# Adaptive Resolution Simulation for Soft Matter and More: Applications and New Developments

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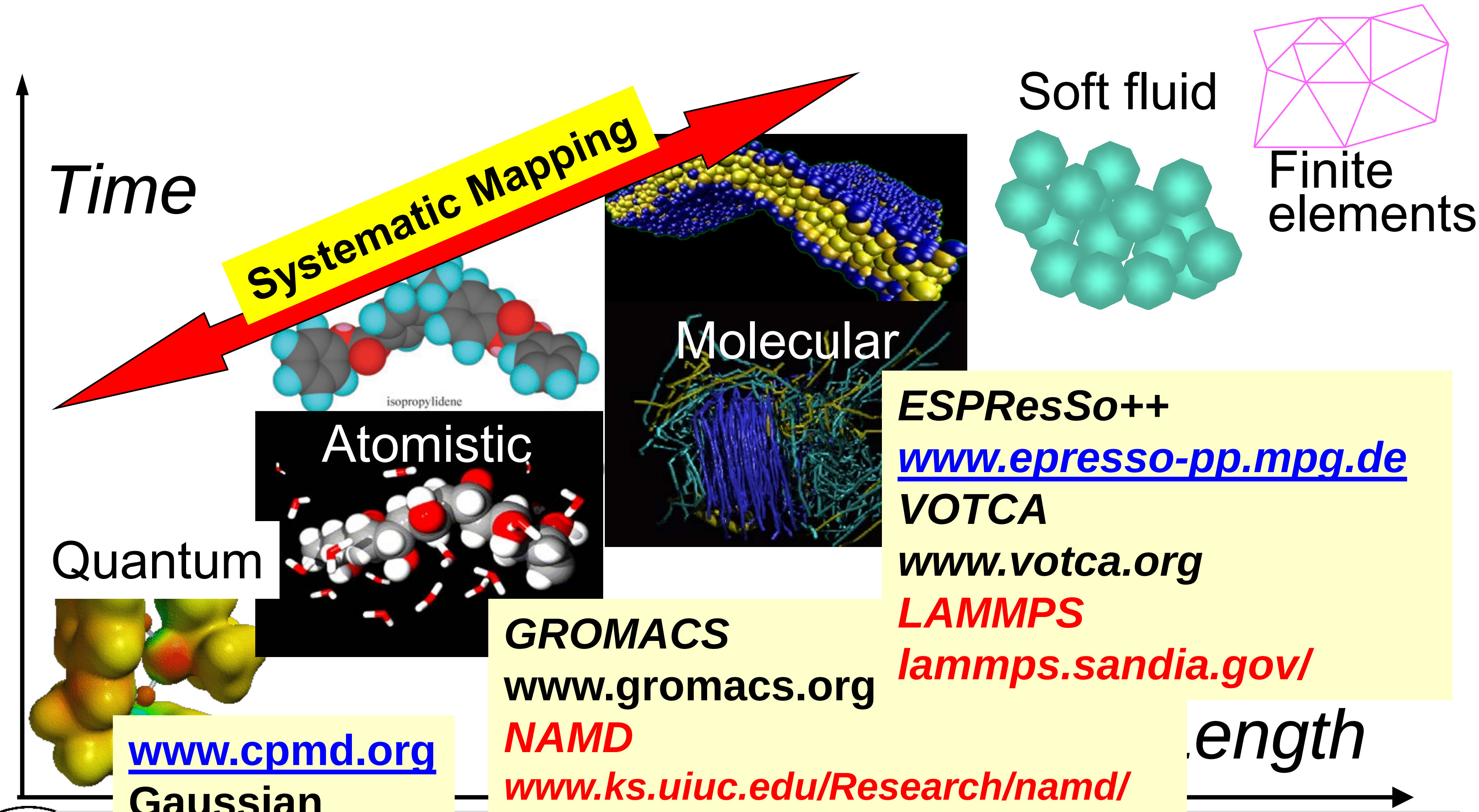
C. Clementi and her group (Rice), G. Ciccotti (Rome), …

**Support:** MMM Initiative of the MPG, Volkswagen Foundation, DAAD, KITP(NSF), DFG, ERC …

# Characteristic Time and Length Scales




Local Chemical Properties --- Scaling Behavior of Nanostructures
Energy Dominance --- Entropy Dominance of Properties

# Energy Scale $k_BT$ for T=300K

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

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

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

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

$$kT \approx 4.1\, p$$

$kT$

$mol$

$k \ldots kJ/mol$

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

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

**Elec**

**mbranes, AFM**

**ctroscopy**

**Chemical Bond**

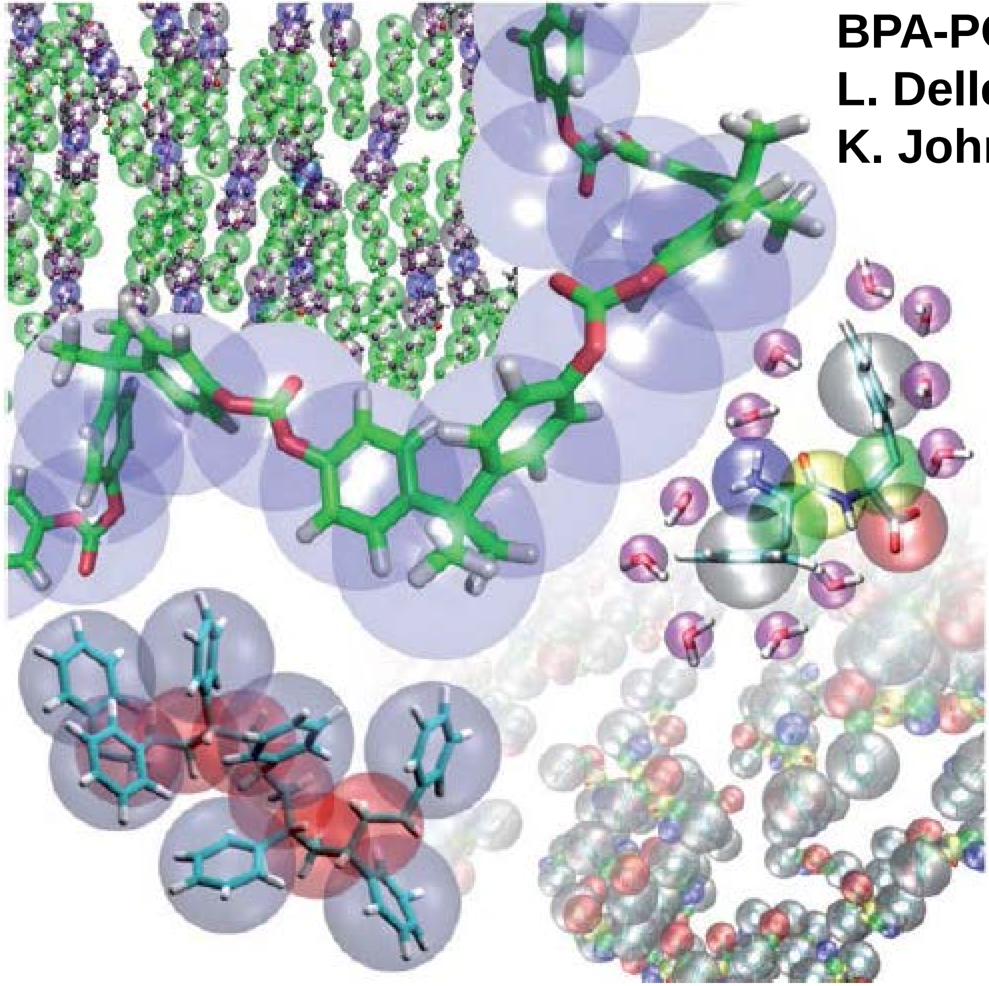
**Hydrogen Bond**

**True challenge for simulations:**
**All atom force fields not transferable and usually not accurate enough!**

# Coarse Graining of Macromolecules: Examples

**Azo Benzene LCs**
**C. Peter, L. Delle Site,**
**D. Marx**

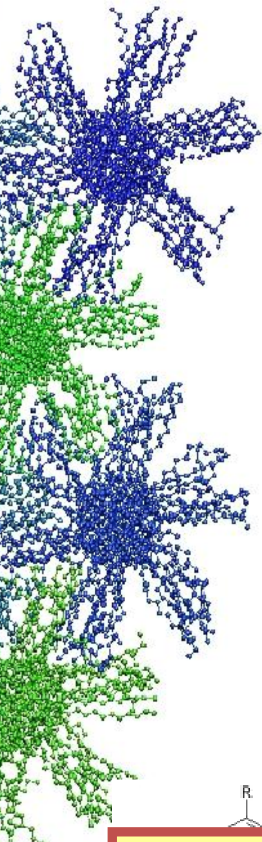
**BPA-PC**
**L. Delle Site, C. Abrams**
**K. Johnston** (1998ff)

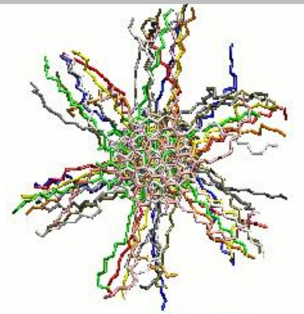


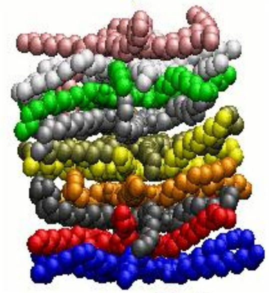
**Peptides**
**C. Peter**

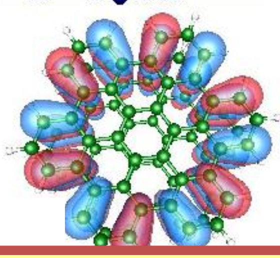
**Polystyrene,**
**(w/wo additives)**
**V. Harmandaris,**
**D. Fritz**
**N. Van der Vegt**

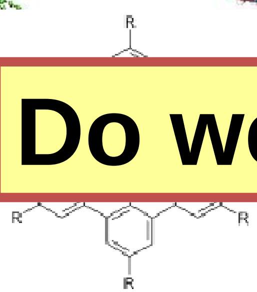
# Standard Approach:
# Run whole system on one level of resolution.

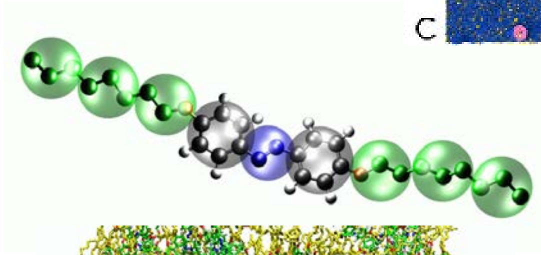


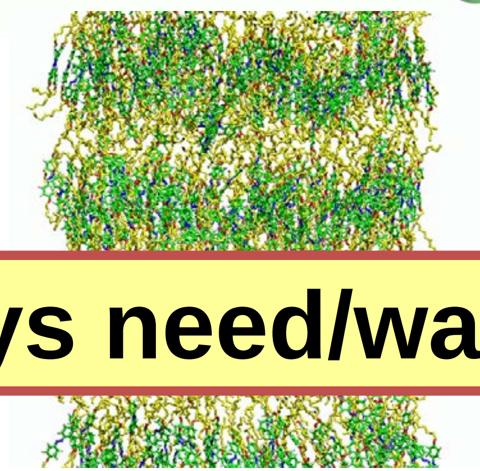


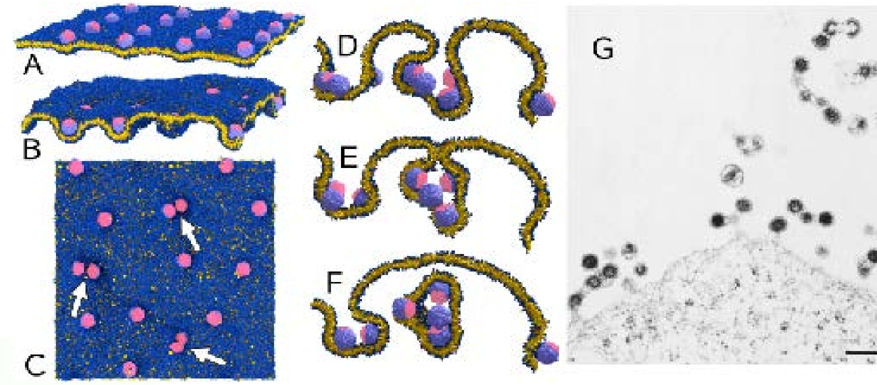












**Do we always need/want to do that?**

Andrienko et al,
PRL 98, 227402 (2007)

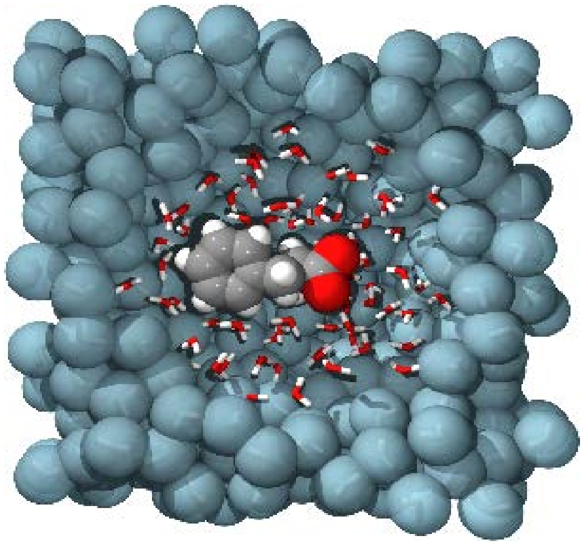
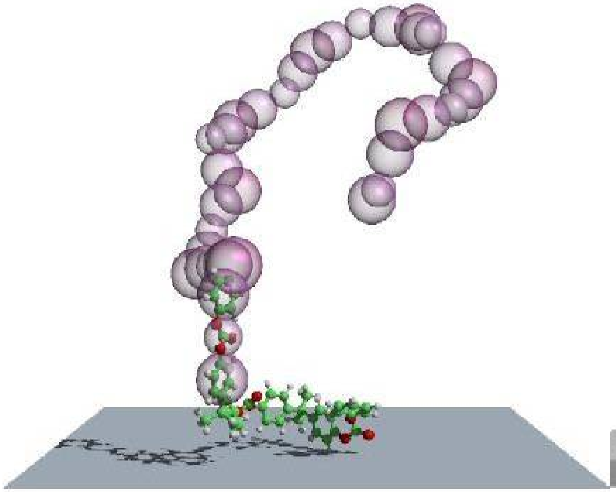
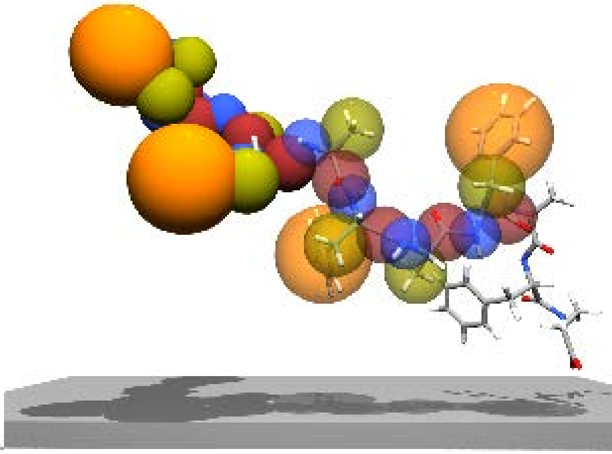
C. Peter et al, 2008ff

M. Deserno et al.,
Nature, 2007

# AdResS: Adaptive Resolution Simulations

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

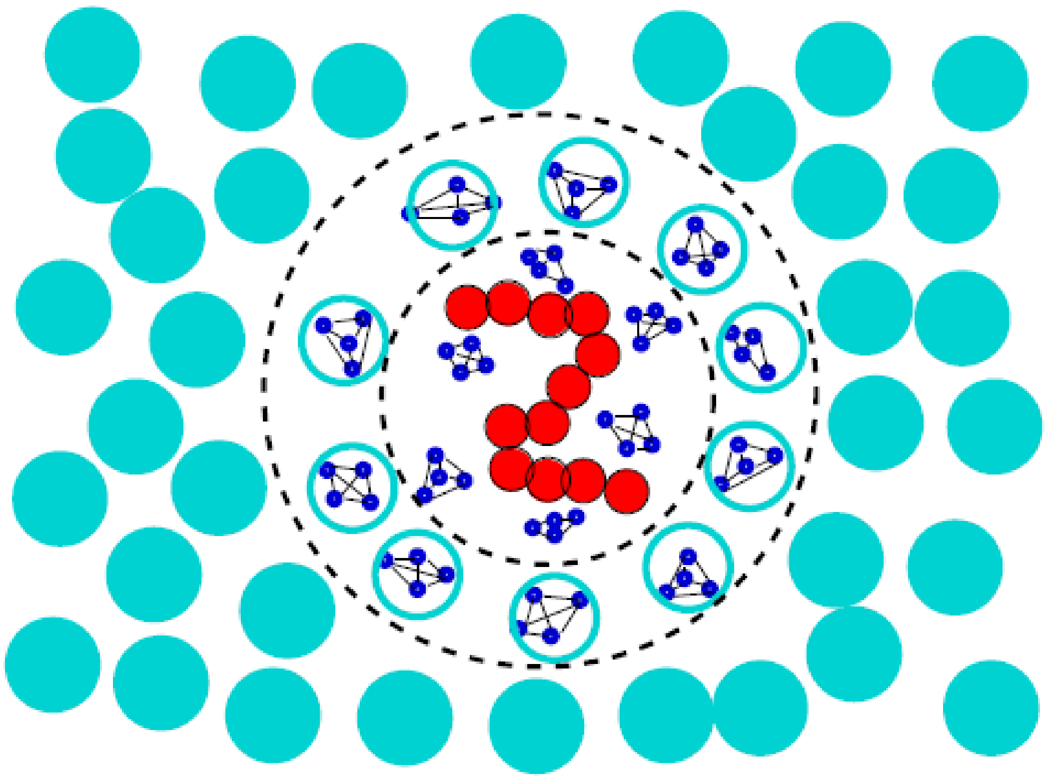
***Free exchange of molecules/particles between regimes with different levels of resolution:*** **equilibrium between both regimes, no kinetic barrier**

**C. Peter, B. Hess, N. van der Vegt, C. Junghans, S. Poblete…**

**Method: Praprotnik, Delle Site, KK: J. Chem. Phys. 123, 224106 (2005) & Phys. Rev. E 73, 066701 (2006)**

**Theory: M. Praprotnik, KK, L. Delle Site, PRE 75, 017701 (2007), JPhys A MathTh F281 (2007)**



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

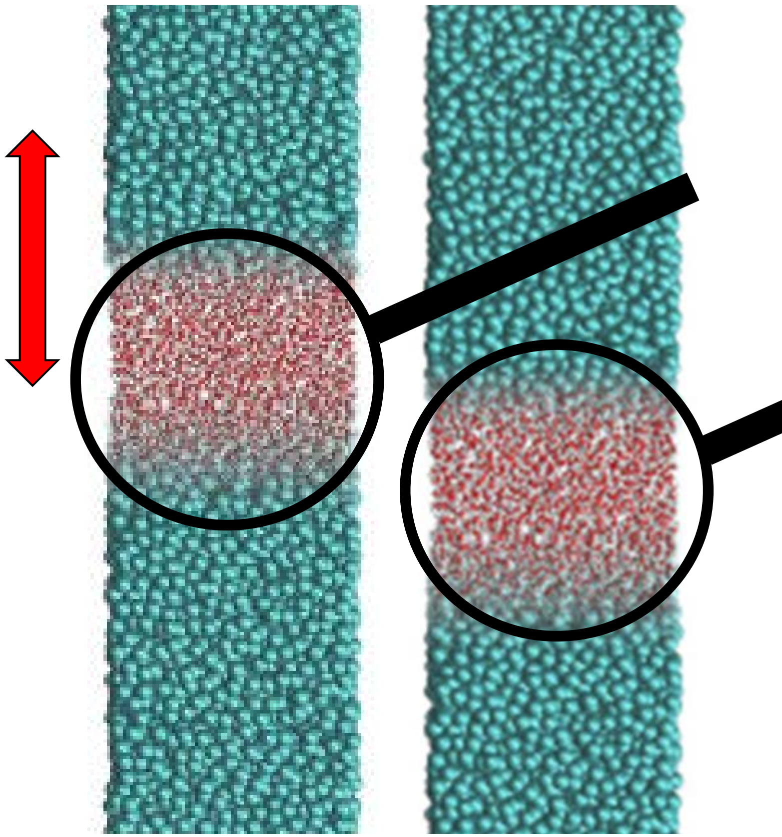
**Requirements**

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

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

- (Simple two body potential)

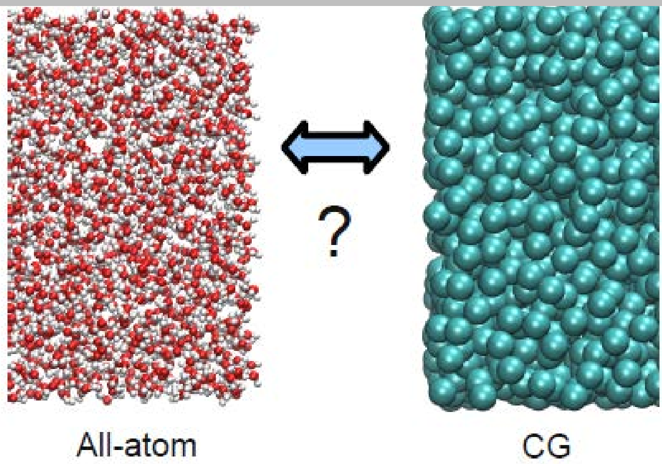
⇒ "Some similarities" to 1st order phase transition
⇒ "Phase equilibrium"



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

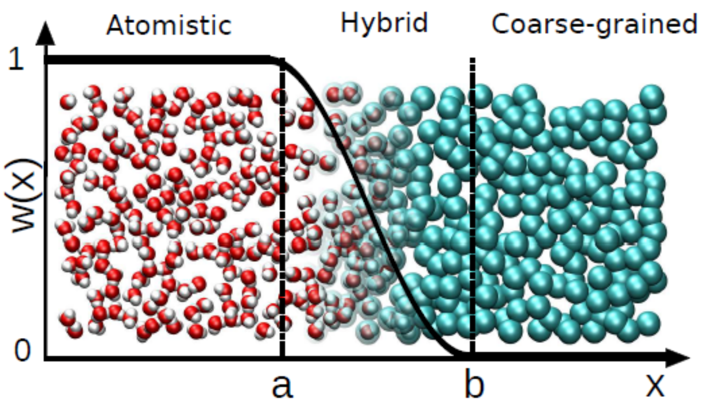
# Adaptive Methods:

## How to couple all-atom and coarse-grained models?




## Requirements:

- Free exchange of molecules
- NO (free) energy barriers
- Smooth transition forces
- Structure and dynamics preserved
  - (at least in all atom region)




$$w(x) = \begin{cases} 1 & : \text{atomistic/explicit region} \\ 0 < w < 1 & : \text{hybrid region} \\ 0 & : \text{coarse-grained region} \end{cases}$$

## Different Interpolation schemes:

- Force should be antisymmetric on exchange of particles $\alpha \leftrightarrow \beta$, => Newton 3rd law
- Force interpolation, no Hamiltonian
- Energy interpolations, MC possible, Ensembles → Newton 3rd law not exactly fulfilled

JCP 2005, PRL 2012,2013,
Ann Rev Phys Chem 2008

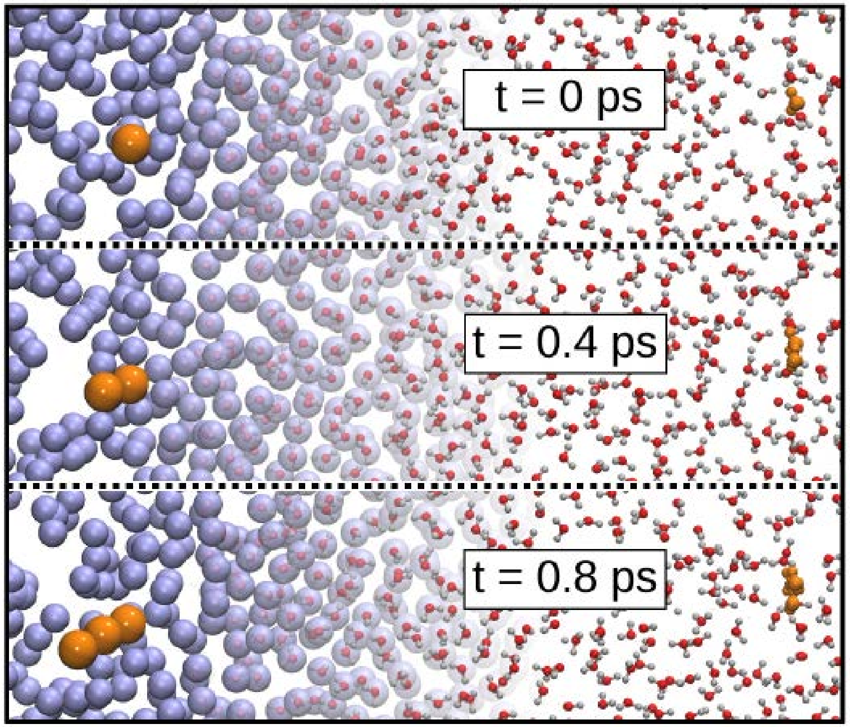
# Applications, Extensions

- **Coupling to an ideal gas**
- Path integral quantum description
- Large solutes in solvents
- Cosolvent Effects for (Bio-) Polymers

  ‘stimuli responsive’ or ‘smart polymers’

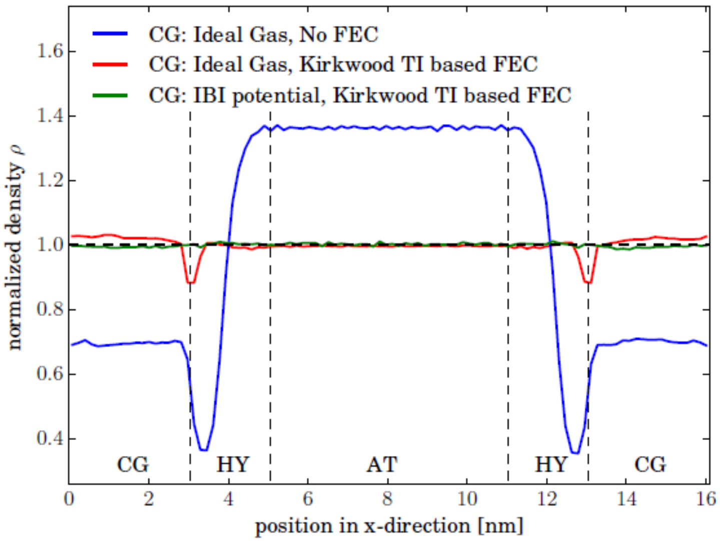
# Free energy compensation in transition zone allows coupling to ideal gas

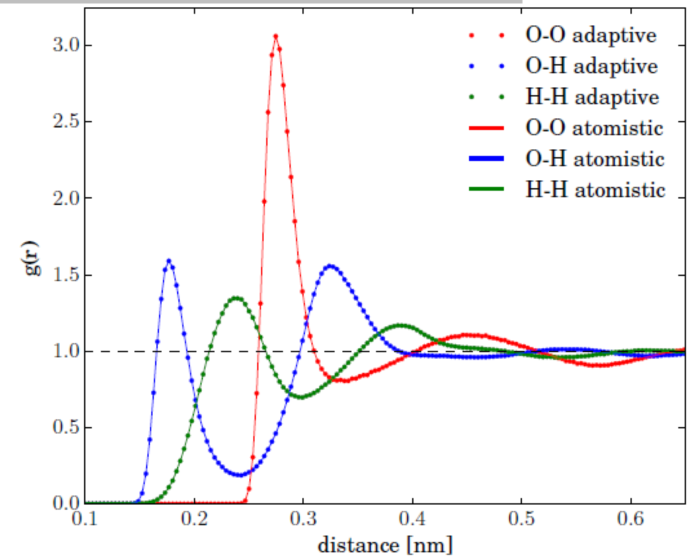
- AT region: SPC water model
- CG region: ideal gas
- The chemical potential compensates density imbalances

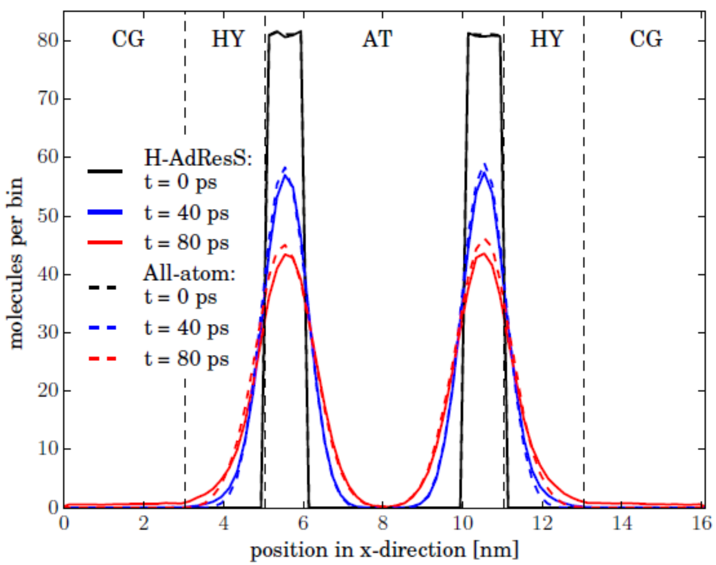


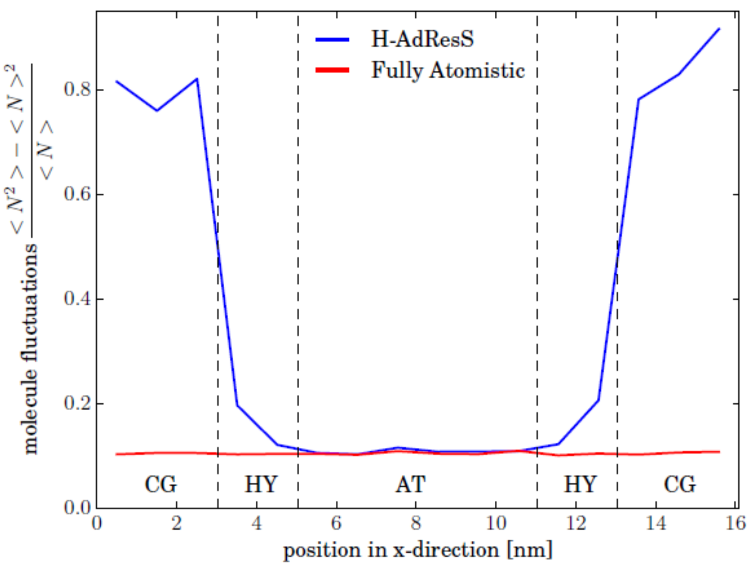

K. Kreis, A.C. Fogarty, KK, R. Potestio, EPJE 2015

# Free energy compensation in transition zone allows coupling to ideal gas



# Applications, Extensions

- Coupling to an ideal gas
- **Path integral quantum description**
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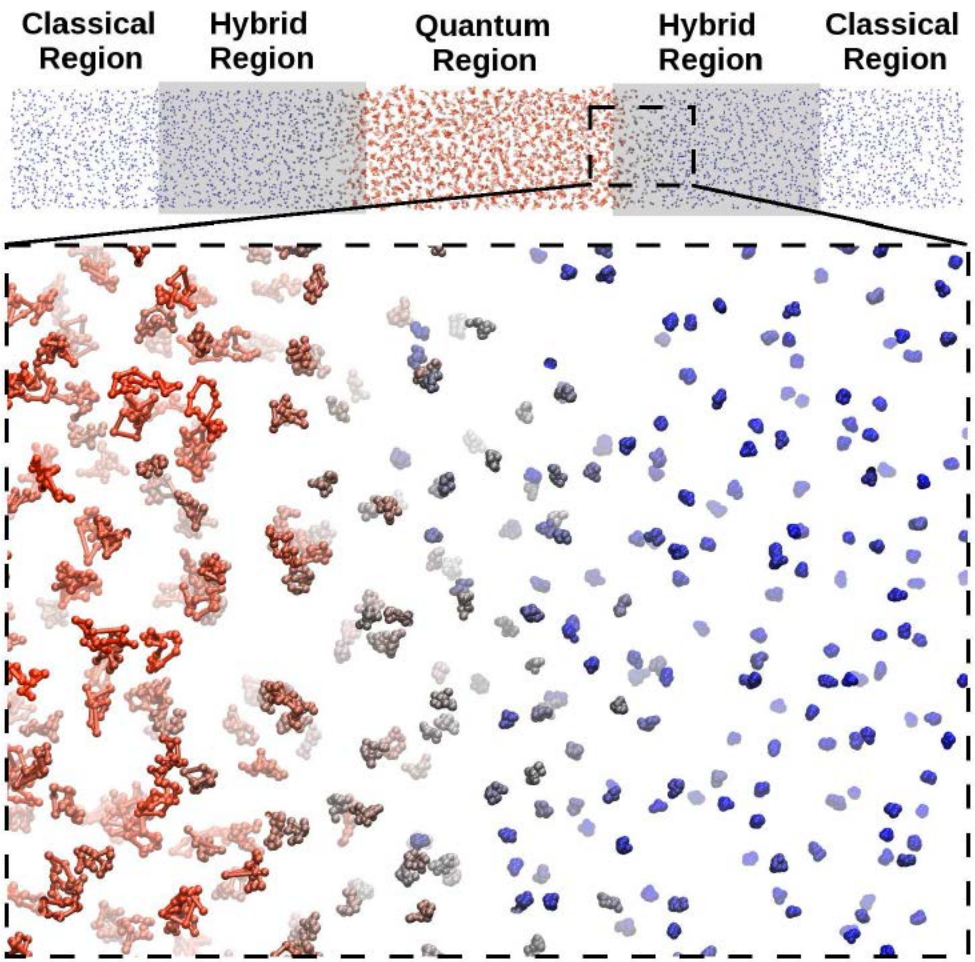
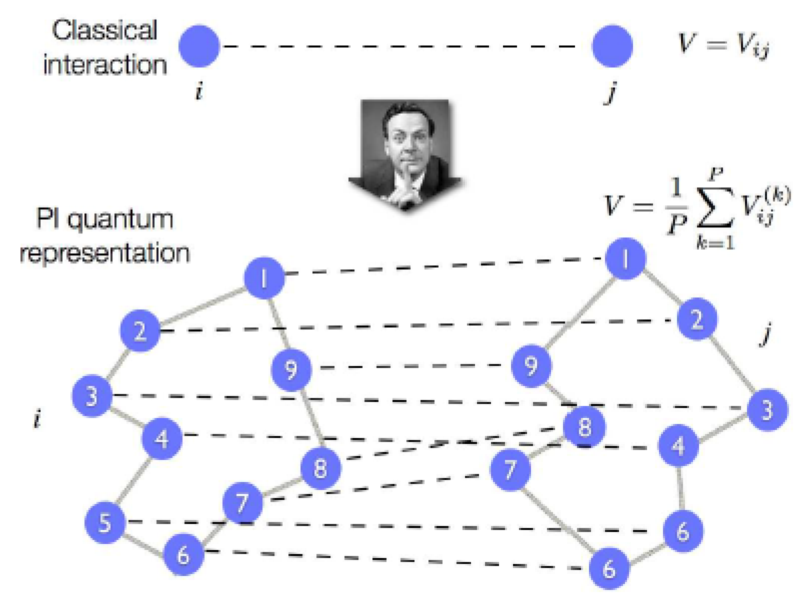
  ‘stimuli responsive’ or ‘smart polymers’

# Path integral quantum AdResS

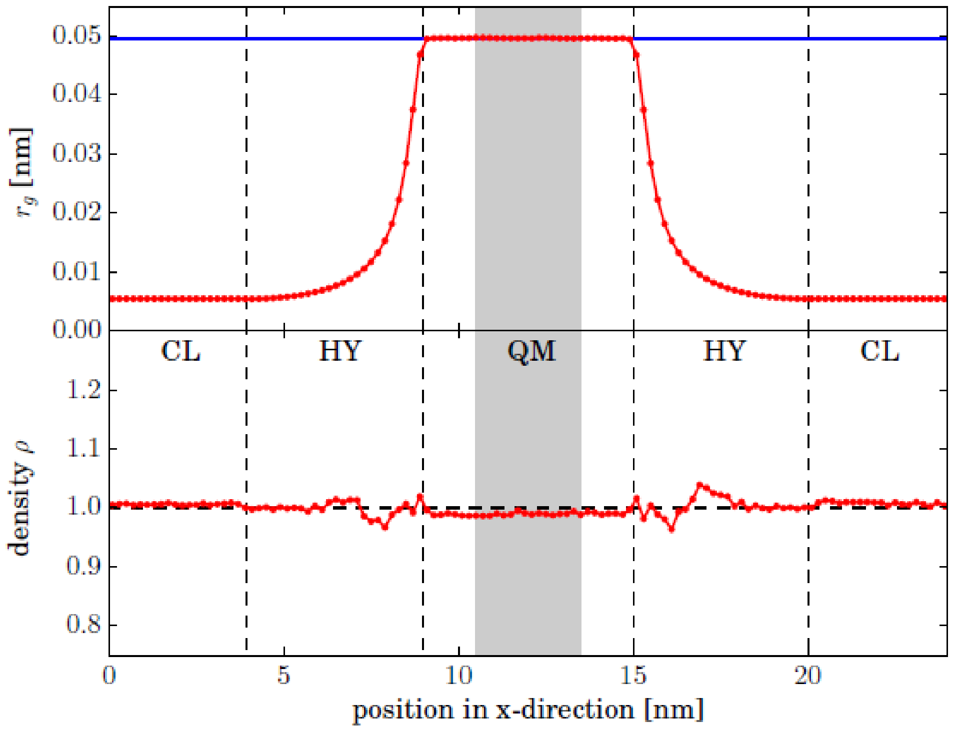


# Path integral quantum AdResS

**Classical – quantum: vary mass of particles in pearls**

$$m \rightarrow \mu(\lambda) = \lambda m + (1 - \lambda) M$$




**Interpolate between quantum (light mass m) and classical particle (heavy mass M)**

**$0 \leq \lambda \leq 1$**

**Feynman:**
**quantum particle as a classical ring polymer of light particles of mass m**

K. Kreis, M. Tuckerman, D. Donadio, KK, R. Potestio ,2015

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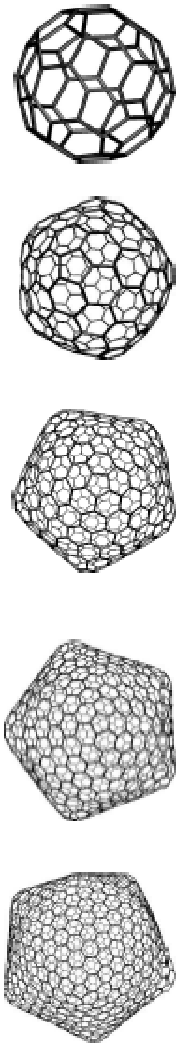
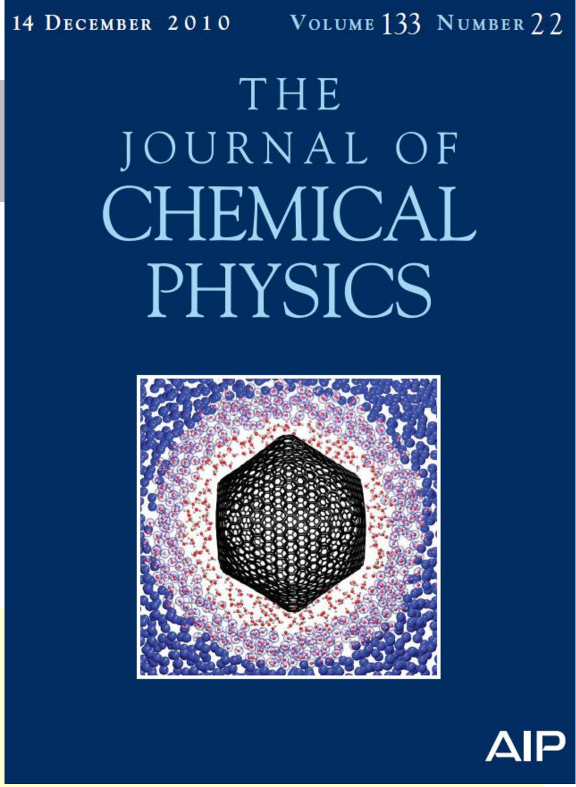
# Hydrophobic Solutes



$C_{60}$

$C_{2160}$



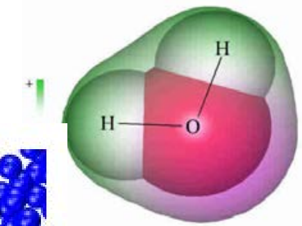

**Influence of bulk H-bond structure on surface layer**

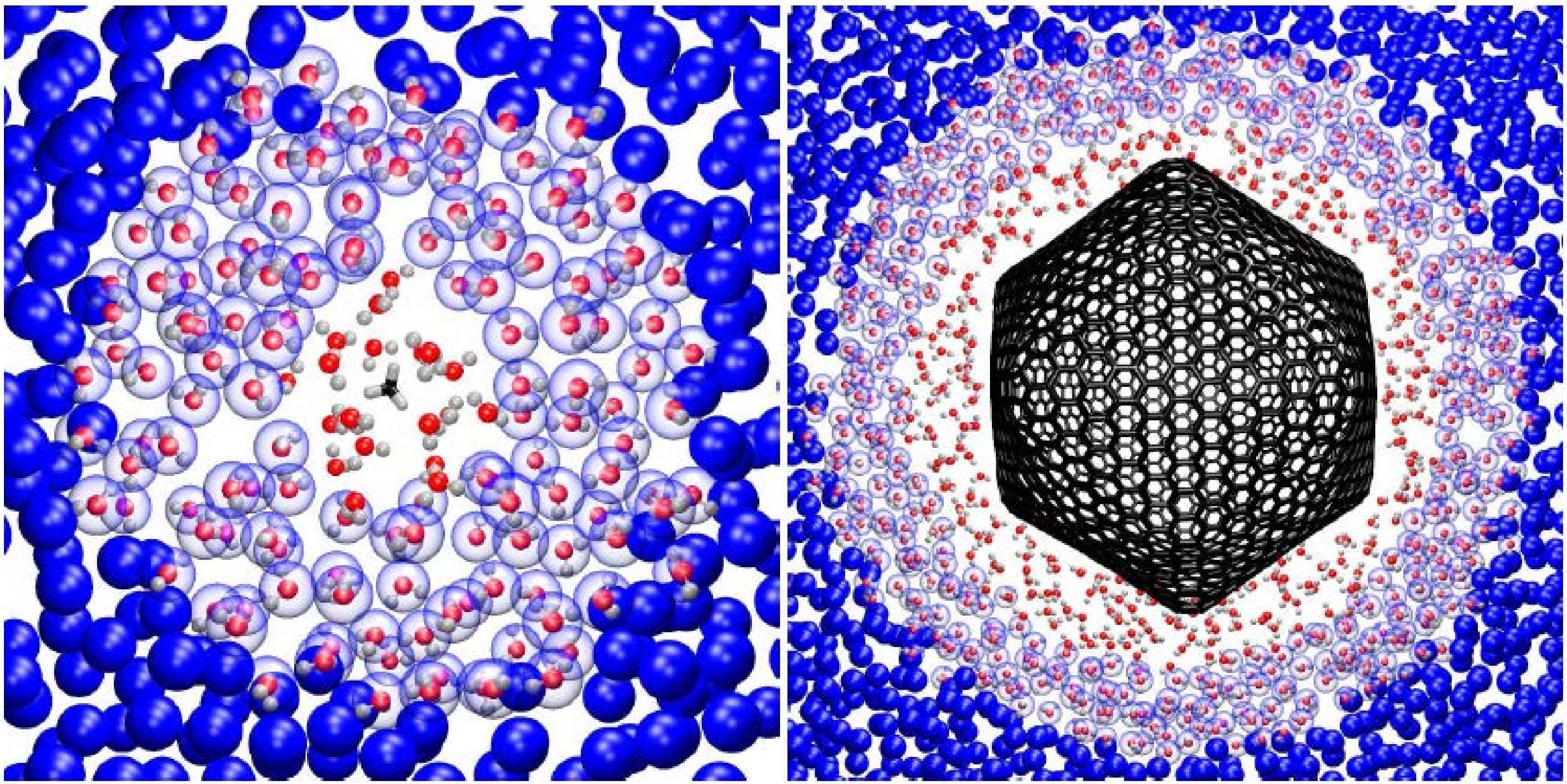
**# two surface potentials**

- **standard (weak) Lennard Jones**
  **($\varepsilon_{CO}$=0.2$k_BT$, $\sigma_{CO}$=0.34nm)**
- **purely repulsive ($r^{-12}$)**

**# variable width of explicit layer**

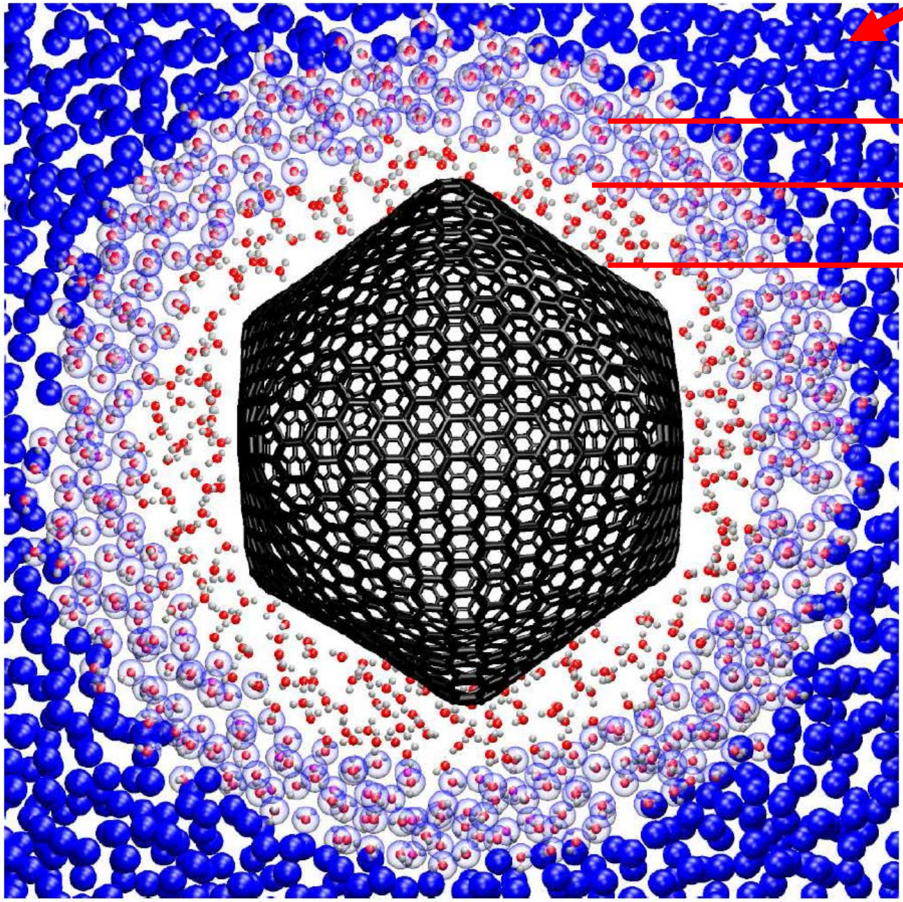
# 3rd Application Hydrophobic Solutes

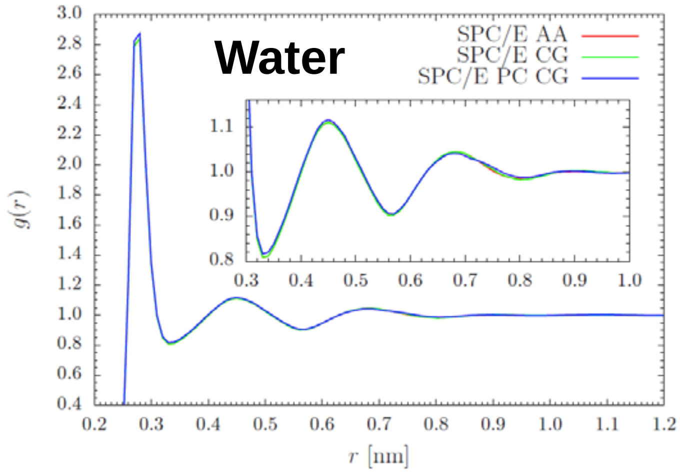


C. Junghans, B. P. Lambeth, C. Clementi, L. Delle Site, KK JCP 2010

# Hydrophobic Solutes: Surface vs Bulk



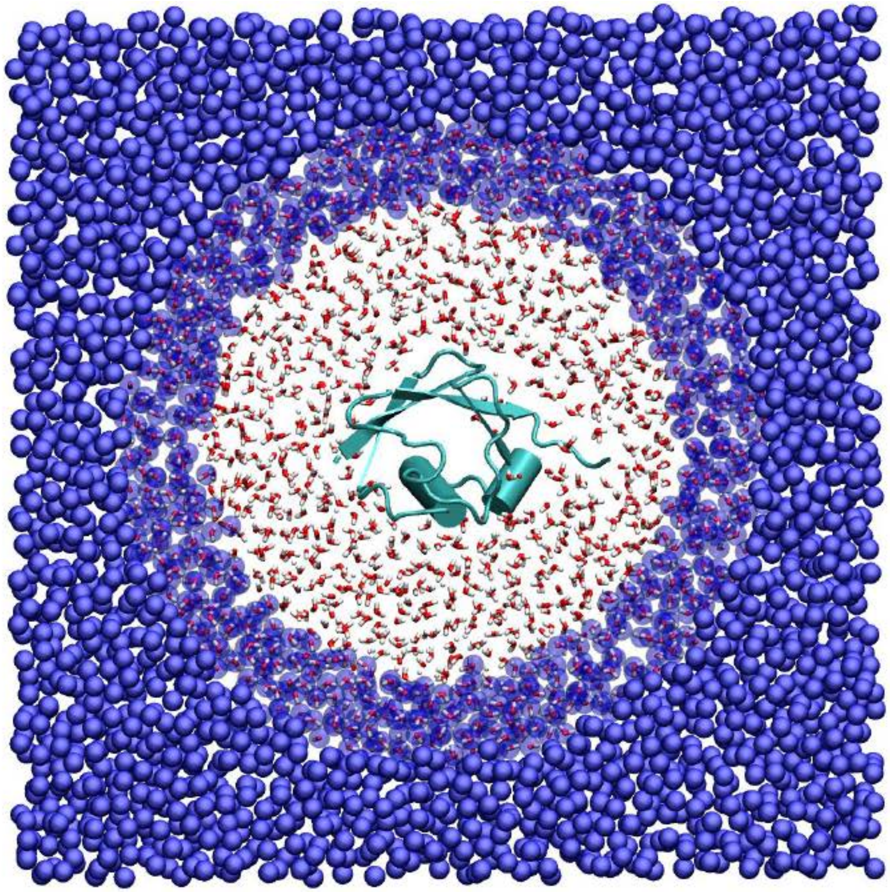



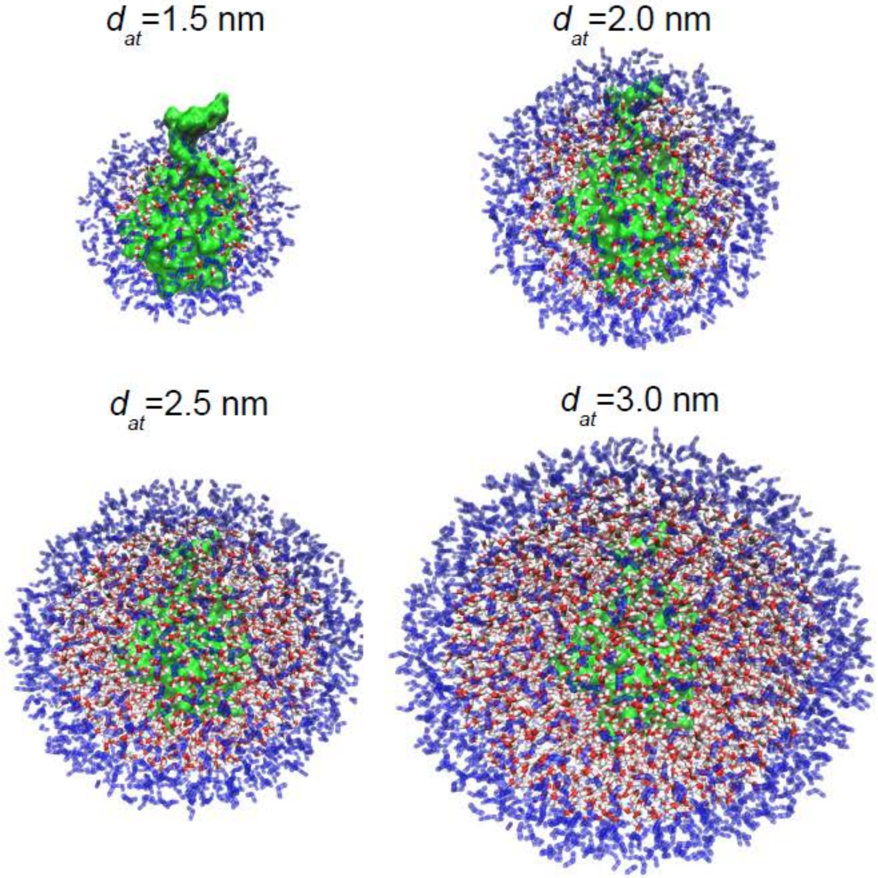

**cg water reproduces g(r) but NOT tetrahedral packing!**

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

# Applications, Extensions

- Ubiquitin  in water, …






A. C. Fogarty, R. Postestio, KK, JCP 2015

# Applications, Extensions

- Coupling to an ideal gas
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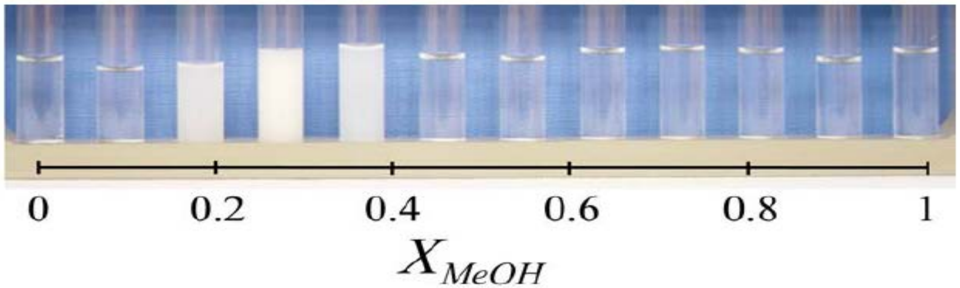
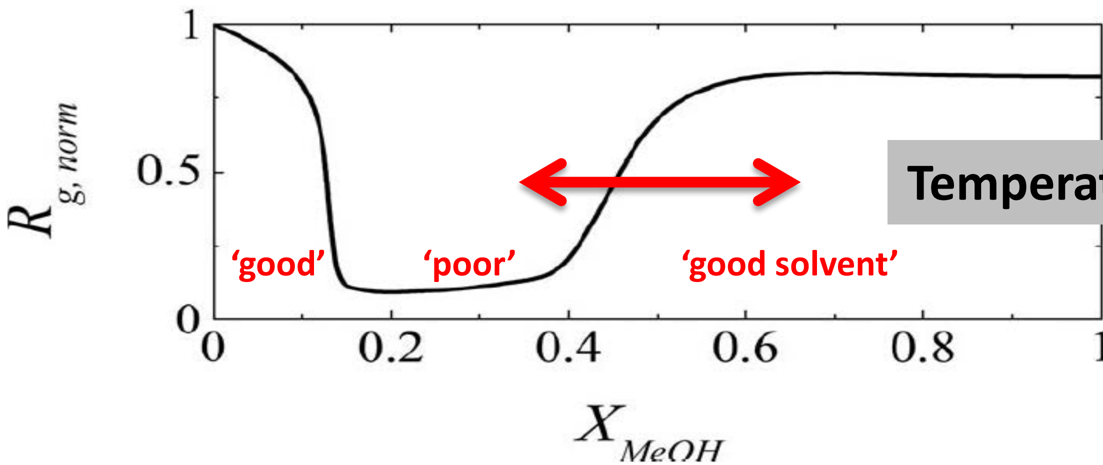
- Large solutes in solvents
- **Cosolvent Effects for (Bio-) Polymers**

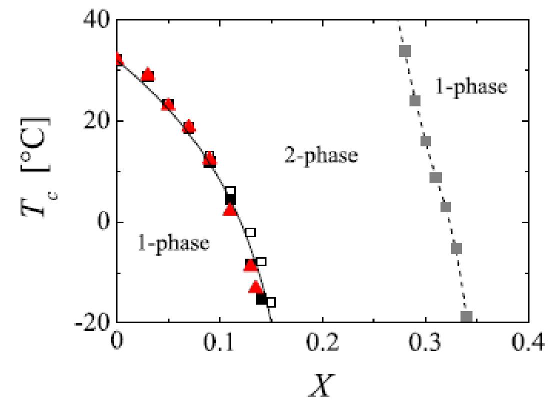
  **‘stimuli responsive’ or ‘smart polymers’**

# Co (Non-) Solvency of Poly(NIPAm) in Water Alcohol Mixtures

Bischofberger et al. Soft Matter 10,8288 (2014)



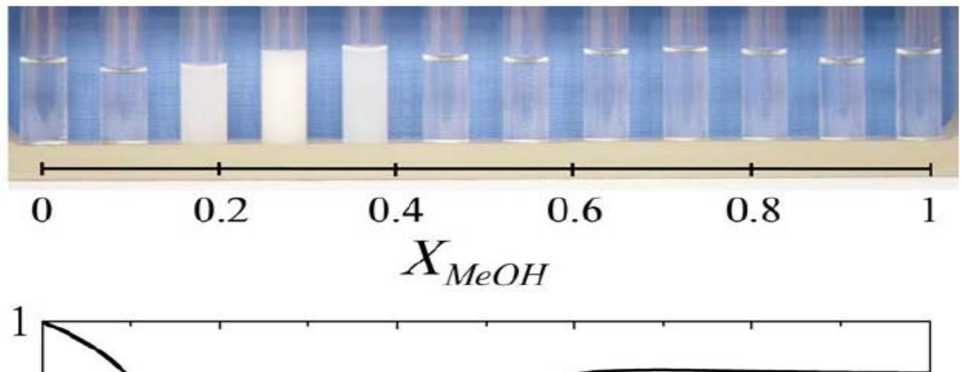



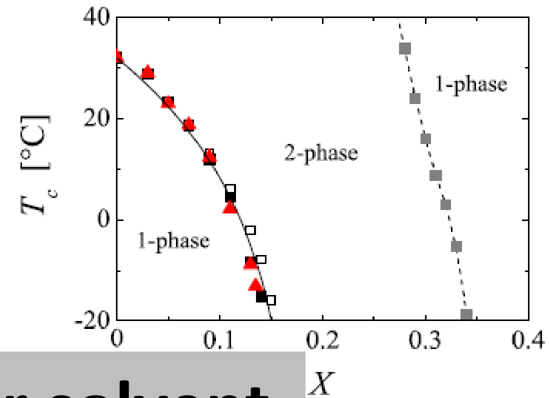

**Temperature fixed**

- Water and alcohol are both good solvents
- water and alcohol are miscible

# Co (Non-) Solvency of Poly(NIPAm) in Water Alcohol Mixtures

Bischofberger et al. Soft Matter 10,8288 (2014)



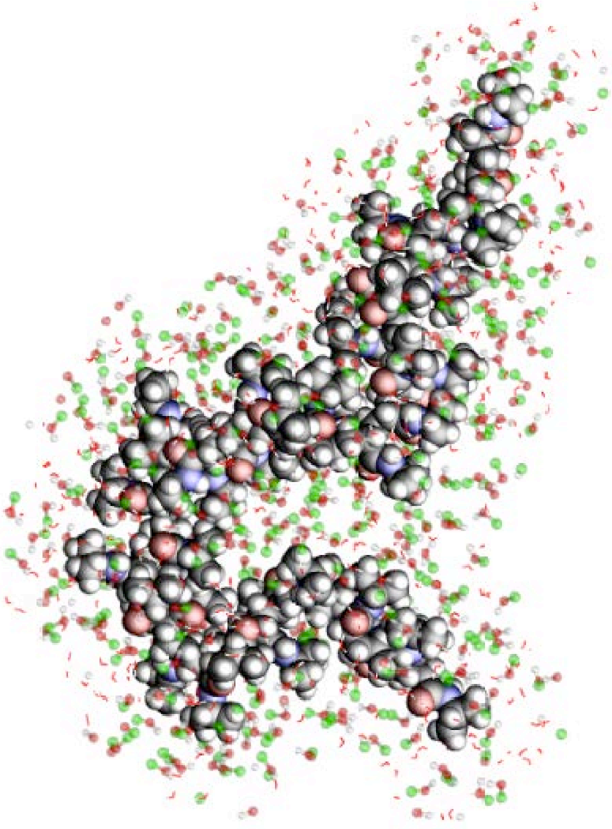

**Two mixed good solvents result in a poor solvent**

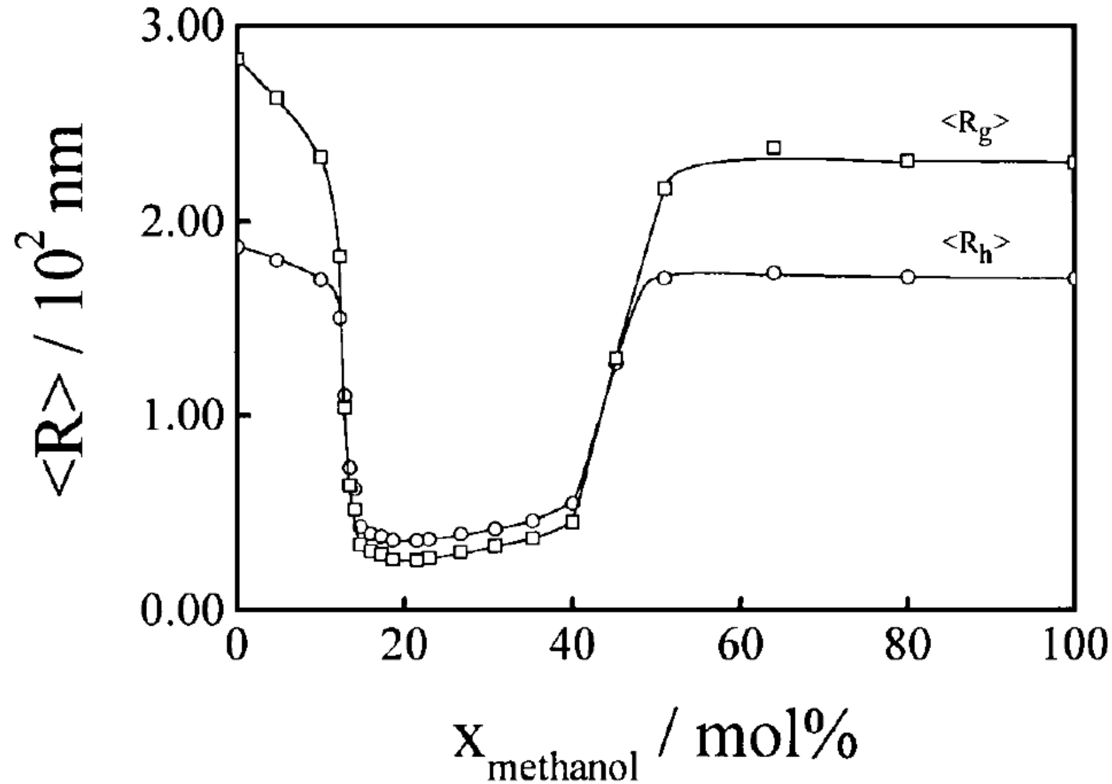
**How can this be possible?**

$X_{MeOH}$

- **Water and alcohol are both good solvents**
- **water and alcohol are miscible**

# Co (Non-) Solvency of Poly(NIPAm) in Water Alcohol Mixtures



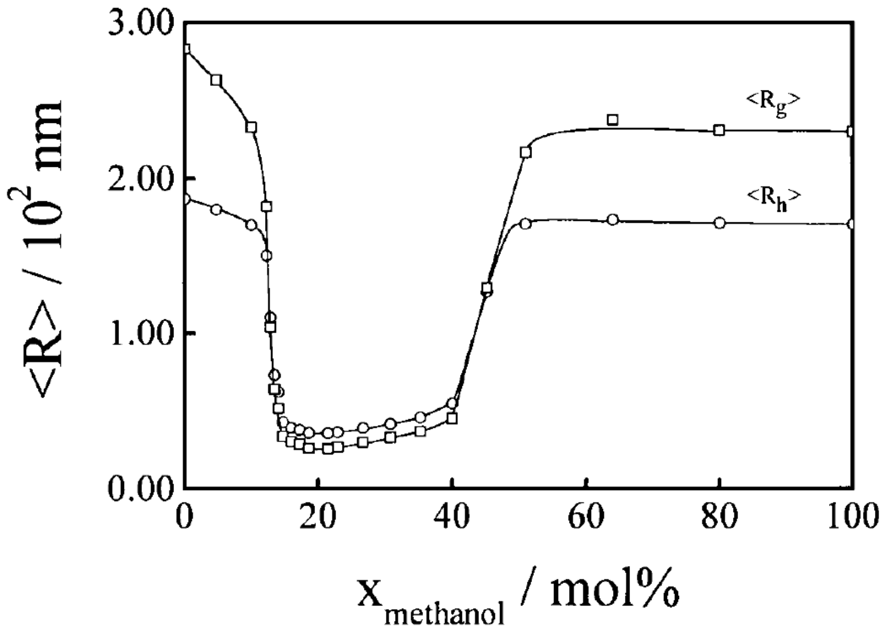


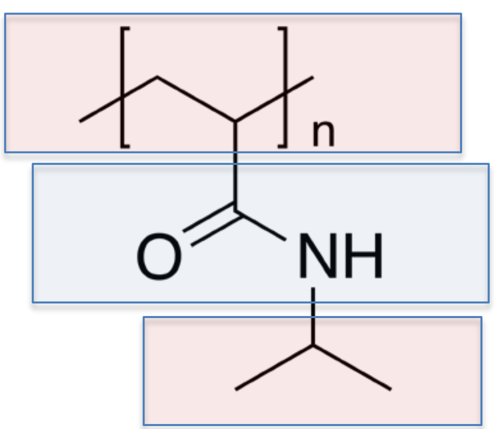

Zhang and Wu, Physical Review Letters 86, 822 (2001).
Mukherji and Kremer, Macromolecules 46, 9158 (2013).

# Co (Non-) Solvency of Poly(NIPAm) in Water Alcohol Mixtures

## Example: Poly(NIPAm) in aqueous alcohol

- **Alcohol and water both good solvents**
- **Alcohol and water well miscible**
- **Pure water: chain expanded**
- **Pure alcohol: chain expanded**
- **Mixture: chain collapses**




hydrophobic

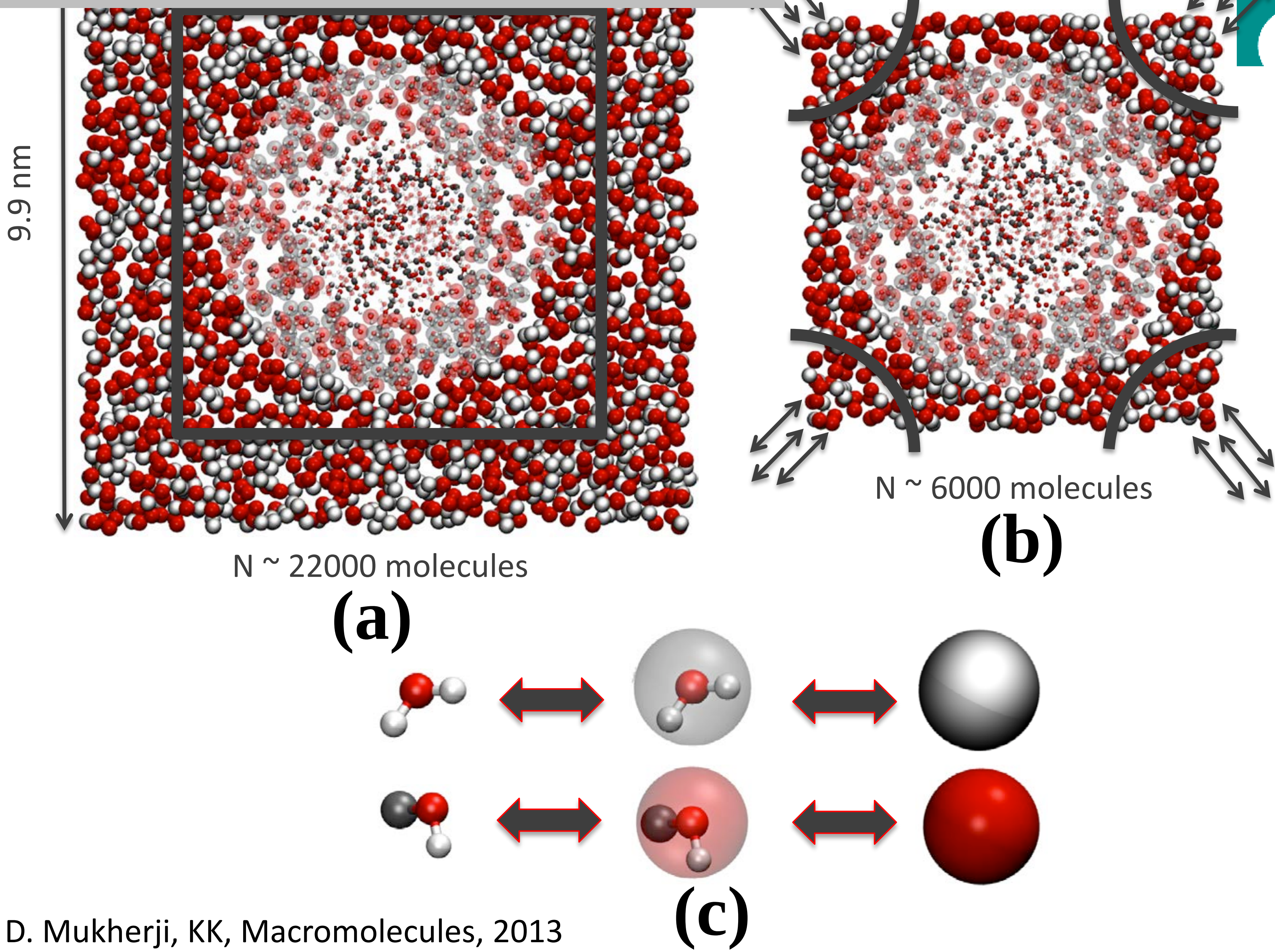
hydrophilic

hydrophobic

Zhang and Wu, Physical Review Letters 86, 822 (2001).

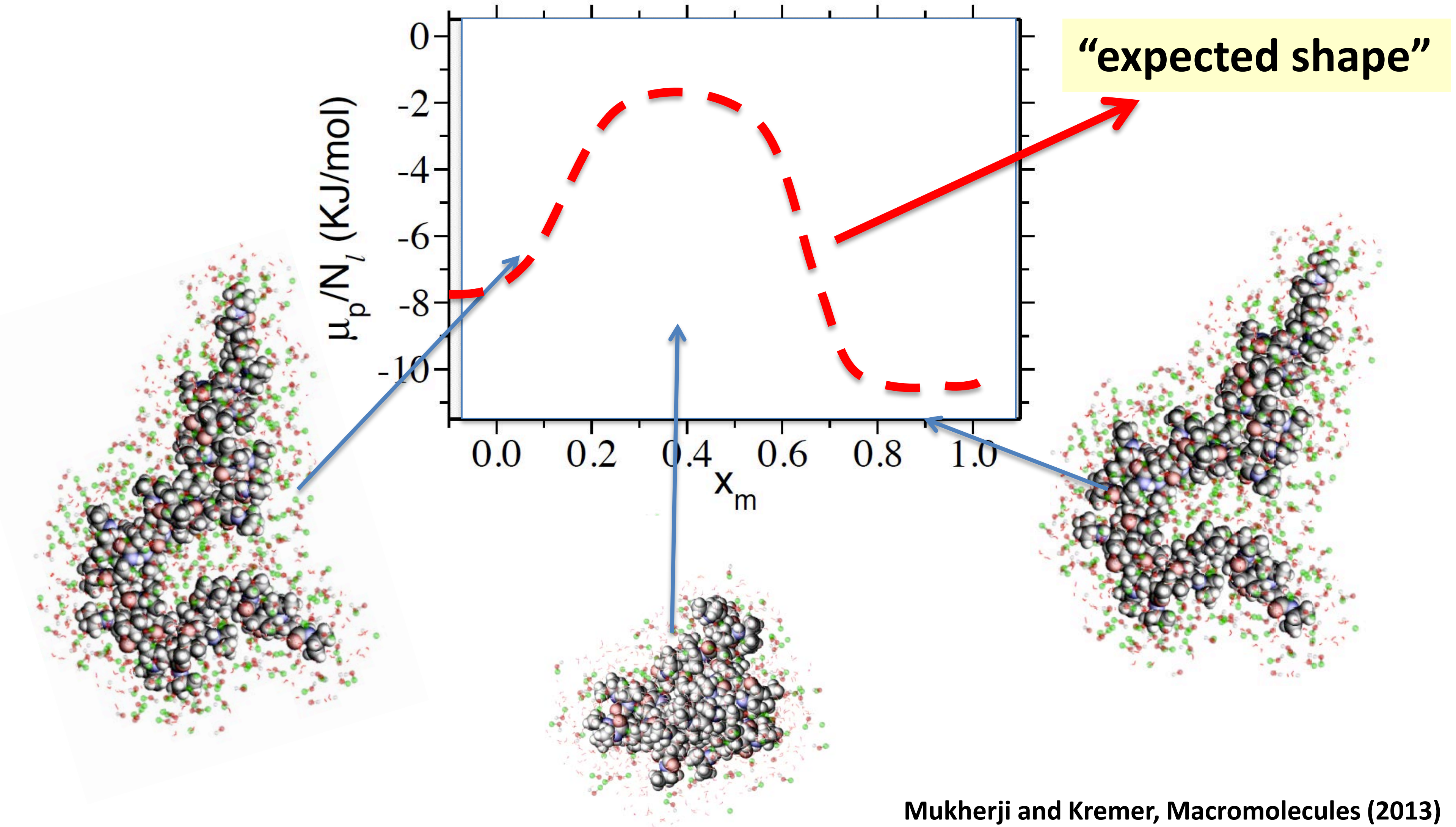
Mukherji and Kremer, Macromolecules 46, 9158 (2013).

# Semi Grand Canonical AdResS




D. Mukherji, KK, Macromolecules, 2013

# Poly-NIPAm chemical potential




Mukherji and Kremer, Macromolecules (2013)

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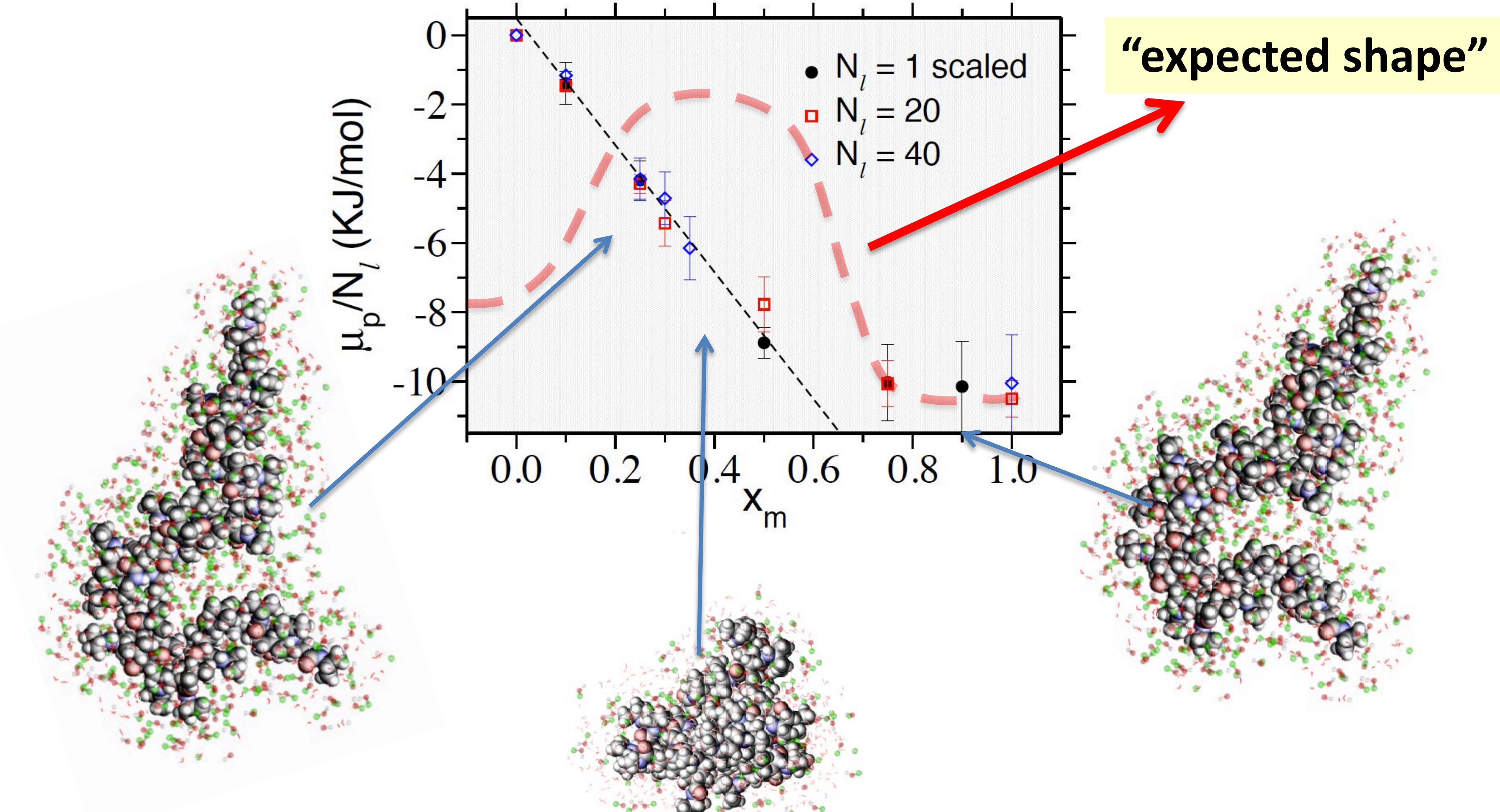


Mukherji and Kremer, Macromolecules (2013)

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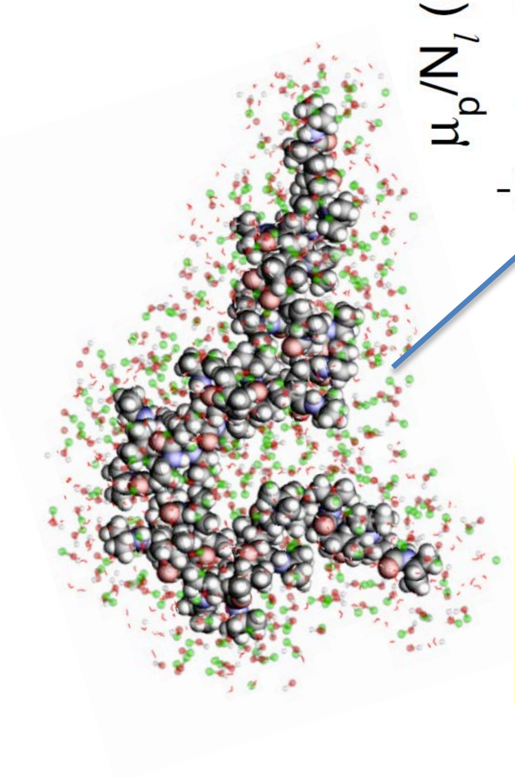
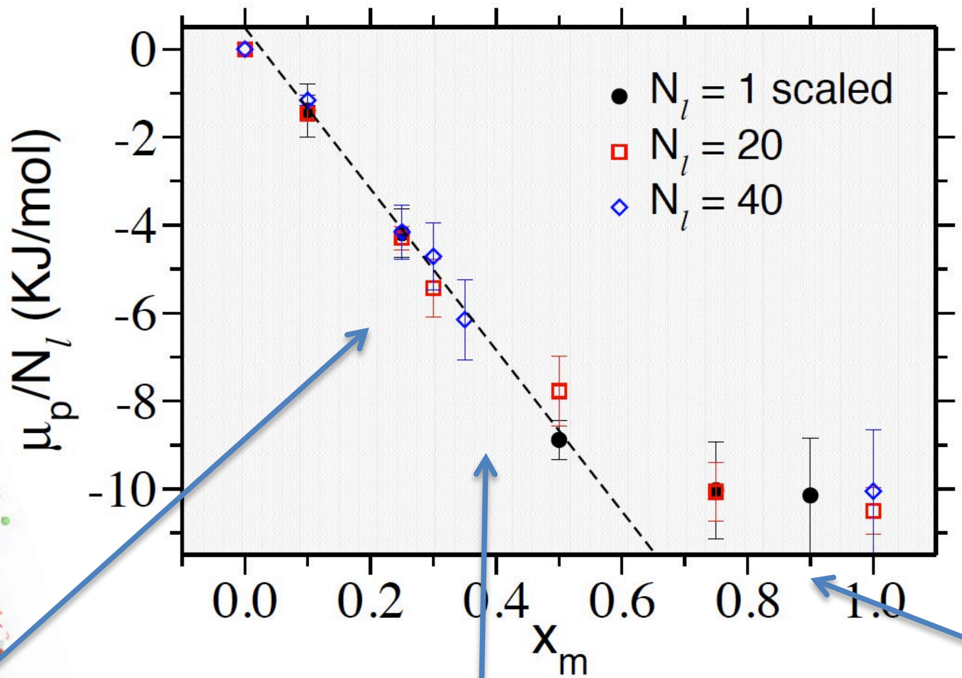
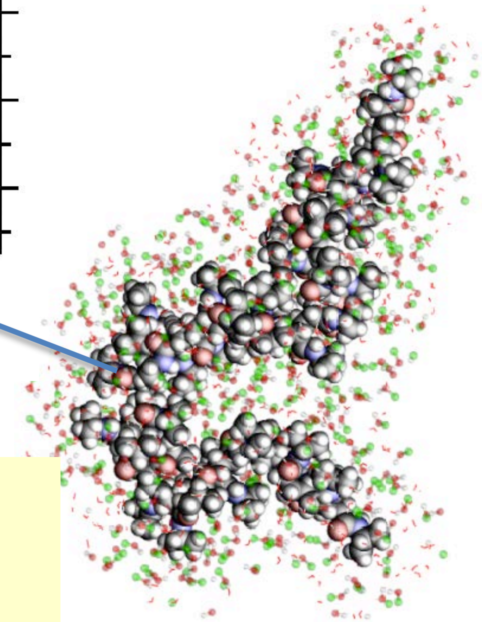
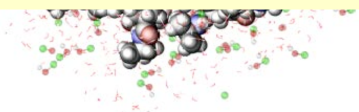




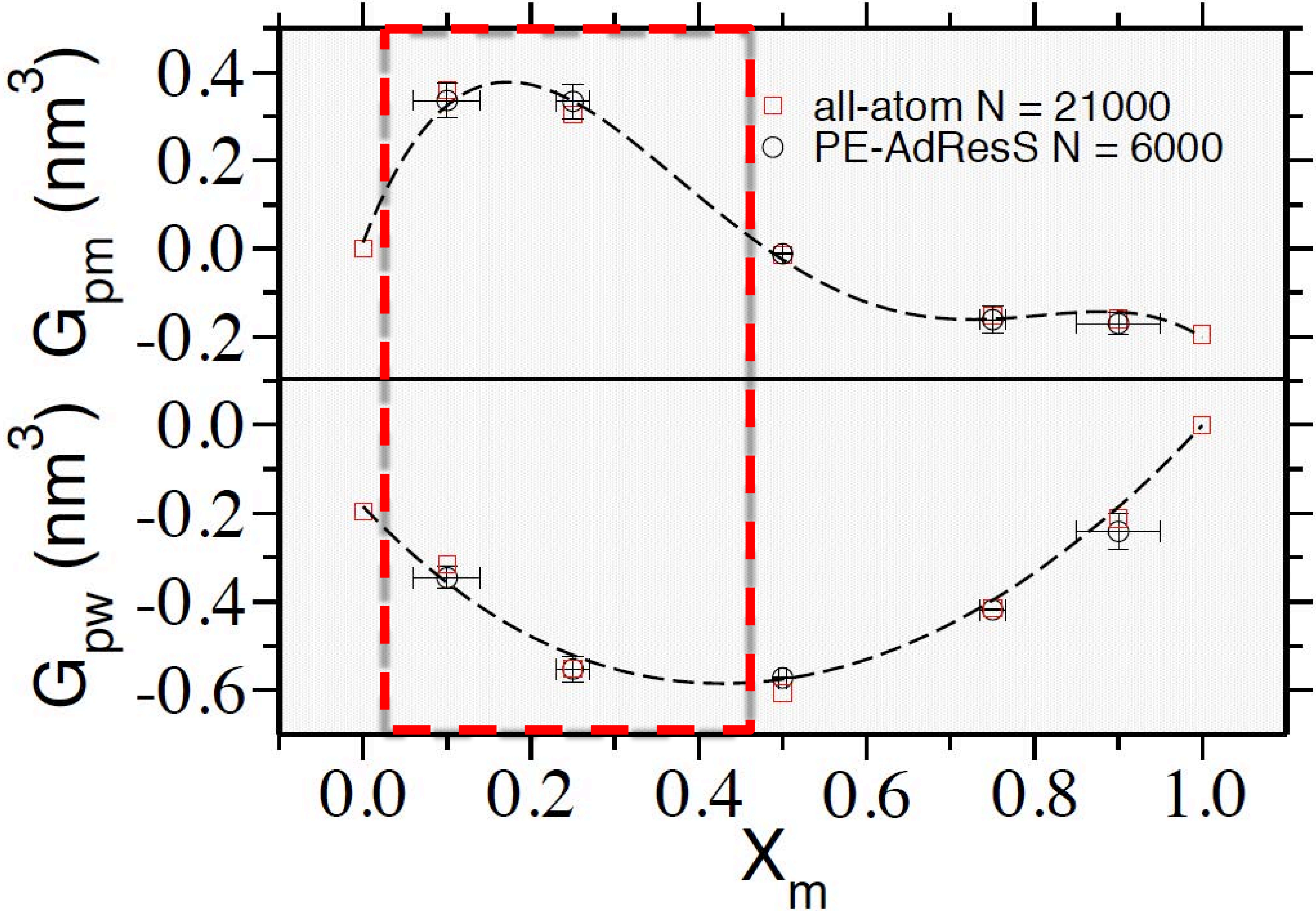



**Chain collapse in good solvent**



**Mukherji and Kremer, Macromolecules (2013)**

# Poly-NIPAm in aqueous methanol

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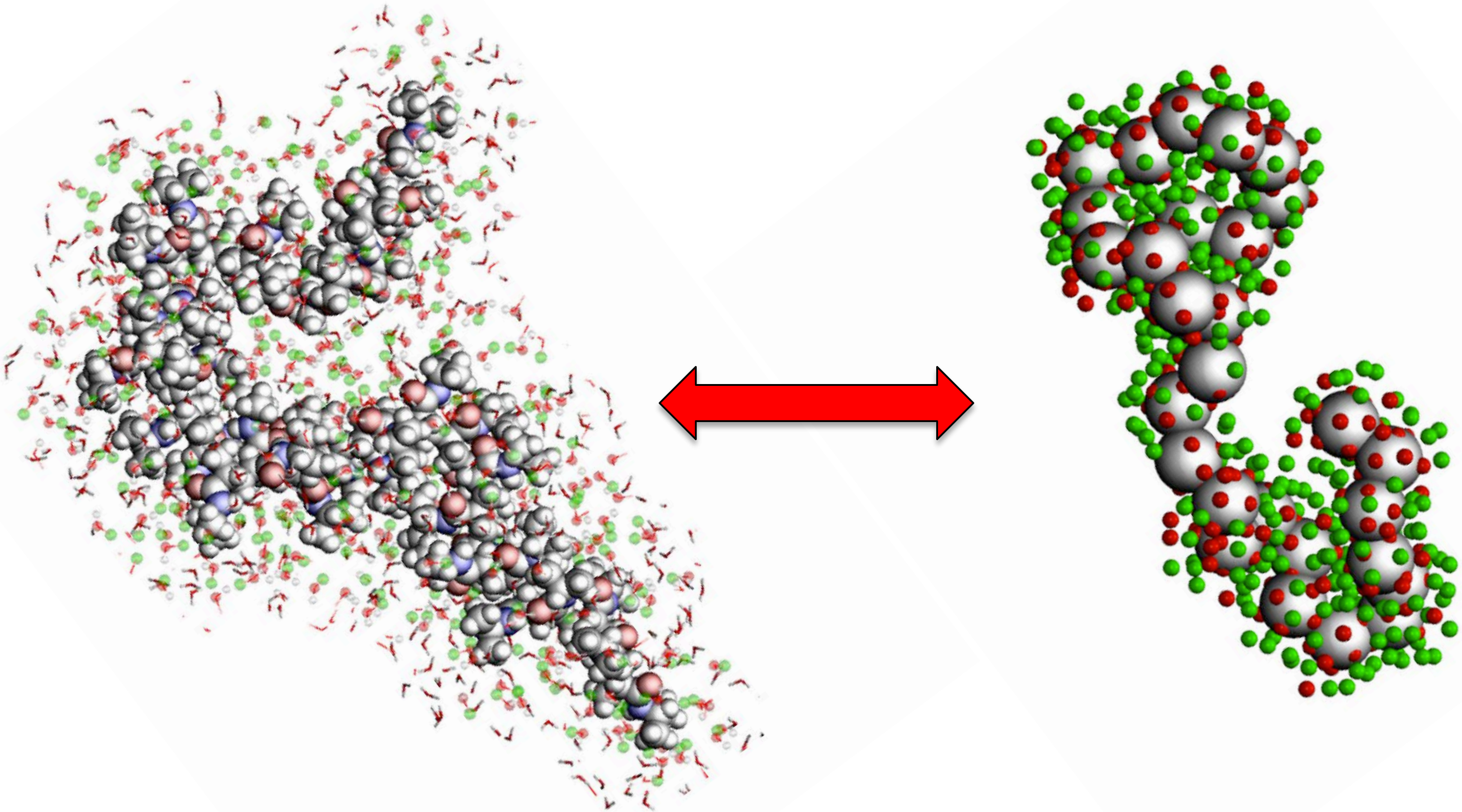
Mukherji and Kremer, Macromolecules (2013).

# Generic Model



Atomistic LJ + FENE

Kremer and Grest, J. Chem. Phys. 92, 5057 (1990).

# So far:
# particle based models
# Bottom up procedures

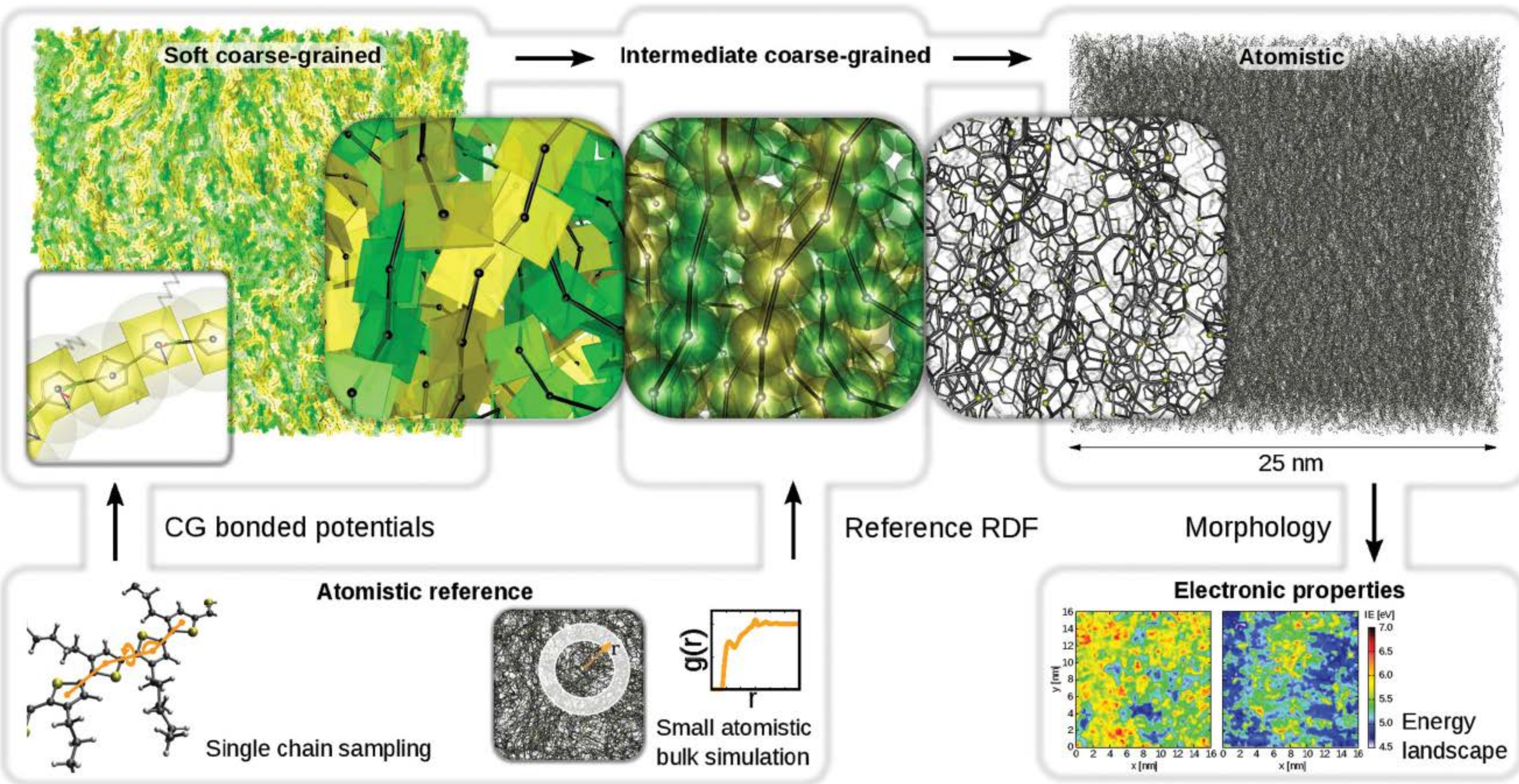
**Complementary strategy:**

**"Soft Models" => particle based generic => all atom**

**Mueller, Daoulas, Guenza, Wang,…**

**Just two pictures**

# Top down:
# Soft models => particle based models




P. Gemünden , C. Poelking , KK, K Daoulas , D. Andrienko , Macr. Rap. Comm. 2015