Modeling Soft Matter: Linking Multiple Length and Time Scales
KITP Conference, Santa Barbara, June 4-8, 2012

Coarse-grained Models for Oligomer-grafted Silica Nanoparticles

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WHERE DISCOVERIES BEGIN

PCCM
Princeton Center for Complex Materials

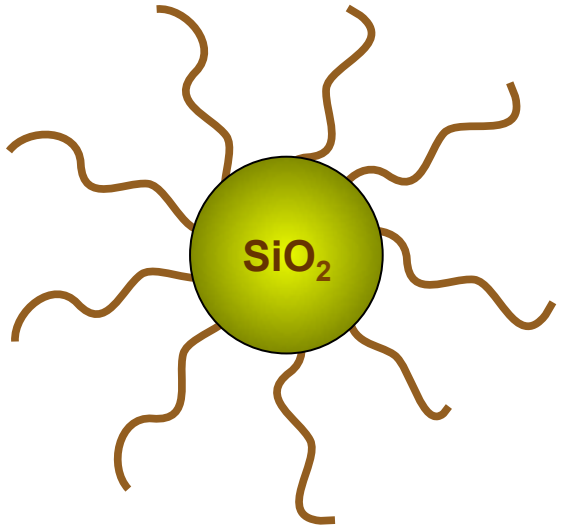
KAUST

Nanoscale ionic & organic hybrid materials

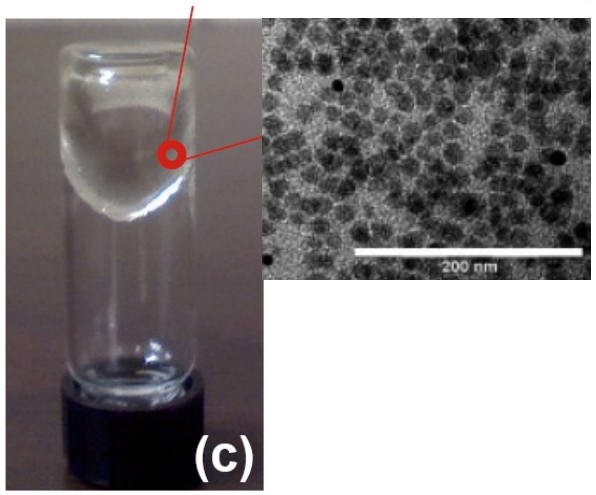
Covalent grafting

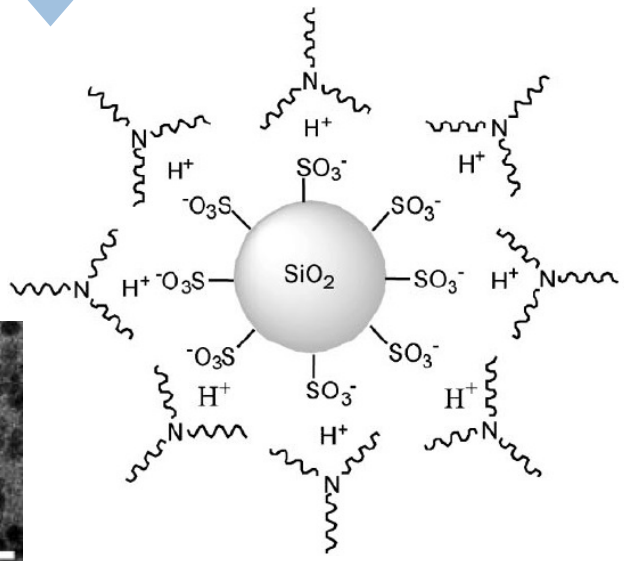
Ionic grafting

-organosilane-PEG



- Viscous liquids
- Solvent-free
- Ultra low vapor pressures
- Many functionalities from cores + chains





J. L. Nugent, L. A. Archer, *Adv. Mater.* **22**:3677-3680 (2010)
P. Agarwal, L. A. Archer, *Phys. Rev. E* **83**:041402 (2011)

A. B. Bourlinos, …, L. A. Archer, E. P. Giannellis, *J. Am. Chem. Soc.* **126**:15358-15359 (2004)
R. Rodriguez, …, L. A. Archer, E. P. Giannelis, *Adv. Mater.* **20**:4353-4358 (2008)

Atomistic reference (PEO chains)

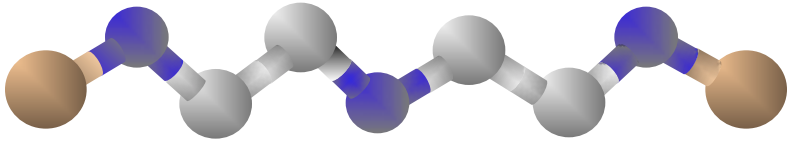
Modified TraPPE potential for $CH_3O[CH_2CH_2O]_nCH_3$

Bond: FENE

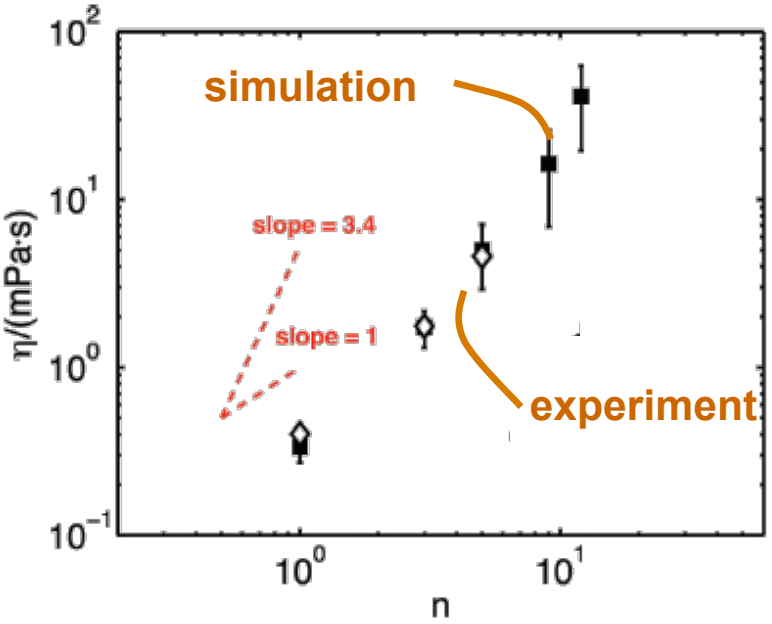
Angle: $u_{\text{bend}} = k_\theta(\theta - \theta_0)^2/2$

Modified Dihedral: $U(\phi) = \sum_{i=1}^{5} A_n \cos^{n-1}(\phi)$

Non-bonded: $U_{\text{NB}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$



n=2



Good agreement of transport properties with experiments (also see next page)

B. B. Hong, F. Escobedo, AZP, *J. Chem. Eng. Data 50*, 4273-4280, 2010

Transport properties of atomistic models for $CH_3O(CH_2CH_2O)_nCH_3$

n	State point		Viscosity (mPa·s)		Diffusivity ($10^{-5}cm^2/s$)	
			sim	expr	sim	expr
1	296.15K, 1bar				3.15±0.02	3.2
	298.15K, 1bar		0.35±0.02	0.394	3.13±0.04	
	303.15K, 10bar		0.34±0.07	0.402	3.47±0.04	
3	303.15K, 10bar		1.7±0.4	1.761	0.61±0.02	
5	303.15K, 10bar	$N = 50$	4.4±3.3	4.588	0.15±0.03	
		$N = 200$	5.0±2.1		0.181±0.008	
		$N = 400$	4.8±2.5		0.187±0.009	
9	303.15K, 10bar		16.3±9.5		0.041±0.005	
	318K, 1bar		11.9±7.0	13.34	0.062±0.005	
12	298.15K, 1bar		33.3±15.0		0.017±0.005	
	303.15K, 10bar		41.1±17.3		0.018±0.002	

Hong, Escobedo, AZP, *J. Chem. Eng. Data*, **55**: 4273-80 (2010)

Coarse-Graining: PEO chains

- **Coarse-grained PEO**

***n*-mer → (N+1)/2–bead chain**

$$CH_3-[O-CH_2-CH_2]-O-CH_3$$

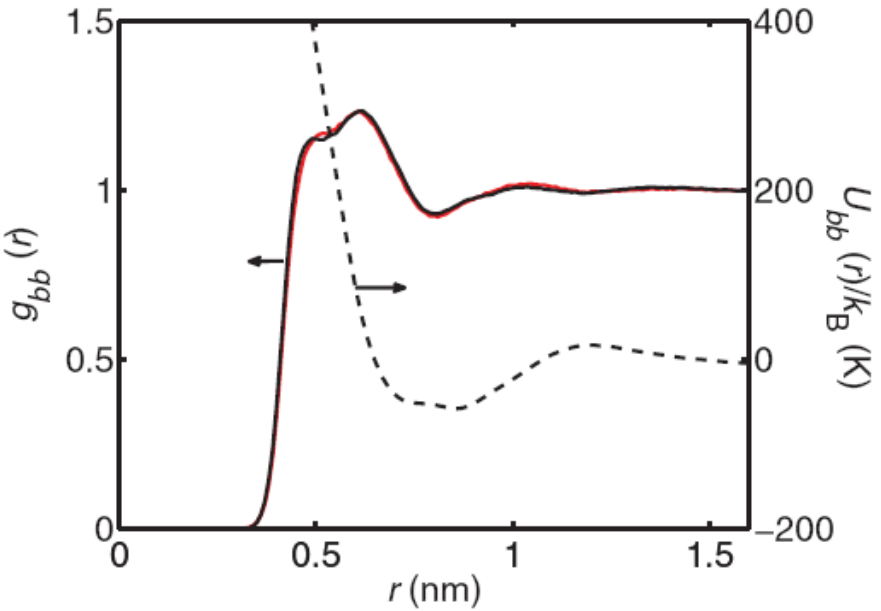
$$\underbrace{[CH_3-O-CH_2]-[CH_2-O-CH_3]}_{\text{One CG bead}}$$

- **Bead-bead potential**

$$U_{i+1}(r) = U_i(r) - x \cdot k_B T \ln \frac{g_{tgt}(r)}{g_i(r)}$$

Iterative Boltzmann Inversion

D. Reith, et al, *J. Comput. Chem. 24*, 1624-636, 2003



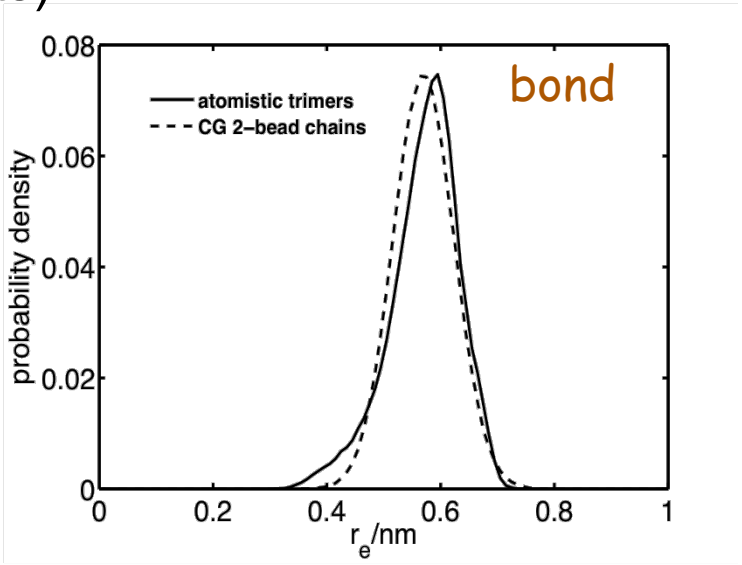
Coarse-Graining: PEO chains

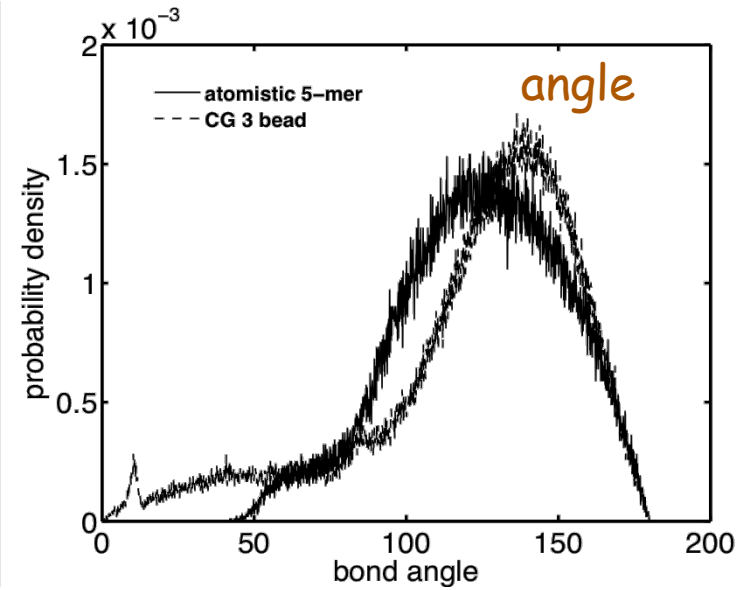
Persistence length:

~ 0.46nm (~3.2 repeat units)

- **Harmonic bond potential**

  Fitted equilibrated bond length between coarse-grained (CG) beads to the distance between two atomistic groups

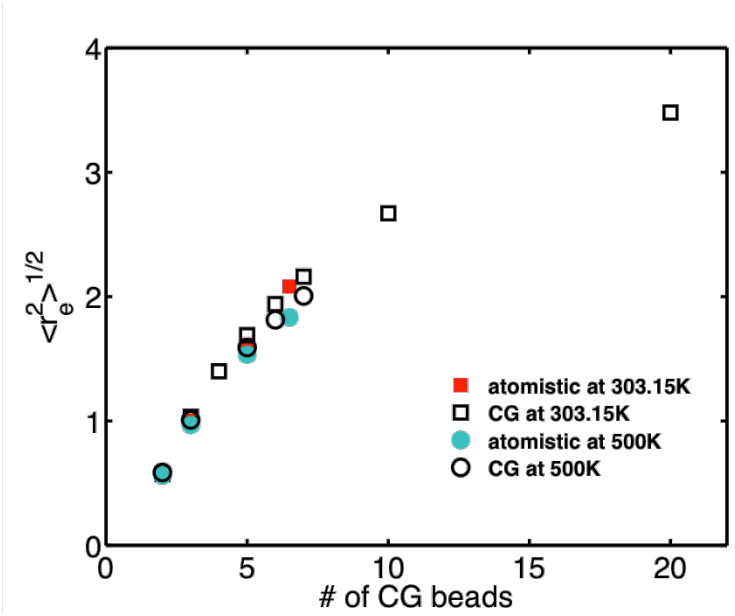




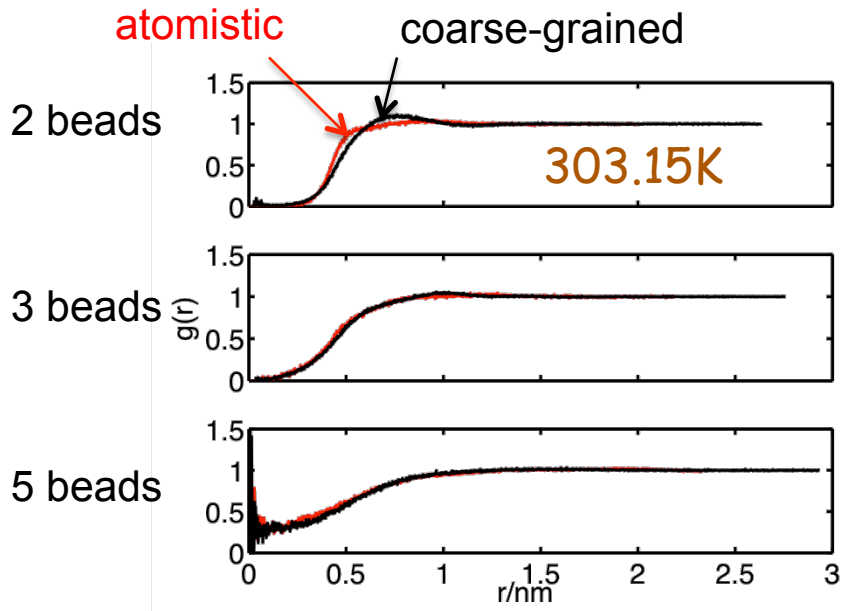
- **Harmonic angle potential**

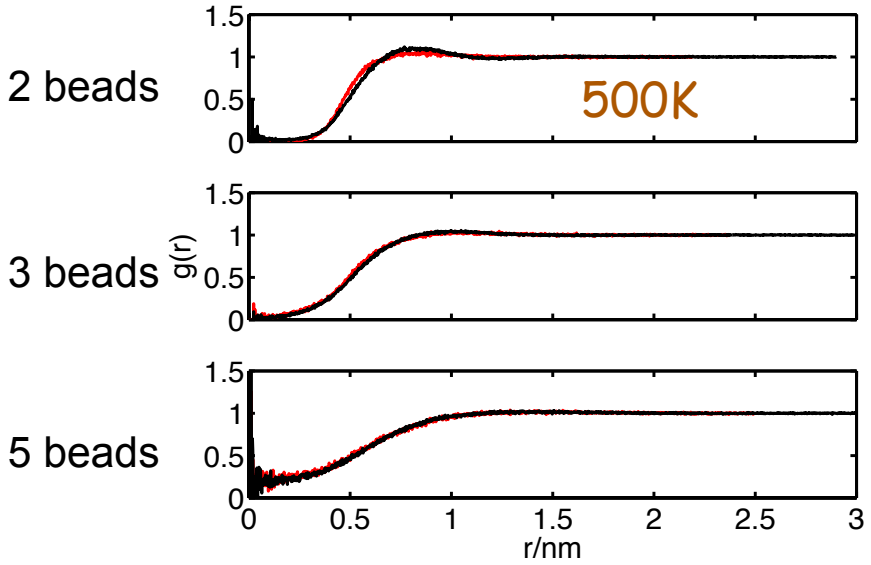
  Determined from matching the end-to-end distance of long CG chains to atomistic simulations

End-to-end distance and structure of CG PEO chains

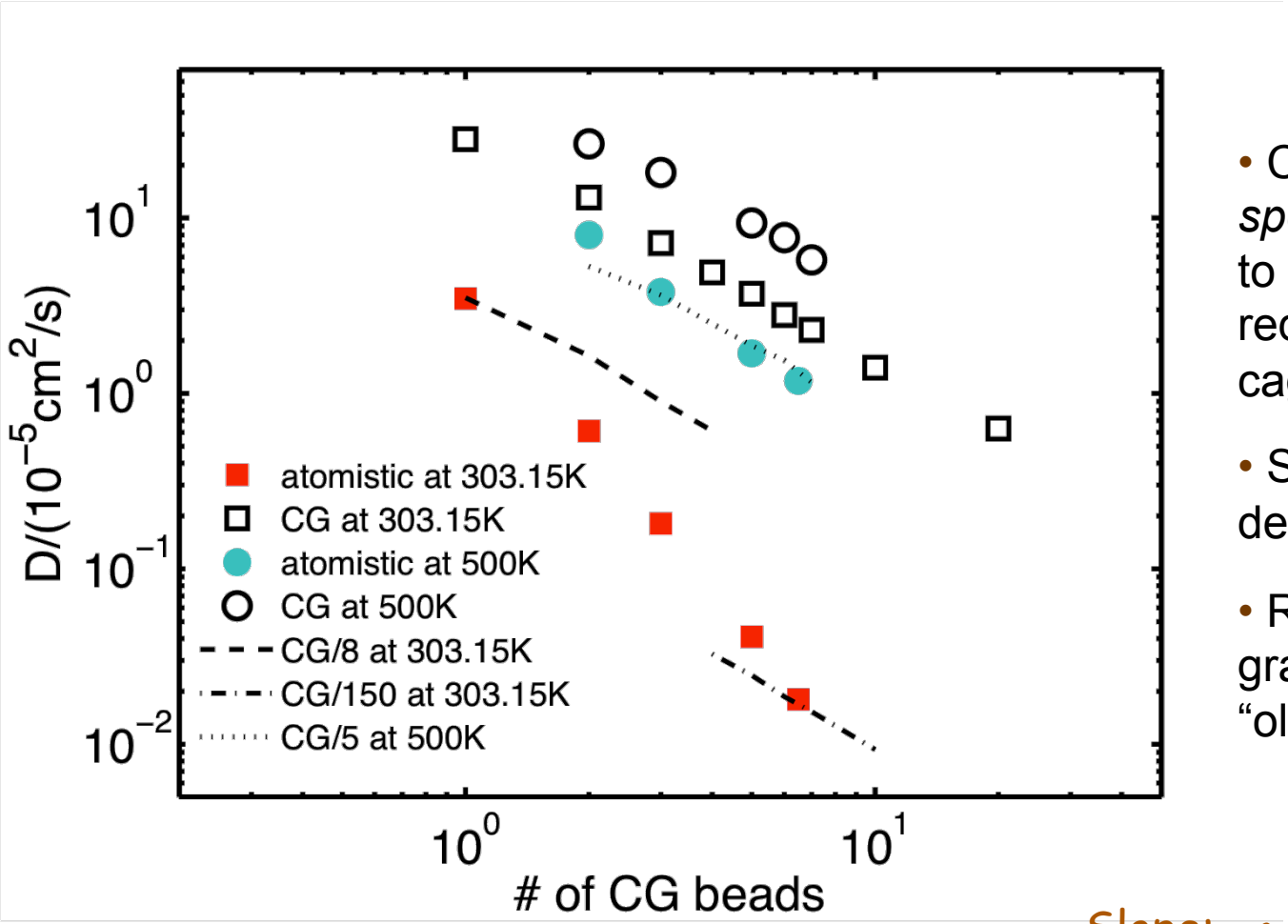


- Good transferability to other *T*'s, chain lengths
- End-to-end distances at higher *T* are slightly smaller (chains less stiff).





Diffusivity of PEO chains



- Coarse-graining *speeds up* dynamics due to softer potentials which reduce the friction of cage escape.
- Speed-up factors depend on *T*
- Raising *T* or coarse-graining shortens the "oligomer" regime.

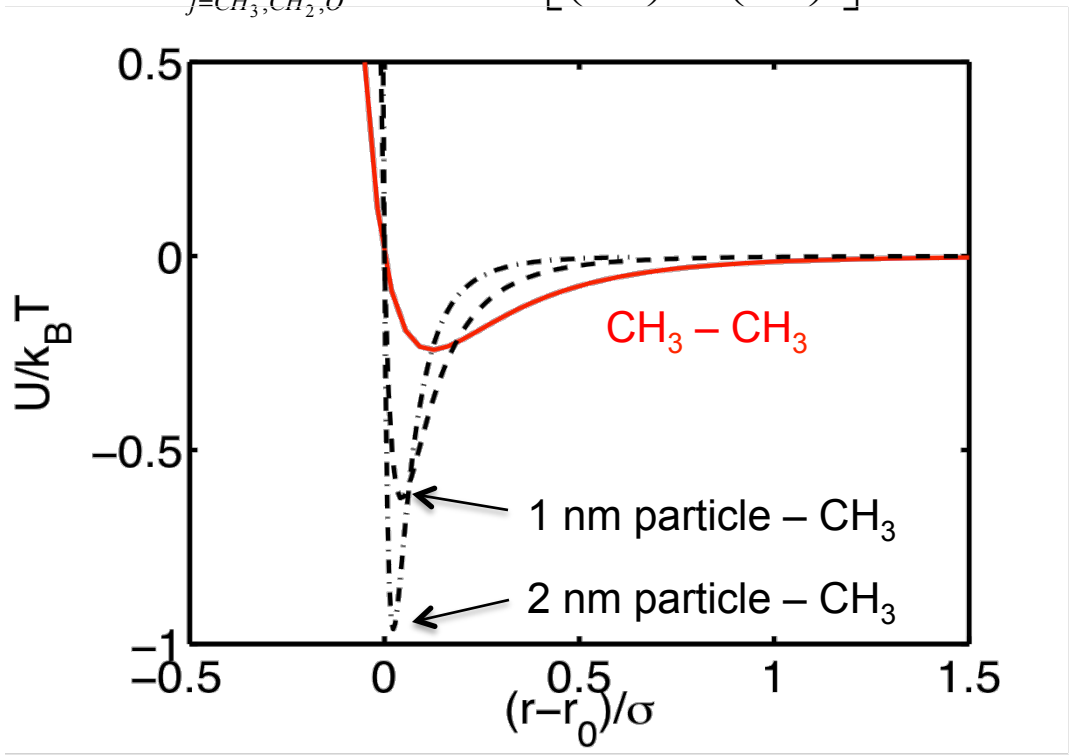
Slope: ~ -2.5 (red squares)
~ -1.3 (others)

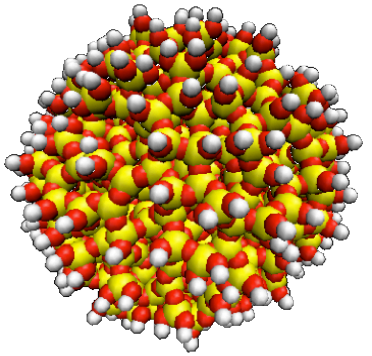
Coarse-graining: core particles

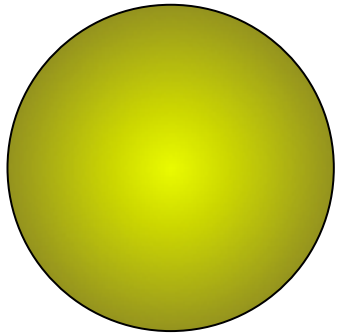
Atomistic reference NOHMs: Integrated LJ

$$U(r) = \sum_{i,j=Si,O} \rho_i \rho_j \int_{sphere\,I} dV_I \int_{sphere\,II} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] dV_{II}$$

$$U(r) = \sum_{\substack{i=Si,O \\ j=CH_3,CH_2,O}} \rho_i \int_{sphere\,I} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] dV_I$$

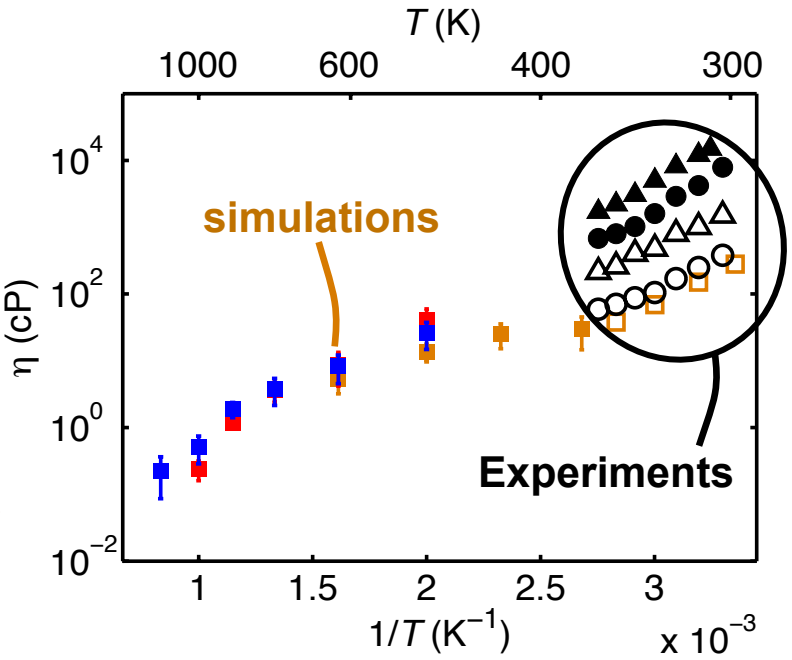


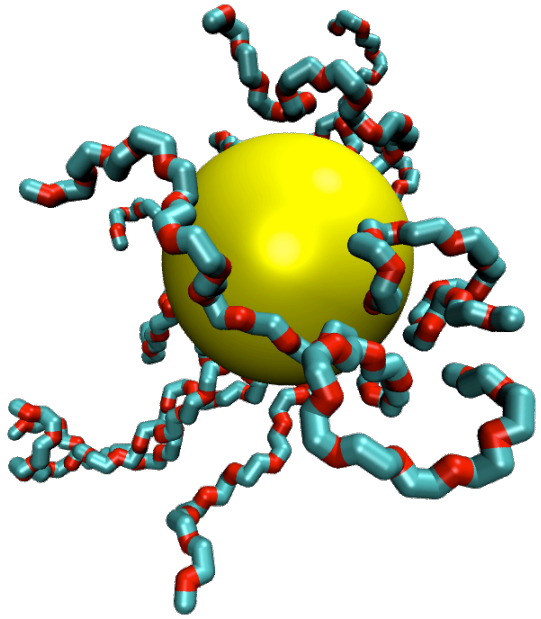




“Semi-atomistic” model: 1-center cores + full chains

Red: 2 nm + 12x6-mer
Blue: 2 nm + 12x12-mer
Brown: 0.9 nm POSS +8x12mer



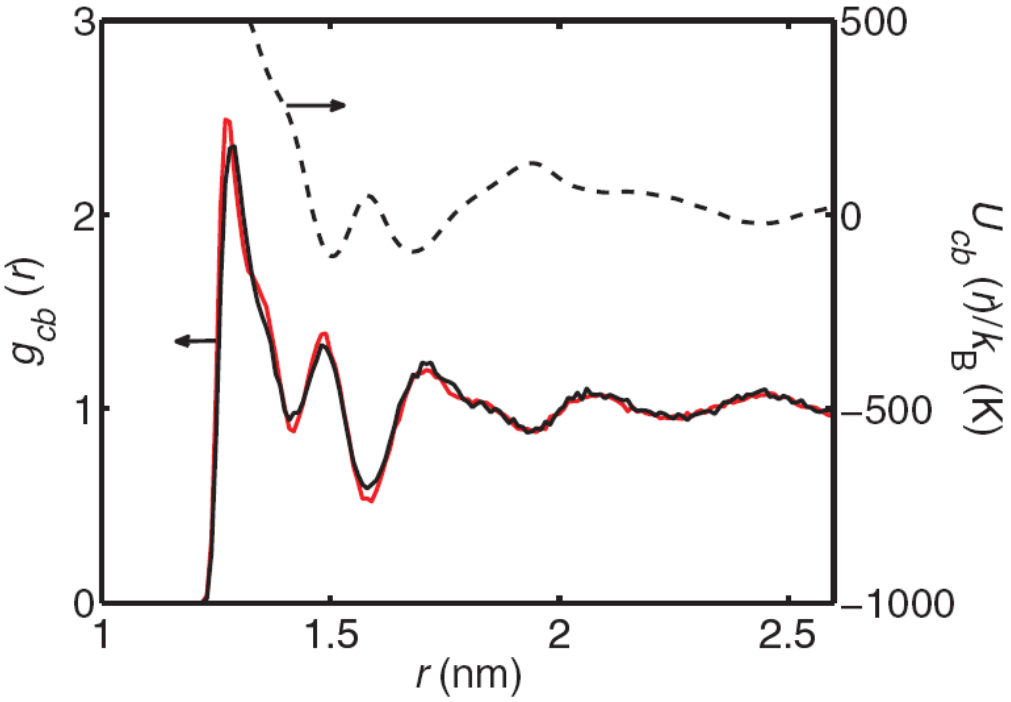


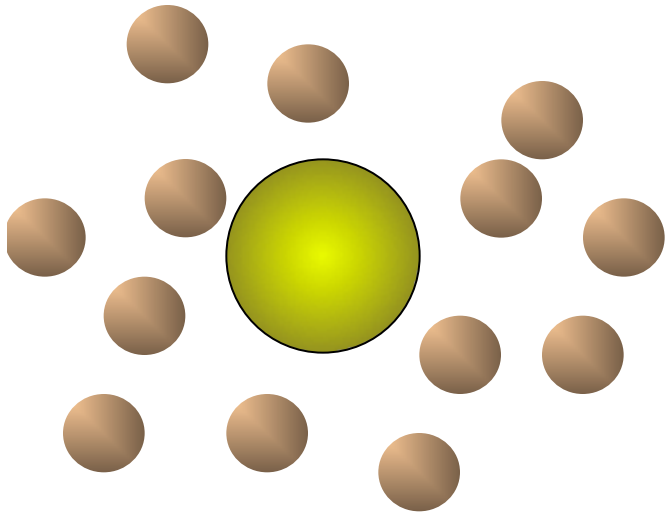
- Large number of interaction sites, slow relaxation
- Simulations only feasible at high *T*

B. B. Hong, AZP, *JPCB* **116**: 2385-2395 (2012)

Core-bead CG interactions

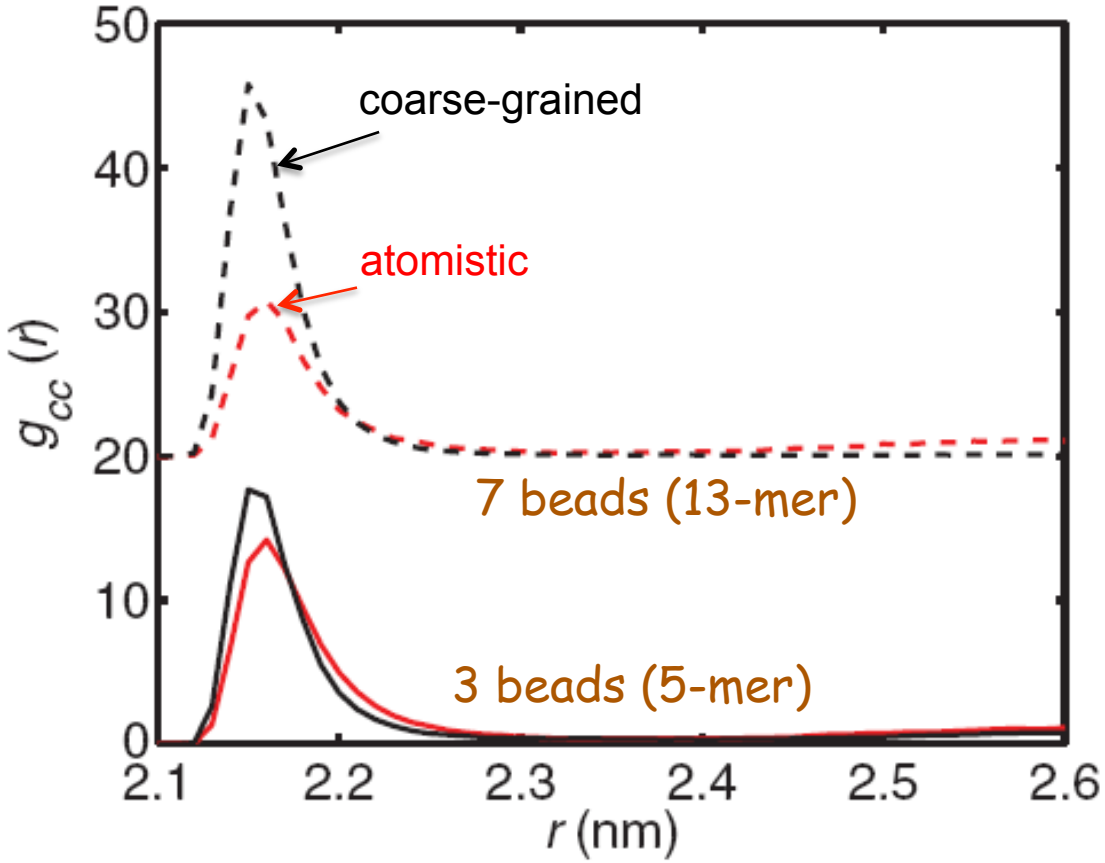
single core in atomistic and CG monomers.

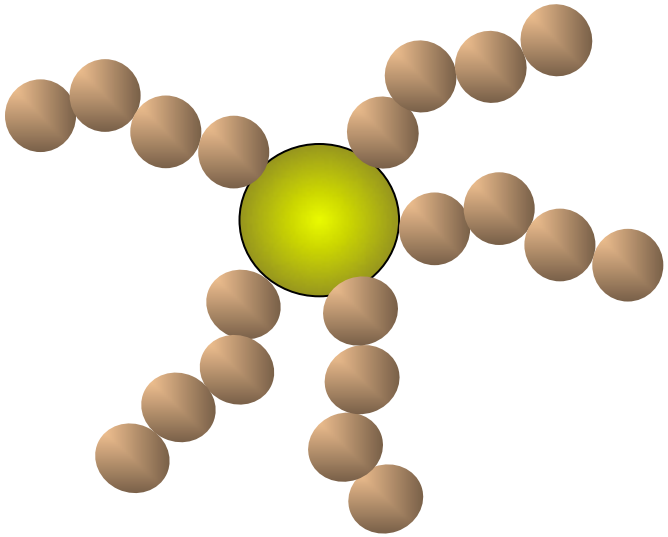




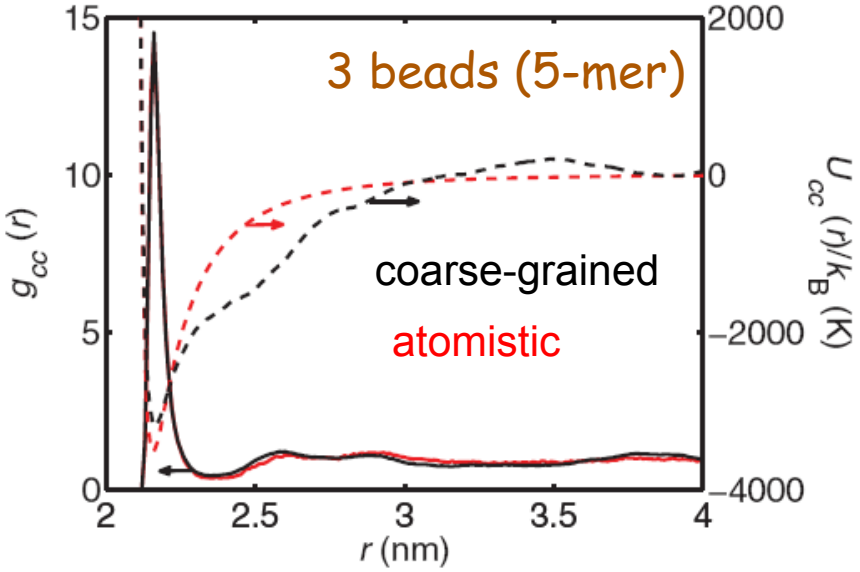
- Iterative Boltzmann Inversion to fit core-bead $g(r)$ at 303.15 K

Core-core interactions also need to be adjusted

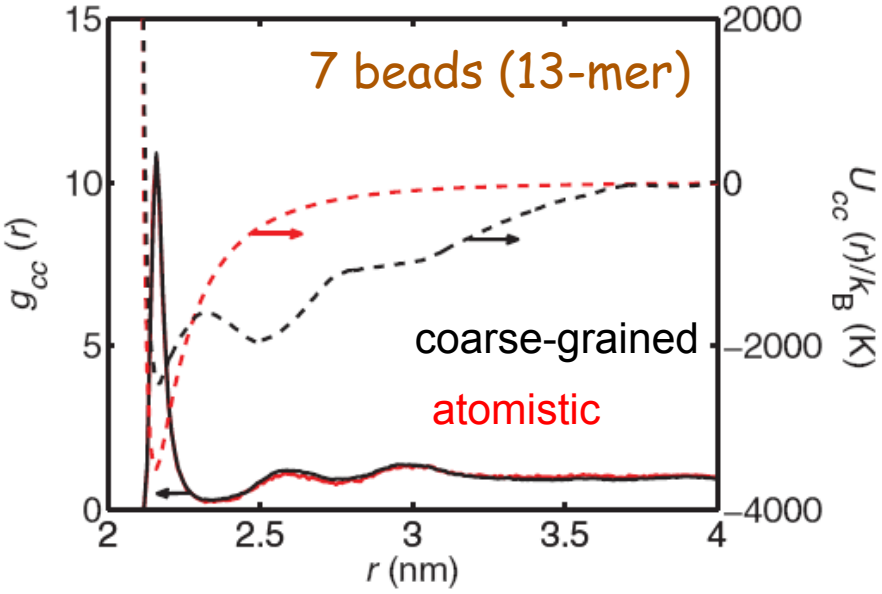




Corrected core-core interactions



Smaller corrections for shorter grafted chains

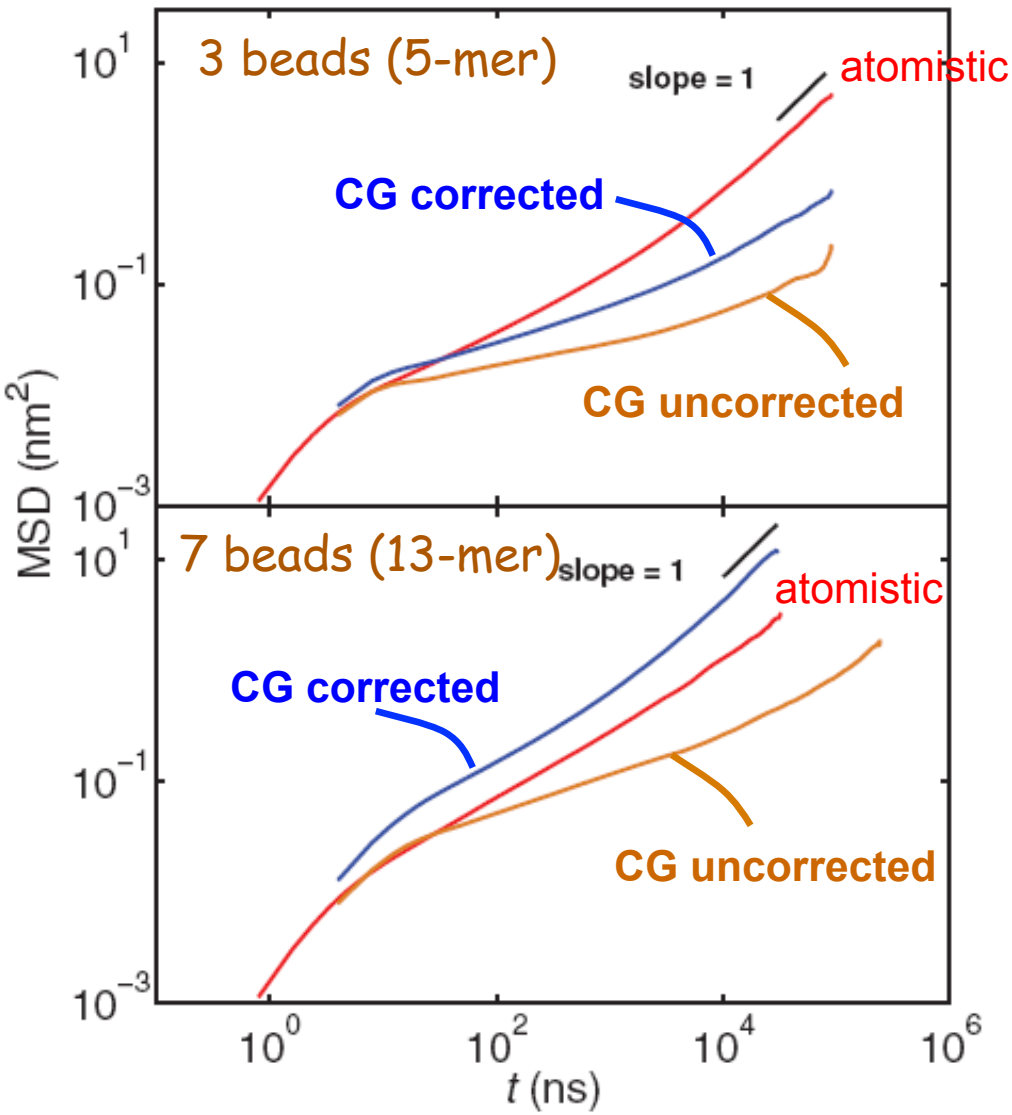


Poor transferability to different *T*'s and chain lengths

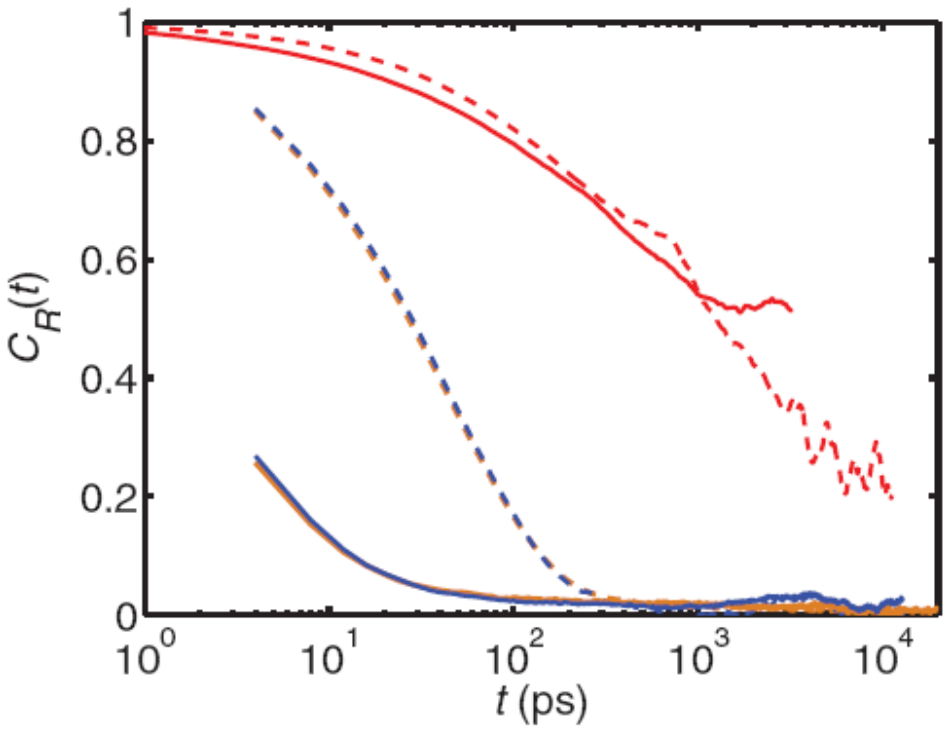
Counter-intuitive core dynamics

NOHMs with uncorrected potentials or short-chain NOHMs with corrected potentials diffuse *more slowly*

Cores grafted with longer chains CG diffuse *faster*



Chain dynamics behave normally



$$C_R(t) = \frac{\langle r_e^2(0) r_e^2(t) \rangle - \langle r_e^2 \rangle^2}{\langle r_e^4 \rangle - \langle r_e^2 \rangle^2}$$

Particle + 13-mer

Particle + 5-mer

Core + 7-bd, corrected *U*

Core + 3-bd, corrected *U*

Core + 7-bd, uncorrected *U*

Core + 3-bd, uncorrected *U*

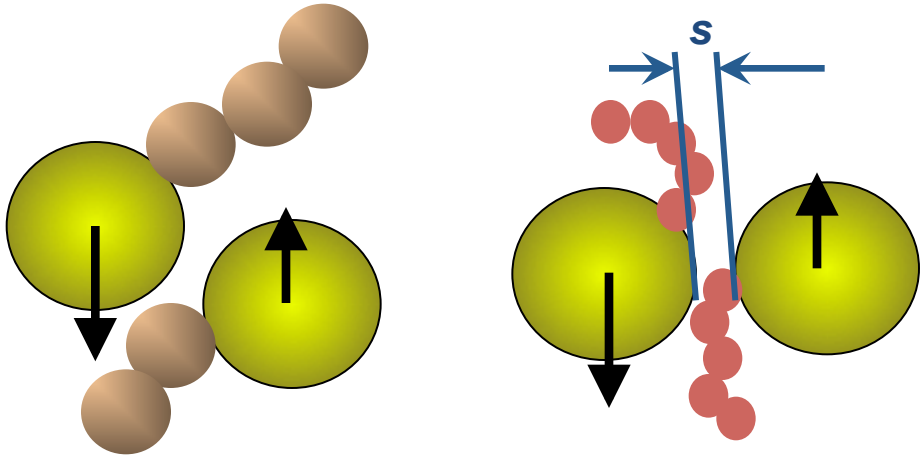
- Coarse-graining speeds up chain relaxations – chain motions are not the cause for core slow-down
- Core potentials have little effect on chain relaxation

Other possible causes for unexpected dynamics?

- **Chain extensions** – no different

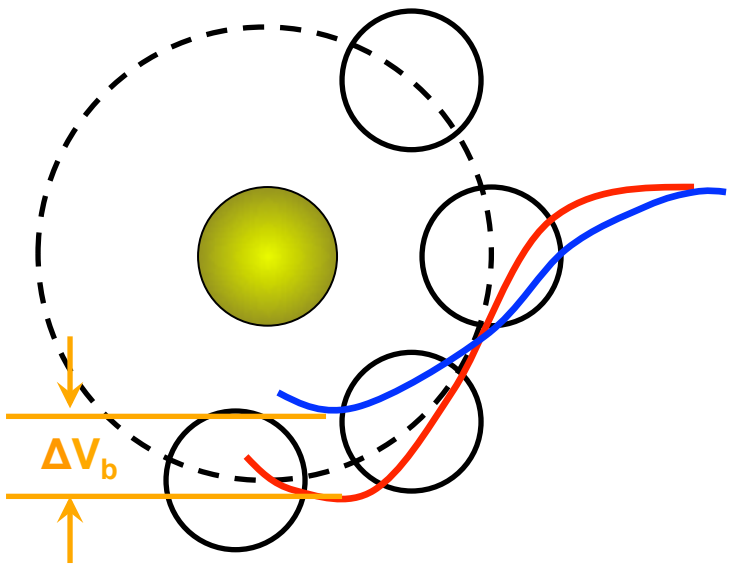
	3-bead NOHMs	7-bead NOHMs
Uncorrected *U*	5 % longer	4 % longer
Corrected *U*	4 % longer	Within errors

- **Grafting topology**
  - g(r) data: space between neighbor cores (*s*) ~ 0.4 nm
    atom ~ 0.3 nm
    bead ~ 0.65 nm



atomistic segments rotate to fit; CG bead are too big

Cage escape dynamics



$$\alpha_b = \exp\left(\langle \Delta V_{\mathrm{b}} \rangle / k_{\mathrm{B}} T\right)$$

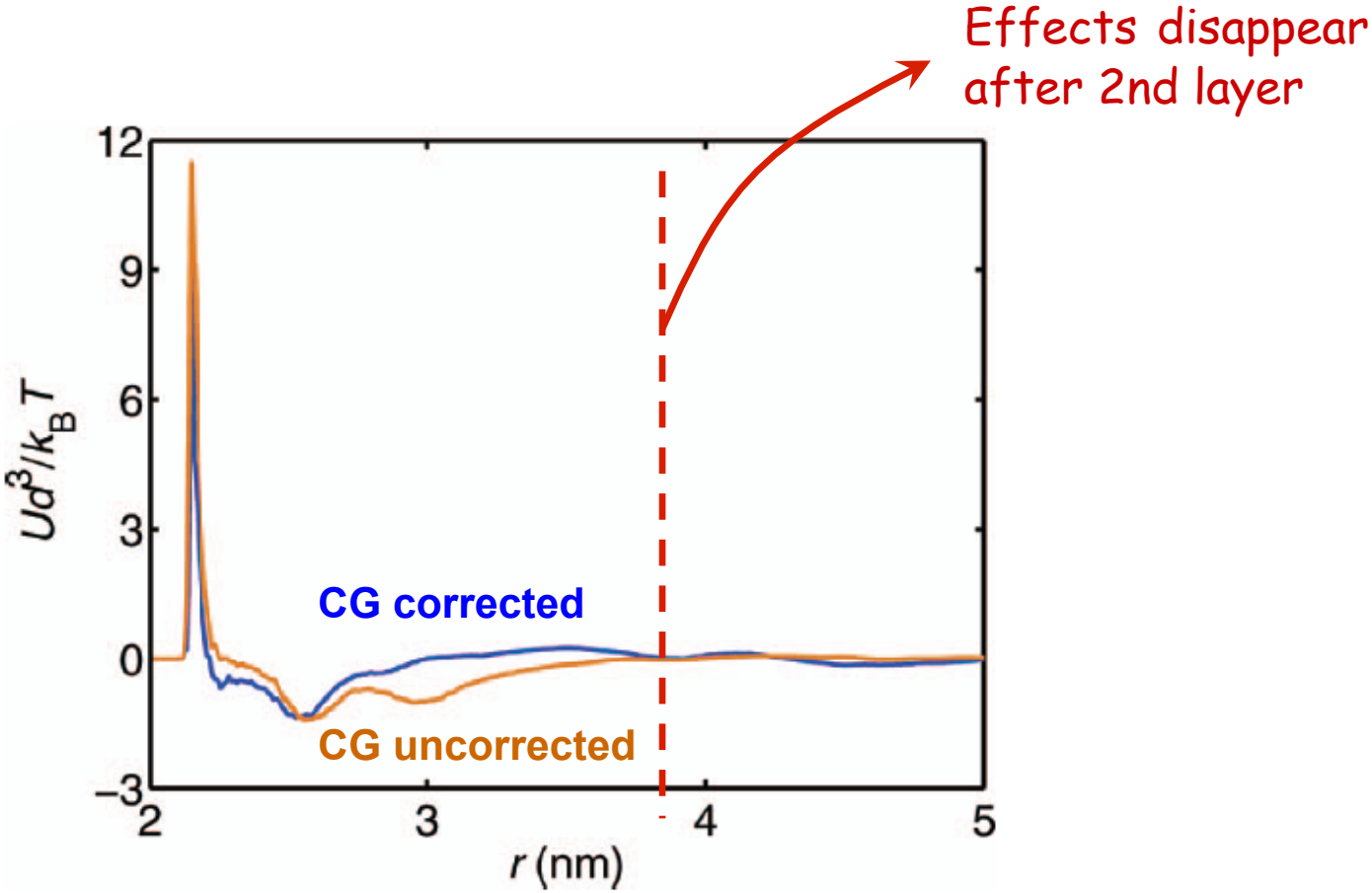
$$\langle \Delta V_{\mathrm{b,cc}} \rangle = \int_{r=0}^{\infty} U \mathrm{d}r = \int_{r=0}^{\infty} \langle N_{cc,CG}(r) \rangle U_{cc,CG}(r) \mathrm{d}r - \int_{r=0}^{\infty} \langle N_{cc,at}(r) \rangle U_{cc,at}(r) \mathrm{d}r$$

P. K. Depa and J. K. Maranas, *J. Chem. Phys.* **123**: 094901 (2005).

D. Fritz, K. Koschke, V. A. Harmandaris, N. F. A. van der Vegt, and K. Kremer, *Phys. Chem. Chem. Phys.* **13**:10412 (2011)

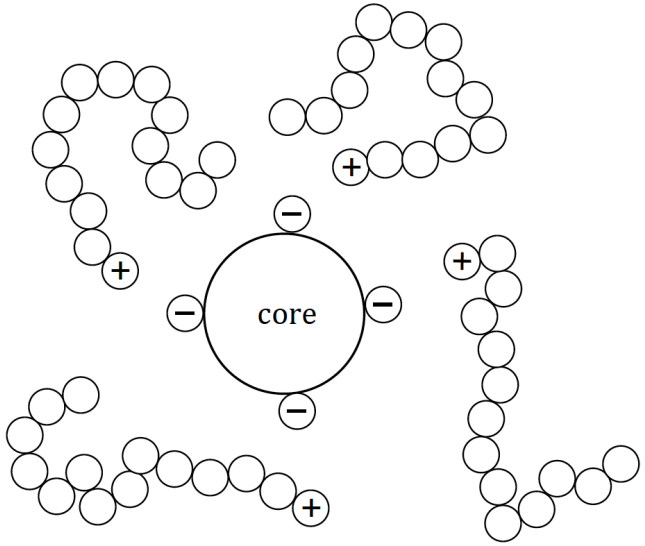
Softer potential → faster cage escape

Integrand for acceleration factor

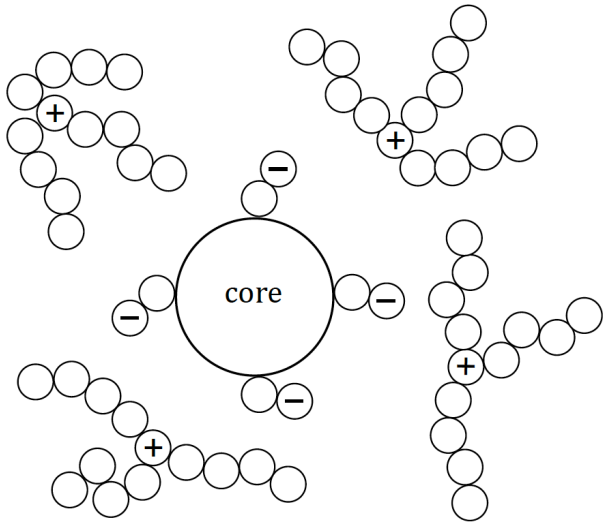


- $\langle \Delta V_b \rangle > 0$ for chains
- $\langle \Delta V_b \rangle < 0$ for cores.
- Speedup or slowdown depends on core/chain content.

Ionic coarse-grained models



Linear (NIMs-L)



Stars (NIMs-S)

Bead LJ parameters from T_C & ρ_C of CH_3-O-CH_3

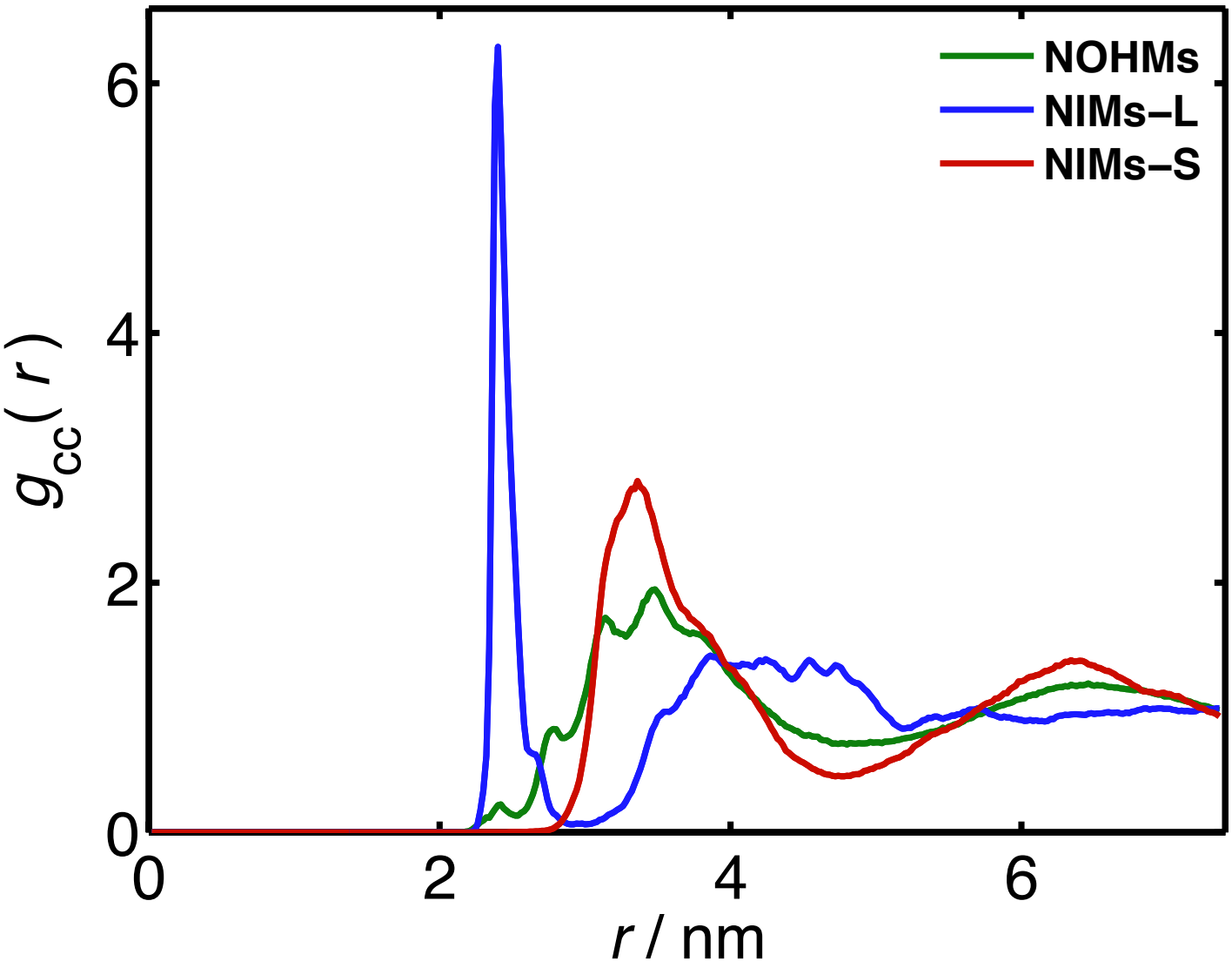
Electrostatic interactions :

$$V_E(r) = \frac{1}{4\pi\varepsilon_0\kappa}\frac{q_i q_j}{r}$$

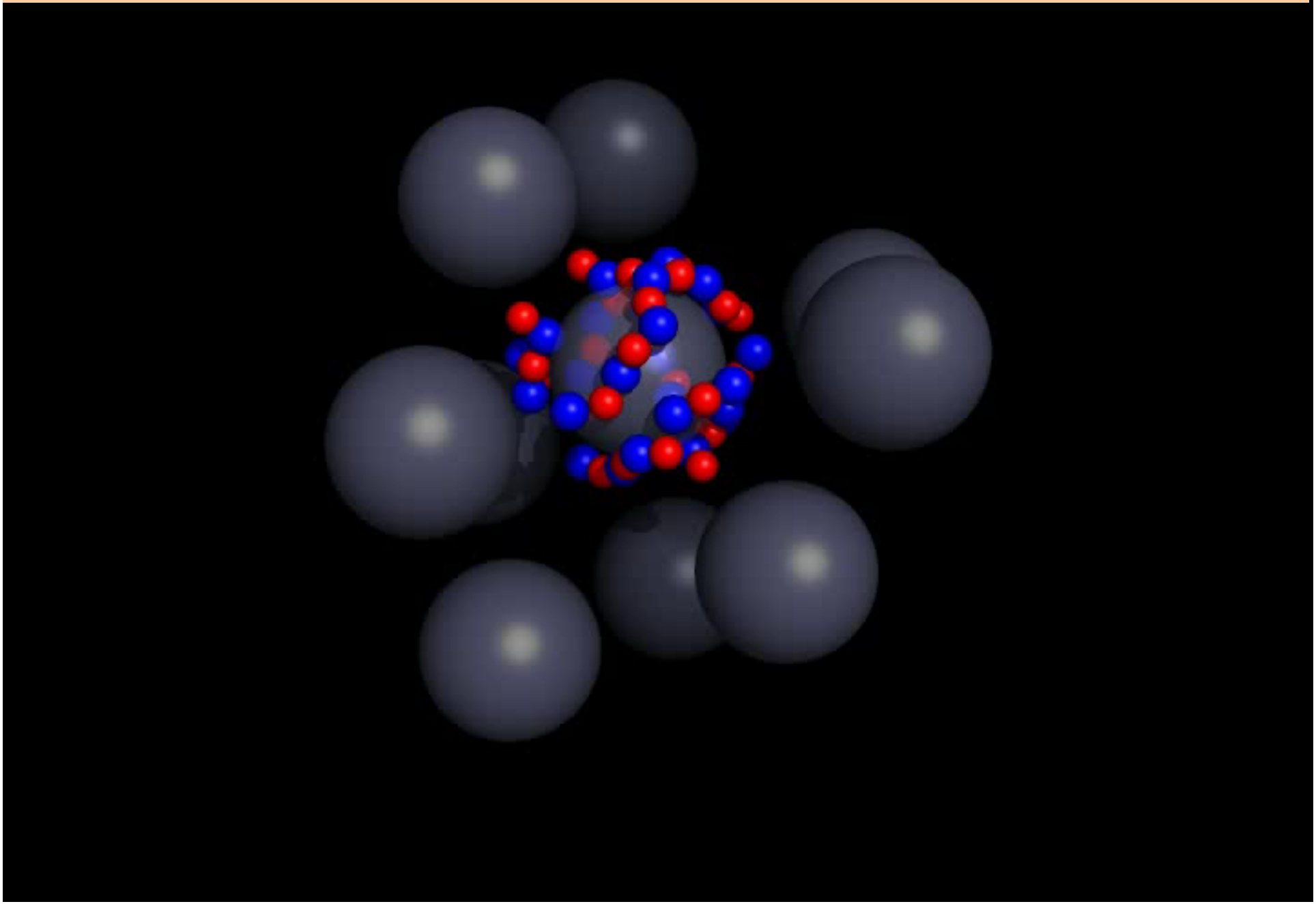
relative permittivity:
κ = 4 (for SiO_2, PEG)

$\Rightarrow V_E(\sigma) = 35 k_B T$

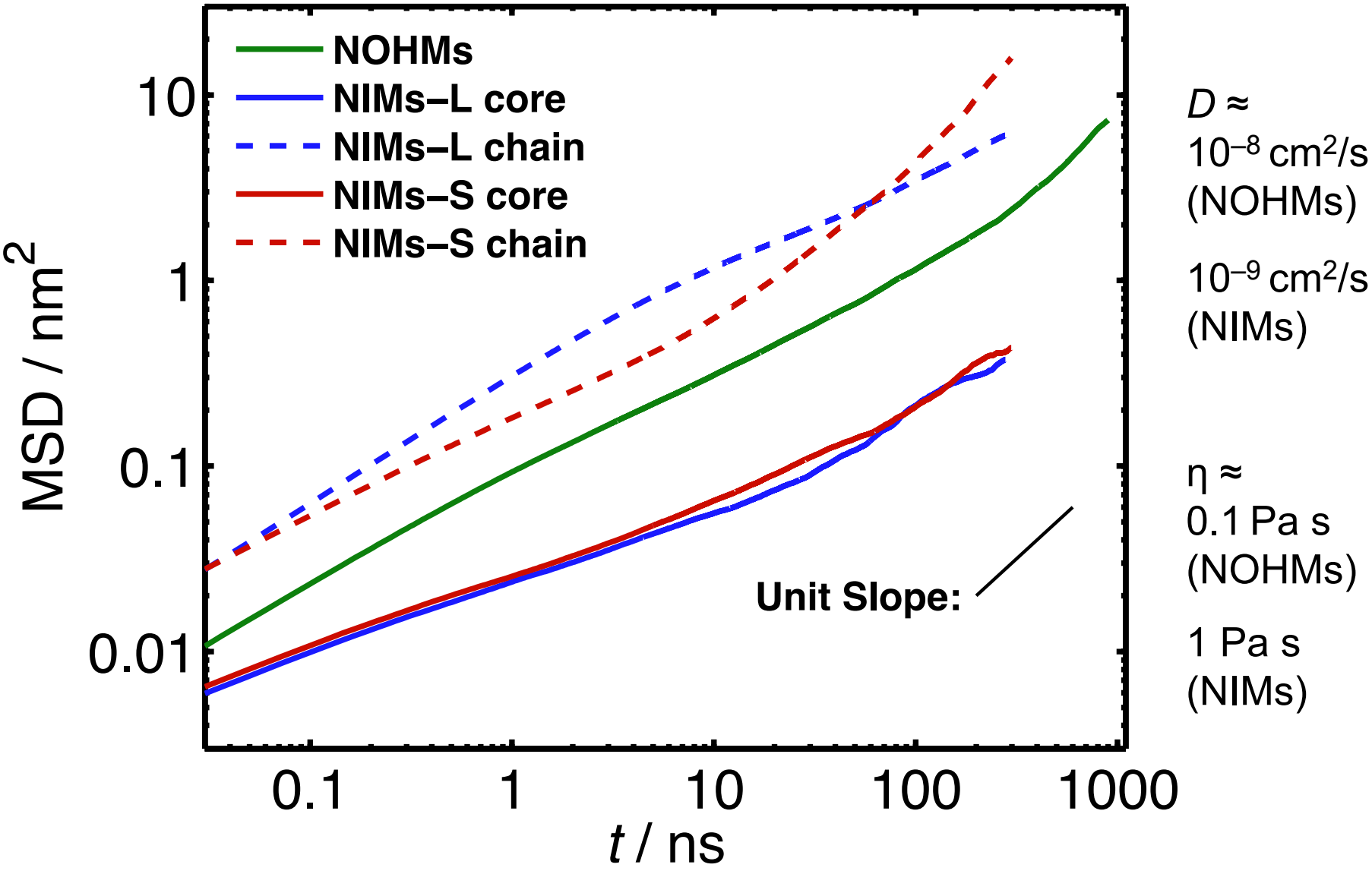
Core-core correlation functions



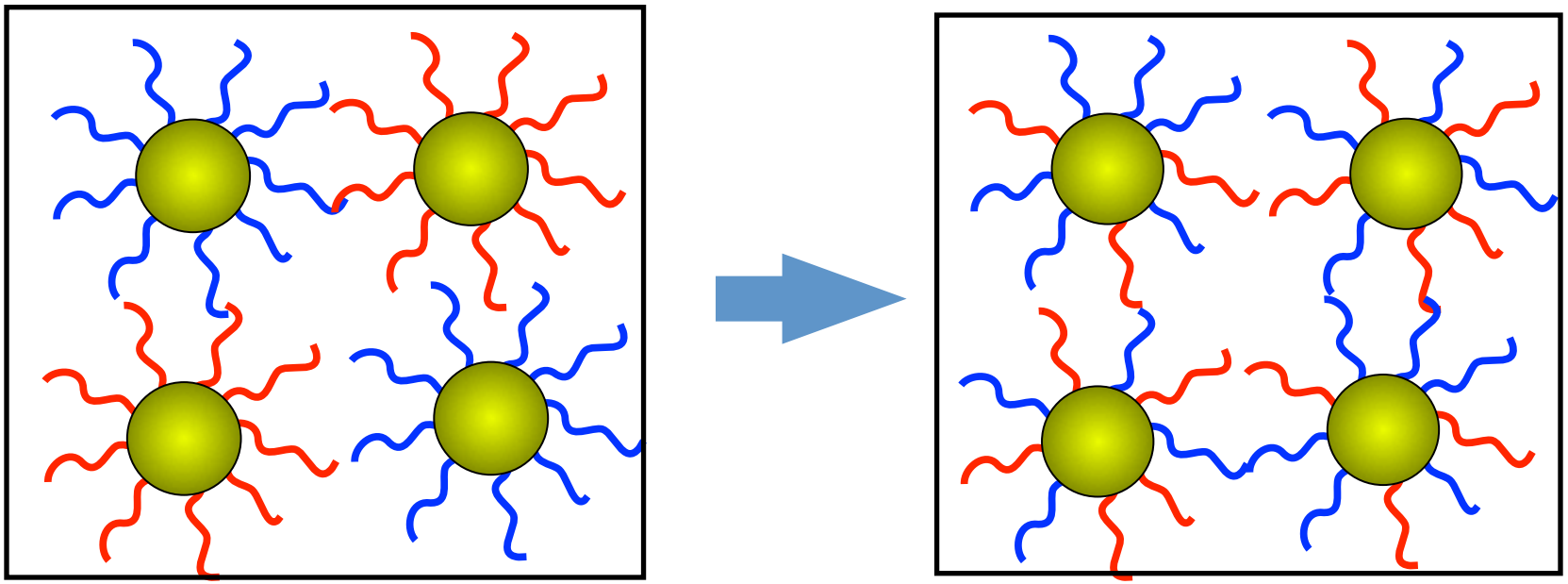
Dynamics: NIMs-S (chains not shown)



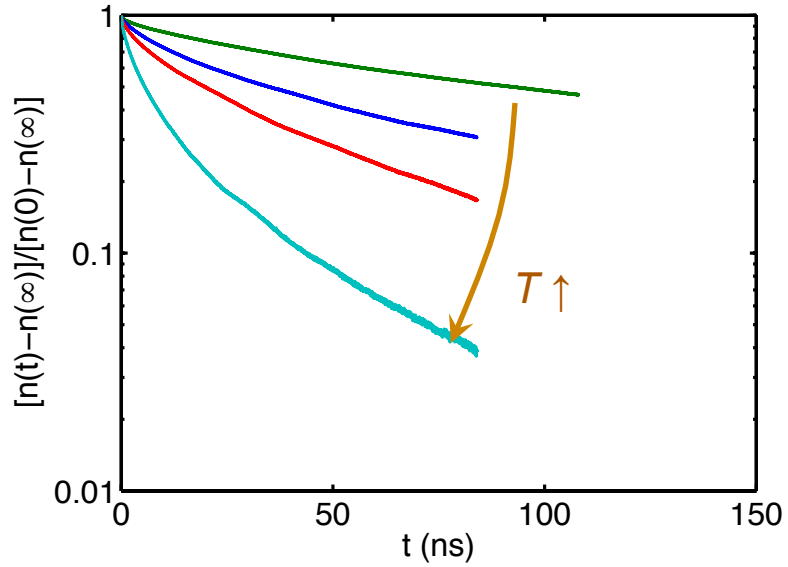
Diffusion of chains and cores

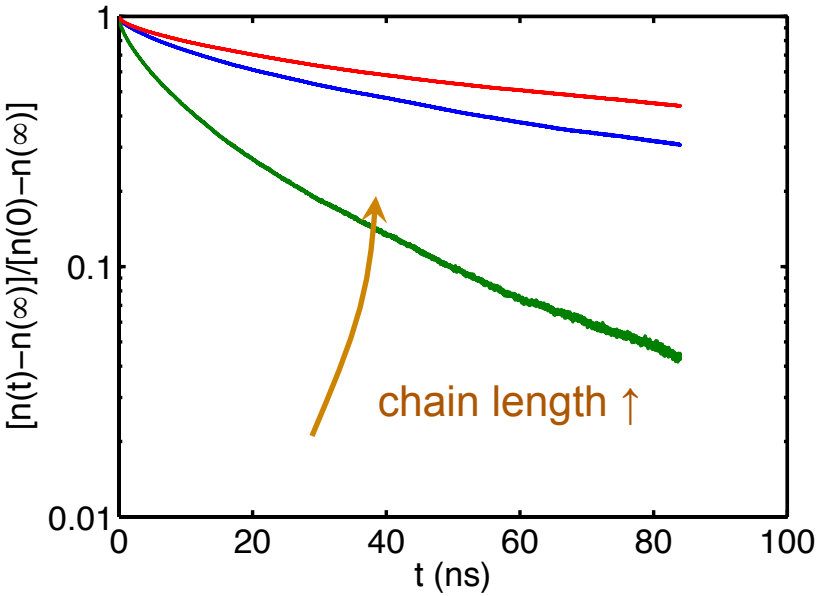


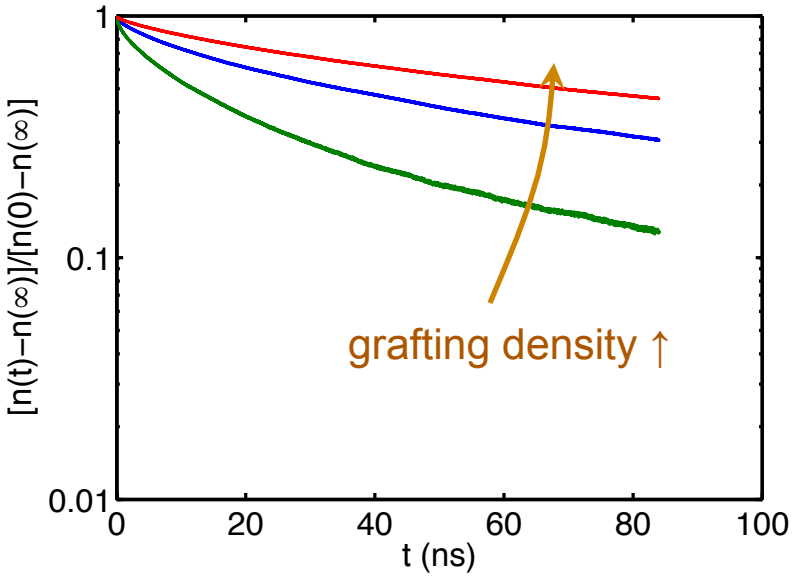
Canopy chain exchange



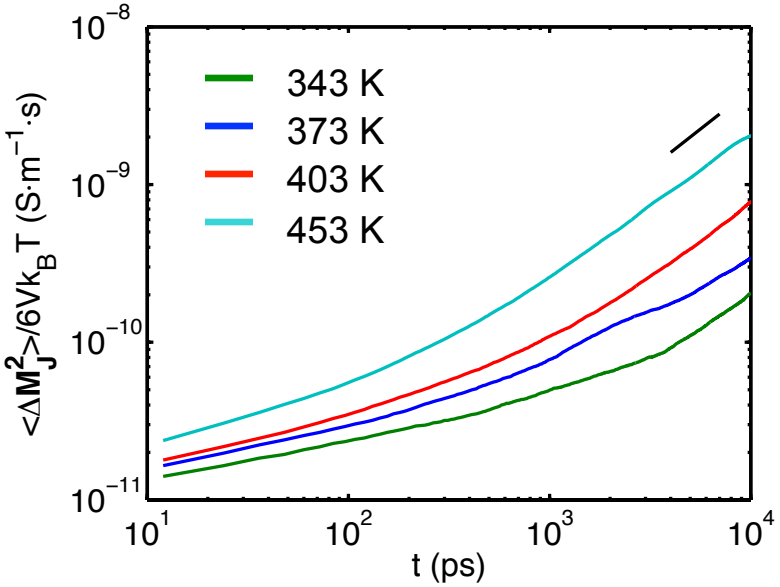
Canopy chain exchange kinetics

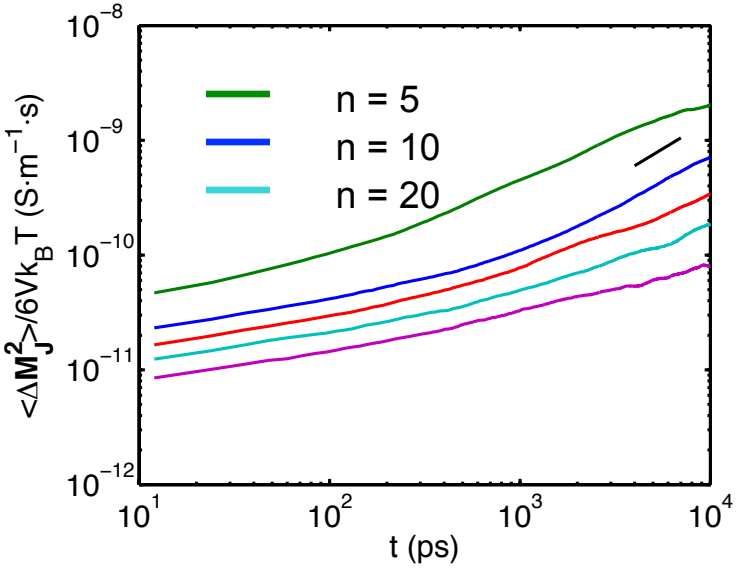


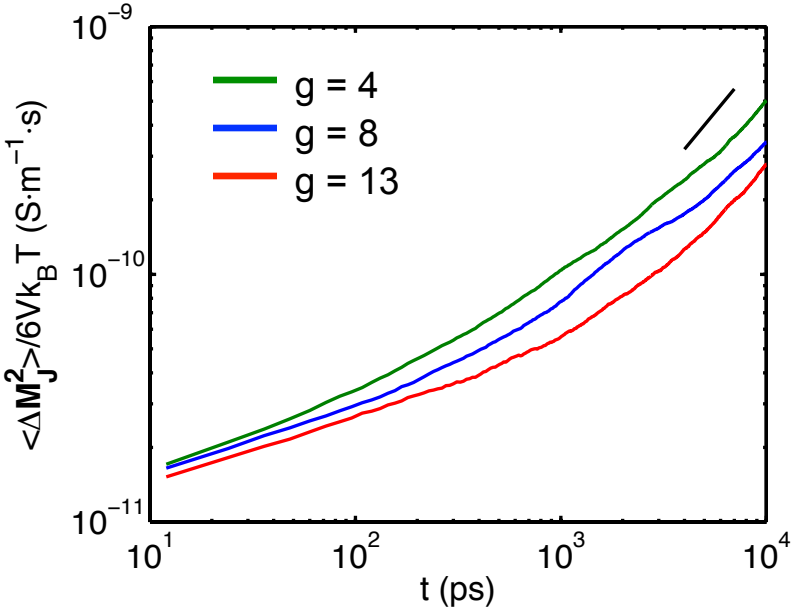




Conductivities







$$\mathbf{M}_J(t) = \sum_i q_i \mathbf{r}_{c.m.i}(t)$$

$$\lim_{t \geq t_c} \left\langle \Delta \mathbf{M}_J^2(t) \right\rangle = \lim_{t \geq t_c} \left\langle \left[\mathbf{M}_J(t) - \mathbf{M}_J(0) \right]^2 \right\rangle = \left[6Vk_B T \sigma(\omega = 0) \right] t + 2 \left\langle \mathbf{M}_J^2 \right\rangle$$

- simulated conductivity 2.5 times the value of polyoxometalates (POM(-)) grafted with two $N(+)(CH_3)(C_{18}H_{37})[(EO)_n][(EO)_m]$ (n+ m = 15) at 373 K.

Summary & discussion points

Bulk PEO chains

- structural properties in good agreement with atomistic models
- diffusion coefficients increase by a nearly constant factor at high *T* only
- non-trivial scaling at low *T*

NOHMs (non-ionic)

Diffusion of nanoparticles can be *slower* in coarse-grained models under some conditions

NIMs (ionic)

- insights on mechanism for fluidity + conductivity
- reasonable agreement with experiments using simple “thermodynamic” CG models

Open question

Is there a way to obtain dynamic scaling of CG models for complex nanoparticle / chain systems?