# Adaptive Resolution Molecular Dynamics: Coupling different levels of resolution

**Luigi Delle Site**

**Max Planck Institute for Polymer Research**

**Mainz**

School on *"Multiscale Modeling and Simulations of Hard and Soft Materials"* JNCASR, Bangalore December 2009

# Outline of Part II (a): The Method

Generalizing AdResS in AdRepS:

- Reformulation of part I (a) in terms of two generic force fields
- Explicit calculation of the latent Heat
- The concept of thermodynamic force
- Examples:
  (i) Two spherical models interfaces adaptively
  (ii) Tetrahedral/spherical adaptive simulation
  (iii) Binary mixture, atomistic/coarse-grained adaptive

# Outline of Part II (b): Applications

Recent (and in progress) developments of AdResS

- Switching resolution for bonded interactions

- Extension to basic quantum description of atoms:
  (i) The Path Integral approach to map a quantum problem onto a classical one
  (ii) Adaptive path integral/atomistic for spherical particles

  (iii) Adaptive path integral/coarse-grained for tetrahedral molecules

- Coupling atomistic and continuum

# Motivations: Why generalise AdResS?

- Target: Identify those DOFs which are strictly required (e.g. small quantum region in a classical "bath")

- For Example: update on the fly (based on quantum calculations) the force field in the region of interest
  G.Csanyi *et al.* Phys.Rev.Lett. 93, 175503 (2004).

- That is: Some force fields may treat differently the DOFs of interest

- Adaptive exchange of particles to properly capture local density fluctuations

# Interfacing two resolutions: Conceptual Aspects

- **(a)** Consider two different force-fields, **f1** and **f2**, describing the same molecule in two (interfaced) regions of space

- **(b)** The exchange of particles must happen in an adaptive way under conditions of equilibrium: $\rho_{f1} = \rho_{f2}, \quad p_{f1} = p_{f2}, \quad T_{f1} = T_{f2}$

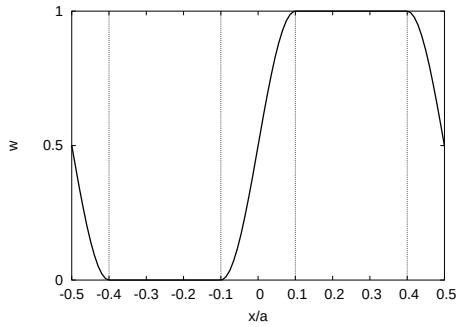
**Problems**

- **(1)** Coupling interactions between the two force-fields

- **(2)** The two representations have (intrinsic) different chemical potentials $\longrightarrow$ How to control the thermodynamic equilibrium

# Coupling Interactions

**Smooth Transition via a Switching Function:**




- **(a)** Smooth coupling of the potentials: Hamiltonian or Lagrangian approach: $U_{coupling} = w(X_\alpha)w(X_\beta)U_{f1} + [1 - w(X_\alpha)w(X_\beta)]U_{f2}$

- **(b)** Smooth coupling of forces: Direct dynamical approach: $\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}^{f1}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}^{f2}_{\alpha\beta}$

# Force approach

$$\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}^{f1}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}^{f2}_{\alpha\beta}$$

- Molecule from **f1** $\longrightarrow$ **f2**: vanishing **contributions** of switching DOF of **f1**, increasing contribution of activating DOF of **f2**
- $w(x)$ smoothly "*freezes*" the **dynamical evolution** and the **contribution to the interactions** of switching DOFs of **f1**
- $w(x)$ smoothly "*activates*" the dynamics and the contributions to the interactions of **f2**
- and vice versa

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

# Thermodynamical equilibrium

- Adaptive force **alone** cannot assure **thermodynamic equilibrium** (**potential energy** cannot be written explicitly)

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

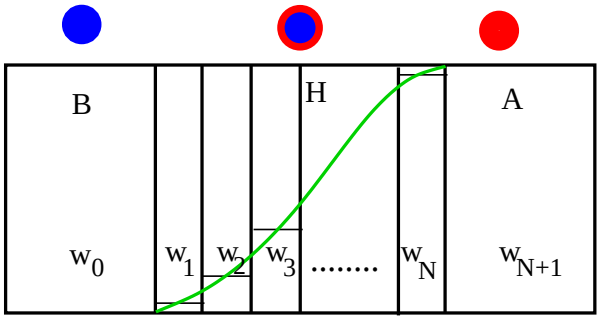
- **preferential tendency** of one species to migrate into the other region that is: $\mu_{f1} \neq \mu_{f2}$

- adaptive system via $w(x) \rightarrow$ local chemical potential $\mu_w(x) \rightarrow \phi(x) = \mu_{f1} - \mu_w(x)$
- **unphysical**: artifact of the different representations.

# Explicit Calculation of $\phi(x)$

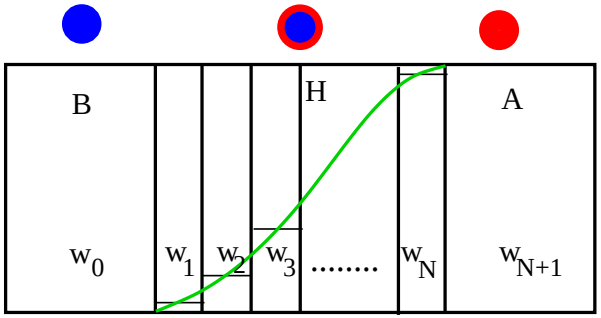
$\phi(x) = \mu_{f1} - \mu(w(x))$ (free energy per particle)

- **(a)**: Excess chemical potential $\mu^{exc}(w_i)$:**insertion particle method (IPM)** for each $i$ (numerical)




- **(b)**: kinetic (ideal gas) contributions $\mu^{kin}(w)$:**formalism of fractional calculus** (analytic)

# Excess chemical potential $\mu^{exc}(w_i)$




- For each $w_i$ apply IPM with:
  $\mathbf{F}_{\alpha,\beta} = w_i w_i \mathbf{F}_{atom} + (1 - w_i w_i)\mathbf{F}_{cg} \Longrightarrow \mu(w_i)$

- $\mu^{exc}(w_i)$: **excess chemical potential the system would have if all the molecules were interacting with some $w_i$ "resolution" (representation)**

# Excess chemical potential: Interacting slabs

- Let us take a generic $w_i$, then one has to applied the IPM using **as an interaction between the particles in the whole box** the formula:
  $\mathbf{F}_{\alpha,\beta} = w_0 w_i \mathbf{F}_{atom} + (1 - w_0 w_i)\mathbf{F}_{cg}$
- This leads to: $\mu_{0i}$: **the chemical potential the system would have if all the molecules were interacting with some** $= w_0 w_i$ **"resolution"(representation)**
- Then this procedure is repeated again but now using:
  $\mathbf{F}_{\alpha,\beta} = w_1 w_i \mathbf{F}_{atom} + (1 - w_1 w_i)\mathbf{F}_{cg}$
  this leads to: $\mu_{1i}$, $\rightarrow$ again with $w_2 w_i$, up to the generic $w_n w_i \rightarrow \mu_{ni}$.
- Then: $\mu_{w_i} = \sum_{n=0}^{N+1} \left[ \frac{N_{w_i} + N_{w_n}}{N_{tot}} \mu_{ni} \right]$
  $N_{w_i}$ is the average number of molecules in the region $w_i$ in the **"adaptive" simulation box** and equivalently $N_{w_n}$, while $N_{tot}$ is the total number of molecules in the system.

# Kinetic Contribution: Fractional formalism

- For **Statistical calculation of physical quantities:**
  **(a)** a DOF $q$, **fully activated** $\rightarrow (\int ...dq)$
  **(b) fully deactivated** $\rightarrow$ no integration over $q$

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

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

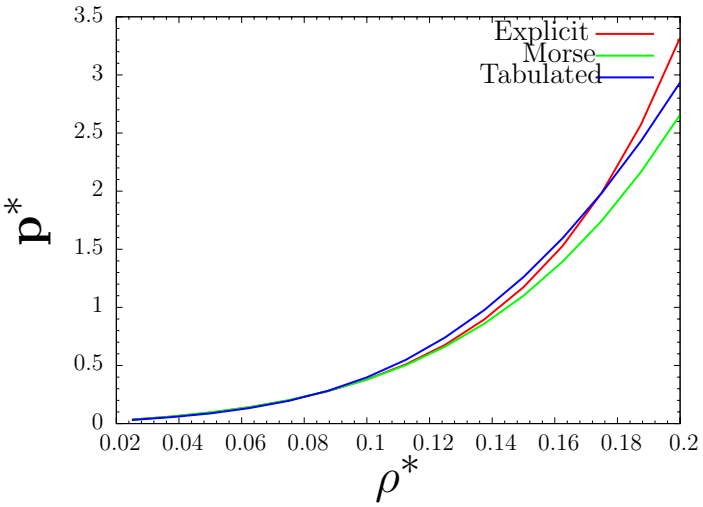
# $\mu^{kin}$ and Temperature

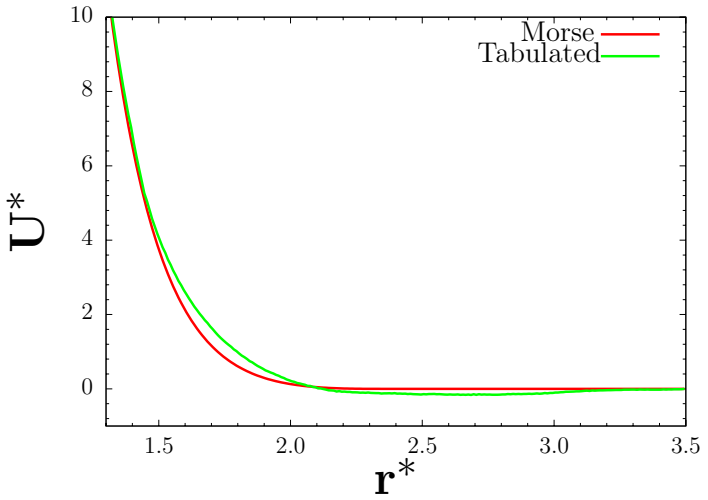
- **kinetic contribution: $\mu^{kin}$:**
  $A_q = -lg[\int e^{-\beta q^2} d^w q] = \mu_q(w) \Longrightarrow \mu^{kin}(w) = \sum_q \mu^{kin}(w)$

- Temperature in the adaptive system:
  **fractional analog of the Equipartition Theorem**:
  $\langle K_w \rangle = \frac{d(\beta A_w)}{d\beta} = \frac{w}{2\beta} = \frac{wT}{2}$
  $\langle K_w \rangle$: average kinetic energy per fractional quadratic DOF with the parametric weight $w$

# Example I: Interfacing two spherical molecular models

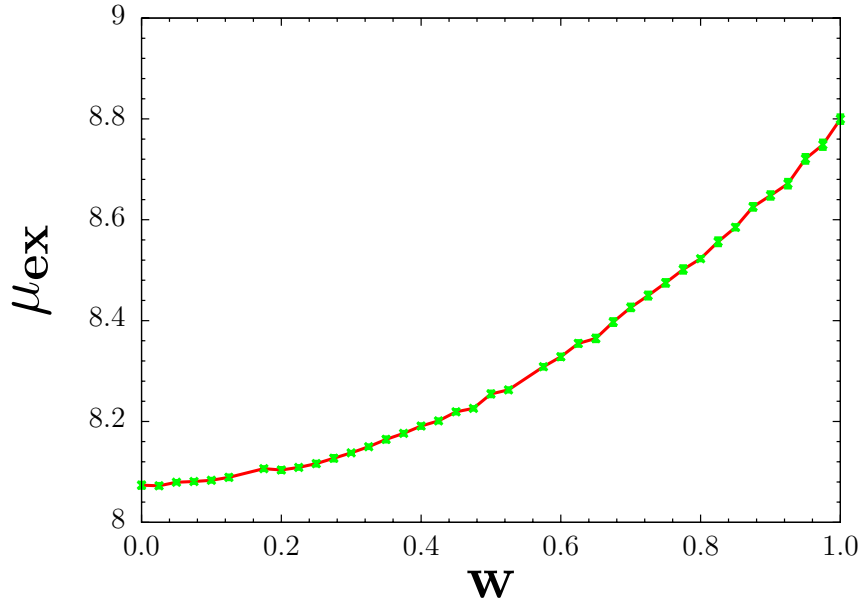
- Two CG models of an atomistic model, interfaced adaptively
- They fit different portion of the atomistic equation of state (high and low density)



# Chemical Potential

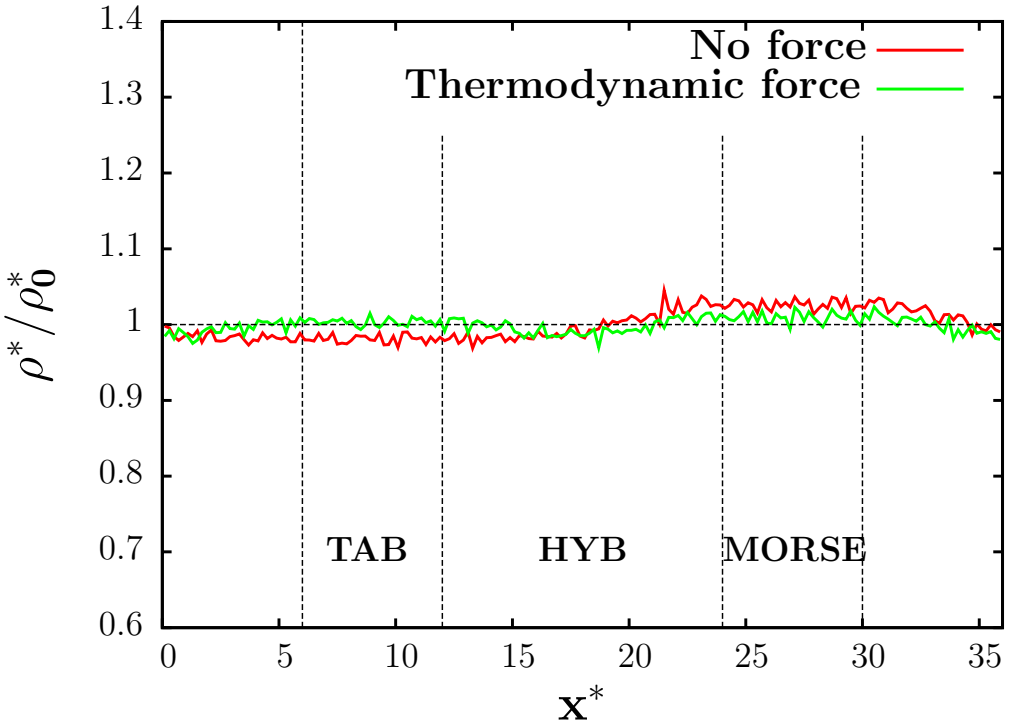
- No kinetic contribution; only excess chemical potential



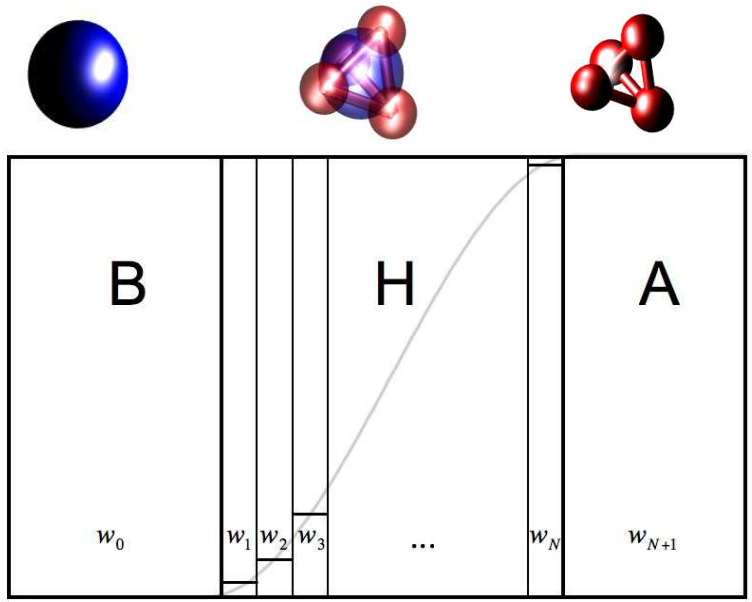
# Thermodynamic Force

How do we use this concepts: addition of a thermodynamic force:

$F_{thm} = -\nabla_x^{exc}\mu(x)$

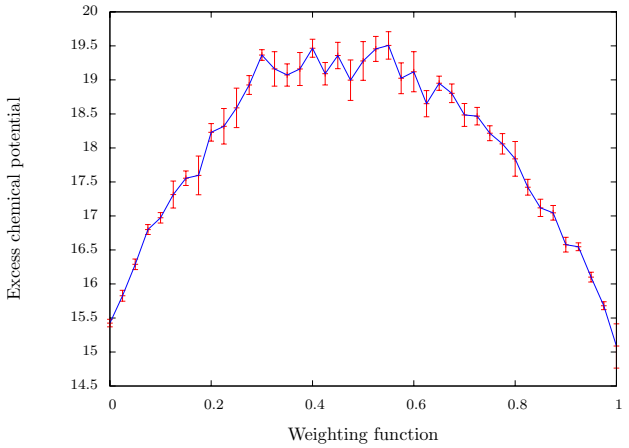


# Example II: Atomistic-CG adaptive



# Calculations

**(a)** Excess Chemical Potential $\mu^{exc}$



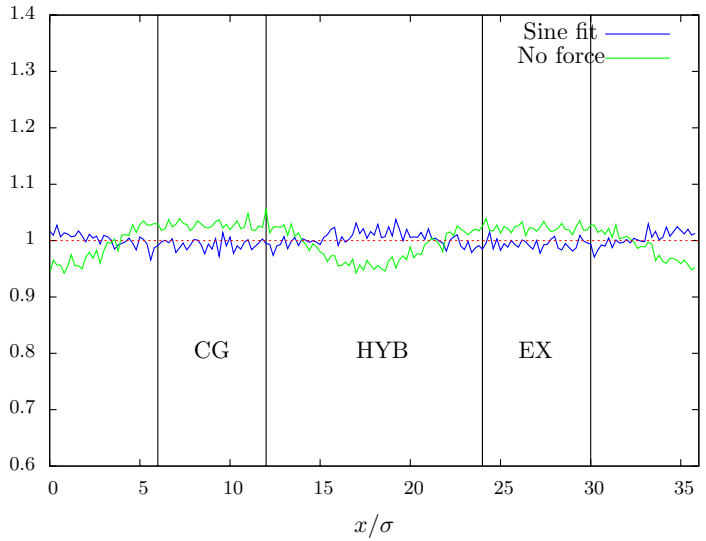

**(b)** Kinetic contribution (internal heat):

$$\mu^{kin} \propto \left(\frac{w}{2}\right) lg(T) + lg\frac{\Gamma\left(\frac{w}{2}\right)}{\Gamma(w)} \longrightarrow \phi(x)^{kin} \propto (1 - w(x))lg(T)$$

# Thermodynamic Force

How do we use these concepts: Part I

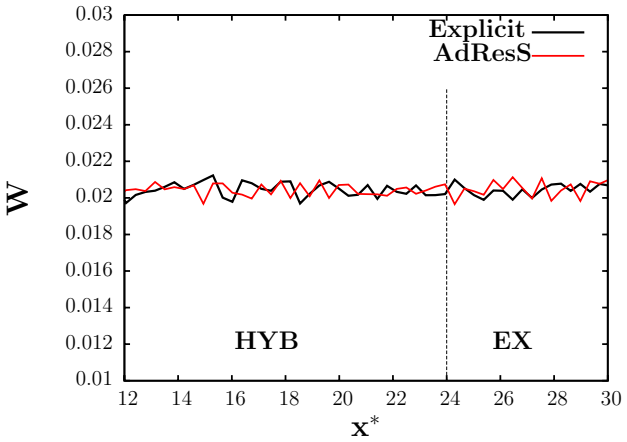
- addition of a thermodynamic force:
  $F_{thm} = -\nabla_x^{exc}\mu(x)$ for the "**interaction part**"




- Thermodynamic force + Thermostat (for the kinetic part/internal heat)

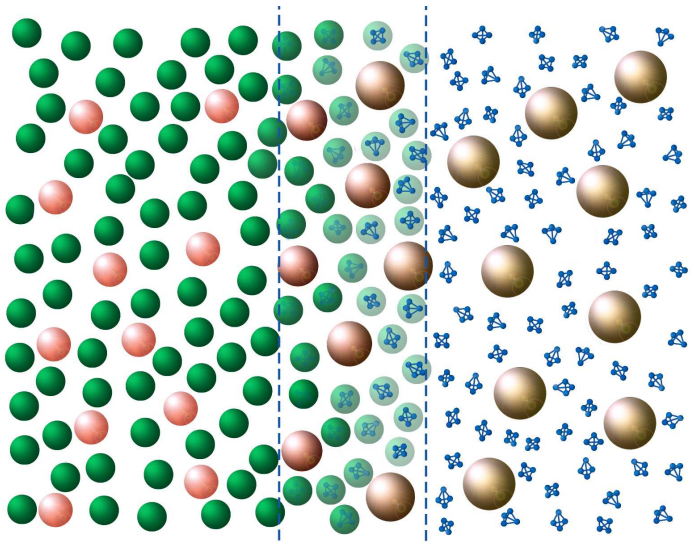
# Internal/latent Heat

- A posteriori check of the heat calculated analytically and "deterministic" control of the system
- internal (latent) heat:
  $Q_{latent} = (1 - w(x))Q_{atom}$ (extra heat to be given due to the deactivated part of a DOF)
  $Q_{fractional/explicit} = w(x)Q_{atom}$ (direct thermalization of the active part of a switching DOF)
  $\longrightarrow Q_{\Delta} = Q_{fractional/explicit} + Q_{latent} = Q_{atom}$



# Mixtures

- Two species, two resolutions each: $\longrightarrow$ 4 different chemical potentials
- how to preserve equilibrium?
- Thermodynamic force proportional to the concentration of the components



# Chemical Potential of Mixtures

$$\mu^{mix}_{tetra} = \mu^{0}_{tetra} + kT \log[c_{tetra}] + f^{mix}_{int}(c_{tetra}, c_{solute}) \qquad (1)$$

$$\mu^{mix}_{solute} = \mu^{0}_{solute} + kT \log[c_{solute}] + g^{mix}_{int}(c_{tetra}, c_{solute}) \qquad (2)$$

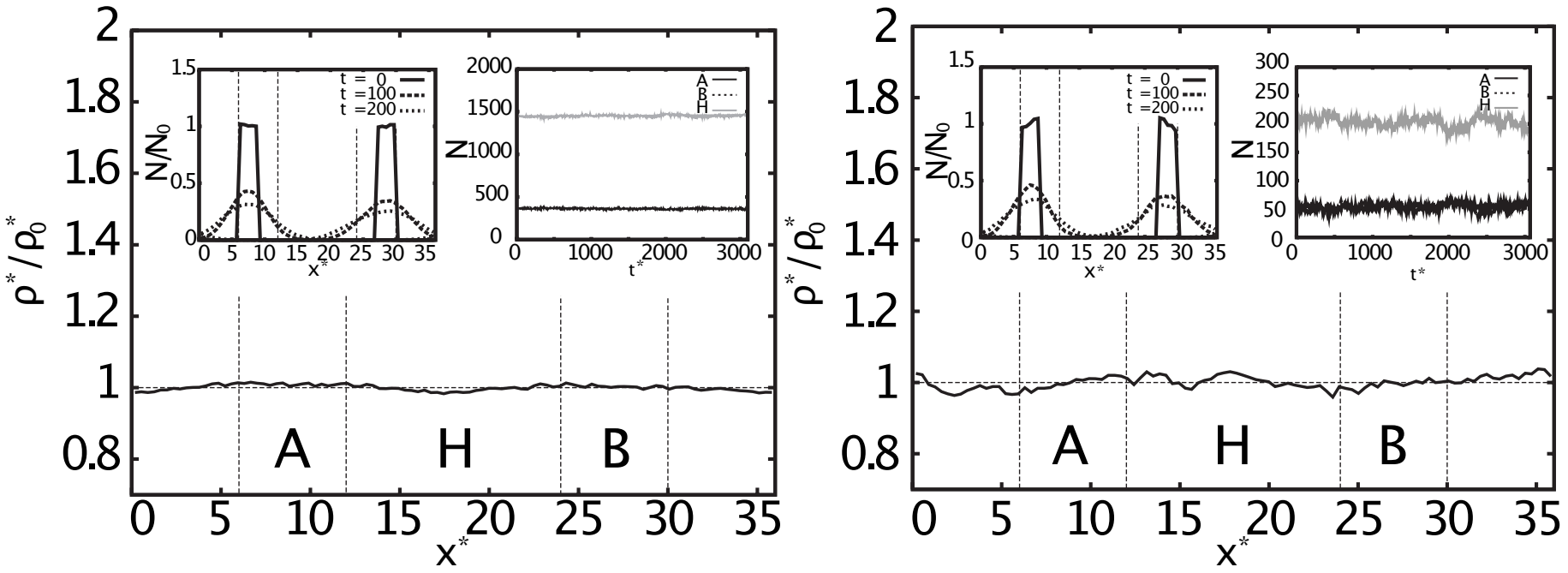
$$f^{mix}_{int}(c_{tetra}, c_{solute}) = \left[\frac{\partial f}{\partial c_{tetra}}\right]_{c^0_{tetra}, c^0_{solute}} \cdot c_{tetra} \qquad (3)$$

$$g^{mix}_{int}(c_{tetra}, c_{solute}) = \left[\frac{\partial g}{\partial c_{solute}}\right]_{c^0_{tetra}, c^0_{solute}} \cdot c_{solute} \qquad (4)$$

# Determination of the unknown coefficients

- **(a)** Use a thermodynamic force without the terms of the mixing: **Result**: a non uniform density profile (or concentration profile) in the transition region.
- **(b)**The mixing terms are functions of the density (concentration) $\longrightarrow$ take **this density profile** and **tune** the unknown coefficients of $f$ and $g$ until the complete thermodynamic force provides a flat profile
- **(c)** Test of consistency: the resulting thermodynamic force will lead to a stationary flat profile independently from the initial (density) condition

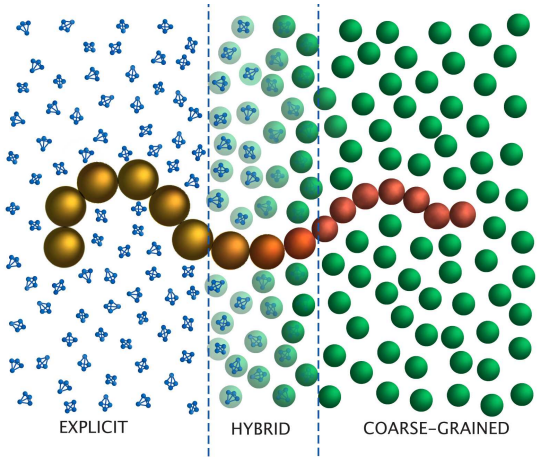
# Results




S.Poblete, M.Praprotnik, K.Kremer and L.Delle Site, *"Coupling different levels of resolution in molecular simulations"*, http://lanl.arxiv.org/abs/0907.5497

# Bonded Interactions

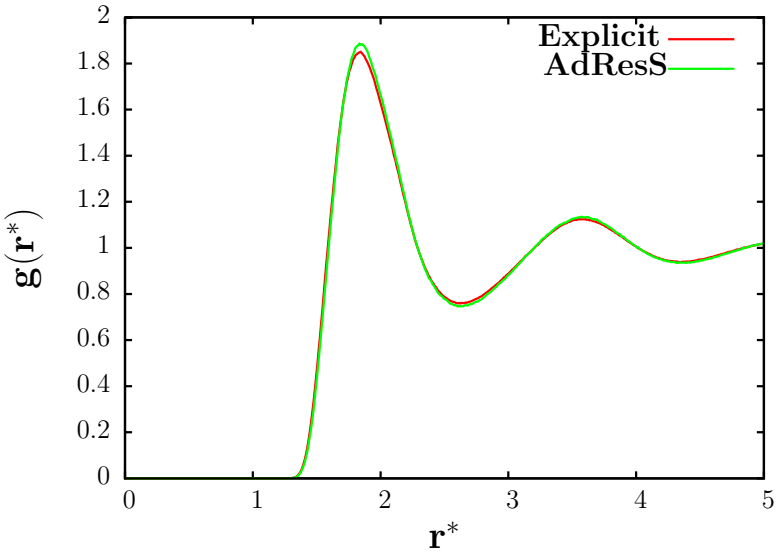
- Reparametrize the bonded interaction between monomers, fitting the bond distribution by using the Iterative Boltzmann Method.

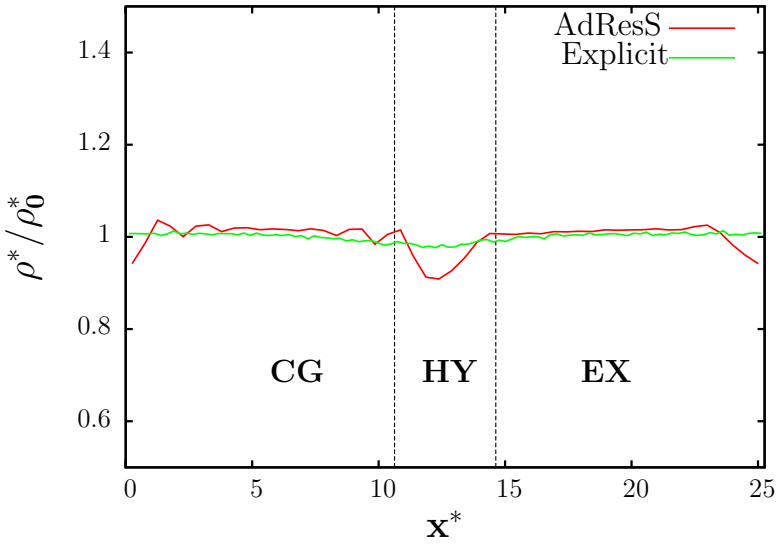



- Perform AdResS simulations interpolating the bonded forces through the same scheme for non-bonded interactions:

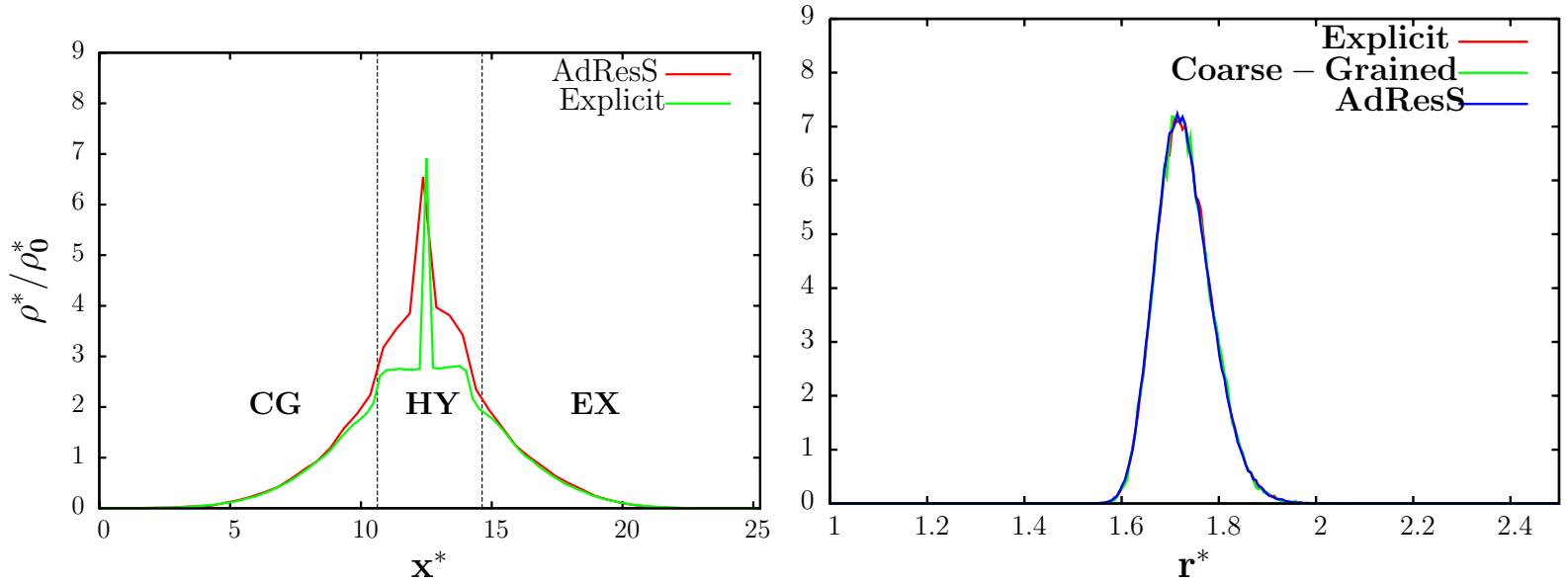
$$\vec{F}_{bond}(\vec{r}_1, \vec{r}_2) = w(\vec{r}_1)w(\vec{r}_2)\vec{F}^{ex}_{bond} + (1 - w(\vec{r}_1)w(\vec{r}_2))\vec{F}^{cg}_{bond}$$

# Static properties of the solvent

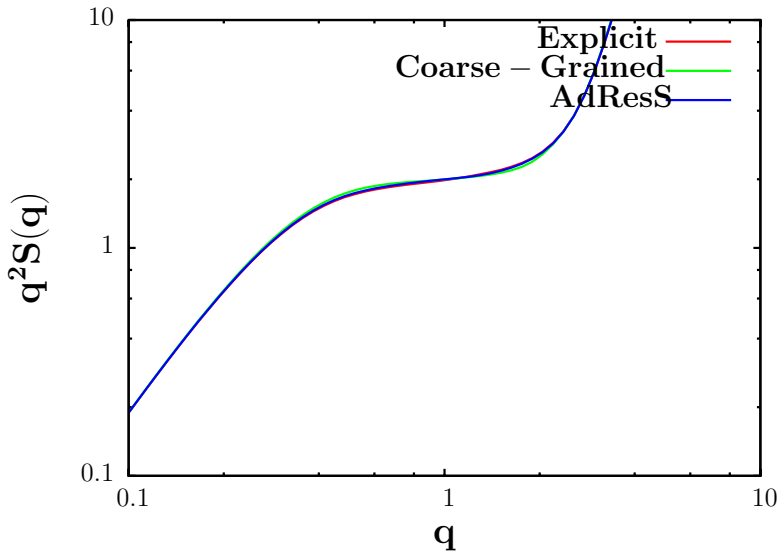


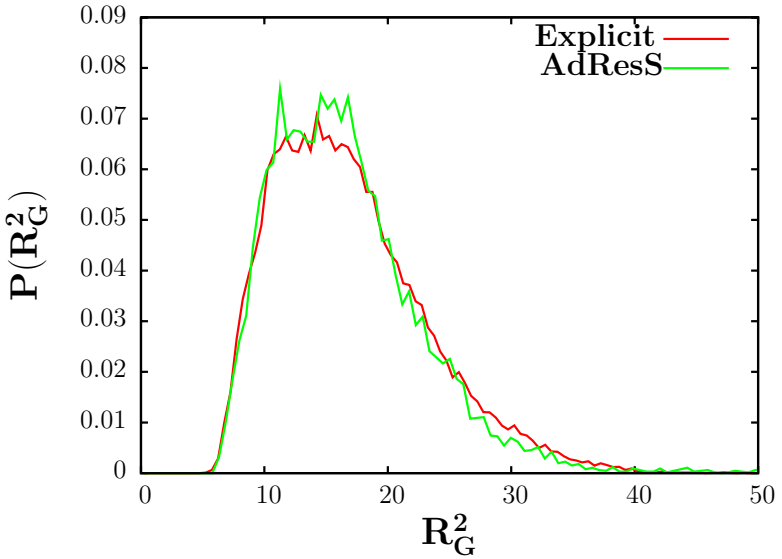



# Static properties of a 20mers polymer (I)



# Static properties of a 20mers polymer (II)



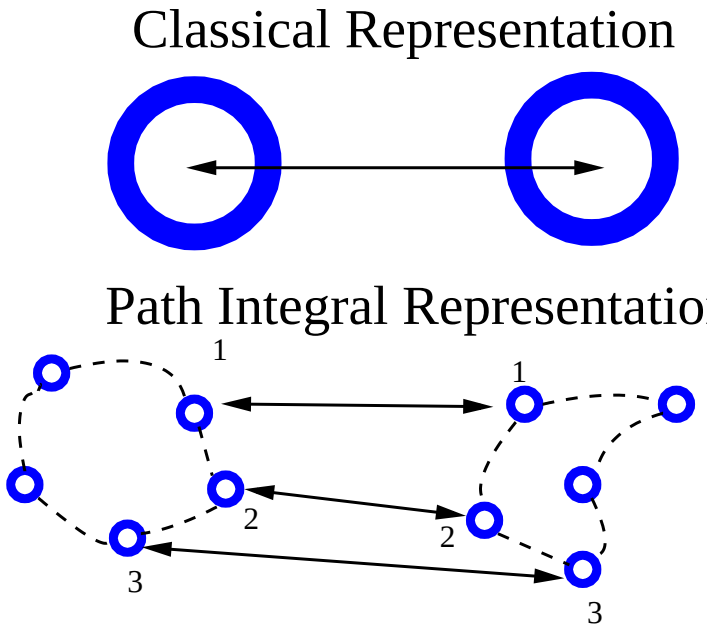
# What about Quantum/Classical adaptive? (I)

Quantum properties based on the electronic structure

- Problem: Interfacing not only two resolutions but also two different **KINDS** of physics
- Adaptive of QM/MM type introduces the process of creation and annihilation of electrons
- However, QM region can be used to update the classical force field on the fly
- Electronic properties (e.g. excited states): Very much questionable

# What about Quantum/Classical adaptive? (II)

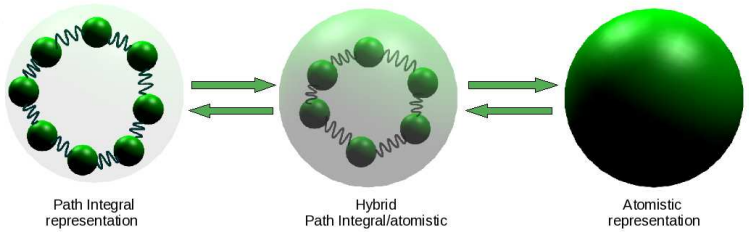
Quantum properties based on the delocalization of atoms




Path Integral (ring polymer) representation of classical atoms
See: M.E.Tuckerman, NIC Series, Vol.10, pg 268 (2002).

# Path Integral/Classical adaptive

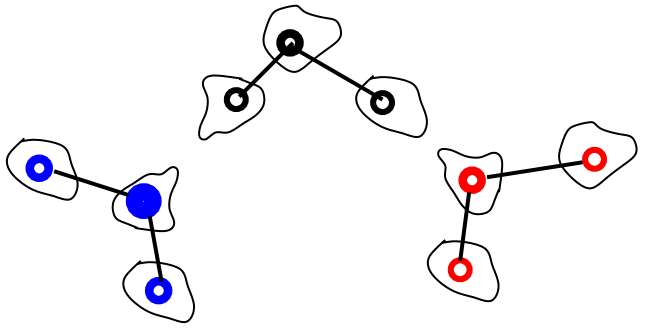
- Path Integral formalism allows to map a quantum object onto a classical one

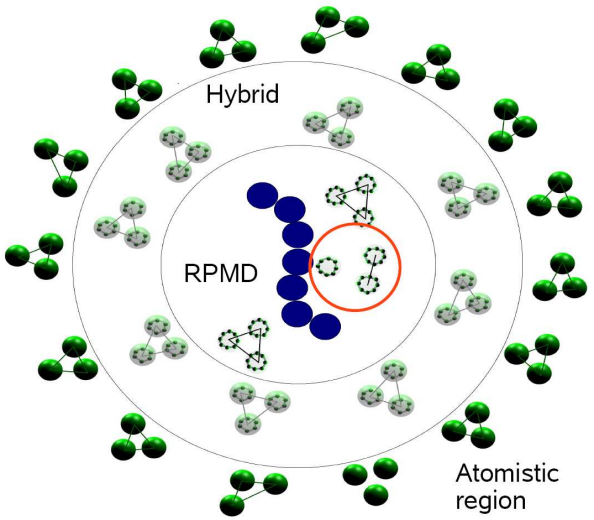



- Principles of the adaptive can be applied straightforward

# Path Integral/Classical adaptive: Useful?

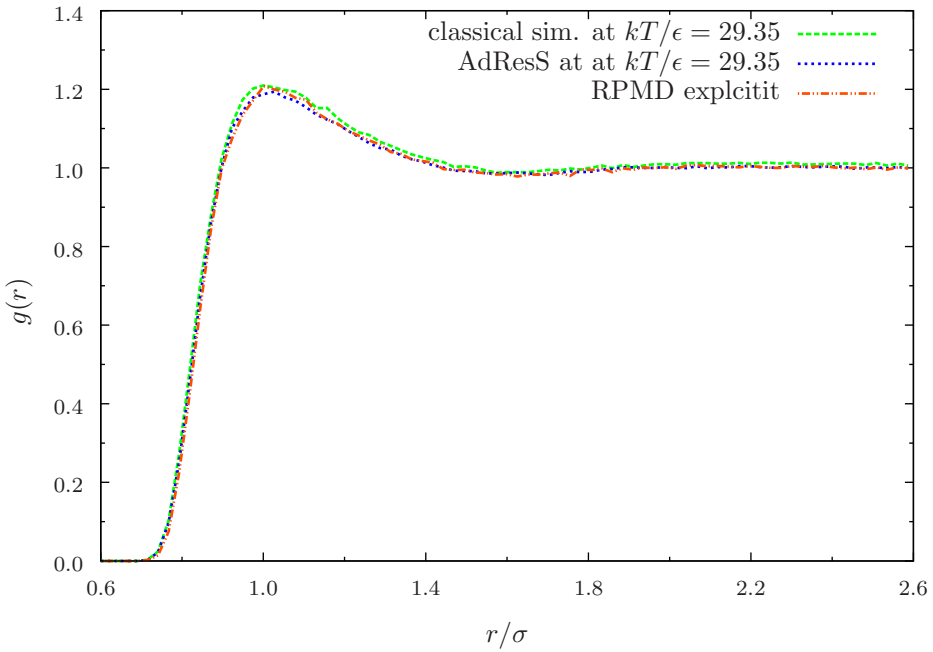
Better description of bonding (hydrogen)

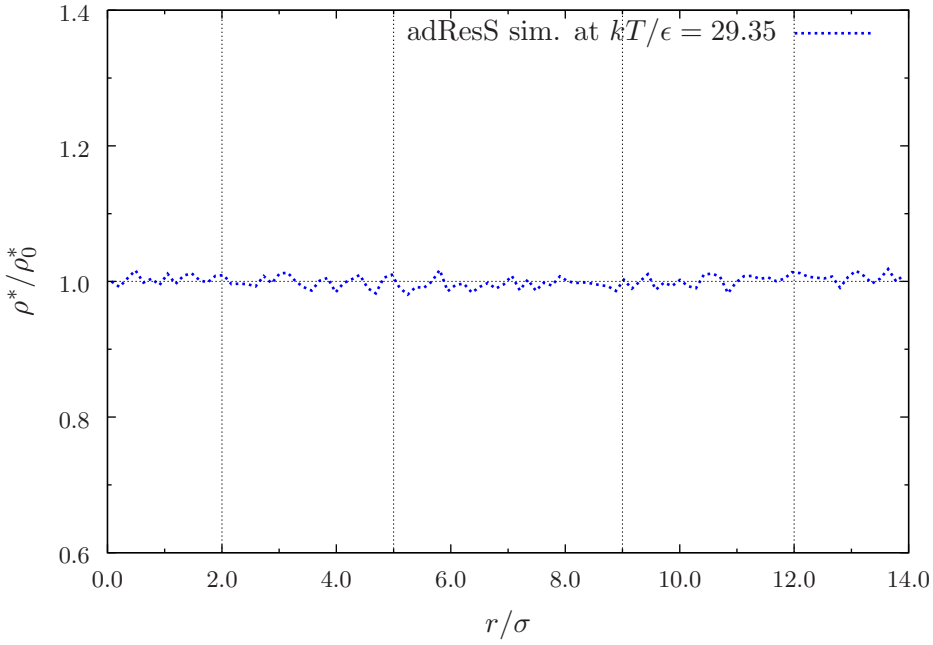




# Lennard-Jones Liquid

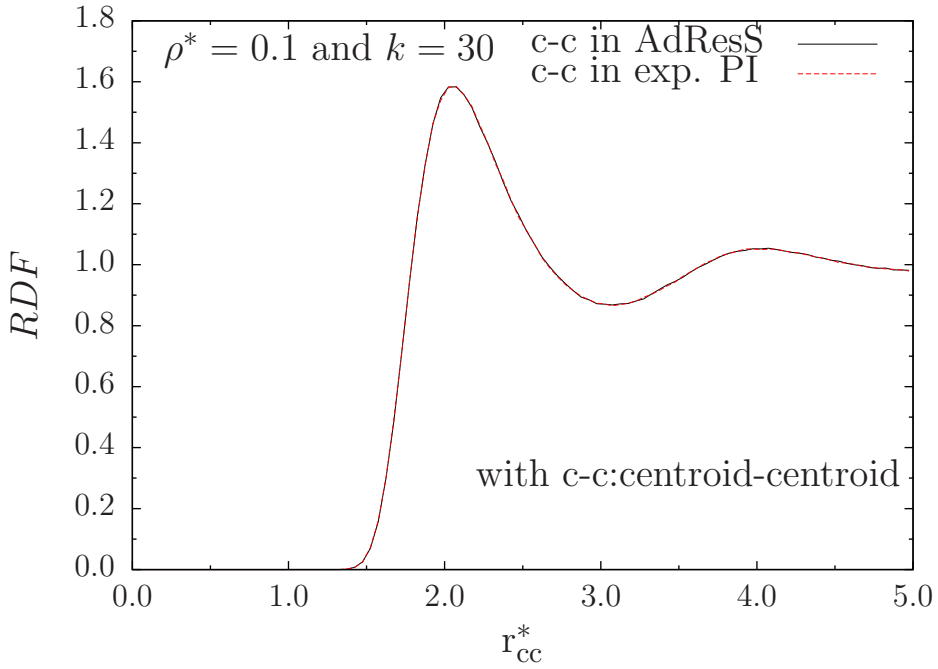
## Lennard-Jones liquid for semirigid rings:

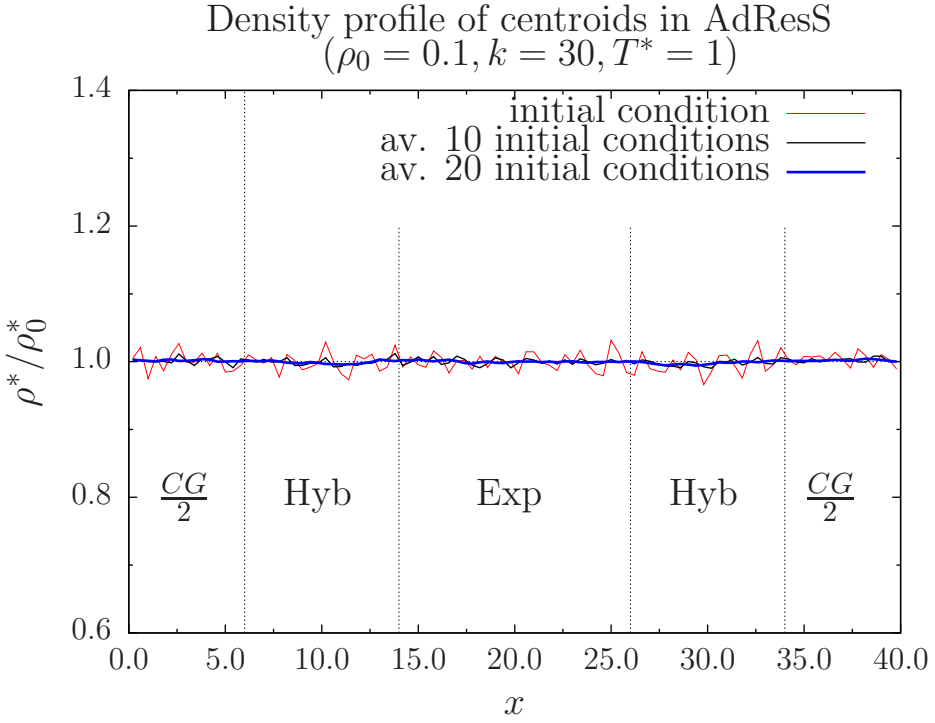


# Morse Potential: Semirigid rings I

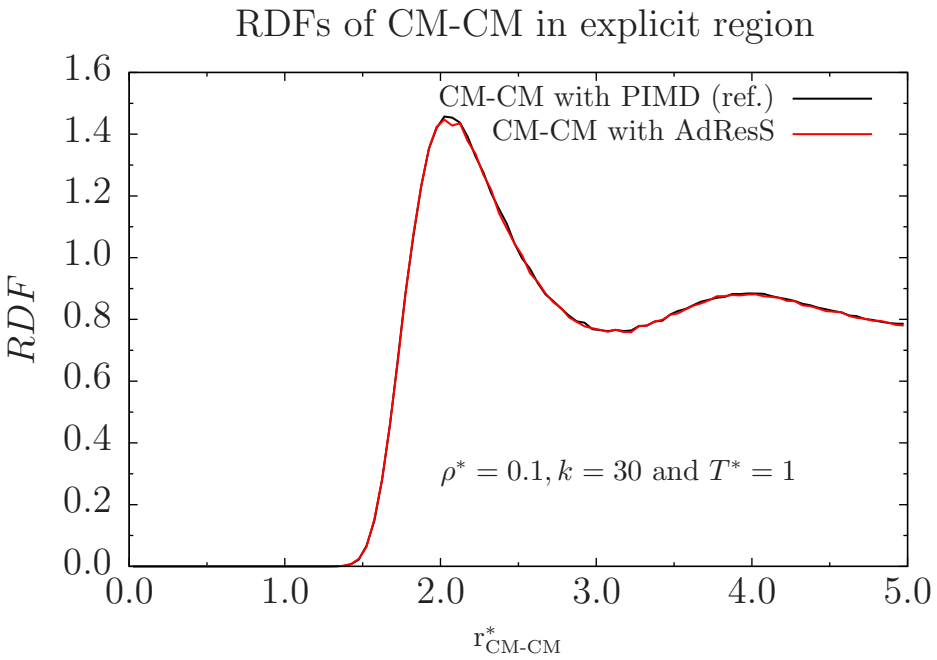
**liquid for semirigid rings ($k = 30$): Global properties**

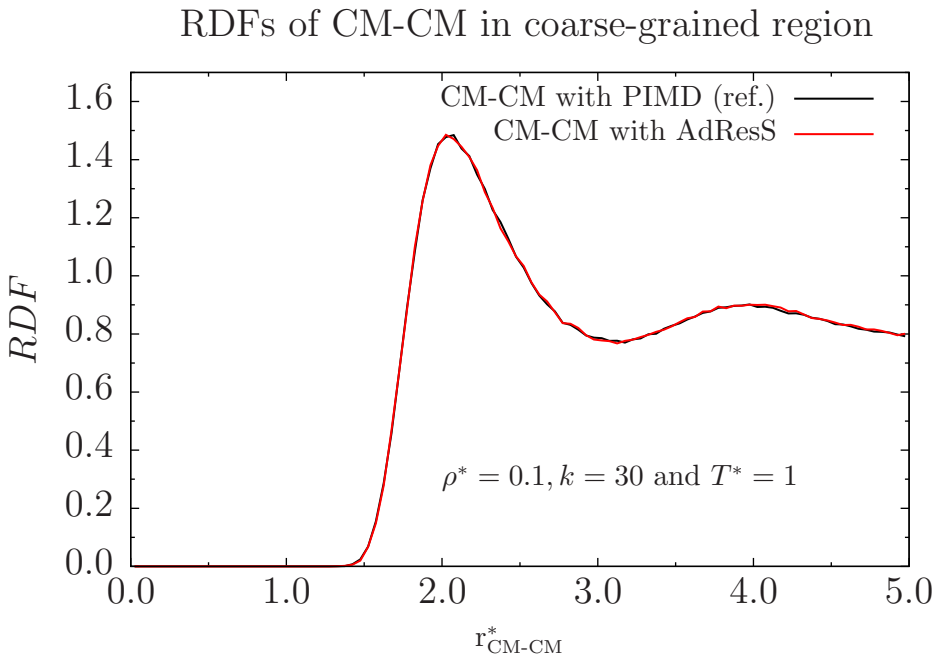


# Morse Potential: Semirigid rings II

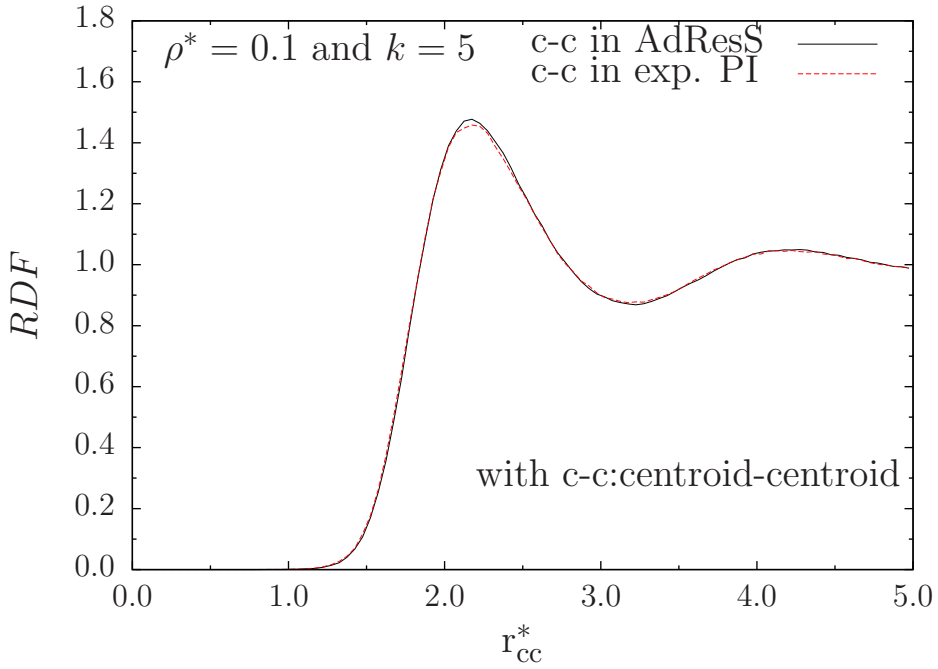
**liquid for semirigid rings ($k = 30$): Local properties**

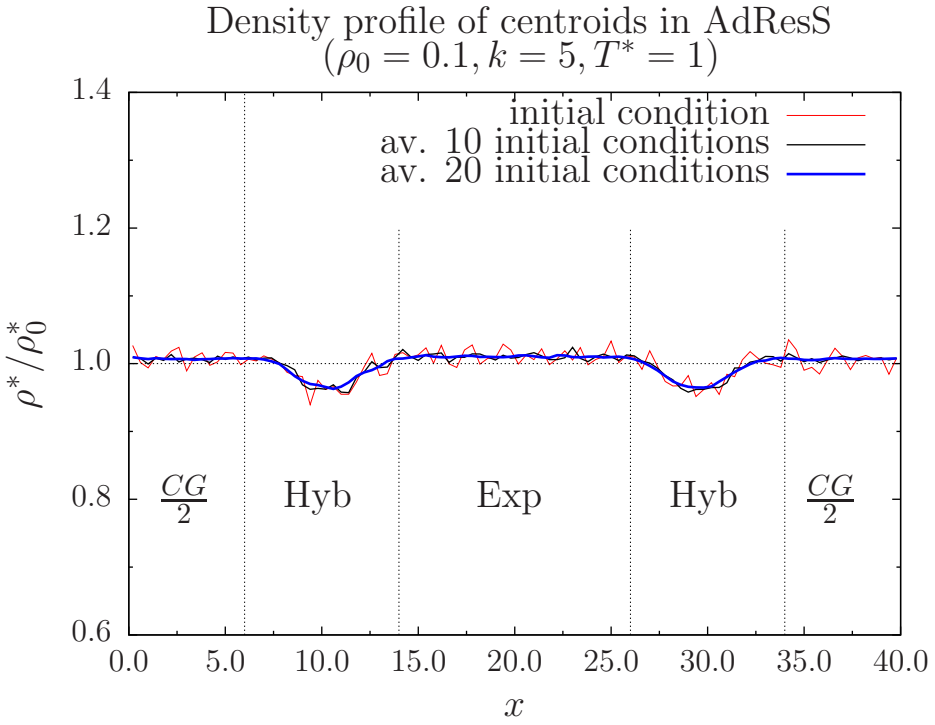


# Morse Potential: Flexible rings I

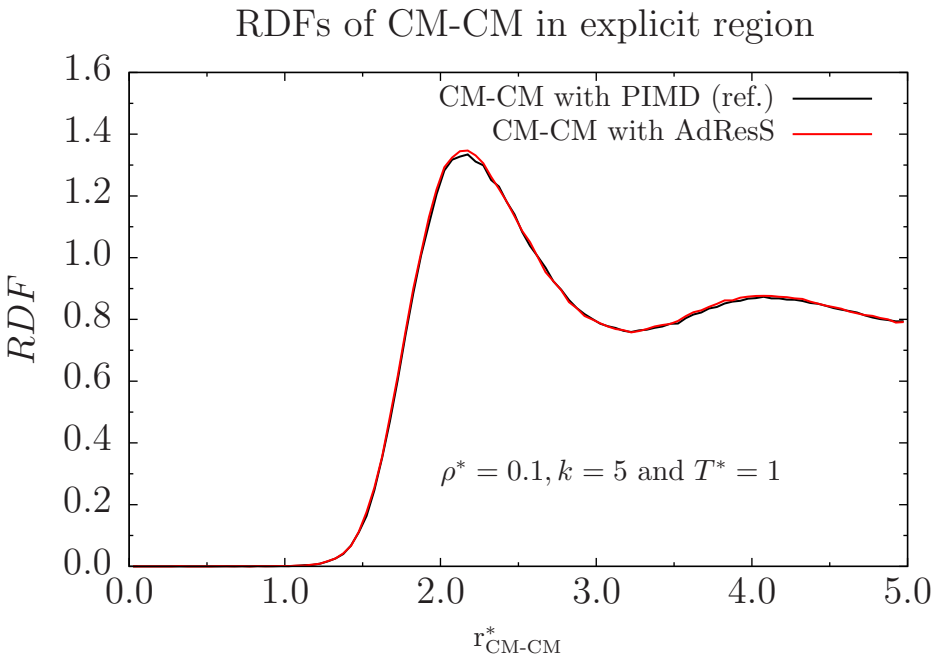
**liquid for flexible rings ($k = 5$): Global properties**

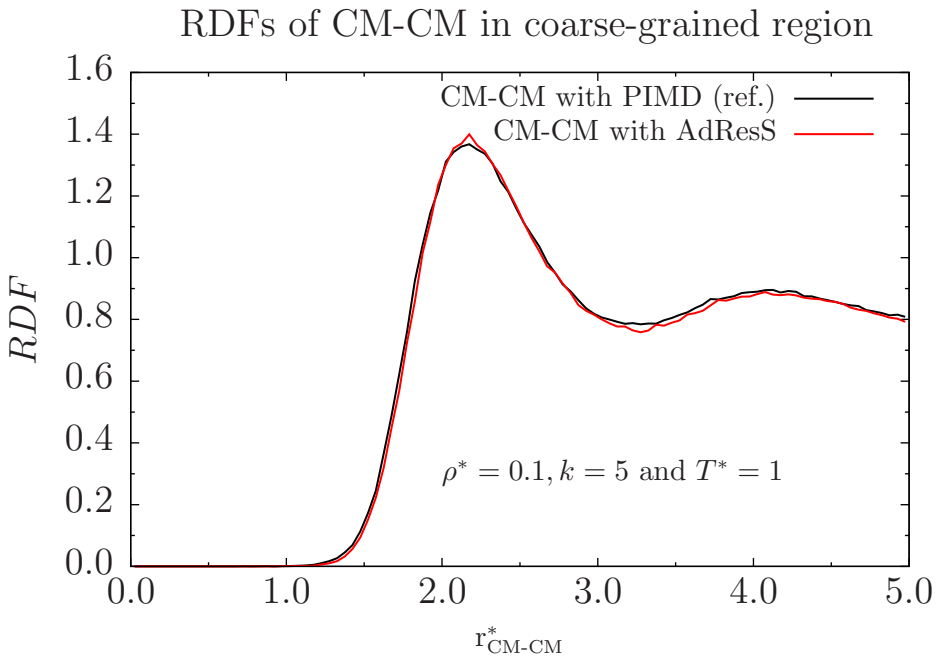


# Morse Potential: flexible rings II

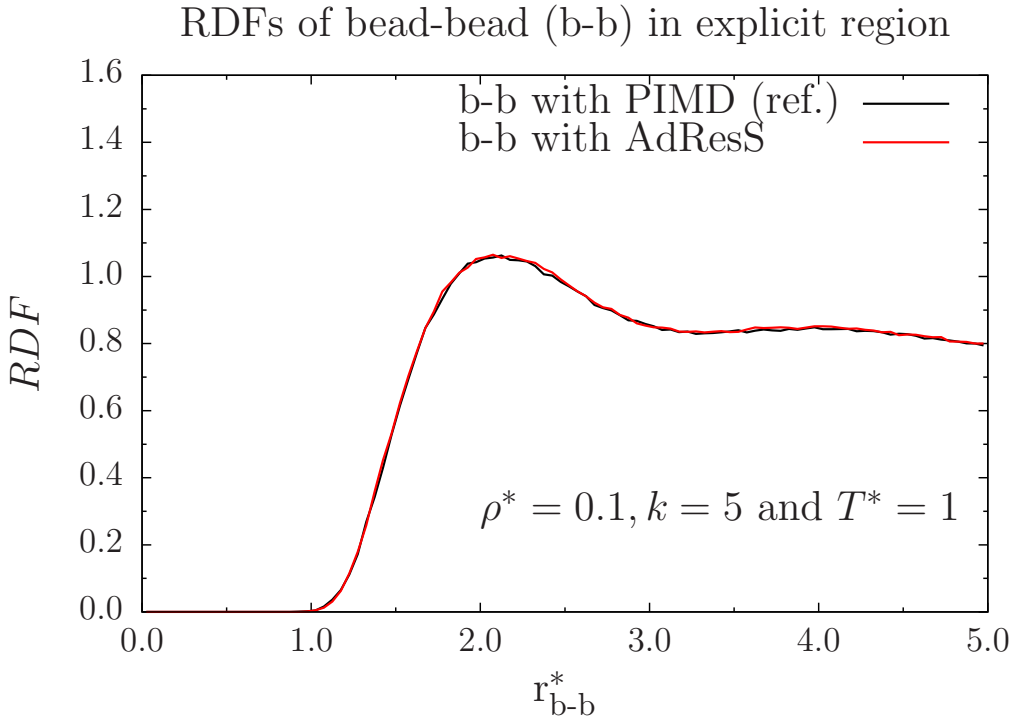
**liquid for flexible rings ($k = 5$): Local properties**



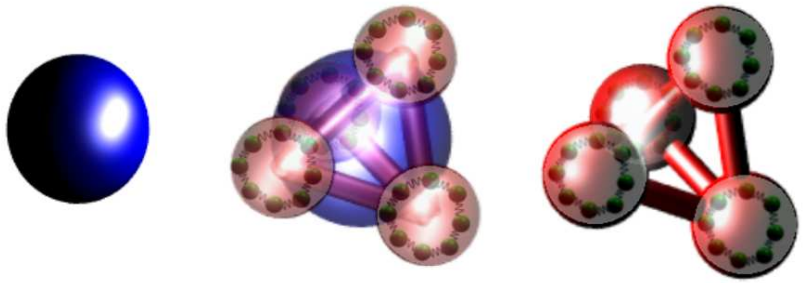



# Morse Potential: flexible rings III

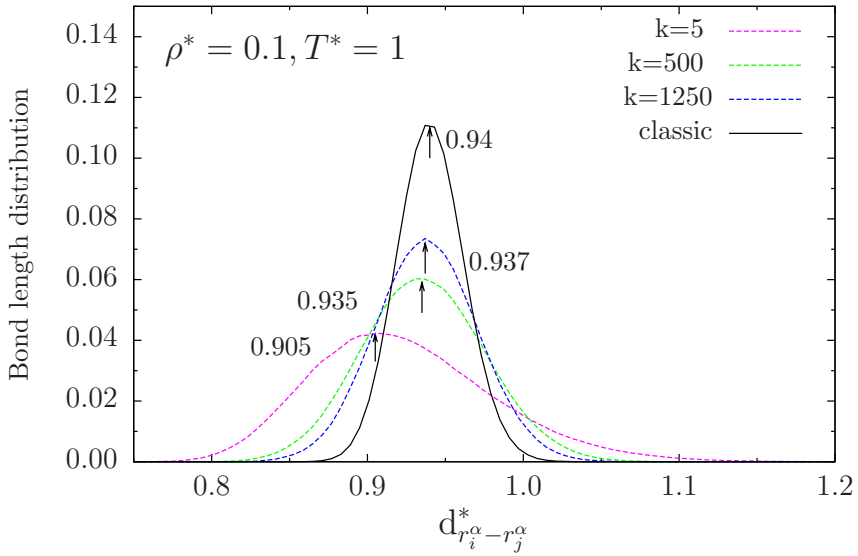
**liquid for flexible rings ($k = 5$): Full quantum properties**



# Tetrahedral Molecules

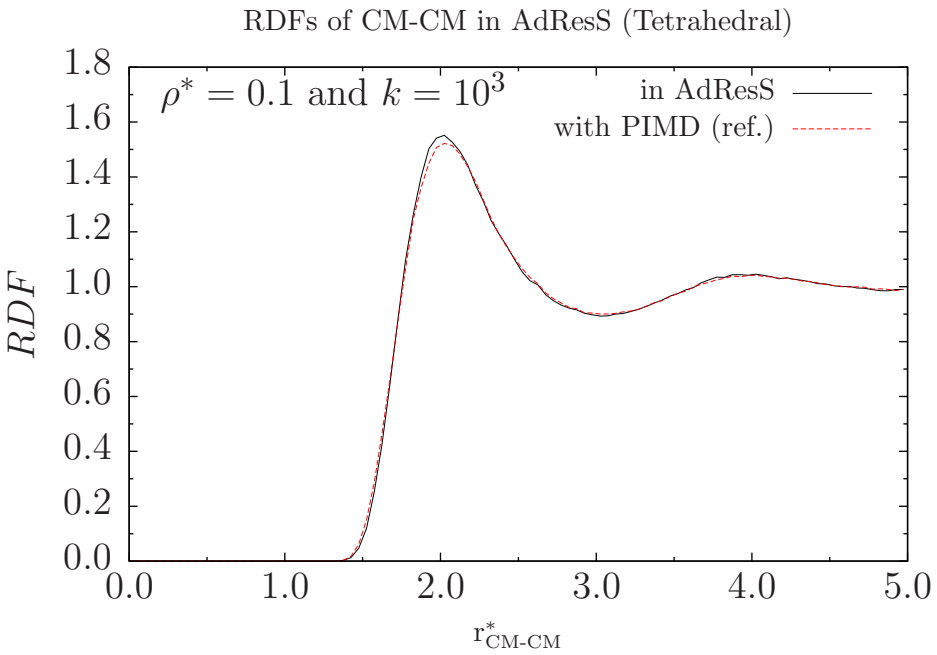


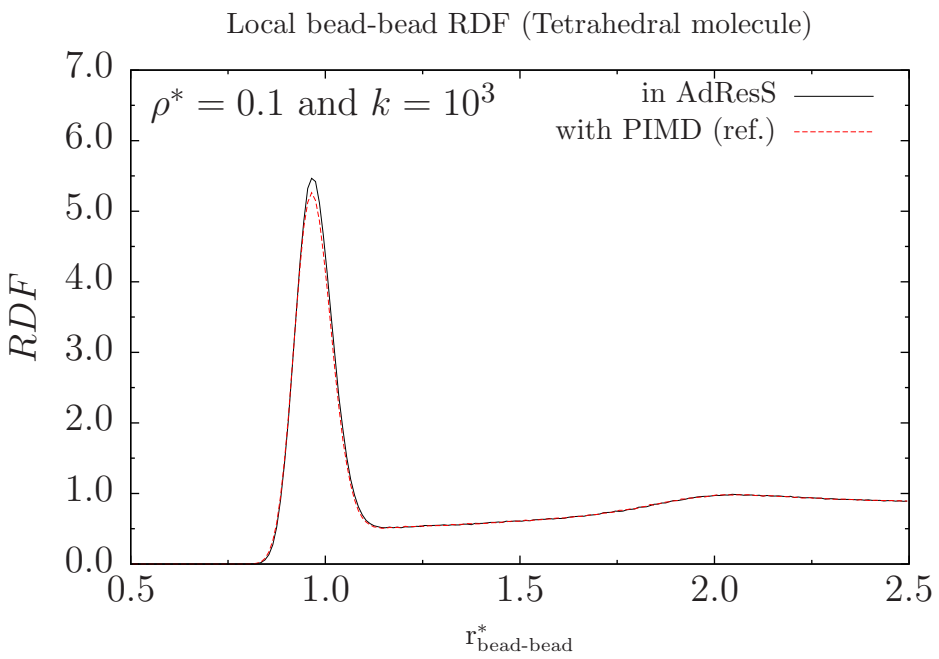
Rigidity of Tetrahedral molecule in PIMD



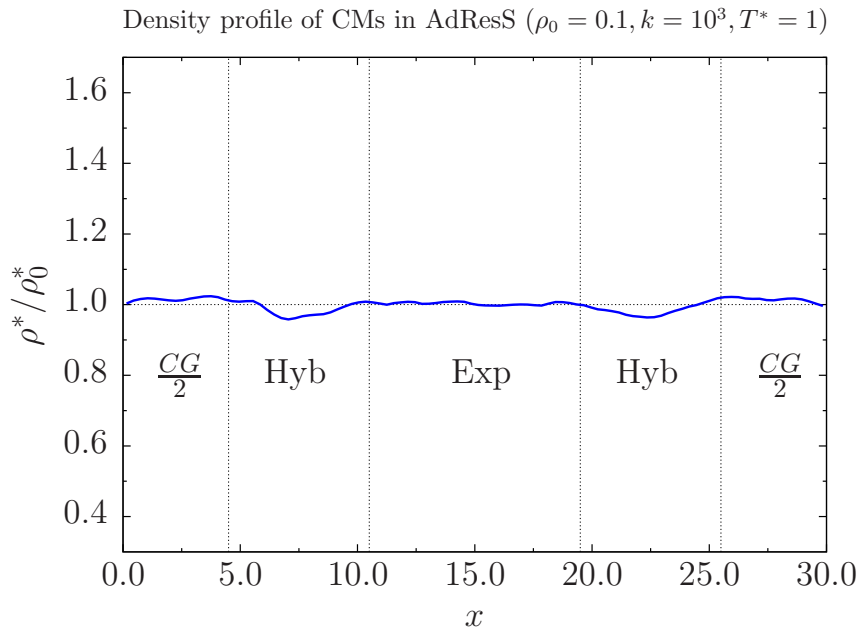
# Tetrahedral Molecules:Results I

semiflexible case: $k = 1000$



# Tetrahedral Molecules:Results II



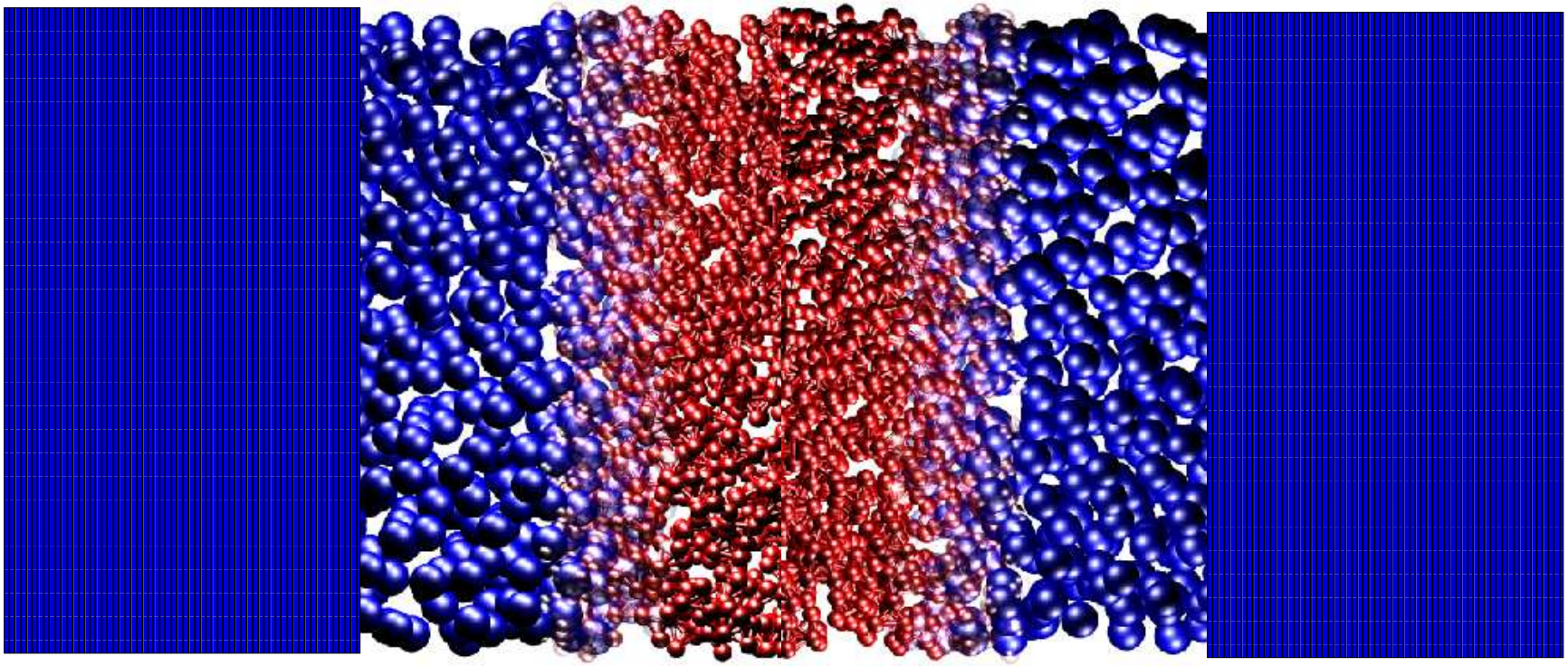
# Extension to Continuum: Concurrent triple-scale simulation

- 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

# Triple-scale model



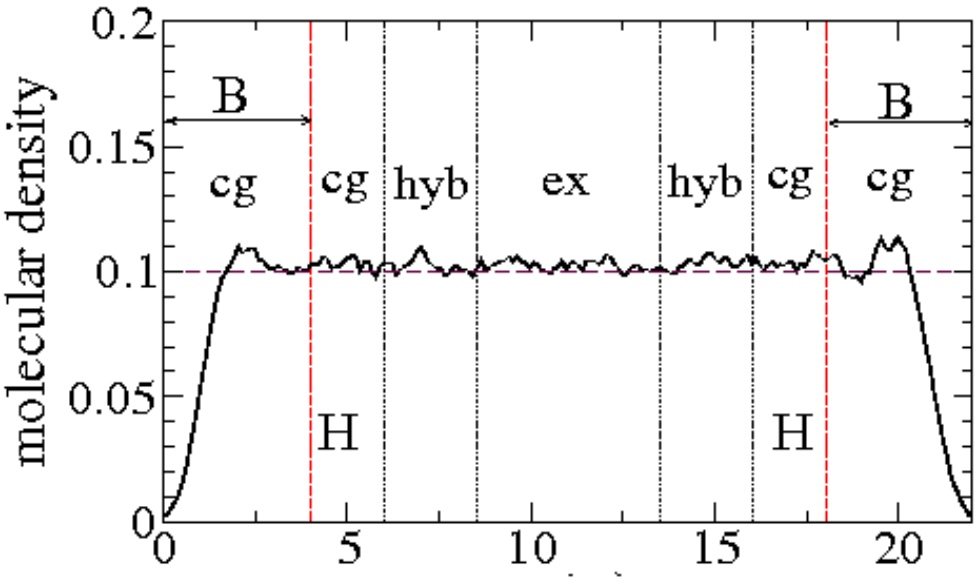
R. Delgado Buscalioni, K. Kremer, MP, J. Chem. Phys. **128**, 114110, 2008.

# HybridMD: Coupling particle-based and continuum descriptions

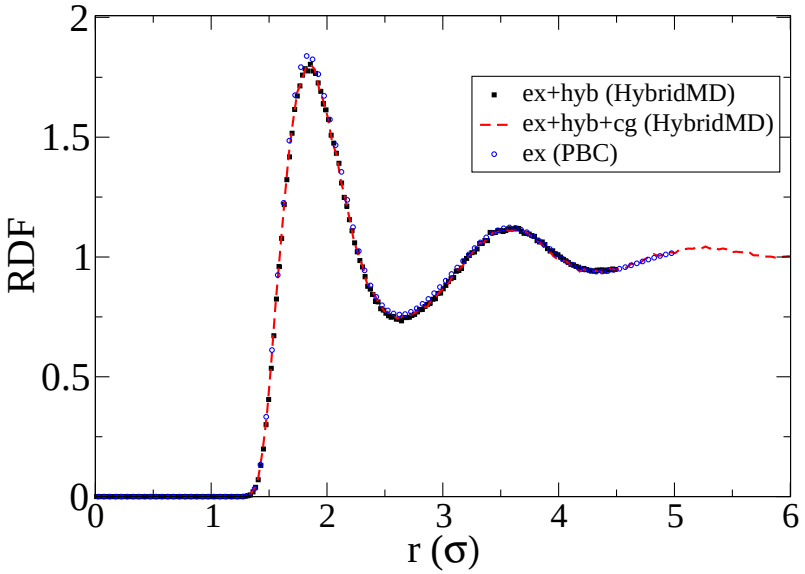
- The hybrid particle-continuum scheme (HybridMD) connects the dynamics of a **"molecular domain"** with a **continuum description** of the surrounding fluid flow.
- The method is based on **flux-exchange**.
- The system is divided in (at least) two domains, described via classical **molecular dynamics (MD)** and **continuum fluid dynamics (CFD)**, i.e., solving the **Navier-Stokes** equations.
- 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.

# Molecular density profile

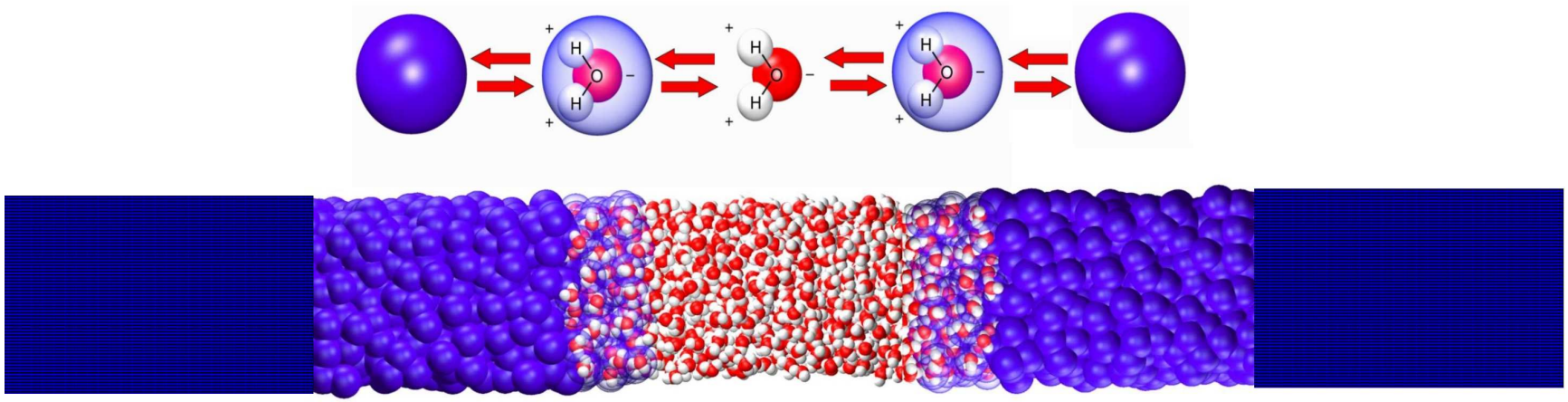


# Radial distribution functions




- 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))

# Triple-scale liquid water




**URL**: http://www.mpip-mainz.mpg.de/∼praprot/

# Adaptive Resolution in MD: Other work

- B.Ensing, S.O. Nielsen, P.B. Moore, M.L. Klein, and M.Parrinello,J. Chem. Theory Comput., 2007, 3 (3), pp 11001105 see also:R.E. Bulo, B.Ensing, J.Sikkema and L.Visscher,J. Chem. Theory Comput., 2009, 5 (9), pp 22122221
- A.Heyden and D.G. Truhlar, J. Chem. Theory Comput., 2008, 4 (2), pp 217221
- M.G.Guthrie, A.D. Daigle and M.R. Salazar,J. Chem. Theory Comput.DOI: 10.1021/ct900449q
- S.Izvekov and G.A. Voth,J. Chem. Theory Comput.,DOI: 10.1021/ct900414p