Multiscale methods for complex fluids

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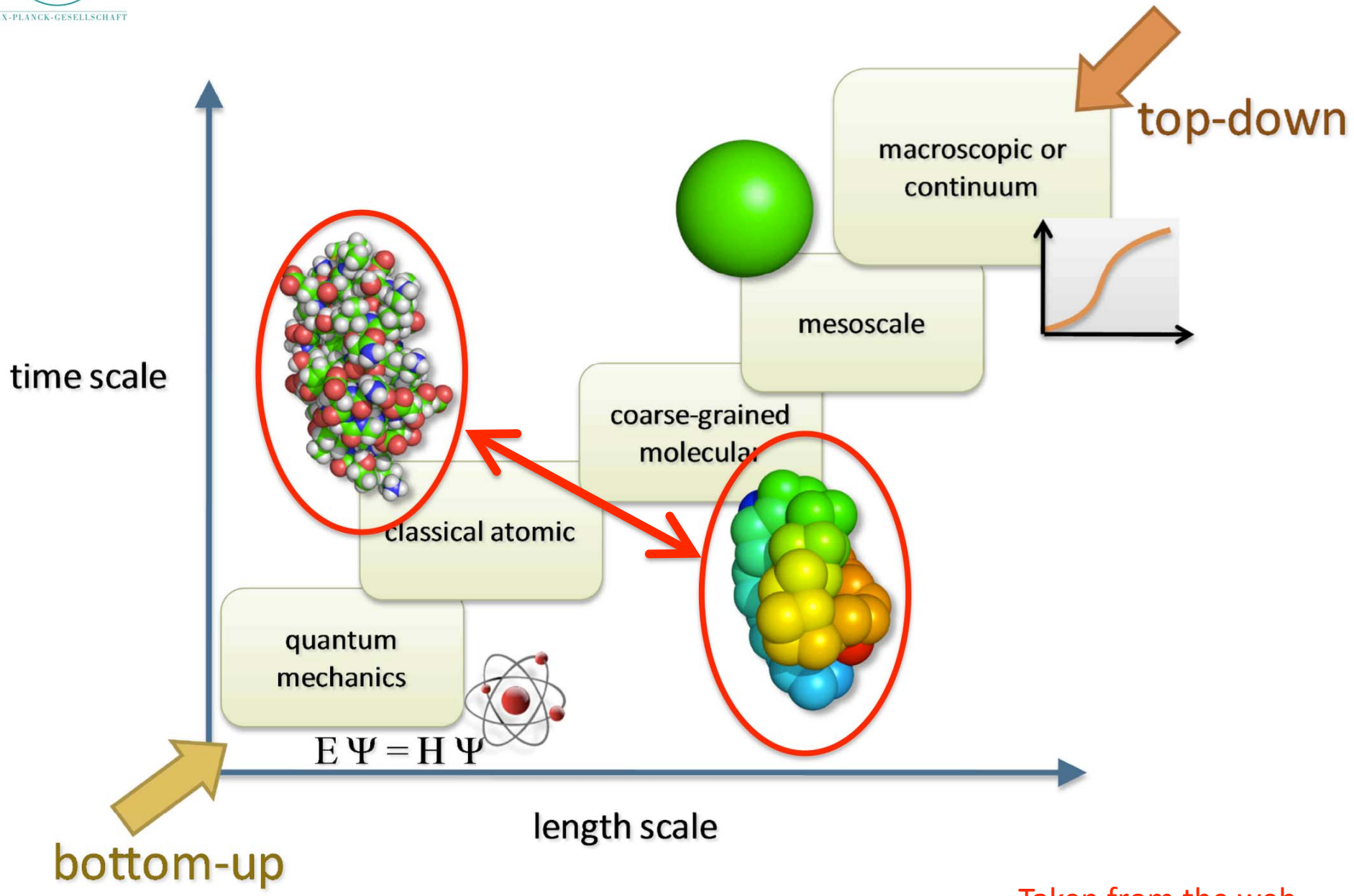


Taken from the web

(Bio-)Macromolecular solvation

- Understanding (bio-)physical properties
- Structure, function and stability of proteins
- Water and organic solvent (effective open boundary)
- Influence of co-solvents
- Mixed solvent (open systems MD is needed)

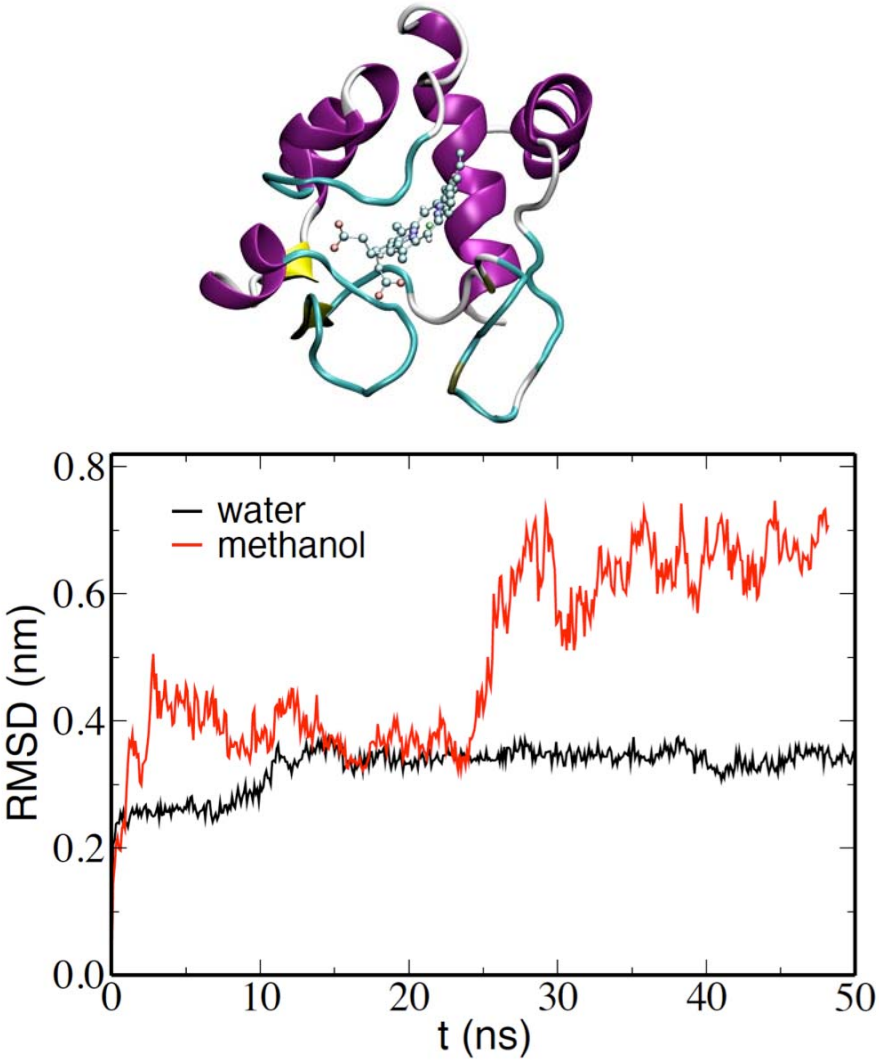
Aim:

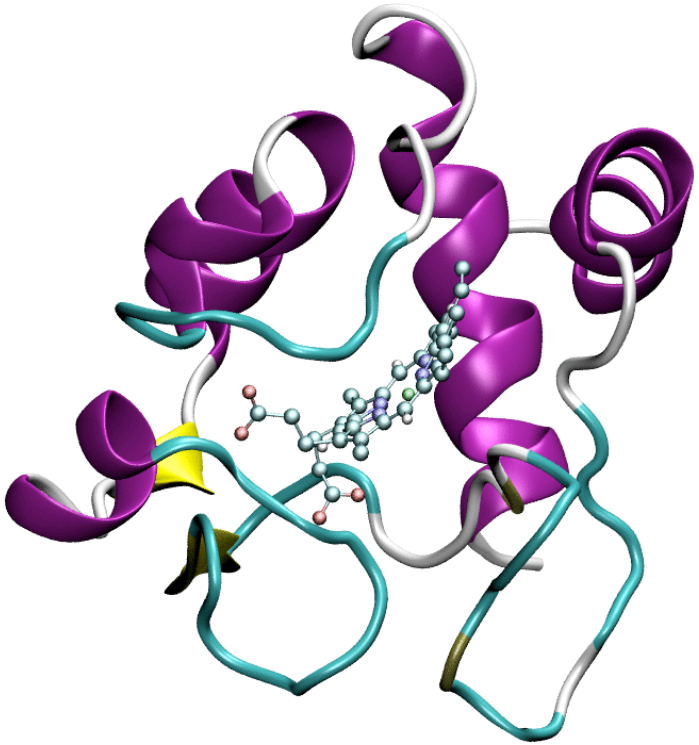
1: Grand (semi) canonical approach for (bio-)molecules in mixed solvents

2: Study large scale conformational transition of macromolecules

Why aqueous mixtures?

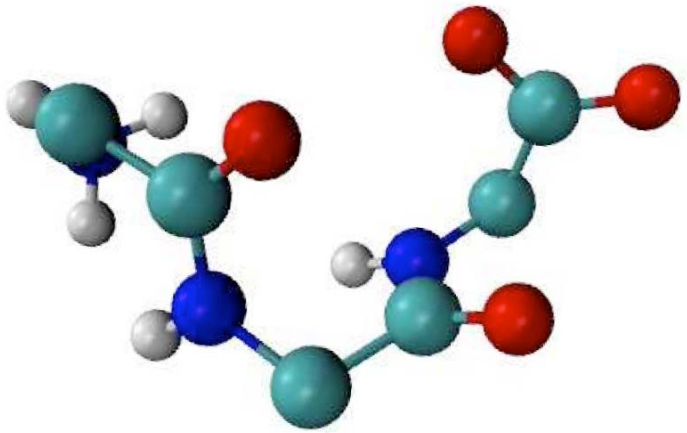
Cytochrome C: Stable structure in water

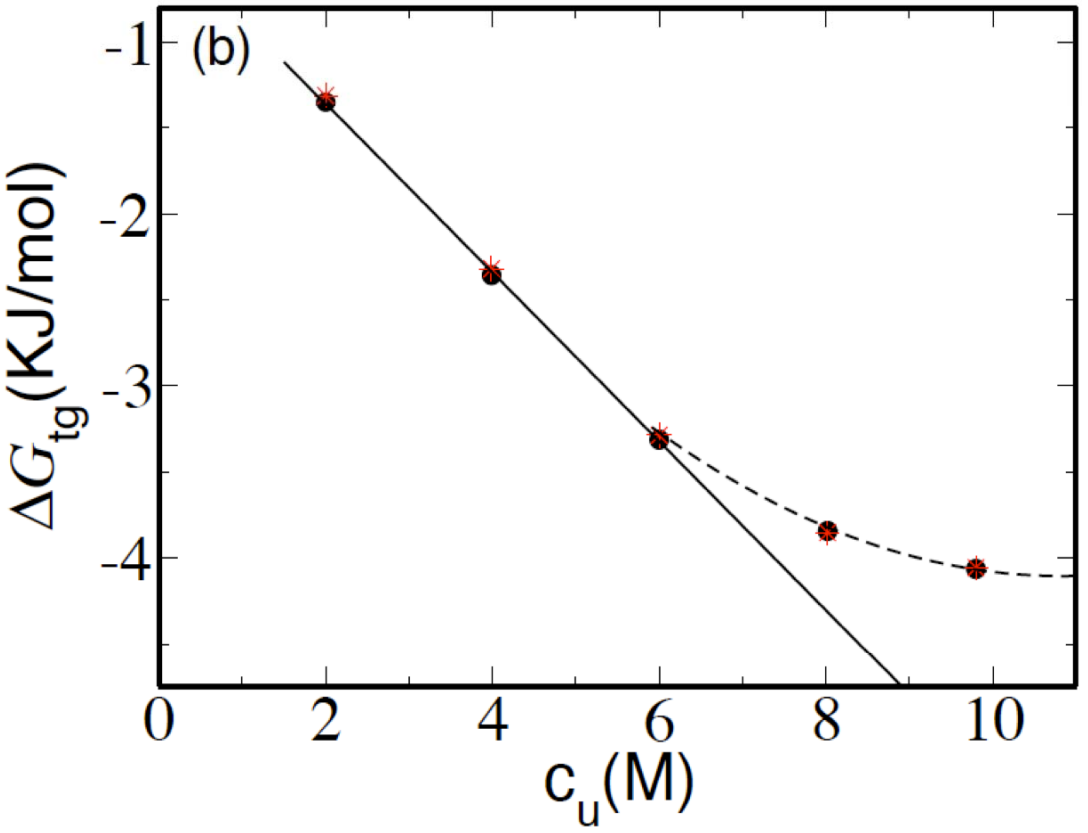




Why aqueous mixtures?

Peptide (tri-glycine) + $CO(NH_2)_2$ + H_2O

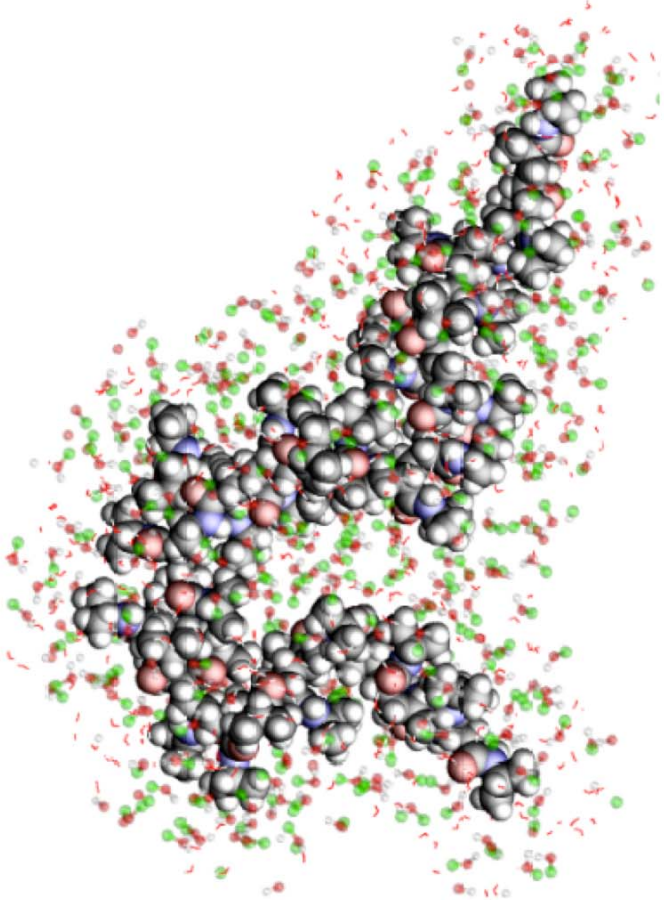


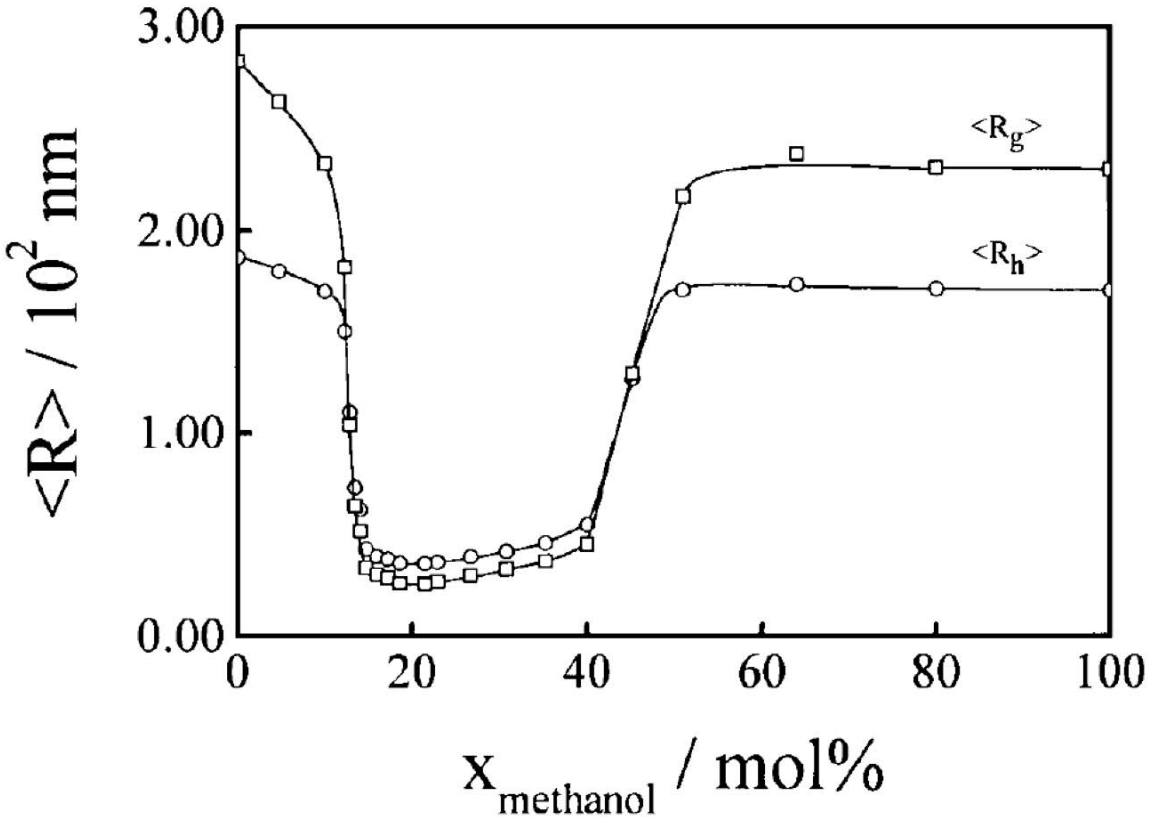


Mukherji, van der Vegt, and Kremer, J. Chem. Theory Comp. 8, 3635 (2012).

Why aqueous mixtures?

PNIPAm + CH_3OH + H_2O

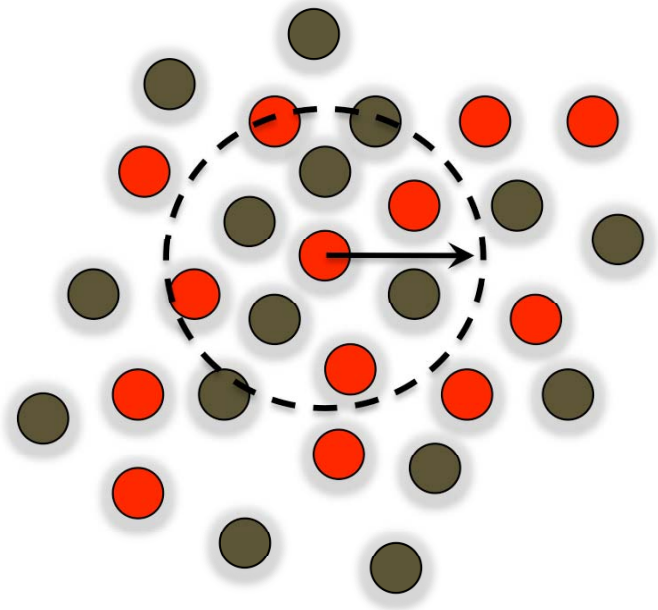




Zhang and Wu, Physical Review Letters 86, 822 (2001).
Mukherji and Kremer, Macromolecules (accepted 2013).

Fluctuation theory of Kirkwood-Buff

Fluctuation theory: Thermodynamic properties from microscopic (pair-wise) molecular distributions



$$G_{ij} = V\left[\frac{\langle N_i N_j\rangle - \langle N_i\rangle\langle N_j\rangle}{\langle N_i\rangle\langle N_j\rangle} - \frac{\delta_{ij}}{\langle N_j\rangle}\right]$$

$$= 4\pi\int_0^\infty \left[g_{ij}^{\mu VT}(r) - 1\right] r^2 dr,$$

Excess (depletion) coordination number

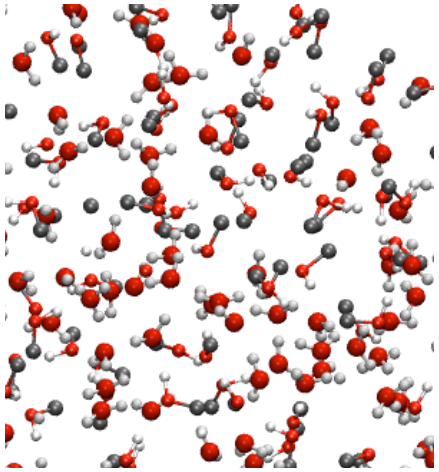
$$\Delta N_{ij} = \rho_j G_{ij}$$

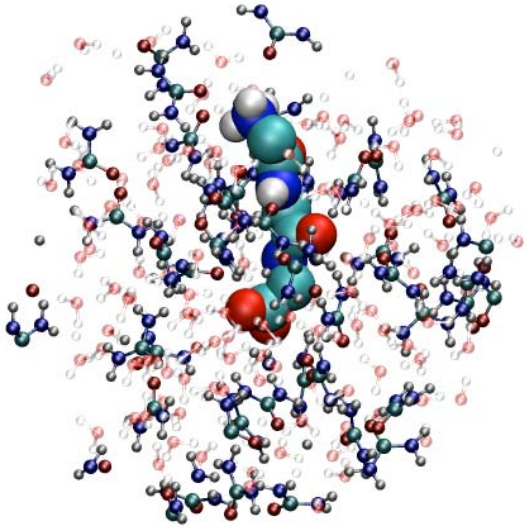
- Solvation energy
- Chemical potential
- Partial molar volume
- Activity coefficient
- Compressibility .....

Kirkwood and Buff, J. Chem. Phys. 19, 774 (1951).

Fluctuation theory of Kirkwood-Buff

Solvation Free Energies





$$\gamma_{cc} = 1 + \left(\frac{\partial \ln \gamma_c}{\partial \ln \rho_c}\right)_{p,T} = \frac{1}{1 + \rho_c \left(\mathrm{G}_{cc} - \mathrm{G}_{cw}\right)}$$

$$k_B T \ln \gamma_c$$

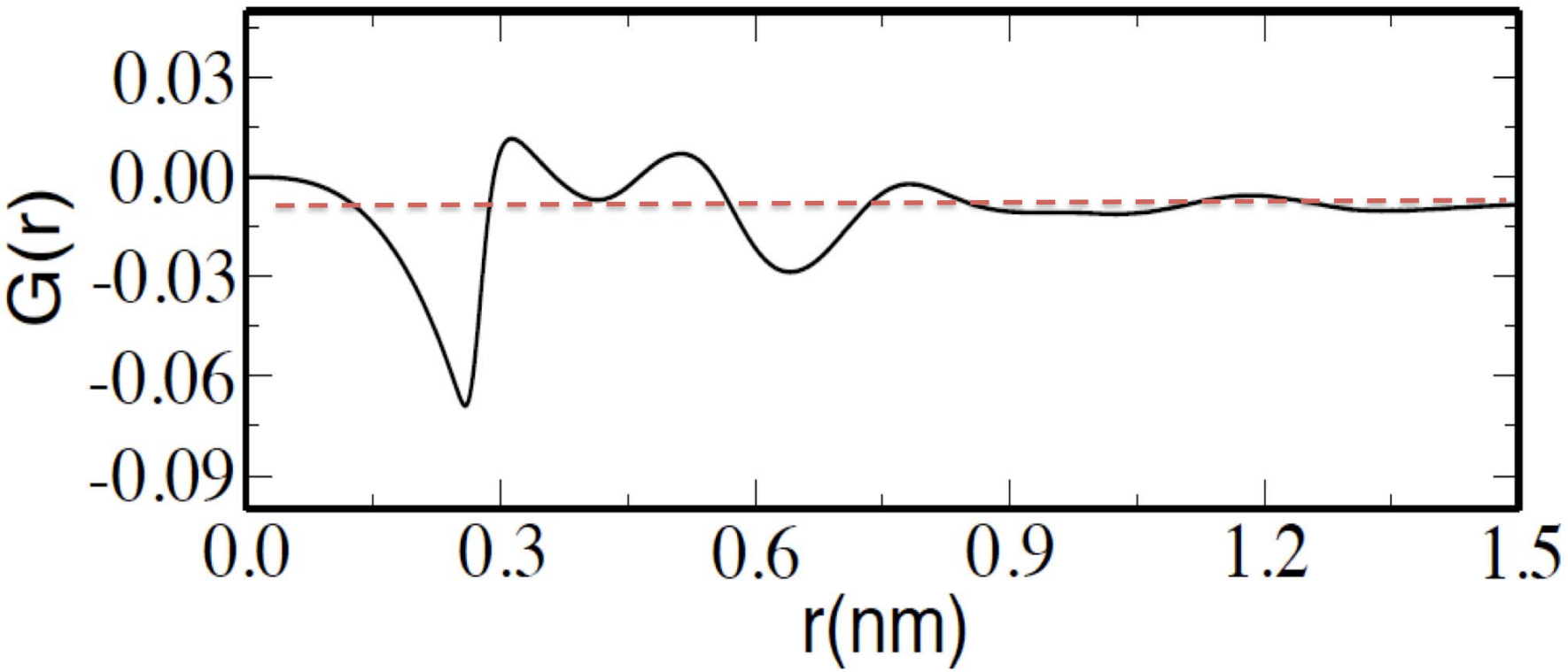
$$\lim_{\rho_s \to 0} \left(\frac{\partial \Delta \mathcal{G}_s}{\partial x_c}\right)_{p,T} = \frac{RT \left(\rho_w + \rho_c\right)^2}{\eta} \left(\mathrm{G}_{sw} - \mathrm{G}_{sc}\right)$$

$$\eta = \rho_w + \rho_c + \rho_w \rho_c \left(G_{ww} + G_{cc} - 2G_{cw}\right)$$

Kirkwood and Buff, J. Chem. Phys. 19, 774 (1951).

Kirkwood-Buff integrals

$$G_{ij}(r) = 4\pi \int_0^r \left[g_{ij}(r') - 1 \right] r'^2 \, dr'$$



Kirkwood and Buff, J. Chem. Phys. 19, 774 (1951).

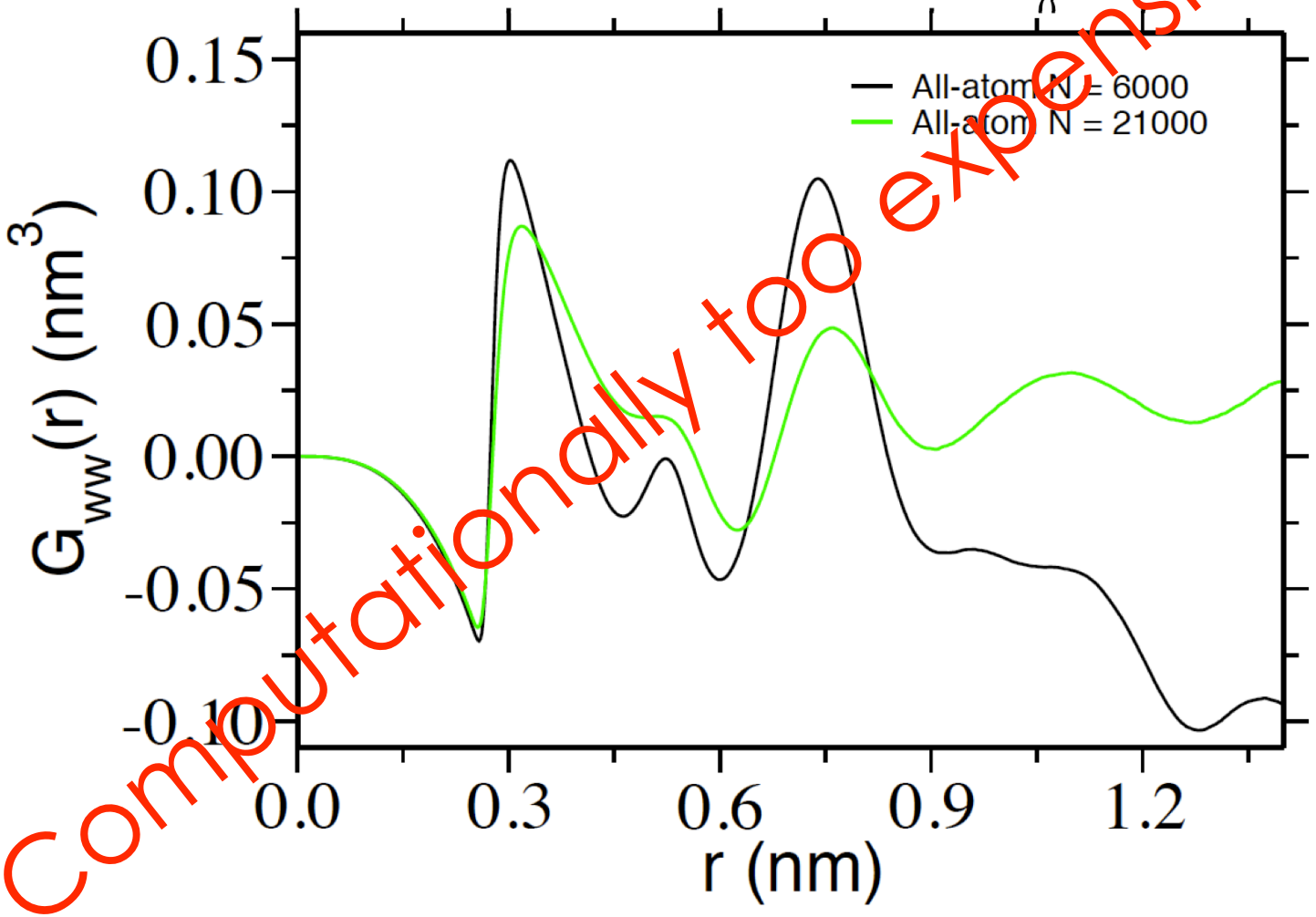
Problems with closed boundary setup

- Non-ideal mixture (water-cosolvent)
- (Bio-)physical processes are intimately linked to large density fluctuations (conformational transition)
- Excess in one region leads to depletion elsewhere
- KBI does not converge
- Thermodynamics away from a protein structure is poorly defined

Test case: methanol water mixture

Where to take the value?

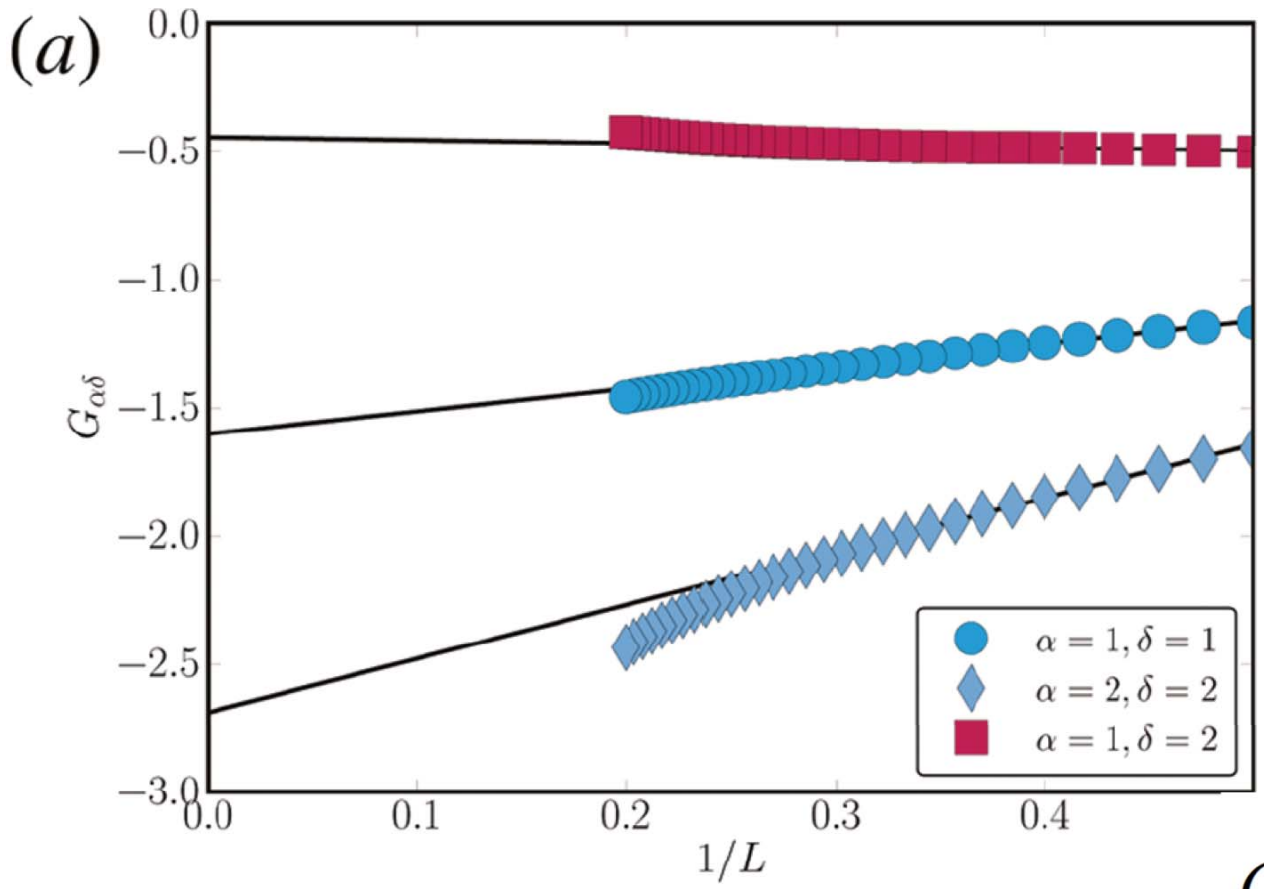
$$G_{ij}(r) = 4\pi \int_0^r \left[g_{ij}(r') - 1 \right] r'^2 \, dr'$$

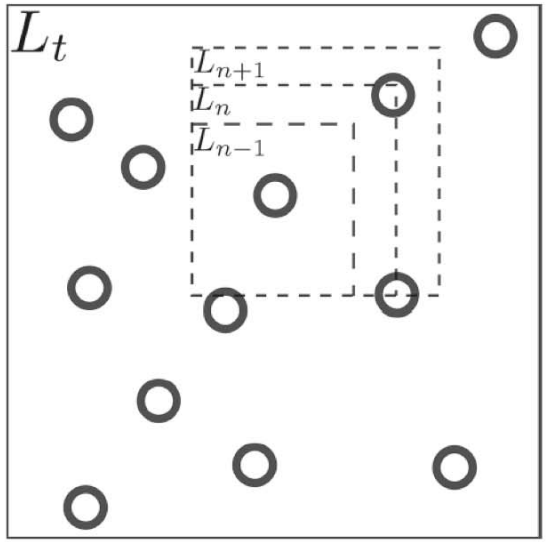


Computationally too expensive

Mukherji, van der Vegt, Kremer, and Delle Site, J. Chem. Theory Comp. (Letter) 8, 375 (2012).

Alternative method

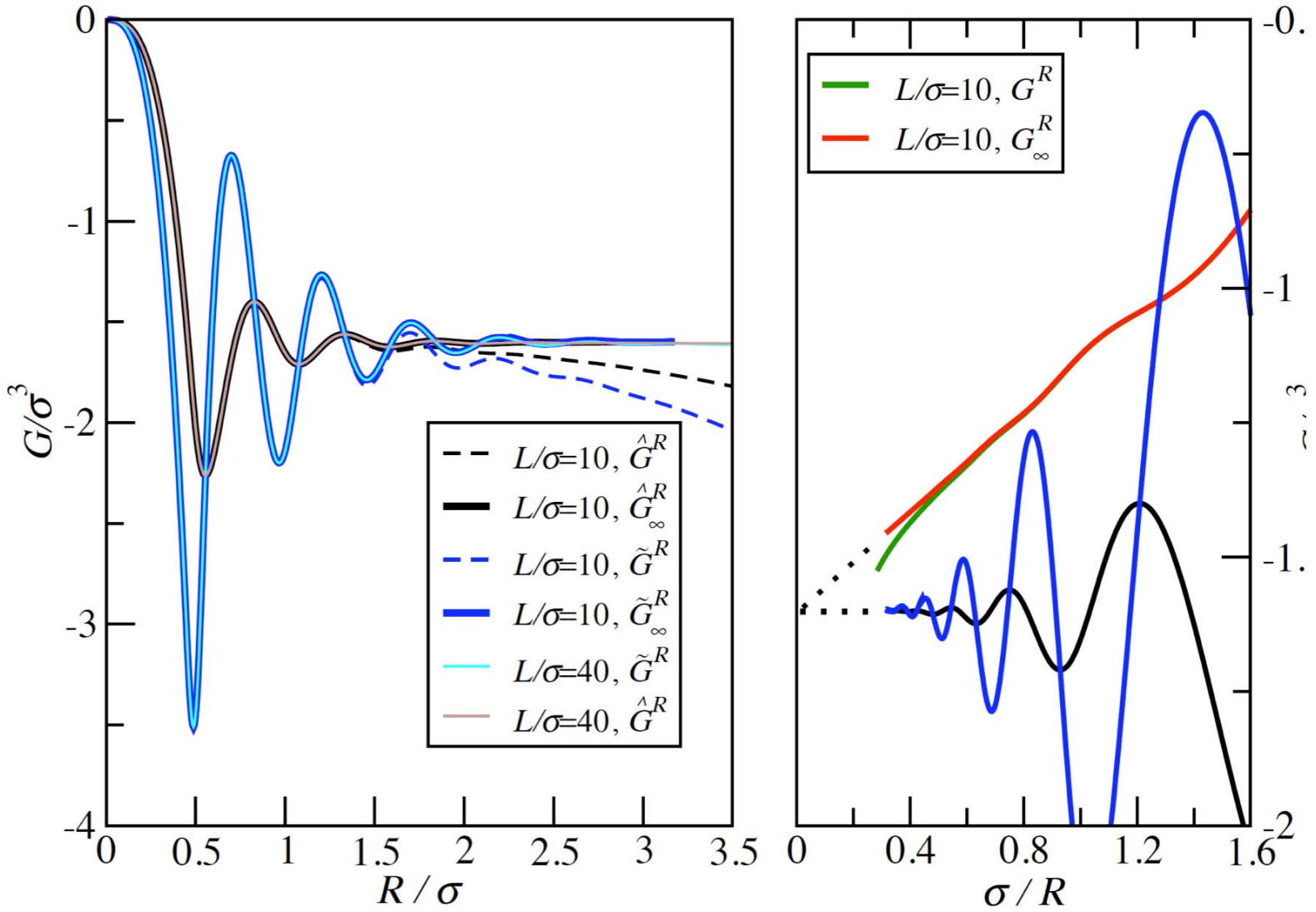




$$G_{ij}(r_s) = G_{ij} + \frac{C}{r_s}$$

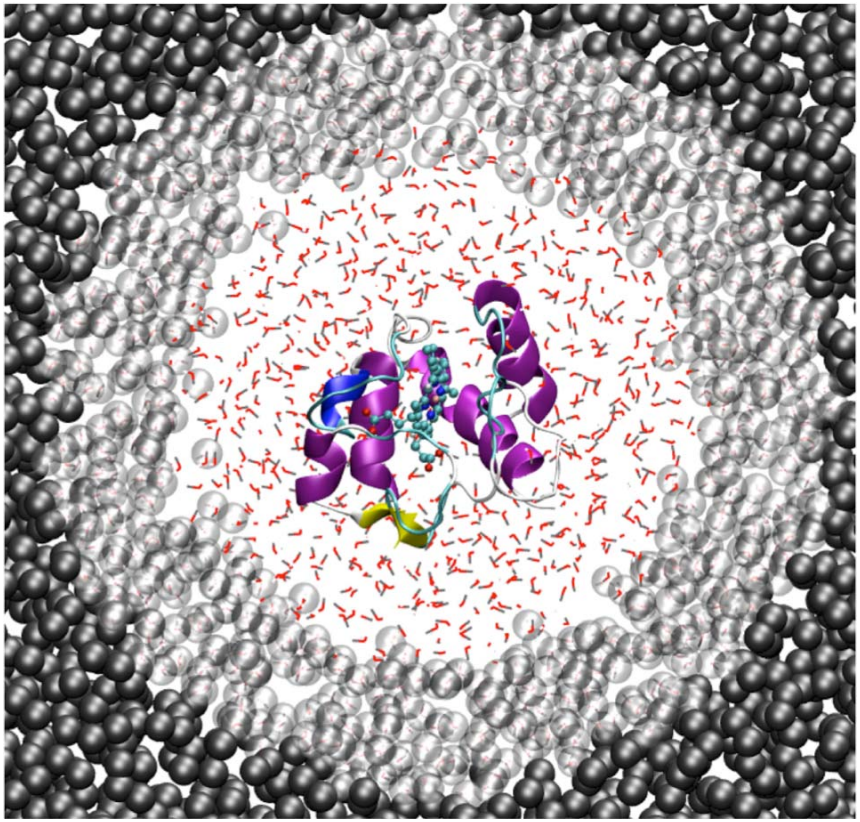
Schnell et al, J. Phys. Chem. B 115, 10911 (2011).

Alternative method

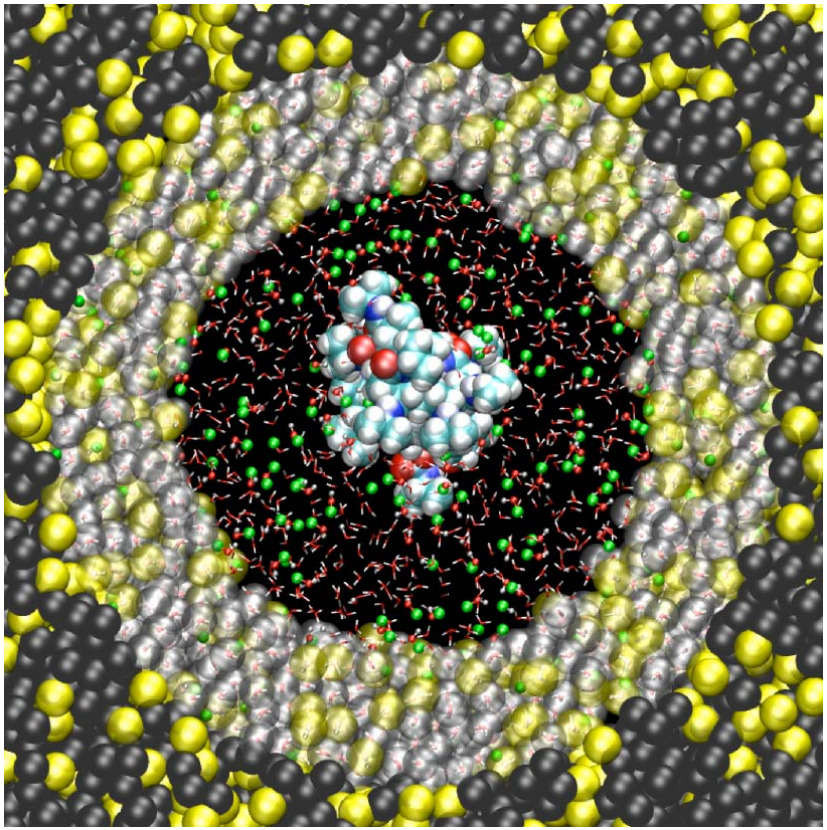


Kruger et al, J. Phys. Chem. Lett. 4, 235 (2013).

(Bio-)Macromolecular solvation



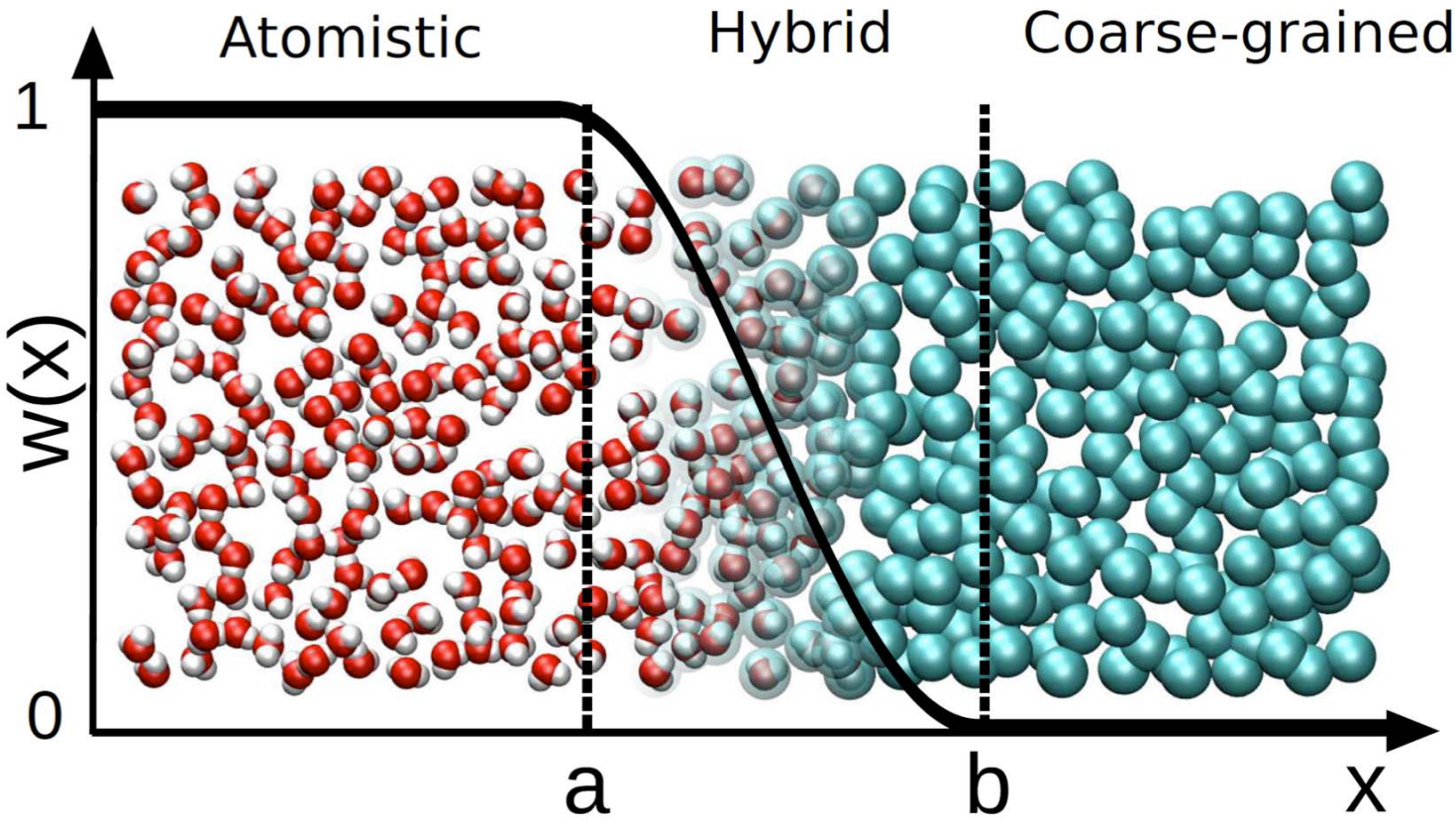
Cytochrome C in organic solvent



PolyNIPAm in mixed solvent

AdResS: Effective open boundary

Adaptive Resolution Molecular Dynamics Scheme

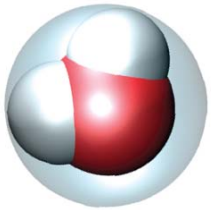


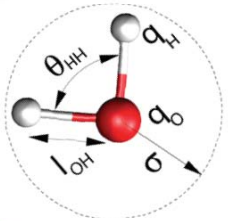
$$\vec{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\vec{F}^{\text{atom}}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\vec{F}^{\text{cg}}_{\alpha\beta}$$

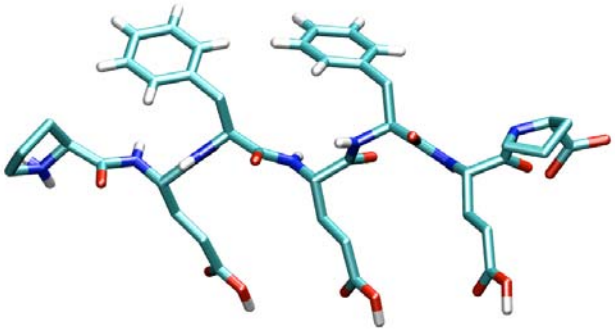
Praprotnik, Delle Site, and Kremer, J. Chem. Phys., 123, 224106 (2005).

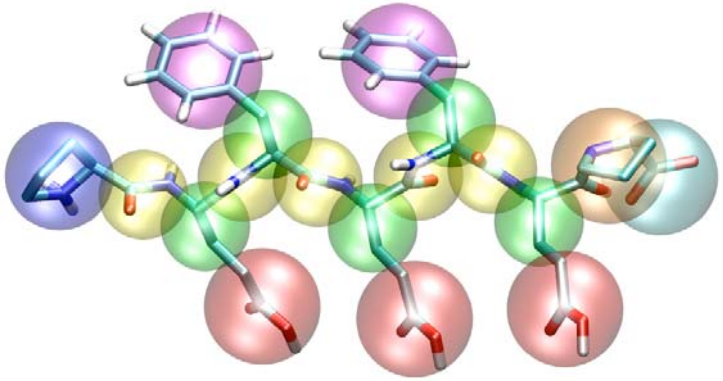
Systematic coarse-graining

- Less degrees of freedom
- Faster dynamics
- Large time and length scales





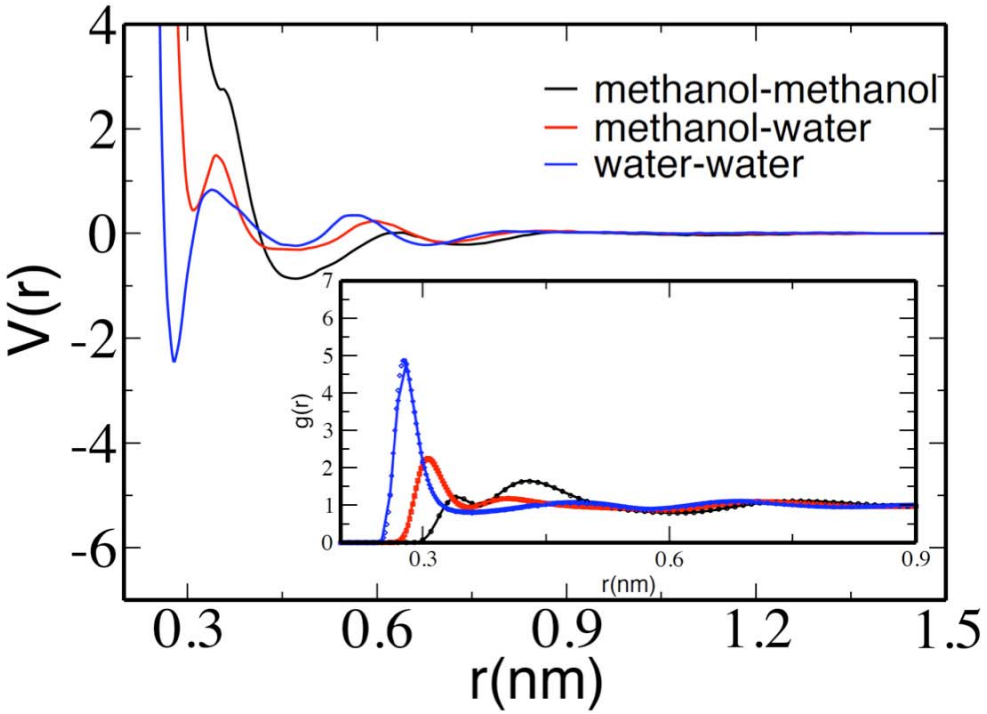


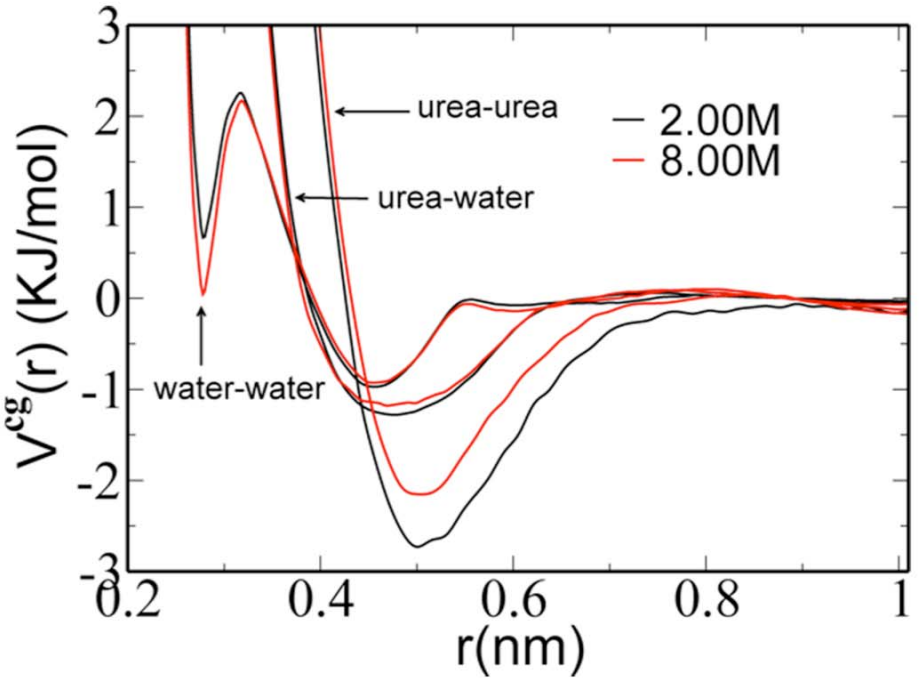


Iterative Boltzmann inversion

$$V_0(r) = -k_B T \ln\left[g_{target}(r)\right] \longrightarrow \text{MD} \longrightarrow g_{new}(r)$$

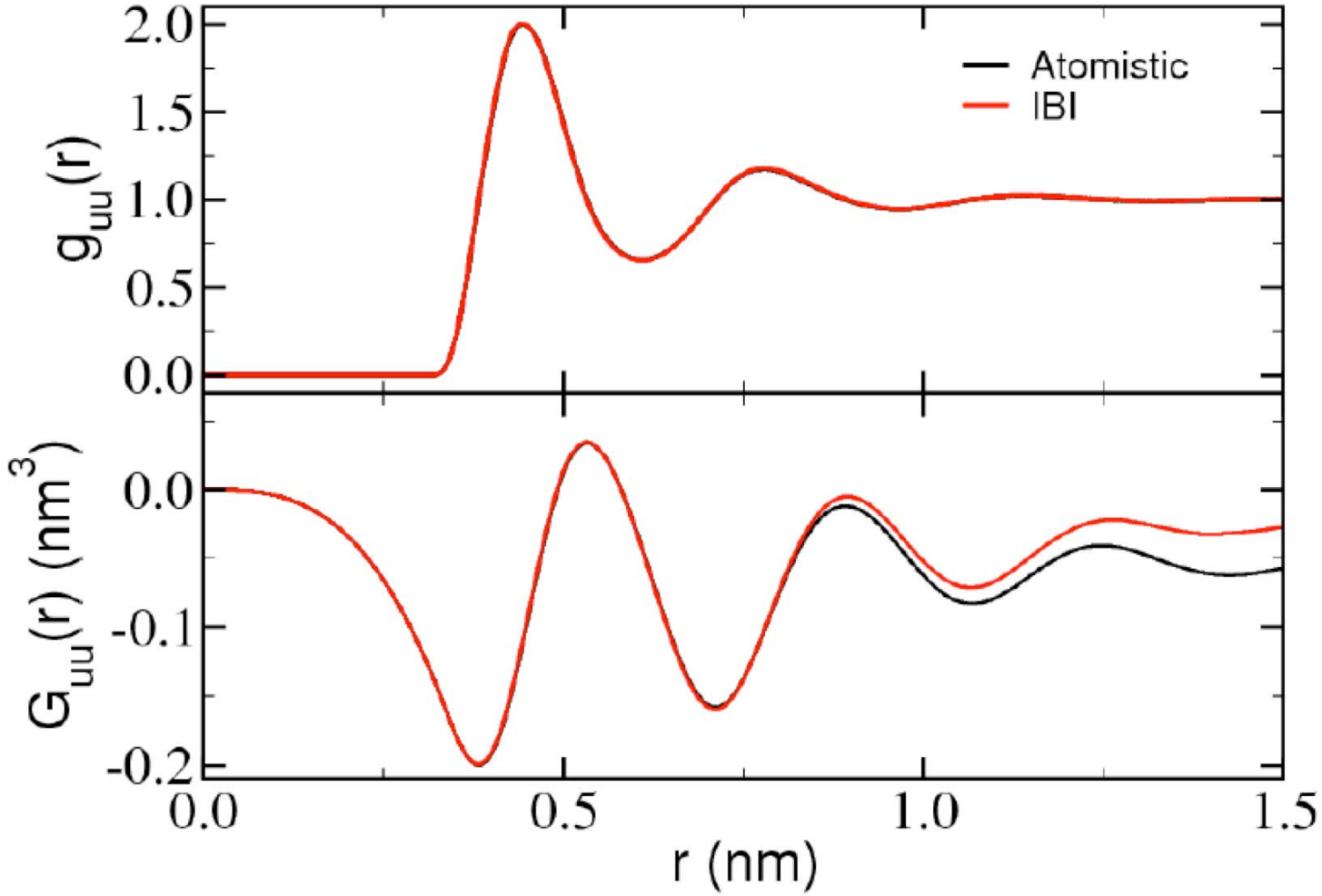
$$V^{cg}{}_n(r) = V^{cg}{}_{n-1}(r) + k_B T \ln\left[\frac{g_{n-1}(r)}{g_{target}(r)}\right]$$





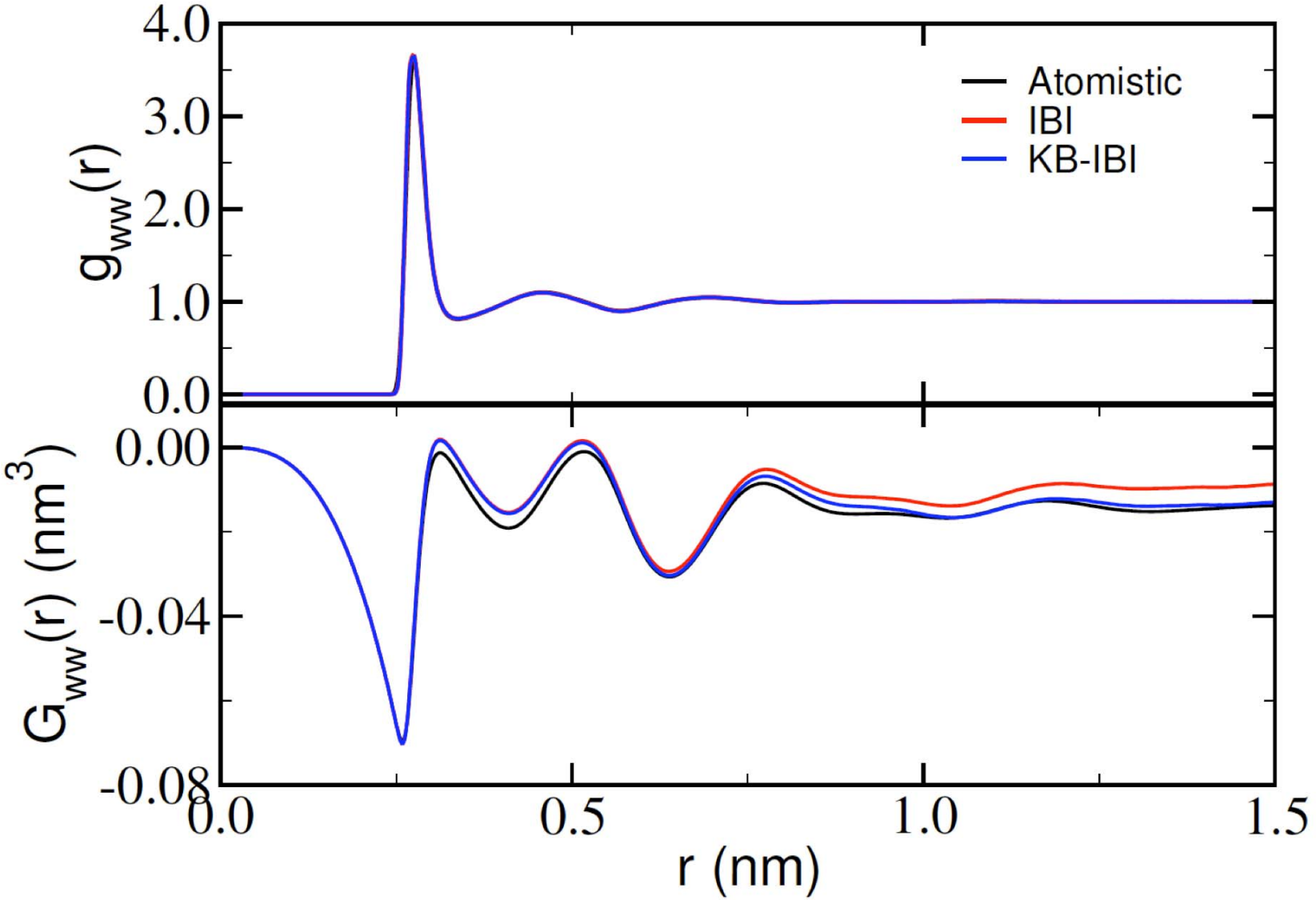
Reith, Pütz, and Müller-Plathe, J. Comp. Chem. Theory Comp. 24, 1624 (2003).

Iterative Boltzmann inversion (Mixture)



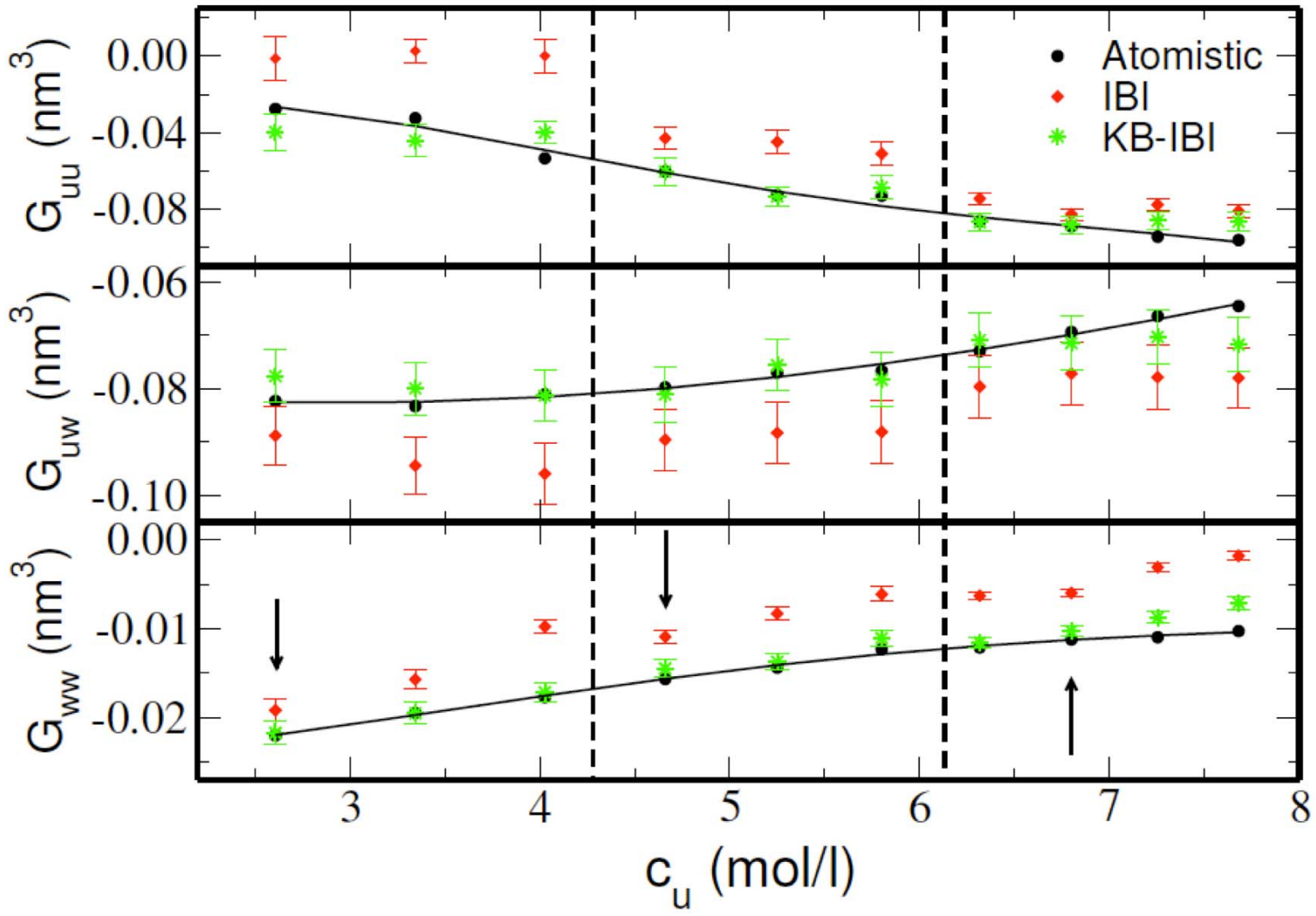
Ganguly, Mukherji, Junghans, and van der Vegt, J. Chem. Theory Comp. 8, 1802 (2012).

Iterative Boltzmann inversion (Mixture)



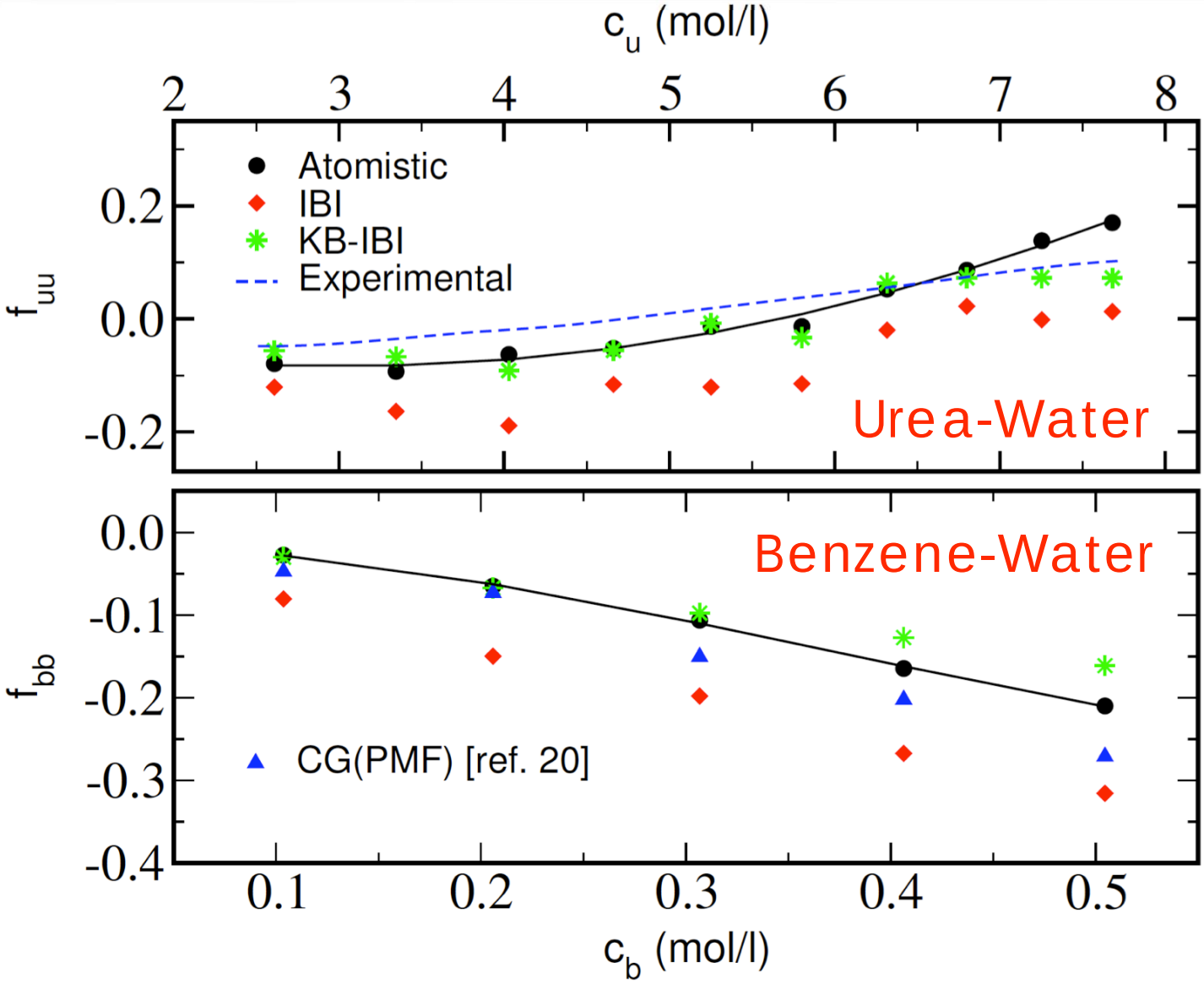
Ganguly, Mukherji, Junghans, and van der Vegt, J. Chem. Theory Comp. 8, 1802 (2012).

KB-IBI: Urea-Water



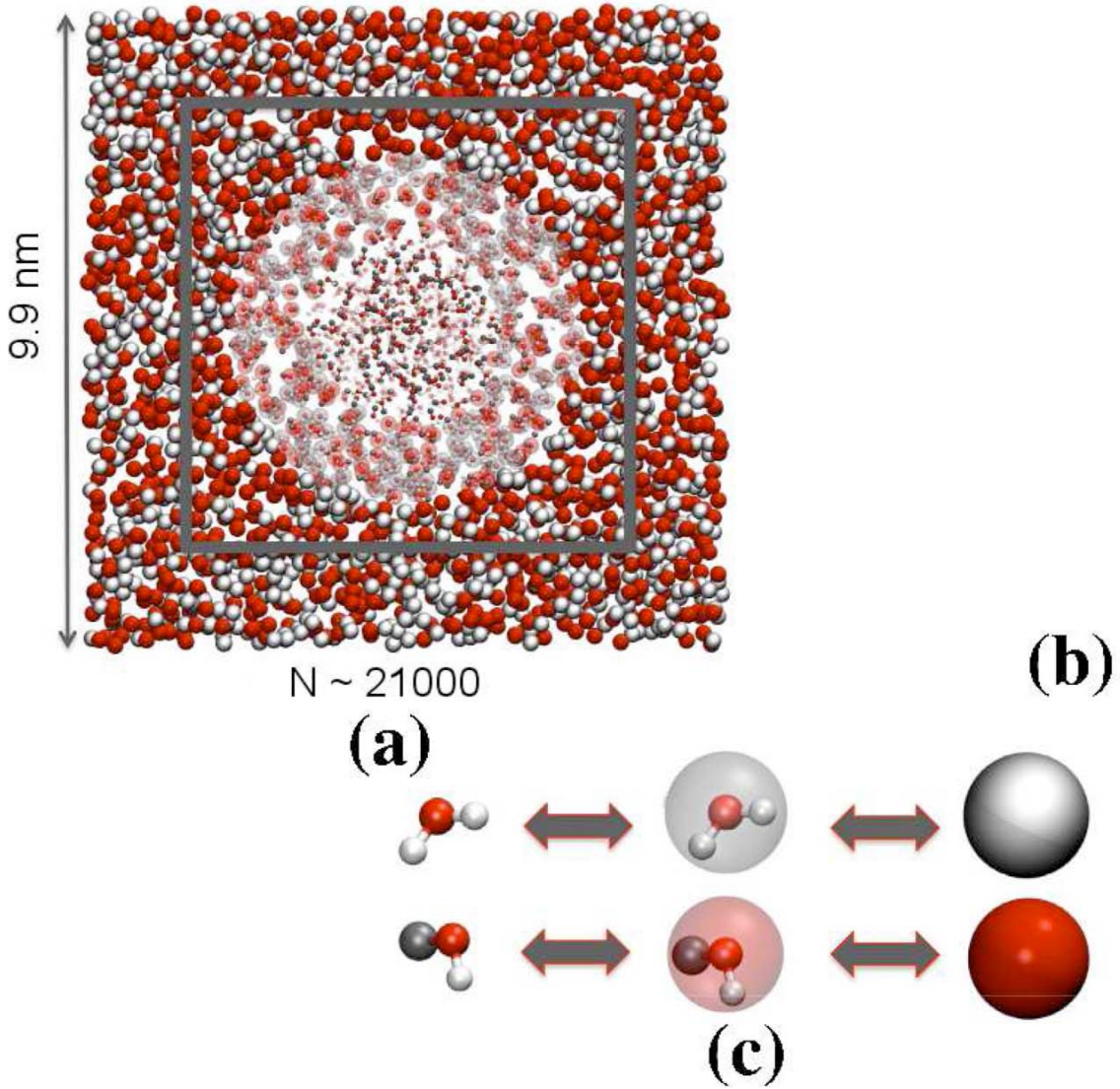
Ganguly, Mukherji, Junghans, and van der Vegt, J. Chem. Theory Comp. 8, 1802 (2012).

KB-IBI



Ganguly, Mukherji, Junghans, and van der Vegt, J. Chem. Theory Comp. 8, 1802 (2012).

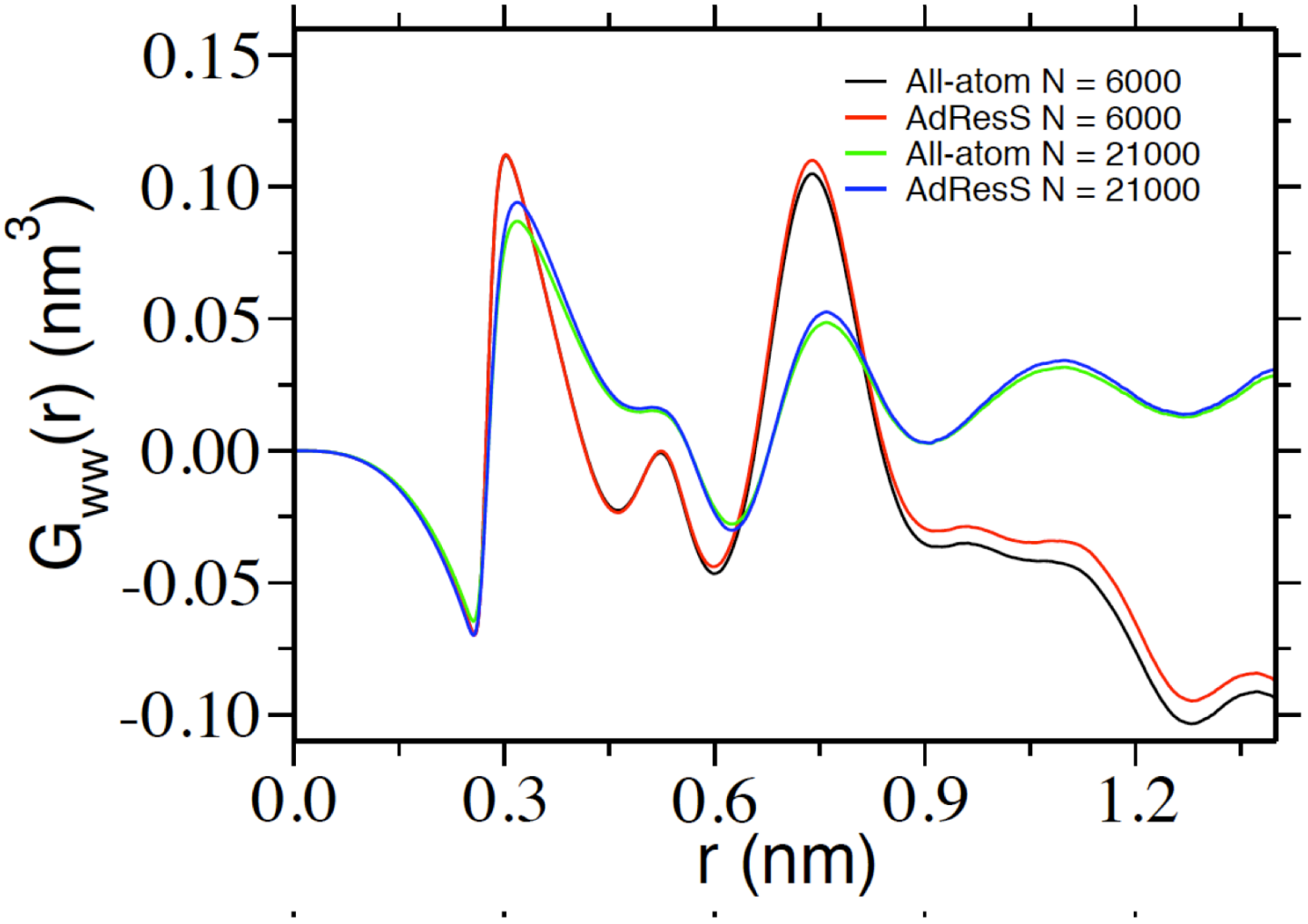
Our Goal



KBI: Methanol-water test case

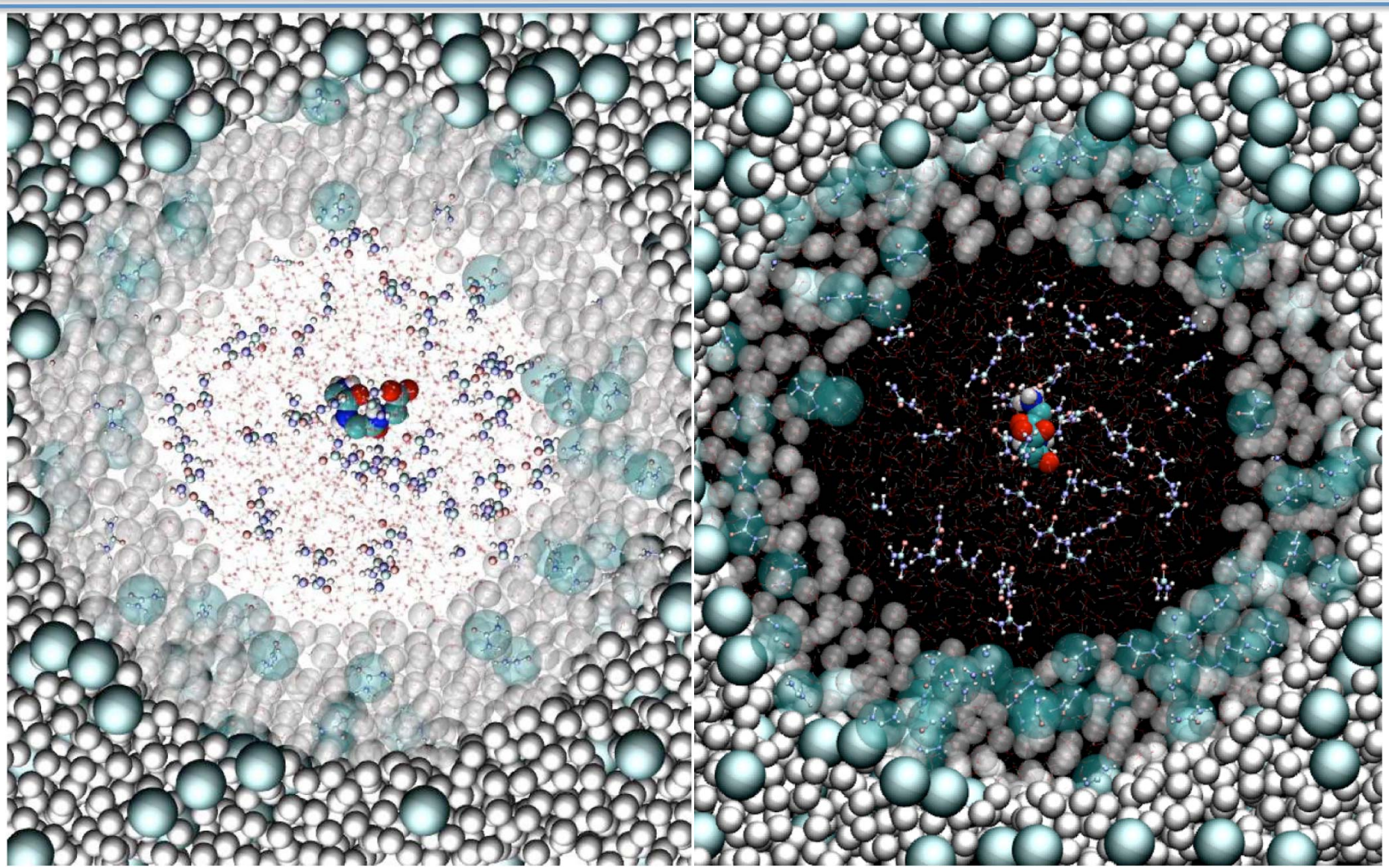
For 0.9 methanol mole fraction

Water-Water



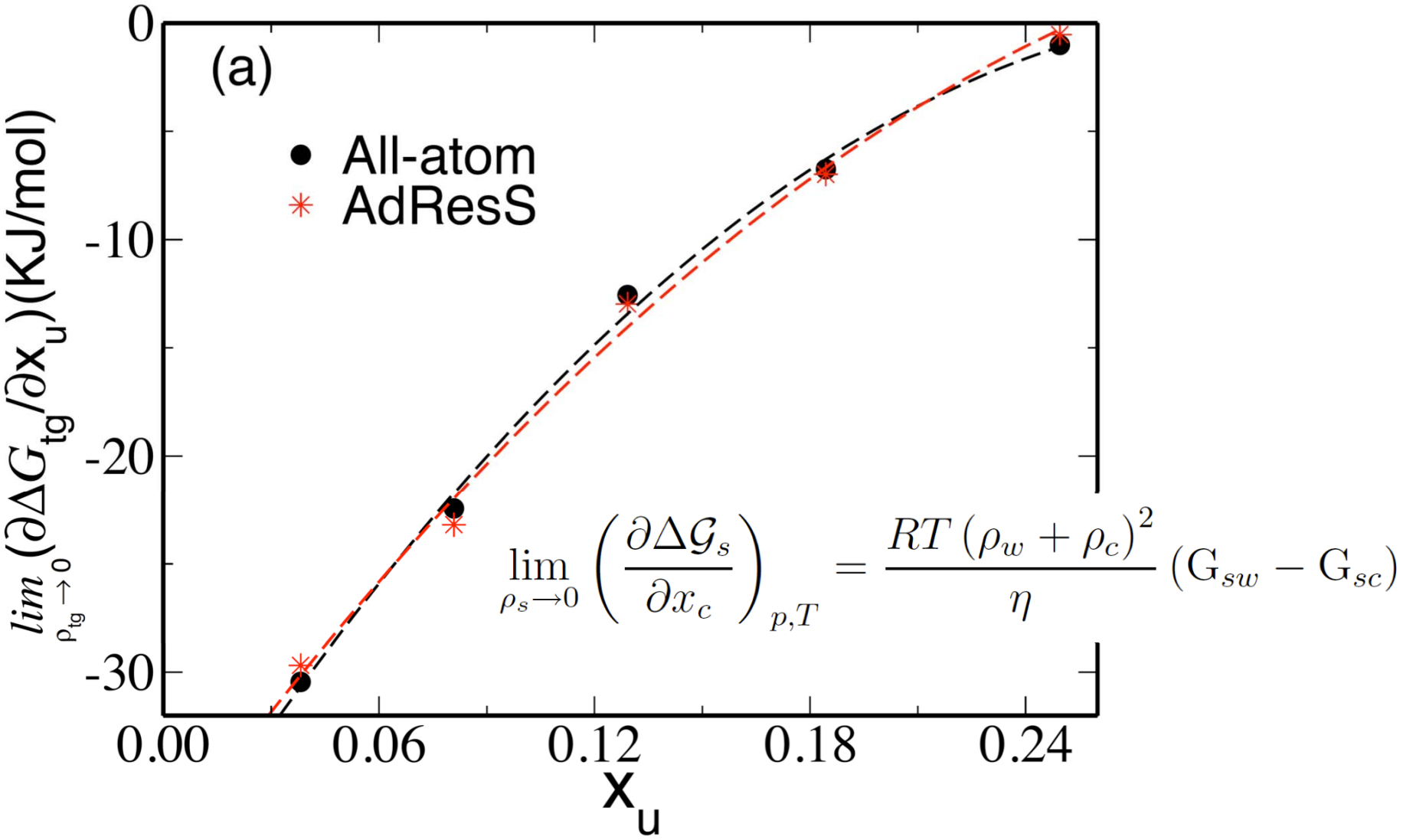
Mukherji, van der Vegt, Kremer, and Delle Site, J. Chem. Theory Comp. (Letter) 8, 375 (2012).

Solvation of tri-glycine: Urea-water



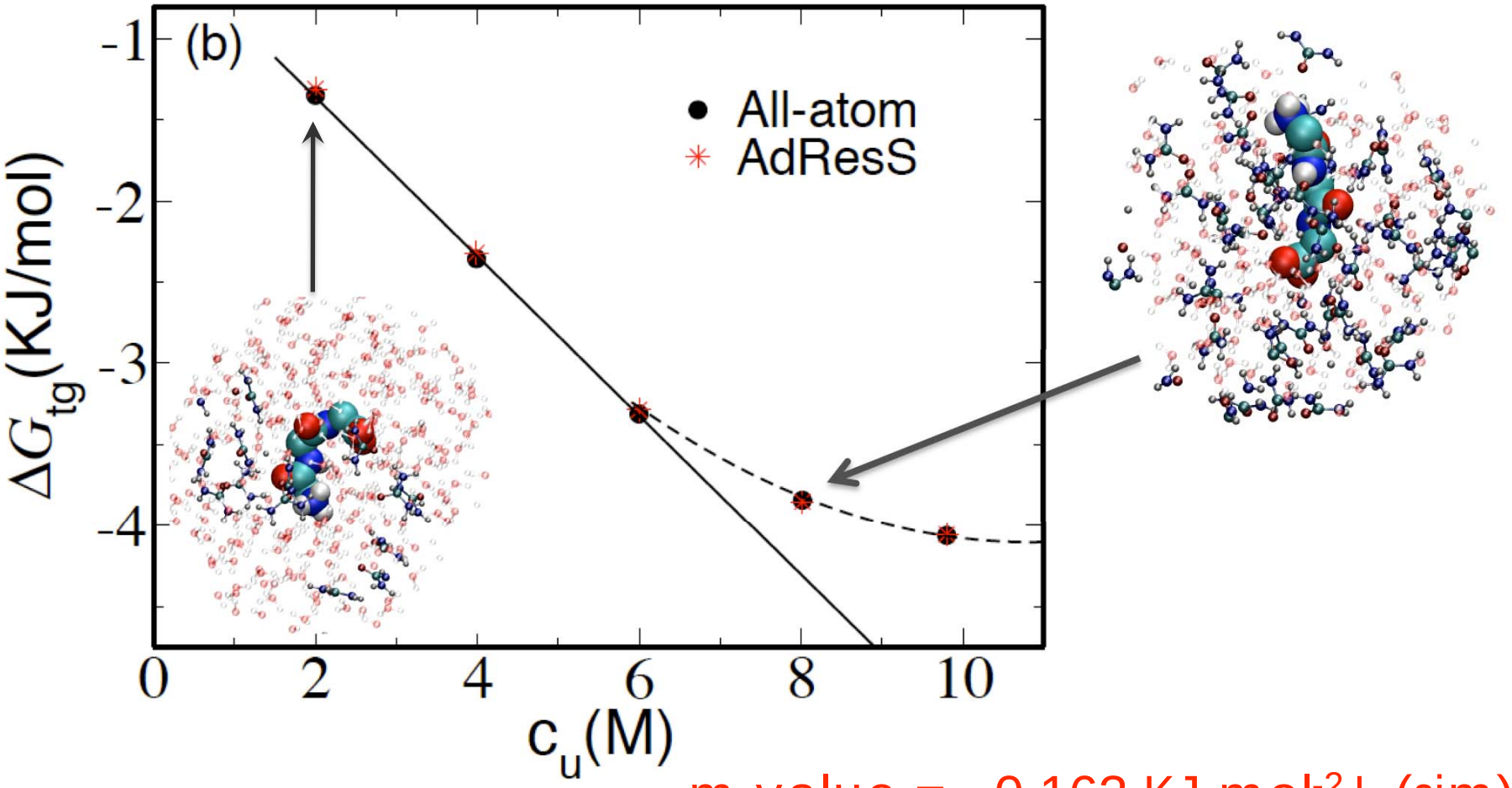
Mukherji, van der Vegt, and Kremer, J. Chem. Theory Comp. 8, 3635 (2012).

Solvation free energy of tri-glycine



Mukherji, van der Vegt, and Kremer, J. Chem. Theory Comp. 8, 3635 (2012).

Solvation free energy of tri-glycine



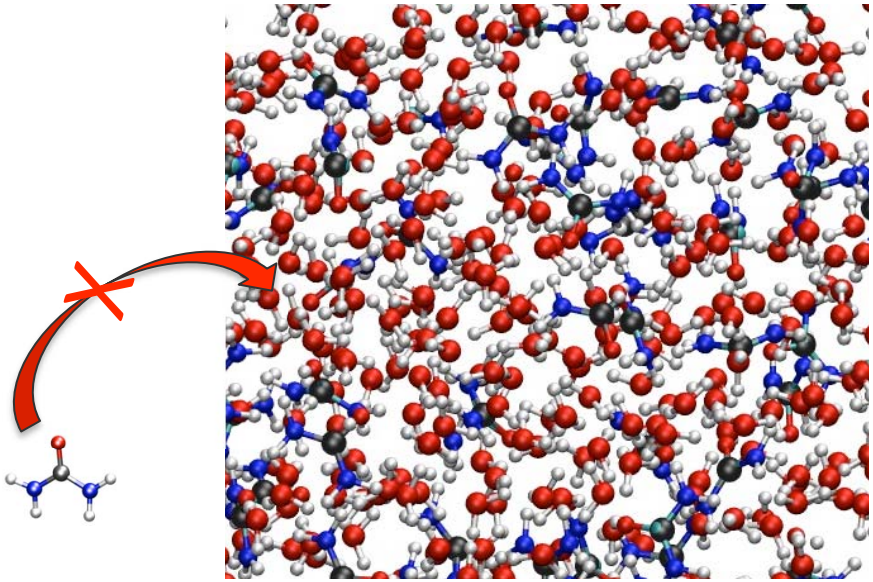
m-value = - 0.163 KJ mol^{-2} L (sim)
= - 0.164 KJ mol^{-2} L (exp)

Auton and Bolen, PNAS 102, 15065 (2005).

Mukherji, van der Vegt, and Kremer, J. Chem. Theory Comp. 8, 3635 (2012).

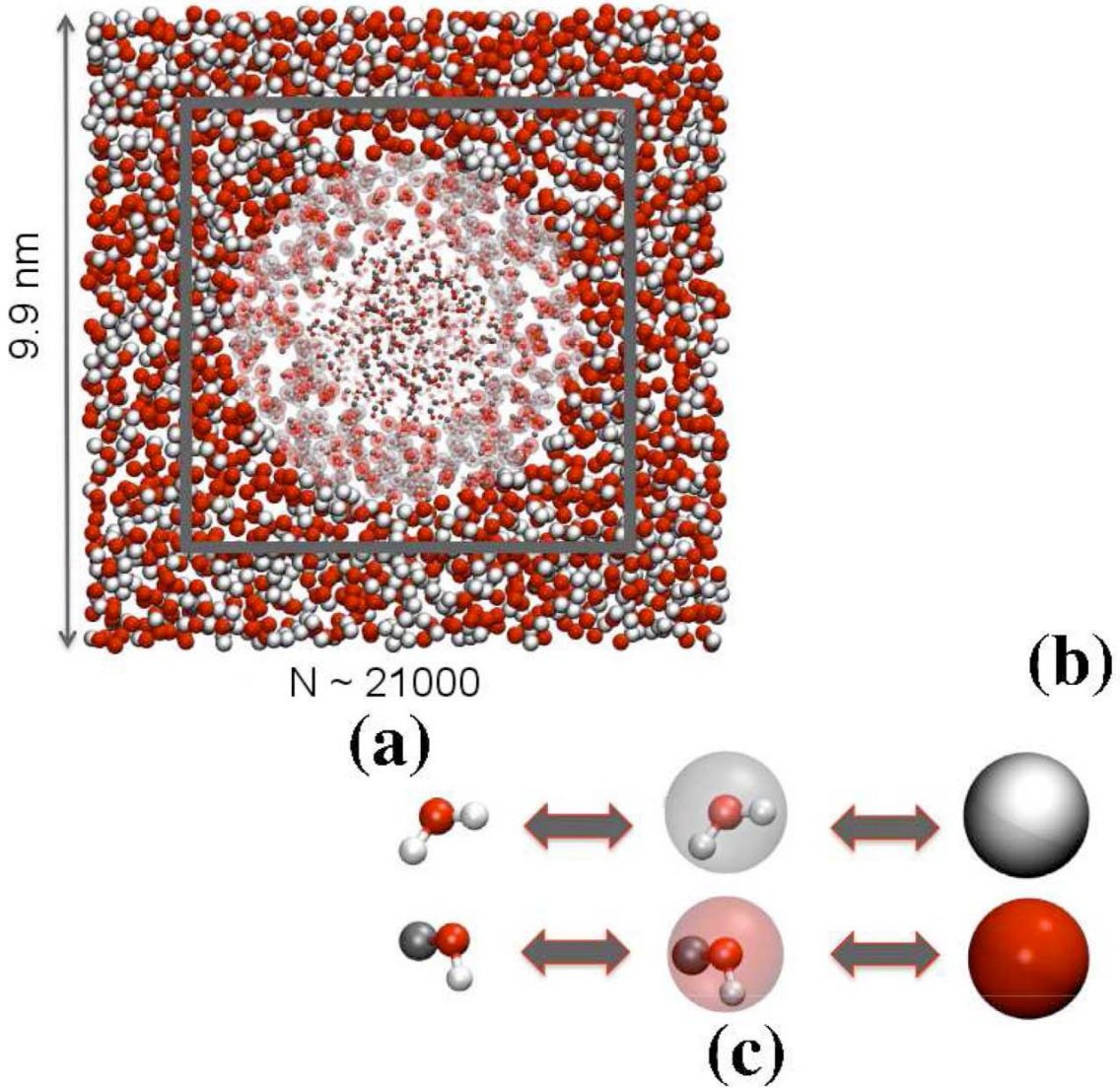
NVT: All-atom+CG

- We are still simulating a big NVT with different regions.

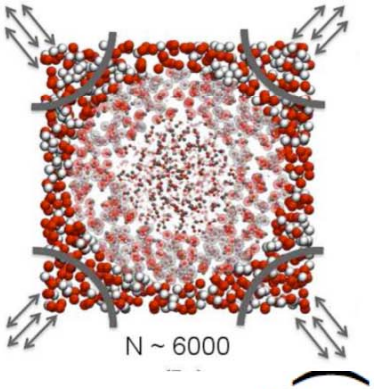


- Particle replacement in all-atom representation of complex incompressible fluid is almost impossible
- It might be possible, if the molecules are represented by spherically symmetric beads

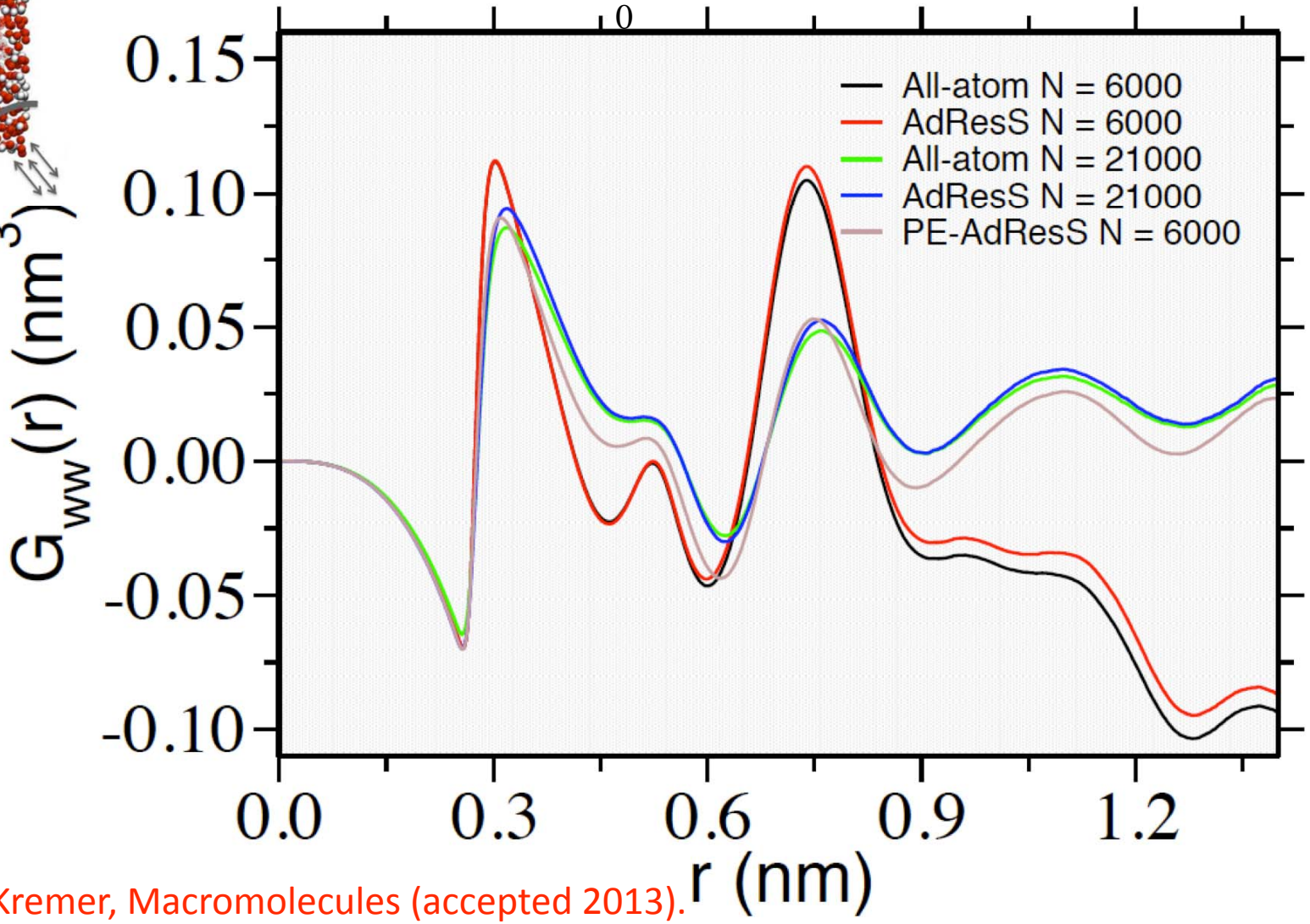
Our Goal: PE-AdResS



KBI: aqueous methanol



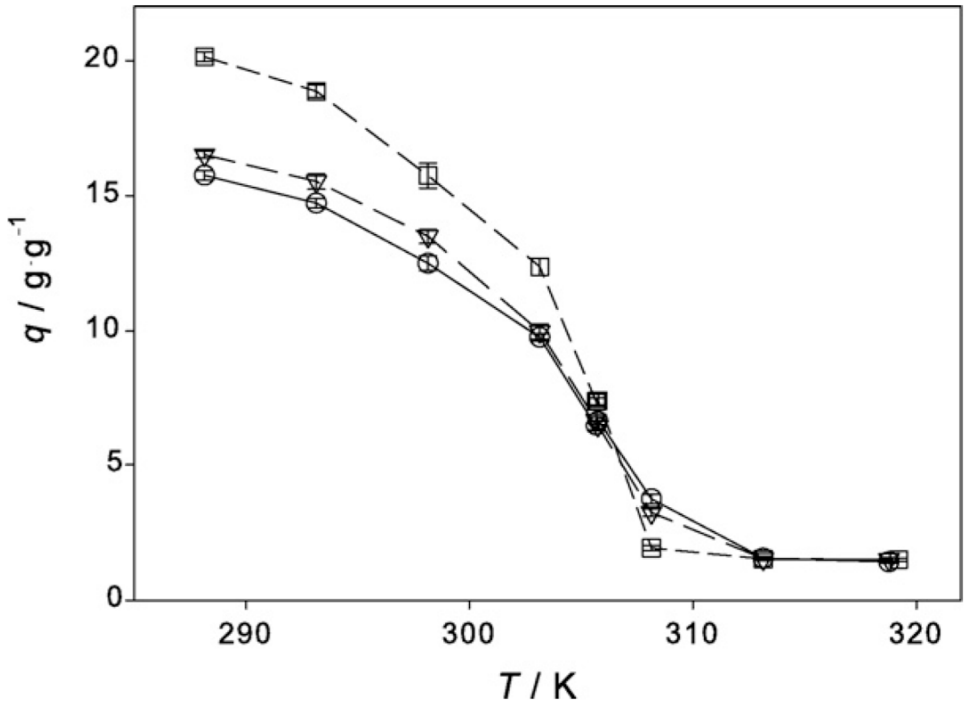
$$G_{ij}(r) = 4\pi \int_0^r \left[g_{ij}(r') - 1 \right] r'^2 \, dr'$$



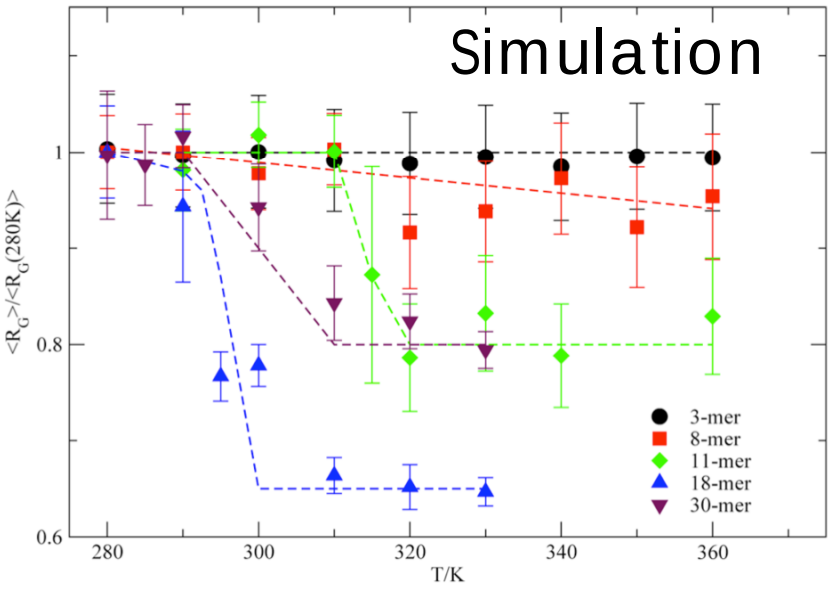
Mukherji and Kremer, Macromolecules (accepted 2013).

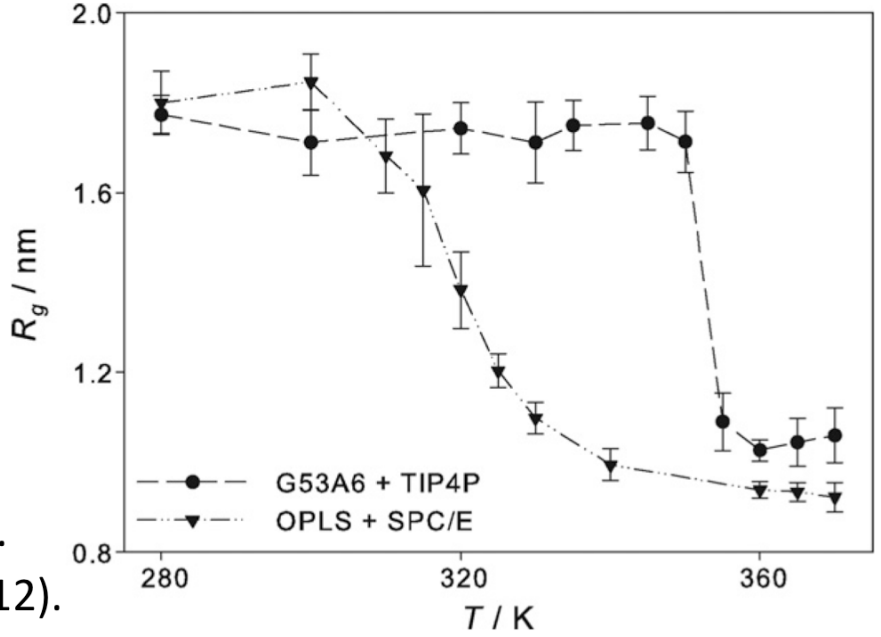
Poly-NIPAm: Thermo responsive

Experiment



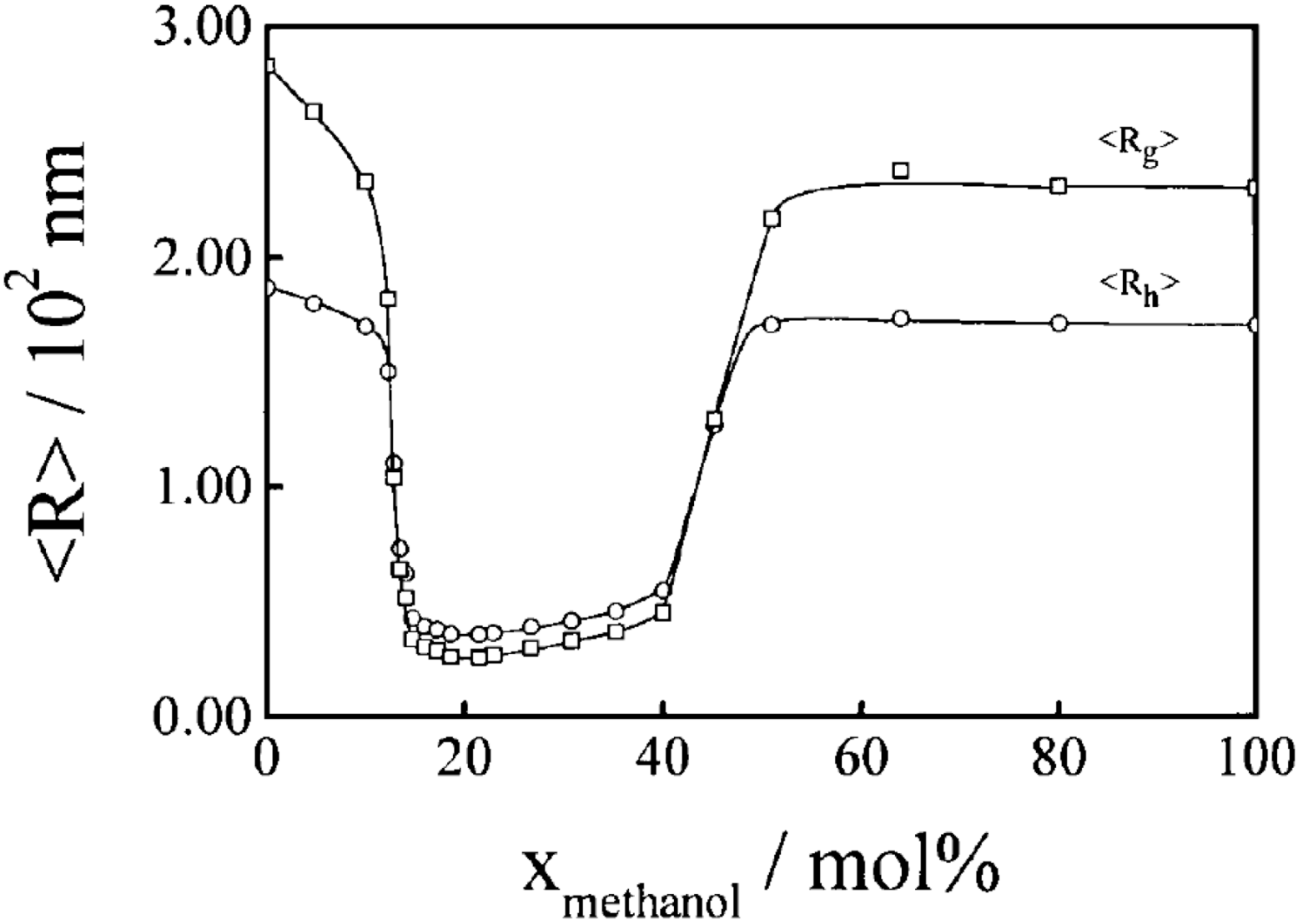
Simulation





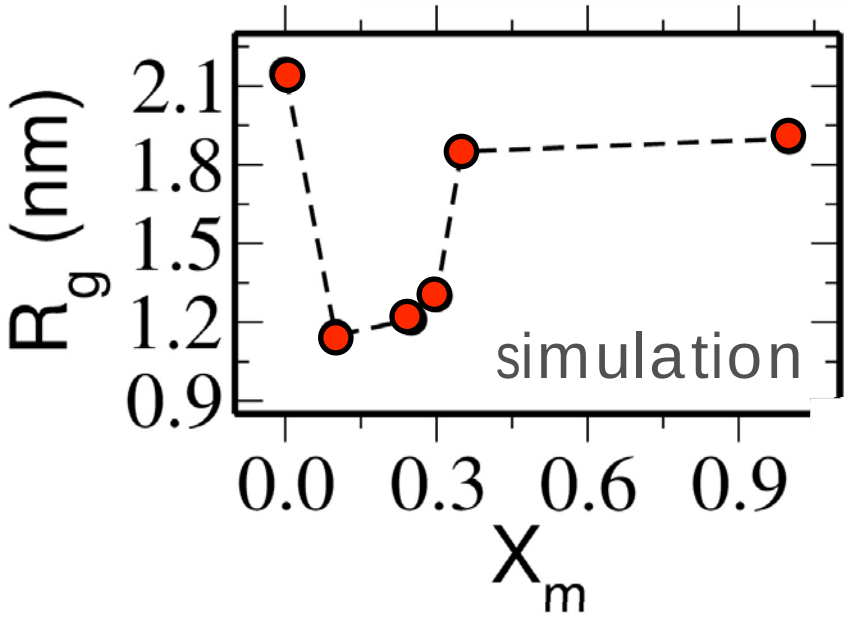
Walter et al. Fluid Phase Equilibria, 296, 164 (2010).
Tucker and Stevens, Macromolecules, 45, 6697 (2012).

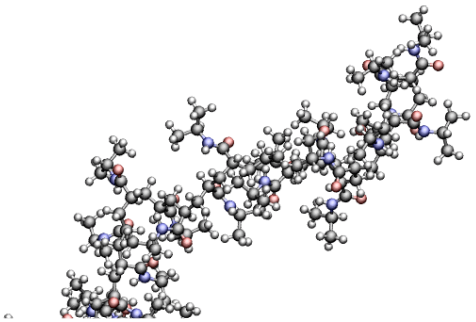
Poly-NIPAm in aqueous methanol

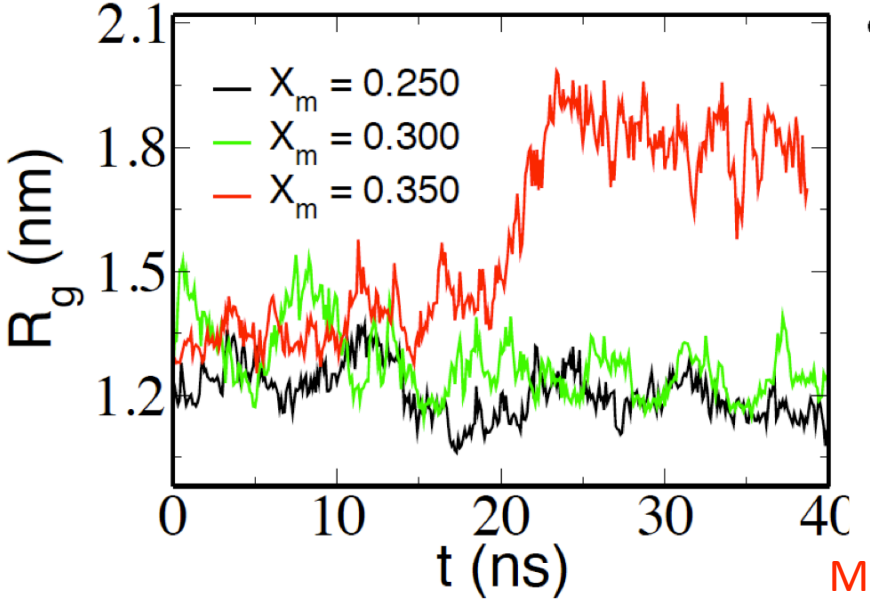


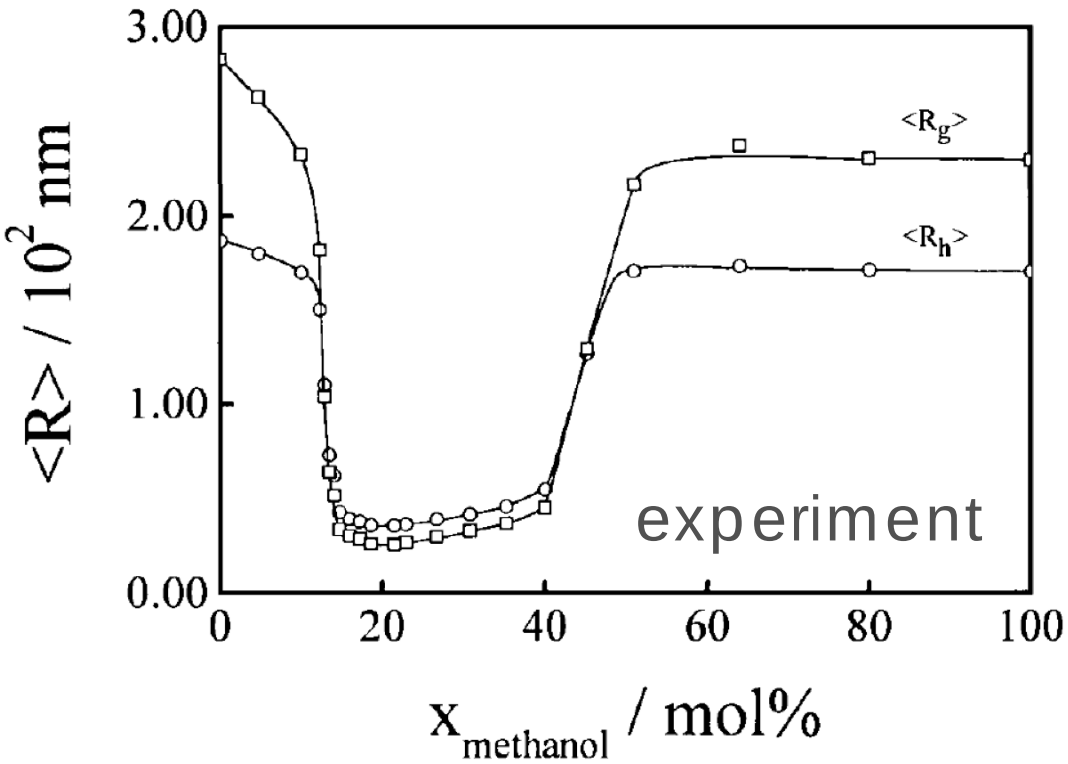
Zhang and Wu, Physical Review Letters, 86, 822 (2001).

Poly-NIPAm in aqueous methanol



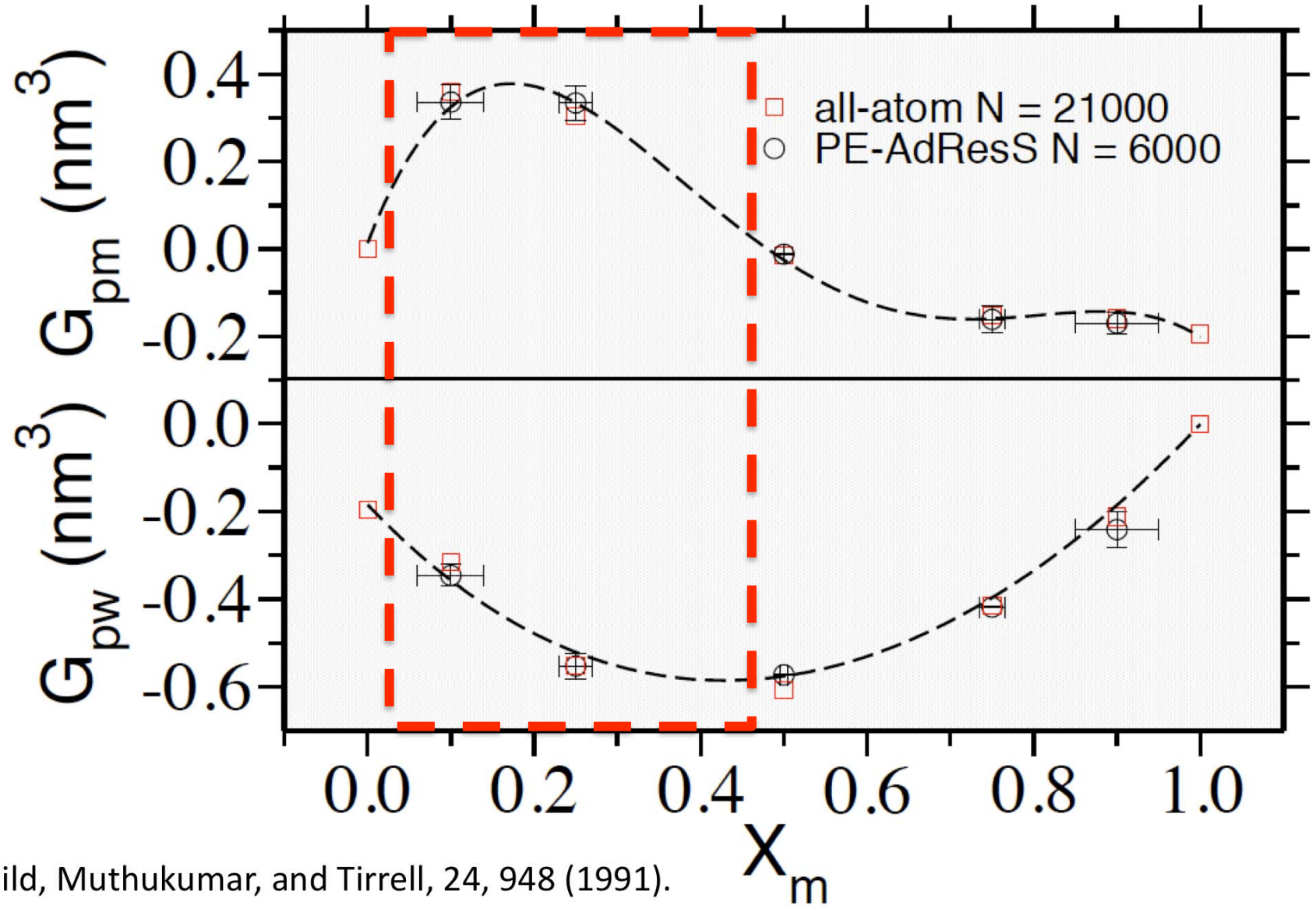






Mukherji and Kremer, Macromolecules (accepted 2013).

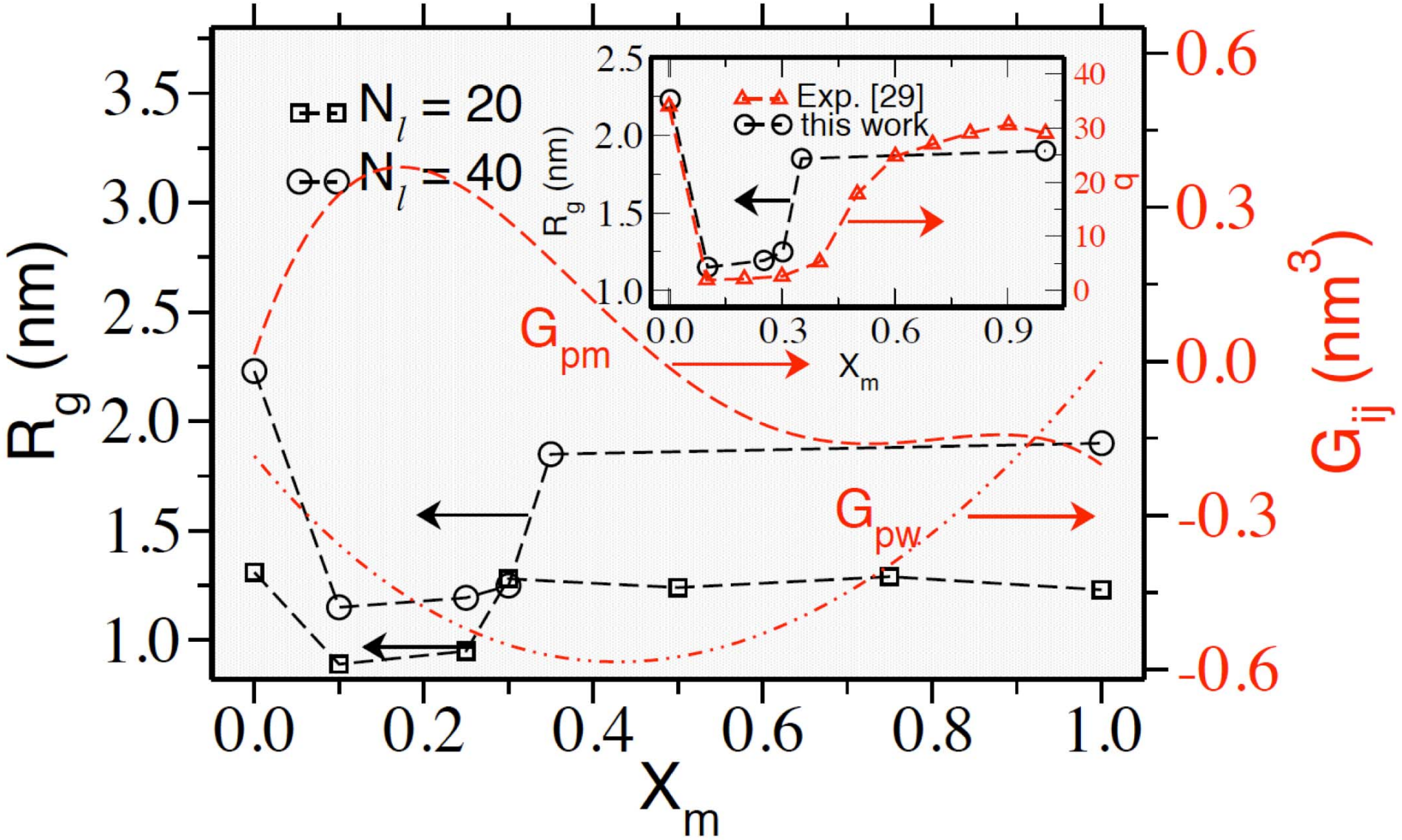
NIPAm in aqueous methanol



Schild, Muthukumar, and Tirrell, 24, 948 (1991).

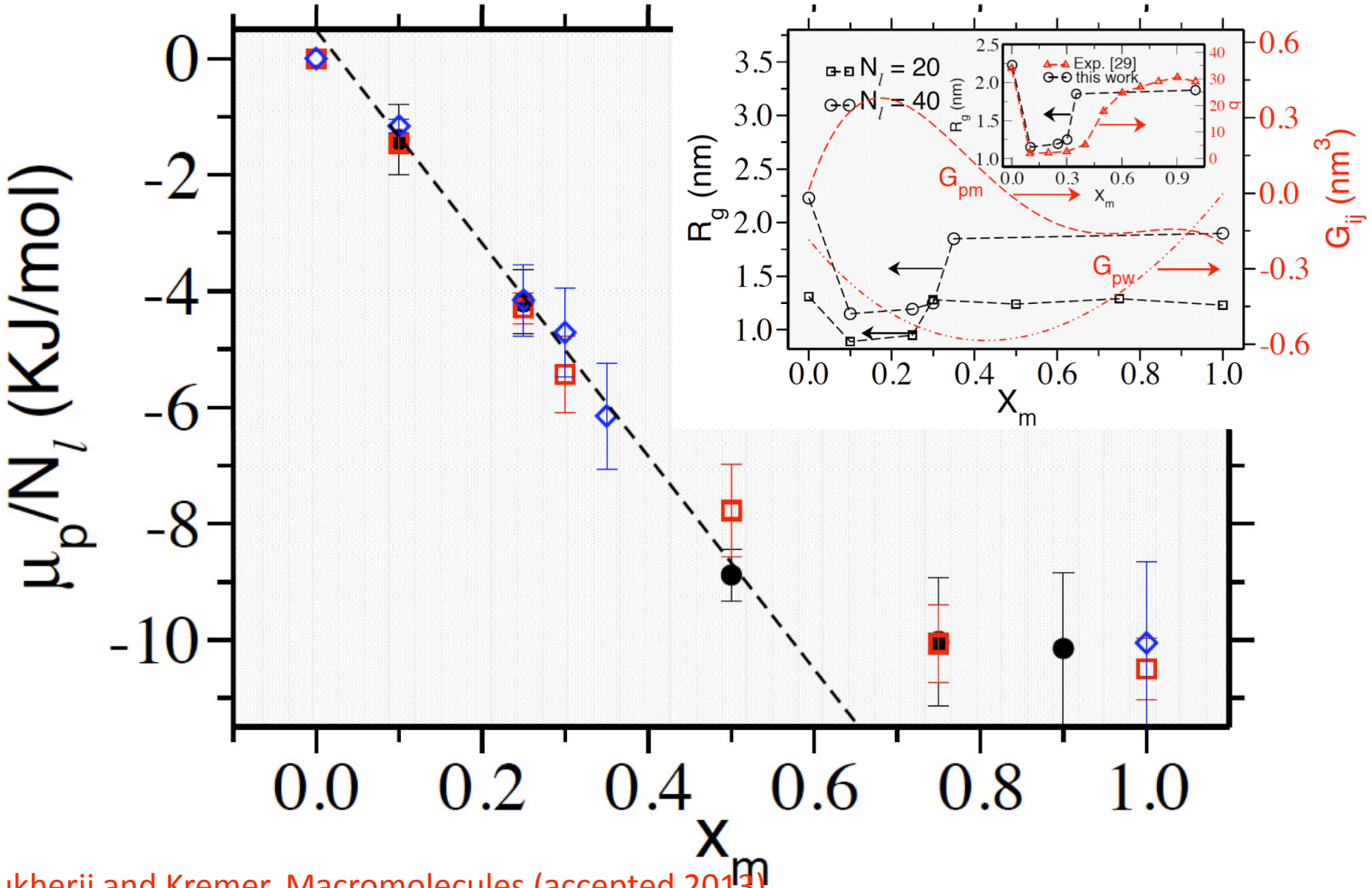
Mukherji and Kremer, Macromolecules (accepted 2013).

Poly-NIPAm in aqueous methanol



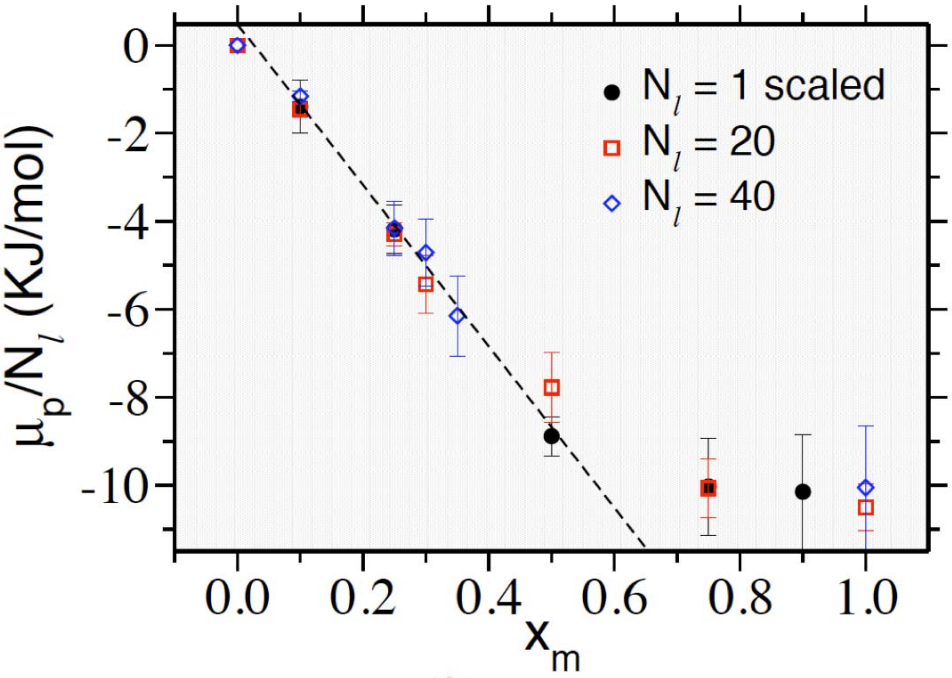
Mukherji and Kremer, Macromolecules (accepted 2013).

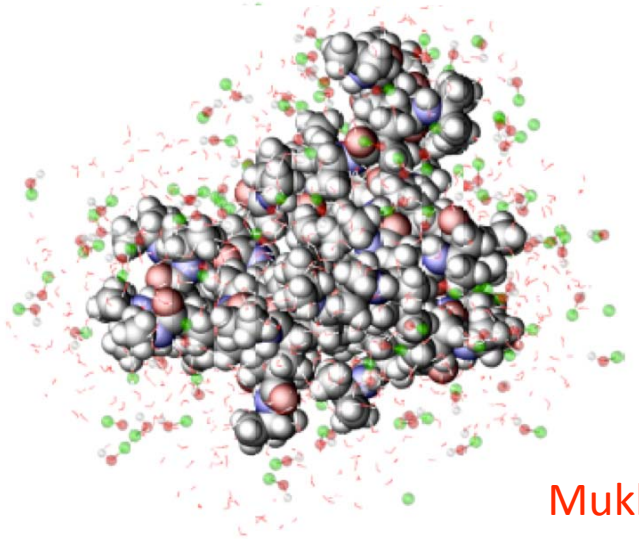
Poly-NIPAm chemical potential

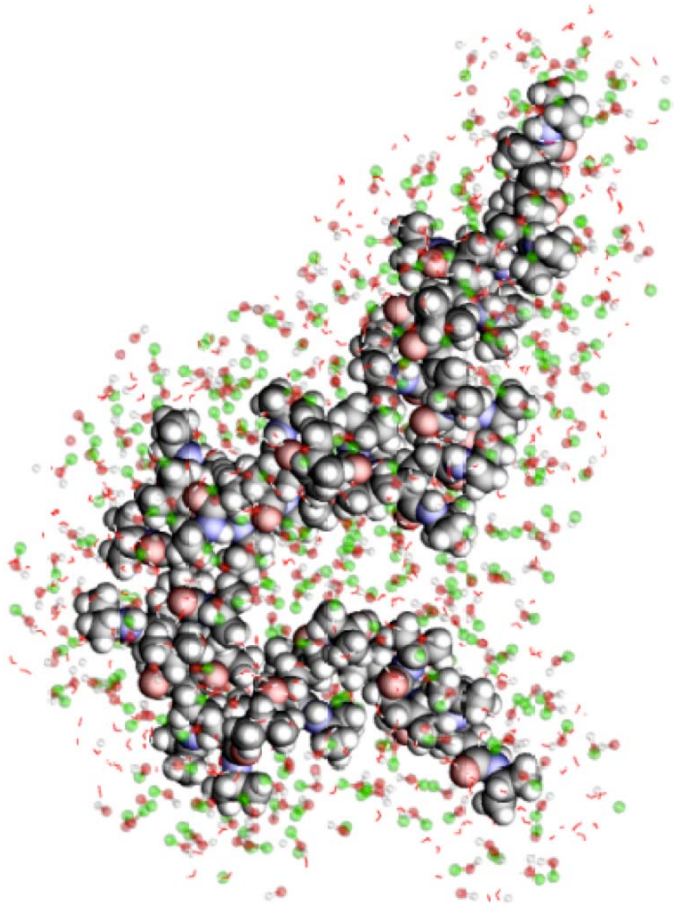


Mukherji and Kremer, Macromolecules (accepted 2013).

Poly-NIPAm chemical potential



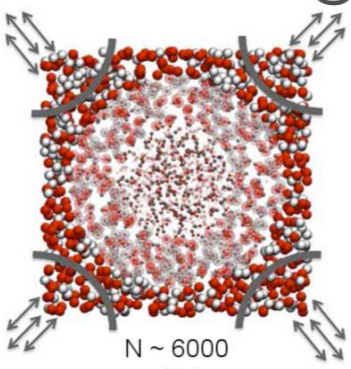


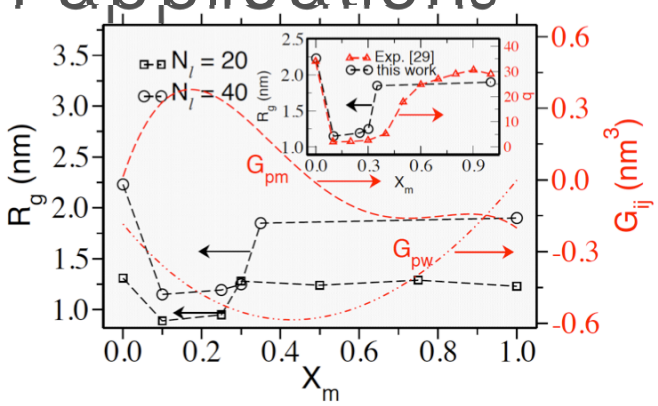


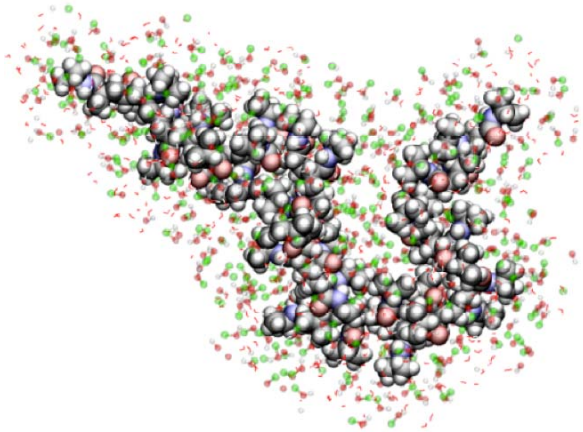
Mukherji and Kremer, Macromolecules (accepted 2013).

Conclusions

- A semi-grand canonical (open boundary) approach for the equilibrium conformational sampling of (bio-)macromolecules
- KBI can be efficiently calculated within reasonable accuracy
- Use the approach for biologically more relevant systems
- General purpose technique that can be used for a broad range of applications







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