Adaptive Resolution Simulations: Towards Open Systems Molecular Dynamics Simulations

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Rutgers University * Dec. 19, 2010

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Support:

MMM Initiative of the MPG, Volkswagen Foundation, DAAD

Outline

- **Motivation: Soft and Nanostructured Matter**
- AdResS: **Ad**aptive **Res**olution MD **S**imulation
  - Method, first Applications
  - Recent developments
- Particle-Continuum: AdResS + Hybrid MD
- Conclusions/Outlook

Soft Matter

"Soft" means:

- low energy density

- nanoscopic length scales (10Å …1000Å)

- large fluctuations

- thermal energy $k_B T$ relevant energy scale

Energy Scale $k_B T$ for T=300K

$$E = 1.38 \cdot 10^{-23}\ J/K \cdot 300\ K$$

$$kT \approx 4.1 \cdot 10^{-21}\ J$$

$$kT \approx 2.5 \cdot 10^{-2}\ eV$$

$$kT \approx 9.5 \cdot 10^{-4}\ E_H$$

$$kT \approx 4.1\ pNnm$$

$$kT \Rightarrow 200\ cm^{-1}$$

$$kT \Rightarrow 0.6\ kcal/mol$$

$$kT \Rightarrow 2.5\ kJ/mol$$

Electronic structure, CPMD

Quantum Chemistry

Biophysics Membranes, AFM

Spectroscopy

$$E \approx 3 \cdot 10^{-19}\ J \approx 80\ kT$$

$$E \approx 4\ kT - 10\ kT$$

Chemical Bond
Hydrogen Bond

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$$kT \approx 4.1\ pNnm$$

$$kT \Rightarrow 20$$

$$kT$$ 3 kcal / mol

$$kT \Rightarrow 2.5\ kJ / mol$$

Green light photon ≈ 2-2.5 eV ≈ 100 kT

Electronic st MD

Qu istry

ophysics Membranes, AFM

Spectroscopy

$$E \approx 3 \cdot 10^{-19}\ J \approx 80\ kT$$

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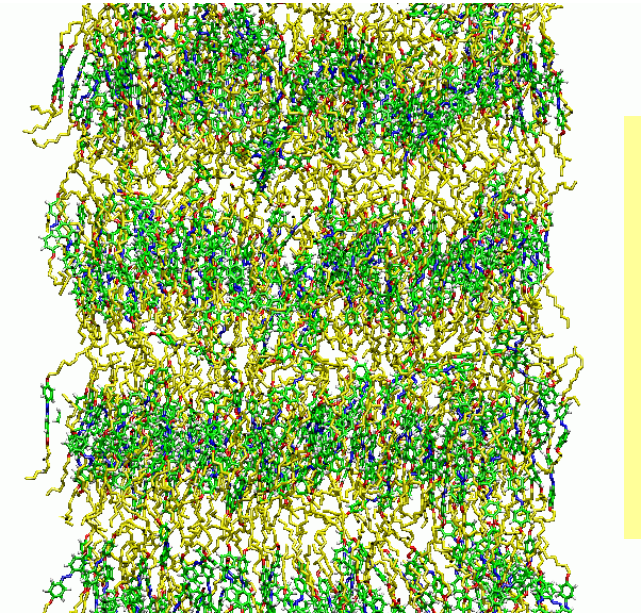
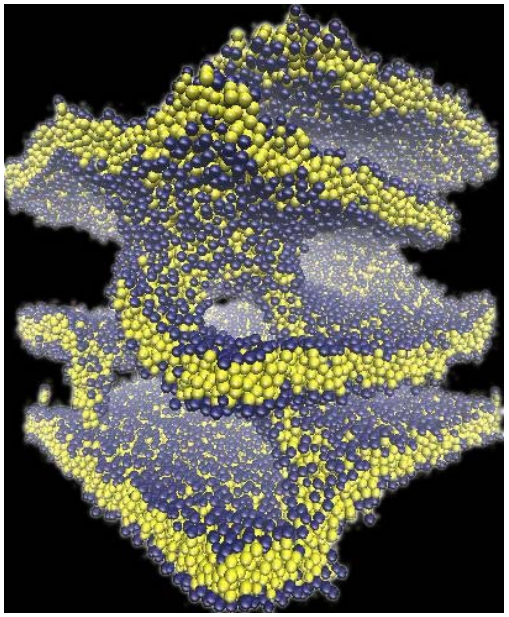
Chemical Bond
Hydrogen Bond

Soft Matter – Nanostructured Matter



Volume
$V = L^3$

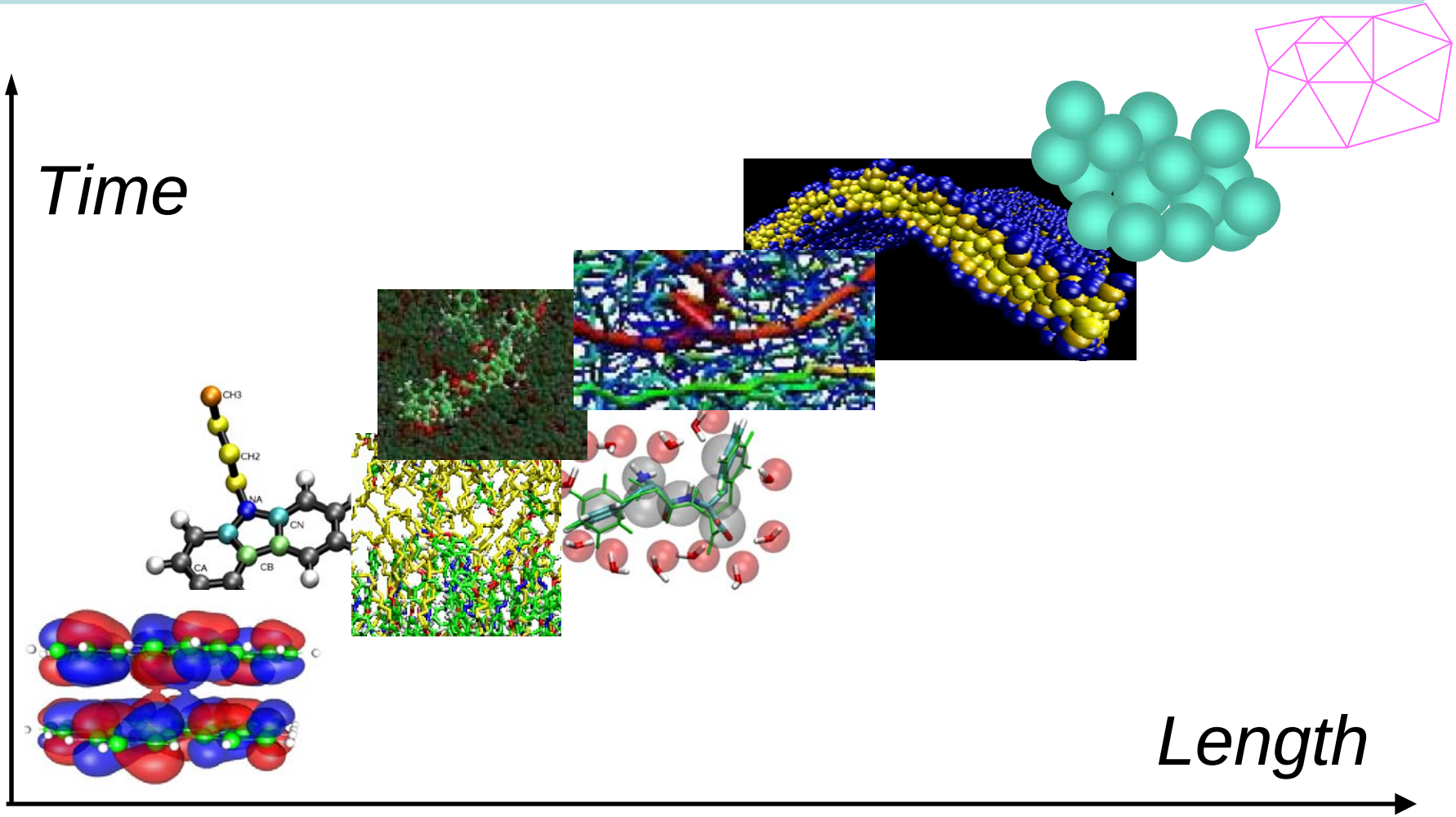
***A*: Surface and Interface Area**



Nanoscopically Structured Material: *V/A* << 1µm =>
Distinction Bulk vs Surface/Interface not usefull

Definition of *A* usually depends on the question studied!

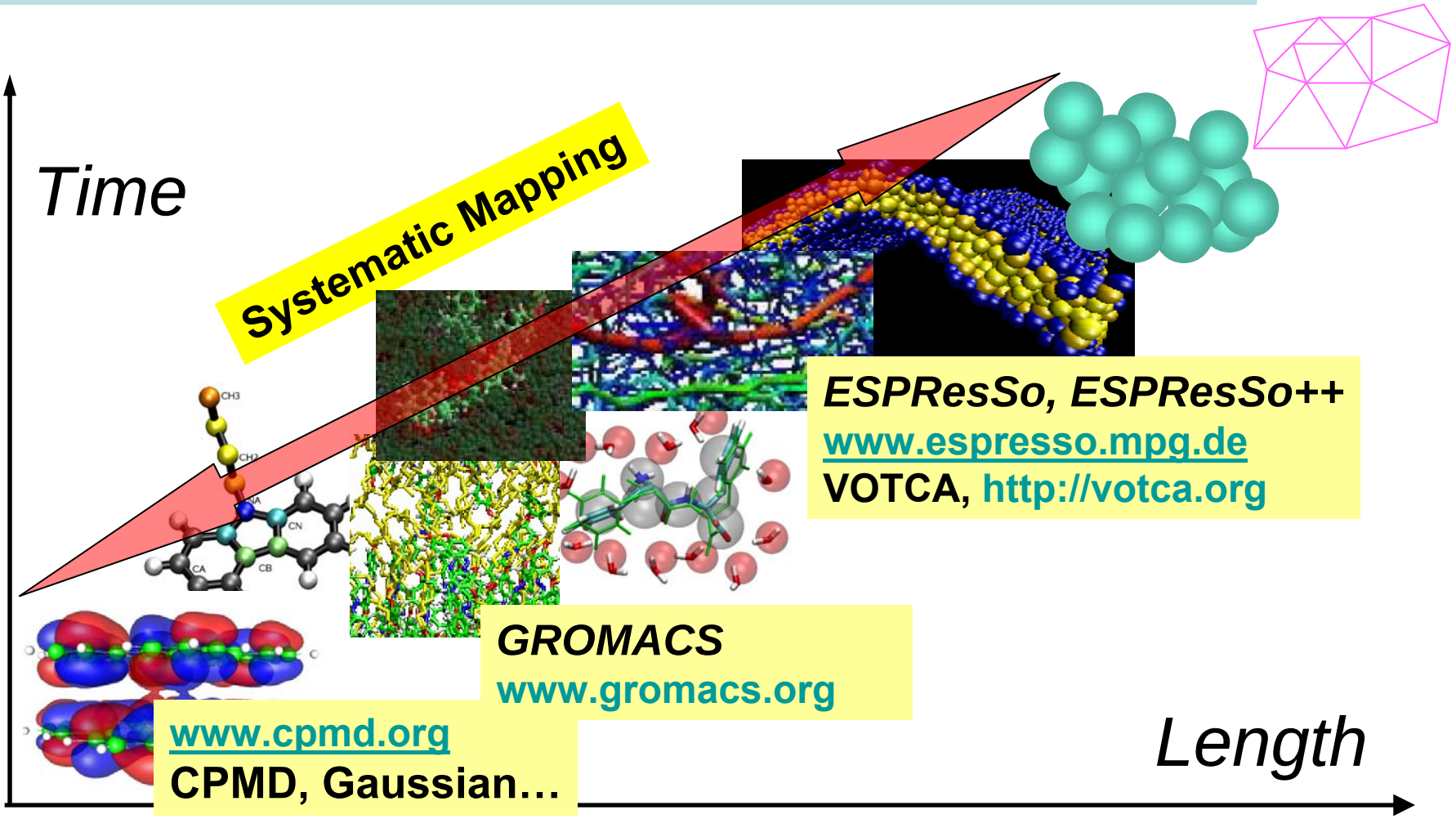
Characteristic Time and Length Scales



Local Chemical Properties --- Scaling Behavior of Nanostructures

Energy Dominance --- Entropy Dominance of Properties

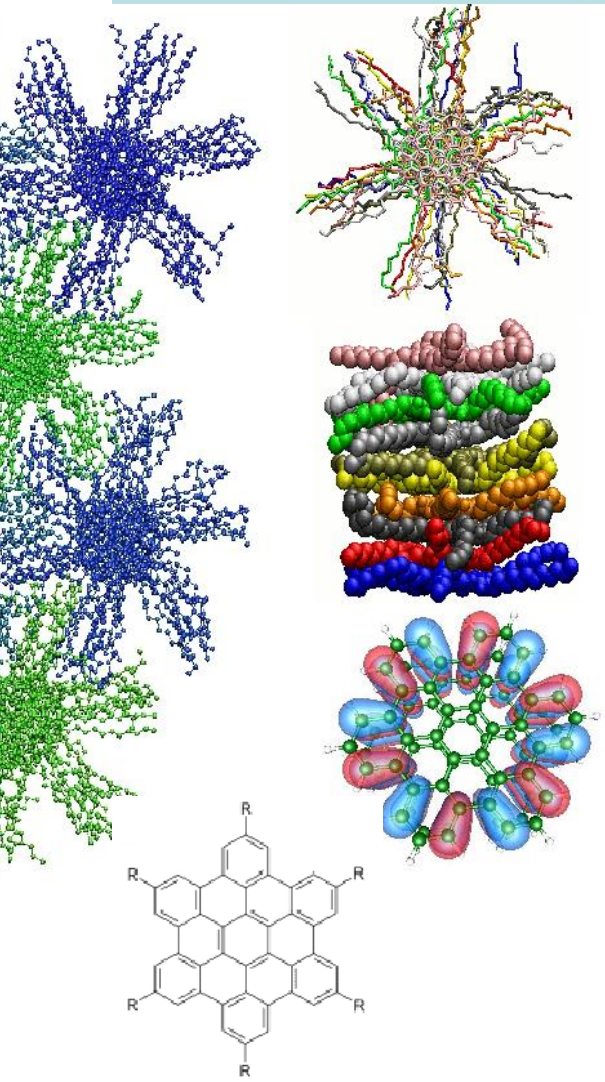
Characteristic Time and Length Scales



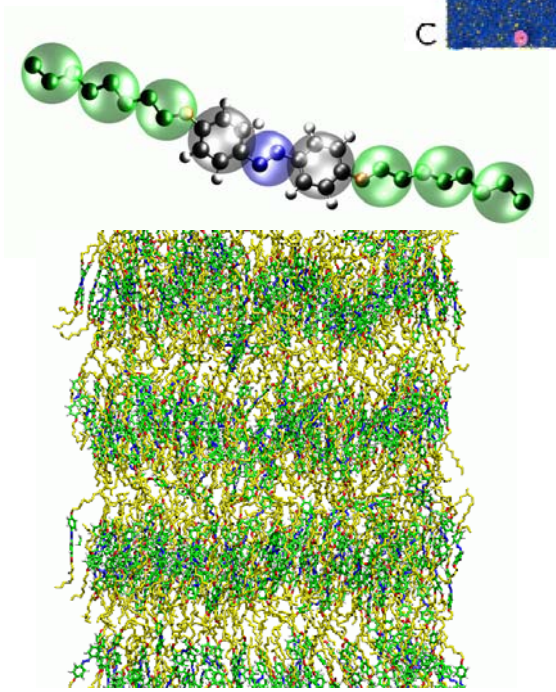
Local Chemical Properties --- Scaling Behavior of Nanostructures

Energy Dominance --- Entropy Dominance of Properties

Standard Approach:
Run whole system on one level of resolution.



Andrienko et al,
PRL 98, 227402 (2007)



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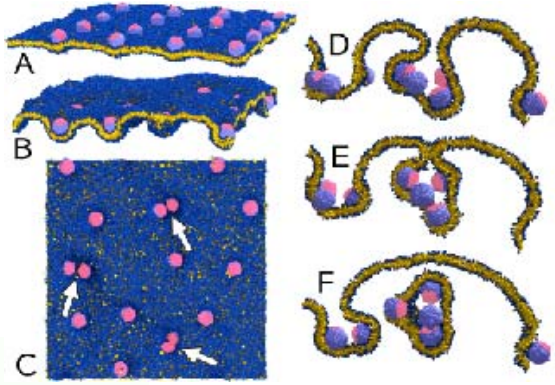

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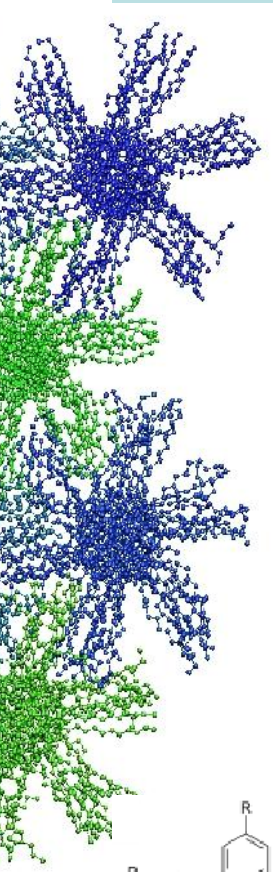

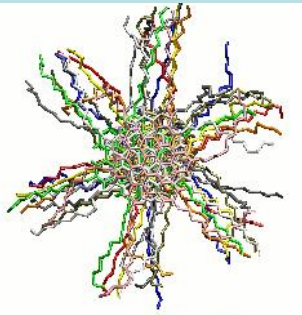

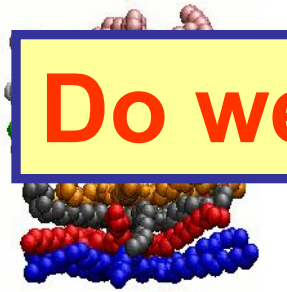

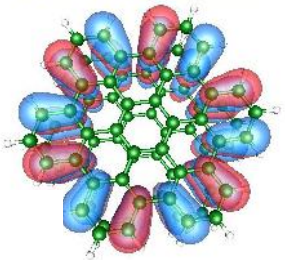

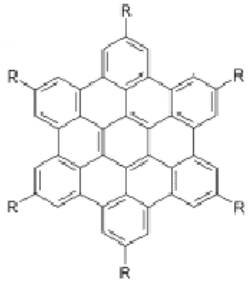

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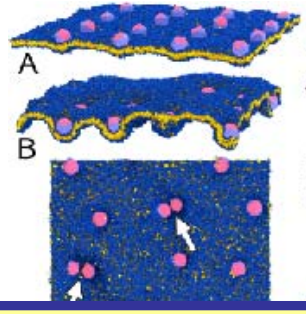
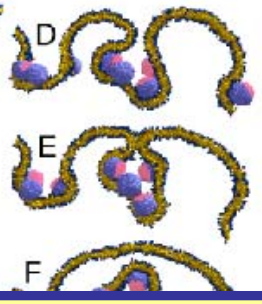
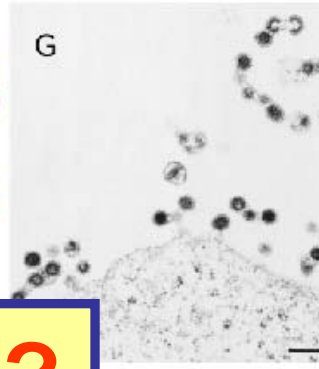
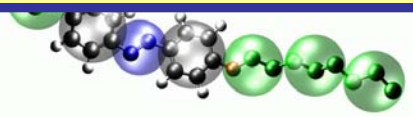
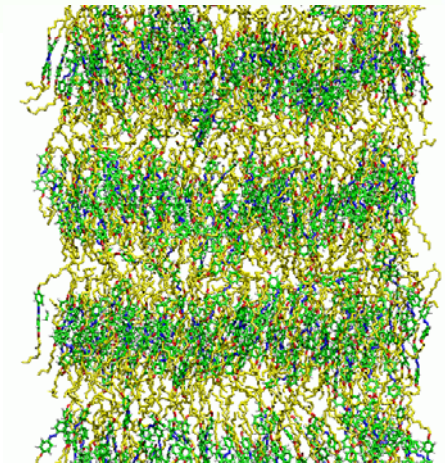






Do we need/want to do that?





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- Particle-Continuum: AdResS + Hybrid MD
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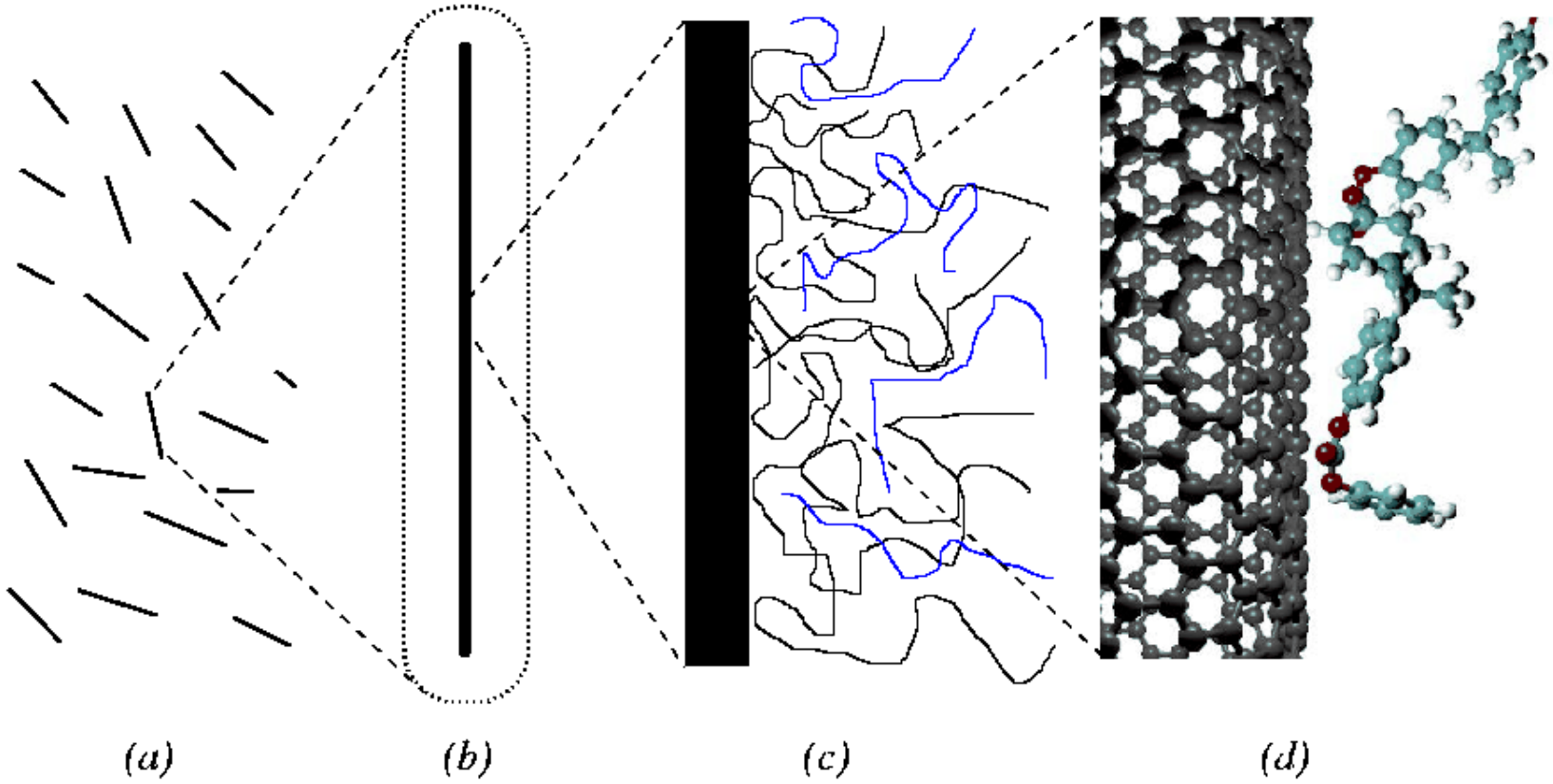
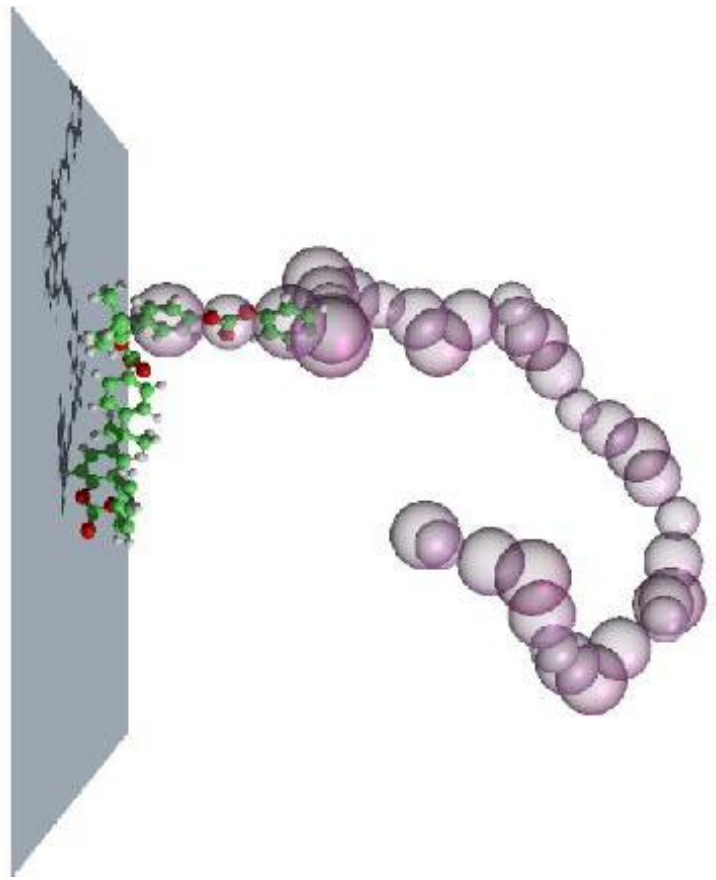
Relevant Levels of Resolution
Example:Polymer/Nanotube Composites



C. F. Abrams, Drexel

Adaptive Inhomogenous Coarse-Graining



Specific atomic-scale energetics dominant at surface

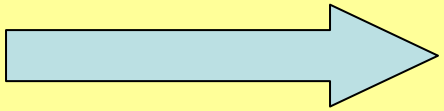
Molecule-scale entropy dominant in bulk

Coarsened fragments provide equilibrated "boundary conditions" for full-blown embedded atomistic simulation

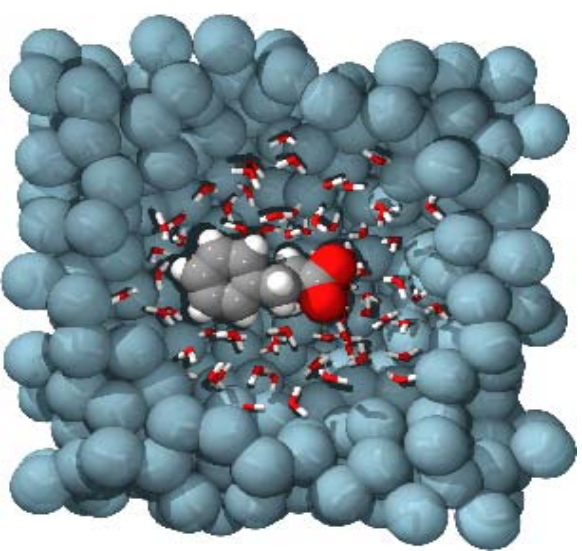
AdResS: Adaptive Resolution Simulations

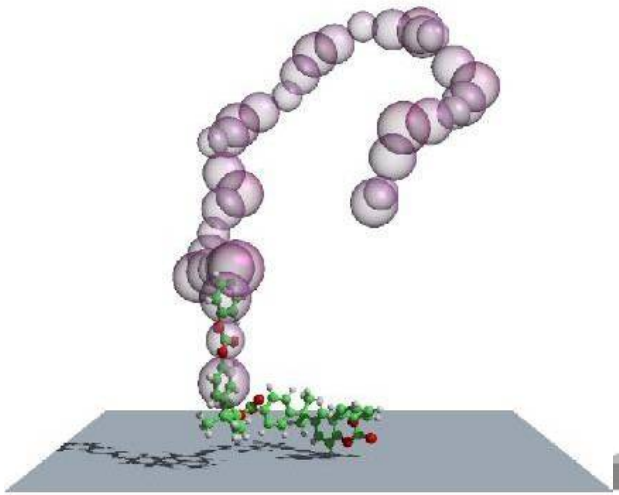
M. Praprotnik, L. Delle Site, KK, Ann. Rev. Phys. Chem. 2008, 59: 545-71

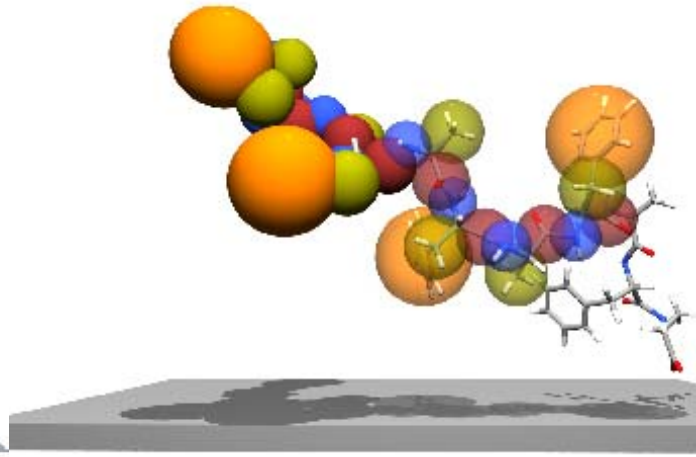
Free exchange of molecules/particles between regimes with different levels of resolution:



equilibrium between both regimes, no kinetic barrier





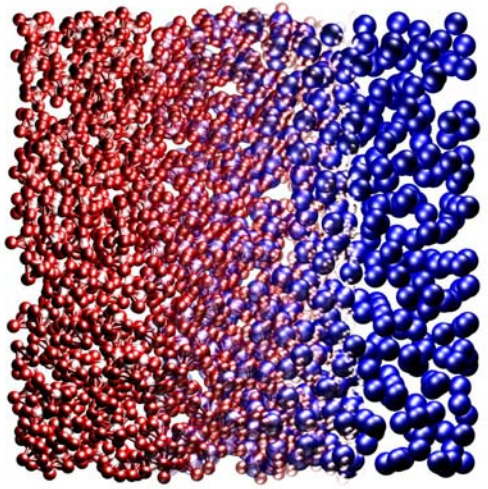


Adaptive Methods: Changing degrees of freedom on the fly

Adaptive multiscale method: Simple test case

Tetrahedron,
repulsive LJ Particles, ⇔ **Hybrids** ⇔ **"Softer"**
Sphere
FENE bonds

Explicit Atom ⇔ **Transition** ⇔ **Coarse Grained**
regime **regime** **regime**

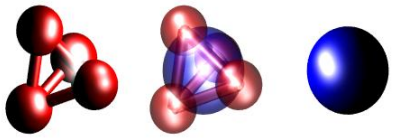


M. Praprotnik, L. DelleSite, KK, JCP 2005

Adaptive Methods:
Changing degrees of freedom (DOFs) on the fly

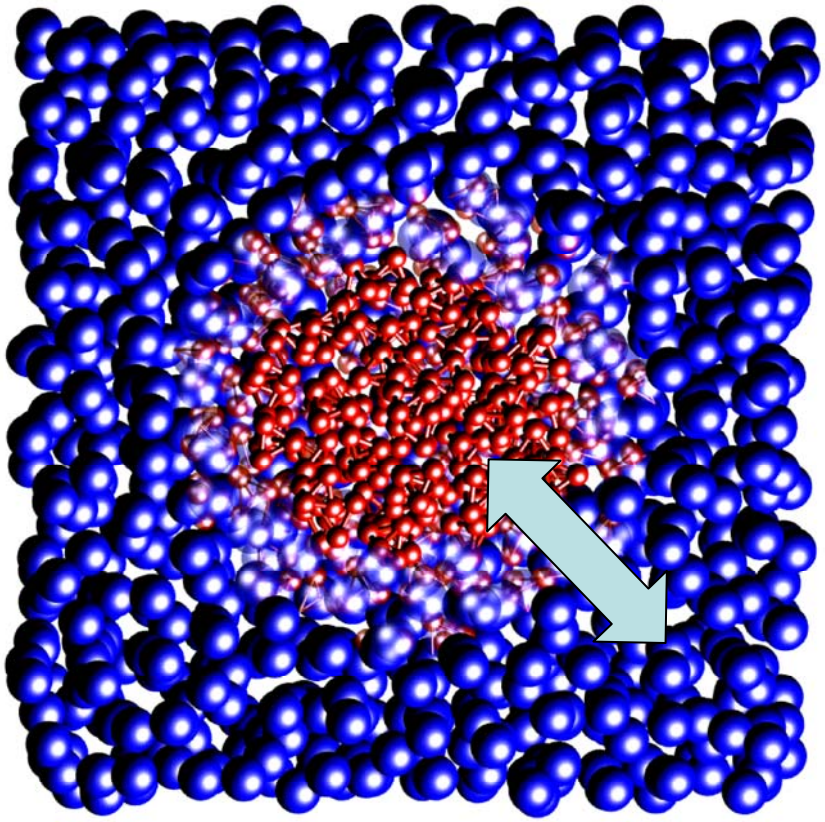
Requirements

- Same mass density
- Same Pressure (=>Eq. of state)
- Same temperature



- Free exchange between regimes
- Same center-center g(r)

- Simple two body potential



VW Foundation Project
M. Praprotnik, L. DelleSite, KK, JCP 2005, PRE (2006)

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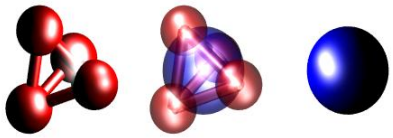

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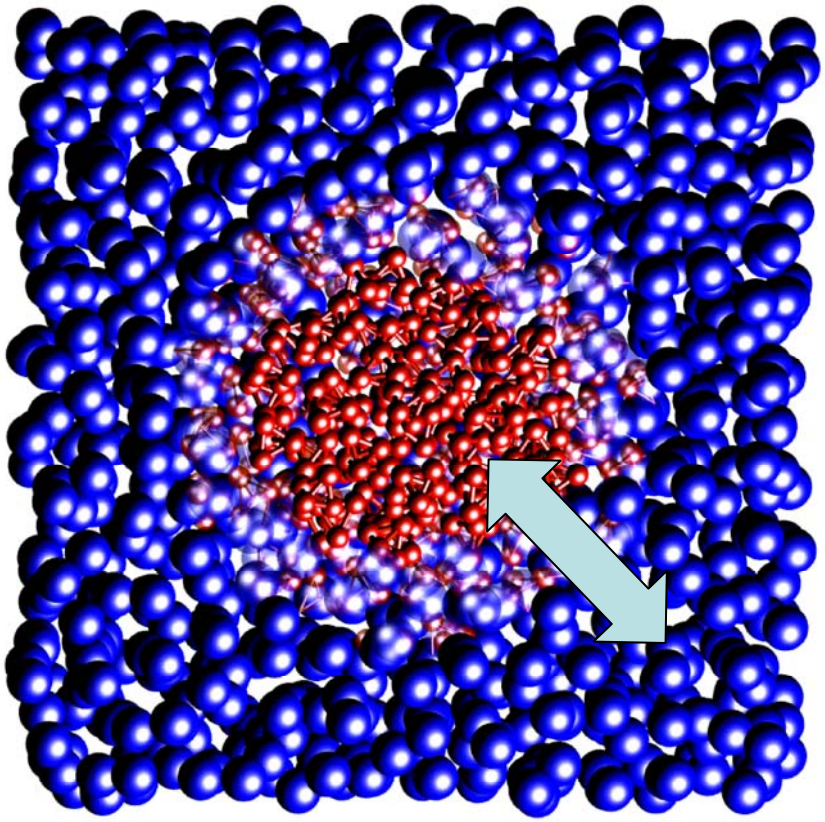
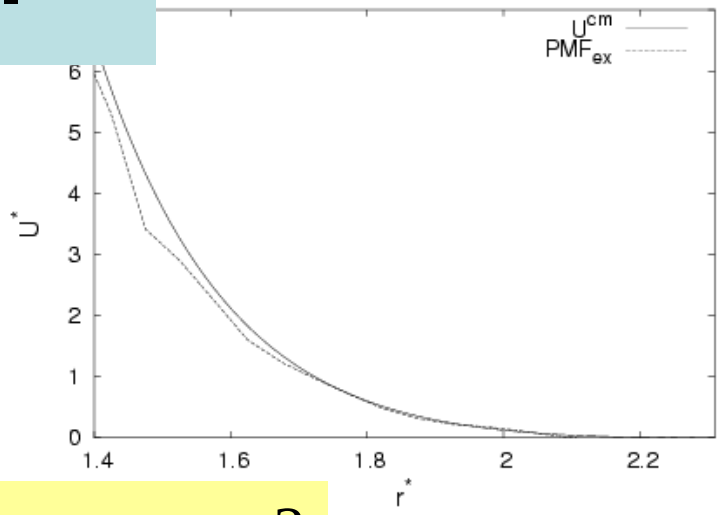


⇒ "Some similarities" to 1st order phase transition
⇒ Phase equilibrium
⇒ Thermostat has to provide/take out latent heat due to change in degrees of freedom

VW Foundation Project
M. Praprotnik, L. DelleSite, KK, JCP 2005, PRE (2006)

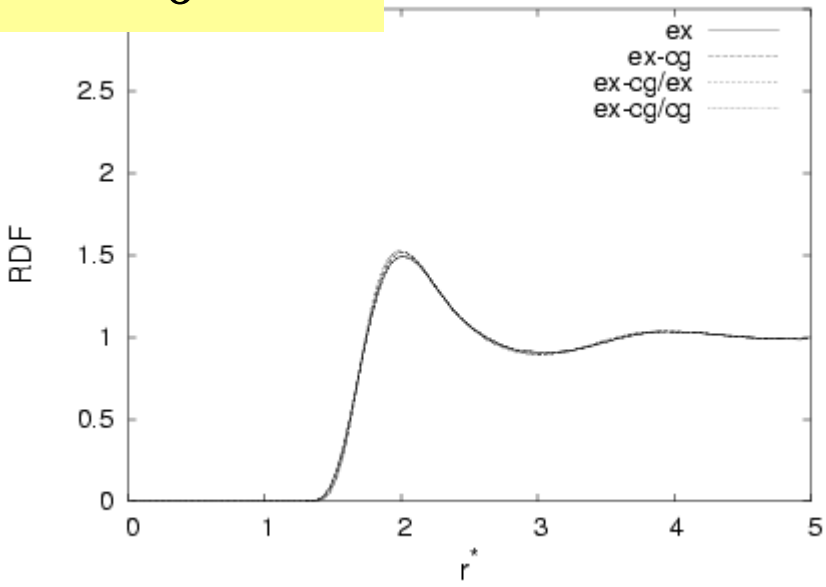
Coarse Grained Model

Study explicite atom and CG system seperately
=> fit CG Interaction Potential:



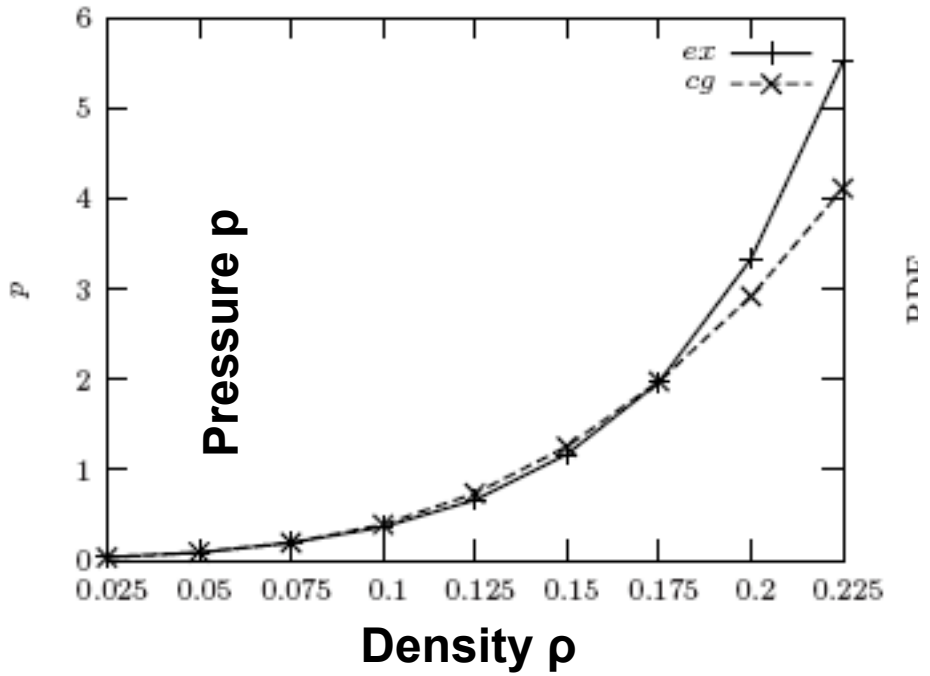
$$U^{cm}(r) = \gamma\{1 - \exp[-\kappa(r - r_0)]\}^2$$

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



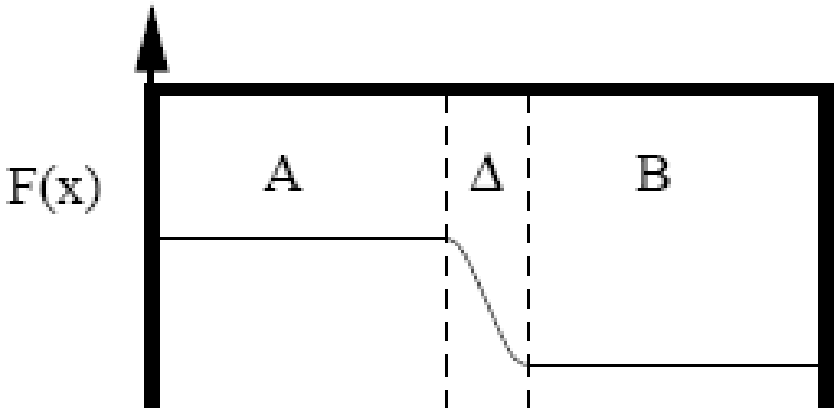
Initial General Considerations

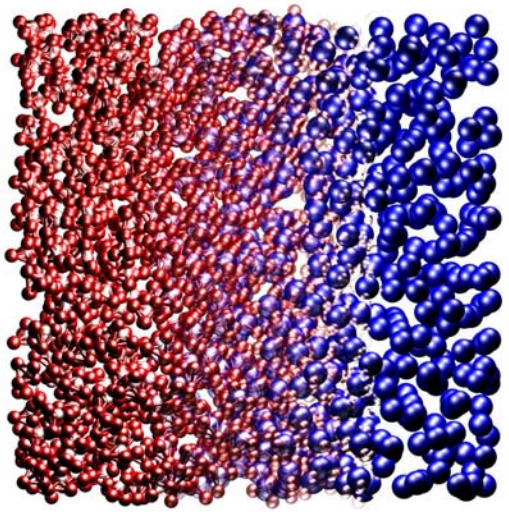
$$\mu_{ex} = \mu_{cg}, \qquad p_{ex} = p_{cg}, \qquad T_{ex} = T_{cg}$$



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

Transition Regime: Changing Degrees of Freedom (DOF): switching function *w(x)* for DOFs

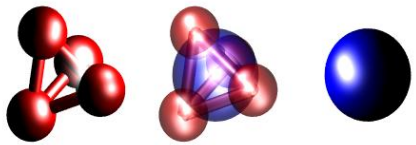


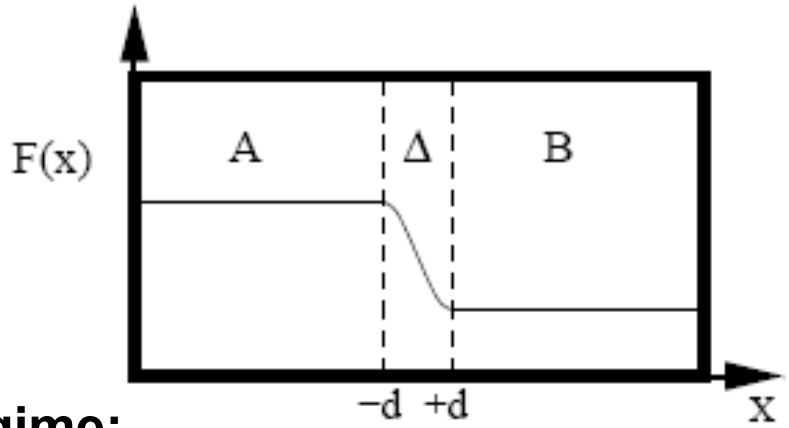


- The number of DOF is $n = n(x)$ with ; $n_A = const_A$; $n_B = const_B$; and $n_\Delta = n(x)$
- The system is in equilibrium which implies: $\lim_{x \to d-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d+} \frac{\partial F_B(x)}{\partial x} = 0$

Transition Regime: Changing Degrees of Freedom (DOF): switching function *w(x)* for DOFs

w=1 . . . w=0





Definition of Temperature in transition regime:
Fractional degrees of freedom, switching function *w(x)*
=> generalization of equipartition theorem
=> Defines thermostat to take out/in "latent heat of the DOFs"

$$dV_w = d^w q \Gamma(w/2) / 2\pi^{w/2} \Gamma(w) = |q|^{w-1} dq / \Gamma(w) = dq^w / w\Gamma(w)$$

$$\Rightarrow H(q) = q^n \qquad \langle H(q) \rangle_w = \frac{w}{n} k_B T$$

w is the fractional dimension of DOF *q*, *w=1 and n=2 standard case*

PRE 2007

Theoretical Basis: Temperature…

- **Change resolution,**
  ⇒ "Latent heat" of fading/emerging degrees of freedom (DOFs)

- **Generalized Equipartition Theorem for DOFs with fractional dimension *w(x)***
  ⇒ Well defined temperature T in Δ, well defined thermostat

- **Smooth switching region Δ with switching function *w(x)***

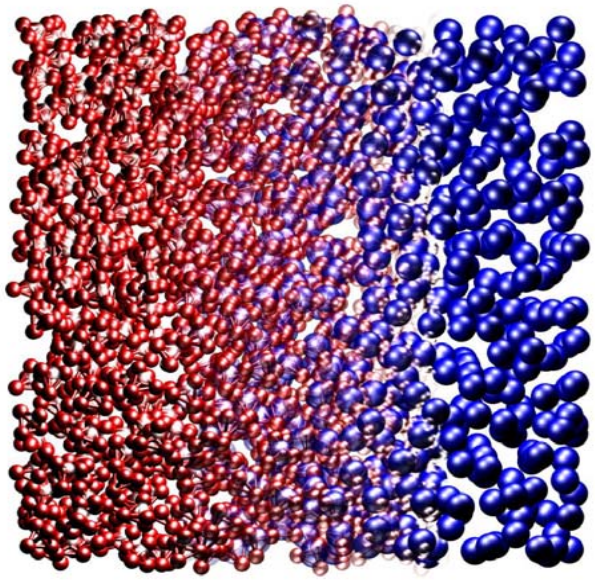
- **Practical Implementation?**

AdResS:
Transition Regime – Energy $U_{\alpha\beta}$ Interpolation?

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

Full atomistic potential

Full coarse grained potential



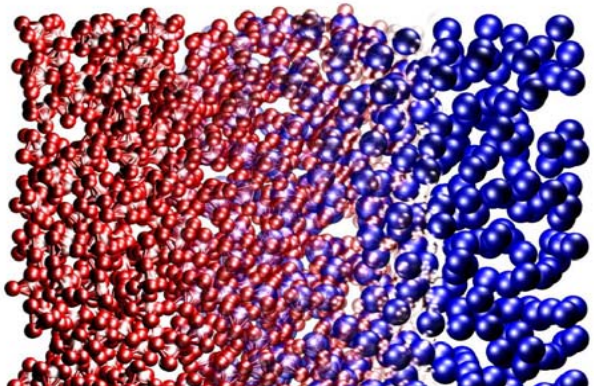
- **Drift terms from *w(x)***
- **Violation of Newton's 3rd law**
- **Mathematical inconsistencies at boundaries**

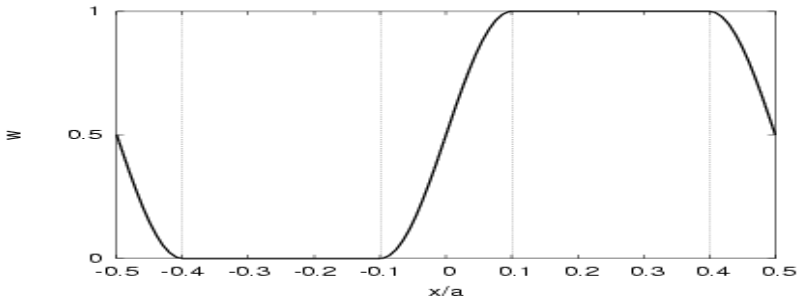
AdResS:
Transition Regime - Force Interpolation

$$F_{\alpha\beta} = w(X_\alpha)w(X_\beta)F^{atom}_{\alpha\beta} + [1 - w(X_\alpha)W(X_\beta)]F^{cg}_{\alpha\beta}$$

Full atomistic force

Full coarse grained force





Interactions

explicit-explicit
CG-CG
hybrid-hybrid

CG- hybrid: CG-CG
explicit-hybrid: explicit-explicit

AdResS: Transition Regime - Force Interpolation

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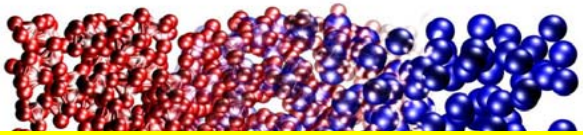
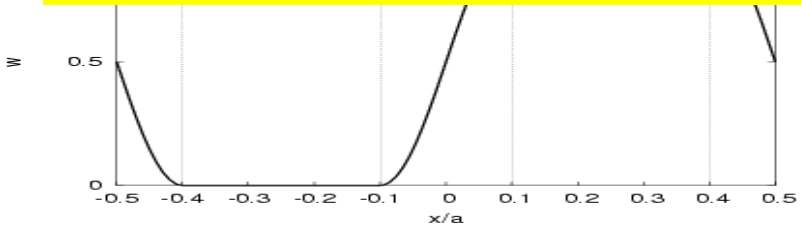
Full atomistic force

Full coarse grained force



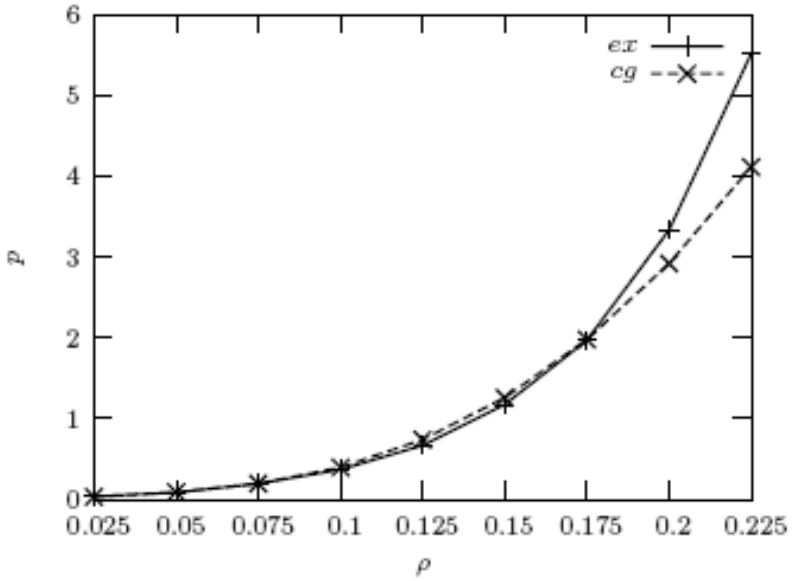
Transition regime: Force interpolation
(Newtons 3rd law fulfilled, no drift forces)

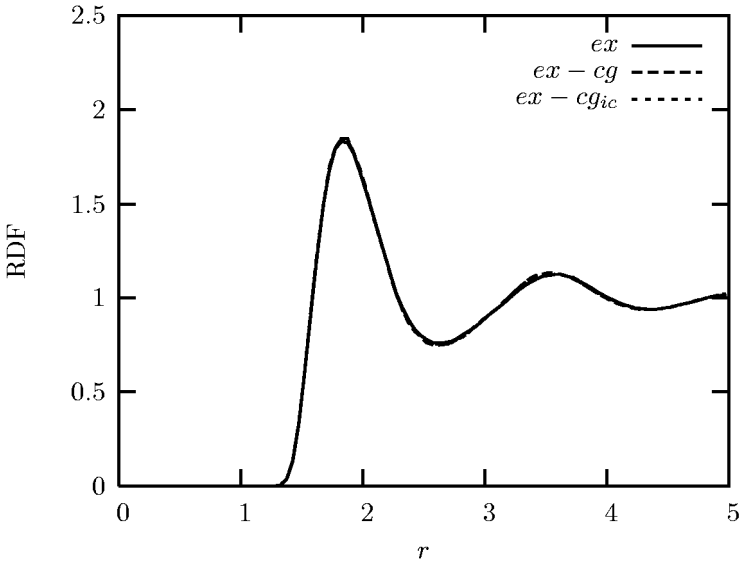
No transition energy function defined!



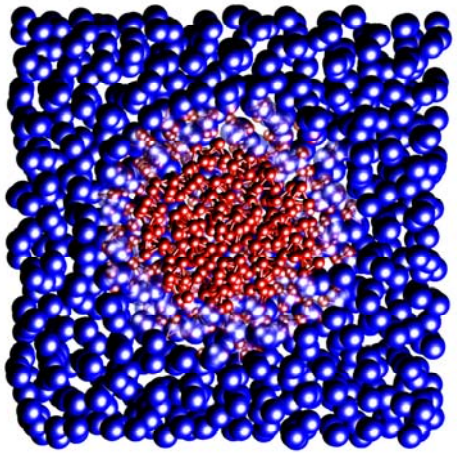
CG- hybrid: CG-CG
explicit-hybrid: explicit-explicit

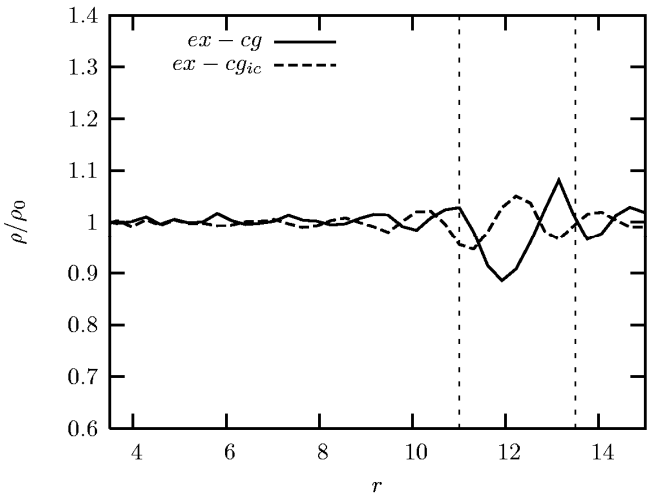
First Test: Radial Distributions, Densities, high density



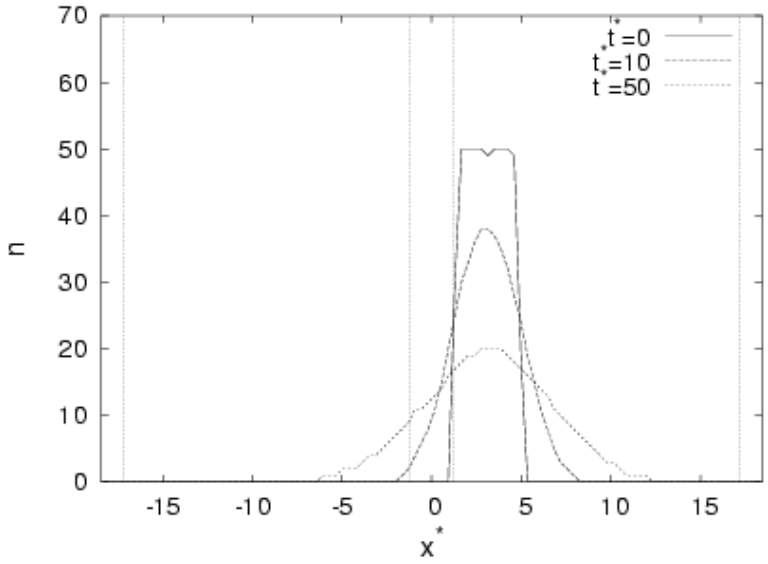


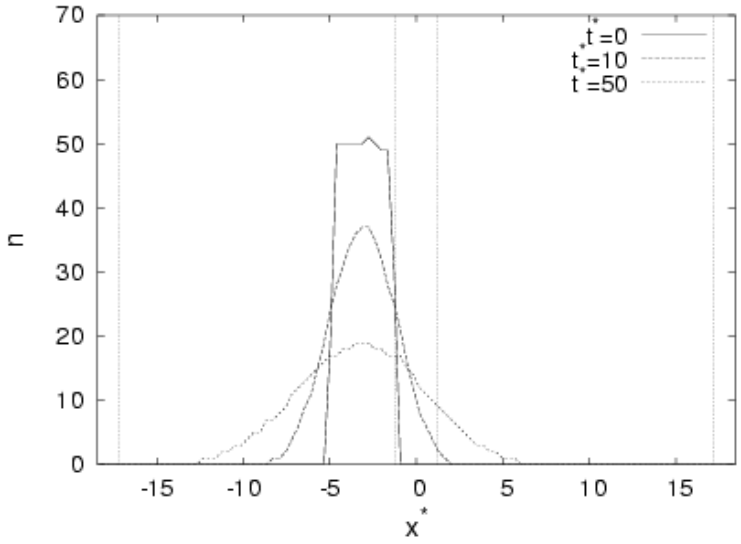
(m) Equation of state for $\rho = 0.175$ and $T = 1$.



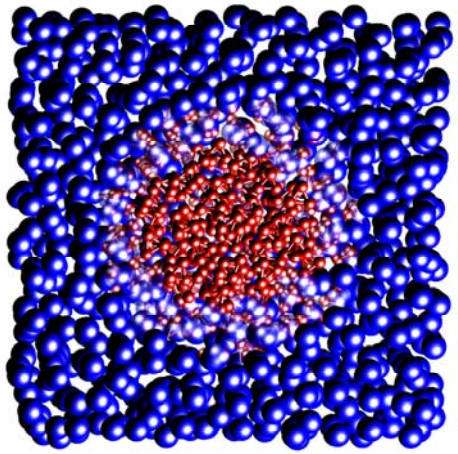


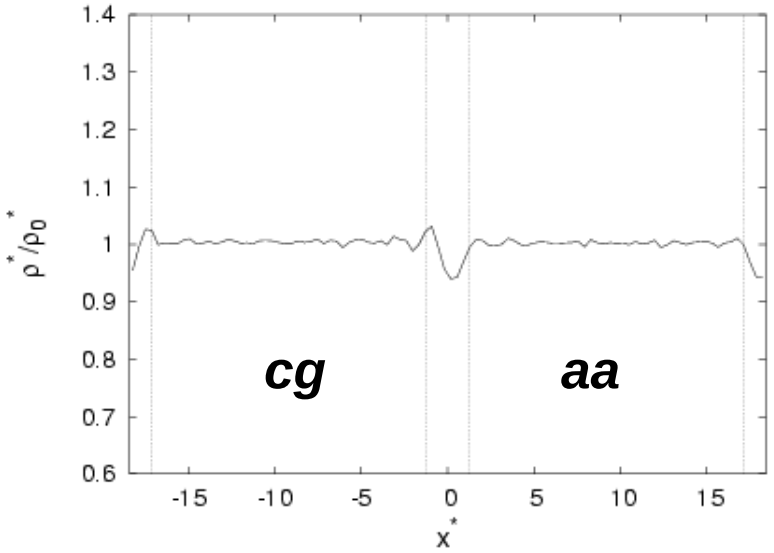
Particle Exchange



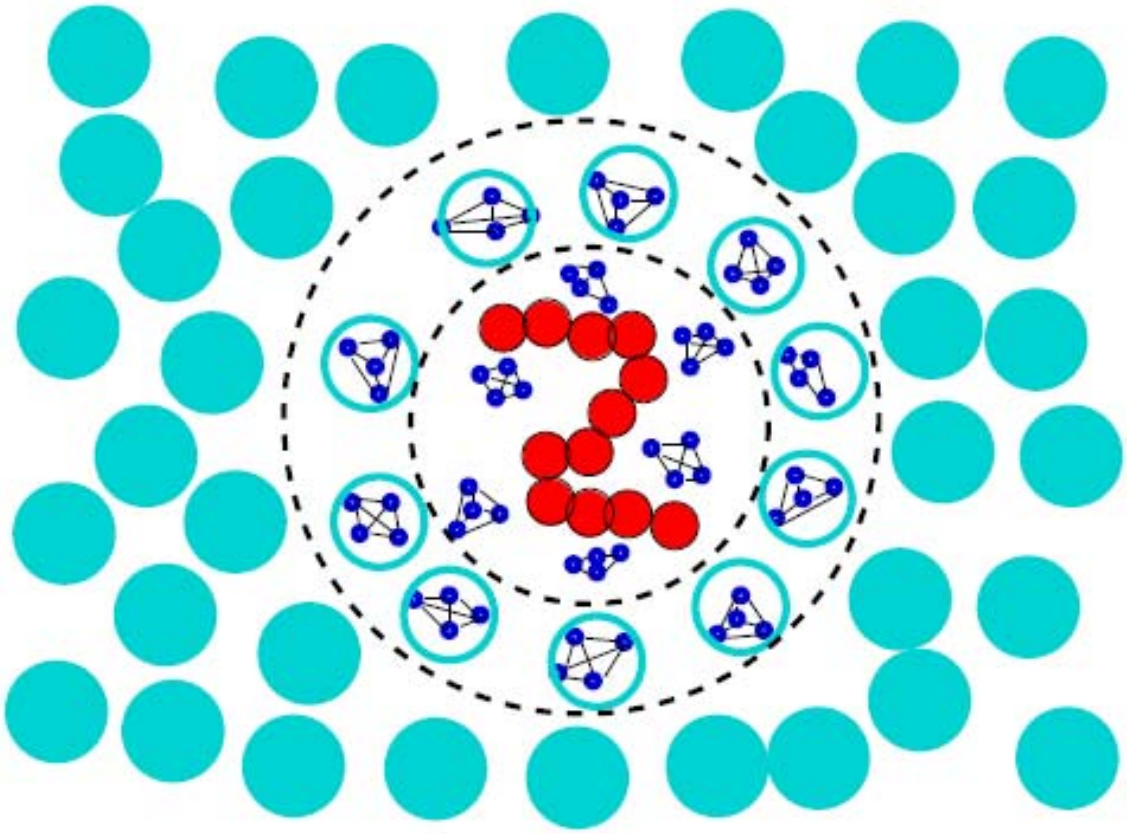


Particle Numbers, Density



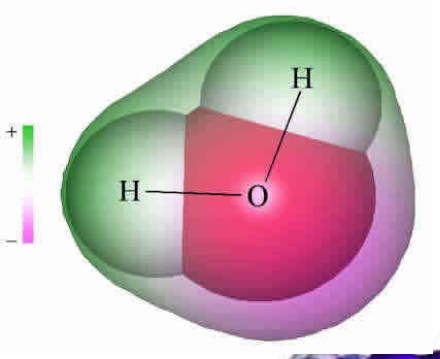


1st Application: Chain in solvent

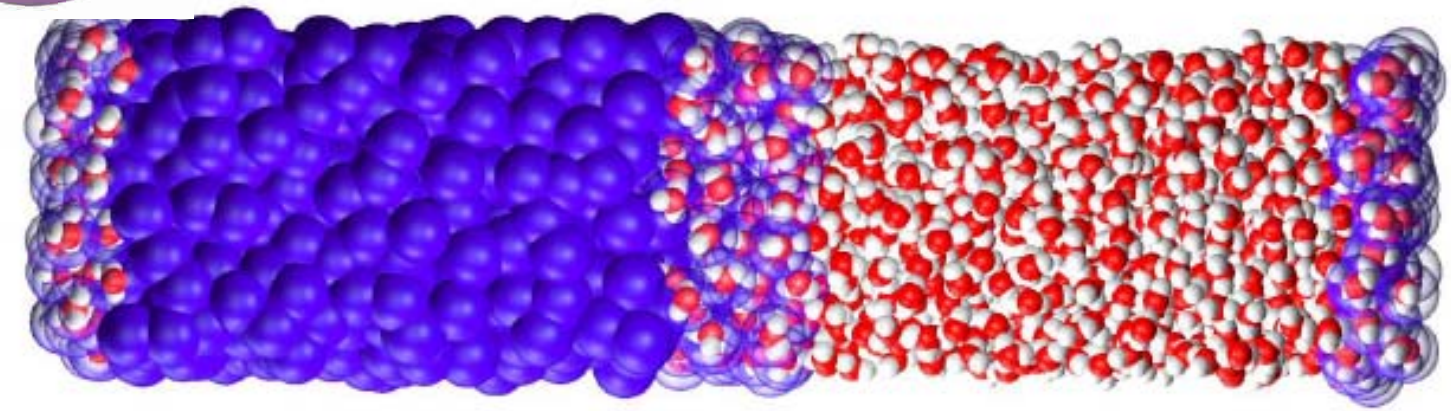


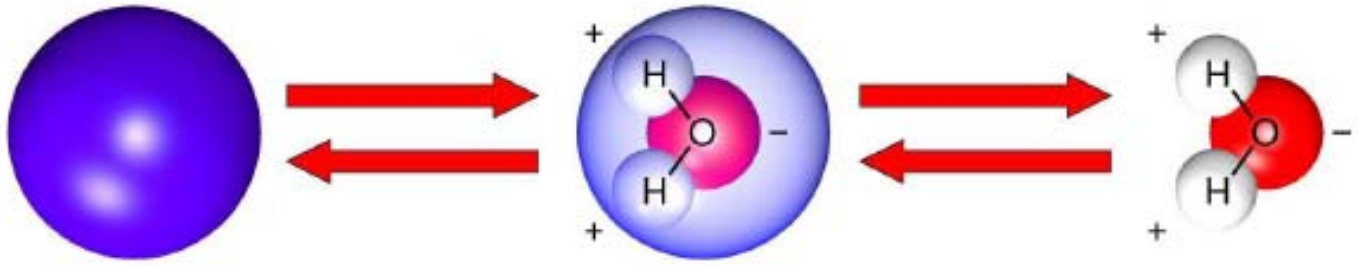
Explicit resolution regime moves with the polymer

M. Praprotnik, L. Delle Site, KK, JCP (2007)



2nd Application TIP3P Water





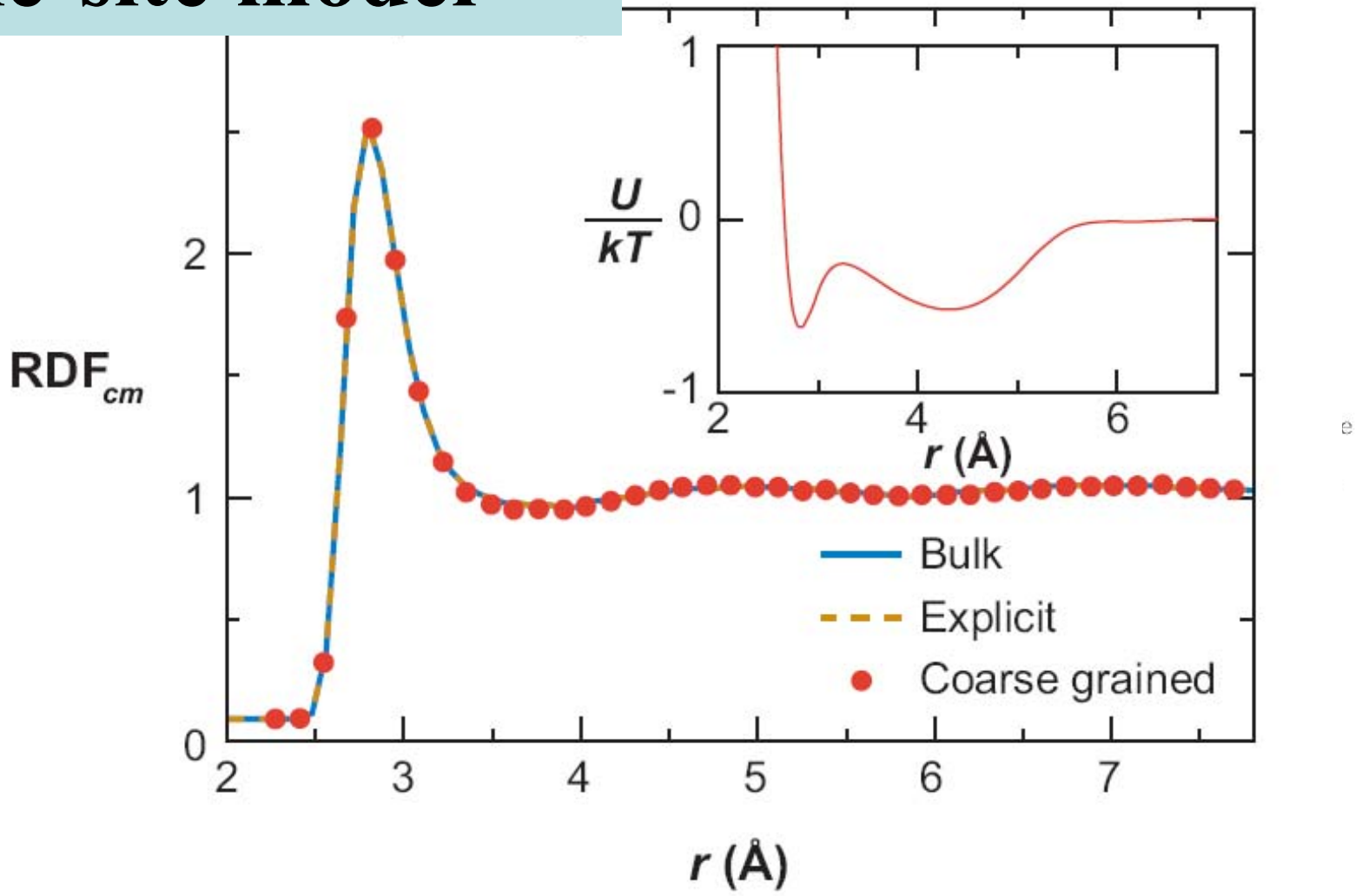
coarse-grained model, effective interactions

adaptive, hybrid scheme to switch from one to the other "on-the-fly"

all-atom model, physical force-field

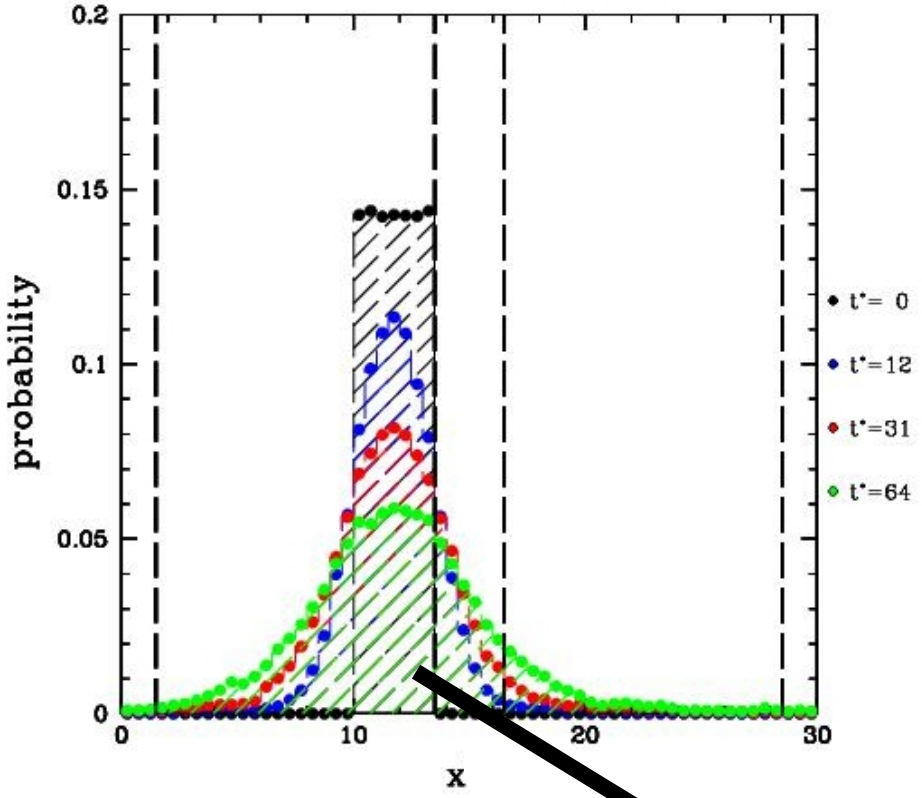
M. Praprotnik, S. Matysiak, L. Delle Site, K. Kremer, C. Clementi; J. Phys.: Condens. Matter; 19, 292201 (2007).

Single-site model

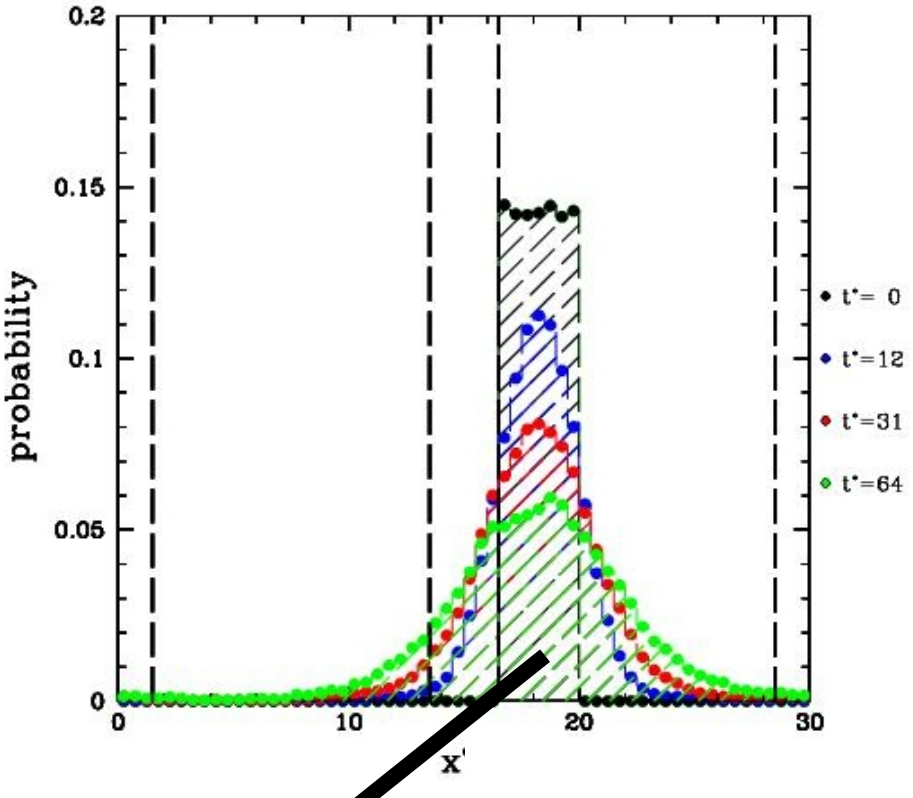


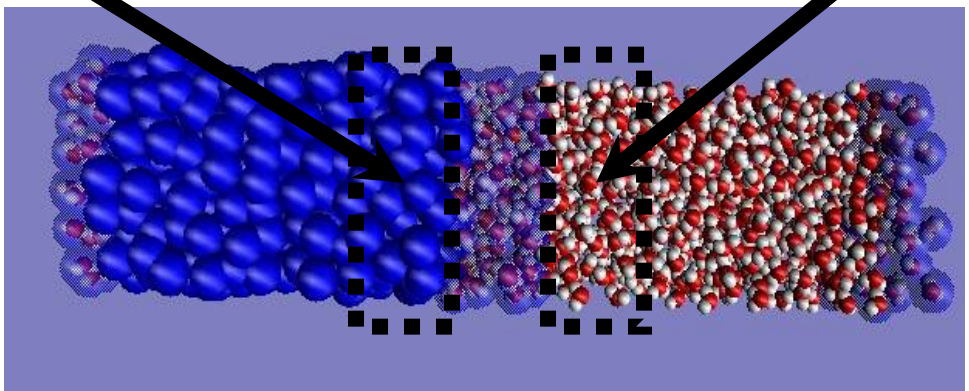
Pressure, temperature are also in excellent agreement, 4 nearest neighbors in first shell,
tetrahedral order in 2nd shell for cg model almost completely lost

coarse grained hybrid explicit

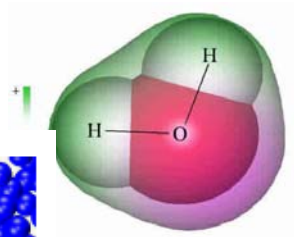


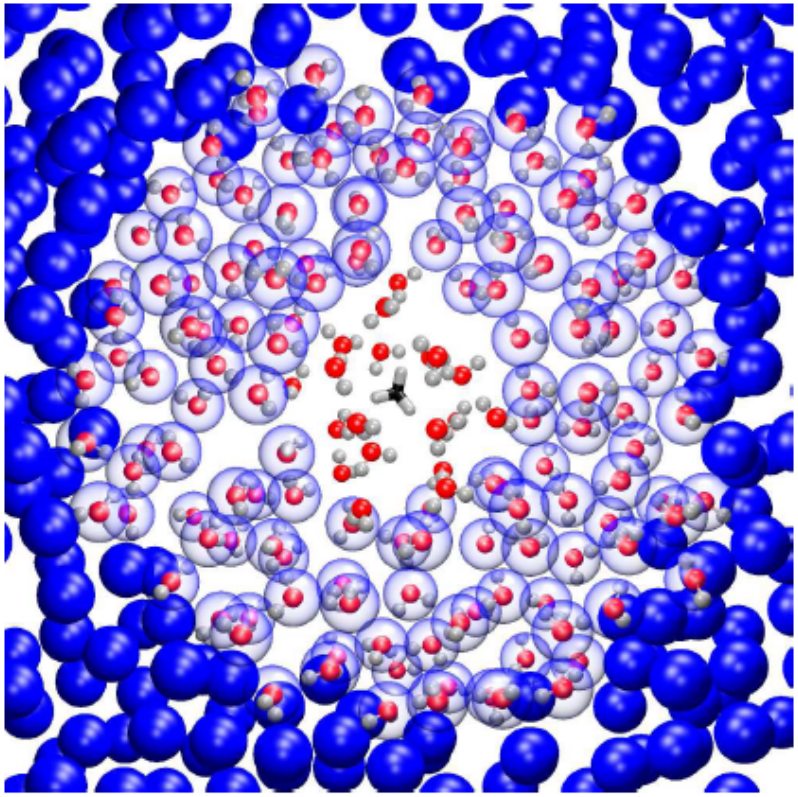
coarse grained hybrid explicit

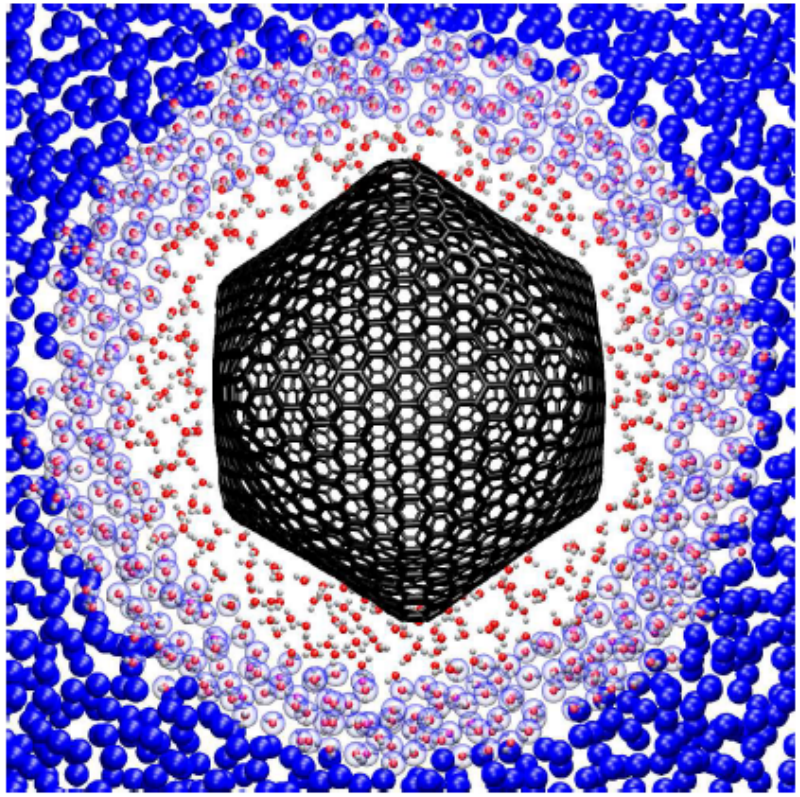




3rd Application Hydrophobic Solutes

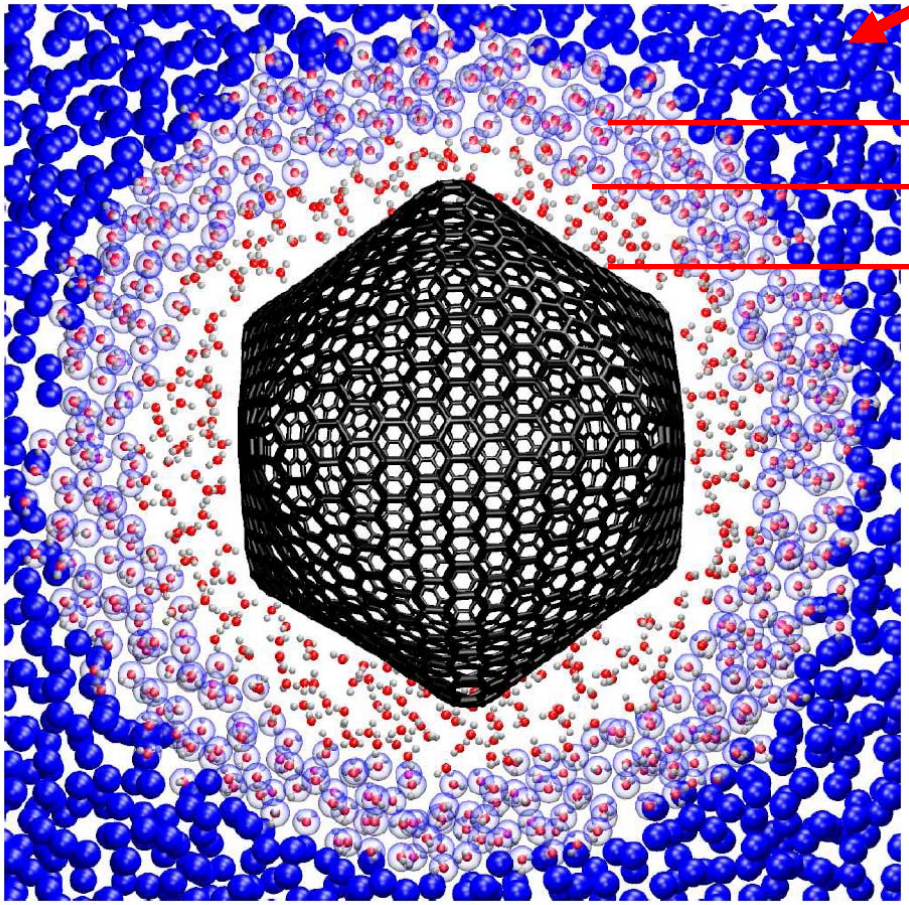






C. Junghans, B. P. Lambeth, C. Clementi, L. Delle Site, KK JCP 2010

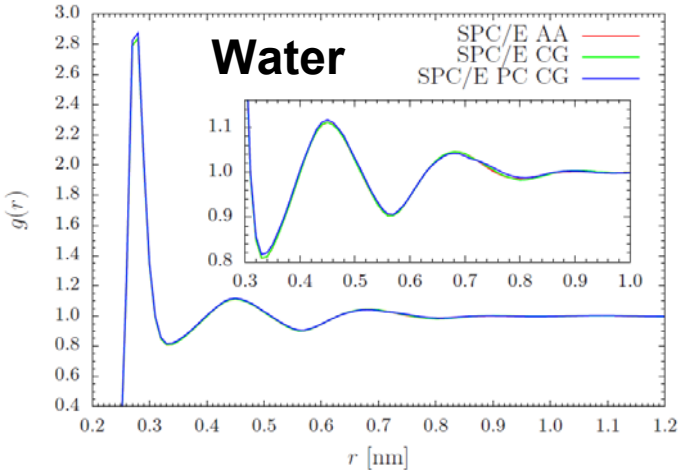
Hydrophobic Solutes: Surface vs Bulk



CG regime

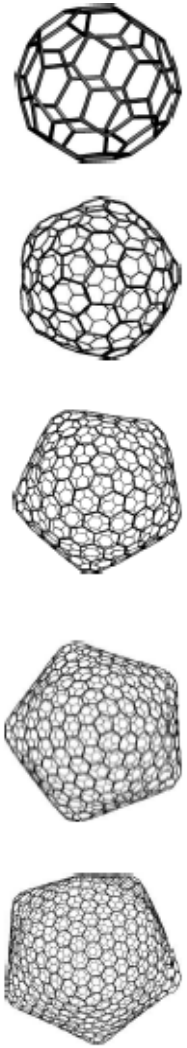
Transition layer

All atom layer, d_{ex}



cg water reproduces g(r)
but NOT tetrahedral packing!

Hydrophobic Solutes

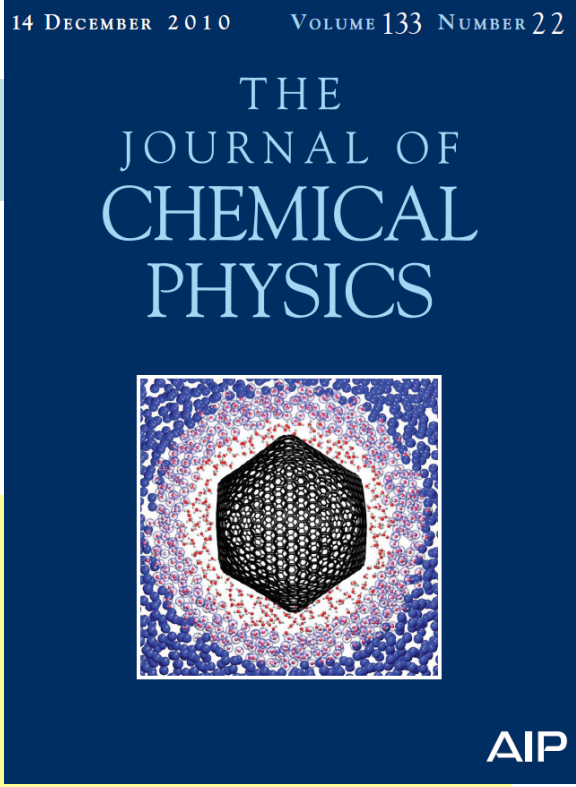


C_{60}

C_{2160}

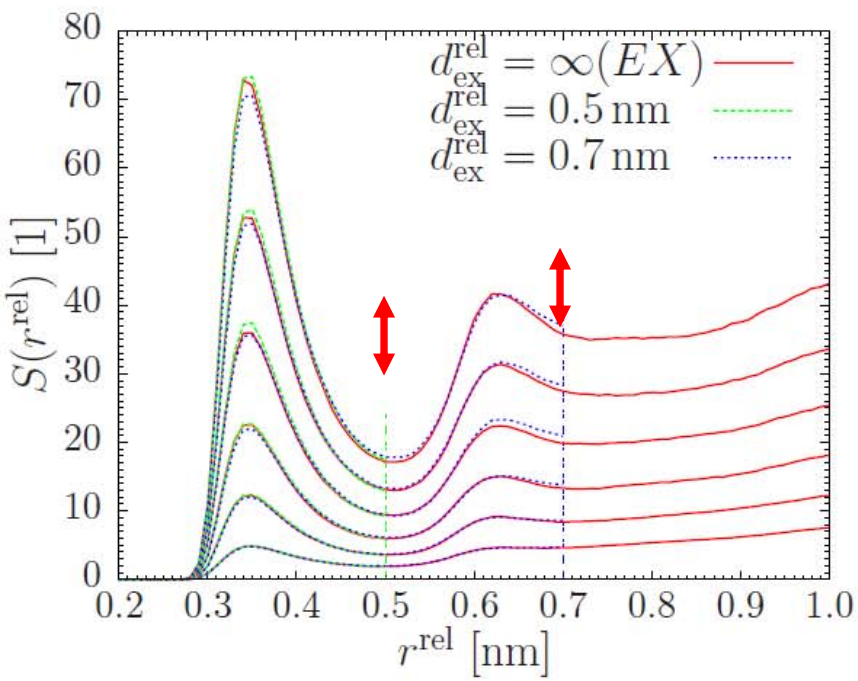
Influence of bulk H-bond structure on surface layer

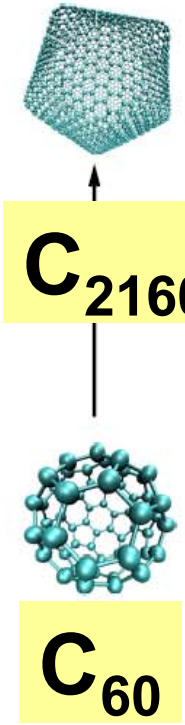
 # two surface potentials
- standard (weak) Lennard Jones
($\varepsilon_{CO} \approx 0.2 k_B T$, $\sigma_{CO} \approx 0.34$nm)
- purely repulsive (r^{-12})
 # variable width of explicit layer



of Water Molecules around Solute, variable all atom water layer

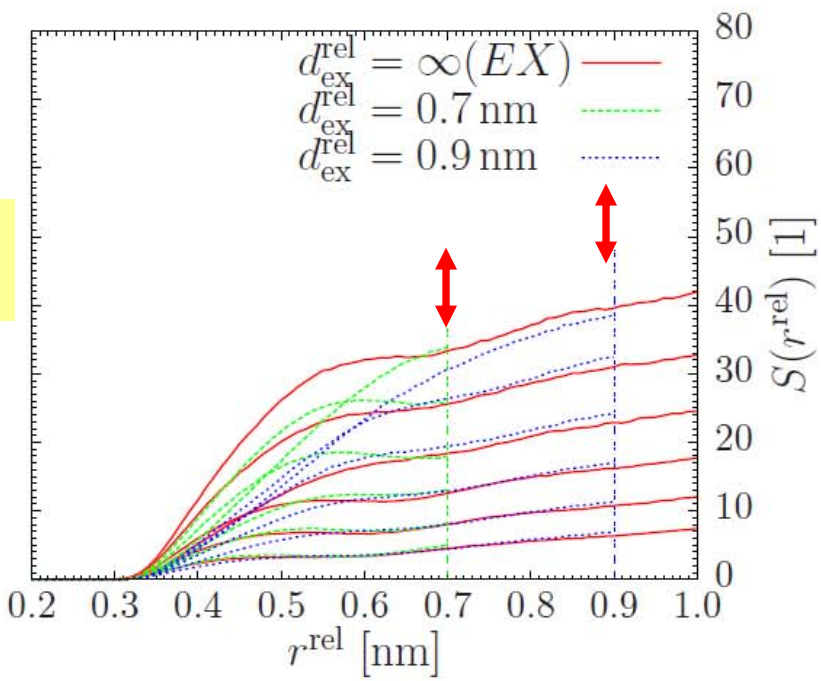
d_{ex} (≈ 1st, 2nd shell, ∞)





C_{2160}

C_{60}

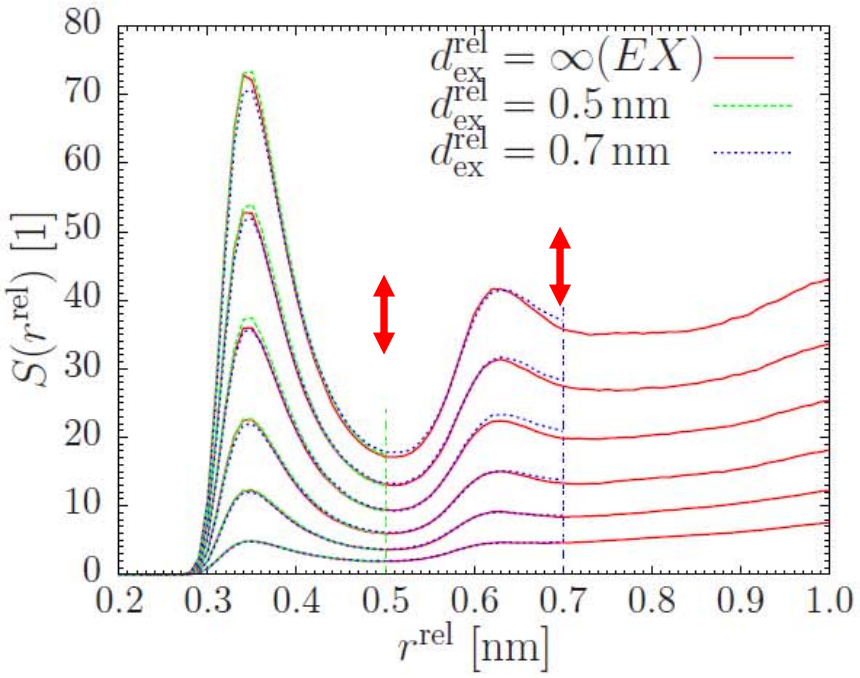


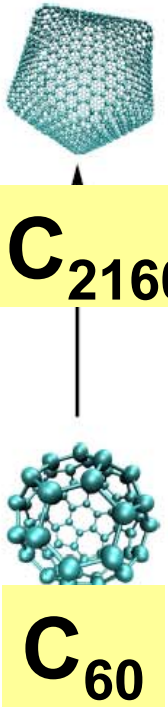
LJ interaction
dominated by surface Interaction

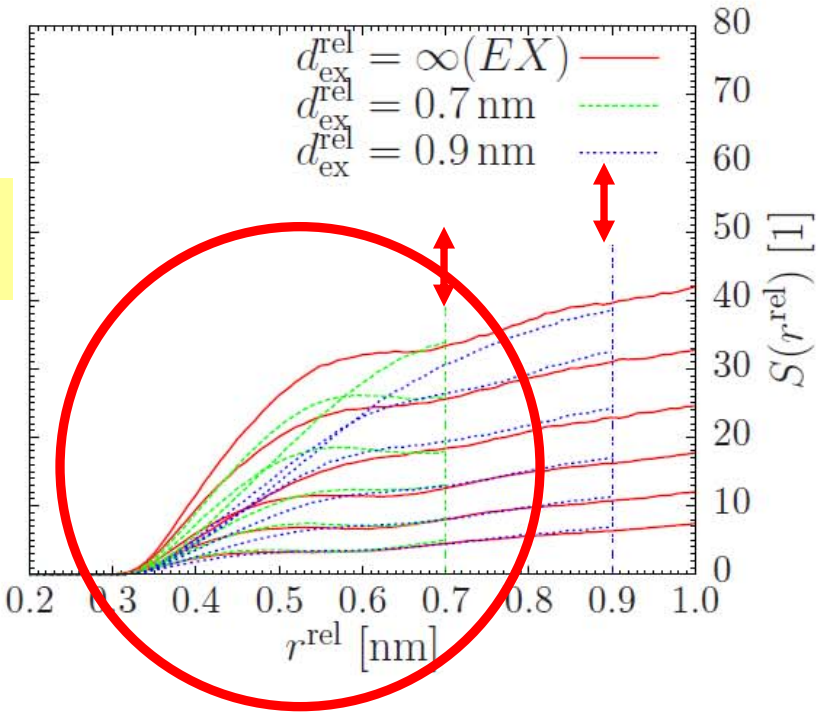
Repulsive
# of waters close to surface strongly depleted

of Water Molecules around Solute, variable all atom water layer

d_{ex} (≈ 1st, 2nd shell, ∞)



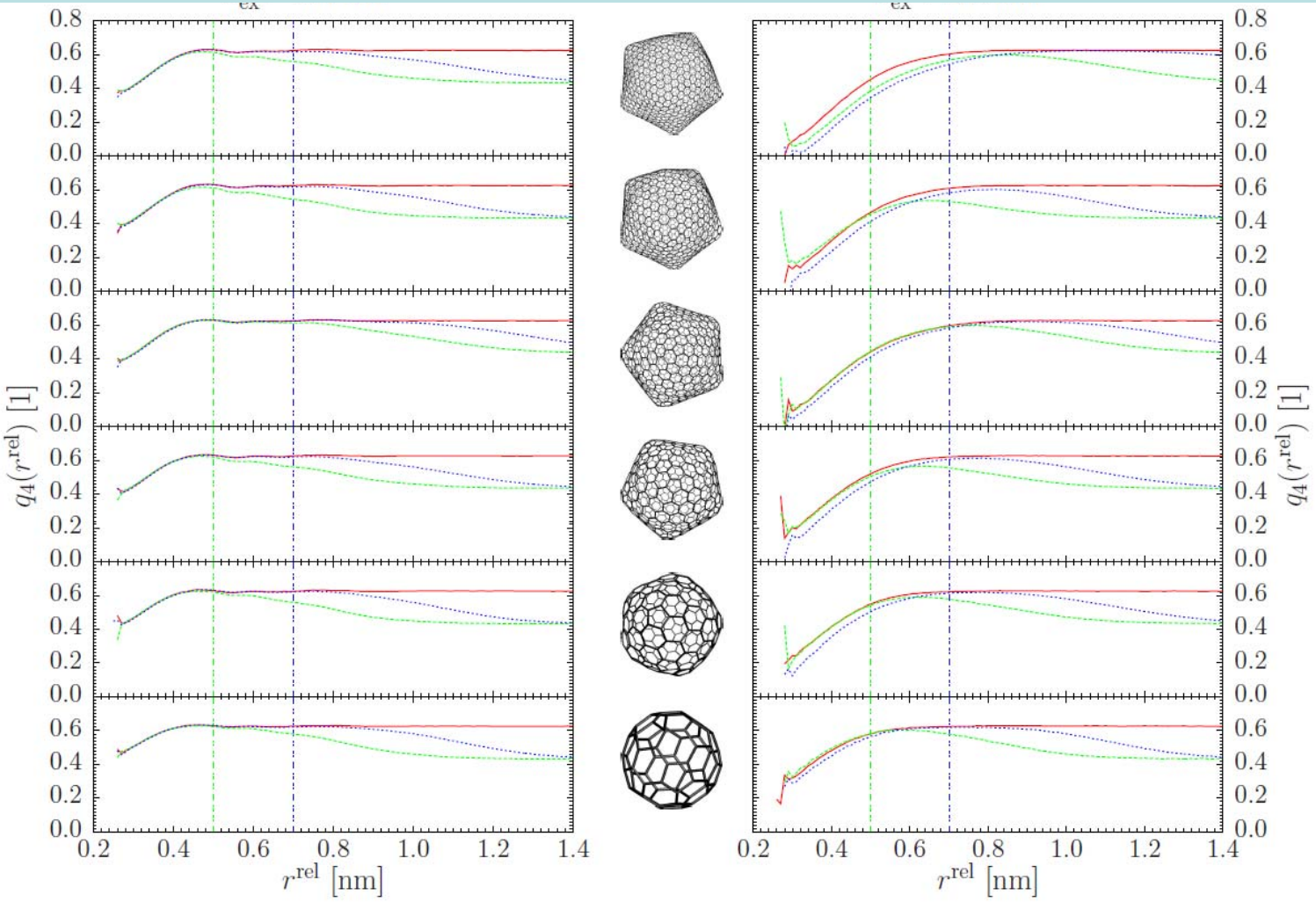




LJ interaction
dominated by surface Interaction

Repulsive
# of waters close to surface strongly depleted

Tetrahedral Order

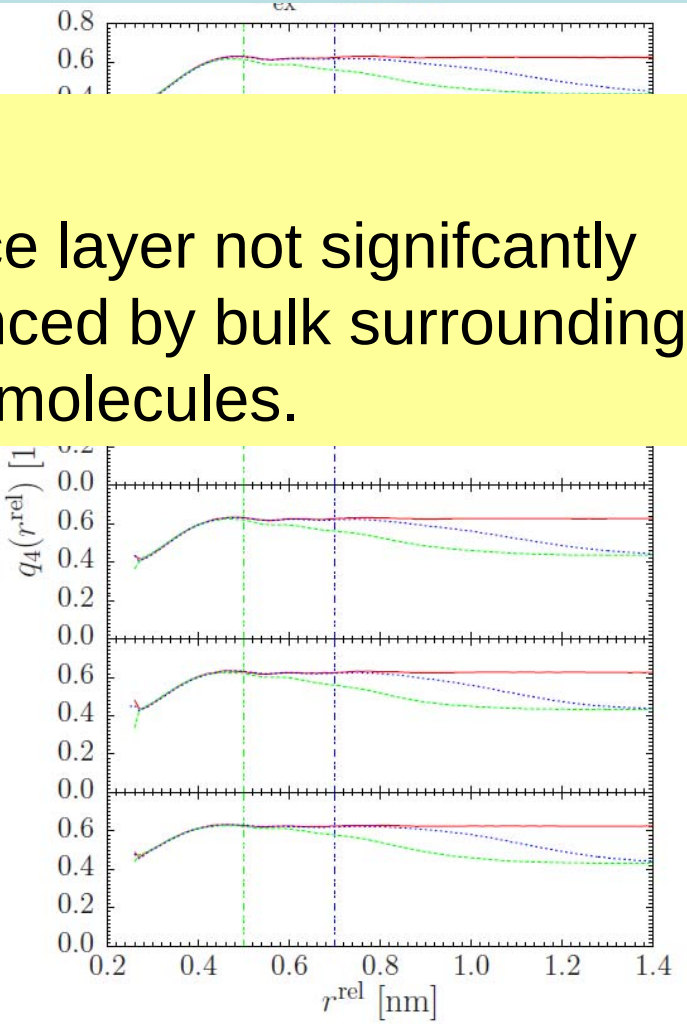


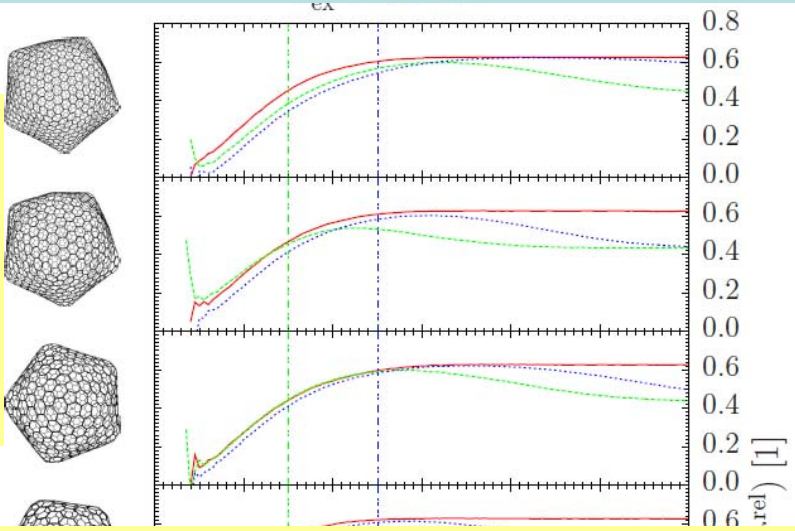
LJ

$$q_4 = 1 - \frac{3}{8}\sum_{i<j}\left[\cos(\theta_{ij}) - \frac{1}{3}\right]^2,$$

Repulsive

Tetrahedral Order





LJ:
Surface layer not signifcantly influenced by bulk surrounding for all molecules.

Repulsive:
Density buildup needs structural support from bulk,
order parameter seems independent of density
(Compensation of effects?).

LJ

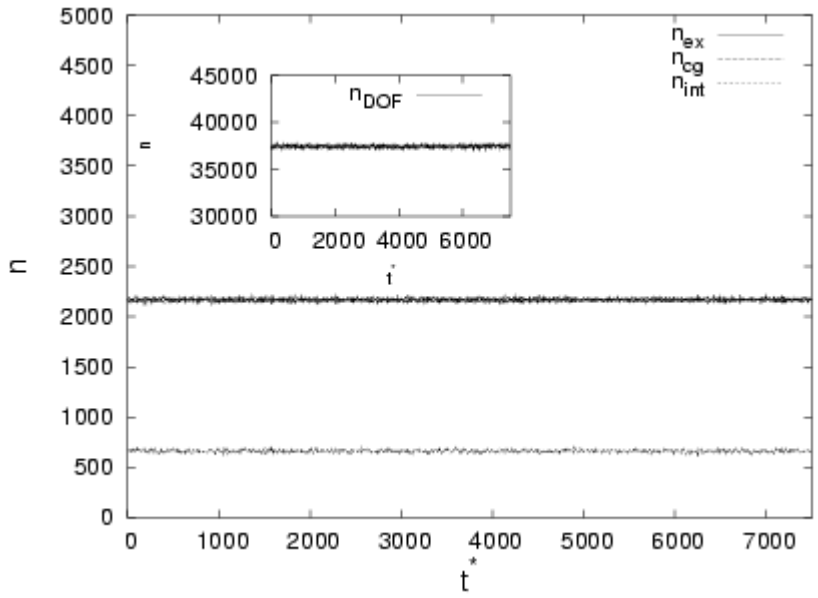
$$q_4 = 1 - \frac{3}{8}\sum_{i<j}\left[\cos(\theta_{ij}) - \frac{1}{3}\right]^2,$$

Repulsive

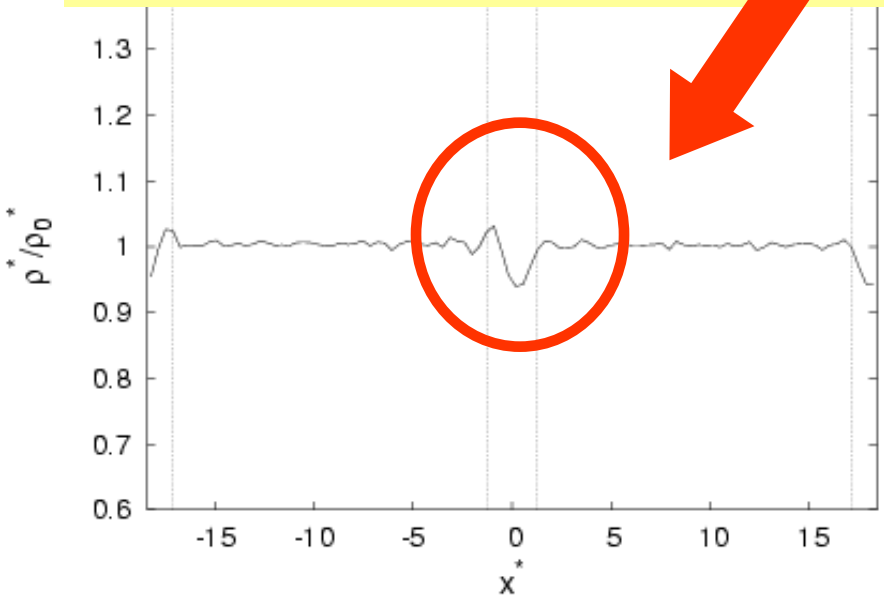
Transition Regime, Generalizations

Density wiggles in transition regime
=> thermodynamic force to level off pressure
Generalization
=> "Open System" MD

Particle Numbers, Density

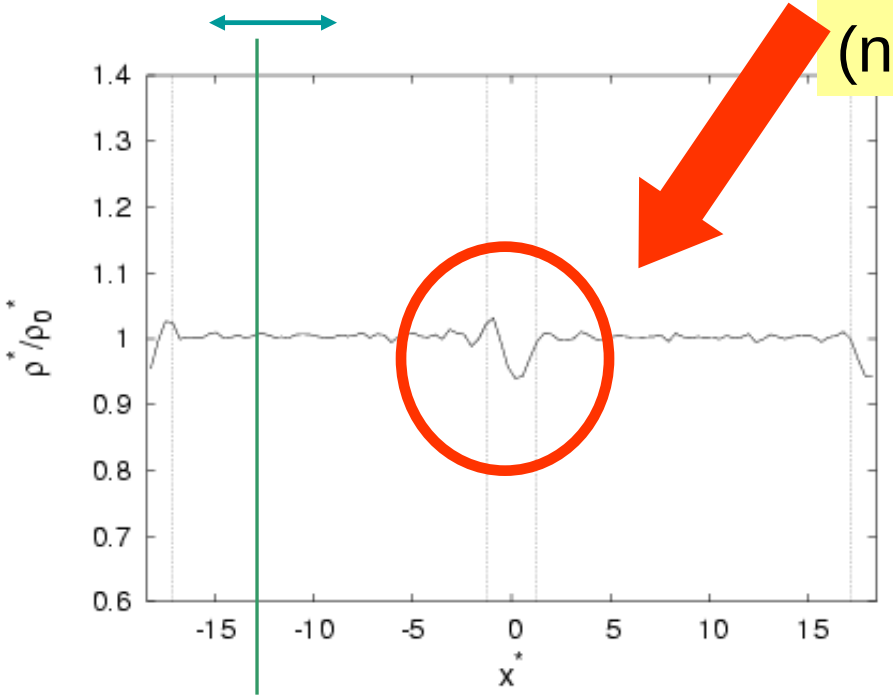


Equation of state in transition Regime not the same!



Pressure

Equation of state in transition regime not the same!
(not surprising)



No potential energy function in whole system,
but
well defined forces and thus well defined pressures

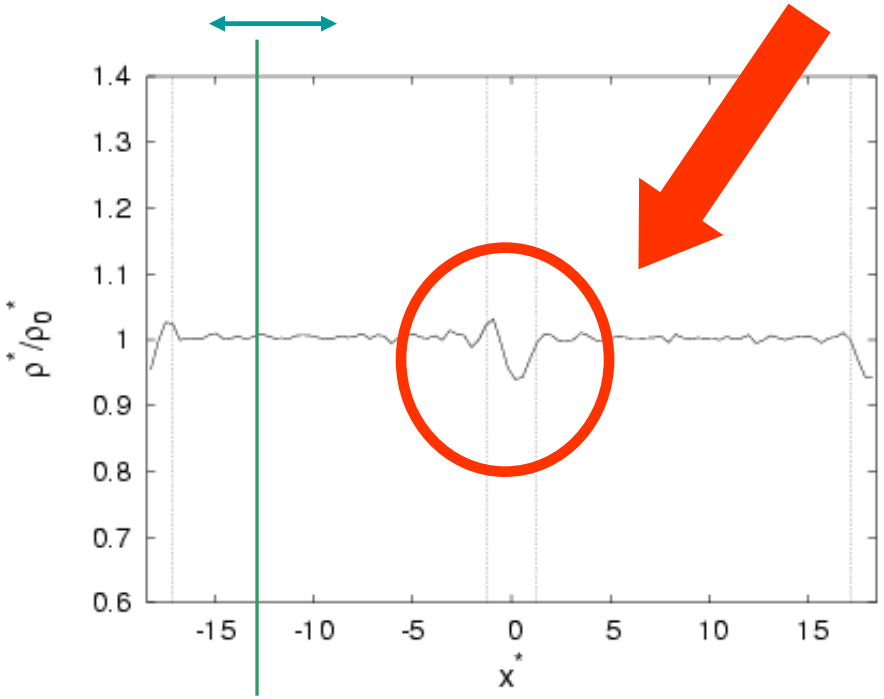
Calculate pressure in a plane ⊥ x **(Todd, Evans, Davies)**

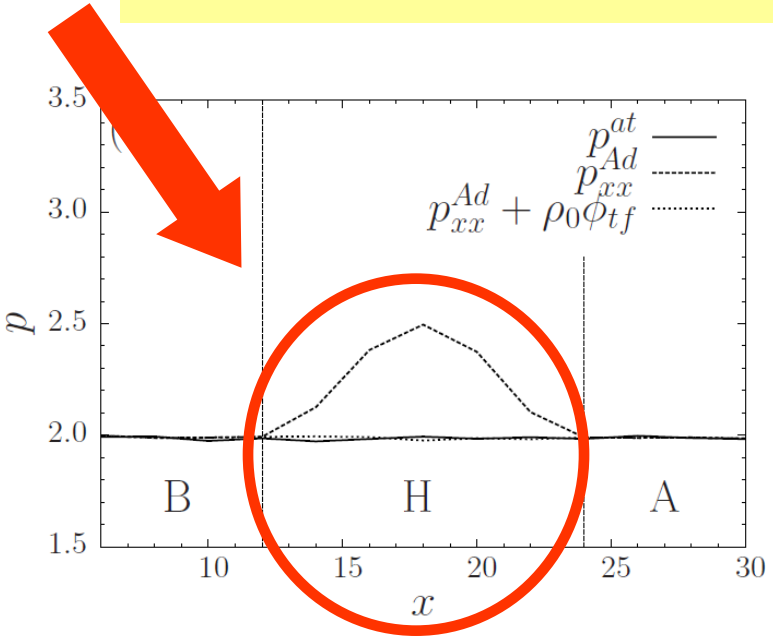
$$\bar{p}_{\beta\alpha}(\alpha) = \frac{1}{2A_\alpha \Delta\alpha}\Big\langle \sum_{\alpha-\Delta\alpha\le\alpha_i\le\alpha+\Delta\alpha} m_i v_{i\beta} v_{i\beta}\Big\rangle + \frac{1}{2A_\alpha}\Big\langle \sum_{i=1}^{N} F_{i\beta}\, sgn(\alpha_i-\alpha)\Big\rangle$$

S. Poblete, S. Fritsch, G. Ciccotti, KK, L. Delle Site, in prep.2010

Pressure

If density fixed to constant value
⇒Pressure bump in hybrid zone





Calculate pressure in a plane ⊥ x **(Todd, Evans, Davies)**

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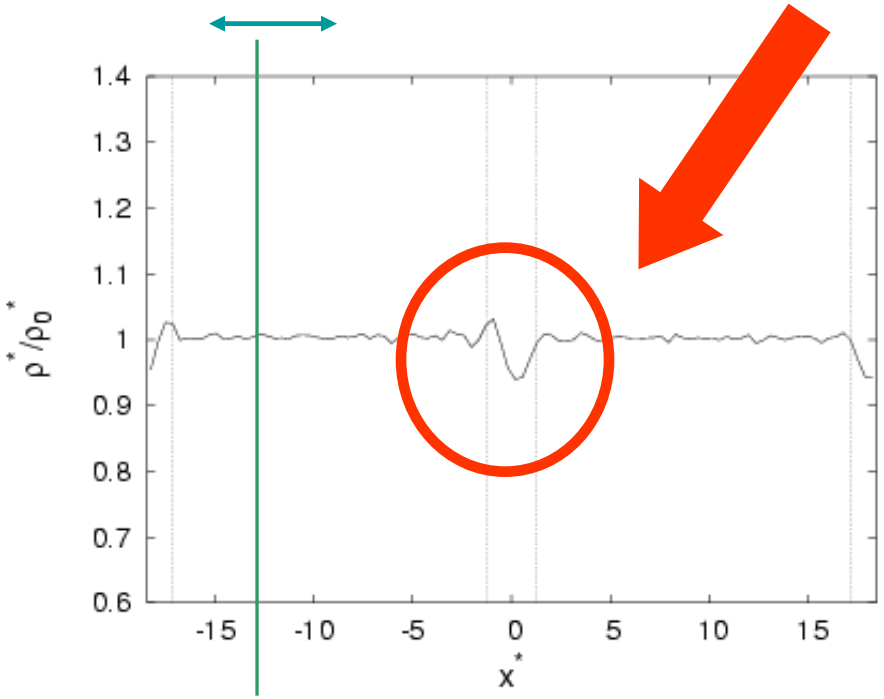
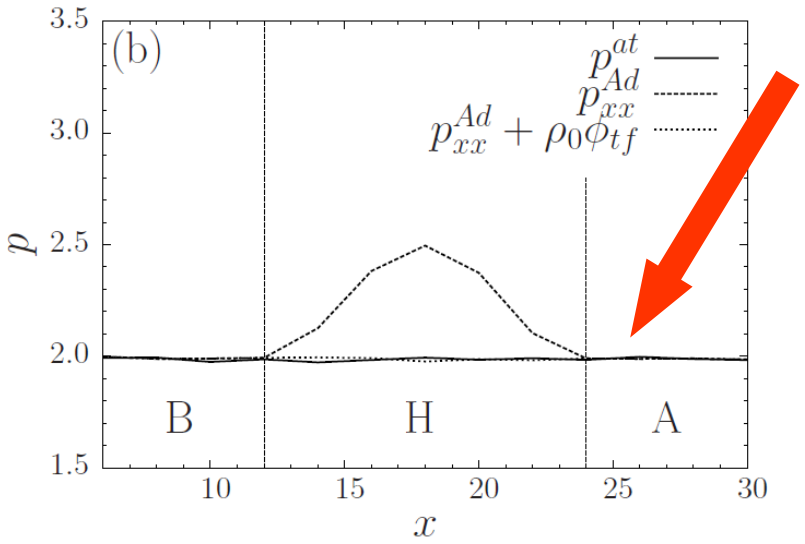
Pressure

If density fixed to constant value
⇒Pressure bump in hybrid zone
⇒Thermodynamic force, iterate

$$f_{th} = \frac{1}{\rho_0}\nabla p_f$$

Well defined constant pressure ensemble





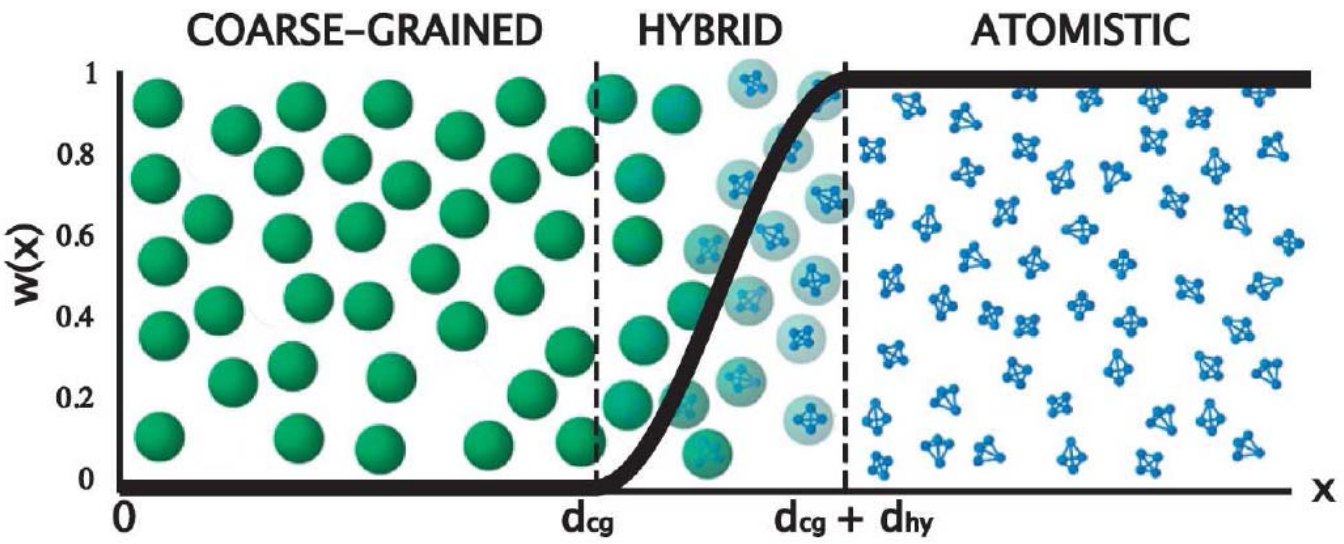
Calculate pressure in a plane ⊥ x

(Todd, Evans, Davies)

$$\bar{p}_{\beta\alpha}(\alpha) = \frac{1}{2A_\alpha \Delta\alpha}\Big\langle \sum_{\alpha-\Delta\alpha\le\alpha_i\le\alpha+\Delta\alpha} m_i v_{i\beta} v_{i\beta}\Big\rangle + \frac{1}{2A_\alpha}\Big\langle \sum_{i=1}^{N} F_{i\beta}\, sgn(\alpha_i - \alpha)\Big\rangle$$

Pressure based “Thermodynamic Force”

(alternative route via chemical potential, S. Poblete, M. Praprotnik, KK, L. Delle Site, JCP, 132, 114101 (2010))



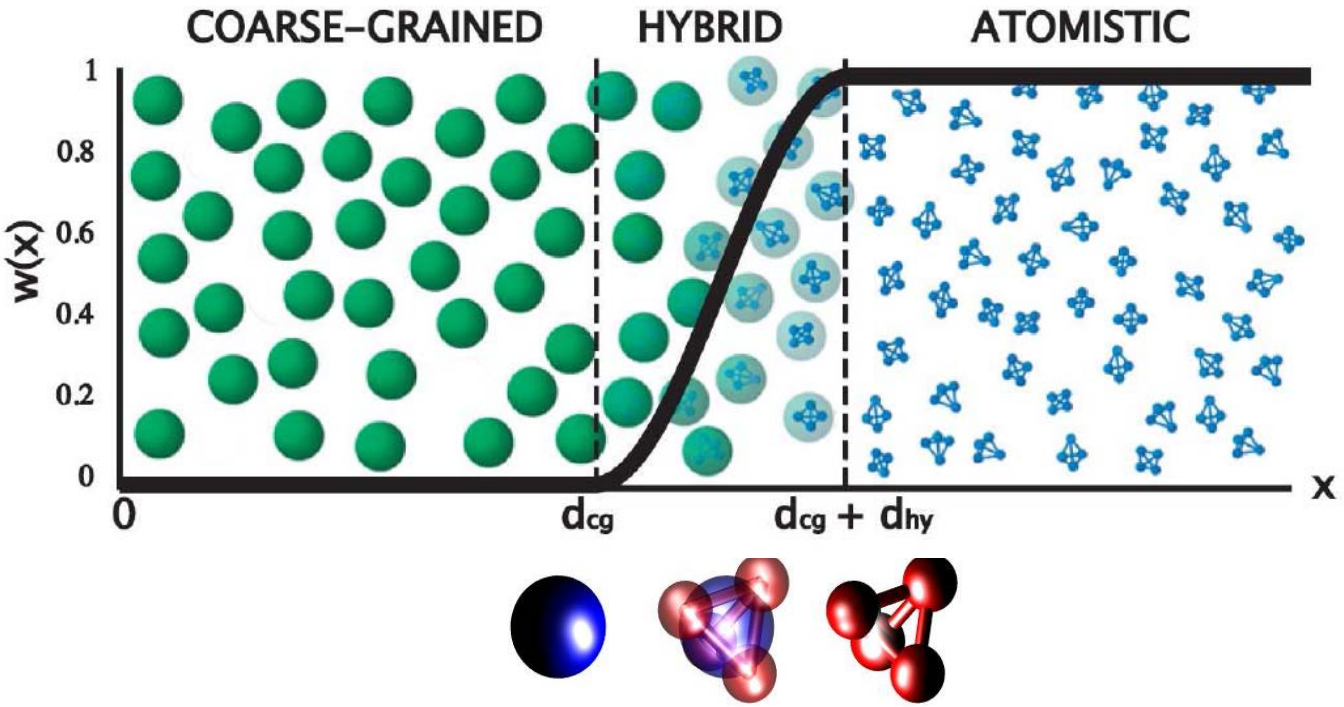
$$p(\mathbf{r}, \rho(\mathbf{r} = \rho_0)) \approx p_{ad} + \frac{1}{\rho_0 \kappa_T(\mathbf{r})} \left(\rho_0 - \rho_{ad}(\mathbf{r})\right)$$

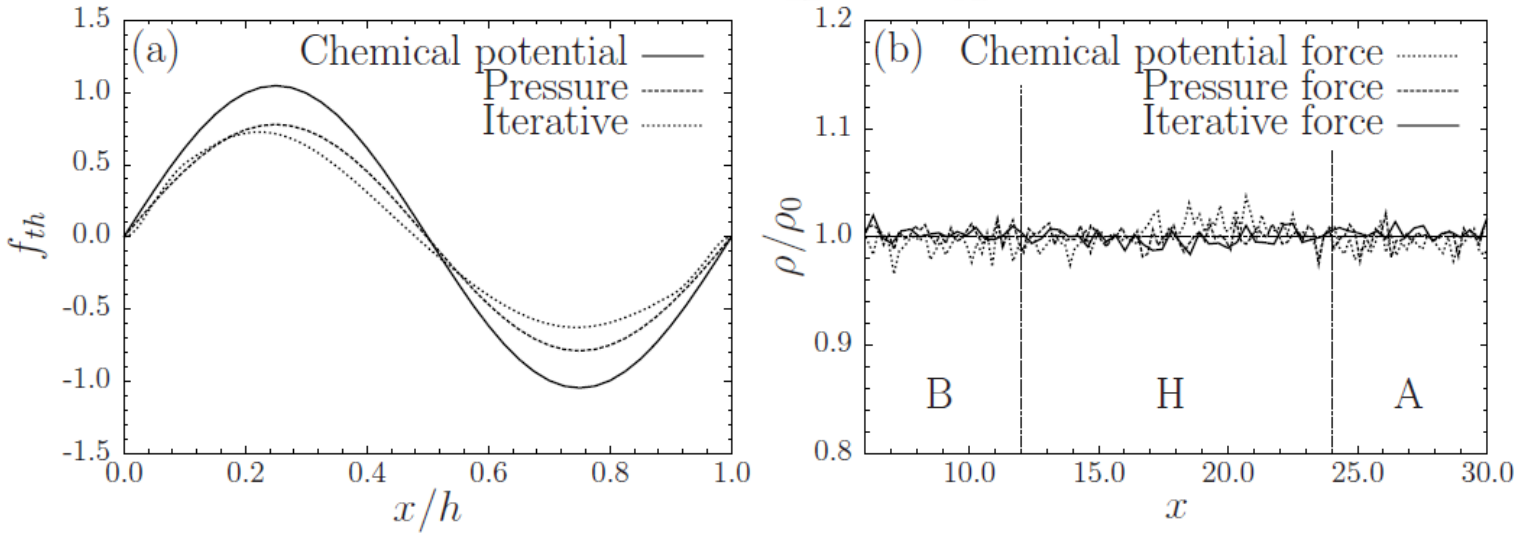
$$\mathbf{f}_{th} = -\frac{1}{\rho_0} \nabla \left(p_{at} - p(\mathbf{r})\right)$$

$$\mathbf{f}_{th}^{i+1}(\mathbf{r}) = \mathbf{f}_{th}^{i}(\mathbf{r}) - \frac{1}{\rho_0^2 \kappa_T^{at}} \nabla \rho_i(\mathbf{r})$$

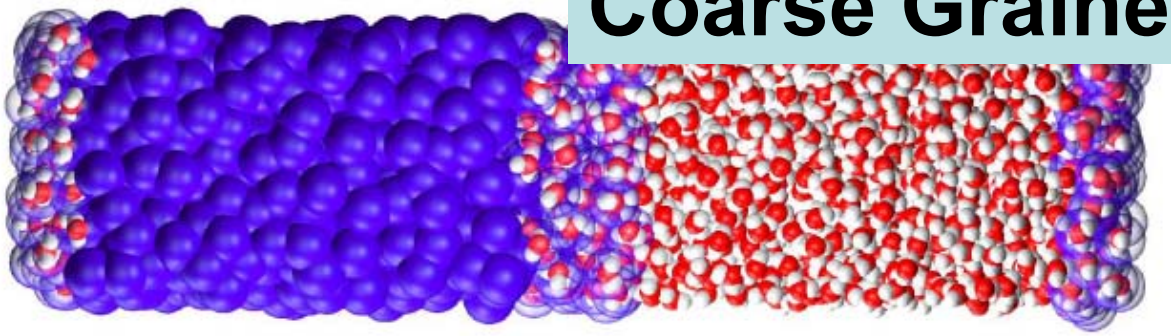
S. Poblete, G. Ciccotti, I. Delle Site, KK, in preparation

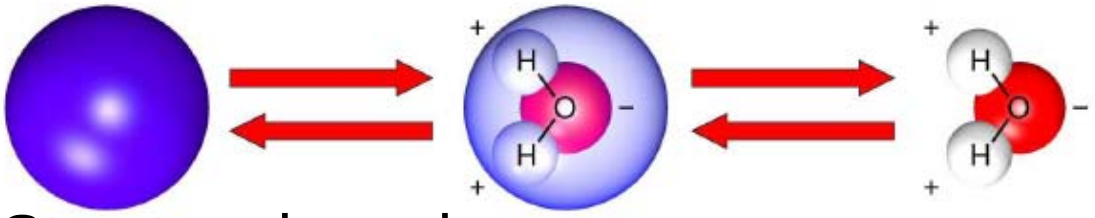
Pressure based Thermodynamic Force





Coarse Grained Water: SPC/E





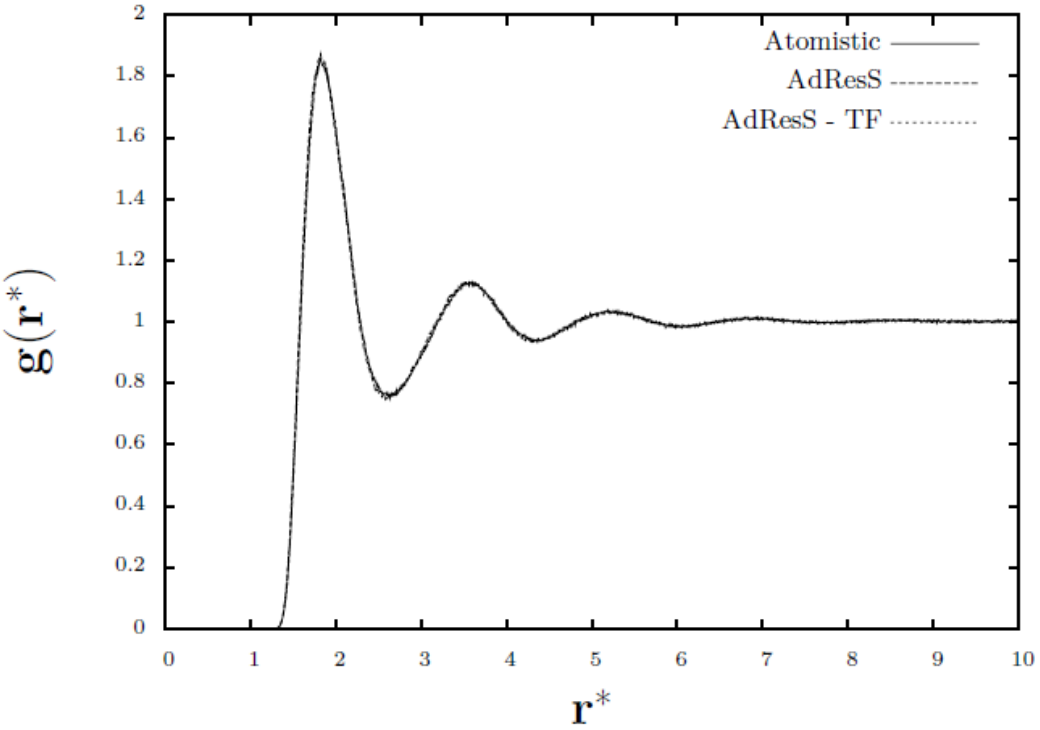
Structure based
Coarse Graining:

Perfect match of g(r)
all atom – coarse grained

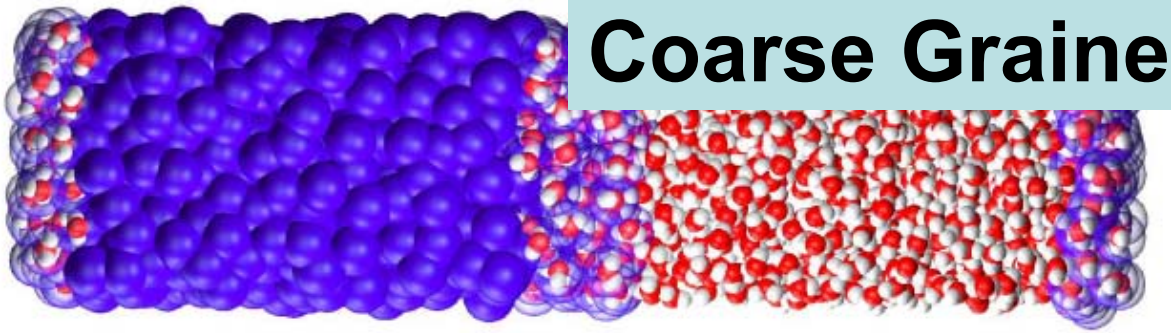
$\kappa_{atomistic} = \kappa_{cg}$

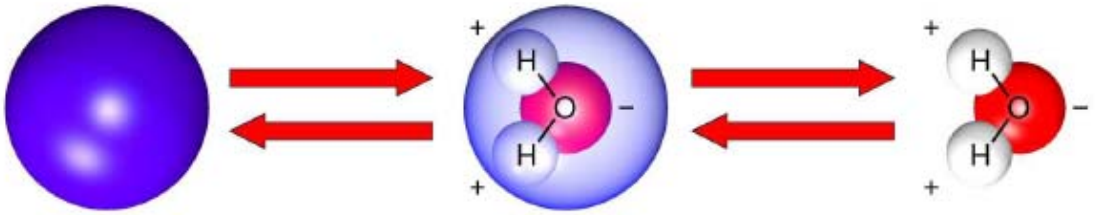
BUT

$p_{cg} = 6200 p_{atomistic}$



Coarse Grained Water: SPC/E





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Perfect match of g(r)
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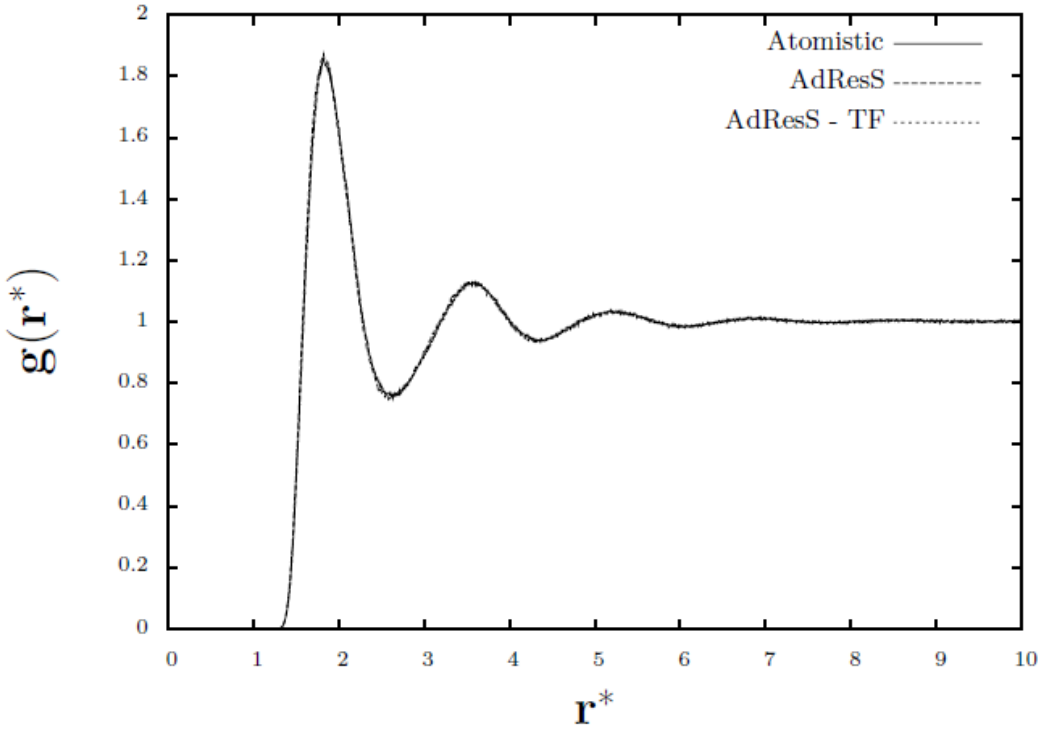
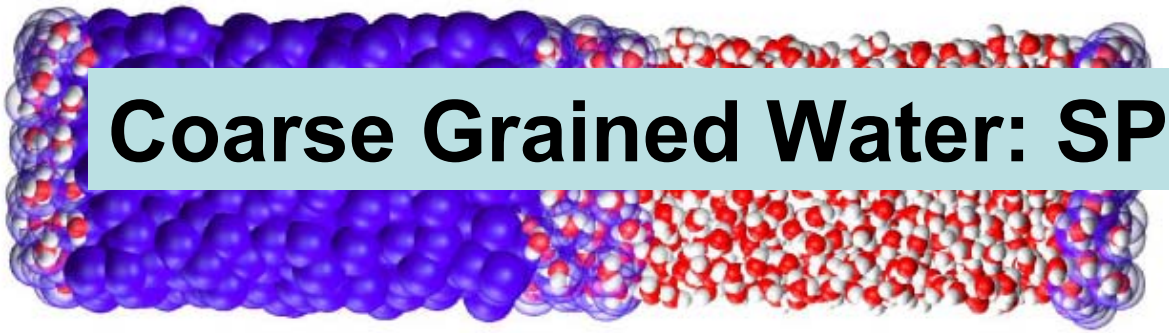
BUT

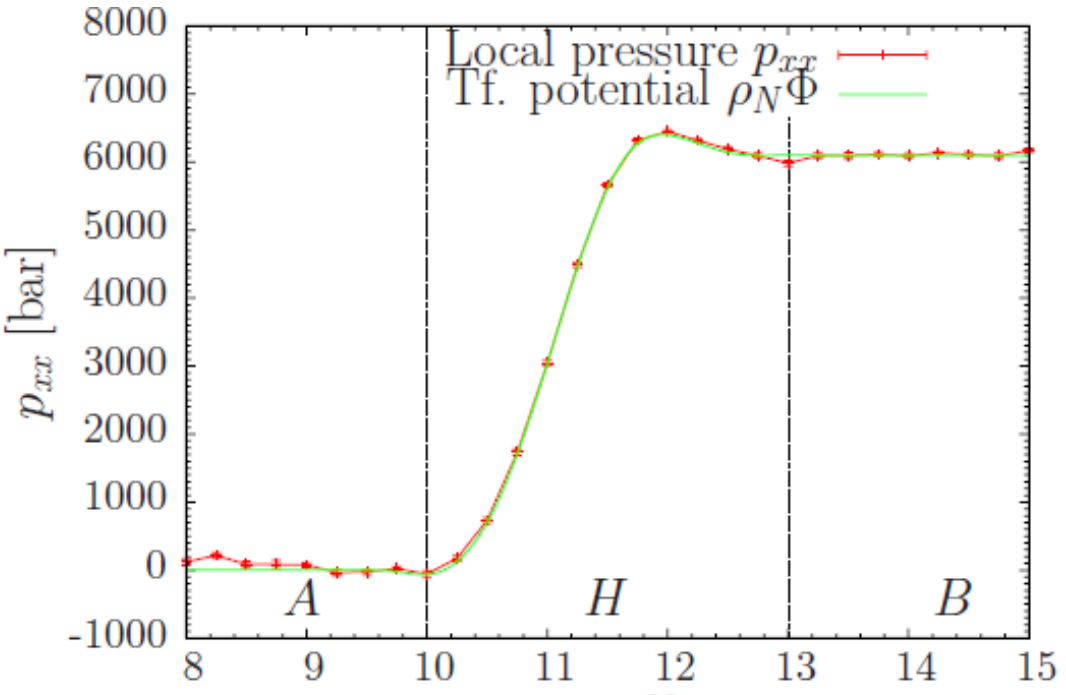
$p_{cg} = 6200 p_{atomistic}$



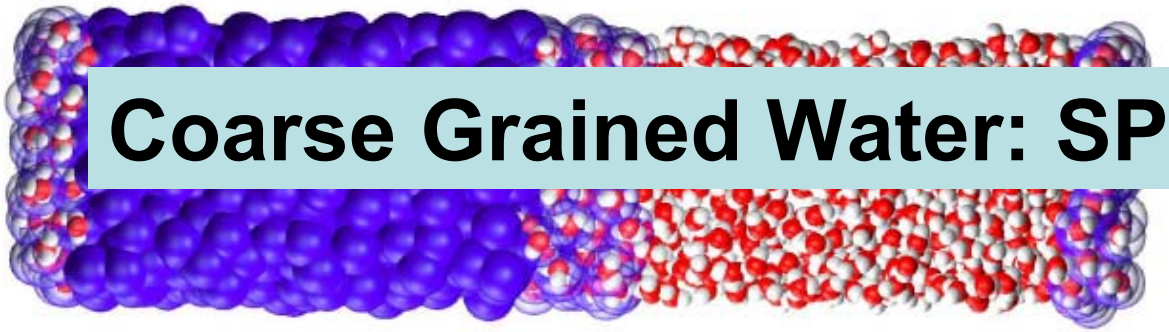


Coarse Grained Water: SPC/E

Structure based Coarse Graining: apply pressure based thermodynamic correction force

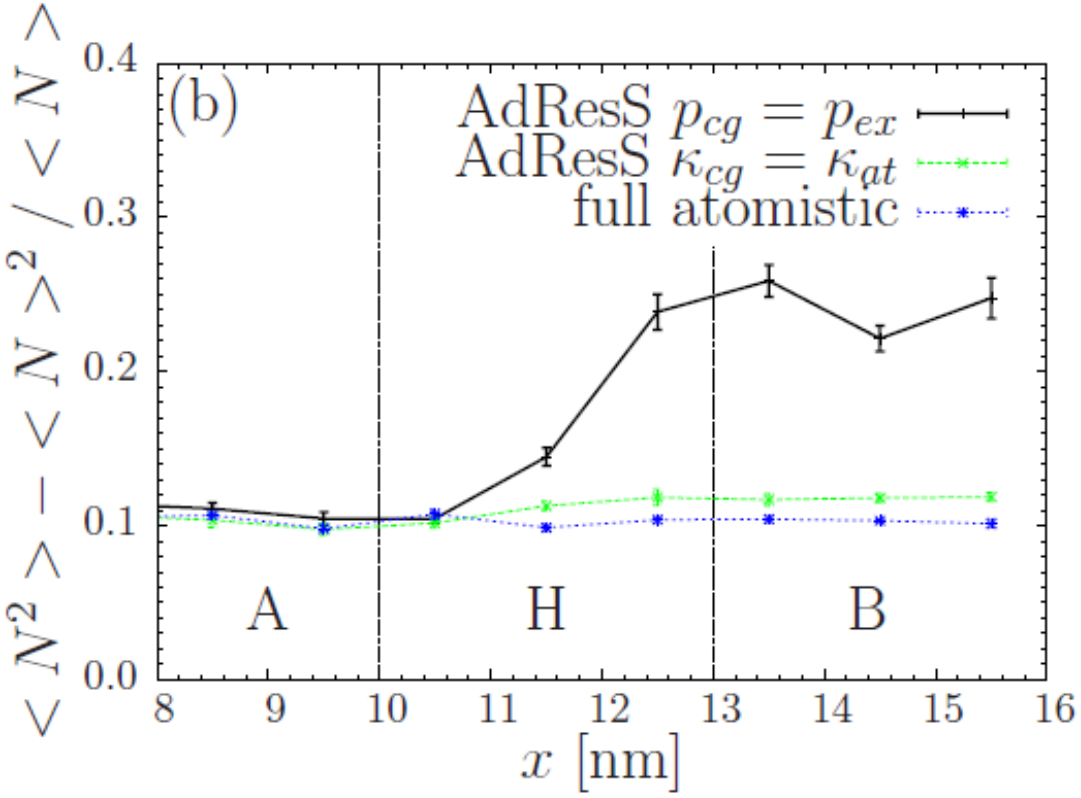


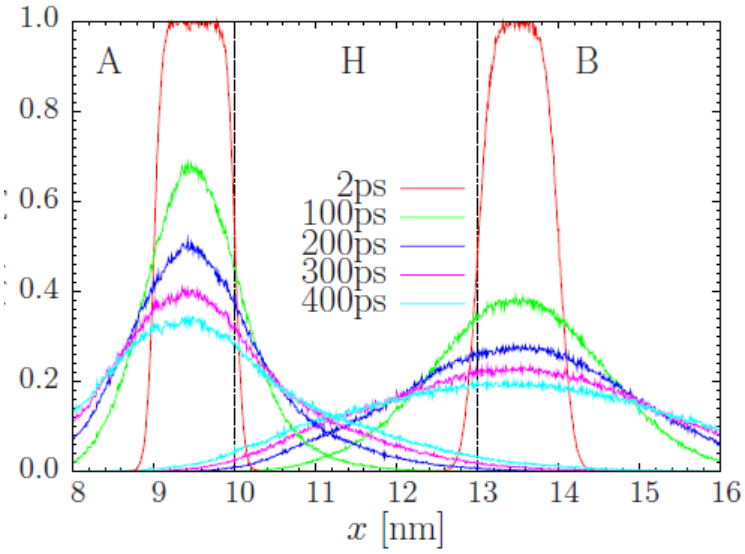
$$\bar{p}_{\beta\alpha}(\alpha) = \frac{1}{2A_\alpha \Delta\alpha}\Big\langle \sum_{\alpha-\Delta\alpha\le\alpha_i\le\alpha+\Delta\alpha} m_i v_{i\beta} v_{i\beta} \Big\rangle + \frac{1}{2A_\alpha}\Big\langle \sum_{i=1}^{N} F_{i\beta}\, sgn(\alpha_i - \alpha)\Big\rangle$$



Coarse Grained Water: SPC/E

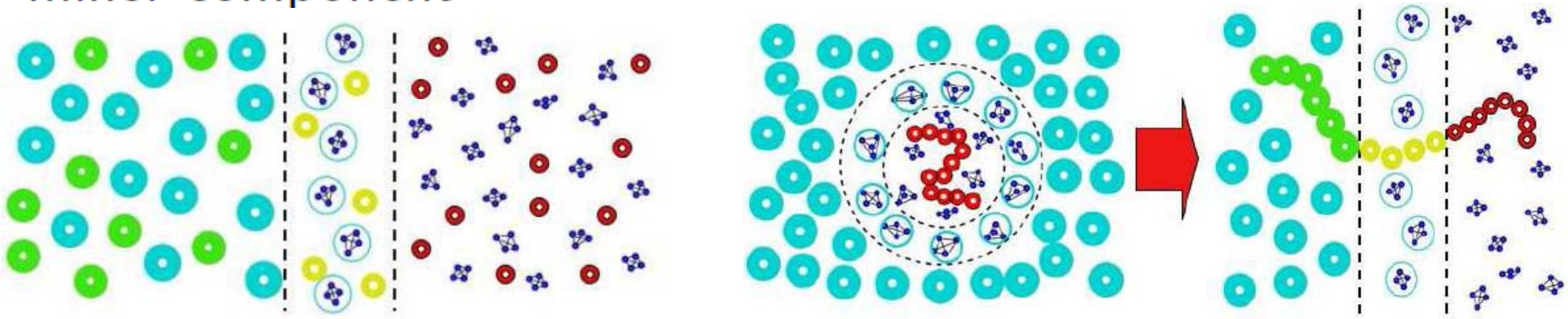
Structure based Coarse Graining: apply pressure based thermodynamic correction force



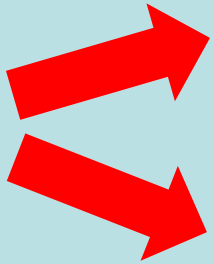


Extensions : Mixtures…

- (a) fundamental questions about the coarse-graining procedure: Structure reproduced, **but** how much of the thermodynamics?
- (b) Two species, two resolutions each: $\longrightarrow$ 4 different chemical potentials
- how to preserve equilibrium?
- Thermodynamic force proportional to the concentration of the minor component



Extensions AdResS:

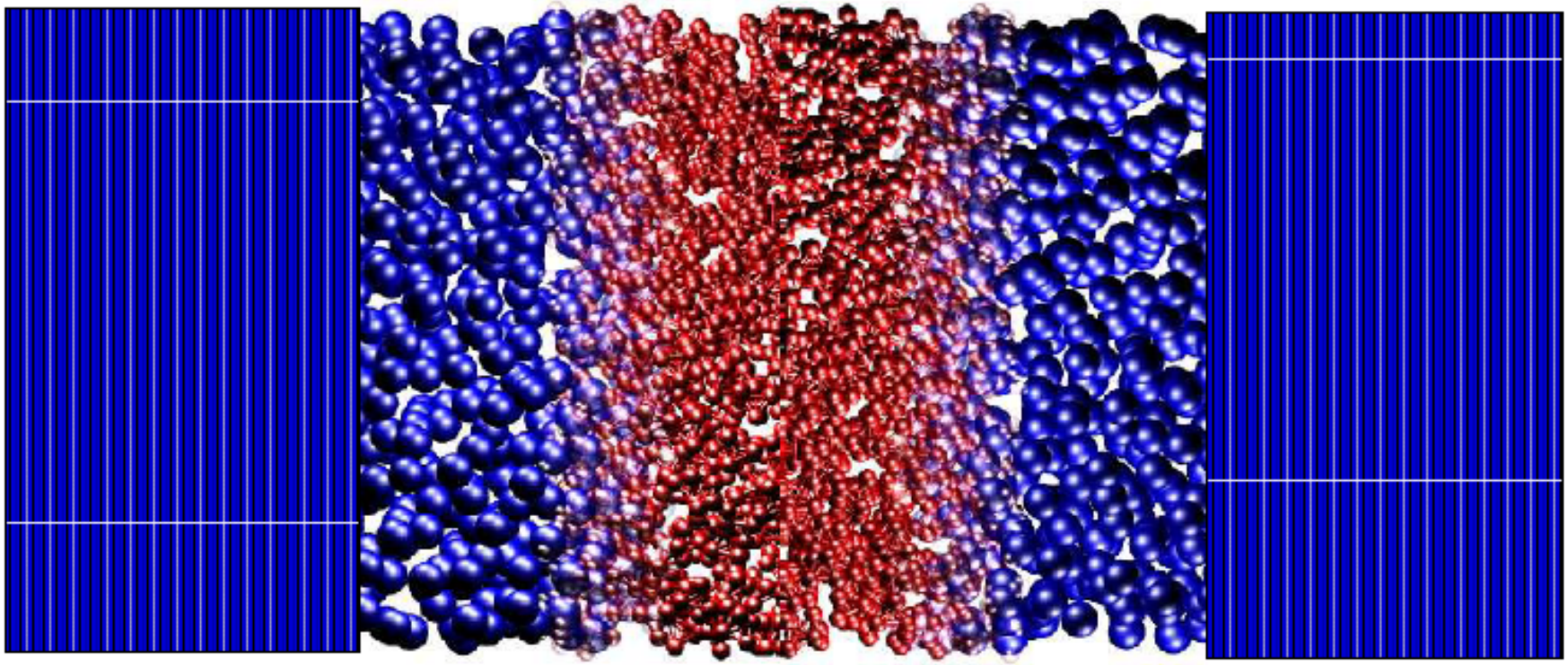


Continuum

QM Description

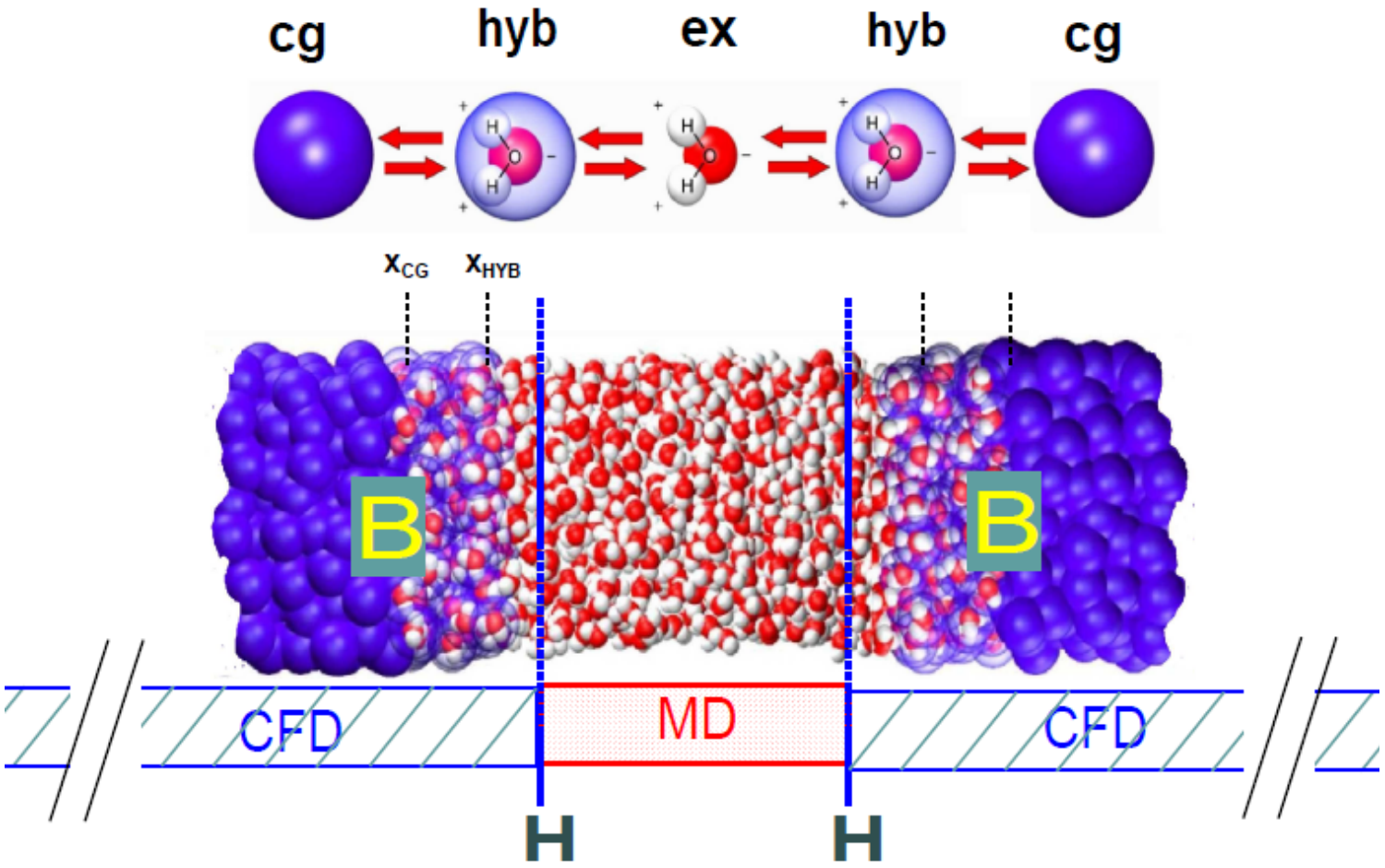
Extension I:

Concurrent Triple-Scale Simulation of Molecular Liquids



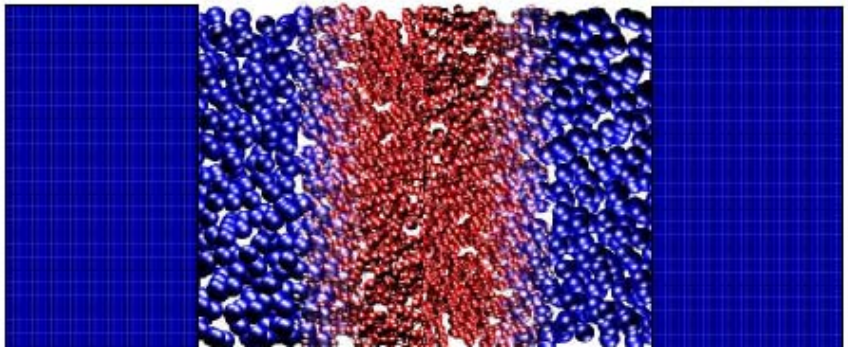
R. Delgado Buscalioni, KK, M. Praprotnik, JCP 128, 114110 (2008)

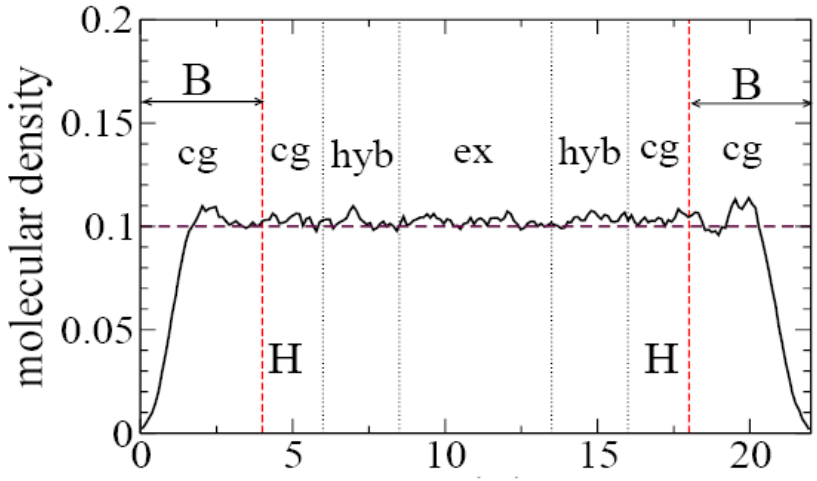
AdResS-HybridMD: Water 2nd Scheme



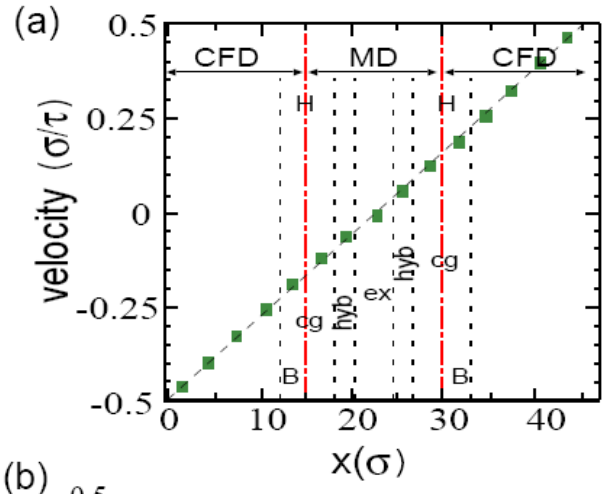
R. Delgado Buscalioni, KK, M. Praprotnik, JCP 131, 244107 (2009)

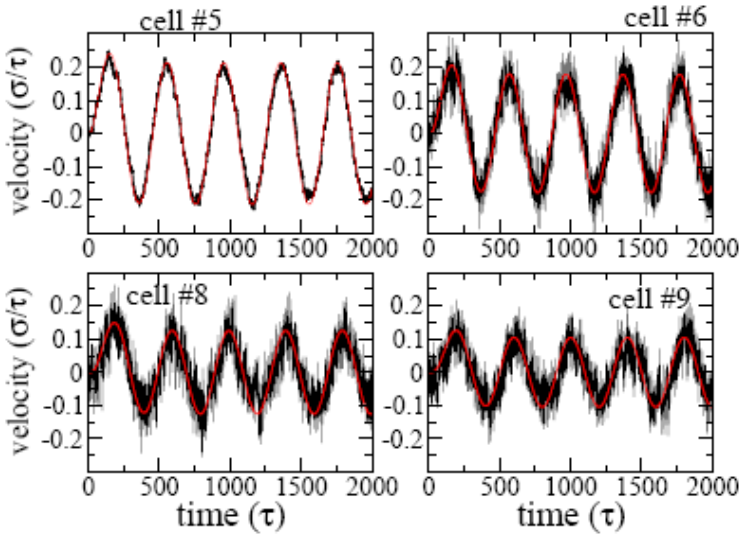
Concurrent Triple-Scale Simulation of Molecular Liquids





Simple shear





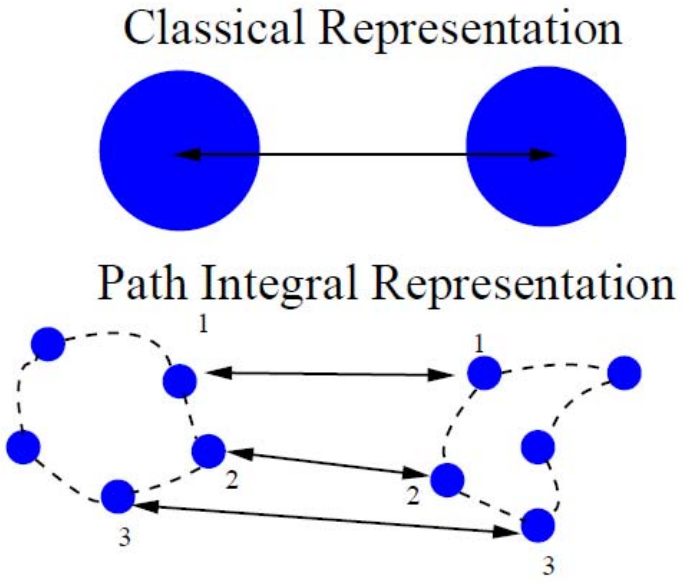
Oscillatory shear

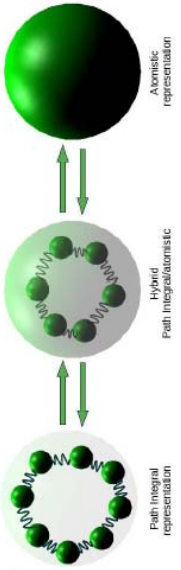
(------ exact solution)

QM-AdResS

A. Poma, L. Delle Site PRL 2010

Quantum properties based on the delocalization of atoms



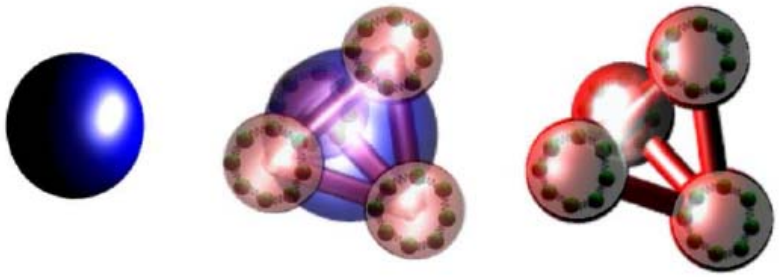


Path Integral (ring polymer) representation of classical atoms

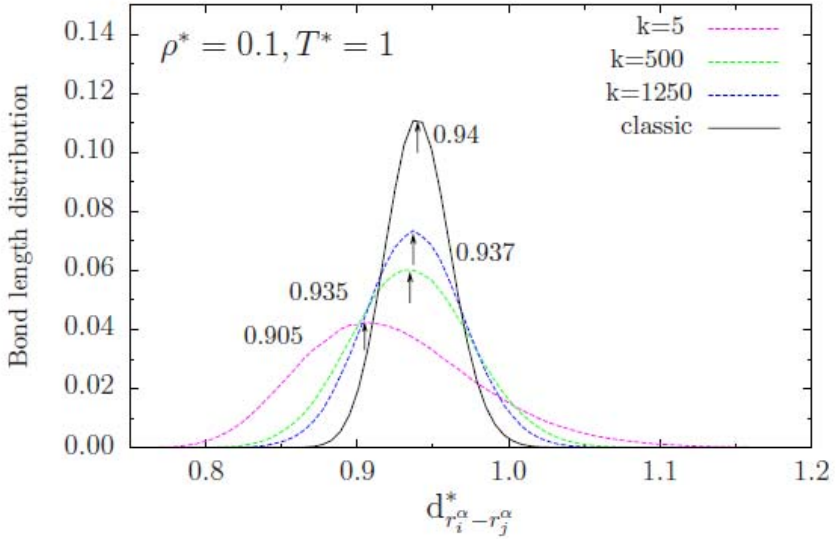
See: M.E.Tuckerman, NIC Series, Vol.10, pg 268 (2002).

QM-AdResS

A. Poma, L. Delle Site PRL 2010



Rigidity of Tetrahedral molecule in PIMD



Conclusion / Challenges

- **Dual-Triple… Scale Simulations/Theory**
  - **Adaptive** quantum⇔force field⇔coarse grained …
  - **Grand Canonical** i.e. salt etc
  - **Thermodynamic Force:** couple rather different systems
- **Nonbonded Interactions: NEMD, Structure Formation, Morphology…**
- **Conformations ⇔ Electronic Properties**
- **Structure Formation, Aggregation**
- **Online Experiments:**
  - **Nanoscale Experiments, long Times**

KITP UCSB Program 2012

- **Physical Principles of Multiscale Modeling, Analysis and Simulation in Soft Condensed Matter**

- **Apr 2, 2012 - Jun 29, 2012**
- **Application deadline: August 15, 2011**
- **Coordinators: Paul Atzberger, Kurt Kremer, Mark Robbins**