Adaptive Resolution Molecular Dynamics

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Outline of Part I (a): The Method

- Concept of **adaptive**: Changing the number of degrees of freedom (DOF) on the fly

- Test system: Liquid of tetrahedral molecules

- The coupling formula on forces and the transition region

- Limitations regarding the control of the thermodynamic equilibrium

- Concept of switching as continuous change of phase space dimensionality and latent heat for equilibrium

- Why forces and not potentials

- Is the method working? Numerical tests

Outline of Part I (b): Applications

- Solvation of polymer in a liquid of tetrahedral molecules:
  (i) The solvent properties, adaptive v.s. full atomistic
  (ii) The polymer properties, adaptive v.s. full atomistic

- Liquid water:
  (i)How to treat long range interactions
  (ii)Properties of the liquid, adaptive v.s. full atomistic
  (iii)Diffusion and position dependent thermostat

Collaborators

- **Matej Praprotnik**, Mainz

- **Kurt Kremer**, Mainz

- Simon Poblete, Mainz

- Adolfo Poma, Mainz

- Christoph Junghans, Mainz

- Cecilia Clementi, Rice University, Houston

- Silvina Matysiak, Rice University, Houston
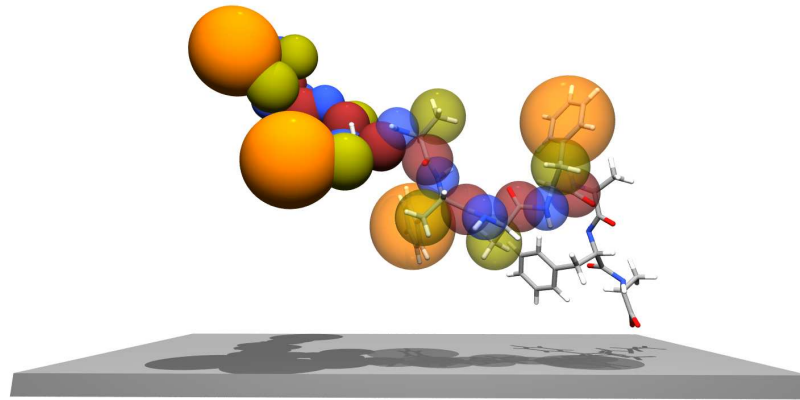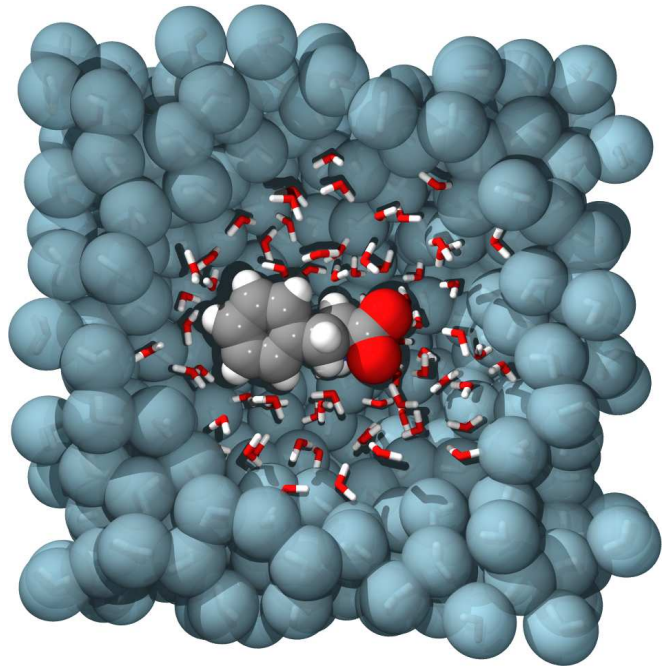
- Brad Lambeth, Rice University, Houston

Motivations

- many problems in condensed matter are inherently **multiscale**

- **main aspect**: scales' interplay $\implies$ simultaneous treatment of **all** the relevant scales

- **optimal computational approach**: treat only those degrees of freedom strictly required

- **different regions** may require **different resolution**

Examples

MD Simulation

All-Atom MD simulation:

- Atomistic (chemical) details

- (often) incapable to bridge the gap between a wide range of length and time scales

Coarse-Grained MD simulation:

- reduced number of degrees of freedom $\implies$ longer length and time scales

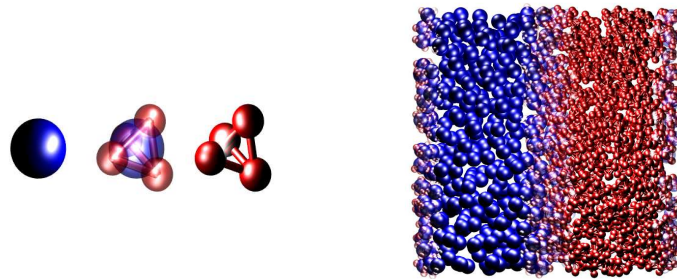- specific chemical details are lost

Solution:

- Hybrid Adaptive MD Schemes

Method and model: General Idea

Adaptive Resolution MD Scheme

- on-the-fly interchange between atomistic and coarse-grained description **Hybrid Model**

with: $\rho_{ex} = \rho_{cg}, \quad p_{ex} = p_{cg}, \quad T_{ex} = T_{cg}$

M.Praprotnik, L.Delle Site and K.Kremer; Annu.Rev.Phys.Chem. 59, 545-571 (2008)
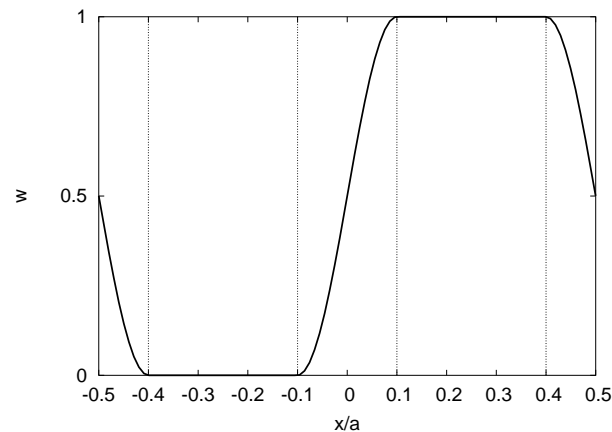
Scale Coupling

Two-stage procedure:

(a) Effective (coarse-grained) pair potential U^{cm} from the reference all-atom system.

(b) $\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}^{atom}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}^{cm}_{\alpha\beta}$
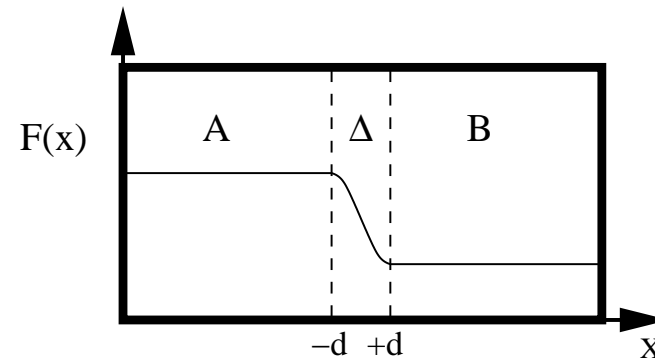
M. Praprotnik L. Delle Site and K. Kremer; J. Chem. Phys.; 123; 224106 (2005)

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

How to define the switching function I

- What happens in Δ ?

- The number of DOF 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:
$\lim_{x \to d^-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d^+} \frac{\partial F_B(x)}{\partial x} = 0$

- If not true $\to$ a free energy density gradient along x within the same level of resolution.

How to define the switching function II

- $\lim_{x \to d-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d+} \frac{\partial F_B(x)}{\partial x} = 0$ can be shown to be equivalent to
  $\lim_{x \to d-} \frac{\partial n_A(x)}{\partial x} = \lim_{x \to d+} \frac{\partial n_B(x)}{\partial x} = 0$

- $w(x)$ is such that $w(x) = 1; \forall x \in A$ and $w(x) = 0; \forall x \in B$, with
  $\lim_{x \to d+} \frac{\partial w(x)}{\partial x} = \lim_{x \to d-} \frac{\partial w(x)}{\partial x} = 0$.

- In accordance with the equation above, we require that the weighting function
  $w(x)$ is continuous up to the first derivative and that goes monotonically from
  the value one to zero in the region Δ.

Spherical Geometry
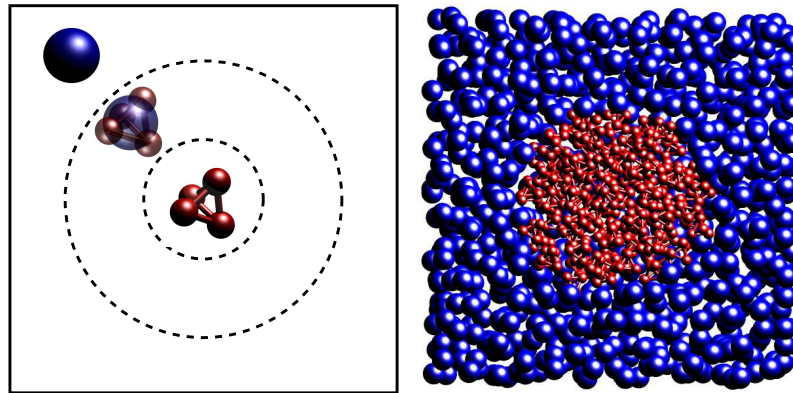
Spherical Symmetry:

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

C.Junghans, M.Praprotnik and L.Delle Site, in **Multiscale Simulation Methods in Molecular Sciences**, NIC Series Volume 42 (2009)

Change of Resolution

- Molecule from **Atom** $\rightarrow$ **cg**: vanishing **contributions** of switching DOFs

- $w(x)$ smoothly "*freezes*" the **dynamical evolution** of such DOFs and their **contribution to the interactions**

- (vice versa) $w(x)$ smoothly "*reactivates*" their dynamics and their contributions to the interactions

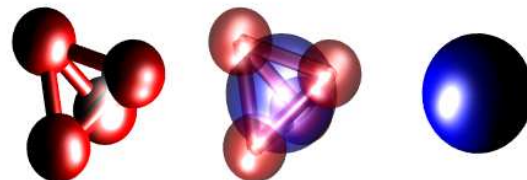by construction the **third Newton's Law** is preserved **(crucial in MD)**.

Technical aspects of the test molecule

A tetrahedral molecule has a defined spatial orientation and $3N = 12$ DOFs:

· 3 translational

· 3 rotational

· $3N - 6 = 6$ vibrational

Molecular Interactions in the Test System

Shifted 12-6 **Lennard-Jones potential:**

$$
U_{LJ}^{atom}(r_{i\alpha j\beta}) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r_{i\alpha j\beta}}\right)^{12} - \left(\frac{\sigma}{r_{i\alpha j\beta}}\right)^{6} + \frac{1}{4}\right]; & r_{i\alpha j\beta} \leq 2^{1/6}\sigma \\ 0; & r_{i\alpha j\beta} > 2^{1/6}\sigma \end{cases}
$$

FENE potential:

$$
U_{FENE}^{atom}(r_{i\alpha j\alpha}) = \begin{cases} -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{r_{i\alpha j\alpha}}{R_0}\right)^2\right]; & r_{i\alpha j\alpha} \leq R_0 \\ \infty; & r_{i\alpha j\alpha} > R_0 \end{cases}
$$

Effective pair potential

- In the limit of $\rho \to 0$:

$$U^{eff} = F(r) = -K_B T \ln g(r) \tag{1}$$

- For $\rho > 0$ we use the above relation as the initial approximation of an **iteration scheme**:

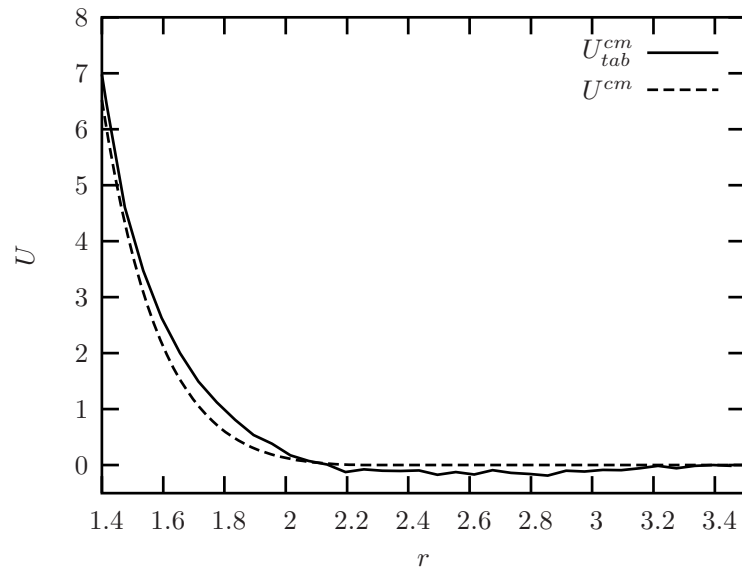$$U_{i+1}^{eff}(r) = U_i^{eff}(r) + k_B T \ln \frac{g_i(r)}{g_{target}(r)} \tag{2}$$

Pressure correction:

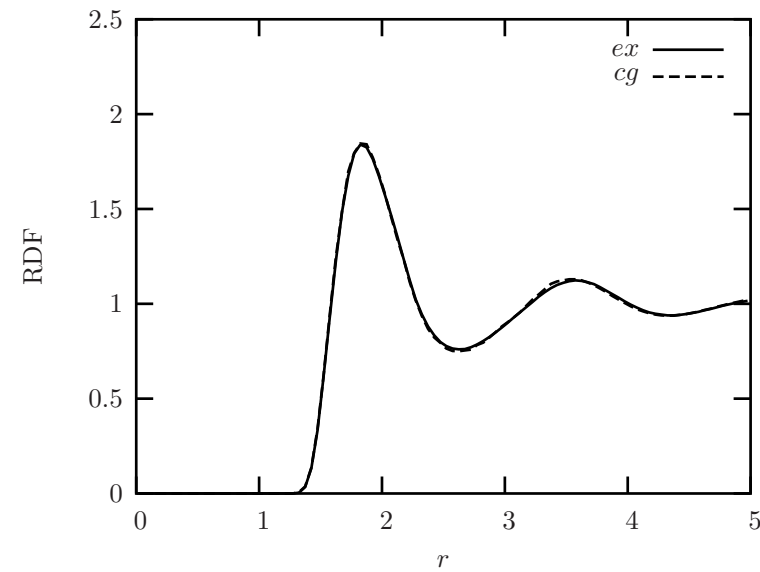$$\Delta V_{lin} = A(1 - \frac{r}{r_{cut}}). \tag{3}$$

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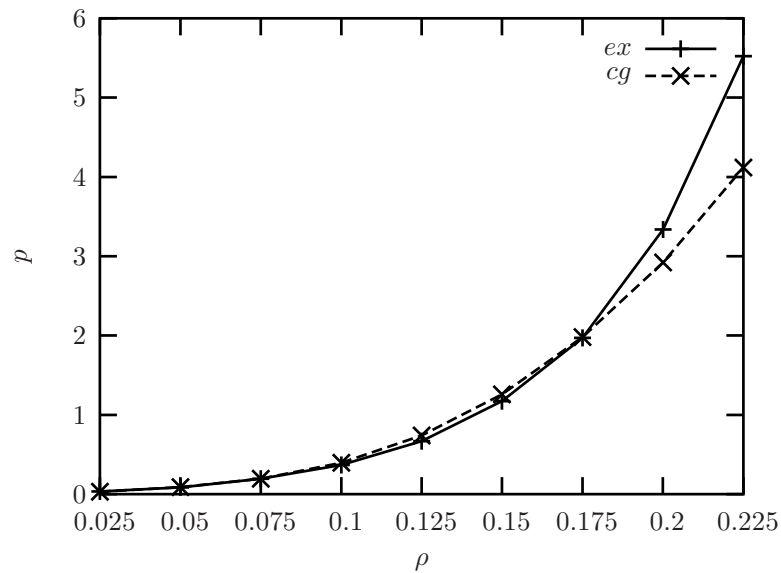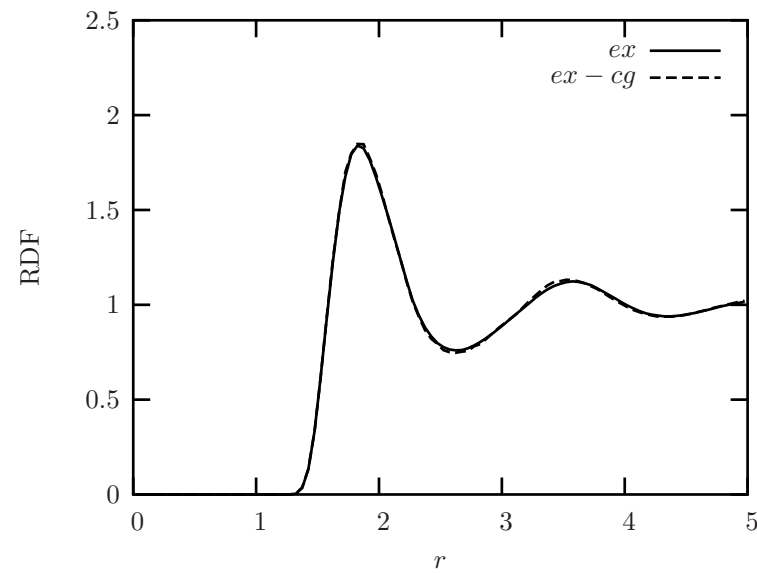
effective pair potentials

(g) Tabulated potential.

(h) RDF$_{cm}$.

Equation of state

(i) Equation of state for $\rho = 0.175$ and $T = 1$.

(j) RDF_{cm}.

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

Control of the thermodynamical equilibrium (I)

- Adaptive force **alone** cannot assure **thermodynamic equilibrium**

- it is not conservative $\implies$ **potential energy** cannot be written explicitly

- **BUT:** statistical mechanics principles of **varying resolution** $\implies$ tools for thermodynamical equilibrium

Control of the thermodynamical equilibrium (II)

- Free energy is an extensive quantity and thus proportional to the number of DOF

- **preferential tendency** of one species to migrate into the other region

- **or equivalently** $\mu_{atom} \neq \mu_{cg}$

- **unphysical**: artifact of the different representations.

Change of resolution and corresponding latent heat

- The change of resolution: change of the number of *active/thermalized* DOF $\implies$ latent heat ϕ

- $\mu_{atom} = \mu_{cg} + \phi$

- Explicit form of ϕ unknown

- **numerical:** couple the system to a position dependent thermostat

- How to define the temperature in Δ

Temperature in the region $\triangle$

- **Equipartition Theorem:** $T_A = \frac{2\langle K_A \rangle}{n_A}$; $T_B = \frac{2\langle K_B \rangle}{n_B}$

- in $\triangle$: $T_\triangle = \frac{2\langle K_\triangle \rangle}{n_\triangle}$?; **What is $\langle K_\triangle \rangle$?**

- **2-dimensional example:**
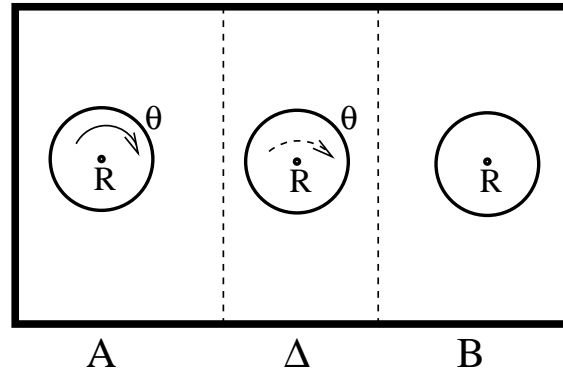
- $K_A = \frac{1}{2}[\dot{\mathbf{R}}^2 + p_\Theta^2] = \frac{1}{2}[\dot{R_x}^2 + \dot{R_y}^2 + \dot{\Theta}^2]$; $K_B = \frac{1}{2}\dot{\mathbf{R}}^2 = \frac{1}{2}[\dot{R_x}^2 + \dot{R_y}^2]$

- R_x, R_y, and Θ, contribute each with $T/2$ to the kinetic energy

- Hence, $T_A = \frac{2<K_A>}{3}$, $T_B = \frac{2<K_B>}{2}$

Adaptive resolution via a continuous change of the phase space dimensionality

- **Statistical calculation of physical quantities:**
  (a) a DOF **fully counts** in the atomistic region $(\int ...d\theta)$
  (b) it **does not count at all** in the coarse-grained region (no integration over θ)

- In Δ $(0 < w(x) < 1)$: switching **equivalent to** continuously change **the dimensionality of the phase space**

- **mathematical formalism:** fractional calculus $\Longrightarrow$
  $$dV_w = d^w q\, \Gamma(w/2)/2\pi^{w/2}\Gamma(w) = |q|^{w-1}dq/\Gamma(w) = dq^w/w\Gamma(w)$$
  (for a fixed value of w, and generic DOF q)

Temperature in the region $\triangle$: The extension of the Equipartition Theorem to non integer DOF

- **partition function** for the fractional quadratic DOF Θ:

$$\exp(-\beta F_w) = C \int \exp(-\beta p_\Theta^2/2)\, dV_w =$$

$$2C \int_0^\infty \exp(-\beta p_\Theta^2/2)\, |p_\Theta|^{w-1}\, \frac{dp_\Theta}{\Gamma(w)} = \frac{2^{w/2} C \Gamma(w/2)}{\Gamma(w)} \beta^{-w/2} \sim \beta^{-w/2}$$

- **fractional analog of the Equipartition Theorem**:

$$\langle K_w \rangle = \frac{d(\beta F_w)}{d\beta} = \frac{w}{2\beta} = \frac{wT}{2}$$

$\langle K_w \rangle$: average kinetic energy per fractional quadratic DOF with the parametric weight w

- In equilibrium $T_A = T_B = T_\triangle = T$ and thus: $n_\triangle = 2 + w$ (proof of consistency)

Fractional DOF: A more general view

- A generic statistical average of a quantity A in the canonical ensemble:

$$< A >= \frac{\int_0^\infty e^{-\beta H(q)} A(q) dq}{\int_0^\infty e^{-\beta H(q)} dq}. \tag{4}$$

- with a fractional degrees α:

$$< A >_\alpha = \frac{\int_0^\infty e^{-\beta H(q)} q^{\alpha-1} A(q) dq}{\int_0^\infty e^{-\beta H(q)} q^{\alpha-1} dq}. \tag{5}$$

- If $H(q) = |q|^m; m > 0$ and $A(q) = C_n |q|^n; n > 0$ then:

$$< A >_\alpha = \frac{C_n \int_0^\infty e^{-\beta |q|^m} q^{\alpha+n-1} dq}{\int_0^\infty e^{-\beta |q|^m} q^{\alpha-1} dq}. \tag{6}$$

$$< A >_\alpha = \frac{\Gamma(\frac{\alpha+n}{m})}{\Gamma(\frac{\alpha}{m})} \beta^{-n/m}. \tag{7}$$

- if $m = n \rightarrow < H(q) >_\alpha$:
  $< H(q) >_\alpha = \frac{\alpha}{n} \beta^{-1}$ that is $< H(q) >_\alpha = \alpha < H(q) >$

The average molecular bond: An example of adaptive representation

Consider the case of the average length of a diatomic molecule

- $<|l|>_\alpha = \dfrac{\int_o^\infty l^\alpha e^{-\beta l^2}\,dl}{\int_o^\infty e^{-\beta l^2}\,dl}$

- $<|l|>_\alpha = \dfrac{\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{\alpha+1}{2}\right)}{\Gamma\left(\frac{\alpha}{2}\right)} <|l|>$
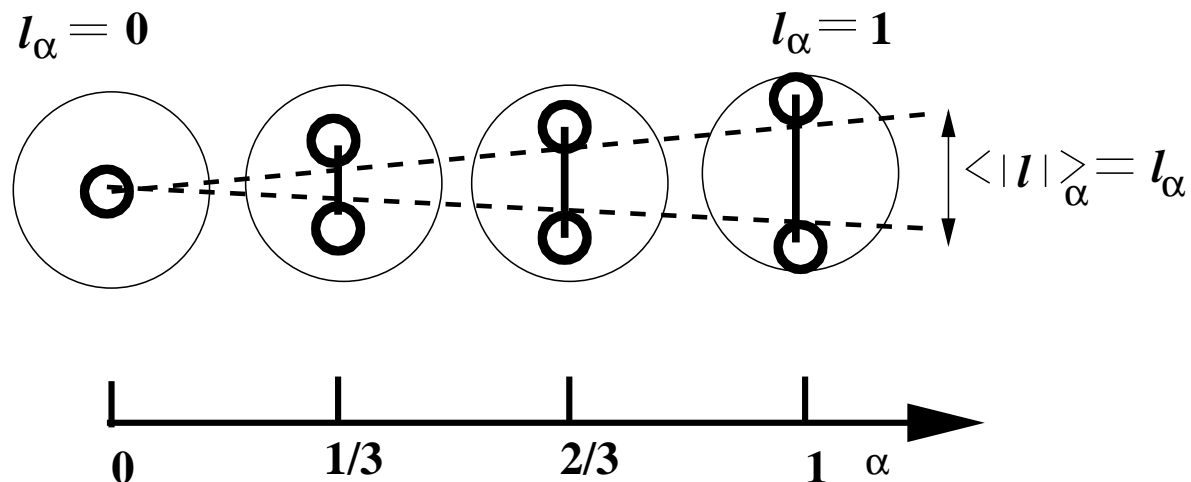
Theoretical Basis: Conclusions

- **(1)** Changing Resolution $\rightarrow$ Latent Heat $\rightarrow$ position dependent Thermostat

- **(2)** The temperature in the switching region, T_Δ, can be obtained by **extending the equipartition theorem to non integer dimensions**

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

  M.Praprotnik, K.Kremer and L.Delle Site, J.Phys.A:Math.Th.40, F281 (2007).

- **Still to address** : Why **forces** and not **potentials**

Coupling the atomistic and mesoscopic scales via a POTENTIAL approach

Why the forces and not the Potentials?

- Coupling potentials:

$$U_{\alpha\beta} = w(x_\alpha)w(x_\beta)U_{\alpha\beta}^{atom} + [1 - w(x_\alpha)w(x_\beta)]U_{\alpha\beta}^{cg}$$

- Consequence: $\mathbf{F}_{drift} = U_{atom}\frac{\partial w}{\partial x} + U_{cg}\frac{\partial w}{\partial x}$

  (a) if considered *physical* $\longrightarrow$ **violation of Third Newton's law**

  M.Praprotnik, K.Kremer and L.Delle Site, J.Phys.A:Math.Th.40, F281 (2007)

  (b) if removed $\longrightarrow$ mathematical inconsistency

  L.Delle Site, Phys.Rev.E, 76, 047701 (2007)

Violation of the Third Newton's law I

- if: $V_{\alpha\beta} = w(x_\alpha)w(x_\beta)V_{\alpha\beta}^{atom} + [1 - w(x_\alpha)w(x_\beta)]V_{\alpha\beta}^{cg}$

- Then: $\mathbf{F}_{\alpha\beta} = -\dfrac{\partial V_{\alpha\beta}}{\partial \mathbf{r}_\alpha}$

- $-\dfrac{\partial V_{\alpha\beta}}{\partial \mathbf{r}_\alpha} = w(x_\alpha)w(x_\beta)\mathbf{F}_{\alpha\beta}^{atom} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}_{\alpha\beta}^{cg}$
  $+ \left(\dfrac{\partial w(x_\alpha)}{\partial x_\alpha} w(x_\beta) \left[V_{\alpha\beta}^{cg} - V_{\alpha\beta}^{atom} \right], 0, 0 \right)$

- The force acting on the molecule β is: $\mathbf{F}_{\beta\alpha} = -\dfrac{\partial V_{\alpha\beta}}{\partial \mathbf{r}_\beta}$

- $-\dfrac{\partial V_{\alpha\beta}}{\partial \mathbf{r}_\beta} = w(x_\alpha)w(x_\beta)\mathbf{F}_{\beta\alpha}^{atom} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}_{\beta\alpha}^{cg}$
  $+ \left(\dfrac{\partial w(x_\beta)}{\partial x_\beta} w(x_\alpha) \left[V_{\alpha\beta}^{cg} - V_{\alpha\beta}^{atom} \right], 0, 0 \right)$

- where $\dfrac{\partial}{\partial \mathbf{r}} = (\dfrac{\partial}{\partial x}, \dfrac{\partial}{\partial y}, \dfrac{\partial}{\partial z})$, $\mathbf{F}_{\alpha\beta}^{atom} = -\dfrac{\partial V_{\alpha\beta}^{atom}}{\partial \mathbf{r}_\alpha}$, and $\mathbf{F}_{\alpha\beta}^{cg} = -\dfrac{\partial V_{\alpha\beta}^{cg}}{\partial \mathbf{r}_\alpha}$.

Violation of the Third Newton's law II

- Using $\mathbf{F}_{\beta\alpha}^{atom} = -\mathbf{F}_{\alpha\beta}^{atom}$ and $\mathbf{F}_{\beta\alpha}^{cg} = -\mathbf{F}_{\alpha\beta}^{cg}$ we obtain:

- $-\mathbf{F}_{\beta\alpha} = w(x_\alpha)w(x_\beta)\mathbf{F}_{\alpha\beta}^{atom} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}_{\alpha\beta}^{cg}$
  $- \left(\frac{\partial w(x_\beta)}{\partial x_\beta} w(x_\alpha) \left[V_{\alpha\beta}^{cg} - V_{\alpha\beta}^{atom} \right], 0, 0 \right)$

- In order that the force satisfies Newton's Third Law:
  $\frac{\partial w(x_\alpha)}{\partial x_\alpha} w(x_\beta) = -\frac{\partial w(x_\beta)}{\partial x_\beta} w(r_\alpha)$

- implying that: $\frac{1}{w(x_\alpha)} \frac{\partial w(x_\alpha)}{\partial x_\alpha} = -\frac{1}{w(x_\beta)} \frac{\partial w(x_\beta)}{\partial x_\beta}$

- whose solution is $w(x_\alpha)$ and $w(x_\beta)$ are constants!

The Mathematical Problem I

- A generalization to the potentials using two generic weighting functions $f(x)$ and $g(x)$ writes: $U^{coupling} = f(X_\alpha, X_\beta)U_{cg} + g(X_\alpha, X_\beta)U_{atom}$

- $\mathbf{F}_{drift} = 0 \rightarrow$

$$U_{cg}\frac{\partial f(X_\alpha, X_\beta)}{\partial X_\alpha} + U_{atom}\frac{\partial g(X_\alpha, X_\beta)}{\partial X_\alpha} = 0$$

$$U_{cg}\frac{\partial f(X_\alpha, X_\beta)}{\partial X_\beta} + U_{atom}\frac{\partial g(X_\alpha, X_\beta)}{\partial X_\beta} = 0. \tag{8}$$

equations of first order, each 2 boundary conditions **(system overdetermined)**

- If generalized: $U^{coupling} = f(X_\alpha, X_\beta)U_{cg} + g(X_\alpha, X_\beta)U_{atom} + \Phi$: $\rightarrow$ overdetermination shifted from f and g to Φ.

The Mathematical Problem II

Above all:

- $\int [U_{cg} \frac{\partial f(x)}{x} + U_{atom} \frac{\partial g(x)}{x} U_{atom}] dx + \Phi_0 = \Phi(x)$

- cannot be a solution, since one **must** have either
  $\Phi(x_0) = \Phi_0 = 0$ (atomistic region) or
  $\Phi(x_1) = \Phi_0 = U_{atom} - U_{cg}$ (coarse-grained region)
  but not both!

- Overdetermination of $\Phi \rightarrow$ Conserved Energy does not correspond to
  dynamical equations

Does the method work?

Comparison of the results of AdResS with those of full atomistic simulations:

- Global and local structures are reproduced

- There is no net flux across the transition region

- The diffusion occurs in a correct way

- Method successfully reproduces statistical properties of the model liquid.

see in particular:

medium dense liquid: M.Praprotnik, L.Delle Site and K.Kremer, J.Chem.Phys.123,224106 (2005).

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

Results for a medium dense liquid
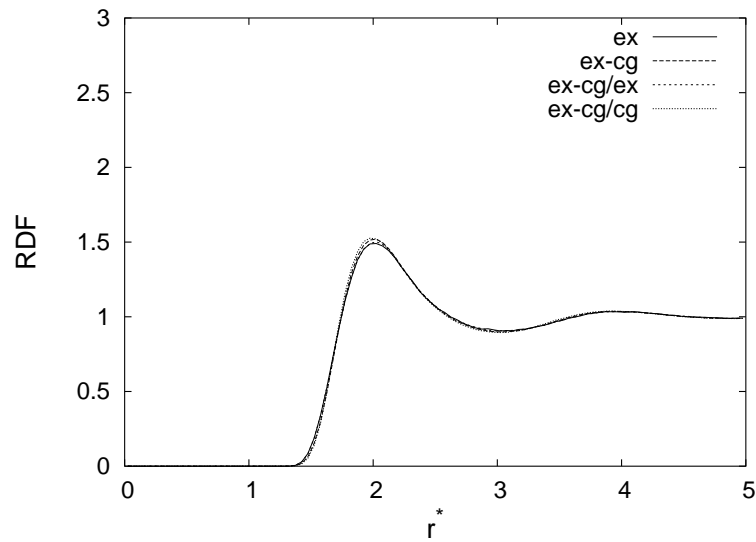
(k) RDF$_{cm}$.
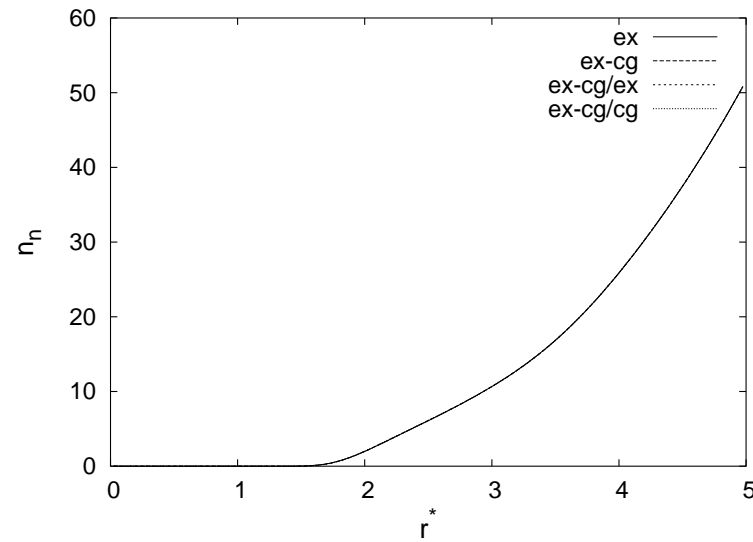
(l) Number of neighbors.

Global and local structure are properly reproduced

Number of DOFs
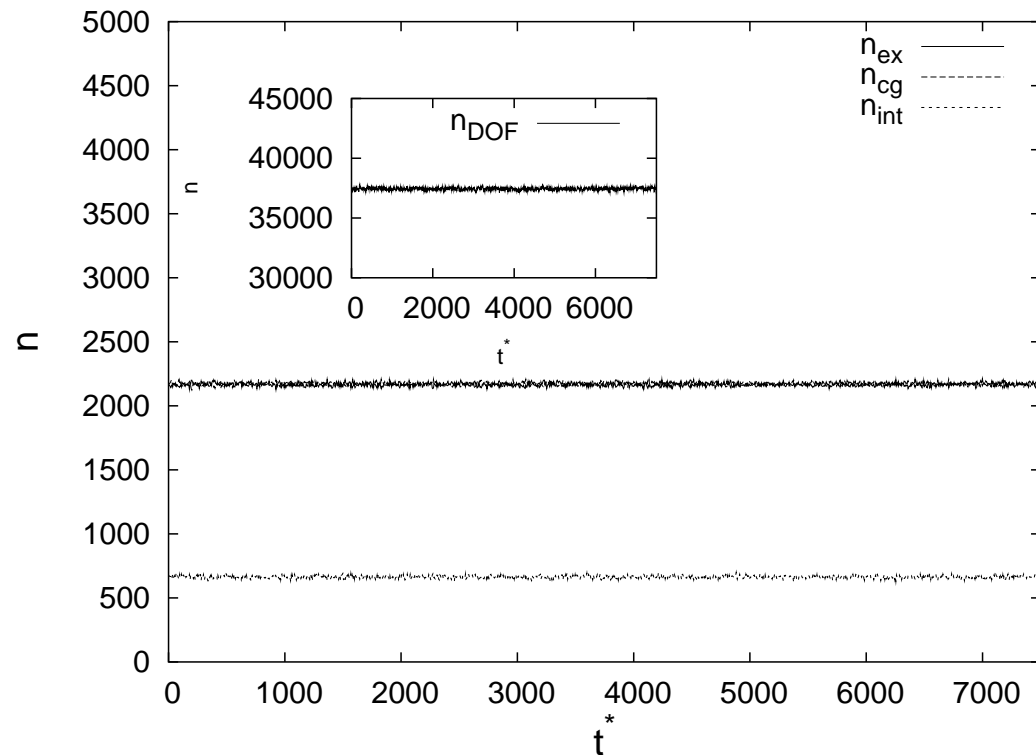
$$n_{DOS} = 3n[4w + (1 - w)]$$

Numerical proof of the "Zero Flux"

Diffusion across the transition regime
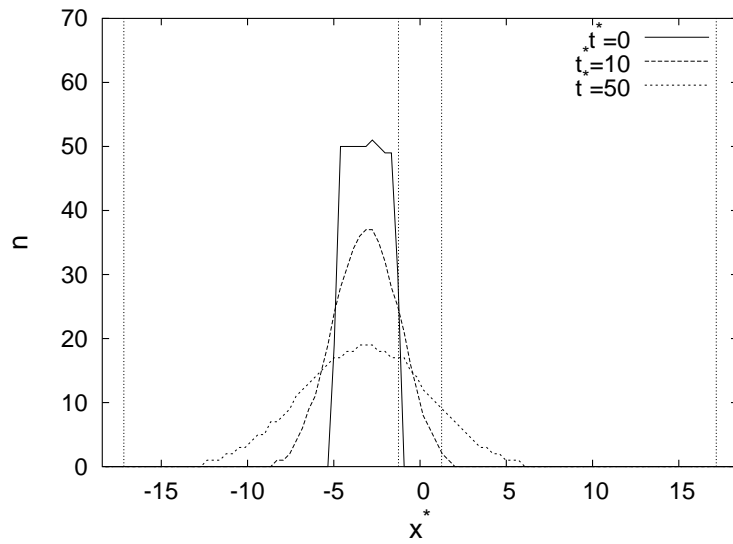
(m) Coarse-grained side.
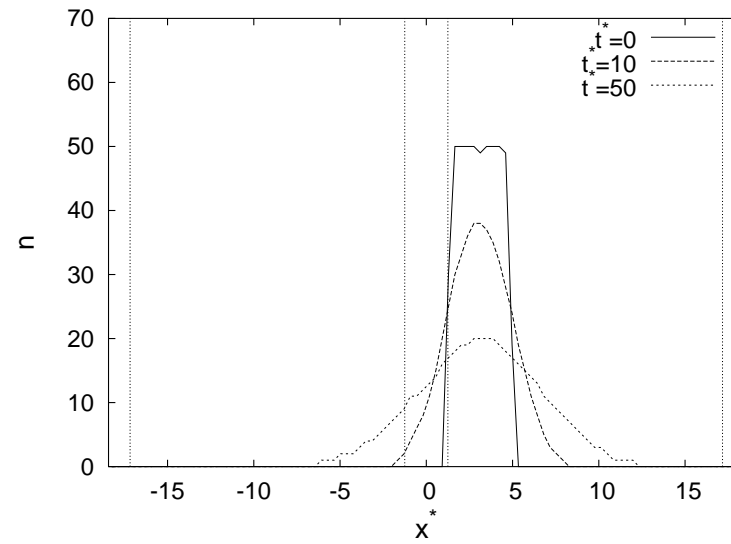
(n) Explicit side.

Further application: Solvating a Polymer
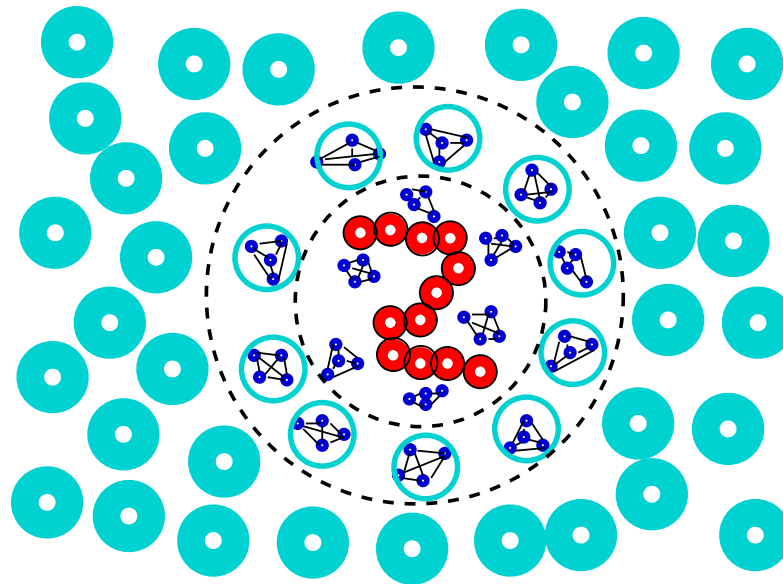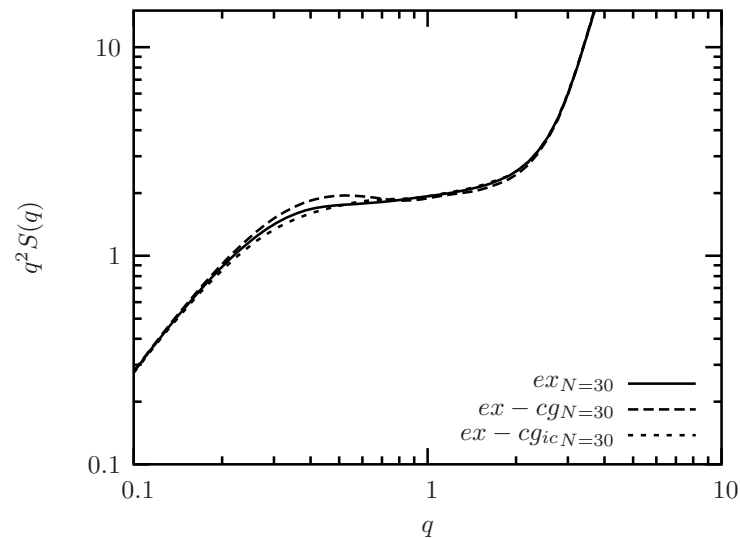

A generic Polymer solvated by a Tetrahedron Liquid
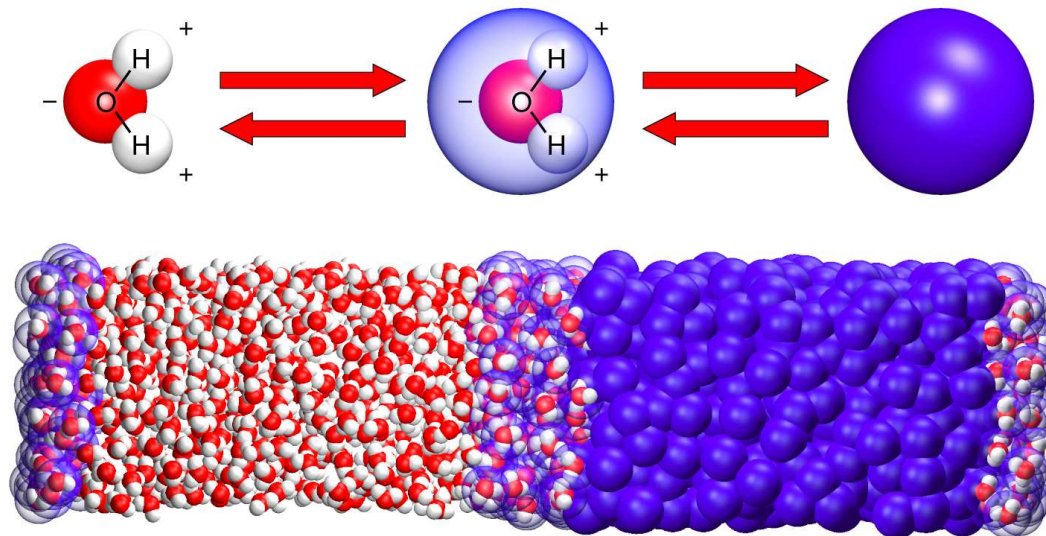
Static properties of the solvent
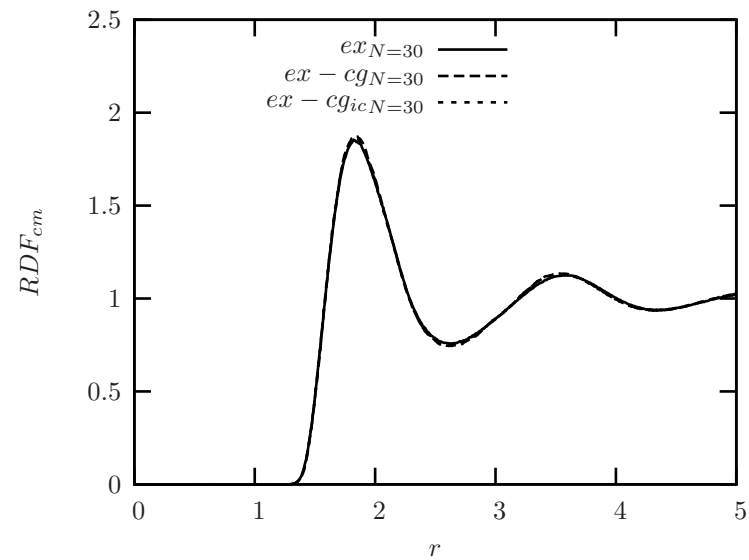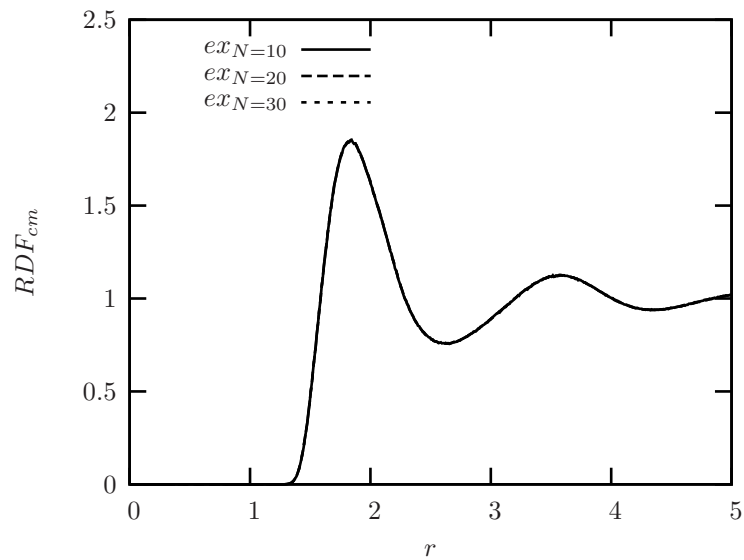
Static properties of the polymer
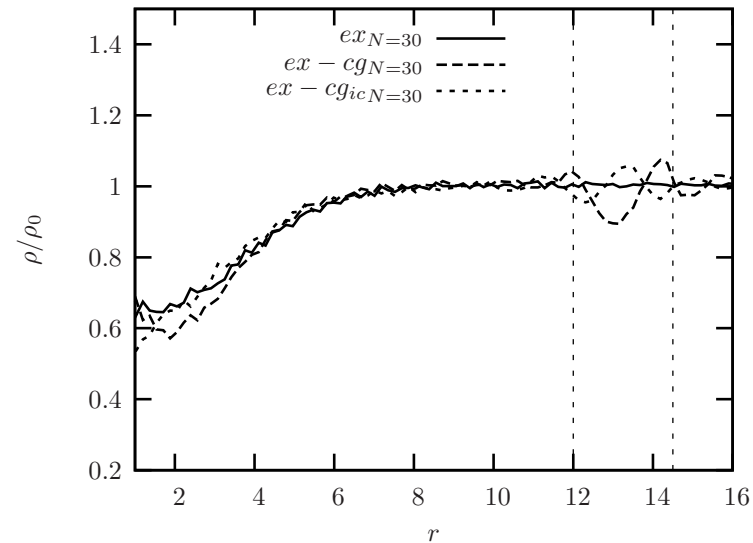
$$S(q) = \frac{1}{N} \left\langle \sum_{ij} \exp(i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \right\rangle$$

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

Liquid Water

The simulation speed-up is $\sim 17 - 20$ compared to atomistic simulations
M.Praprotnik, S. Matysiak, L. Delle Site, K. Kremer, C. Clementi, J. Phys.:
Condens.Matter, 19, 292201, 2007.

Reaction field method for Electrostatics

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

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

The RF is suitable to be used with AdResS because:

- it is pairwise

- like AdResS it must also be applied with a thermostat
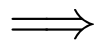
Results for water
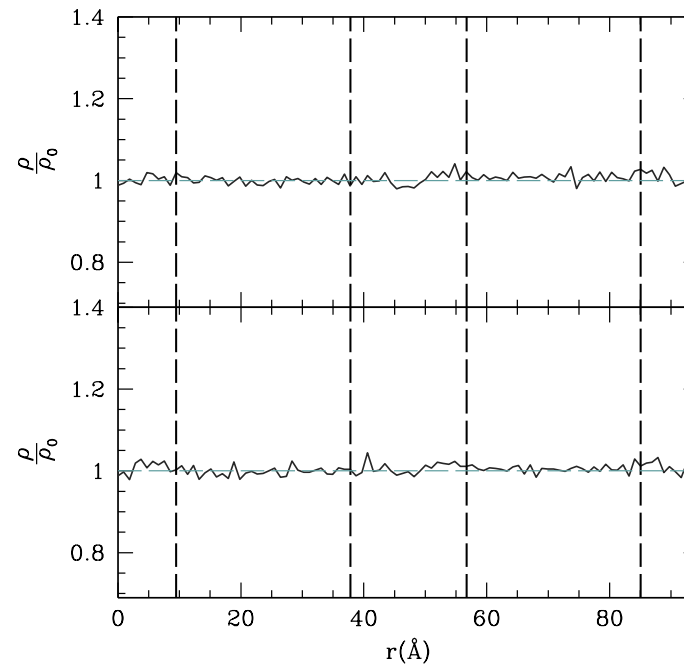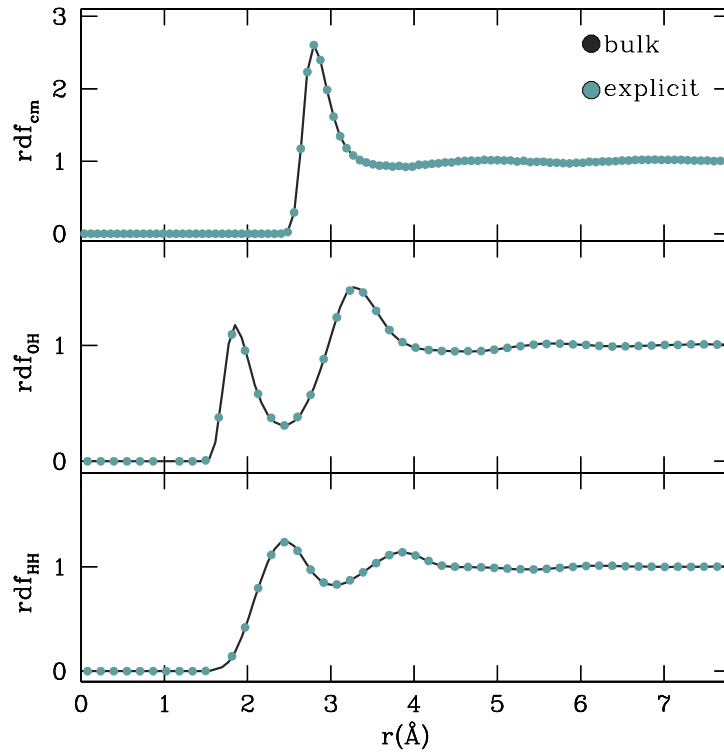
S.Matysiak, C.Clementi, M.Praprotnik, K.Kremer and L.Delle Site;
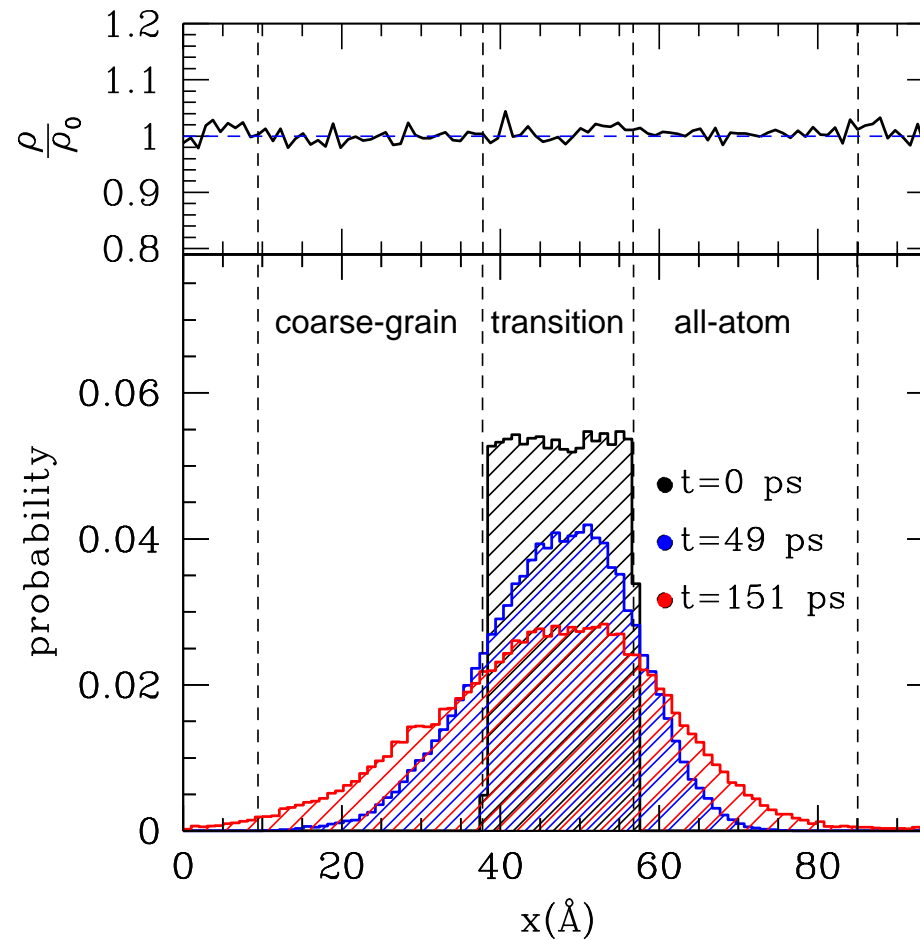J.Chem.Phys.128, 024503 (2008).

Interface effect of the cg water
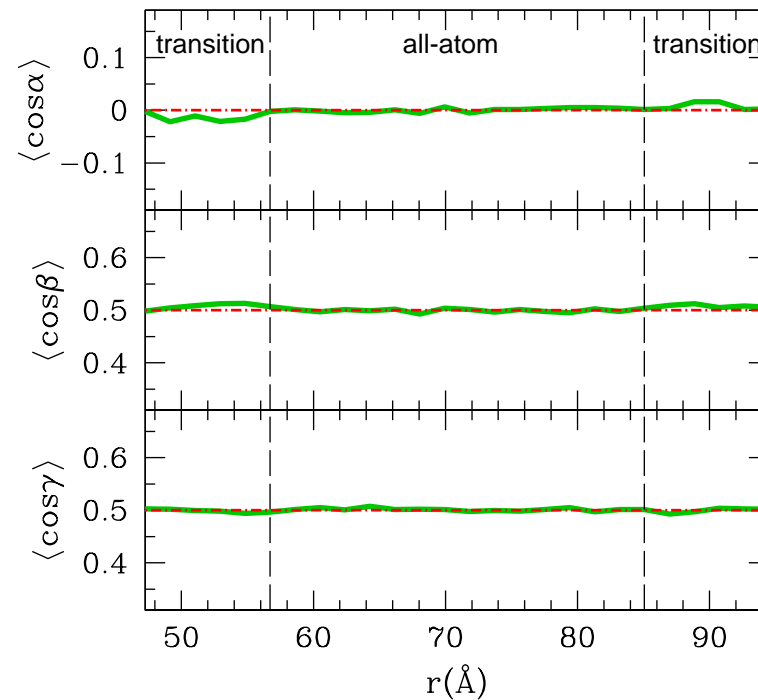
The transition regime neutralizes the interface effect of the *c*g water

$\implies$

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

Diffusion across the transition regime

Position dependent Langevin thermostat

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

$$m_i dv_i/dt = F_i - m_i \Gamma(x) v_i + R_i(x, t) \tag{9}$$

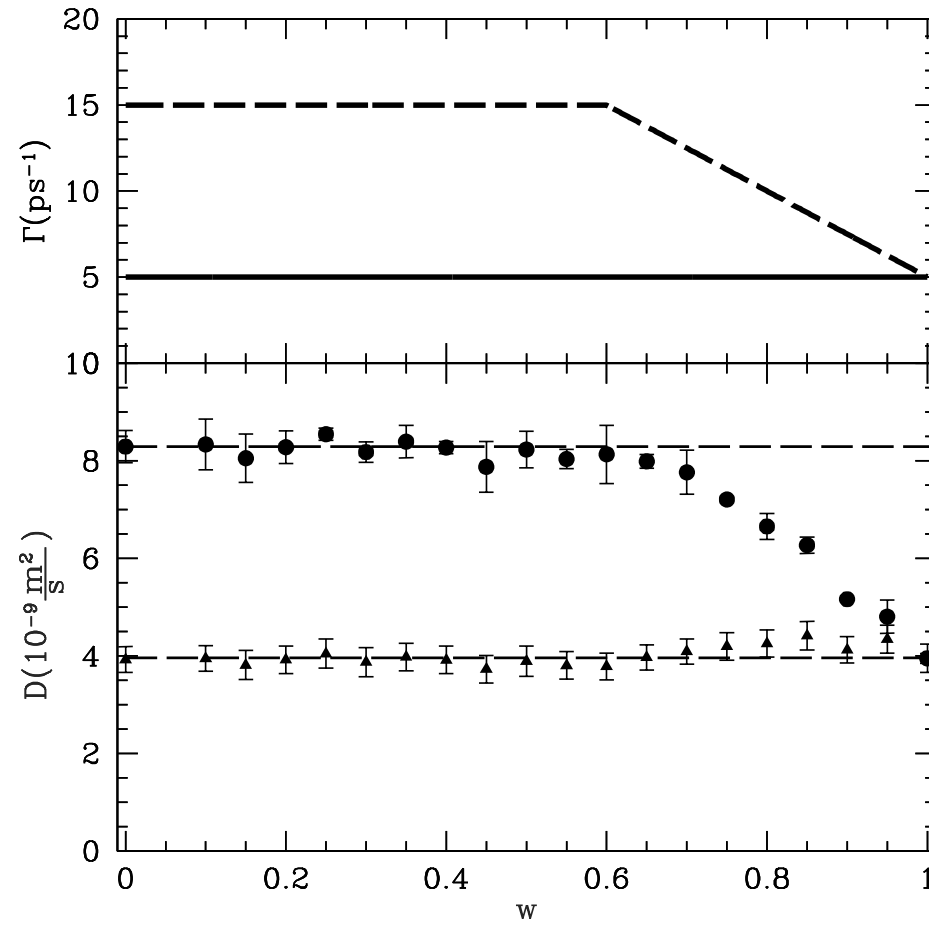where $R_i(x, t)$ is:

$$\langle R_i(x, t) \rangle = 0, \tag{10}$$

$$\langle R_i(x, t_1) R_j(x, t_2) \rangle = 2\Gamma(x) m_i kT \delta(t_1 - t_2) \delta_{ij} \tag{11}$$

$$\Gamma(x) = \begin{cases} \Gamma_{cg} & \text{if } x \leq 0.6 \\ \alpha x + \beta & \text{if } 0.6 < x \leq 1.0 \end{cases} \tag{12}$$

This choice provides a simple interpolation between the two limit values of $\Gamma(0.6) = \Gamma(0) = \Gamma_{coarse-grained}$ and $\Gamma(1) = \Gamma_{all-atom}$
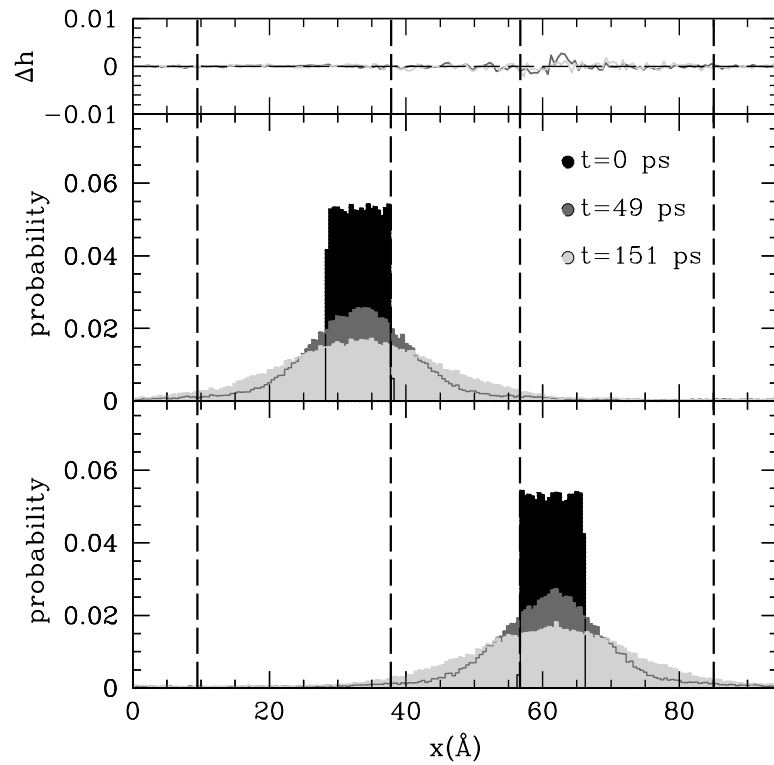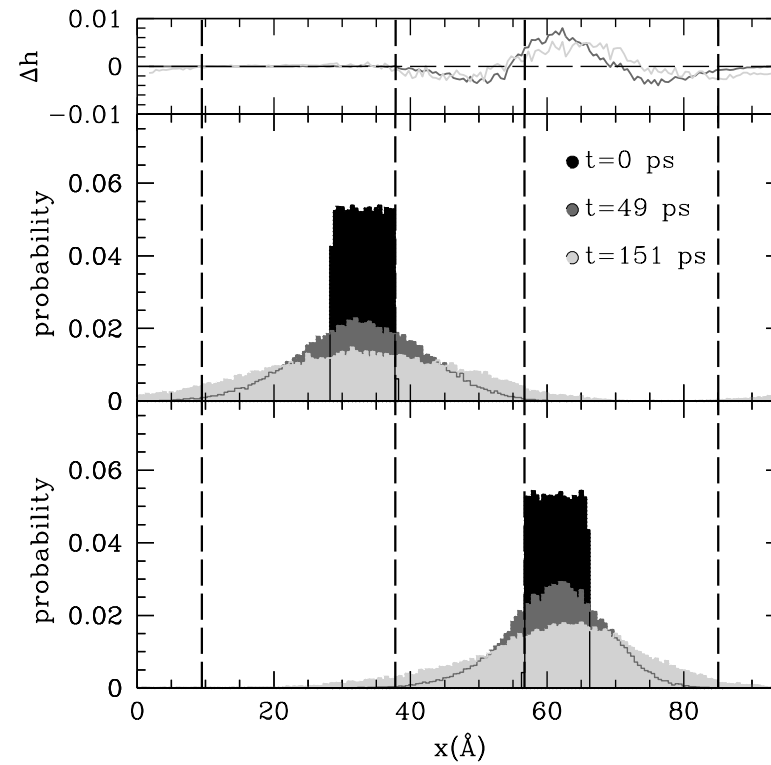
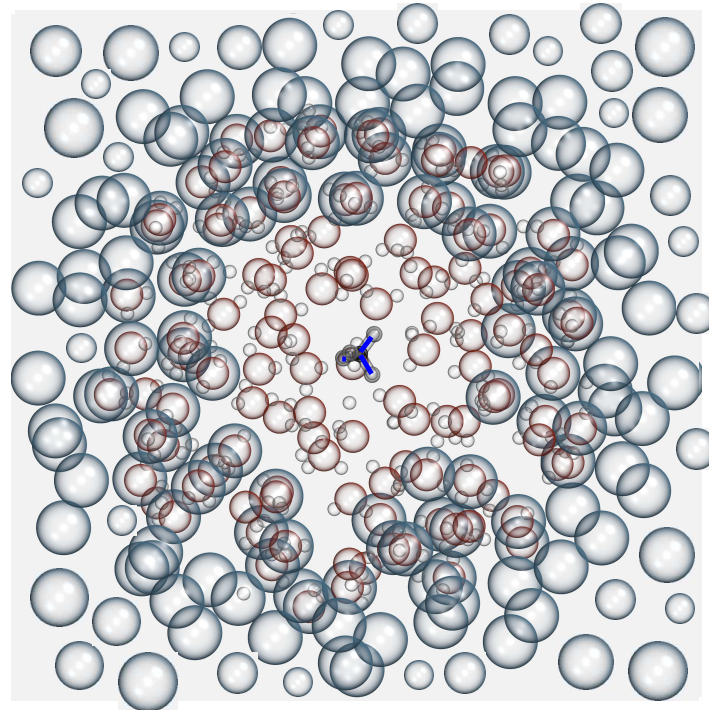# Diffusion coefficient across the simulation box II.

(v) Position dependent thermostat

(w) Regular thermostat

Next: Hydrophobic solvation via adaptive simulation

What is the range of influence of the hydrogen bonding network of the bulk in the formation of the hydration structure around the solute?