COARSE-GRAINING AND MULTISCALE MODELING OF MACROMOLECULAR LIQUIDS: THERMODYNAMIC CONSISTENCY AND DYNAMIC RECONSTRUCTION

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•Division of Material Research-Material Theory & Chemistry Division - Theoretical Chemistry
•TERAGRID- XSEDE
•NSF-MRI Cloud Computer - ACISS

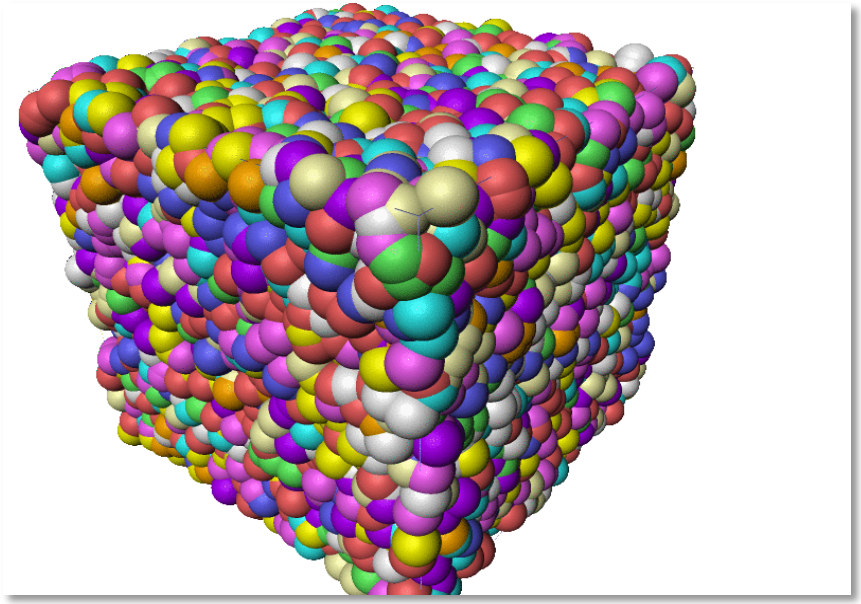
Advantages and Challenges in Coarse-graining

Local degrees of freedom are averaged out → Changes in Entropy

Free energy landscape is simplified → Thermodynamic consistency

Simulation speeds up improving resolution on large length and time scales

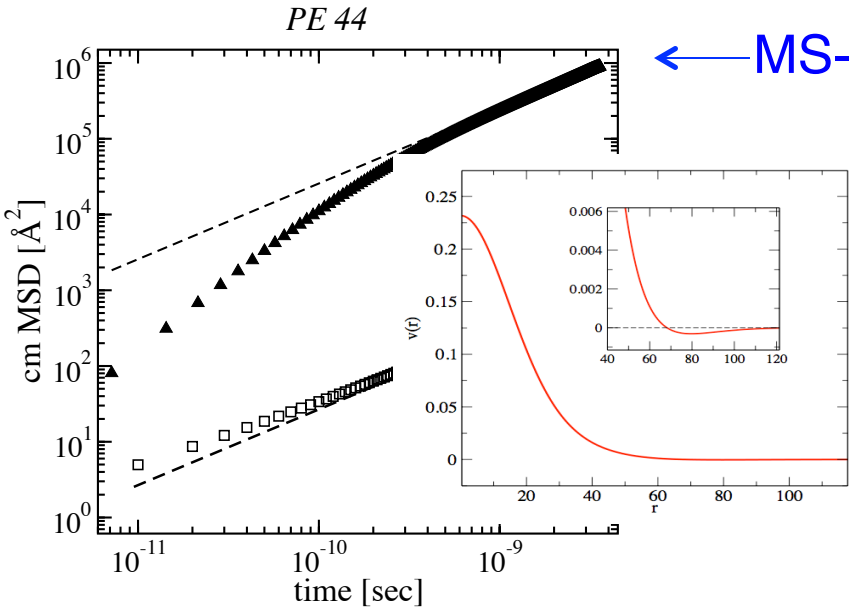
→ Dynamics is unrealistically fast



Challenges in CG with NUMERICALLY OPTIMIZED POTENTIALS

> *"Beware of density dependent pair potentials"*
> *A.A.Louis* J. Phys. Condens. Matter **14** (2002) 9187

Dynamical Rescaling: CG dynamics is unrealistically accelerated



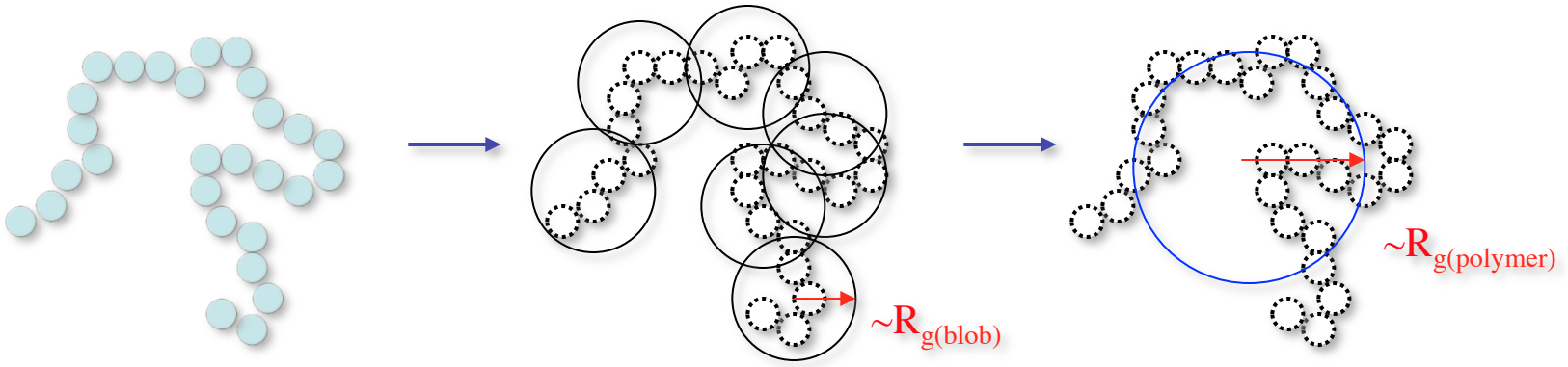
←MS-MD

ID

An analytical coarse-grained model

J. McCarty, I. Lyubimov, M. G. Guenza J. Phys. Chem. B 113, 11876-11886 (2009).
A. J. Clark, and M. G. Guenza J. Chem. Phys. 132, 044902-12 (2010).
J. McCarty, I, Y, Lyubimov, and M. G. Guenza, Macromolecules 43, 3964-3979 (2010).
Y. Lyubimov, J. McCarthy, A. Clark, and M. G. Guenza J. Chem. Phys. 132, 2249031-2249035 (2010).
J. McCarty, and M. G. Guenza J. Chem. Phys. 133,094904-094918 (2010)
Y. Lyubimov, and M. G. Guenza Phys. Rev. E 84, 031801-19 (2011).

ANALYTICAL COARSE-GRAINING OF MACROMOLECULAR LIQUIDS



Monomer-size, l
Microscopic scale

Blob or Block size
Mesoscale description

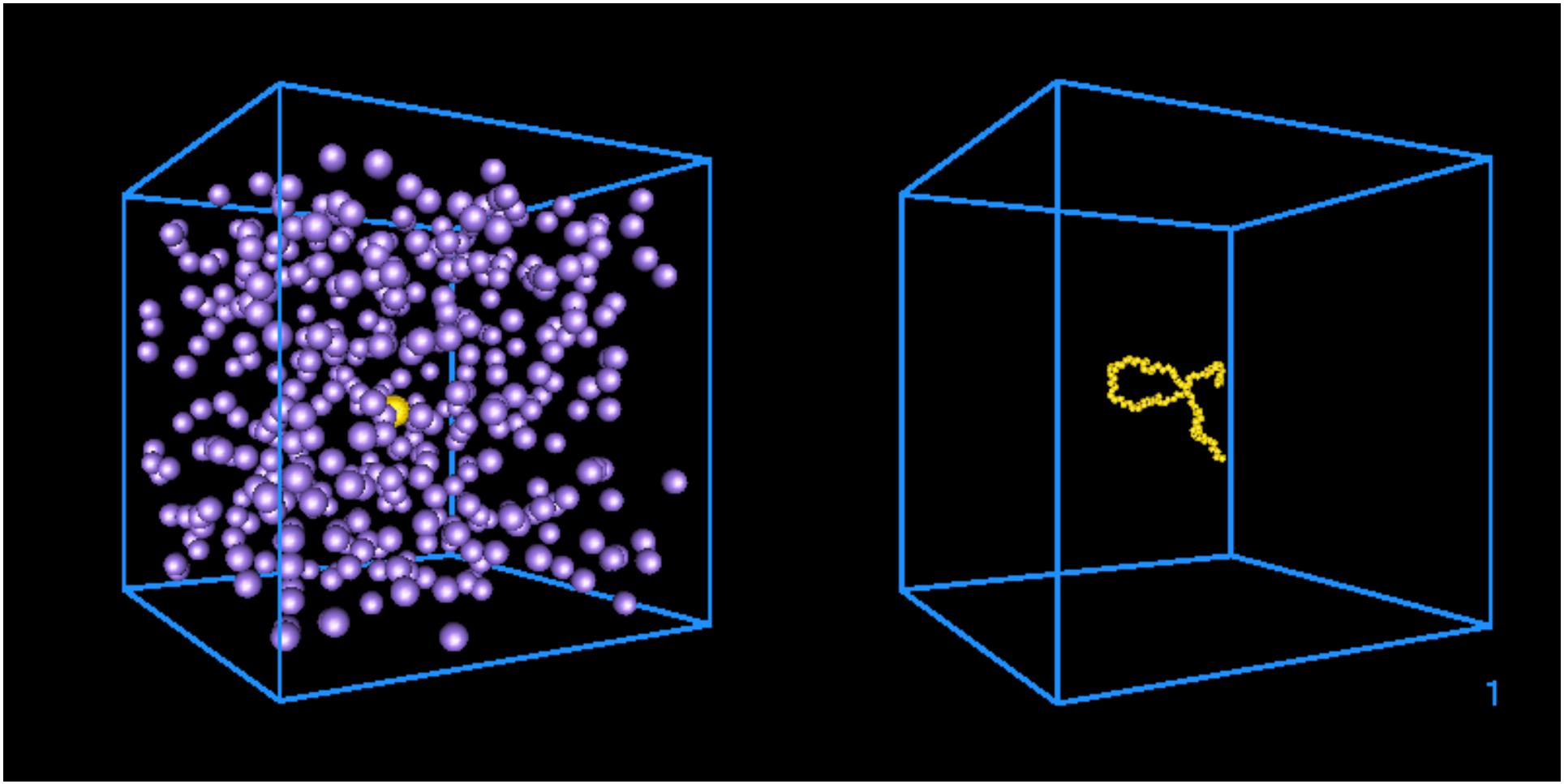
Polymer-size
R_g radius of gyration
Mesoscale description

GOAL: Reproducing Radial Distribution Function g(r) or total correlation function h(r)=g(r)-1, i.e. probability of finding beads belonging to different molecules at a relative distance r.

Any isotropic potential which reproduces the correct pair structure of a fluid is **unique** up to a constant - *R. L. Henderson Phys. Lett. A **49**, 197 (1974)*

From g(r) --> Thermodynamic properties
D. A. Mc Quarrie "Statistical Mechanics" (University Science Book, Sunsalito, 2000)
J. –P. Hansen & I. R. McDonald "Theory of Simple Liquids" (Academic Press, 1991)

A Soft-Sphere Representation of Polymer Liquids



THEORETICAL APPROACH: Ornstein-Zernike equation for real (monomer) and auxiliary (center-of-mass of coarse-grained unit) sites

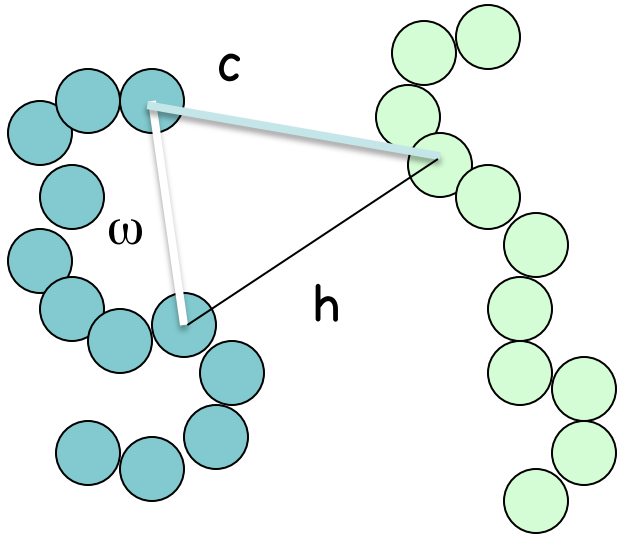
Mapping of polymers into soft colloidal particles

Not a novel idea: Flory, Hall, Hansen, Kremer, Likos, Louis, and more.

Derive Total Correlation Function from analytical solution of Ornstein-Zernike equation for real (monomer) and auxiliary (center-of-mass of coarse-grained unit) sites.

$$h^{cc}(k) = \left[\omega^{mc}(k)/\omega^{mm}(k)\right]^2 h^{mm}(k)$$

V. Krakoviack, J.-P. Hansen, A. A. Louis Europys. Lett. 58, 53 (2002).



N monomers in a chain

RISM - Chandler & Andersen 1972
PRISM - Curro & Schweizer 1990

$$h^{mm}(r) = \frac{\xi_\rho}{r}\left[\exp\left(-r/\xi_\rho\right) - \exp\left(-r/\xi_c\right)\right]$$

$$\xi_\rho = 3/\left(\pi\rho l^3\right)$$

Density-fluctuation correlation length

$$\xi_c = R_g/\sqrt{2}$$

Correlation hole length scale

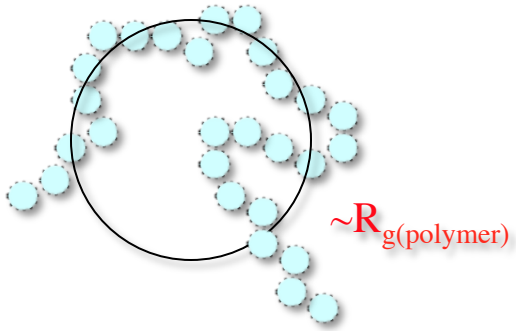
$$R_g = Nl^2/6$$

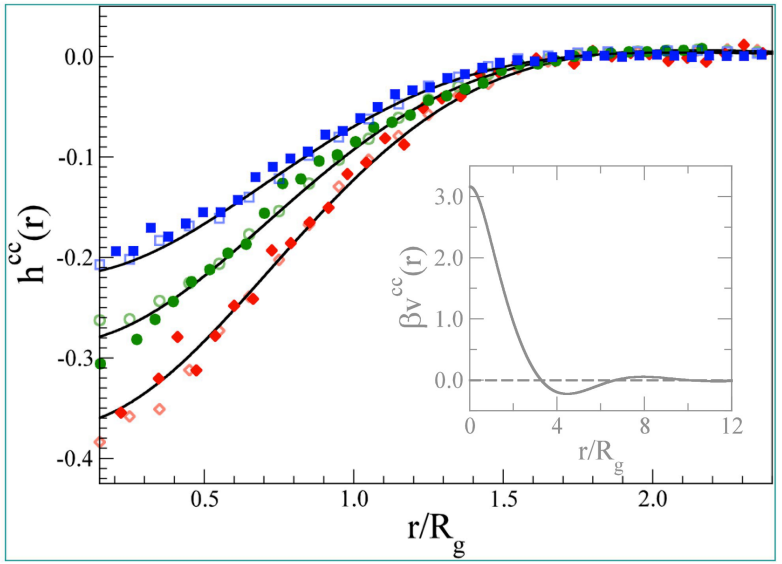
Analytical Coarse-Grained model from Ornstein-Zernike Equation

$$h(\tilde{r},\xi_\rho) \approx -\frac{39\sqrt{3}}{16\sqrt{\pi}}\tilde{\xi}_\rho\left(1+\sqrt{2}\tilde{\xi}_\rho\right)\left[1-\frac{9}{26}\tilde{r}^2+O\left(\tilde{r}^4\right)\right]\exp\left(-\frac{3}{4}\tilde{r}^2\right)$$

$$\tilde{\xi}_\rho = \xi_\rho / R_g \qquad \tilde{r} = r/R_g$$

in the large N limit





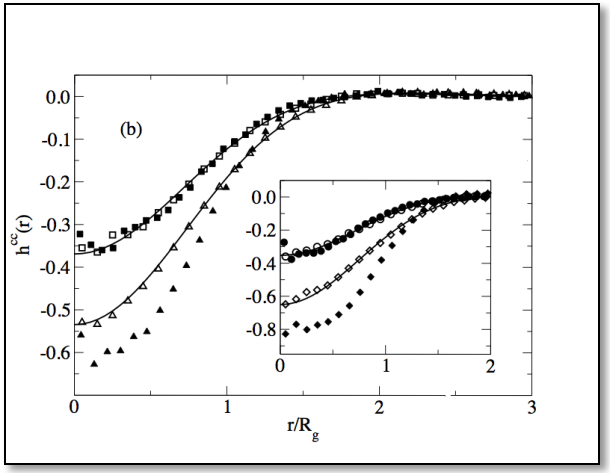
Polyethylene N=44◆, 64●, 96■

Filled symbols:UA-MD simulation (Grest) (24 h, 1600 particles, 64-node cluster)

Open symbols: MS-MD simulation (4 h, 6000 particles, 1 CPU)

G.Yatsenko, E.J. Sambriski, M.A. Nemiroskaya, M. G. Guenza, Phys. Rev. Lett. 93, 257809 (2004).

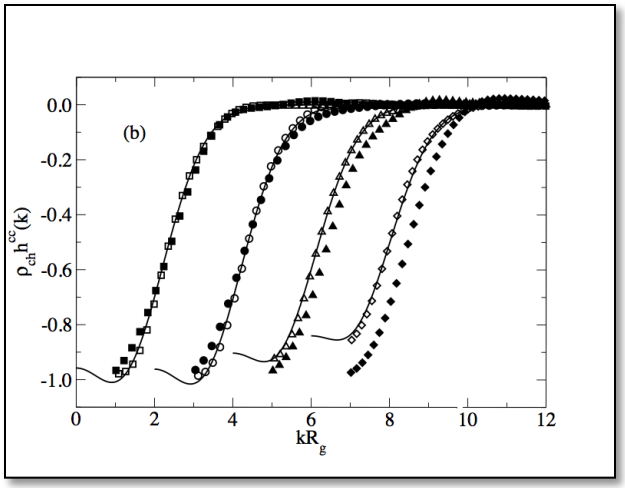
Transferability: *an effective pair potential optimized at one set of conditions (molecular structure and thermodynamic) will not generally be transferable to another set of conditions*

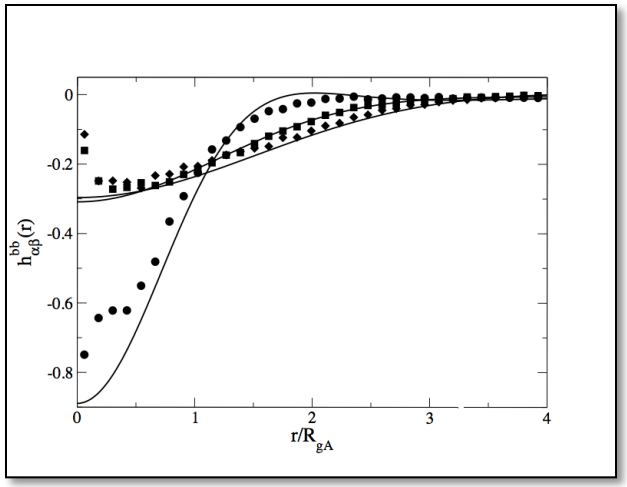


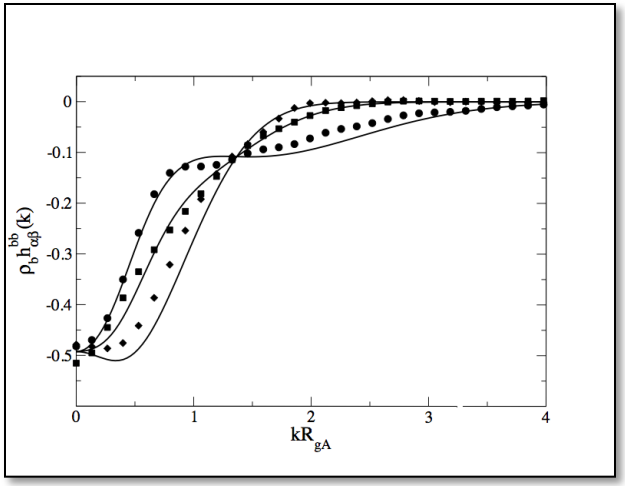
Different architectures

iPP(▲) sPP(●)

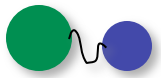
hhPP(■) PIB (◆)







Blockcopolymer melts
Here $f=N_A/N_B=0.25$
AA (●), BB (◆), AB (■)



E.J. Sambriski, M. G. Guenza, PRE 76, 051801 (2007)
Multiblock polymer A. J. Clark, and M. G. Guenza J. Chem. Phys. 132, 044902-12 (2010).

Coarse-graining Description for Polymer Mixtures

$$h^{AA}(r)=\frac{1-\phi}{\phi}I_{\phi}^{AA}(r)+\gamma^{2}I_{\rho}^{AA}(r),\quad h^{BB}(r)=\frac{\phi}{1-\phi}I_{\phi}^{BB}(r)+\gamma^{-2}I_{\rho}^{BB}(r),$$

$$h^{AB}(r)=-I_{\phi}^{AB}(r)+I_{\rho}^{AB}(r)$$

$\sigma=\sigma_A/\sigma_B$ semiflexibility ratio

$$I_{\lambda}^{\alpha\beta}(r)=\frac{3}{4}\sqrt{\frac{3}{\pi}}\tilde{\xi}_{\rho}\vartheta_{\alpha\beta1}\left(1-\frac{1}{2\tilde{\xi}_{\lambda}^{2}}\right)\mathrm{e}^{-3\tilde{\mathrm{r}}^{2}/4}-\frac{1}{2}\frac{\tilde{\xi}_{\rho}}{\tilde{\mathrm{r}}}\vartheta_{\alpha\beta2}\left(1-\frac{1}{2\tilde{\xi}_{\lambda}^{2}}\right)^{2}\mathrm{e}^{1/\left(3\tilde{\xi}_{\lambda}^{2}\right)}$$

$$\times\left[\mathrm{e}^{\tilde{\mathrm{r}}/\tilde{\xi}_{\lambda}}\mathrm{erfc}\left(\frac{1}{\tilde{\xi}_{\lambda}\sqrt{3}}+\frac{\tilde{\mathrm{r}}\sqrt{3}}{2}\right)-\left[\mathrm{e}^{-\tilde{\mathrm{r}}/\tilde{\xi}_{\lambda}}\mathrm{erfc}\left(\frac{1}{\tilde{\xi}_{\lambda}\sqrt{3}}-\frac{\tilde{\mathrm{r}}\sqrt{3}}{2}\right)\right]\right].$$

$\tilde{\xi}_{\lambda}$ with $\{\lambda\in(\rho,\phi)\}$

$$\xi_{\phi}=\sqrt{\left[\phi\sigma_{B}^{2}+(1-\phi)\sigma_{A}^{2}\right]/\left[24(\chi_{s}-\chi)\phi(1-\phi)\right]}$$

The potential depends on the concentration fluctuations correlation length

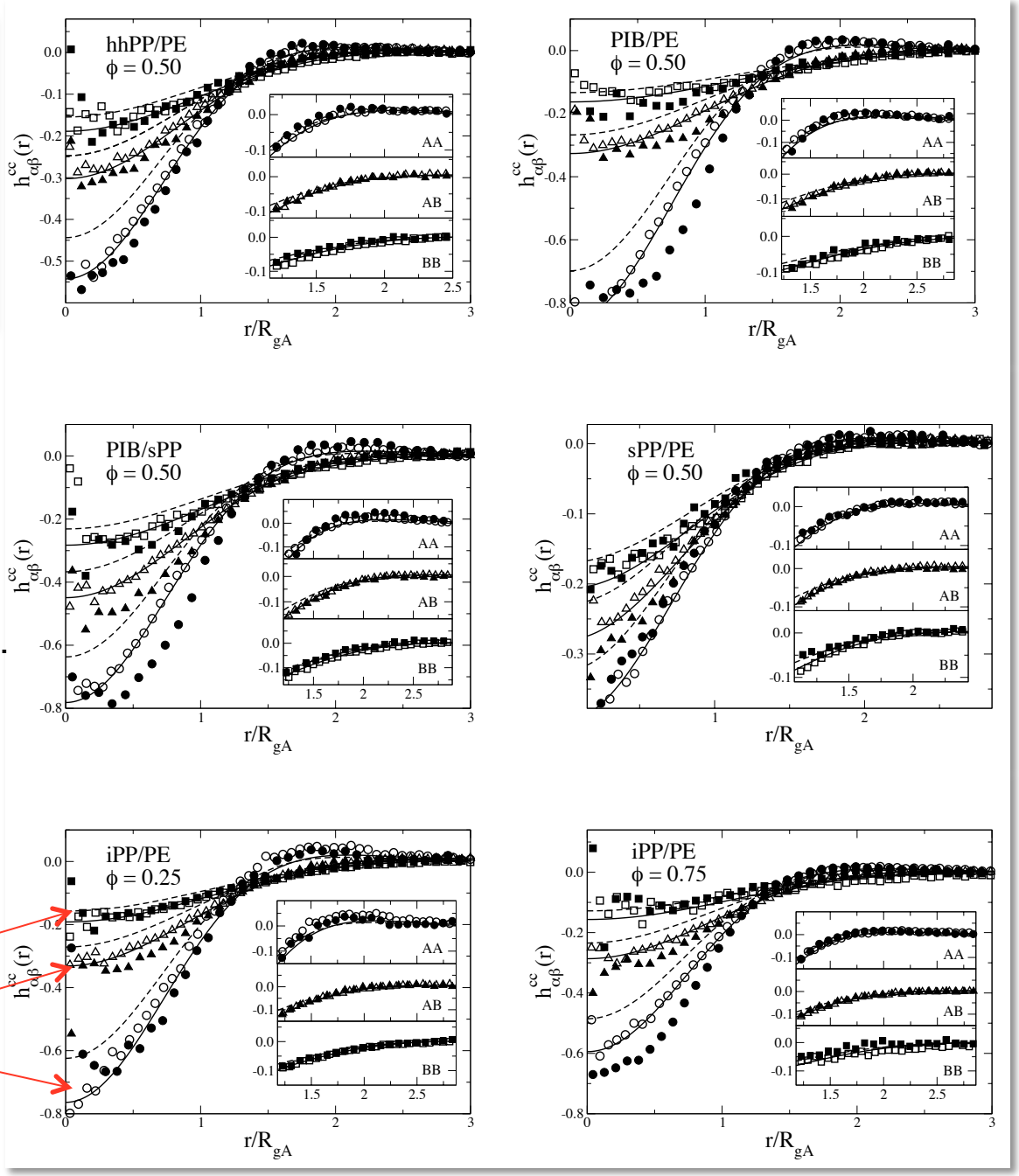
Center-of-mass TCF

Comparison of theory (full line) with UA-MD (filled symbols) and MS-MD(open symbols)

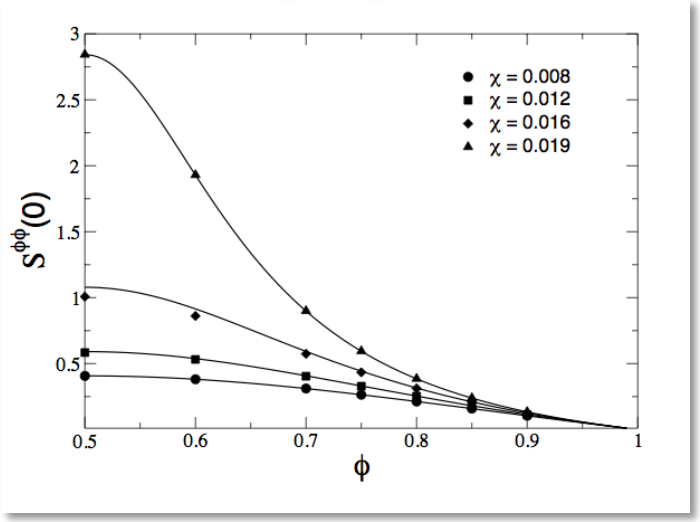
T=453K – athermal regime
$N_A=N_B=96$
Data from Heine et al JCP 2003, Jaramillo et al JCP 2004.

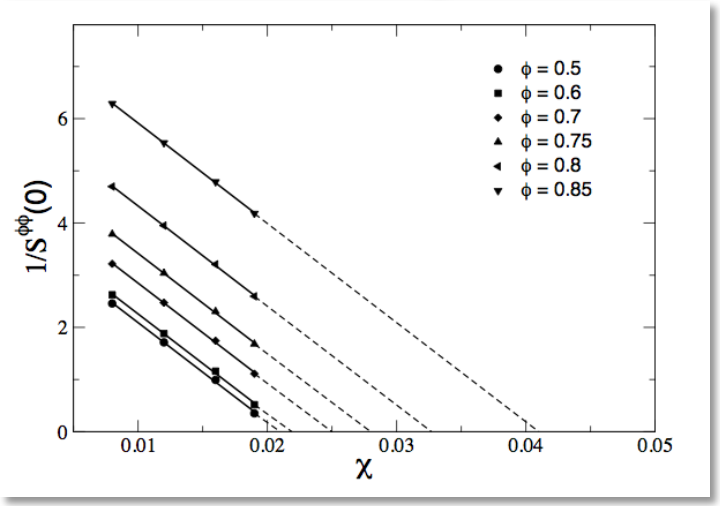
J. McCarty, I. Y. Lyubimov, M.G.G. Macromol. 43, 3964 (2010).

h_{BB}
h_{AB}
h_{AA}



Multiscale Modeling of Polymer Mixtures: Scale Bridging in the Athermal and Thermal Regime hhPP/PE



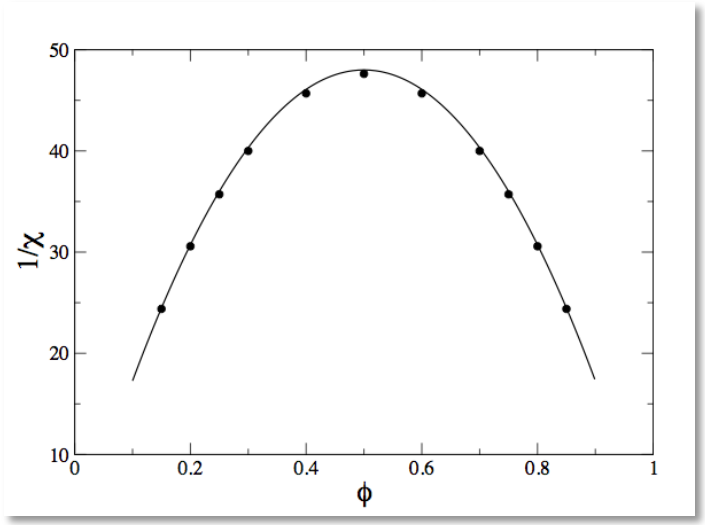


Concentration fluctuation structure factor $S^{\phi\phi}(0)$ diverges at the phase transition (spinodal).

The interaction parameter $\chi \sim T^{-1}$
The polymer volume fraction ϕ

J. McCarty, I. Y. Lyubimov, M. G. Guenza
Macromol. 43, 3964 (2010).
J. McCarty, and M. G. Guenza
J. C. P. 133, 094904 (2010).

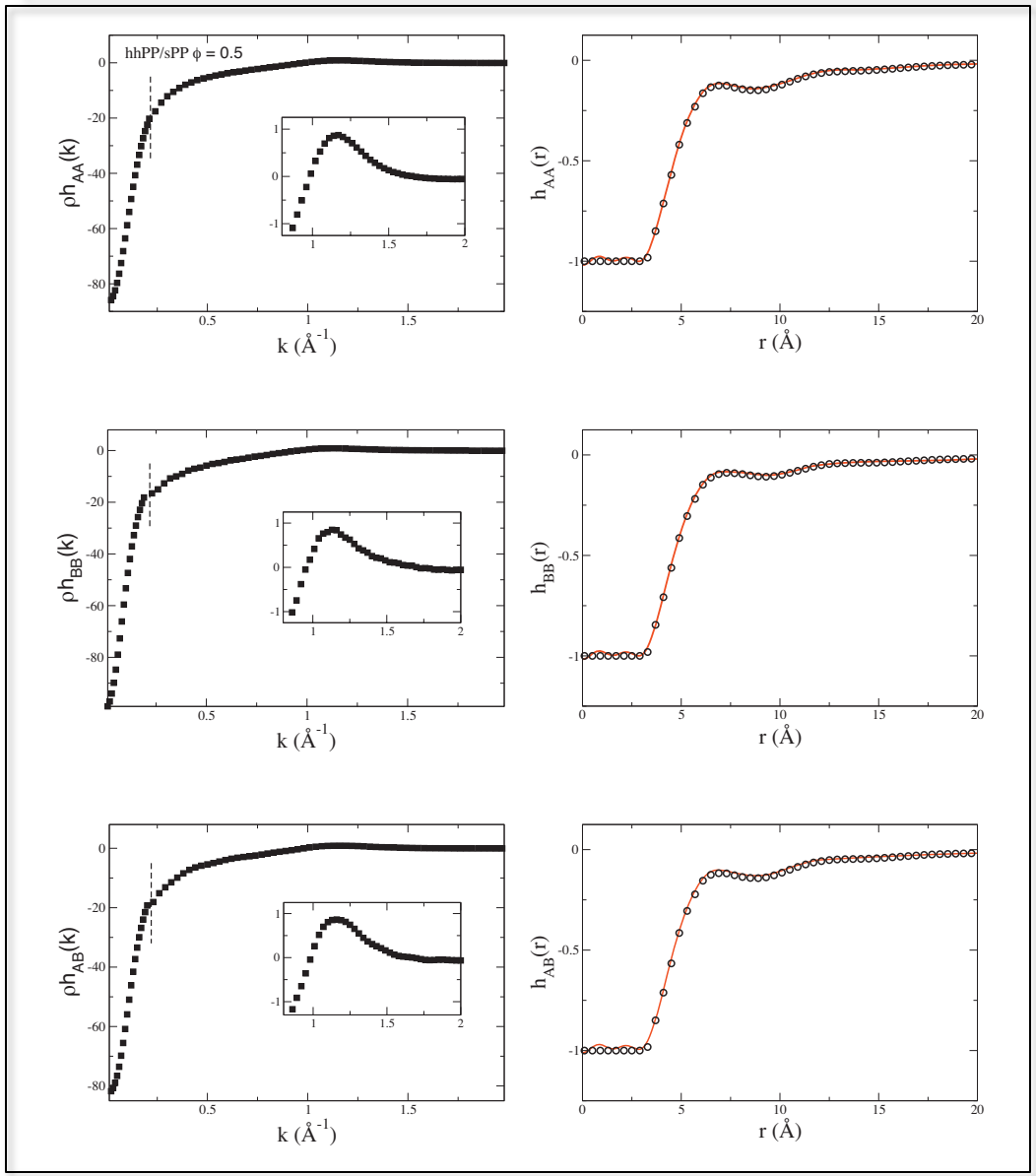
hhPP/PE Phase diagram from MS-MD



Jay McCarty

How to include the atomistic structure back: Multiscale Modeling of Polymer Mixtures

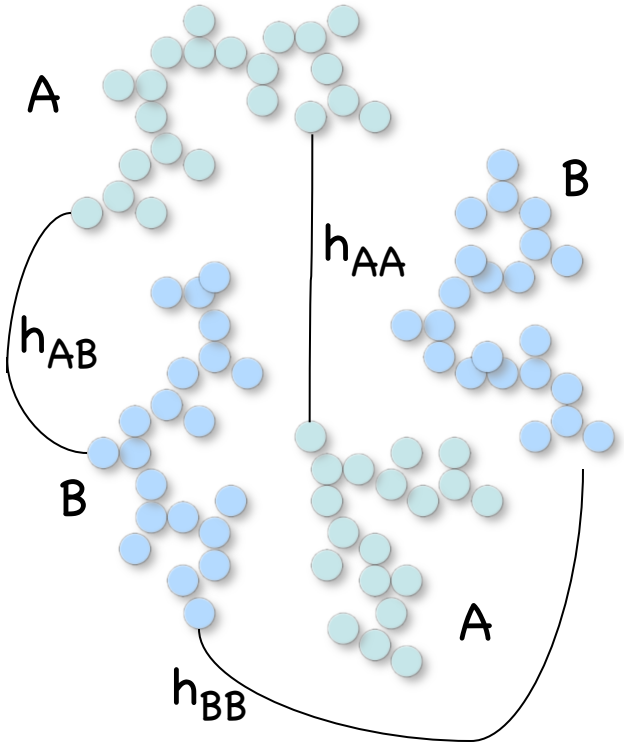
Monomer TCF



hhPP
sPP

Athermal T
Circle: UA-MD, Line: theory

$$h^{cc}(k) = \left[\omega^{mc}(k)/\omega^{mm}(k)\right]^2 h^{mm}(k)$$



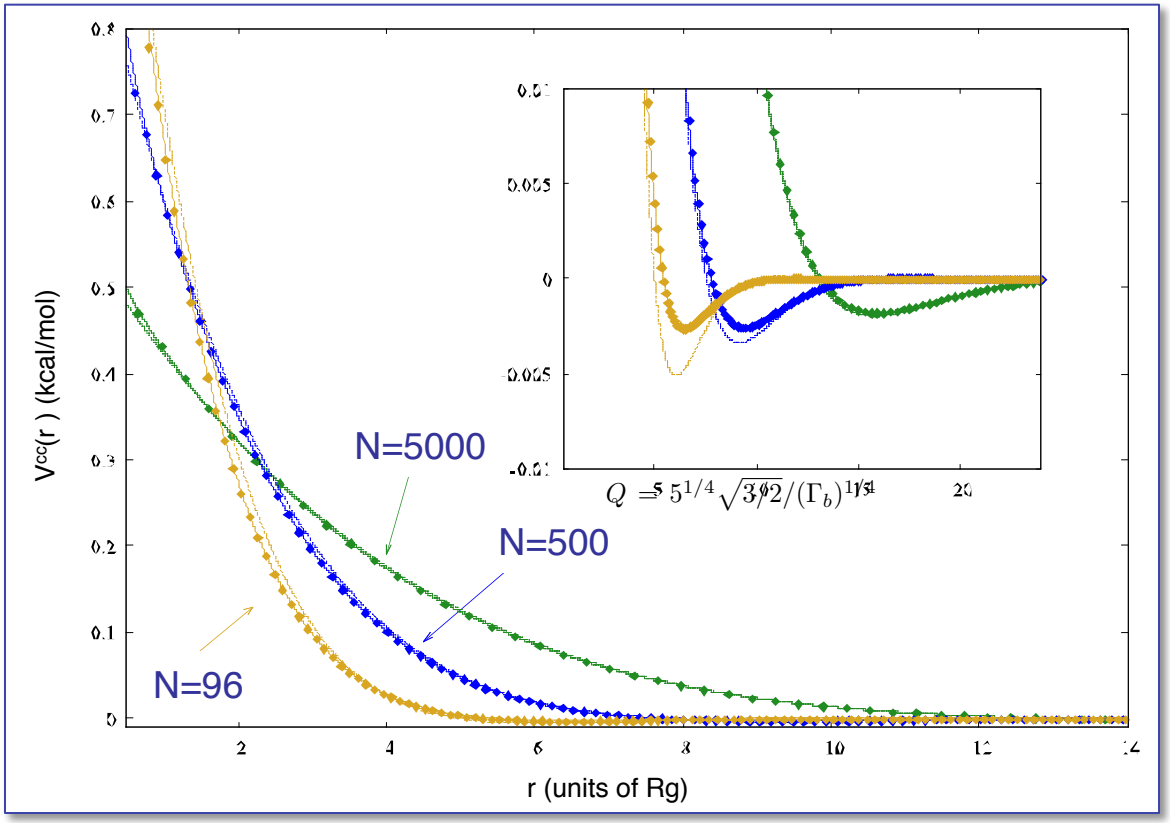
J. McCarty, and M. G. Guenza
J. C. P. 133, 094904 (2010).

Representability: *even at the correct state conditions numerical potential optimized to reproduce one quantity, e.g. the correct radial distribution function, will not necessarily reproduce any other, such as the correct pressure or energy.*

Analytical Effective Potential between two Soft Spheres

HNC closure

$$V_{HNC}(r) = -k_B T\left[c(r) - h(r) + \ln(1+h(r))\right] \approx -k_B T\, c(r)$$



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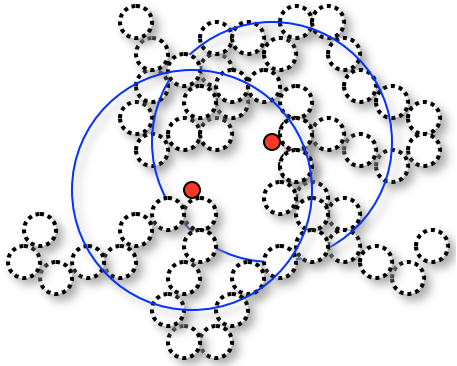


$$c^{cc}_{(0)}(r) \approx -\frac{45}{(5^{1/4})8\pi}\sqrt{\frac{2}{3}}\frac{\Gamma^{1/4}}{\rho_{ch}R_g^3}\frac{\sin(Qr)}{Qr}e^{-Qr}$$

$$Q = 5^{1/4}\sqrt{3/2}\,(\Gamma)^{1/4}$$

$$\Gamma \equiv N|c_o|\rho$$

Thermodynamic Consistency: Eq. of State for Soft Colloids (an example)

Compressibility Route

$$\frac{P}{k_B T} = \int_0^{\rho_{ch}} d\rho[\hat{S}^{cc}(0,\rho)]^{-1}]$$

Assuming c_0 is no density dependent

$$Z_c = \frac{N|c_0|\rho}{2}$$

Thread model

$$Z_c = \frac{\pi\rho\sqrt{N}\sigma^3}{6\sqrt{3}} + \frac{2}{3}\frac{\pi^2\rho^2 N\sigma^6}{216}$$

Consistency with Atomistic description

$$h^{cc}(k) = \left[\omega^{mc}(k)/\omega^{mm}(k)\right]^2 h^{mm}(k)$$

$$k \to 0 \quad \omega^{mc}(0) = \omega^{mm}(0) = N\,h^{cc}(0) = h^{mm}(0)$$

$$Z_c = \frac{\pi\rho\sqrt{N}\sigma^3}{6\sqrt{3}} + \frac{2}{3}\frac{\pi^2\rho^2 N\sigma^6}{216}$$

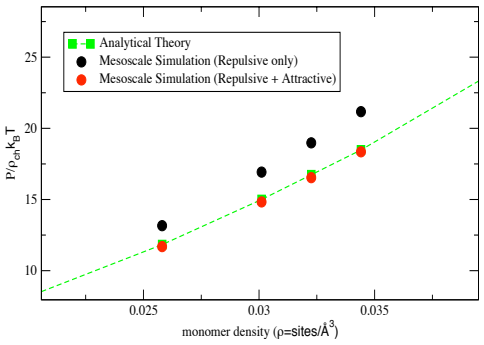
Virial Route
Analytical form of v(r)~ - k_BT c(r)

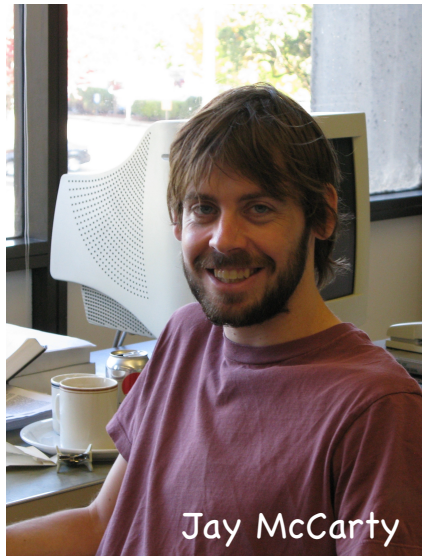
$$\frac{P}{\rho_{ch}k_B T} = 1 - \frac{2\pi\rho_{ch}}{3k_B T}\int_0^\infty g(r)\frac{dv(r)}{dr}r^3 dr,$$

$$Z_v = 1 + \frac{N|c_0|\rho}{2}.$$

Thread model

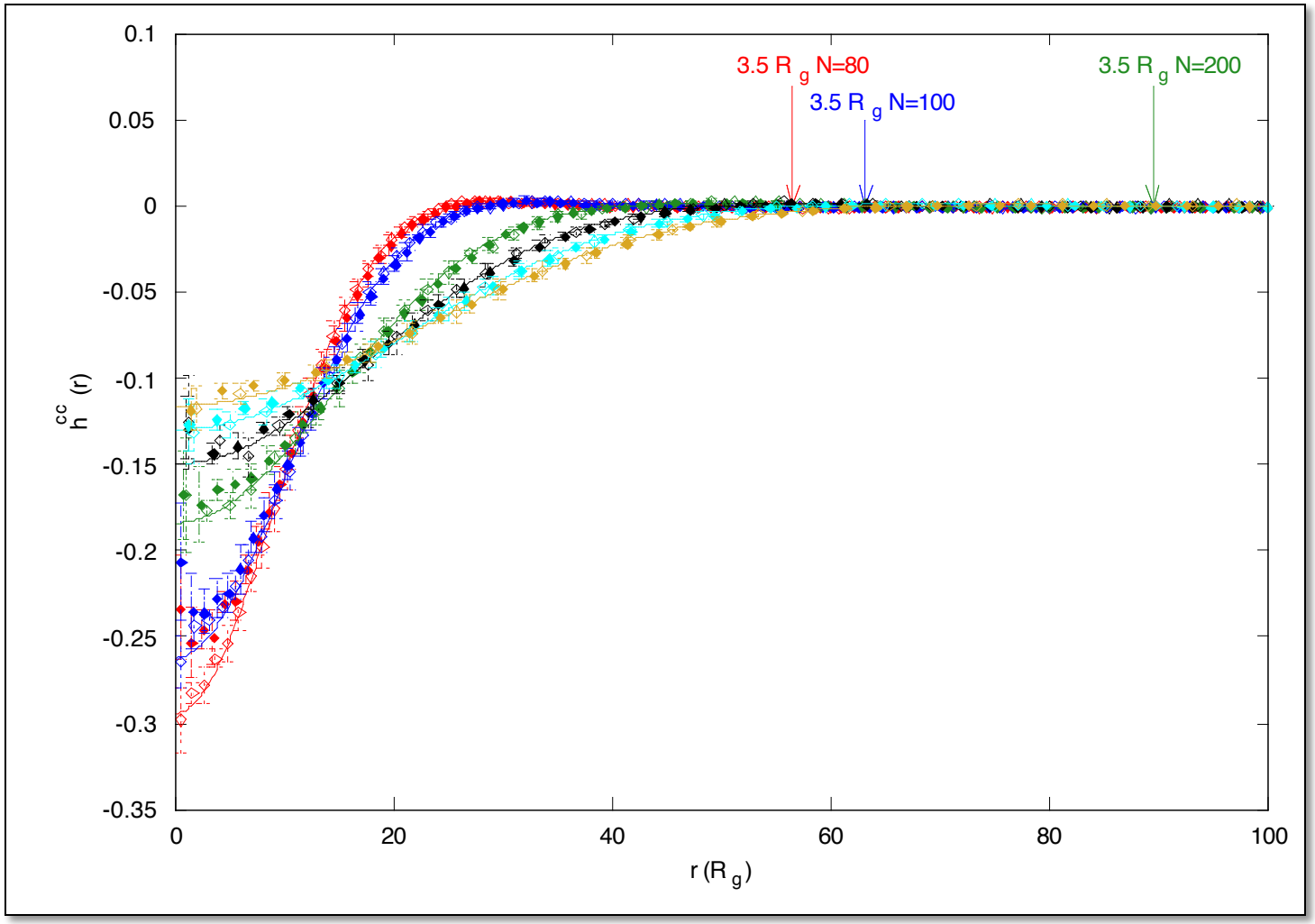
$$Z_v = 1 + \frac{\pi\rho\sqrt{N}\sigma^3}{6\sqrt{3}} + \frac{\pi^2\rho^2 N\sigma^6}{216}$$





Thermodynamic Consistency

Thermodynamic Inconsistency due to Numerical Optimizations



Theory (full lines), and MS-MD data from simulations that use the full potential (open circles), or the potential calculated using h(r) cut at 3.5 R_g (full circles). N=80, 100, 200, 300, 400, 500

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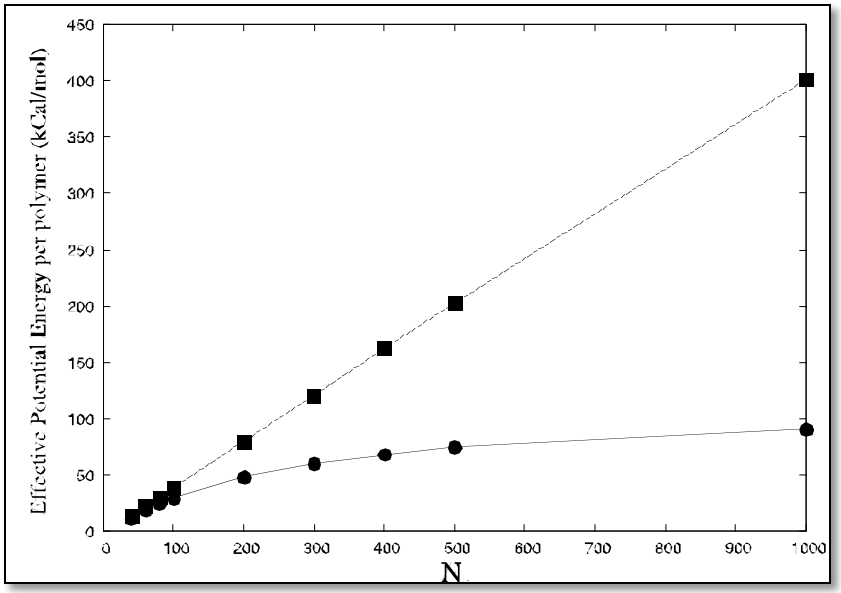
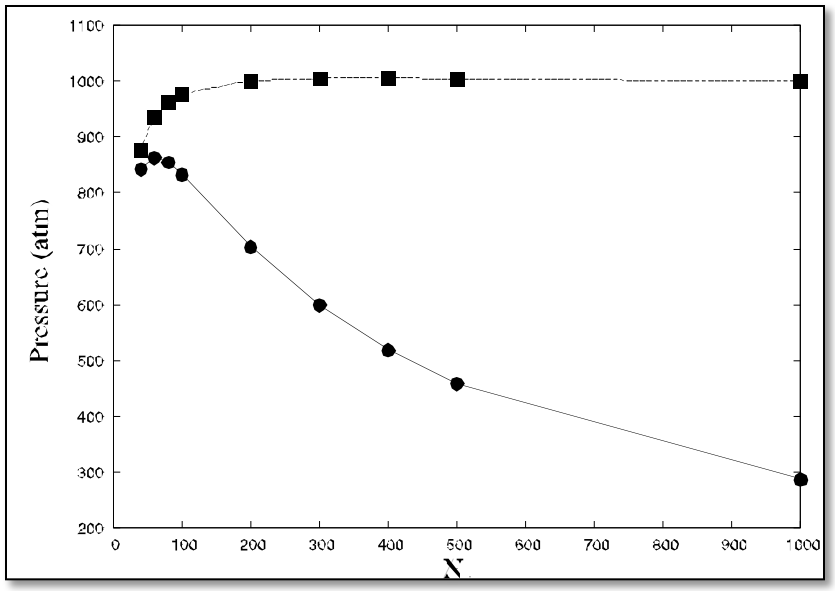
Thermodynamic Inconsistency due to Numerical Optimizations



Energy and Pressure from MS-MD simulations, using the full potential (squares) or the potential with h(r) cut at 3.5 Rg (circles)

$T = 450\,K \quad \rho_m = 0.0328\,\text{Å}$

- *Cutting the potential affects the structure of the simulated CG liquid within the error of the procedure.*
- *However it greatly affects the measured thermodynamic properties.*
- *Enhanced at large N*

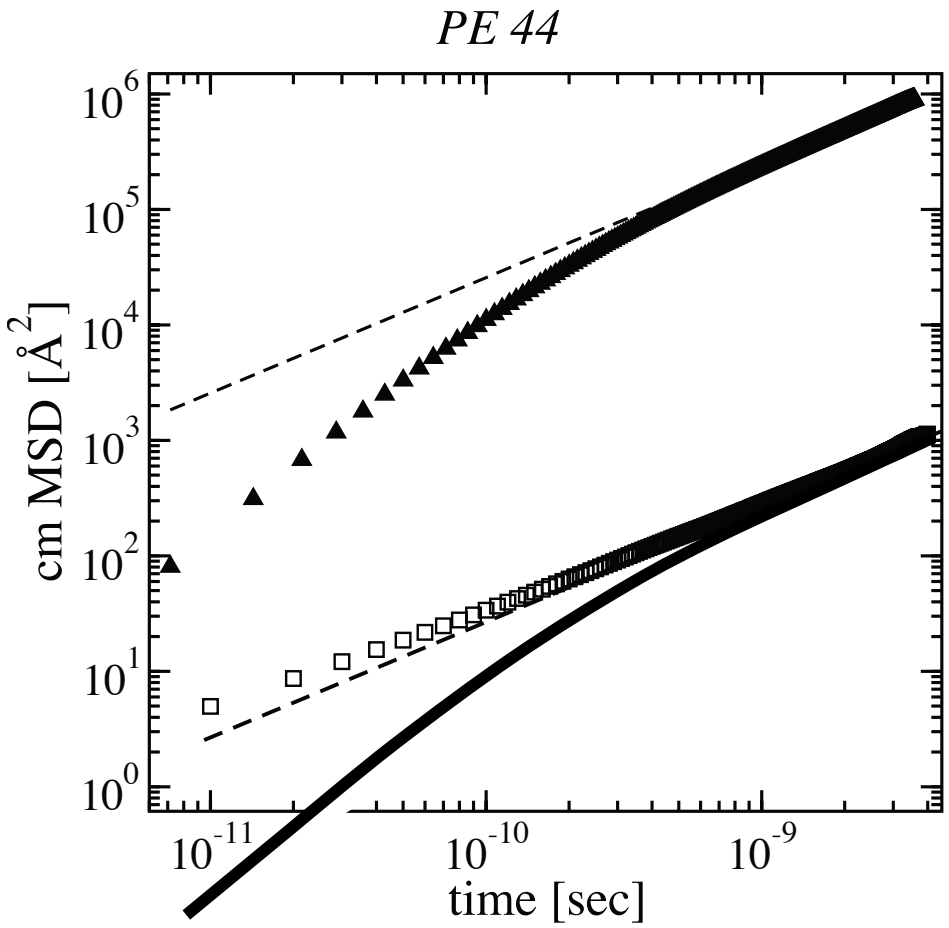


Anthony Clark

The dynamics measured in mesoscale simulations of the coarse-grained system is unrealistically fast and needs to be rescaled

I. Y. Lyubimov, J. McCarthy, A. Clark, and M. G. Guenza J. Chem. Phys. 132, 2249031 (2010).
I. Y. Lyubimov, and M. G. Guenza Phys. Rev. E 84, 031801-19 (2011).

Rescaled dynamics from mesoscale simulations of coarse-grained polymers. Conventional method: the calibration curve.

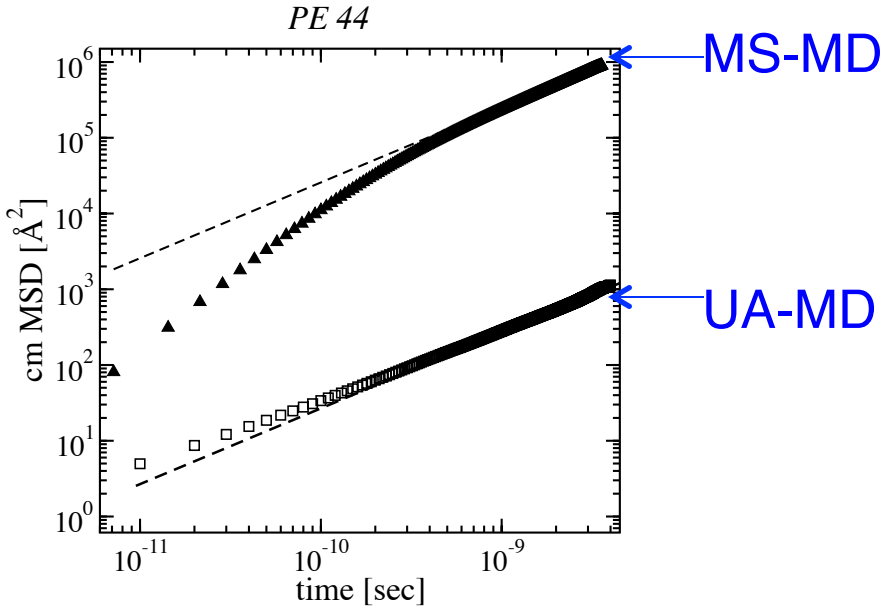


← MS-MD

← UA-MD

Problem: the method is not predictive

Predictions of Single-chain Diffusion Coefficients from mesoscale simulations of coarse-grained polymers



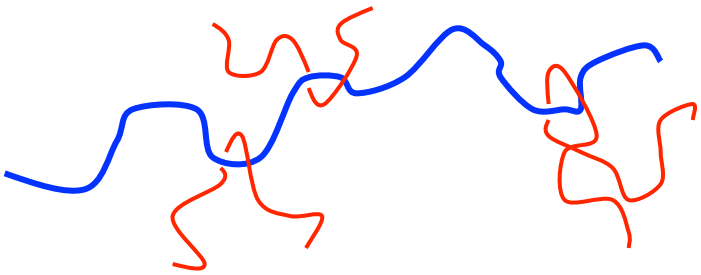
1) MS MD --> diffusion D^{MS}

2) $D^{MS} \xrightarrow{\text{time rescaling–ENTROPY}} D^{MS}_{time}$

3) Re-scale friction

$$D = D^{MS}_{time} \frac{\zeta_{soft}}{N\zeta_m}$$

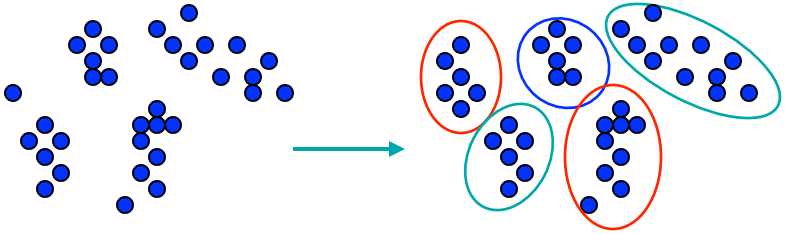
Rescaling is calculated from the ratio between MS and UA properties, solved analytically. MS-MD input: ρ, T, R_g



Entanglements relax on the same timescale than the entangled chain: one loop perturbation

$$D\beta\zeta_m' = N\left(D\beta\zeta_m\right)^2$$

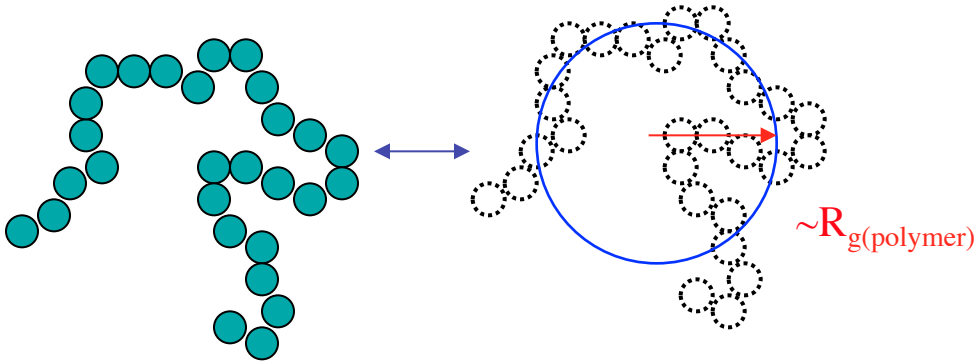
COARSE-GRAINING and DYNAMICAL RESCALING - 1



Grouping of microstates (blue dots) into progressively coarser states (ellipses) leads to **increasing entropy** (number of microstates in the corresponding ellipse)

H. C. Öttinger *Beyond Equilibrium Thermodynamics* (Wiley, Hoboken, N.J. 2005).

Time rescaling due to **increasing entropy**



$$t = t_{simul} R_g \sqrt{3mN/2k_B T}$$

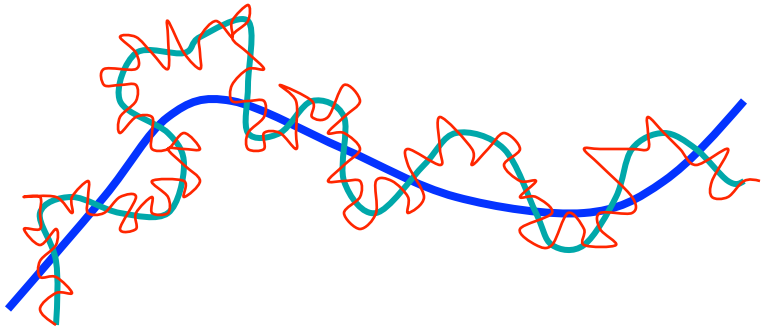
Obtained solving the LE for monomers dynamics

$$\zeta_m \frac{d\mathbf{r}_i(t)}{dt} = -\frac{\partial U(r)}{\partial \mathbf{r}_i(t)} + \mathbf{F}_i^Q(t)$$

$$U(r) = 3k_B T/(2l^2) \sum_{i,j=1}^{N} \mathbf{A}_{i,j} \mathbf{r}_i \cdot \mathbf{r}_j$$

COARSE-GRAINING and DYNAMICAL RESCALING - 2

A polymer on three levels of description: an increasing number of fast processes are eliminated in favor of random fluctuations for the coarser description --> **increasing friction**.

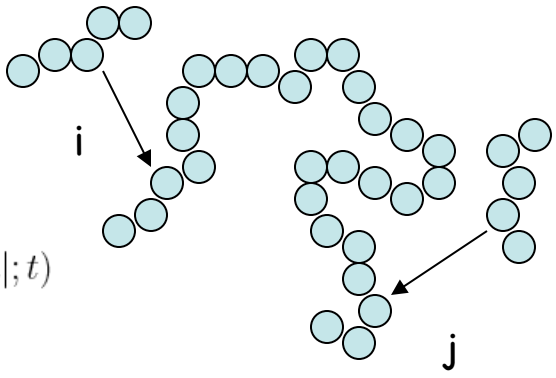


H. C. Öttinger *Beyond Equilibrium Thermodynamics* (Wiley, Hoboken, N.J. 2005).

2) Rescaling of the **friction coefficient**

Monomer $\zeta_m \cong \frac{1}{N}\sum_{j,i=1}^{N}\int_0^\infty d\tau \Gamma_{i,j}(\tau)$

$$\Gamma_{i,j}(t) \cong \frac{\beta}{3}\rho_m \int d\mathbf{r}\int d\mathbf{r}' g(r)g(r')F(r)F(r')\,\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'\int d\mathbf{R}\, S^Q_{i,j}(R;t)S^Q(|\mathbf{r}-\mathbf{r}'+\mathbf{R}|;t)$$



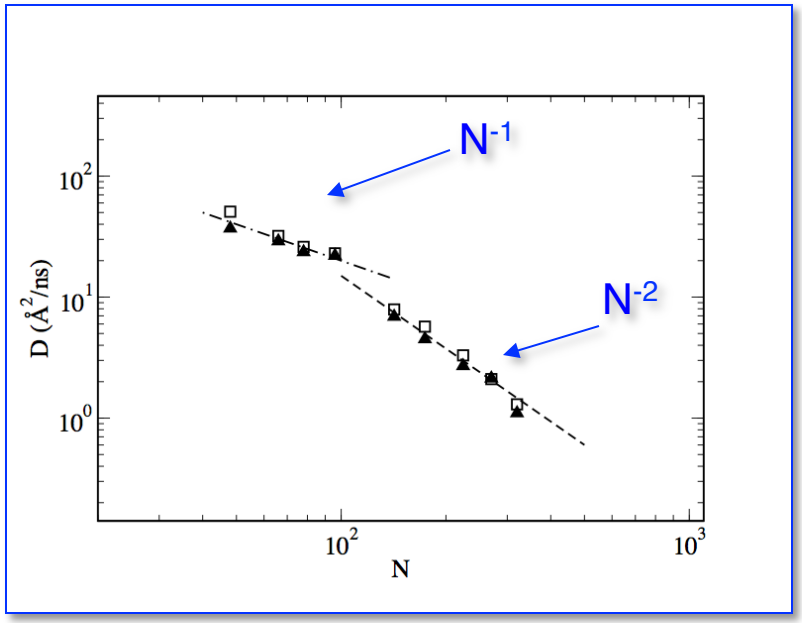
LJ CH_2 UA mapped onto a hard-sphere d=2.1 A

Soft-colloid

$$\zeta_{\text{soft}} = \frac{4}{3}\sqrt{\pi}(D\beta)^{-1}\rho_{ch}R_g\xi_\rho^2\left(1+\frac{\sqrt{2}\xi_\rho}{R_g}\right)^2\frac{507}{512}\left[\sqrt{\frac{3}{2}}+\frac{1183}{507}\rho_{ch}h_0+\frac{679\sqrt{3}}{1024}\rho_{ch}^2h_0^2\right] \qquad h_0=(\xi_\rho^2/\xi_c^2-1)/\rho_{ch}$$

Comparison with Simulations I

From rescaled MS-MD friction coefficient → local dynamics from Langevin Equation

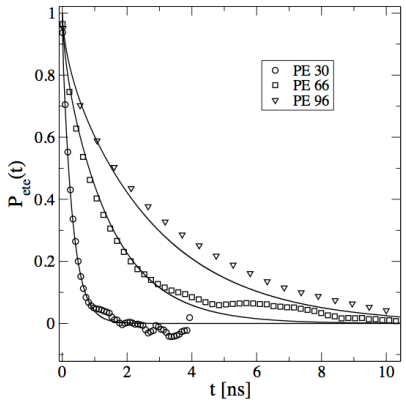


□ UA-MD simulations

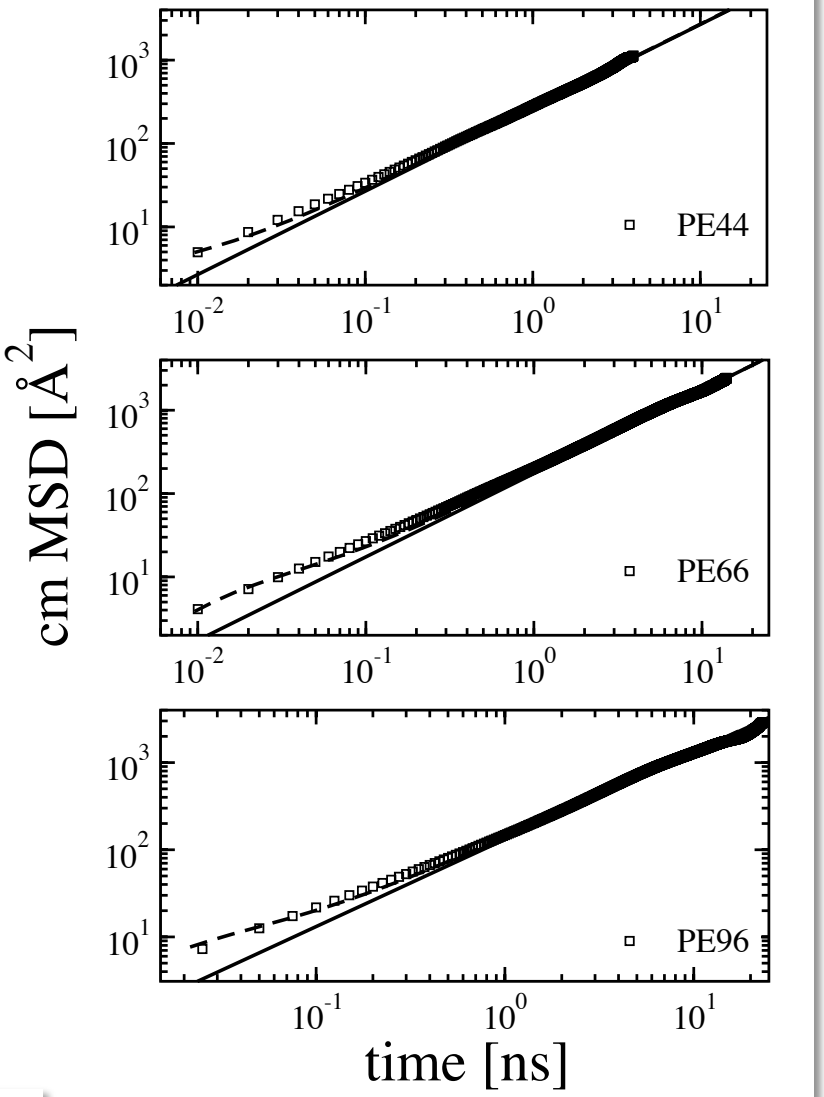
▲ **MS-MD simulations**

Data from: a) Mondello & Grest JCP 106, 327 (1997)
b) Uhlherr et al. Europhys. Lett. 57, 506 (2002).

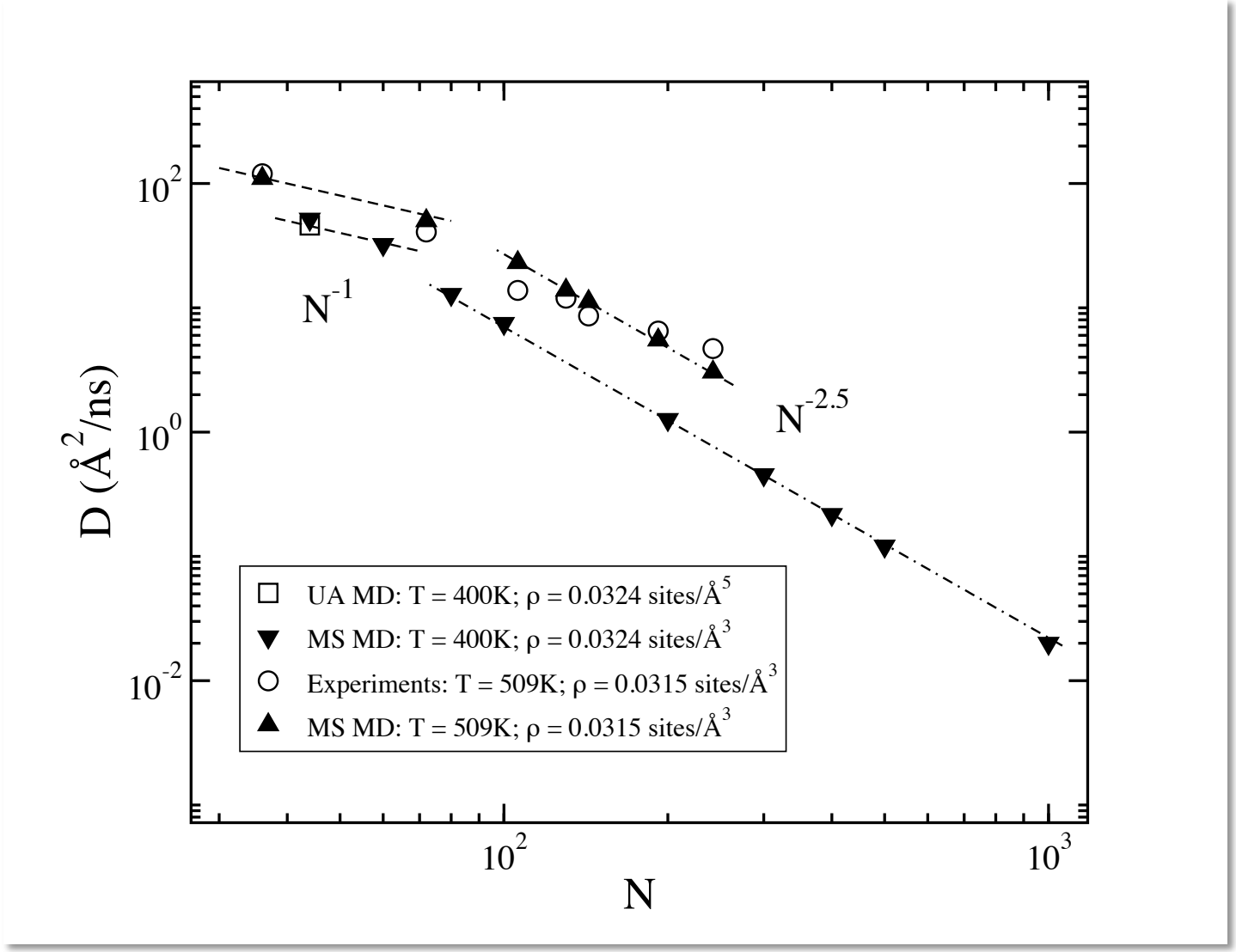
Polymer	N	T [K]	ρ [sites/Å^3]	R_g [Å]
PE30[a]	30	400	0.0317	7.97
PE44[a]	44	400	0.0324	10.50
PE48[b]	48	450	0.0314	10.54
PE66[a]	66	448	0.0329	13.32
PE78[b]	78	450	0.0321	14.35
PE96[a]	96	448	0.0328	16.79
PE142[b]	142	450	0.0327	20.51
PE174[b]	174	450	0.0328	22.92
PE224[b]	224	450	0.0329	26.28
PE270[b]	270	450	0.0330	29.27
PE320[b]	320	450	0.0330	31.31



Rotational End-to-End TCF

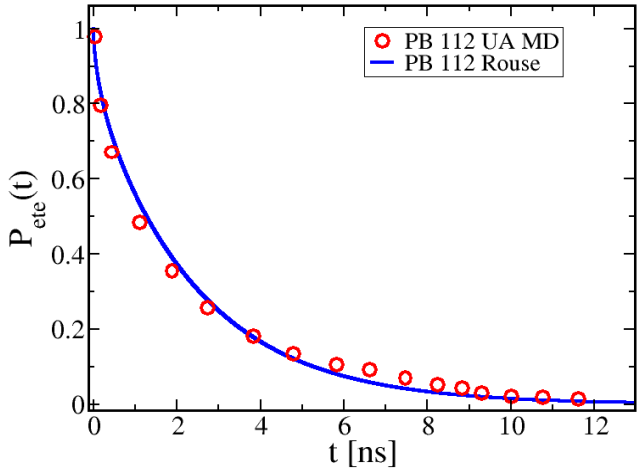


Comparison with experiments and predictions of new data

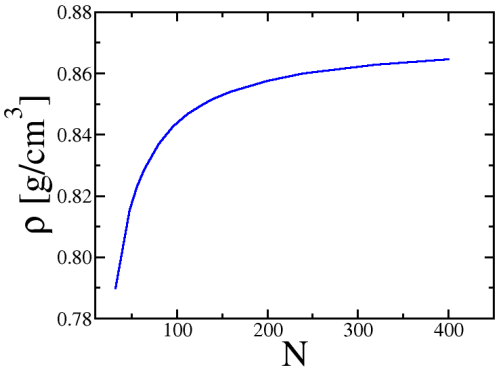


Data from: Seggern at al., 1991; Richter et al., 1993 Pearson et al., 1994; Zamponi et al., 2008.

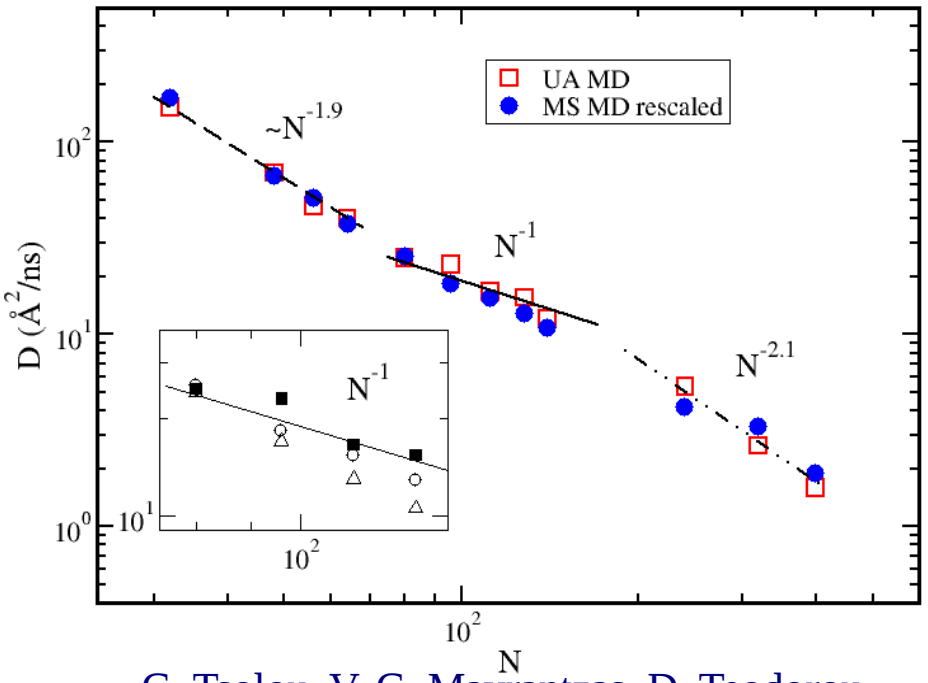
Comparison with simulations of a different polymer: PB
Simulation in the NPT ensemble



Decorrelation of the
end-to-end vector orientation



d = 1.468Å (PB 56)



G. Tsolou, V. G. Mavrantzas, D. Teodorou,
Macromol. **38**, 1478 (2005).

The procedure is general, transferable, and predictive (different molecules, density, temperature, molecular weighs).

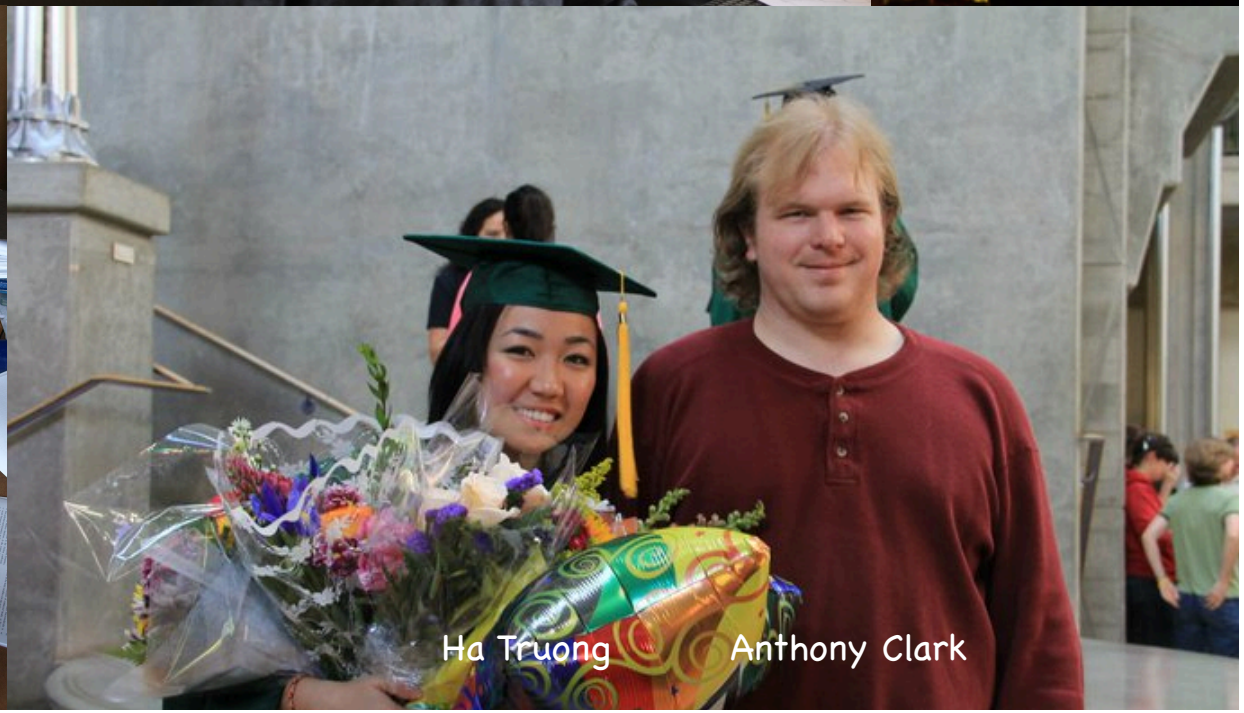
GUENZA'S LAB 2010-2012


Jeremy Copperman


Jay McCarty


Anthony Clark


Ivan Lyubimov


Ha Truong

Anthony Clark

CONCLUSIONS

Analytical h(r) from OZ Eq.

1) Structural consistency

2) Thermodynamic consistency

3) Transferable

4) Analytical rescaling of the dynamics

5) Insights on how to achieve thermodynamic consistency in numerical methods

THE END

by Jay