation we resort here to the fractional calculus.
- ⑥ Let us consider a given $w(x) = \alpha$ and use α as a variable parameter.
- ⑥ The infinitesimal volume element of the fractional configurational space is defined as $dV_\alpha = d^\alpha x \Gamma(\alpha/2)/2\pi^{\alpha/2}\Gamma(\alpha) = |x|^{\alpha-1} dx/\Gamma(\alpha) = dx^\alpha/\alpha\Gamma(\alpha)$ where the positive real parameter α denotes the order of the fractional coordinate differential.

MP, K. Kremer, L. Delle Site, Phys. Rev. E 75, 017701, 2007.



The extension of equipartition theorem to non-integer DOFs



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

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

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

MP, K. Kremer, L. Delle Site, Phys. Rev. E **75**, 017701, 2007.

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

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:

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



Mapping of structural properties



Effective pair potential that reproduces the structure of the all-atom system as closely as possible is determined using the RDF_{cm} of the reference all-atom system via the potential of mean force (PMF) as

$$U^{cm}(r) \approx PMF(r) = -k_B T \log g_{ex}^{cm}(r),$$

$g_{ex}^{cm}(r)$ is the all-atom RDF_{cm} and $U^{cm}(r)$ is the effective potential.

Effective potential is:

- ⑥ in general **temperature** and **density** dependent
- ⑥ **softer** than the interatomic potentials



Iterative Boltzmann inversion



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**:

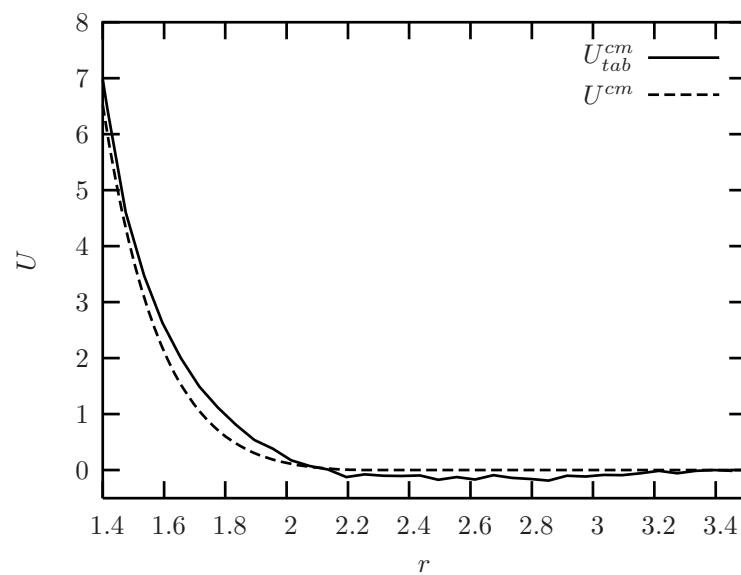
$$U_{i+1}^{eff}(r) = U_i^{eff}(r) + k_B T \ln \frac{g_i(r)}{g_{target}(r)}$$

Ramp pressure correction:

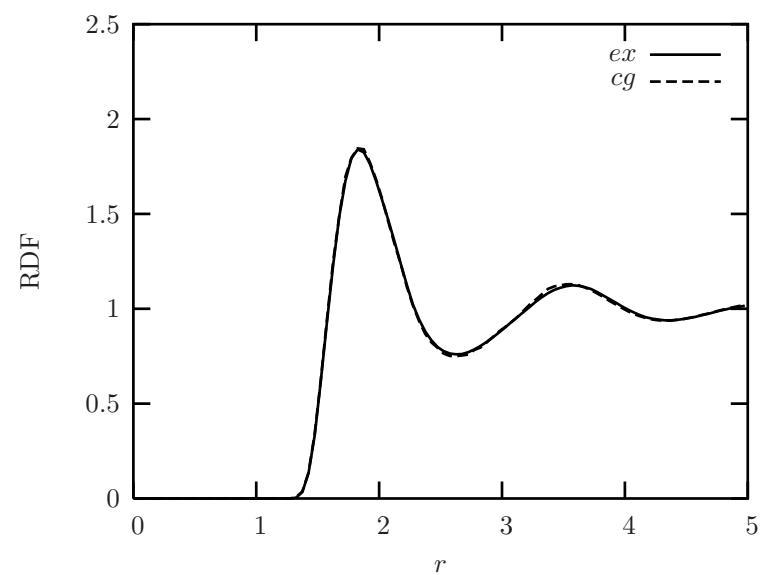
$$\Delta U_{lin} = A \left(1 - \frac{r}{r_{cut}}\right).$$

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

Tetrahedral liquid: effective potential

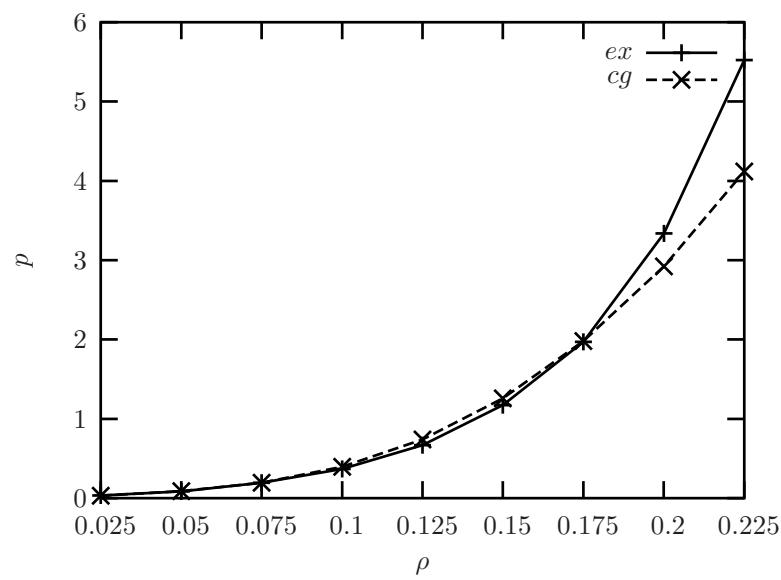


(c) Tabulated effective potential.

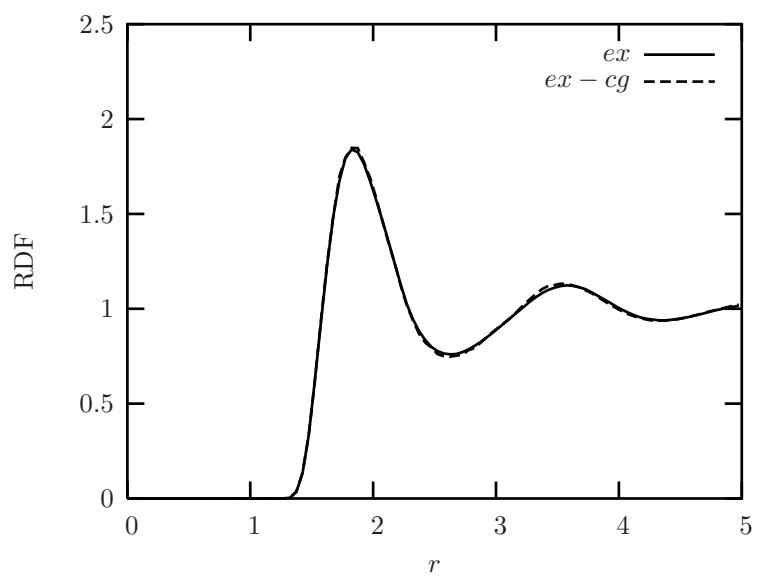


(d) RDF_{cm} .

Equation of state

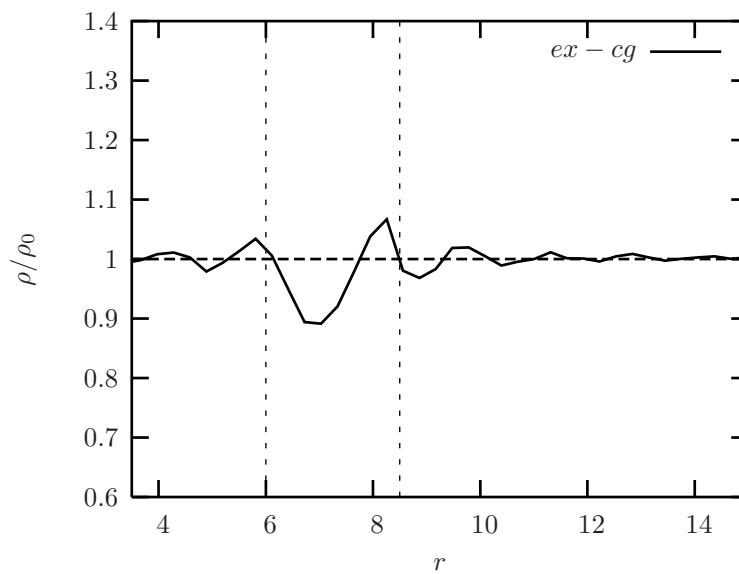


(e) EOS for $\rho = 0.175$ and $T = 1$.

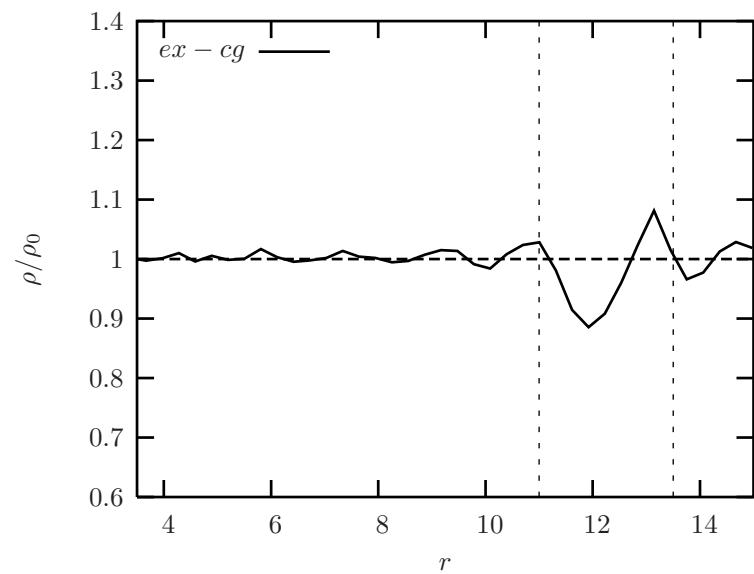


(f) RDF_{cm} .

Density profile profile

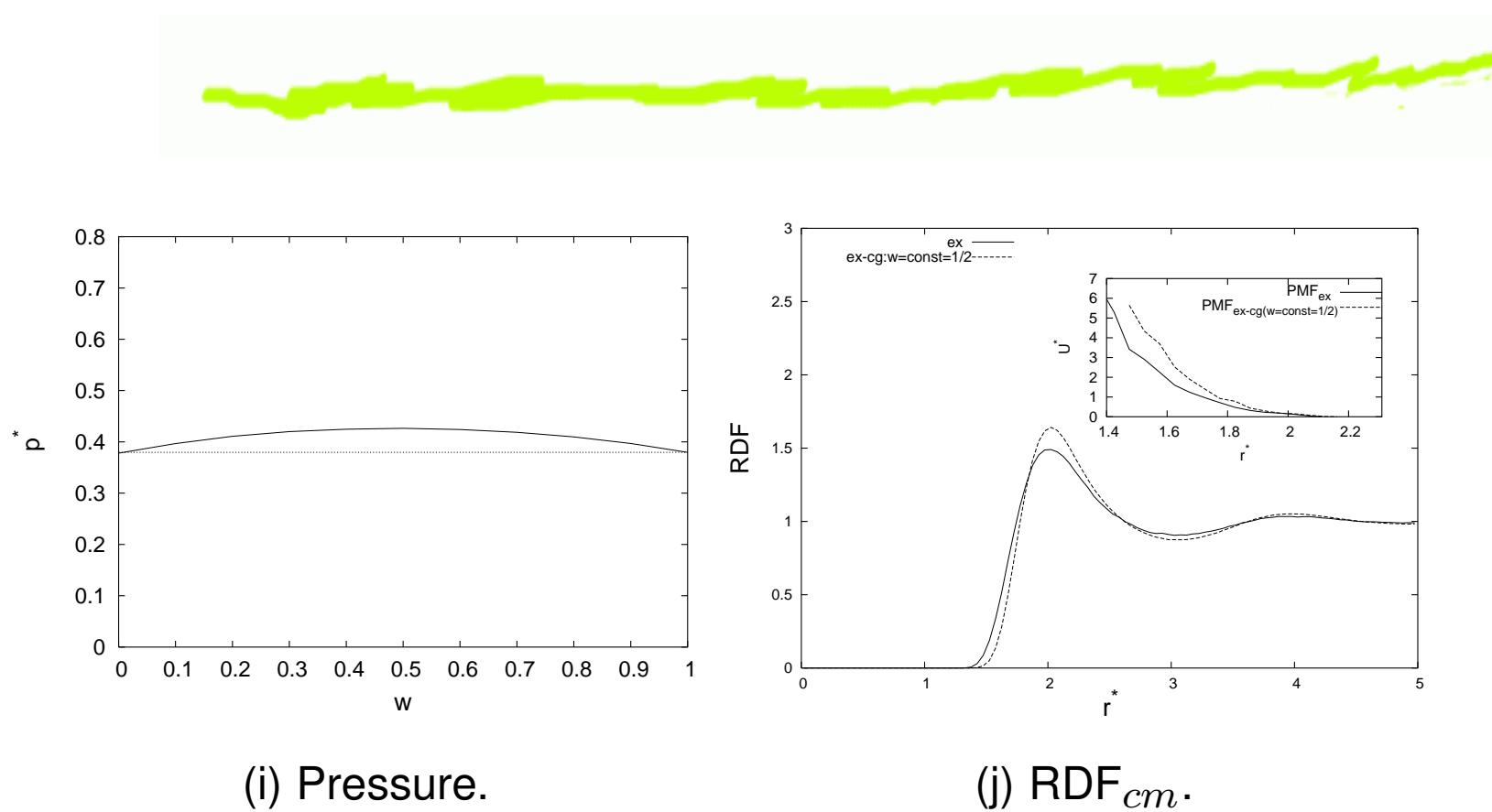


(g) Radius of the explicit regime:
 $r_0 = 6.0.$



(h) Radius of the explicit regime:
 $r_0 = 11.0.$

Artifacts of the method



Interface pressure correction (ic)



$$\mathbf{F}_{\alpha\beta}^{cm} = s[w(R_\alpha)w(R_\beta)]\mathbf{F}_{\alpha\beta_o}^{cm} + (1 - s[w(R_\alpha)w(R_\beta)])\mathbf{F}_{\alpha\beta_{ic}}^{cm}.$$

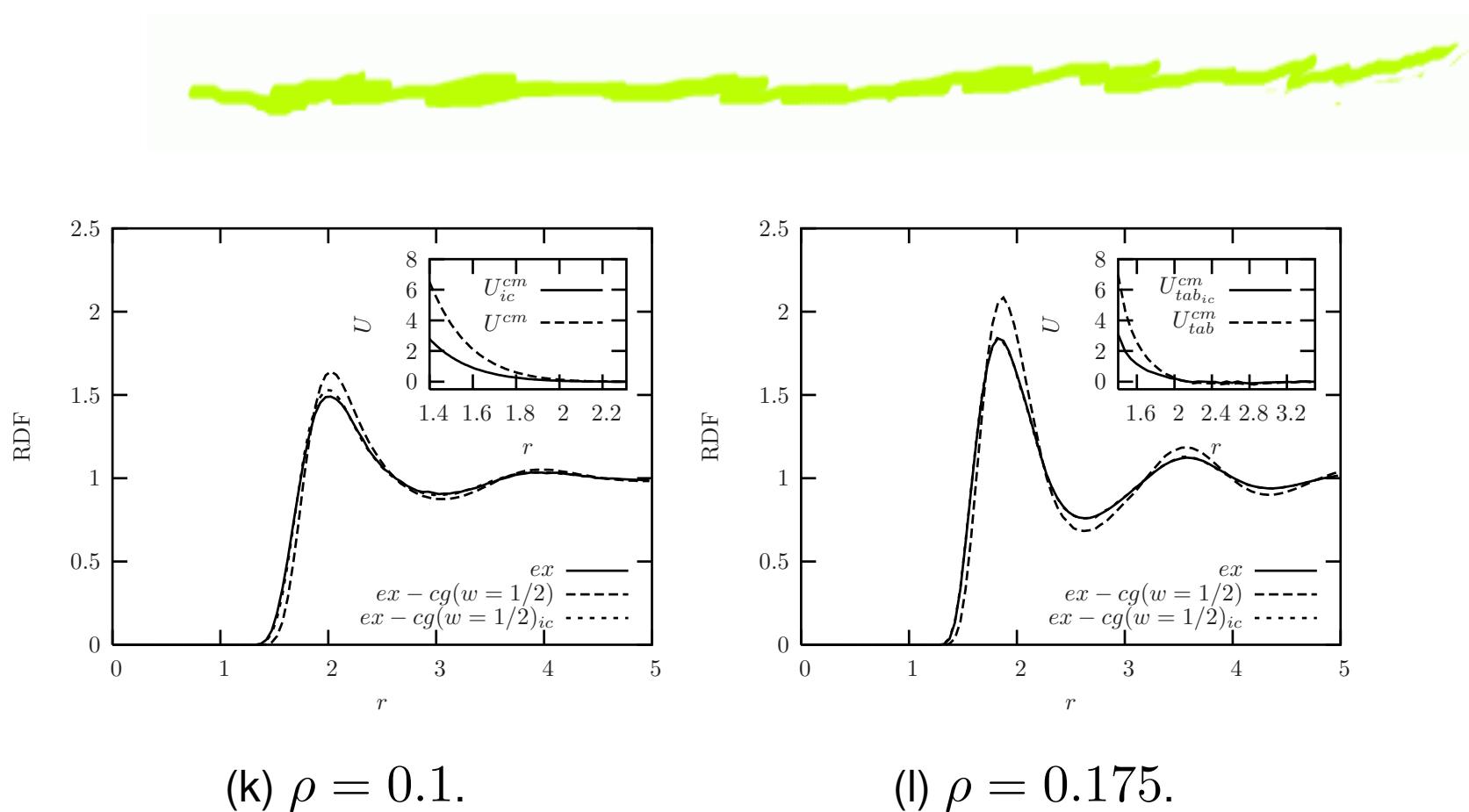
$s \in [0, 1]$ is defined as

$$s[x] = 4(\sqrt{x} - \frac{1}{2})^2,$$

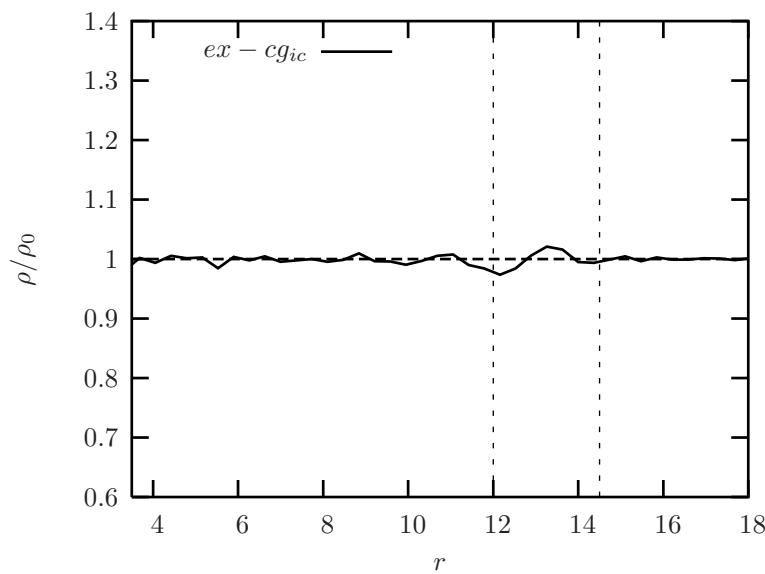
where $s[0] = 1$, $s[1] = 1$ and $s[1/4] = 0$

System of hybrid molecules with

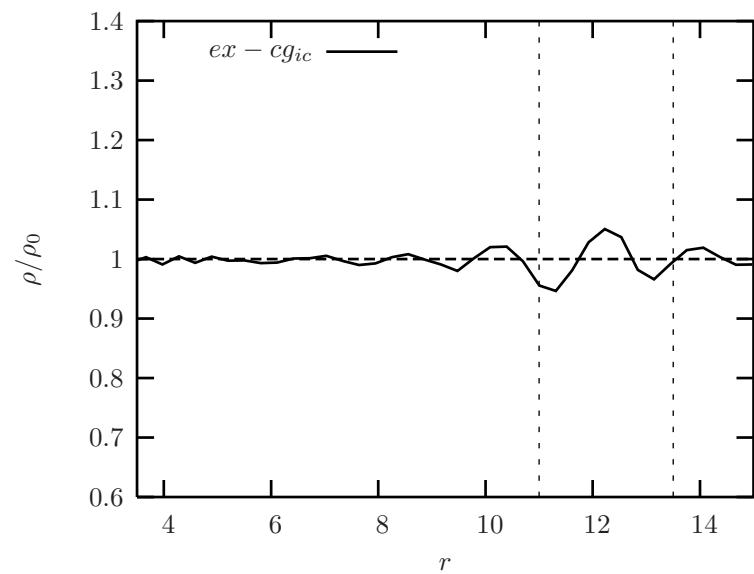
$$w = 1/2$$



Density profile with ic correction



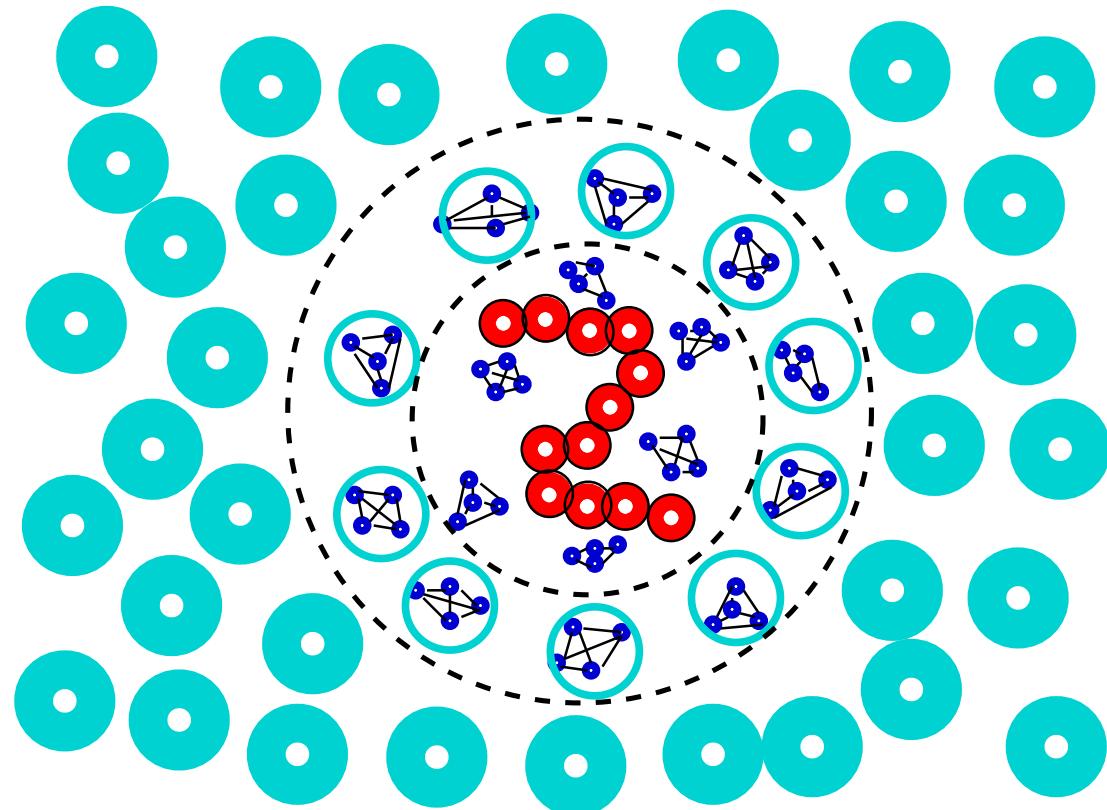
(m) $\rho = 0.1.$



(n) $\rho = 0.175.$

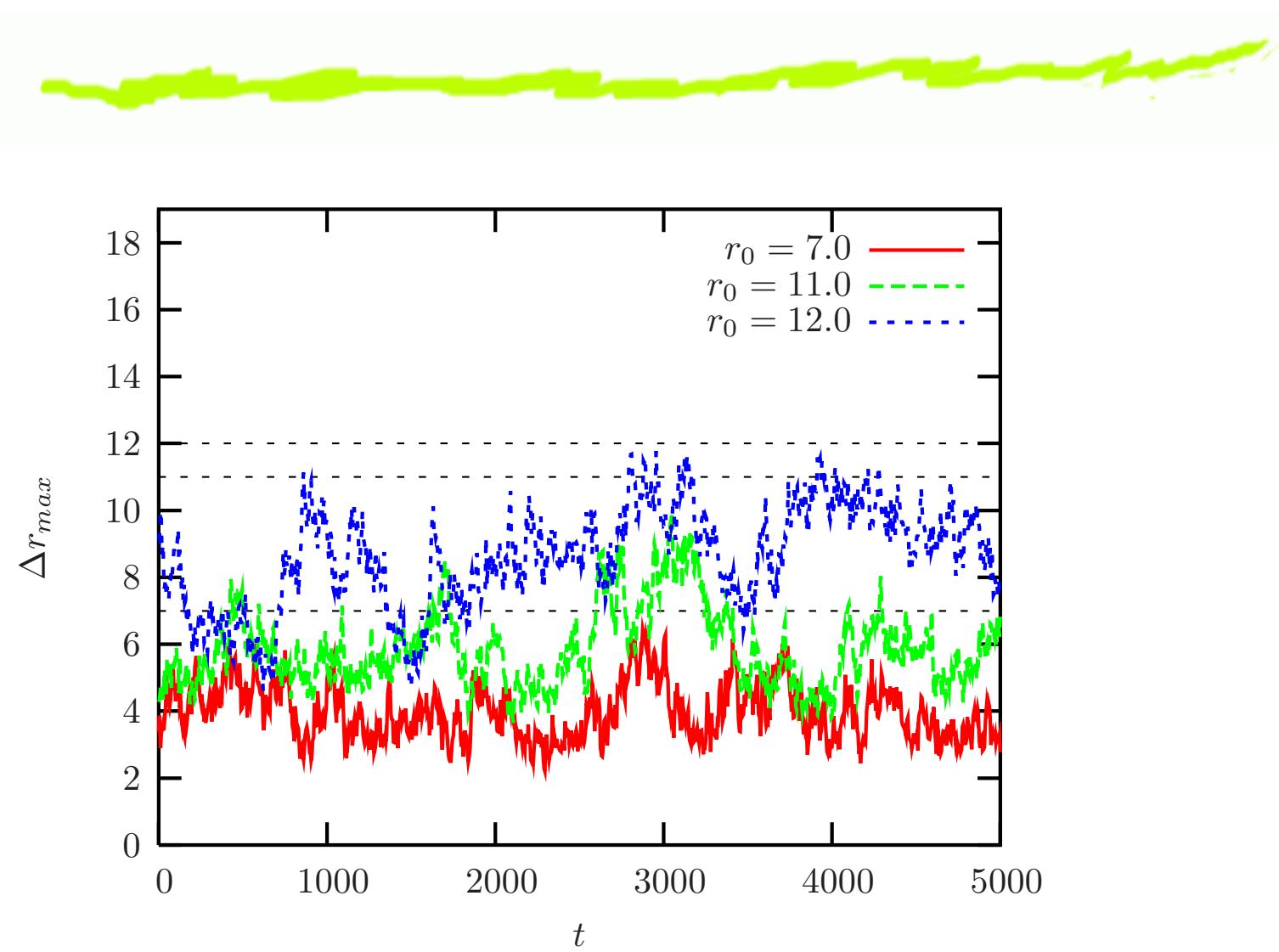


Macromolecule in solvent

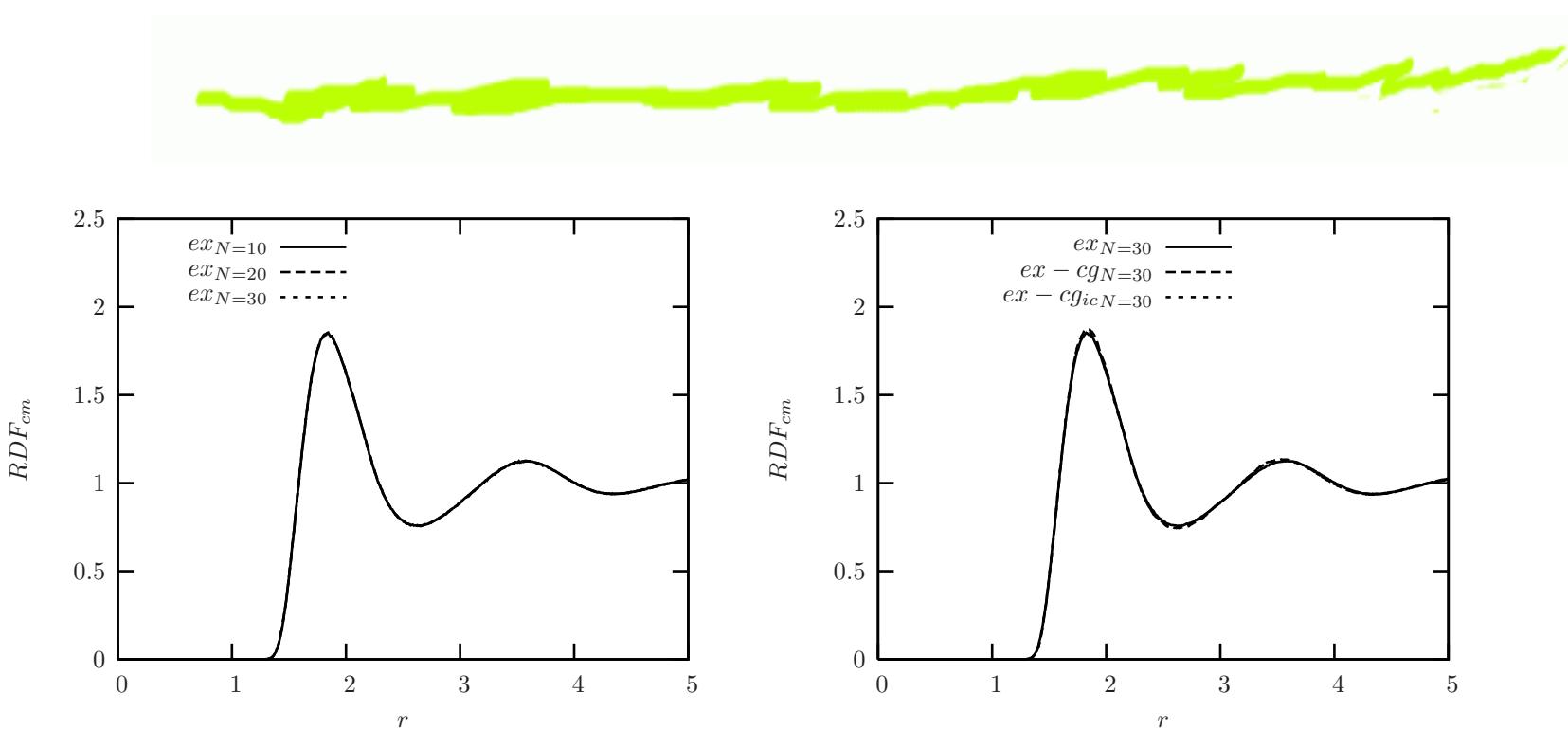


MP, L. Delle Site, K. Kremer, J. Chem. Phys. 126, 134902, 2007.

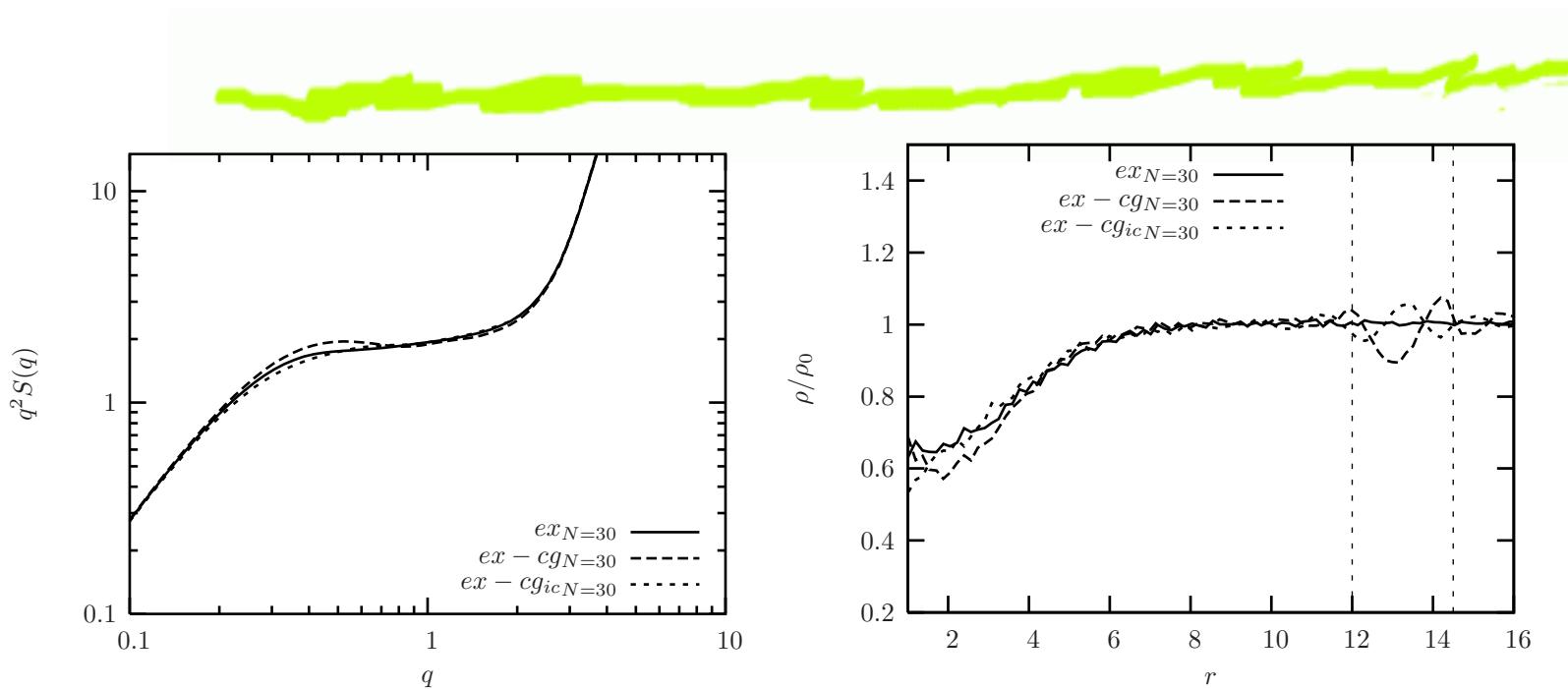
Maximal monomer distance



Static properties of the solvent



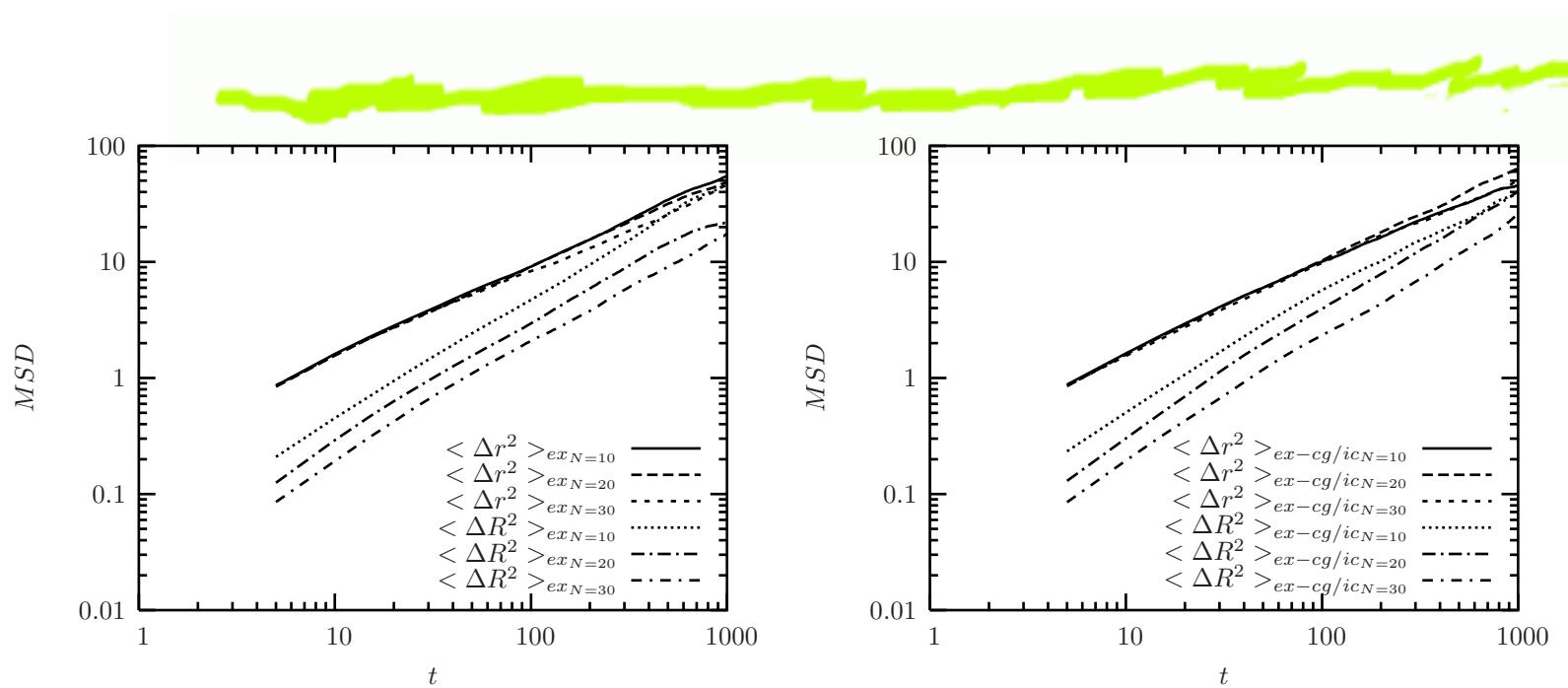
Static properties of the polymer



$$S(q) = \frac{1}{N} \left\langle \sum_{ij} \exp(i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \right\rangle$$

$$S(q) \propto q^{-1/\nu} \rightarrow q^2 S(q) \propto q^{2-1/\nu}, \nu \approx 0.57$$

Dynamic properties of the polymer



$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle}{t} = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle \Delta R^2 \rangle}{t}$$

$$\langle \Delta r^2 \rangle = \langle (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \rangle \propto t^{2/z}, 2/z \approx 0.67 (N = 30)$$

Diffusion constant of the chain



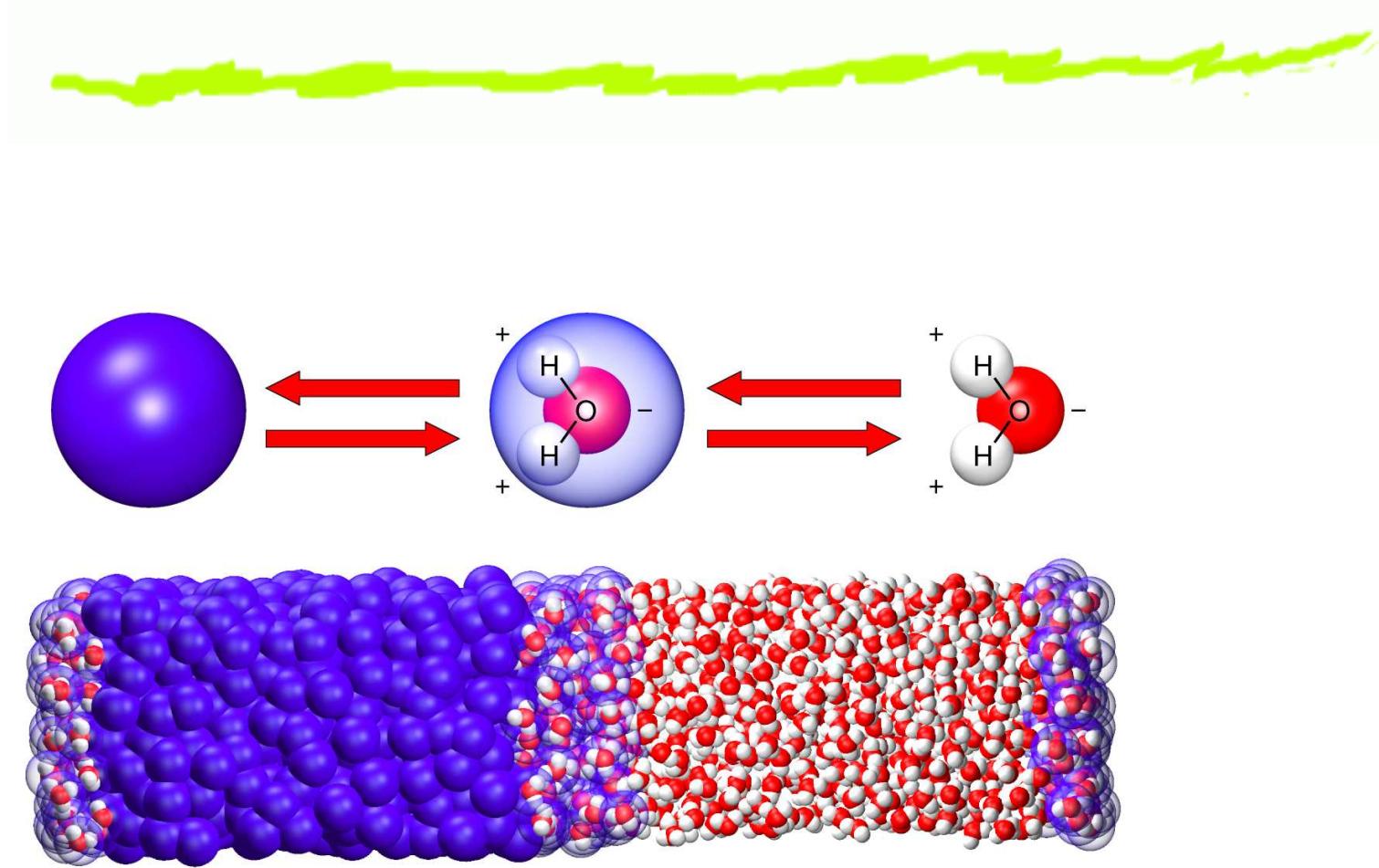
N	10	20	30
$D(ex)$	0.008	0.005	0.003
$D(ex-cg)$	0.009	0.006	0.0045
$D(ex-cg_{ic})$	0.0085	0.006	0.0035

$$D_{bulk_{ex}} = 0.036, D_{bulk_{cg}} = 0.057$$

$$D_{polymer} \ll D_{solvent}$$



Liquid water



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.

Electrostatics: Reaction field method

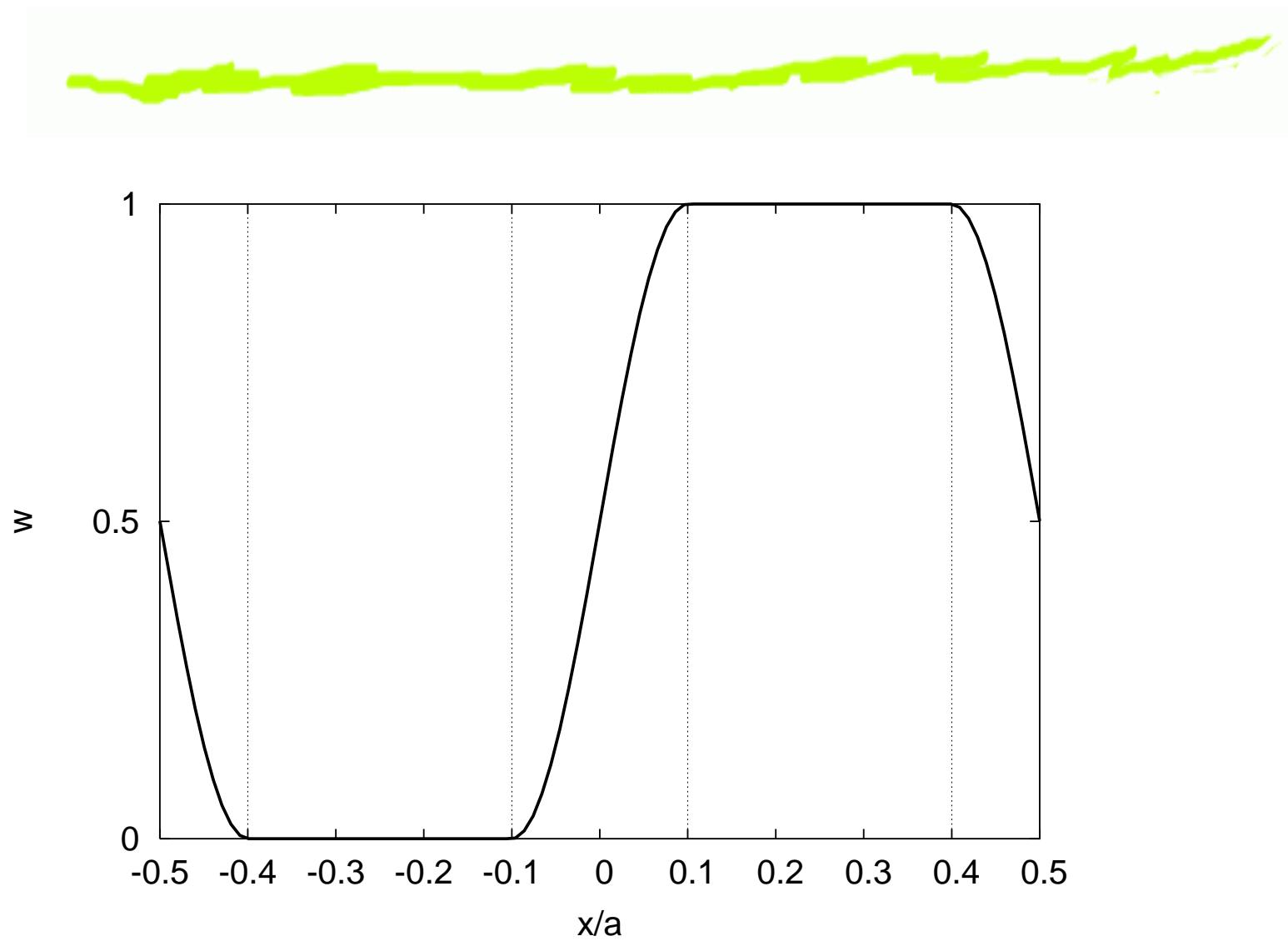
The electrostatic forces interactions are described using the Reaction field (RF) method:

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

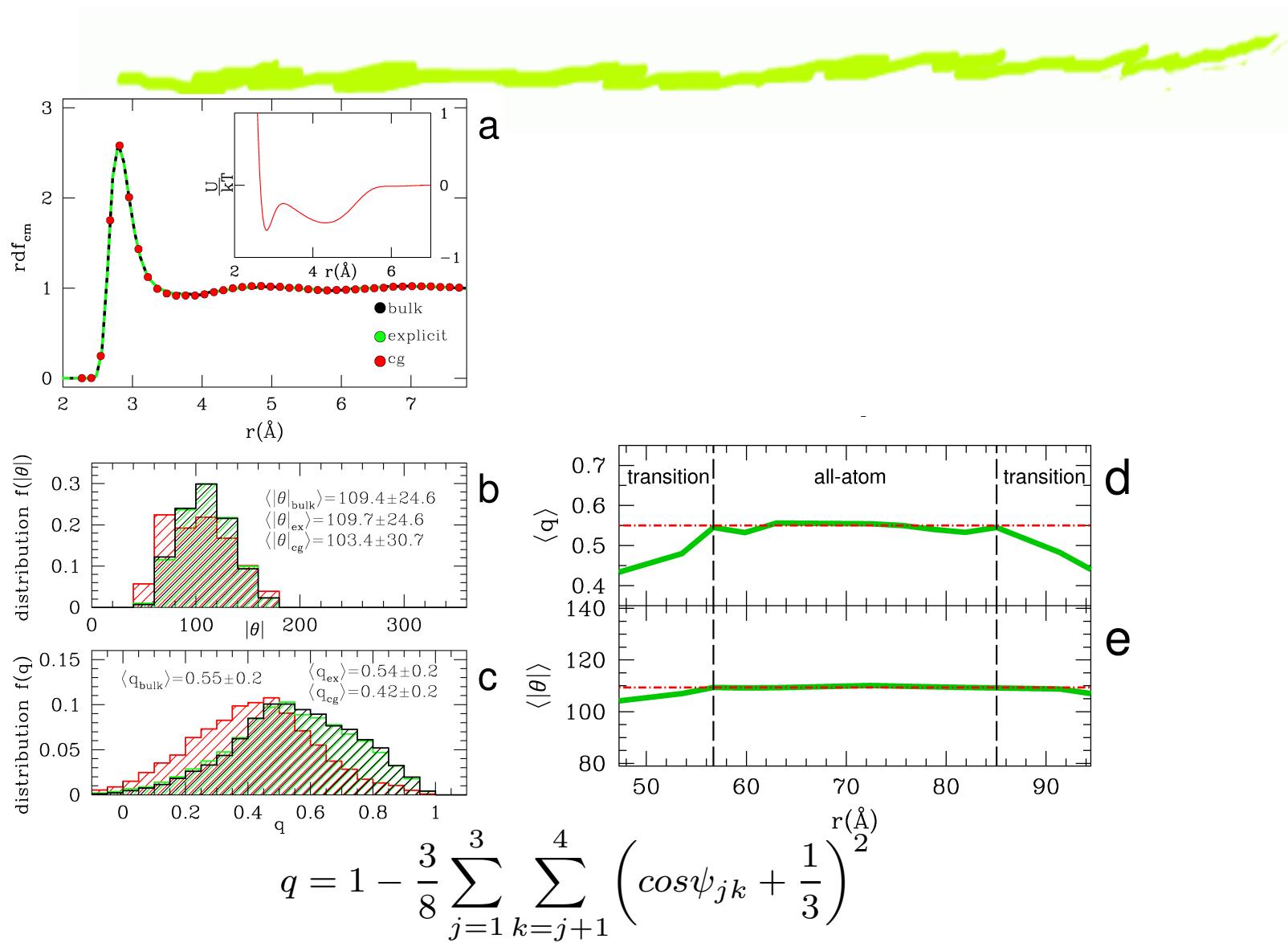
The RF is suitable to be used with AdResS because:

- ⑥ it is pairwise
- ⑥ like AdResS it must also be applied with a thermostat

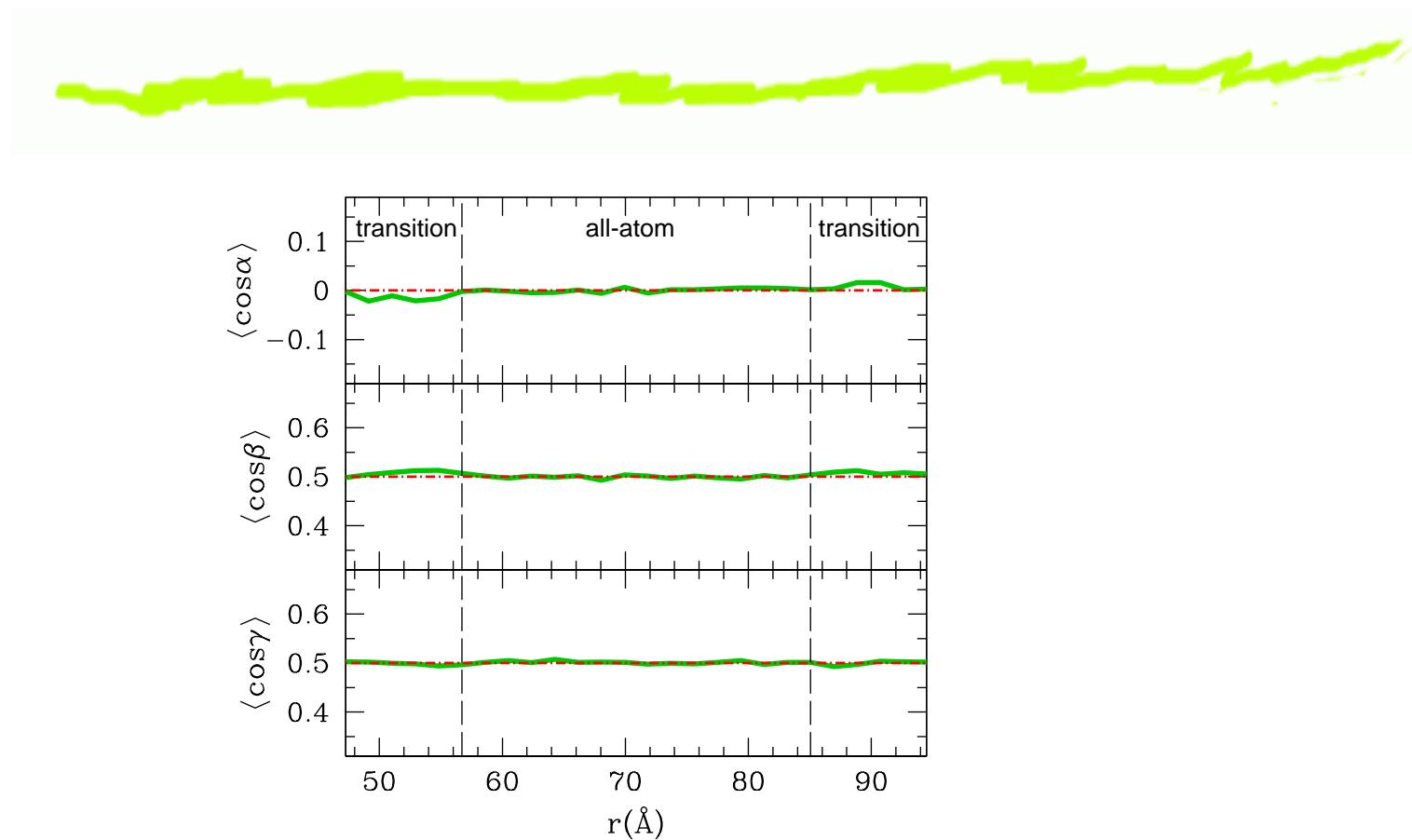
Weighting function for flat geometry



Static properties

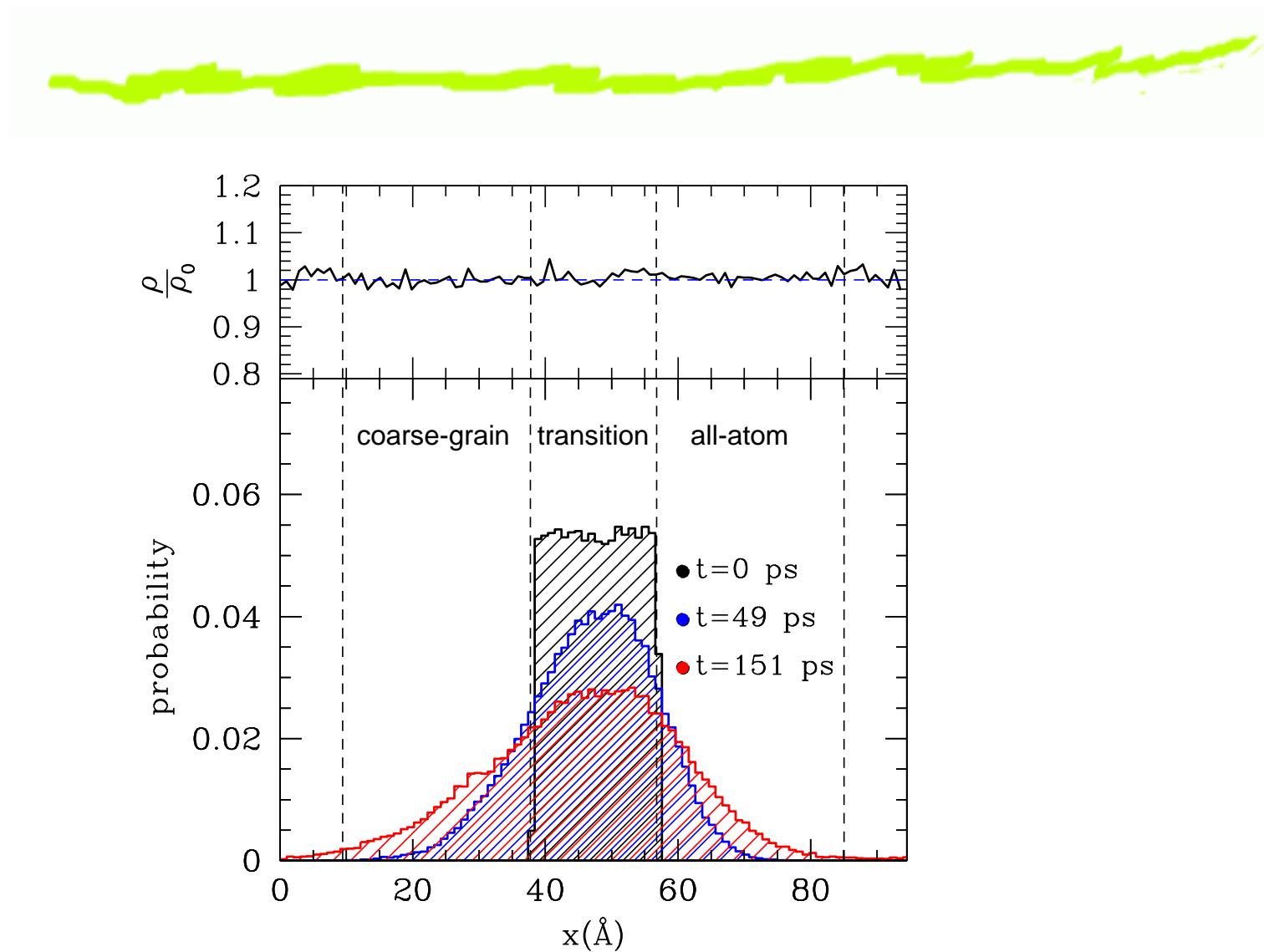


Interface effect of the cg water



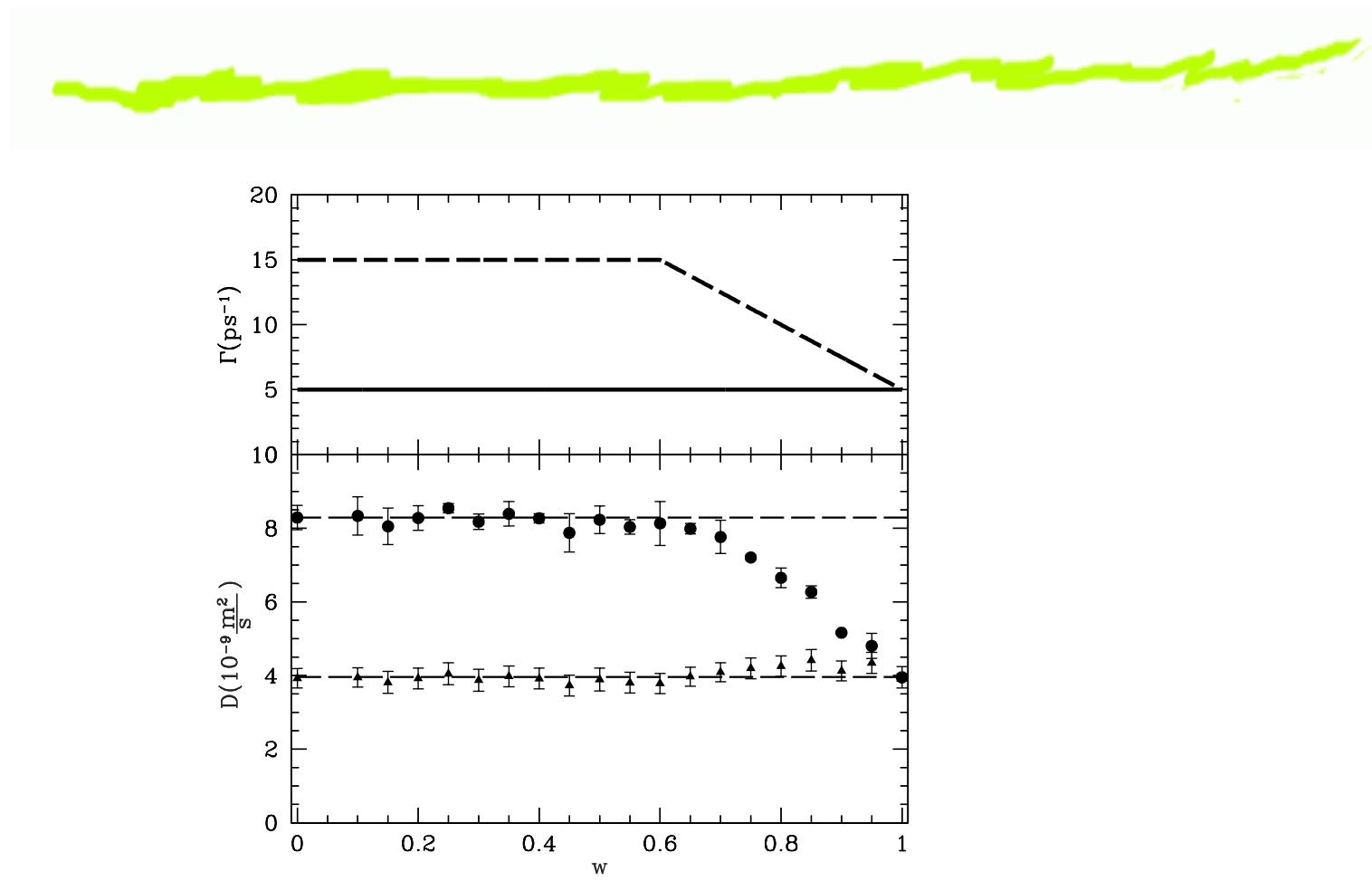
The transition regime neutralizes the interface effect of the cg water \Rightarrow the structure of water in the explicit regime is the same as in the bulk.

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 **128**, 024503, 2008.



Position dependent Langevin thermostat



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

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

where $R_i(x, t)$ is:

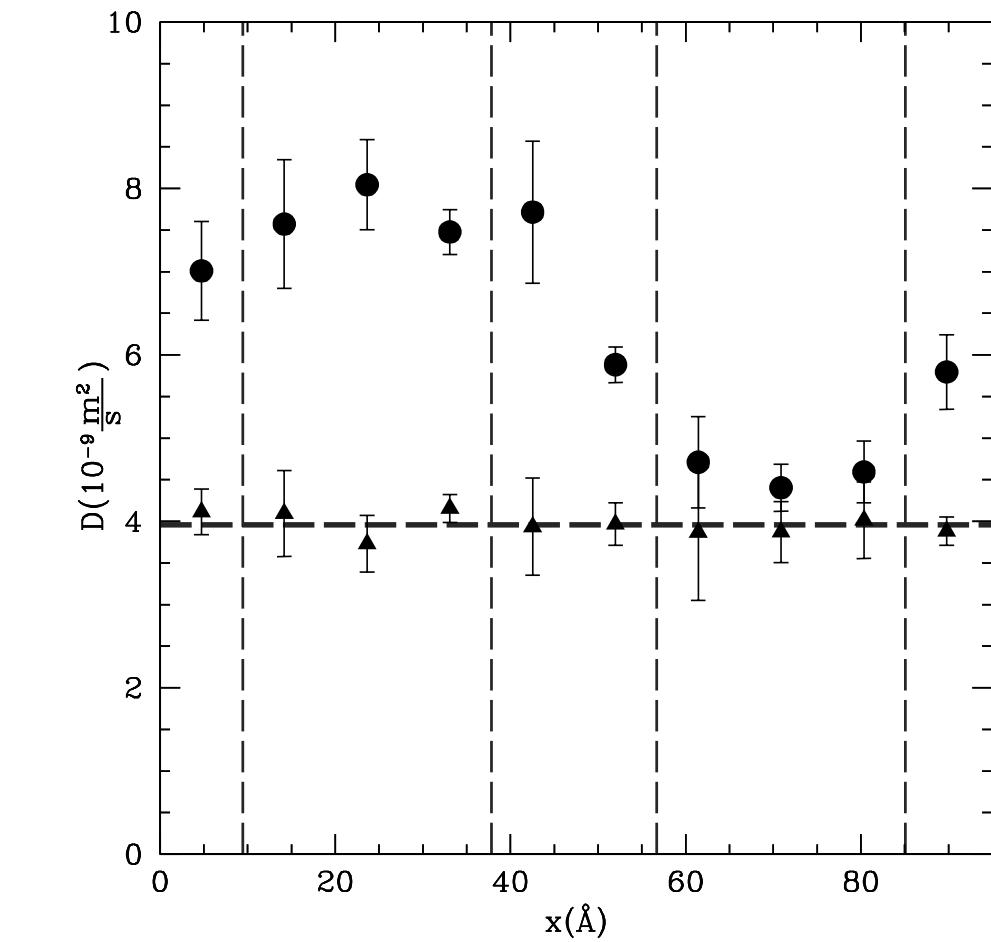
$$\langle R_i(x, t) \rangle = 0, \quad (2)$$

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

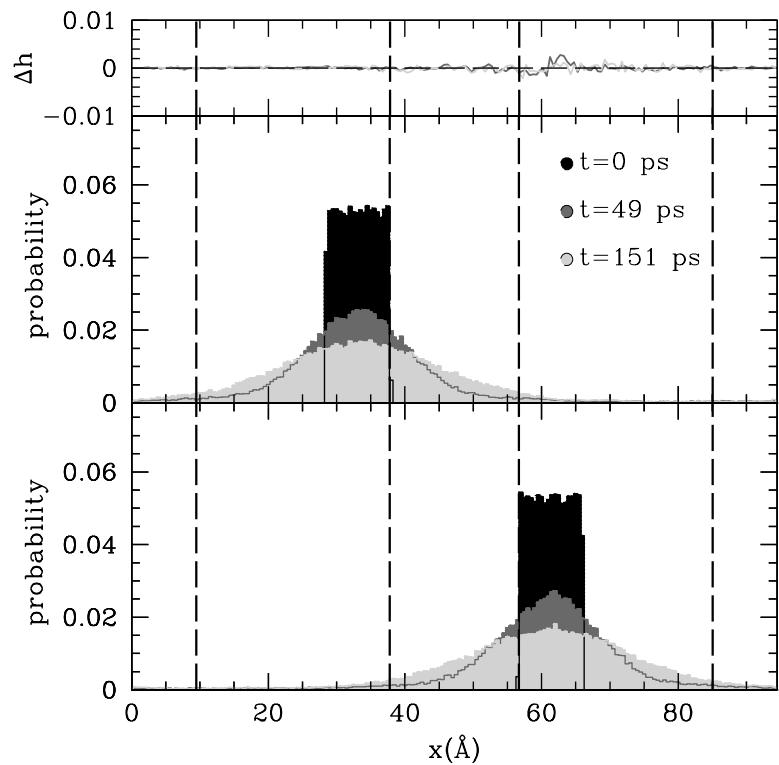
$$\Gamma(x) = \begin{cases} \Gamma_{cg} & \text{if } x \leq 0.6 \\ \alpha x + \beta & \text{if } 0.6 < x \leq 1.0 \end{cases} \quad (4)$$

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.

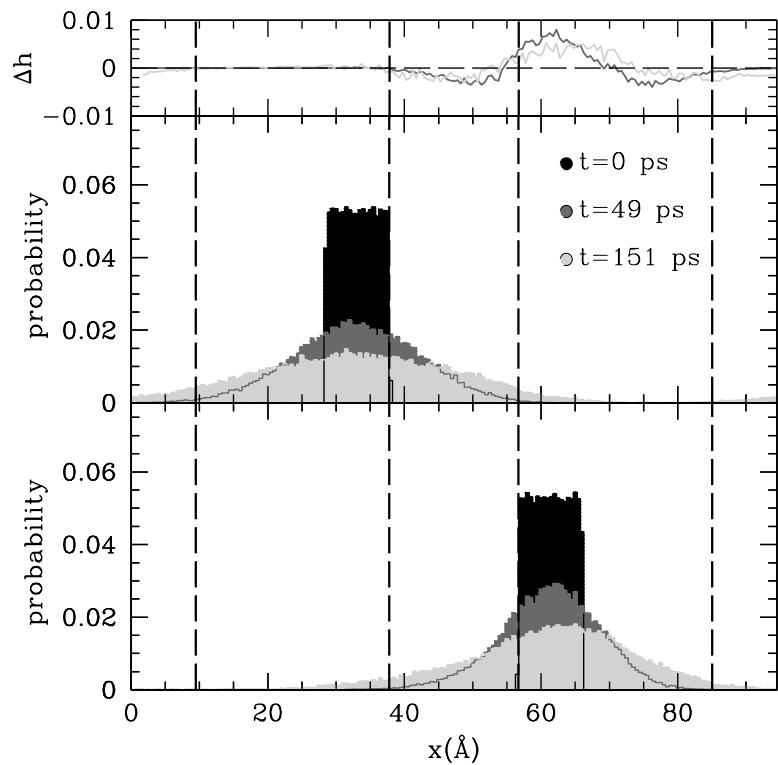
Diffusion coefficient in the hybrid system



Diffusion coefficient across the simulation box II.



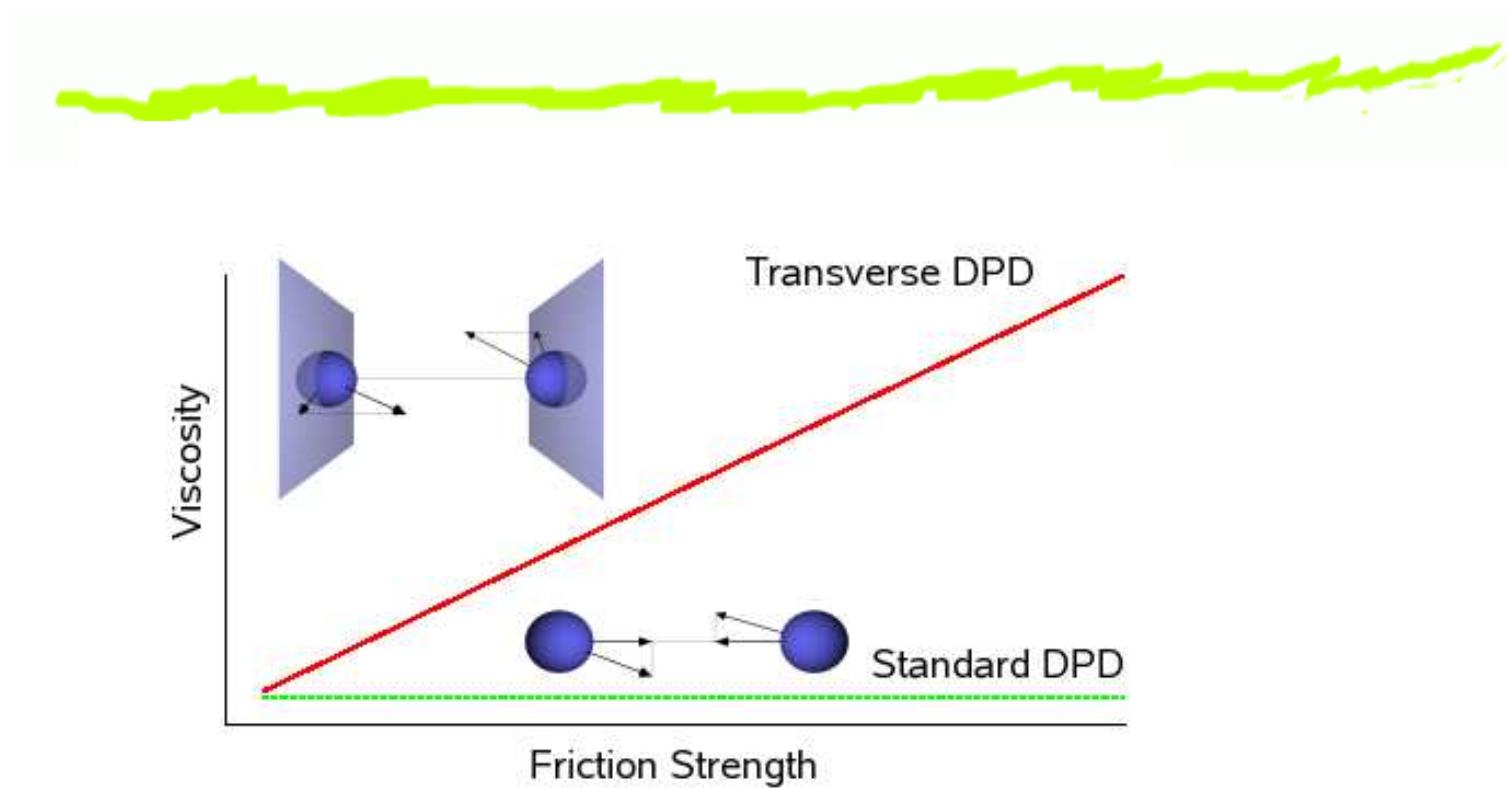
(w) Position dependent thermostat



(x) Regular thermostat



Transverse DPD Thermostat



- ⑥ 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, MP, K. Kremer, Soft Matter 4, 156, 2008.



AdResS: Conclusions



⑥ 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.

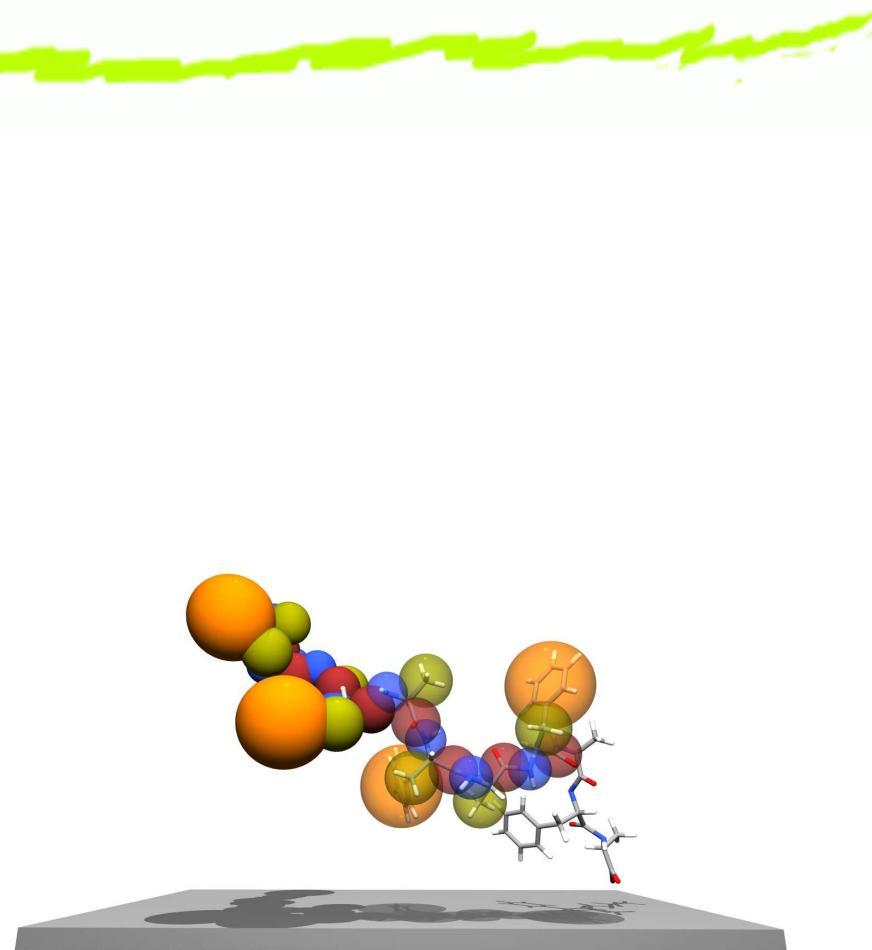
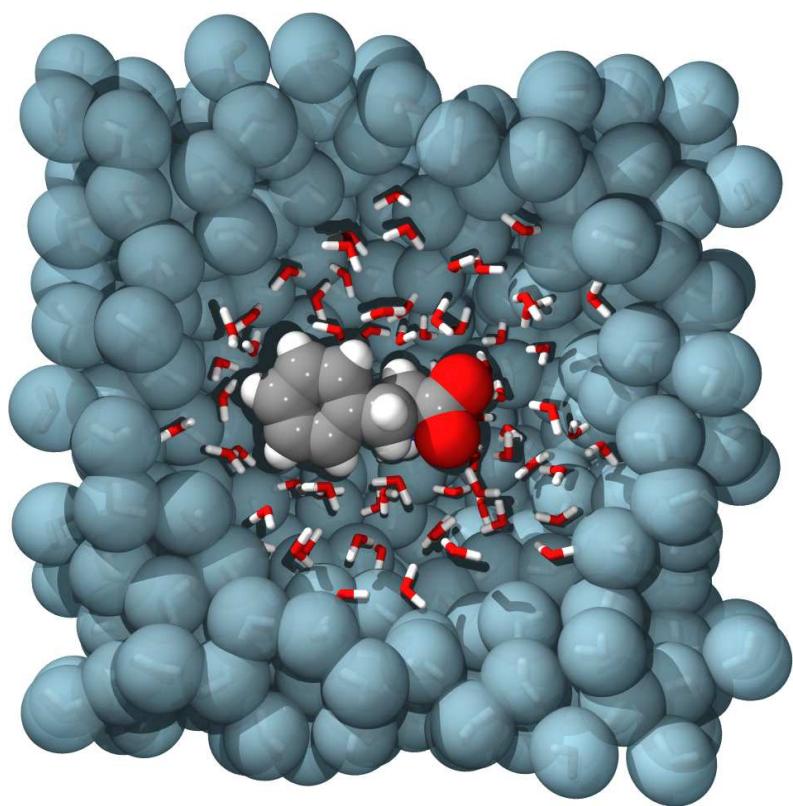
⑥ Hybrid method AdResS:

- △ Allows for a dynamical switching of the spatial resolution.
- △ We treat only as many DOFs as absolutely necessary for the problem considered.
- △ AdResS was so far applied to MD simulations of a simple tetrahedral liquid, a macromolecule in an explicit solvent, and liquid water at standard conditions.
- △ The simulation speed-up for liquid water is $\sim 17 - 20$ compared to atomistic simulations.

⑥ Review:

- △ MP, L. Delle Site, K. Kremer, Annu. Rev. Phys. Chem. **59**, 545, 2008.

AdResS: Future work





Concurrent triple-scale simulation



⑥ Motivation:

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

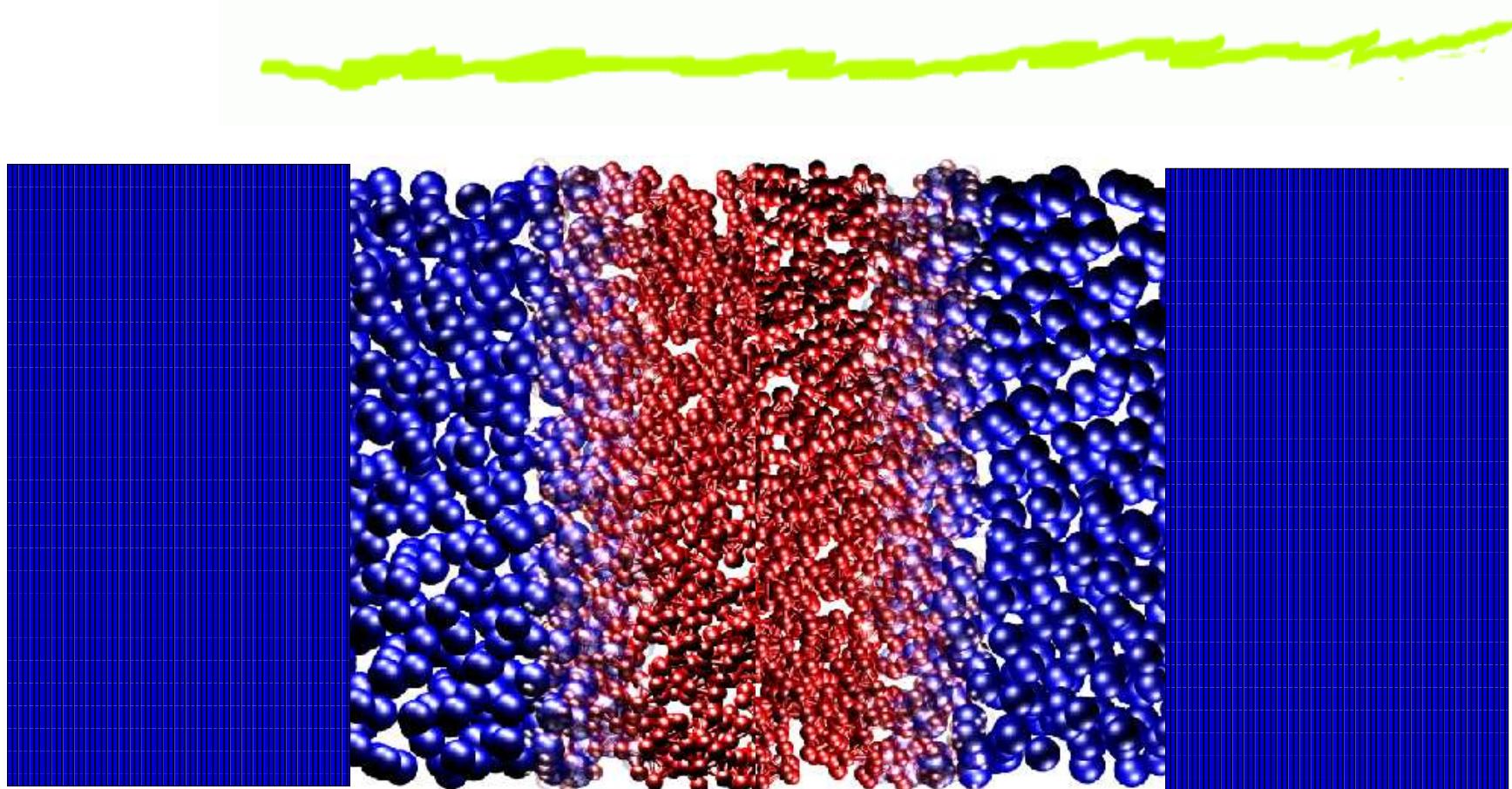
⑥ Method: *Triple-scale AdResS-HybridMD scheme*

- ▷ is a combination of two dual-scale models: a particle-based **Adaptive Resolution Scheme (AdResS)**, which couples the **atomic** and **mesoscopic** scales, and a **hybrid continuum-molecular dynamics scheme (HybridMD)**
- ▷ covers the **length-scales** ranging from the **micro-** to **macro-scale**
- ▷ successfully sorts out the problem of **large molecule insertion** in the hybrid particle-continuum simulations of molecular liquids
- ▷ opens up the possibility to perform efficient **grand-canonical molecular dynamics simulations** of truly open molecular liquid systems

⑥ Results:

- ▷ the **structural** and **dynamical** properties of the liquid are **accurately captured**

Triple-scale model



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



HybridMD: Coupling particle-based and continuum descriptions

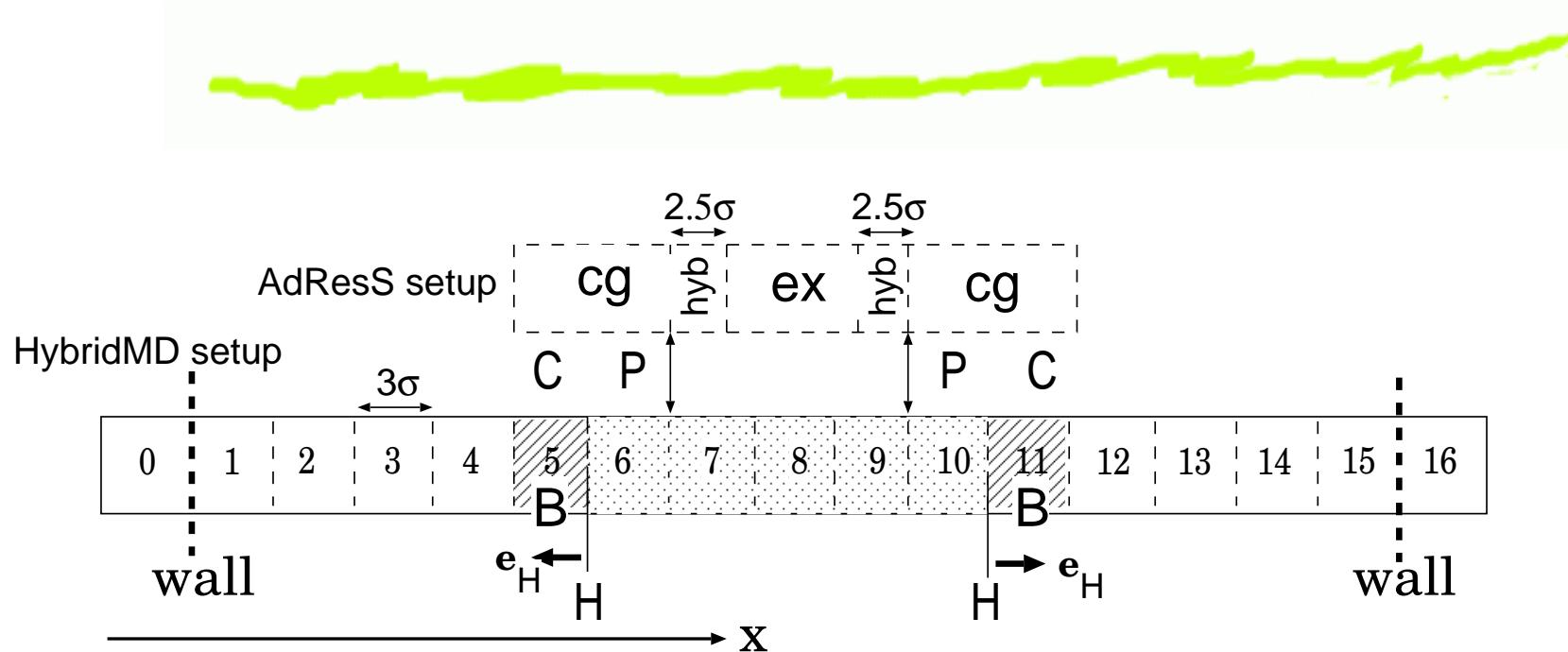


- ➊ The hybrid particle-continuum scheme (HybridMD) is designed to connect the dynamics of a “**molecular domain**” with that obtained from a **continuum description** of the surrounding fluid flow.
- ➋ The method is based on **flux-exchange**.
- ➌ The system is divided in (at least) two domains, described via classical **molecular dynamics (MD)** and **continuum fluid dynamics (CFD)**, i.e., solving the **Navier-Stokes** equations.
- ➍ The MD and CFD domains share one unique “hybrid interface”, H : Flux balance implies the **conservation of mass and momentum** across H .

G. De Fabritiis, R. Delgado Buscalioni, P. Coveney, Phys. Rev. Lett **97**, 134501, 2006.
R. Delgado Buscalioni, G. De Fabritiis, Phys. Rev. E **76**, 036709, 2007.



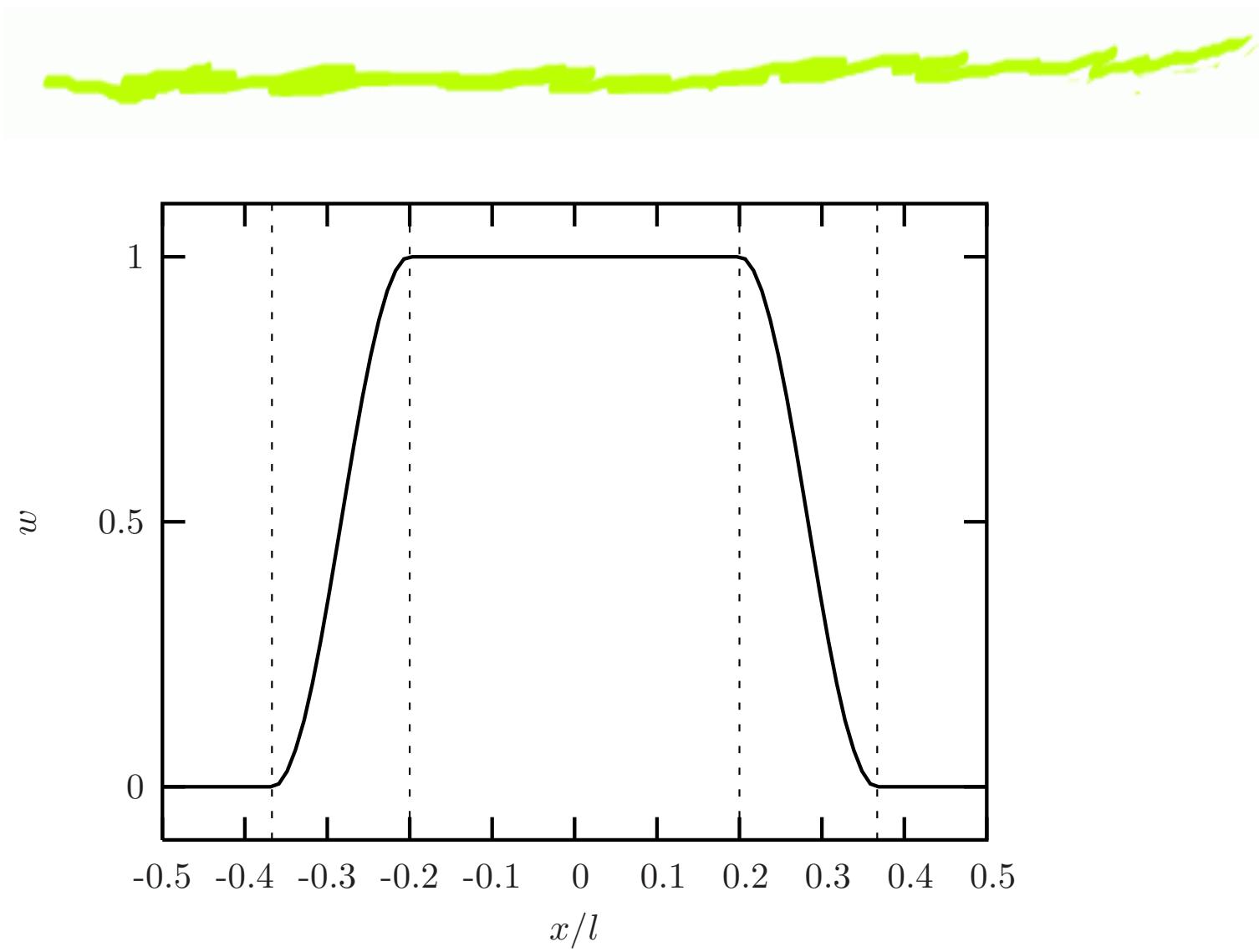
AdResS-HybridMD: Combined scheme



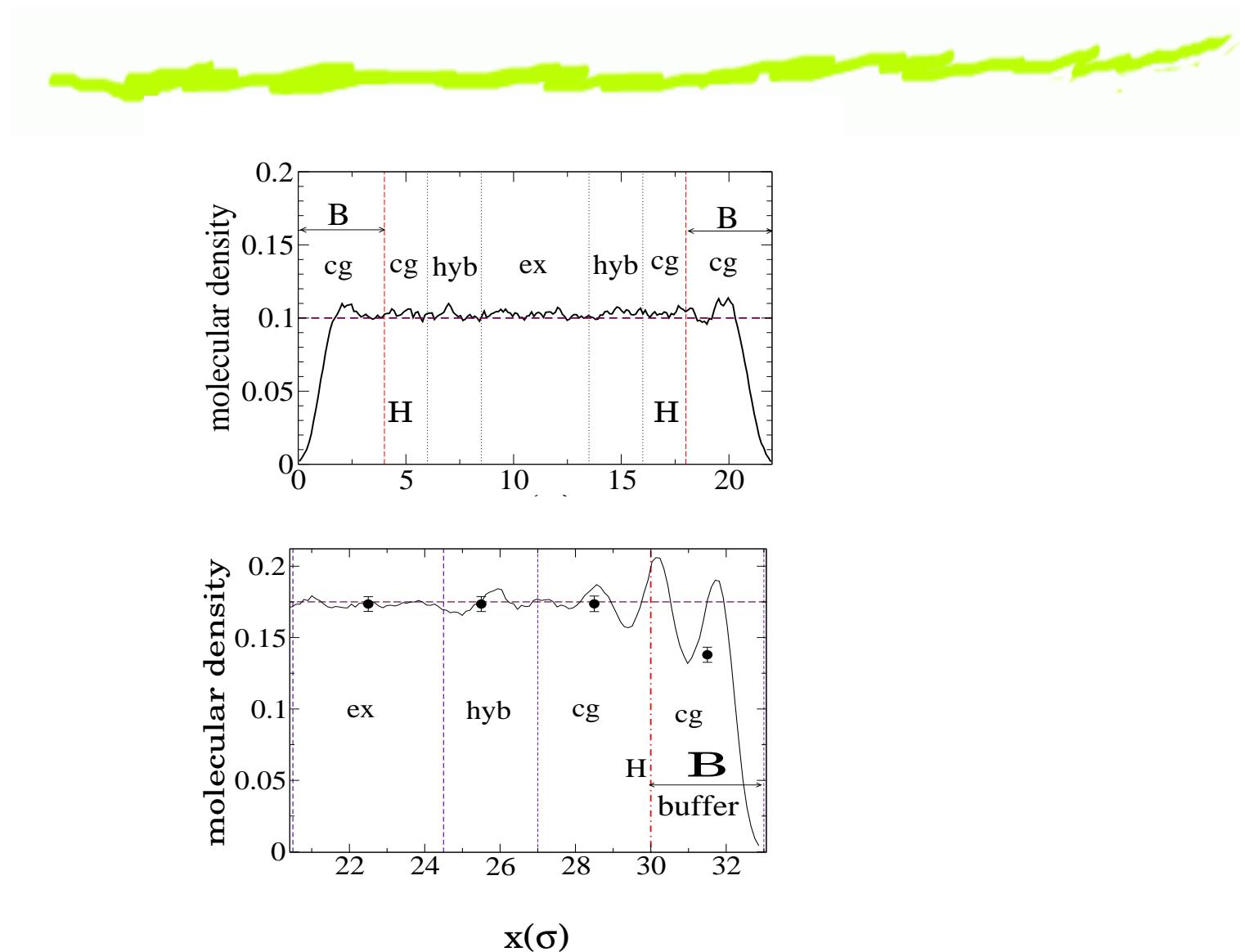
- 6 Domain decomposition of the combined scheme. The top part of the figure shows the location of the fluid model layers (*cg*, *hyb* and *ex*) within the HybridMD setup. The bottom part of the figure shows the set of control cells used in the HybridMD setup.

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

Weighting function



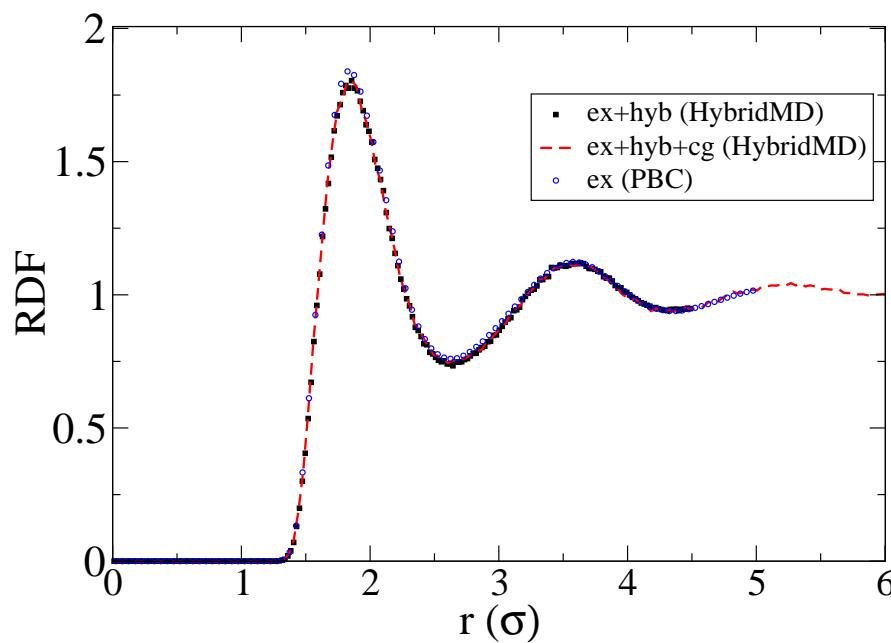
Molecular density profile



6

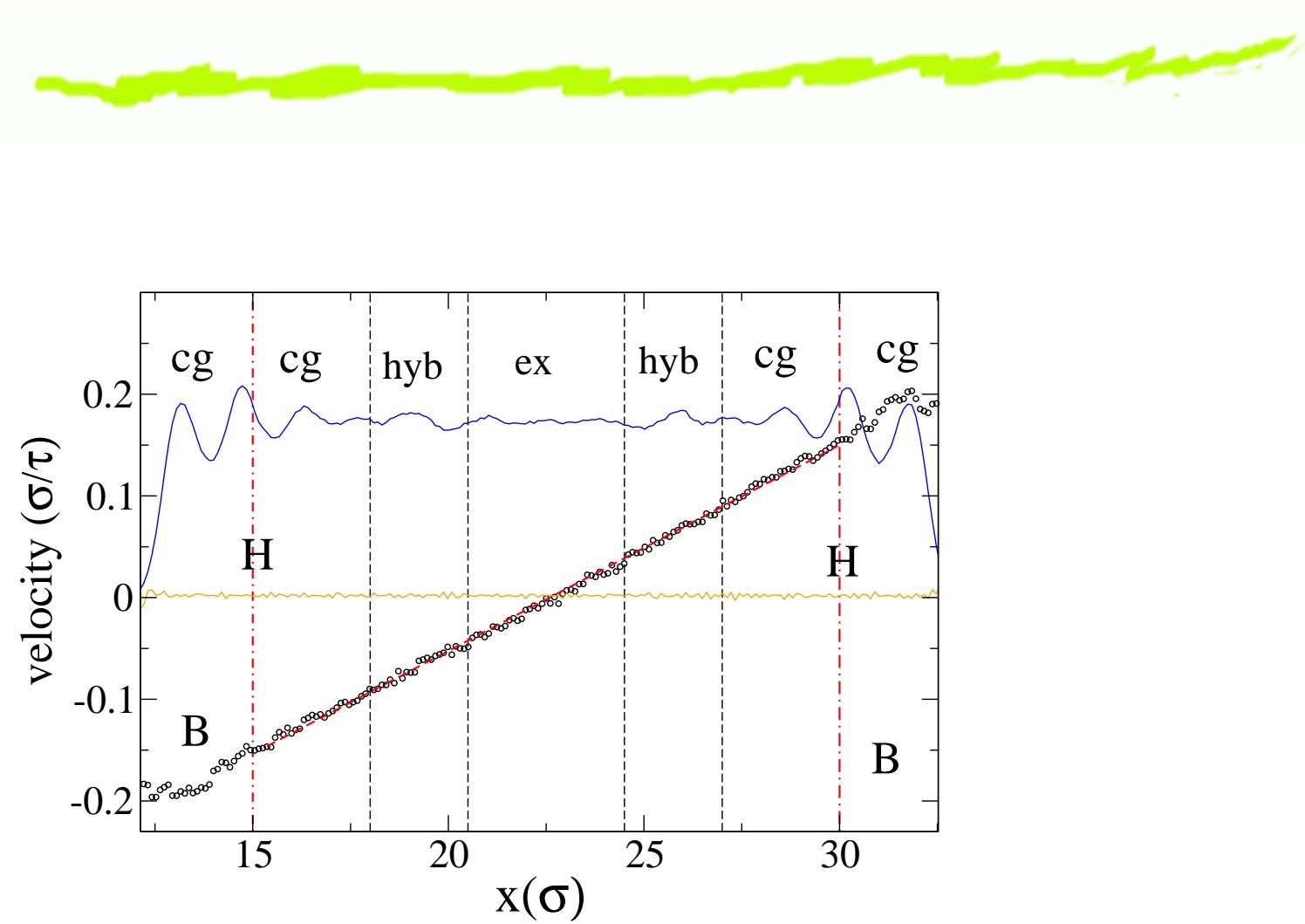
(a) $\rho_m = 0.1\sigma^{-3}$. (b) $\rho_m = 0.175\sigma^{-3}$

Radial distribution functions



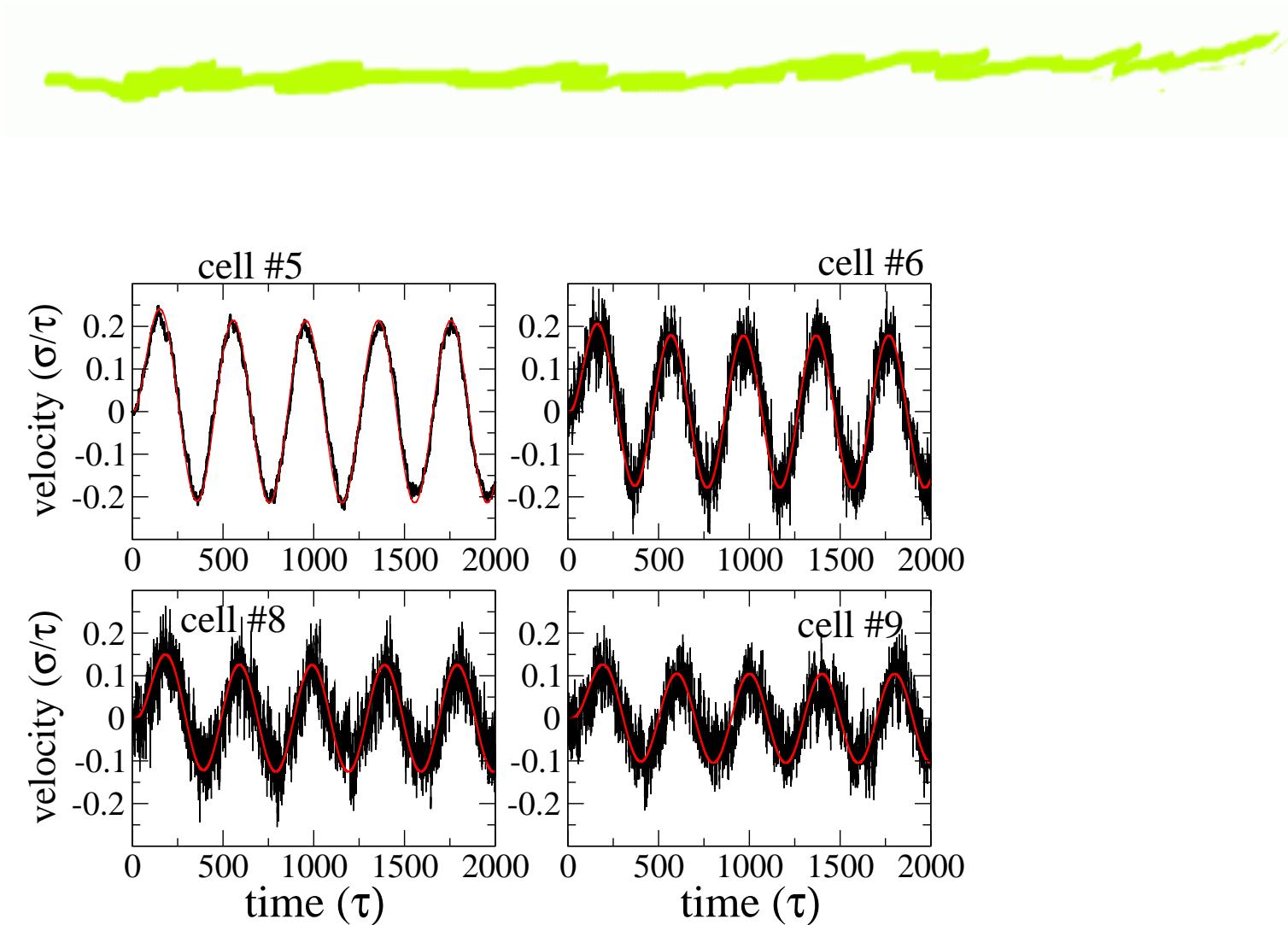
- ⑥ RDF_{cm}s of the liquid in the atomistic and transition domains (*ex + hyb*) and in the total molecular region (*ex + hyb + cg*) of the triple-scale model together with the reference RDF_{cm} of the all-atom system (*ex(PBC)*) at $\rho = 0.175/\sigma^3$.

Couette flow



6 Velocity profile at the particle region of an hybrid simulation of a Couette flow.

Stokes flow



- Velocity in the y-direction at some selected cells in a hybrid simulation of a Stokes flow.



AdResS-HybridMD: Conclusions



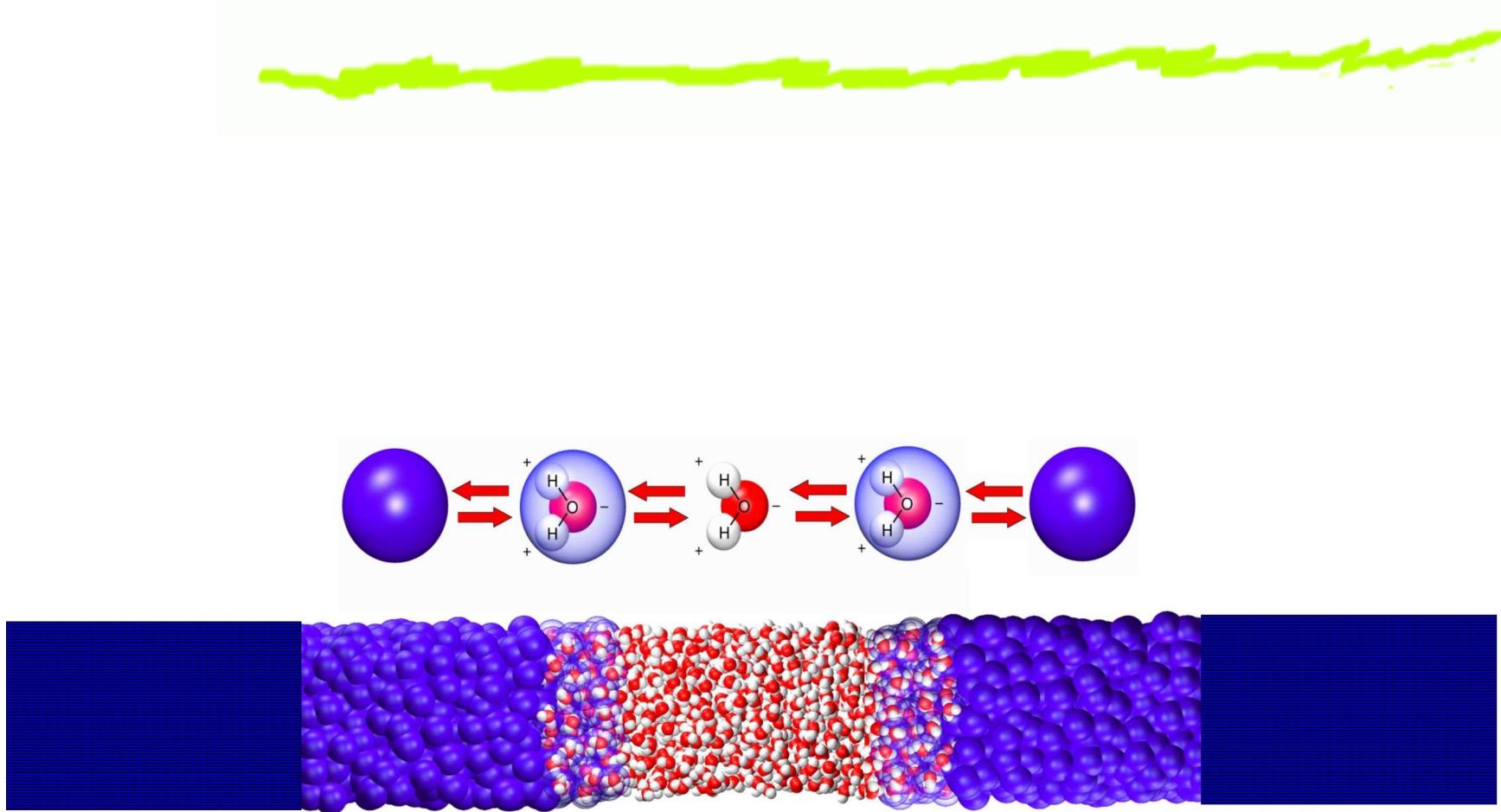
⑥ AdResS-HybridMD Scheme:

- △ We performed a **triple-scale simulation** of a molecular liquid.
- △ Length scales from the **micro- to macro-scale** are concurrently coupled.
- △ The method allows us to perform efficient **grand-canonical molecular dynamics simulations** of molecular liquids.

⑥ Future work:

- △ Application to realistic systems, e.g., liquid water.

Triple-scale liquid water



URL: <http://www.mpi-p-mainz.mpg.de/~praprot/>