Dynamics of Ring-Linear Blends

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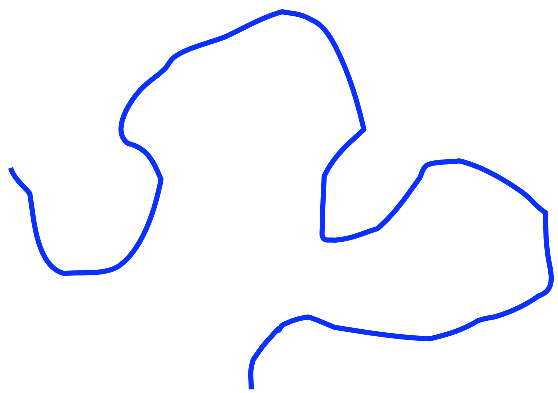
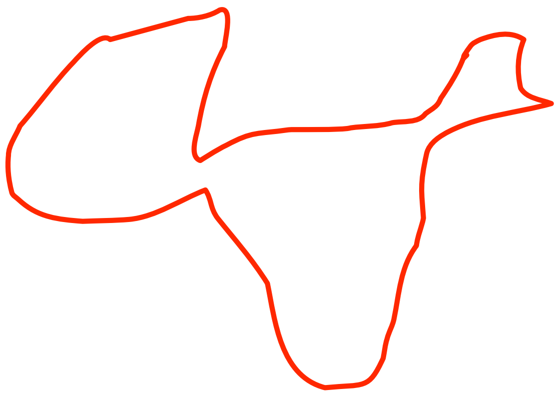
Linear and Ring Polymers



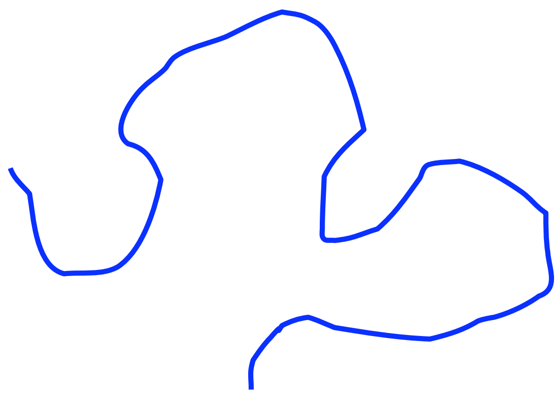
linear chain



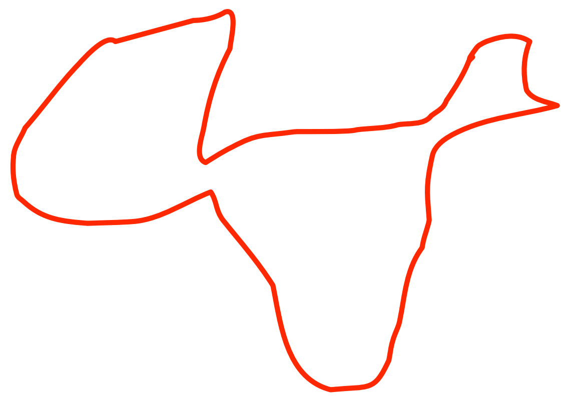
ring molecule

Ring (or cyclic) molecules do not have chain ends

Linear and Ring Polymers



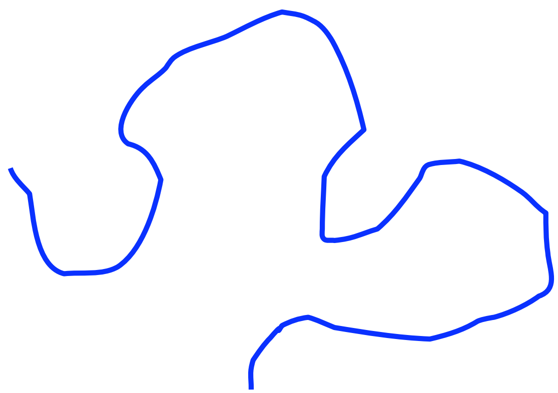
linear chain



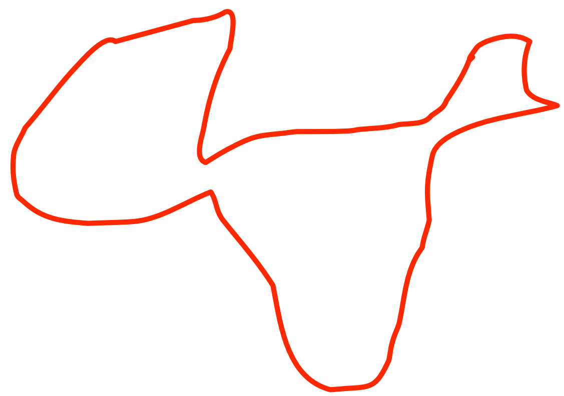
ring molecule

- *Rings are less viscous, diffuse faster*
- *Dynamics of rings are extremely sensitive to linear contaminants*
- *Older data: linear contamination, knotting, concatenation*

Linear and Ring Polymers



linear chain



ring molecule

- *Rings are less viscous, diffuse faster*
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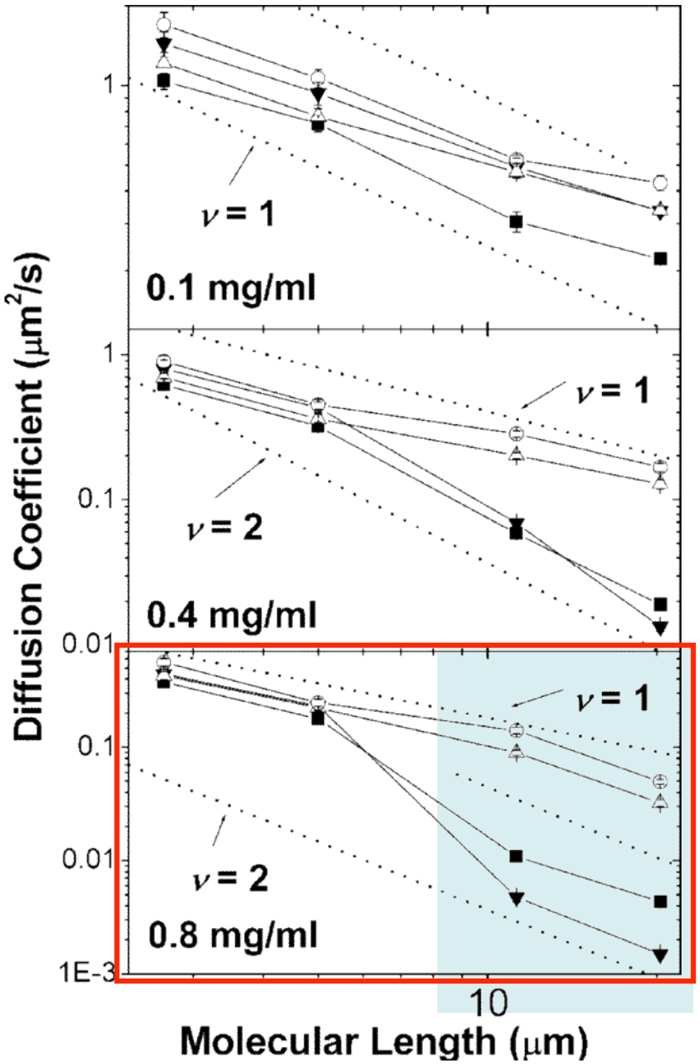
Rings behave differently

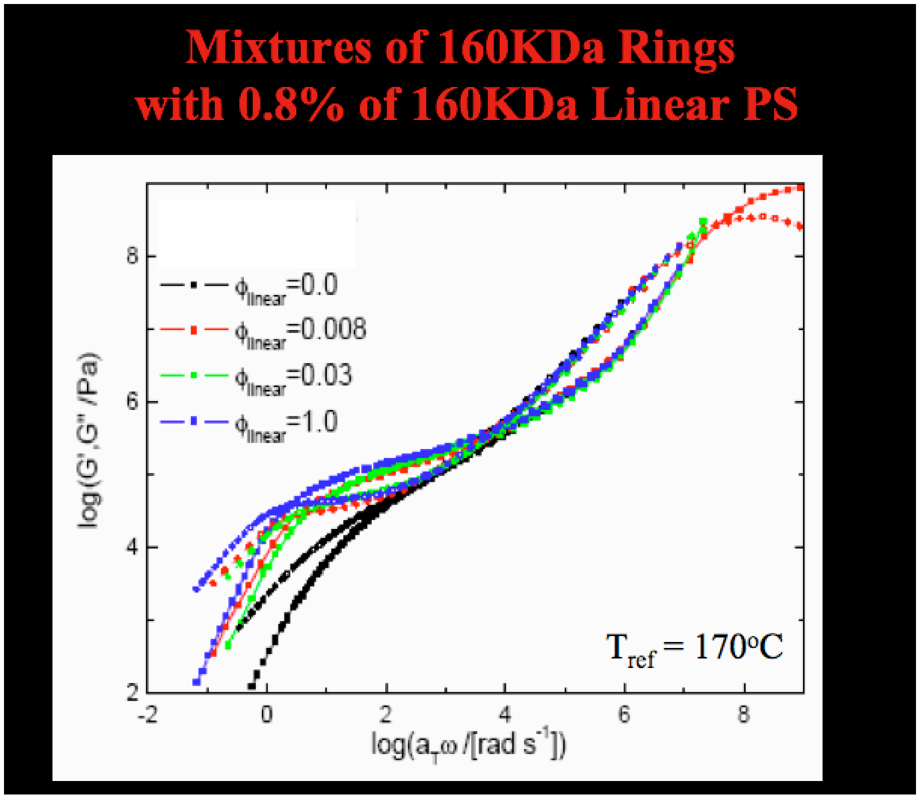


Robertson and Smith, Macromolecules, 2007

Measure self-diffusivity of tracer DNA (ring or linear) in a matrix (ring or linear)

From top to bottom R-**R**, L-**R**, L-**L** and R-**L**

Rings behave differently



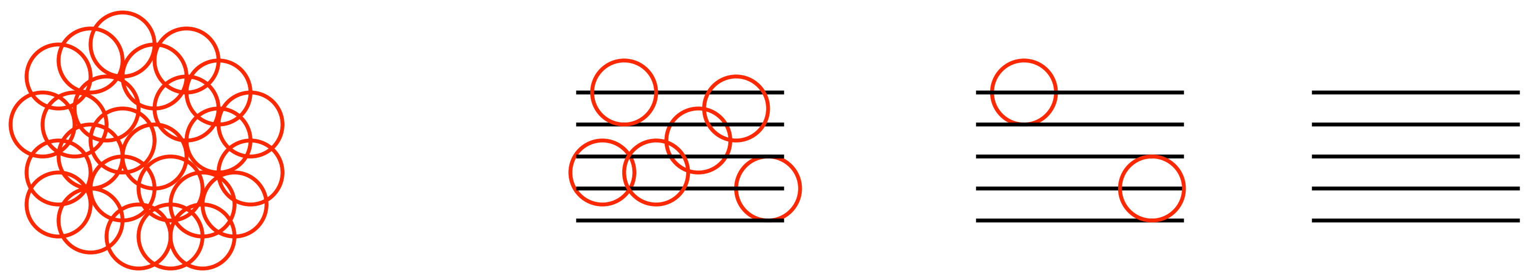
Kapnistos et al., SoR, 2006

1% linear fraction make the LVE response look like linear melt

McKenna and Plazek, 1986 had already reported this extreme sensitivity

Ring-Linear Blends

The idea is to use simulations to study the composition range between pure linear and pure ring polymers



pure ring melt *semidilute rings* *dilute rings* *pure linear melt*

Simulation System

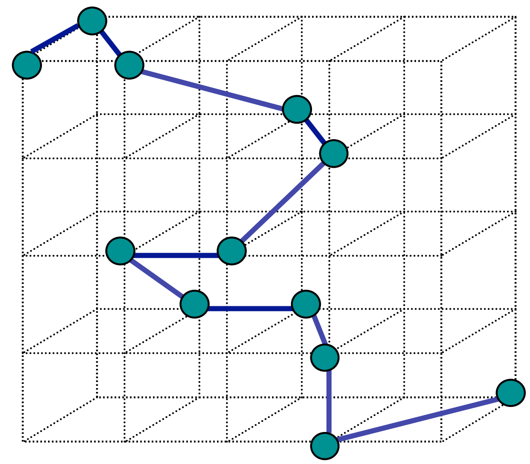
- Non-catenated rings melts are hard to simulate using MD
- With BFM, a brute force equilibration is feasible

Procedure

1. $N_C = N_L = 150$ and $N_C = N_L = 300$
2. $\phi = \phi_C + \phi_L = 0.5$
3. NVT Ensemble: constant density
4. Equilibrate, and do primitive path analysis, using annealing

Iyer et al., *Macromolecules,* **2007**
Geyler and Pakula, *Macromolecules,* **1988**,
Shanbhag and Larson, *PRL*, **2005**

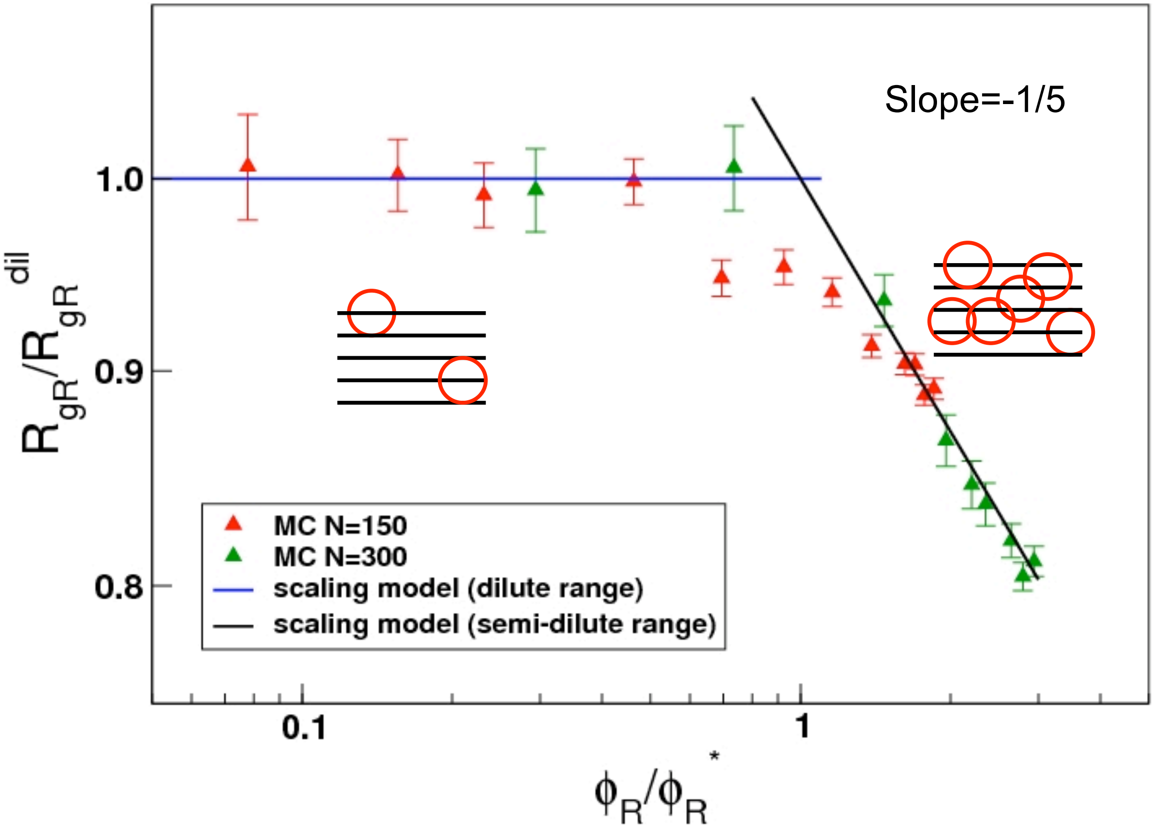
Bond Fluctuation Model



Efficient equilibration of chains

Shaffer, *J. Chem Phys.*, **1994**

Older Results: Size

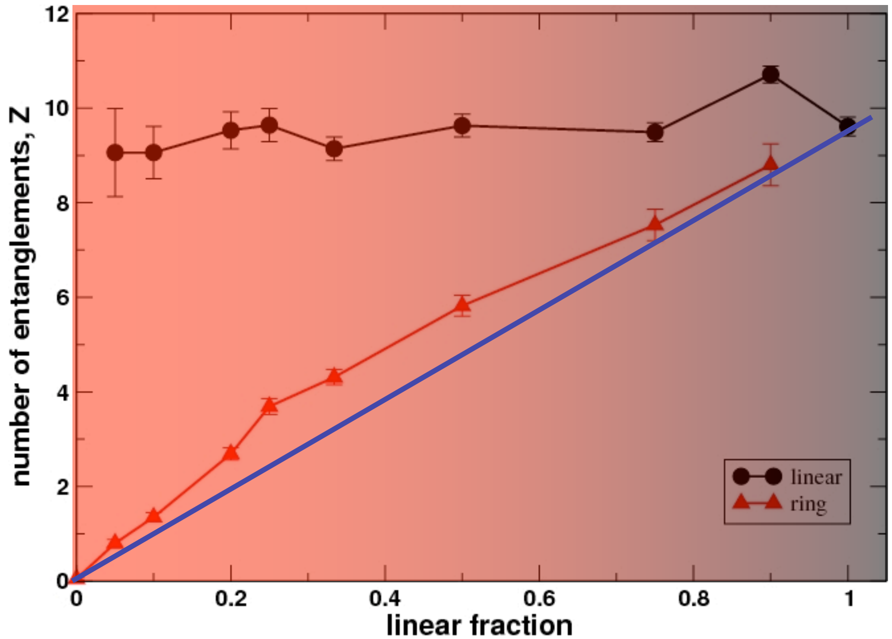


Iyer et al., *Macromolecules,* **2007**

Scaling model to describe the effect of concatenation.

- Rings shrink as the fraction of rings in a ring-linear blend increases
- Linears are insensitive to blend composition

Statics Results: Primitive Path Analysis



For, N = 300

* the linear chain is unaffected by ϕ_L

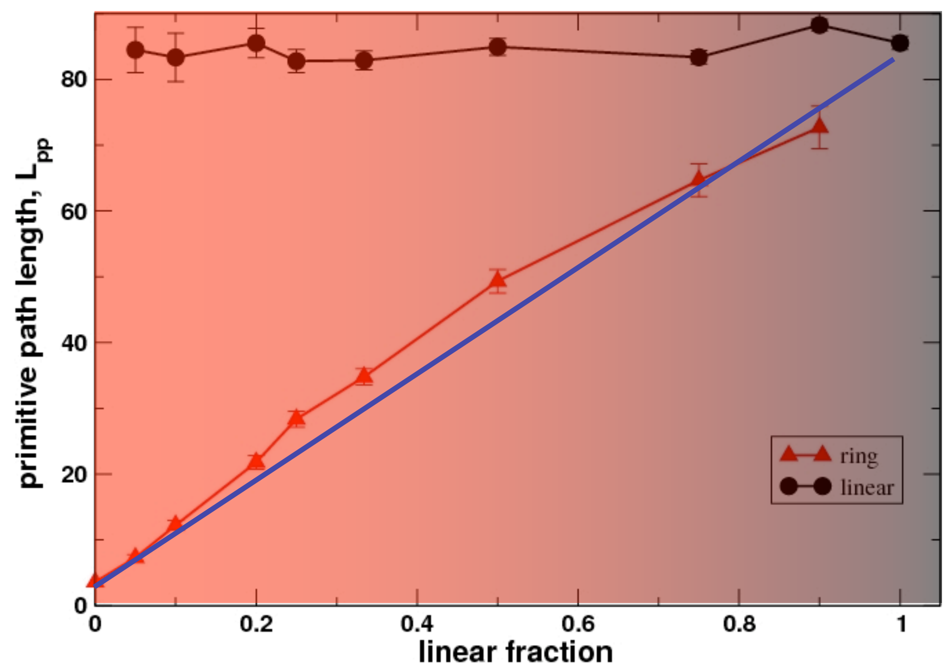
* a pure ring melt has no entanglements

* as the linear fraction increases, the number of entanglements increases

Increase is approximately linear:

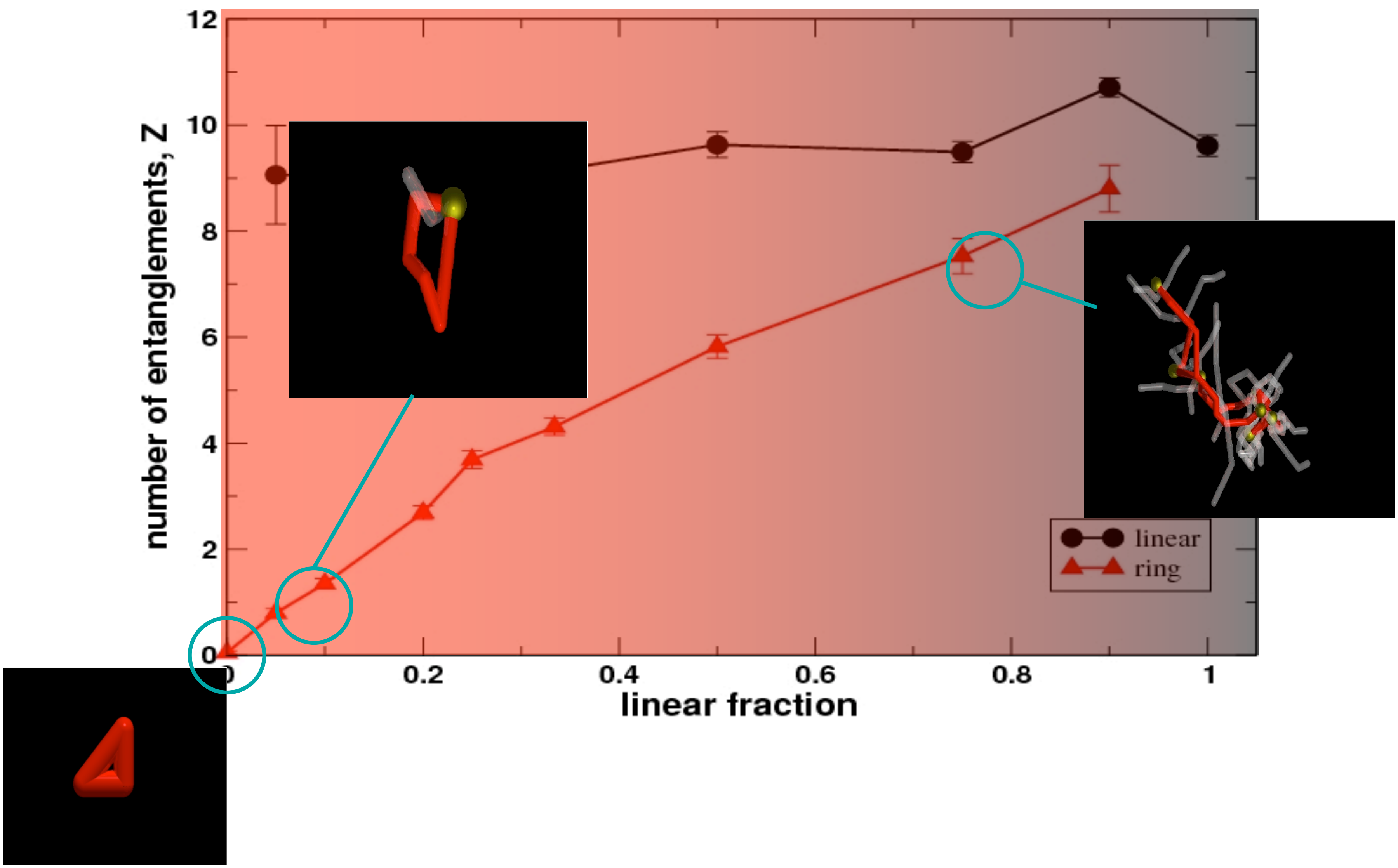
$$L_C(\phi_L) = L_L^*(\phi_L/\phi)$$

$$Z_C(\phi_L) = Z_L^*(\phi_L/\phi)$$



Subramanian and Shanbhag, *PRE*, **2008**

Statics Results

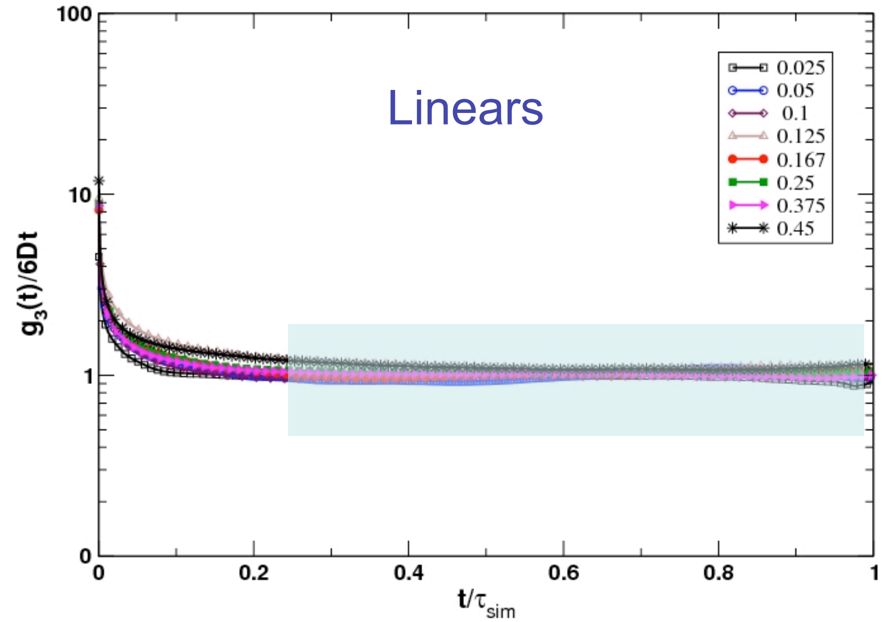


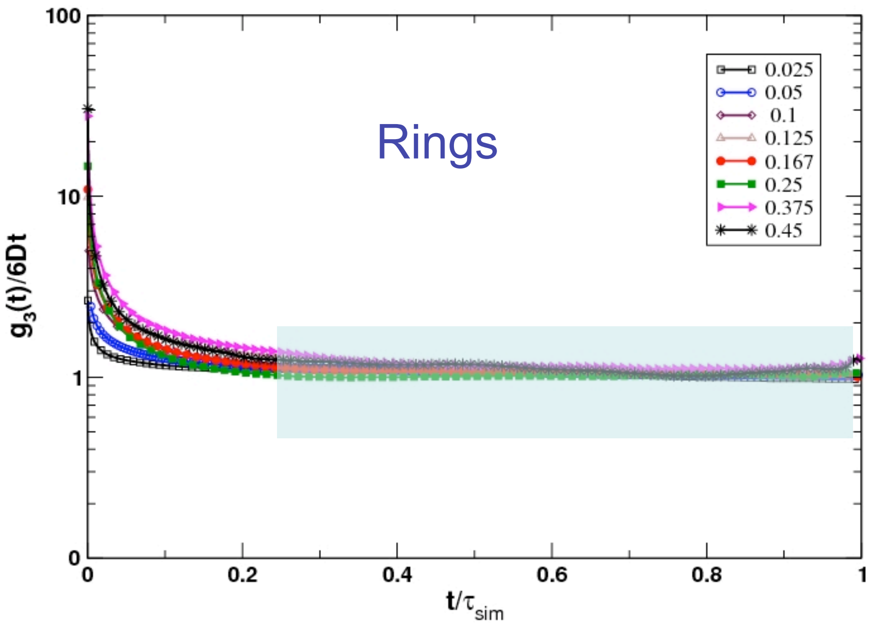
Dynamics Results

* N=300

* Monitor MSD of center of mass $g_3(t)/6t$ for flatness.

* Extract a diffusivity

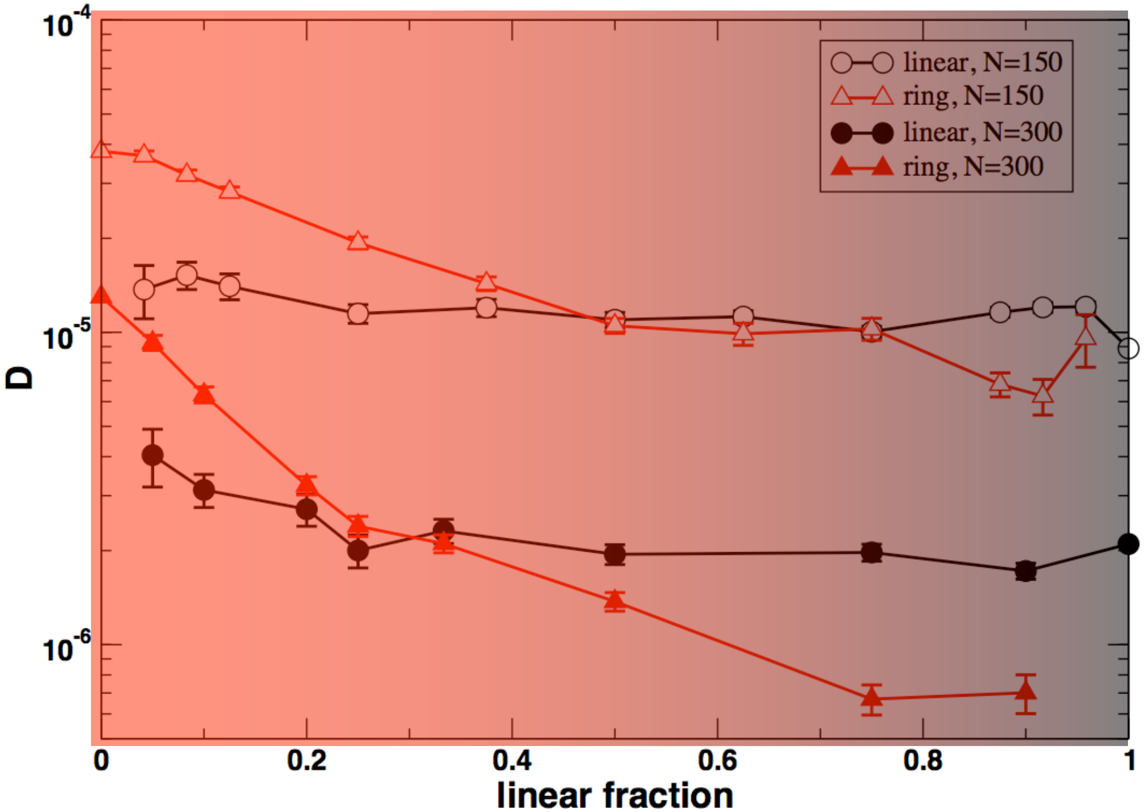




$$D = \lim_{t \to \infty} \frac{g_3(t)}{6t}$$

Subramanian and Shanbhag, *Macromolecules* **2008** (accepted)

Dynamics Results



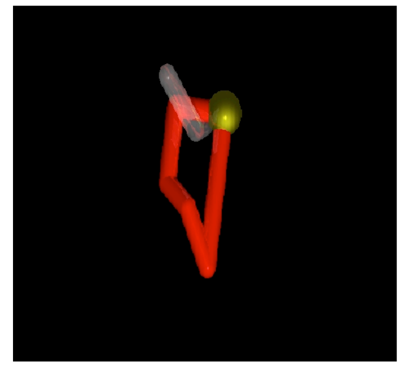
- as $\phi_L \uparrow$, D_C, $D_L \downarrow$
- $D_C \downarrow$ more steep
- qualitatively consistent with experimental data on entangled DNA solutions (1)
- PS rings-linear blends observe D_L is independent of ϕ_L (2)
- this picture reconciles the discrepancy between the two data-sets (if rings contaminated by linears)

1. Robertson and Smith, *Macromolecules*, **2007**.
2. Tead et al., *Macromolecules*, **1992**.

Interpreting the results: Minimal CR Model

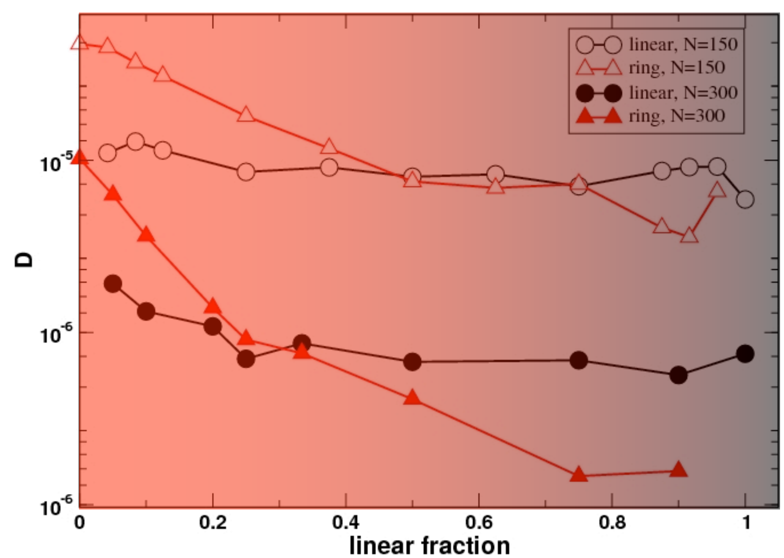
ring-linear blend

+

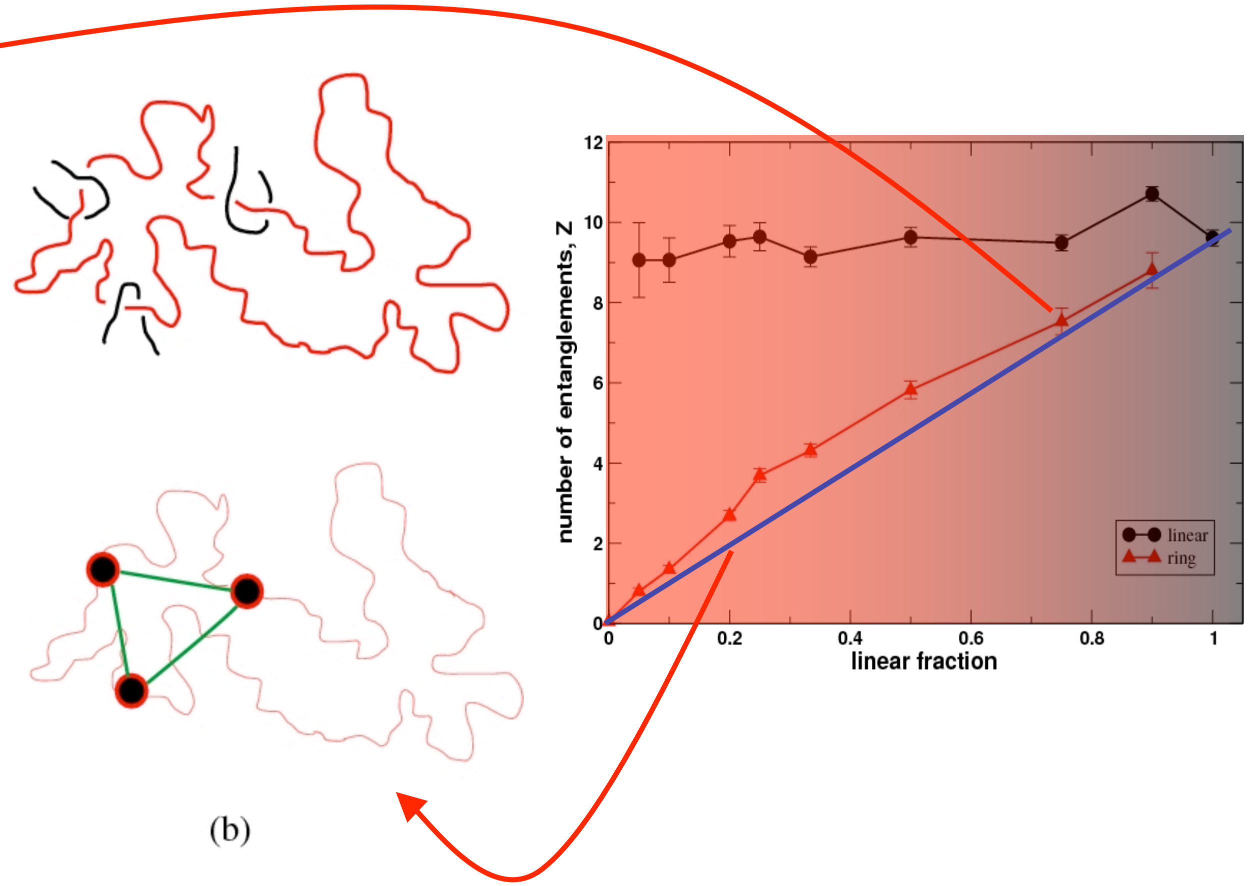


PPA: threading of rings by linears

+



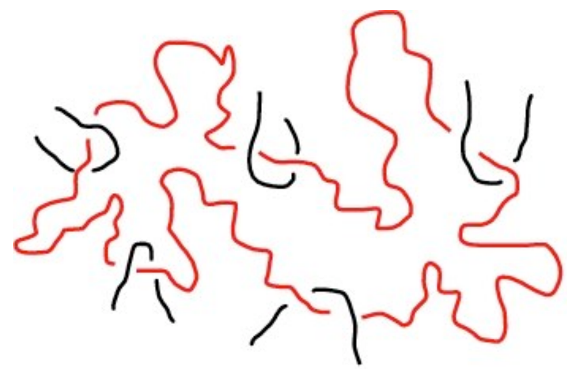
Review: Minimal CR Model



Low Linear fraction

Interpreting the results: Minimal CR Model

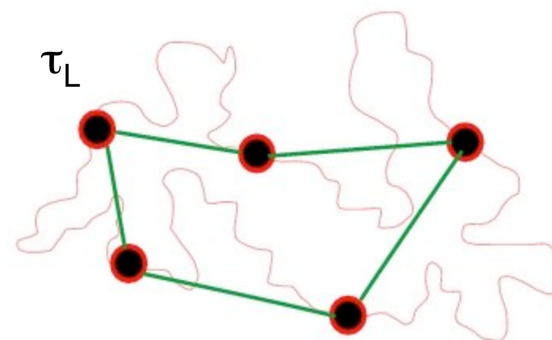
Linears pin down the cyclic polymer



Release and reform entanglements:
Constraint Release Rouse Process

Mean lifetime of the effective Rouse bead is the reptation time, which sets the “hopping” time for CRR.

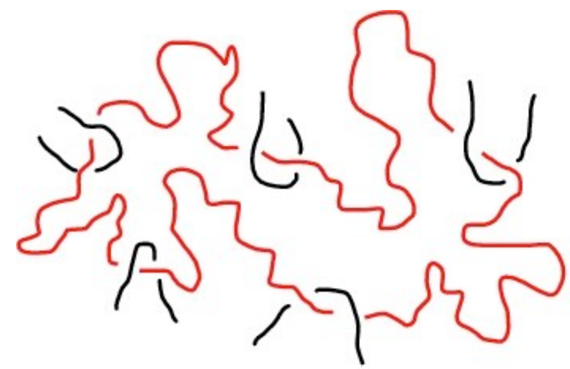
The diffusion of a ring in a blend is thus retarded by the linear constraints



$$\frac{1}{D_C(\phi_L)} = \frac{1}{D_C(\phi_L = 0)} + \frac{1}{D_{CR}(\phi_L)}$$

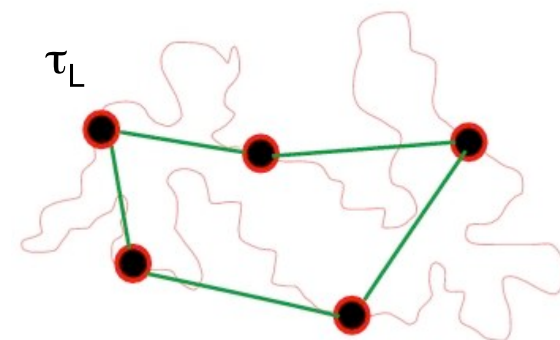
Interpreting the results: Minimal CR Model

A ring will diffuse (by CRR) only after the linear constraints have been renewed several times



$$\frac{1}{D_C(\phi_L)} = \frac{1}{D_C(\phi_L = 0)} + \frac{1}{D_{CR}(\phi_L)}$$

Very different from:



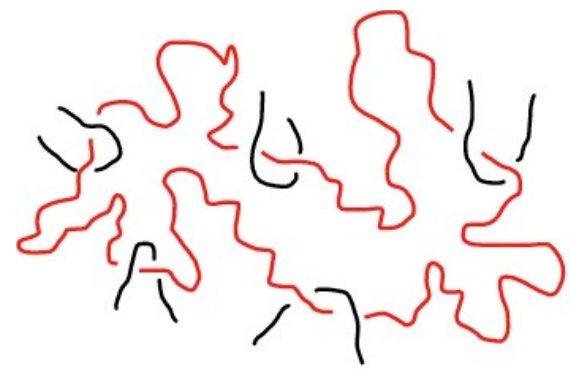
(a) CRR models for binary blends of linear molecules
Rubinstein and Colby, *Macromolecules*, **1988**

(b) Models for ring diffusion
Klein, *Macromolecules*, **1986**

FASTER PROCESS DETERMINES DYNAMICS

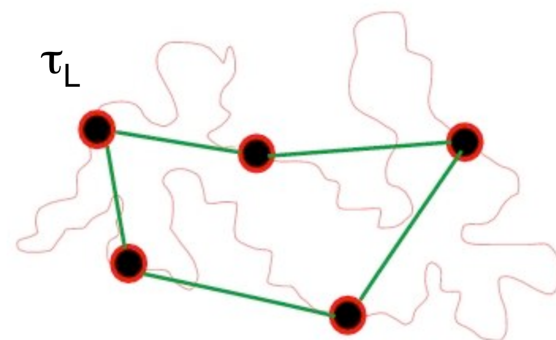
Interpreting the results: Minimal CR Model

$$\frac{1}{D_C(\phi_L)} = \frac{1}{D_C(\phi_L = 0)} + \frac{1}{D_{CR}(\phi_L)}$$



$$\tau_L(\phi_L) = \frac{R_L^{\,2}(\phi_L)}{D_L(\phi_L)};$$

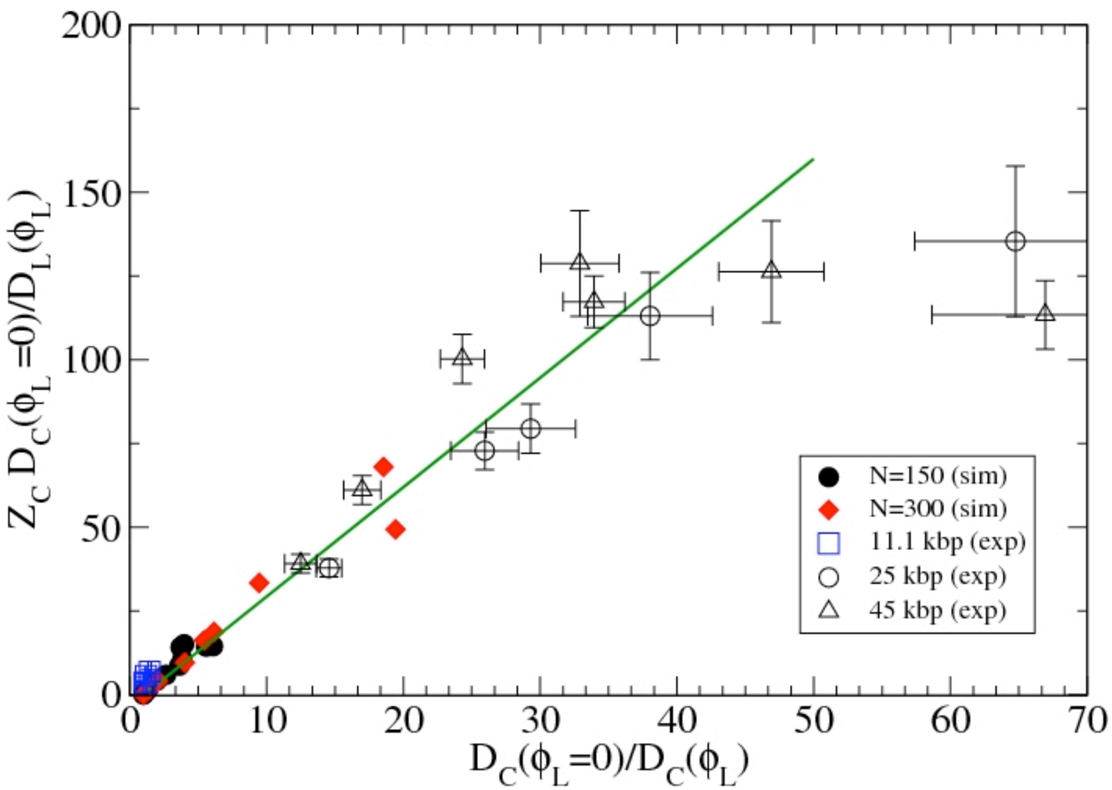
$$D_{CR}(\phi_L) = \frac{kT}{\zeta Z_C} \approx \frac{1}{\tau_L(\phi_L) Z_C(\phi_L)}$$



$$Z_C \frac{D_C(\phi_L = 0)}{D_L(\phi_L)} = c_1 \frac{D_C(\phi_L = 0)}{D_C(\phi_L)} + c_2$$

can be tested on our simulation data

All Together



a very broad range of:
1. MW
2. Blend Composition
3. Concentration

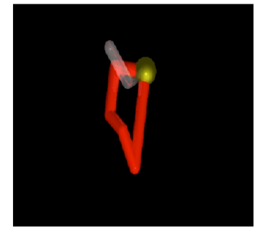
Entangled DNA (Robertson and Smith, 2007)

* Tracer Ring in Linears
* $Z_C = Z_L = (l/l_0)(c/c_0)^{4/3}$
* l_0=3 kbp when c_0=1 mg/ml

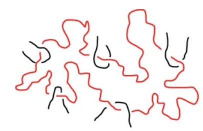
$$Z_C \frac{D_C(\phi_L = 0)}{D_L(\phi_L)} = c_1 \frac{D_C(\phi_L = 0)}{D_C(\phi_L)} + c_2$$

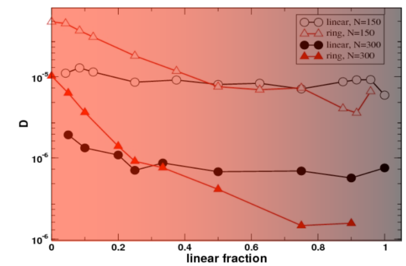
Summary

1. Primitive path analysis: extent threading of rings by linears

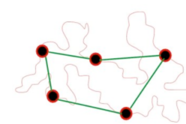


2. Self-diffusion coefficients: how dynamics are influenced by linears

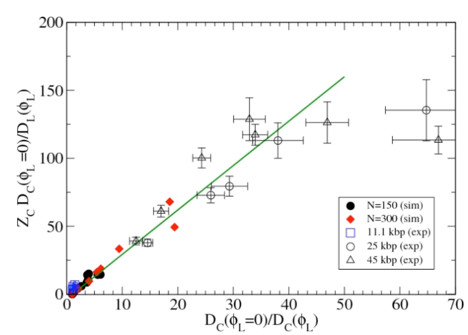




3. Minimal CRR model to put (1) and (2) together



4. The CRR model appears to unify simulation and experimental data over a wide range of MWs, concentrations, and blend compositions.



5. Ring-linear blends may be model systems to learn about constraint release!

Acknowledgements

- Petroleum Research Fund (ing)
- Rae Robertson and Doug Smith (experimental data)
- Richard Graham and Jorge Ramirez (CRR model)
- Ashish Lele and Balaji Iyer
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