Nonlinear Langevin equation (NLE) theory and its application to colloidal polymer glass

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From supercooled liquids to glasses: Current challenges for amorphous materials, KITS 2017

Outline

- Background
- The basics of the NLE theory
- The unique role of bond length in colloidal polymer glass
- Outlook

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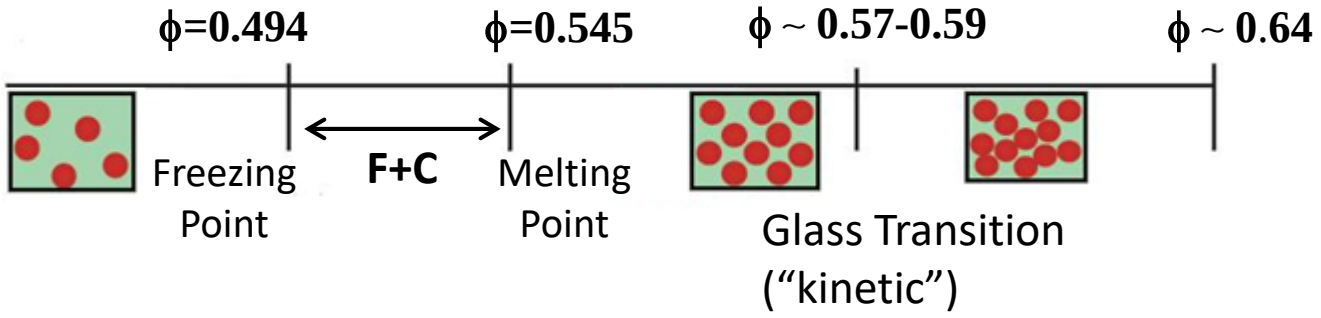
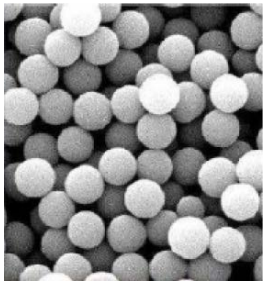
Glass transition

Colloid: athermal





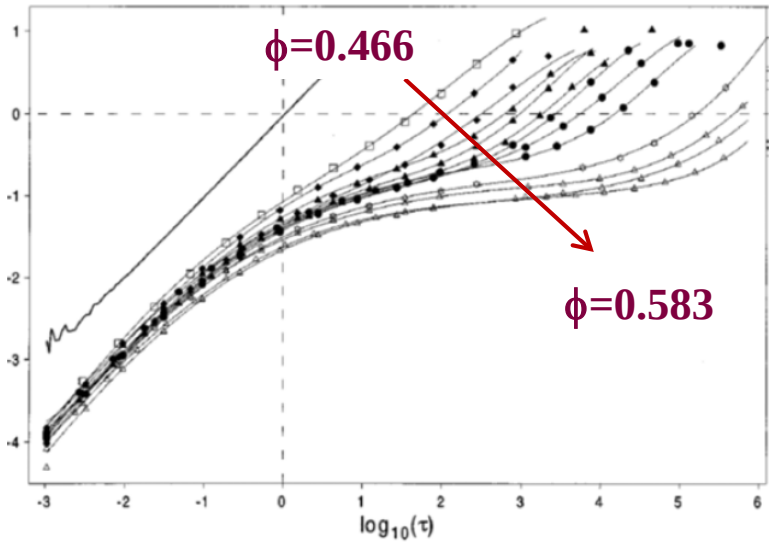
$\sigma \sim$ **100nm-2μm**

Typical Brownian time: $\tau_0 = \sigma^2 / D_0 \sim 0.01 - 30$ sec.

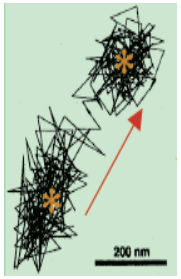
Kinetical vitrification: experimental patience

$\eta \sim 10^{12}\ Pa \cdot s$ or $\tau_\alpha \sim 100 - 10000$ sec.

MSD



Microscopy or Simulation:



Low ϕ

Hydrodynamic like smooth motion

High ϕ

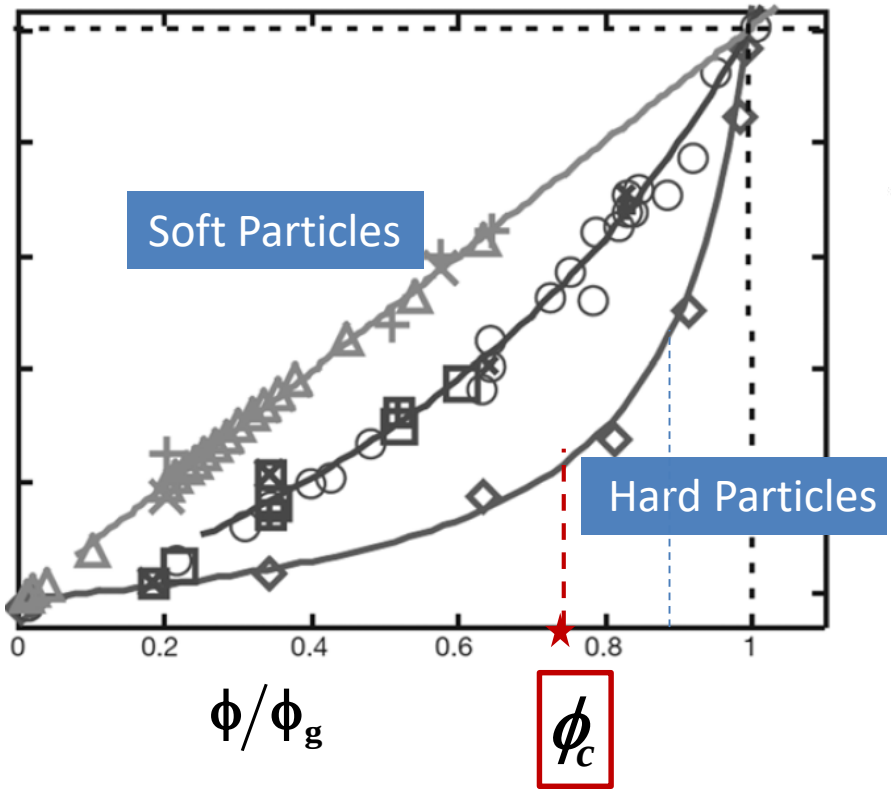
solid like intermittent hopping

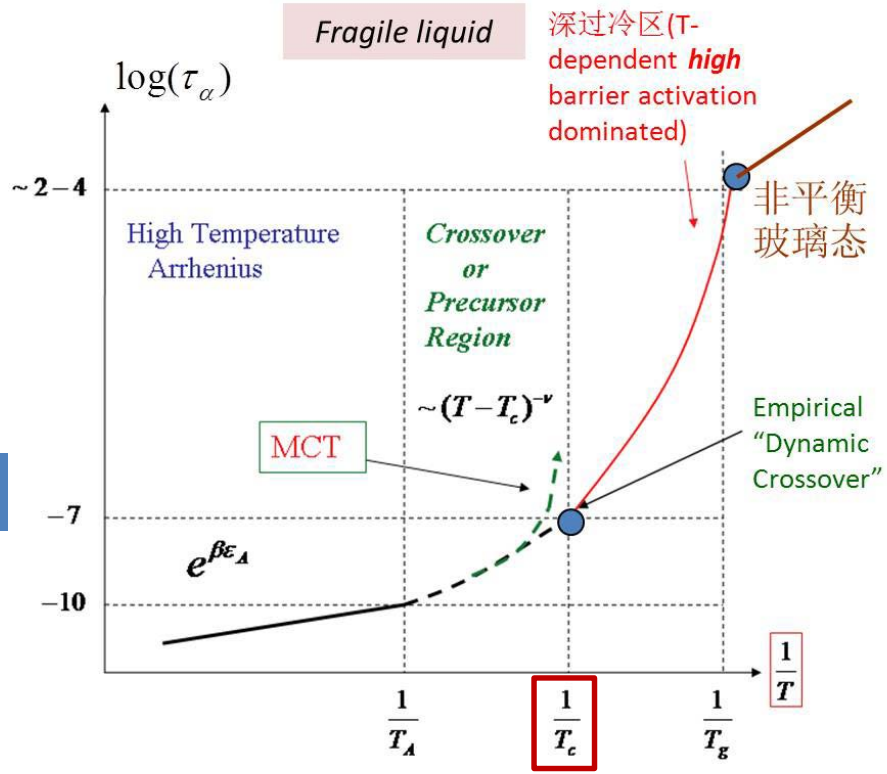
Glass transition

Colloid: athermal

Relaxation time

Polymer: thermal





Naïve: $\phi_c = 0.432$

Full: $\phi_c = 0.52$

Polymer: T_c T_g

Colloid: ϕ_c ϕ_g

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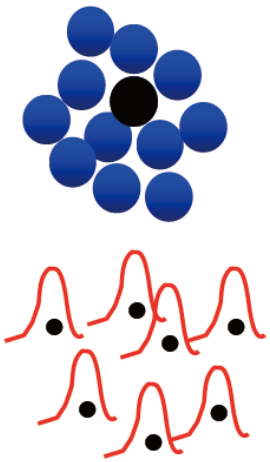
NLE theory for colloidal glass



Locally solid picture

Motion of a single particle: r(t)--scalar

DDFT, Local Equilibrium Approximation, Vineyard Closure

$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{dyn}\left[r(t)\right] + \eta(t)$$

K.S. Schweizer J. Chem. Phys. (2005)

short time friction — white noise

$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{dyn}\left[r(t)\right]$$

$$0 = -\frac{\partial}{\partial r} F_{dyn}\left[r(t)\right]$$

$$\alpha \equiv 3/2 r_{\mathrm{loc}}^2$$

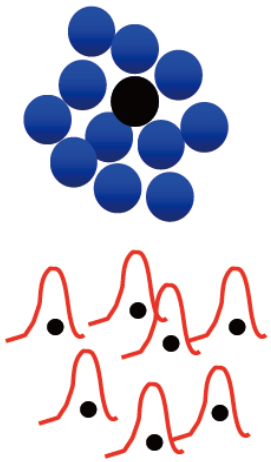
$$\alpha = \frac{1}{2}\beta K(t \to \infty)$$

$$= \frac{1}{6}\int \frac{d\mathbf{q}}{(2\pi)^3} \rho q^2 C^2(q) S(q) e^{-q^2/4\alpha(1+S^{-1}(q))}$$

Naive MCT

Kirkpatrick & Wolynes, 1987

NLE theory for colloidal glass



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$$F_{dyn}(r) = -3k_BT\ln(r) - k_BT\int \frac{d\vec{q}}{(2\pi)^3}\rho C^2(q)S(q)\left[1+S^{-1}(q)\right]^{-1} e^{-q^2r^2\left[1+S^{-1}(q)\right]/6}$$

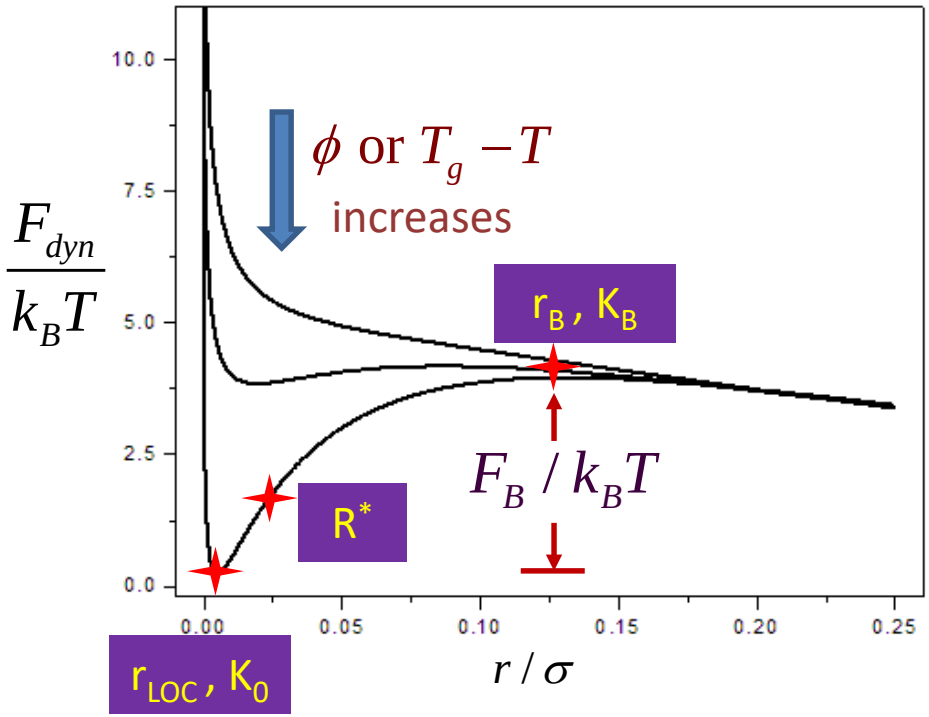
translational entropy favors fluid

Inter-particle interactions (caging effect) localized solid

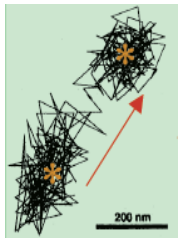
S(q): Static Structure Factor

C(q): Direct Correlation Function

Dynamic free energy



- Crossover: ϕ_c



Localized, activated hopping dynamics

- Characteristic lengths: r_{LOC}, R^*, r_B

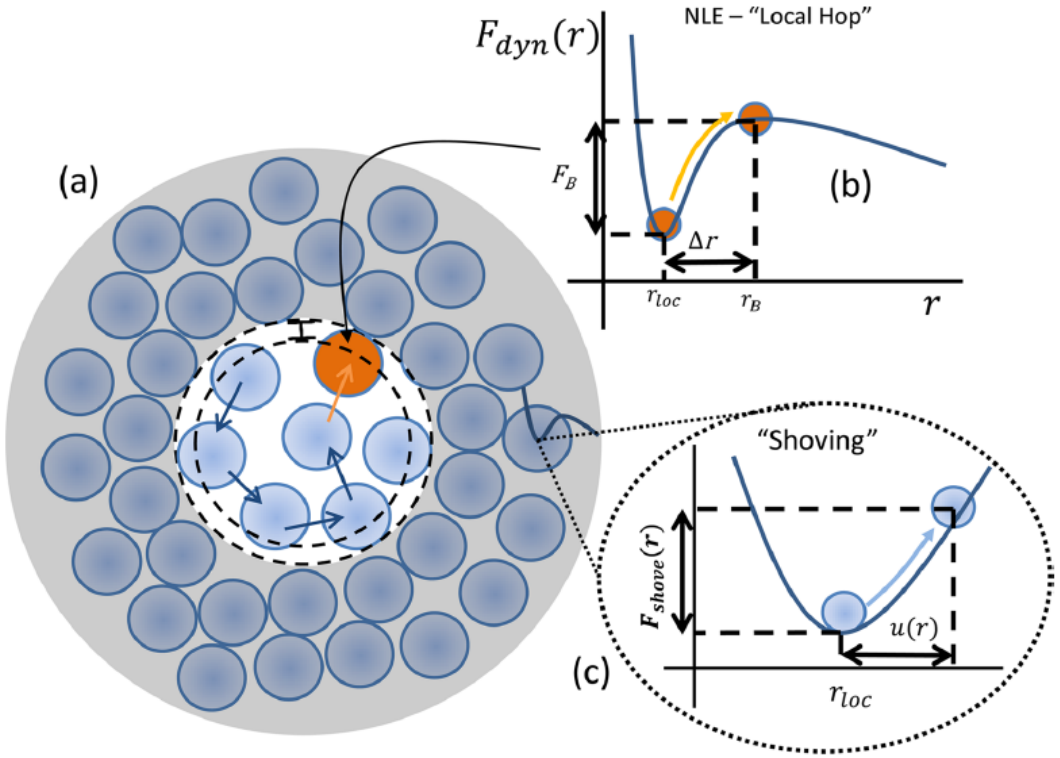
The "confined" space of the particle's motion– "cage size"

Related to the Lindemann length at the crossover

- Barrier and the relaxation time: F_B, τ_α

Structural relaxation ⟺ Escaping the cage ⟺ Activated barrier hopping

Barrier



$$F_B$$

Shoving model: $F_e = G'V_c$

$$F_e = 4\pi\rho\int_{r_{cage}}^{\infty} dr\; r^2 g(r)\left[\frac{1}{2}\frac{\partial^2 F_{dyn}(r)}{\partial r^2}\bigg|_{r_{loc}} u^2(r)\right]$$

$$\approx 12\phi\Delta r_{eff}^2\left(r_{cage}/\sigma\right)^3 K_0$$

$$r_{cage} \approx 1.5\sigma \qquad \xi_s \equiv (6V_c/\pi)^{1/3} \approx 0.3\sigma$$

$$F_{tot} = F_B + F_e$$

Mirigian and Schweizer JPCL 2013

Relaxation time

$$F_{tot} = F_B + F_e$$

Kramers first-passage theory:

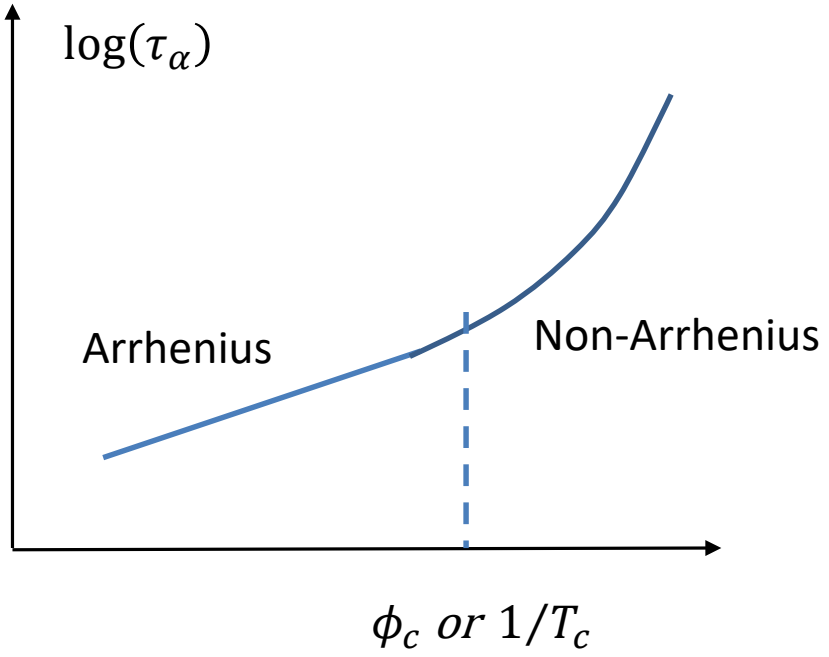
$$\tau_\alpha = \tau(\phi)\exp(F_{tot}/k_B T)$$

For hard-sphere

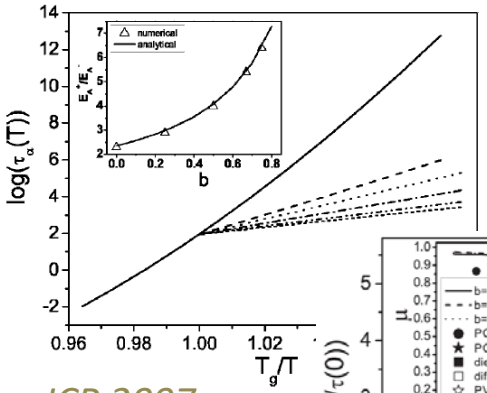
$$\frac{\tau(\phi)}{\tau_0} = \frac{2\pi g(\sigma) k_B T}{\sigma^2 \sqrt{K_0 K_B}}$$

$$\tau_0 = \sigma^2 \zeta_0 / k_B T$$

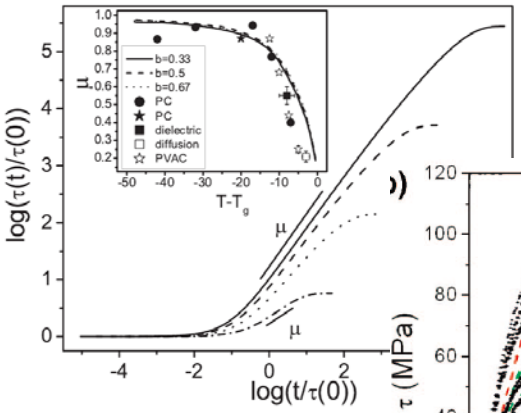
$\tau(\phi)$ is a weak function of volume fraction



Applications of the NLE theory



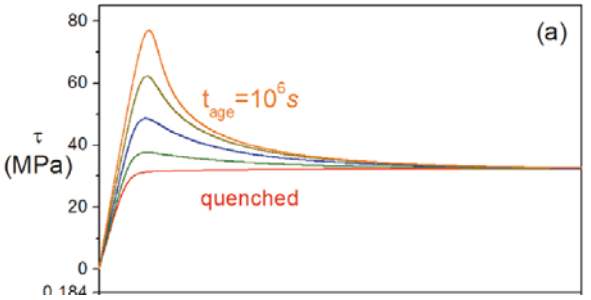
Relaxation & elasticity



Aging

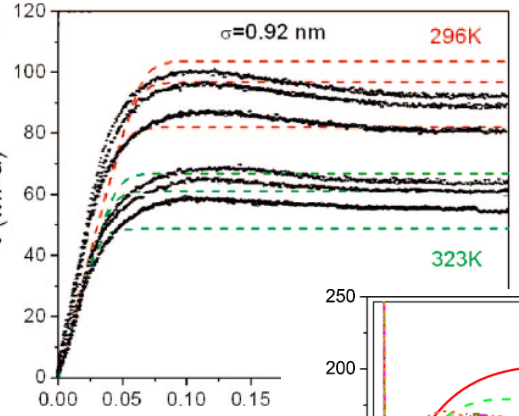
JCP 2007

PRL 2007



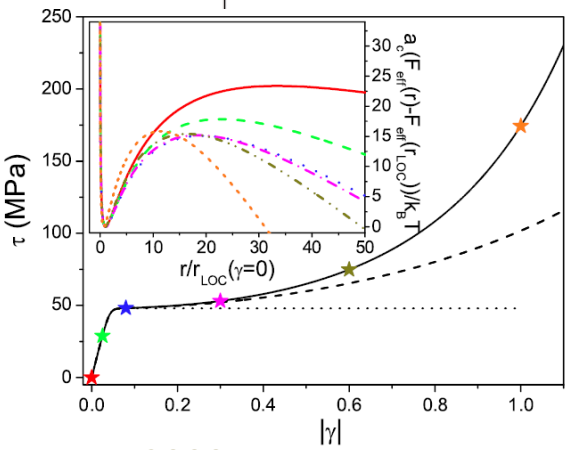
Rejuvenation & strain softening

Macromolecules 2011



Mechanical response

Macromolecules 2008



Strain hardening

PRL 2009

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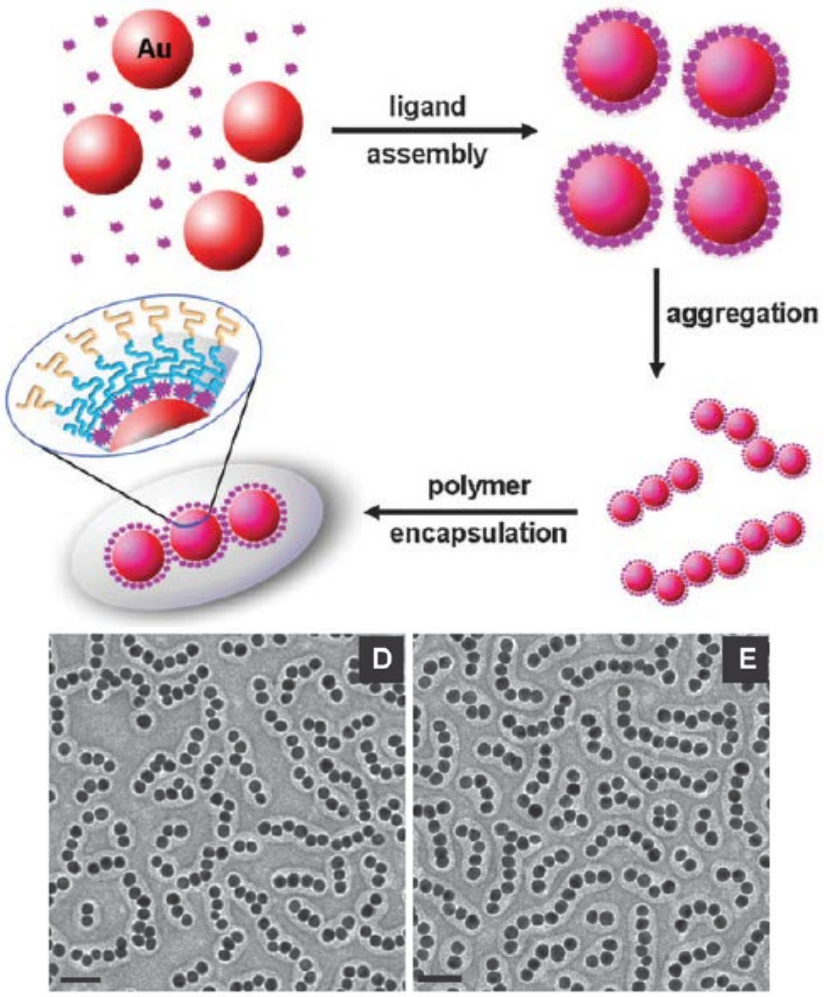
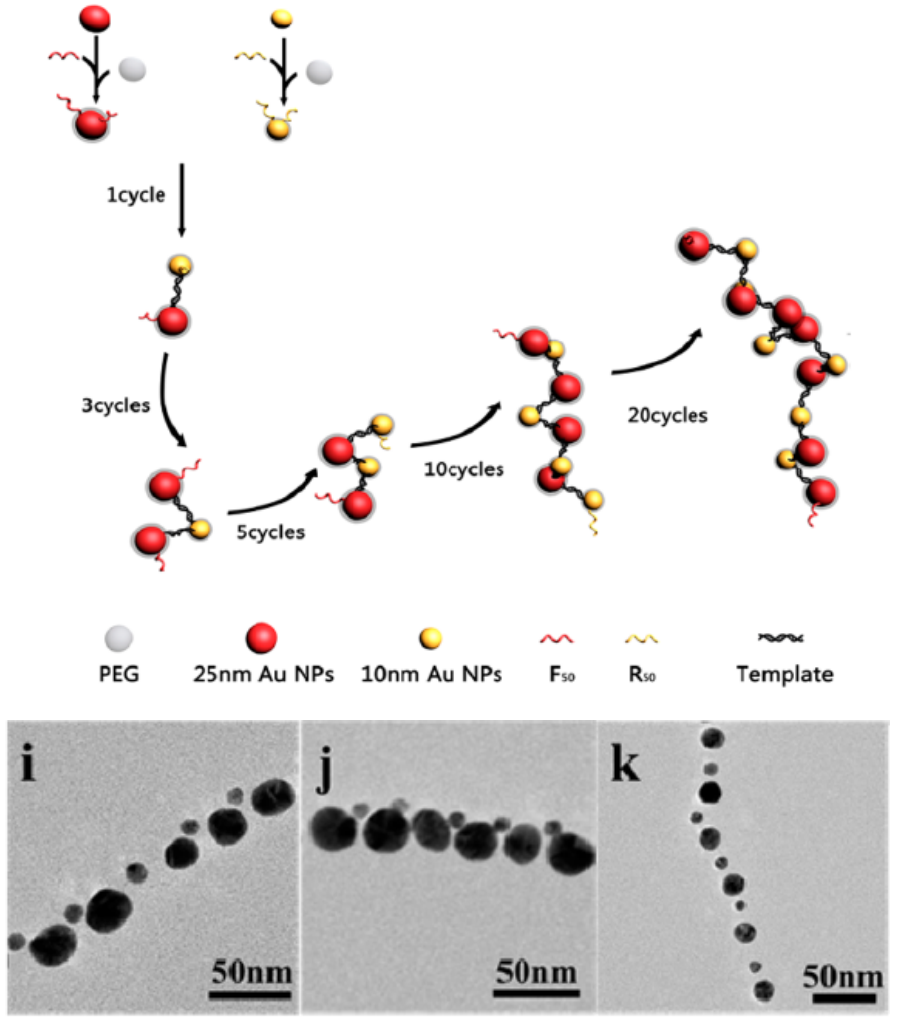
Colloidal polymers



Yang et al., Phys. Chem. Chem. Phys. 2010

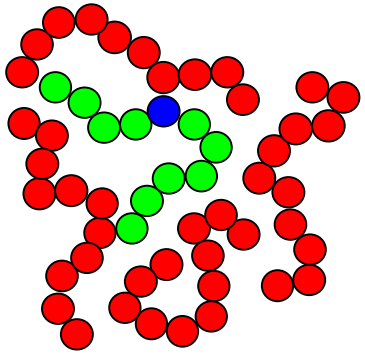


Zhao et al., J. Phys. Chem. Lett. 2013

Motivation

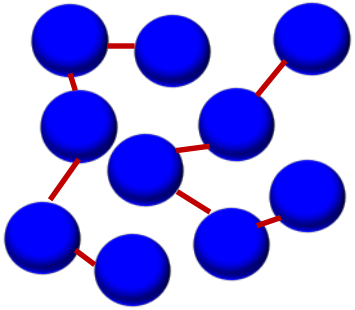
Features of molecular polymer

- Bond length is not a controllable variable
- Ambiguity of the basic unit



Colloidal polymer as a model system

- Unambiguity of the basic unit
- Flexibility in tuning the architecture, especially the bond length



Current theoretical and simulation research

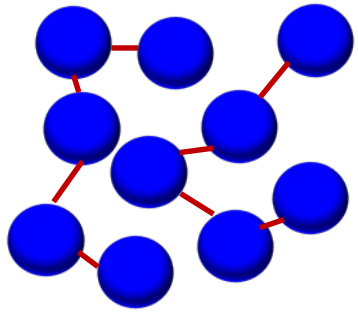
- Based on Gaussian or bead-spring chain
- Focus on the influence of chain length and rigidity

NLE theory for chain molecules

$$F_{dyn}(r) = -3k_BT\ln(r) - k_BT\int \frac{d\vec{q}}{(2\pi)^3}\rho C^2(q)S(q)\left[1+S^{-1}(q)\right]^{-1} e^{-q^2r^2\left[1+S^{-1}(q)\right]/6}$$

$$F_{dyn} = -3k_BT\ln(\mathrm{r}) - k_BT\int \frac{d\vec{q}}{(2\pi)^3}[C^2(\mathrm{q})\rho\,\mathrm{S}(\mathrm{q})\omega(\mathrm{q}) + \mathrm{C}_{\mathrm{intra}}(\mathrm{q})(\omega-1)]$$
$$\times[1+S^{-1}(\mathrm{q})]^{-1}\,\mathrm{e}^{-q^2r^2[1+\mathrm{S}^{-1}(\mathrm{q})]/6}$$

$$\boldsymbol{\omega(\mathbf{q}) = \frac{1}{1-\rho\mathbf{C}_{\mathbf{intra}}(\mathbf{q})}}$$

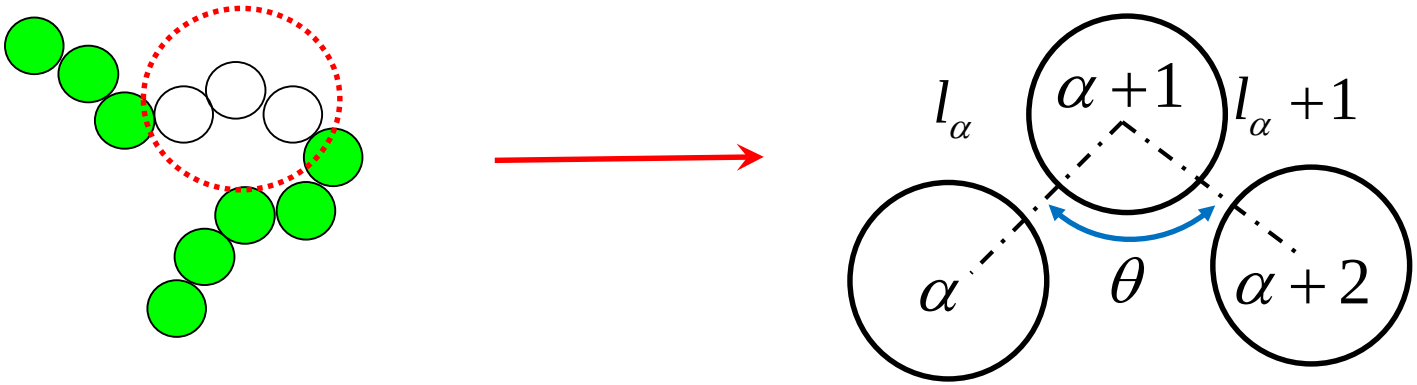


$$h(q) = \omega(q)C(q)[\omega(q)+\rho h(q)] \qquad S(q) = \omega(q)+\rho h(q)$$

Intramolecular correlation function

Koyama distribution for worm-like chain

l : bond length ε : rigidity N: chain length



$$\omega_{ab}(\mathrm{r}) = \frac{1}{8\pi^{3/2}ABr}\left[e^{-(\mathrm{r}-\mathrm{B})^2/4\mathrm{A}^2} - e^{-(\mathrm{r}+\mathrm{B})^2/4A^2}\right]$$

$$A^2 = \left\langle r_{ab}{}^2 \right\rangle (1-\mathrm{C})/6 \;,\quad B^2 = C\left\langle r_{ab}{}^2 \right\rangle \;,\quad C^2 = \frac{1}{2}\left(5 - 3\frac{\left\langle r_{ab}{}^4 \right\rangle}{\left\langle r_{ab}{}^2 \right\rangle^2}\right)$$

Macromolecules 1990,23, 3496-3505

Intramolecular correlation function

$$\left\langle r_{ab}^2 \right\rangle = |a-b| l^2 \left[\frac{1-\langle \cos\theta \rangle}{1+\langle \cos\theta \rangle} + \frac{2\langle \cos\theta \rangle}{n} \cdot \frac{1-(-\langle \cos\theta \rangle)^{|a-b|}}{(1+\langle \cos\theta \rangle)^2} \right]$$

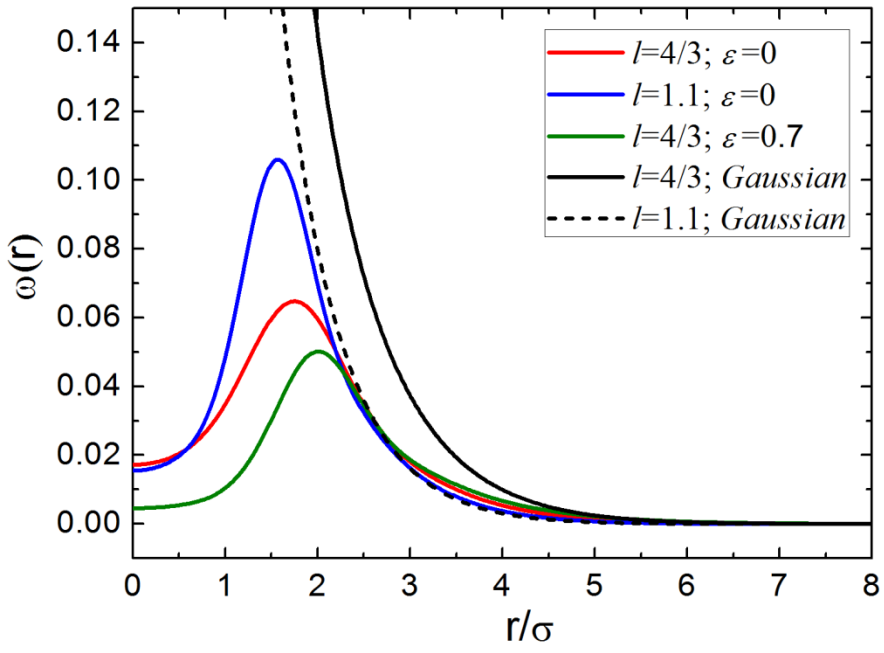
$$\left\langle r_{ab}^4 \right\rangle = \left\langle r_{ab}^2 \right\rangle^2 + D_{ab} l^4 \qquad D_{ab} \longrightarrow D_{ab}(<\cos\theta>, <\cos^2\theta>)$$

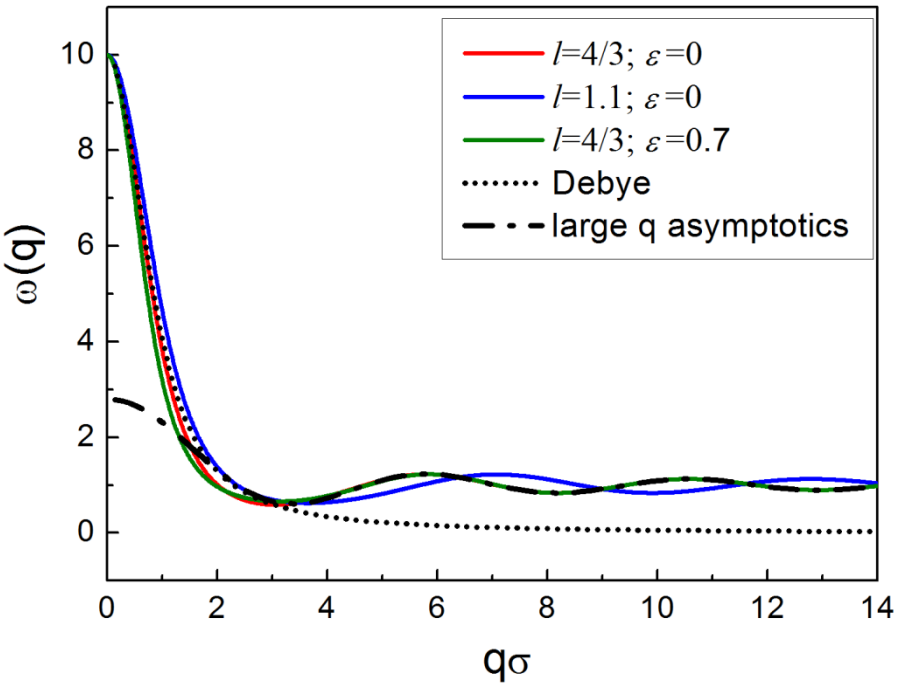
$$\langle \cos\theta \rangle = \frac{\int_{\theta_0}^{\pi} e^{-\varepsilon(1+\cos\theta)} \cos\theta \sin\theta d\theta}{\int_{\theta_0}^{\pi} e^{-\varepsilon(1+\cos\theta)} \sin\theta d\theta} = \frac{1}{\varepsilon} - \frac{e^{\varepsilon} + \cos\theta_0 e^{-\varepsilon\cos\theta_0}}{e^{\varepsilon} - e^{-\varepsilon\cos\theta_0}}$$

$$\langle \cos^2\theta \rangle = \frac{2}{\varepsilon} \langle \cos\theta \rangle + \frac{e^{\varepsilon} - \cos^2\theta_0 e^{-\varepsilon\cos\theta_0}}{e^{\varepsilon} - e^{-\varepsilon\cos\theta_0}}$$

Intramolecular correlation function

N=10





- Partial exclusion between beads
- Exclusion is better satisfied for rigid chains
- Asymptotics between colloidal and Gaussian chain of short bond length

- Debye function

$$\omega(q) = Nf(q^2R_g^2) \quad f(x) = \frac{2}{x^2}(e^{-x} - 1 + x)$$

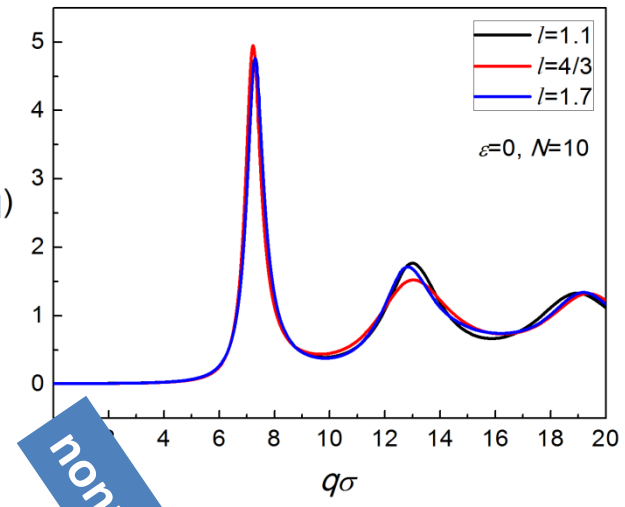
- Large q asymptotics

$$1 + 2(N-1)\sin(ql)/Nql$$

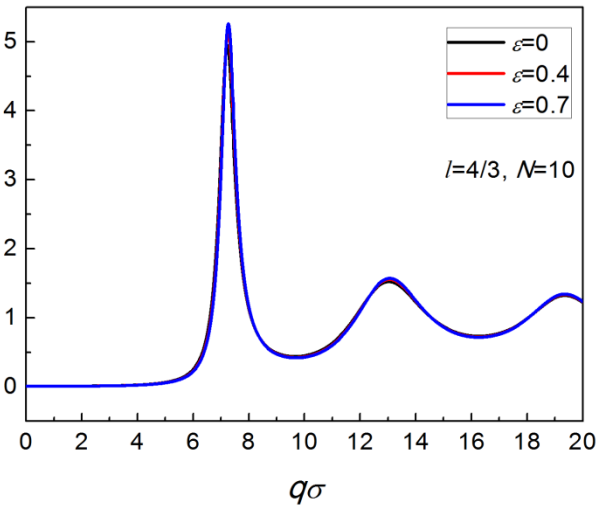
Structure factor

$\phi = 0.57$

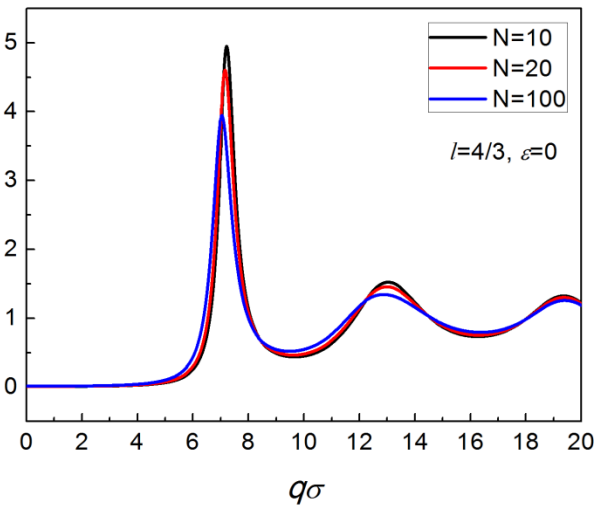
Bond length: *l*



Rigidity: ε



Chain length: N



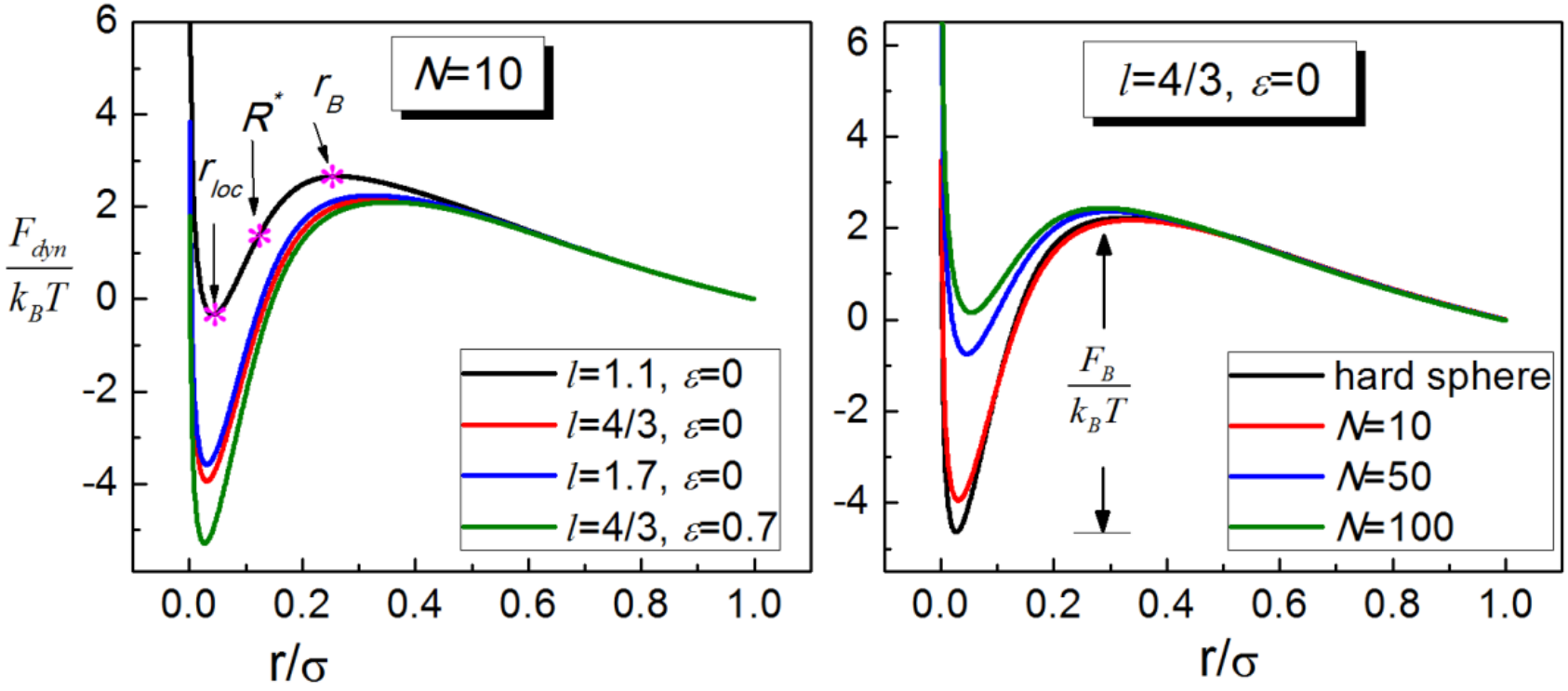
nonmonotonicity

Table I. Values of structure factor at the long-wave-length limit and the first peak. The numbers are corresponding to Fig. 1(c)-(e).

	$\varepsilon = 0, N = 10$			$l = 4/3, N = 10$		$l = 4/3, \varepsilon = 0$	
	$l = 1.1$	$l = 4/3$	$l = 1.7$	$\varepsilon = 0.4$	$\varepsilon = 0.7$	$N = 20$	$N = 100$
S(q=0)	0.00912	0.00806	0.00845	0.00755	0.00733	0.00912	0.012
S(q^*)	4.74	4.95	4.76	5.16	5.26	4.60	3.95

Dynamic free energy

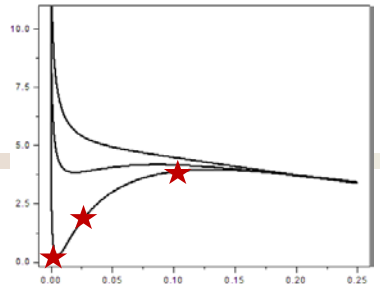
$\phi = 0.55$

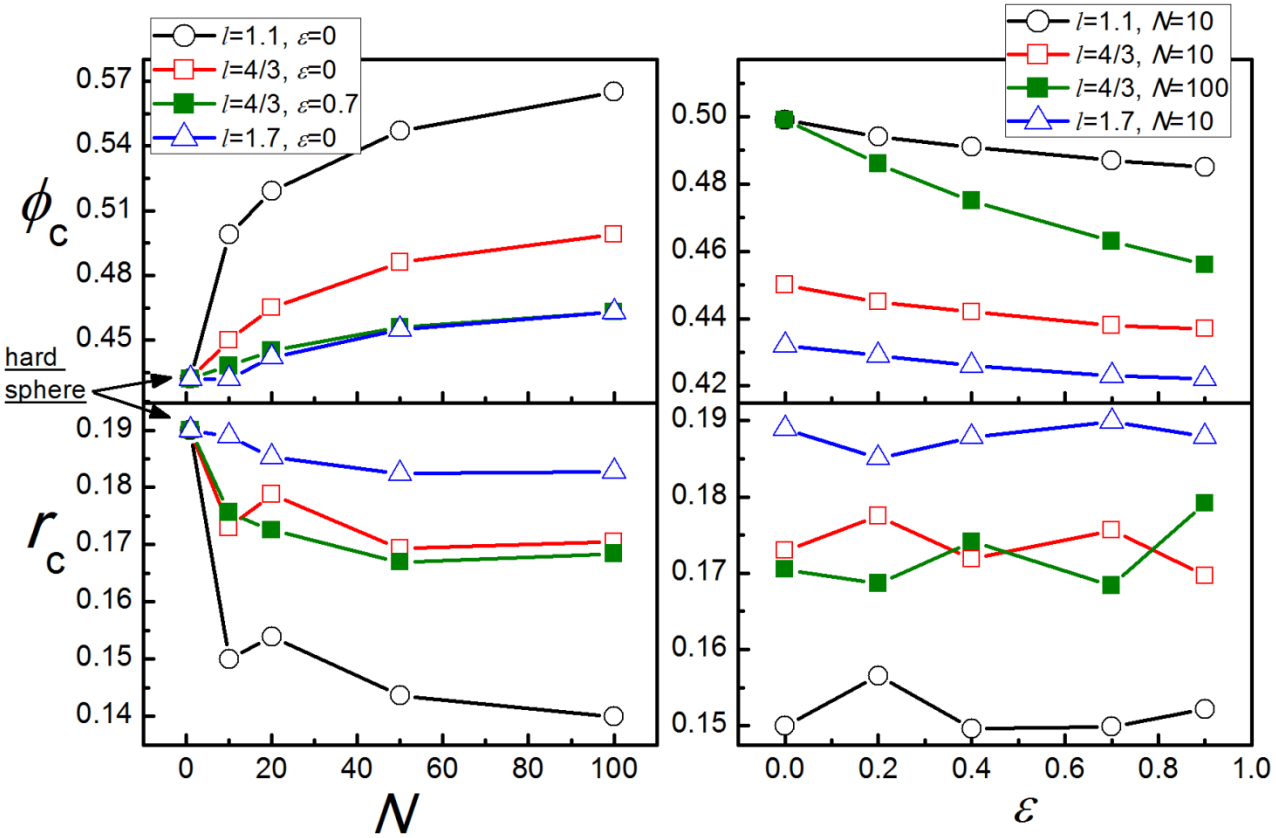


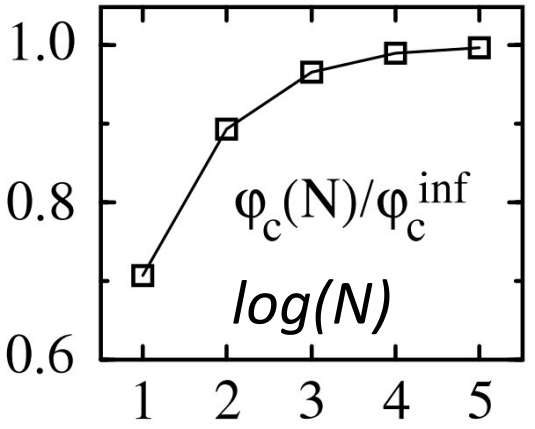
nonmonotonicity

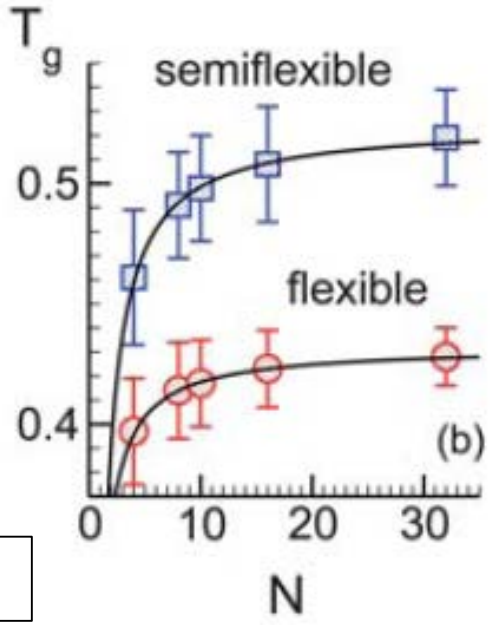
- l=4/3 has the largest barrier height.
- The barrier height increases with the increase of rigidity and decreases with chain length.

Critical point





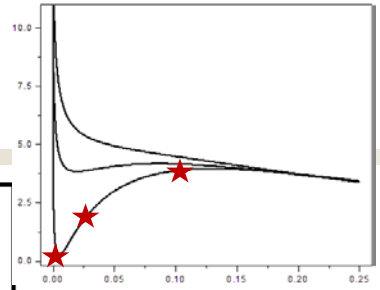


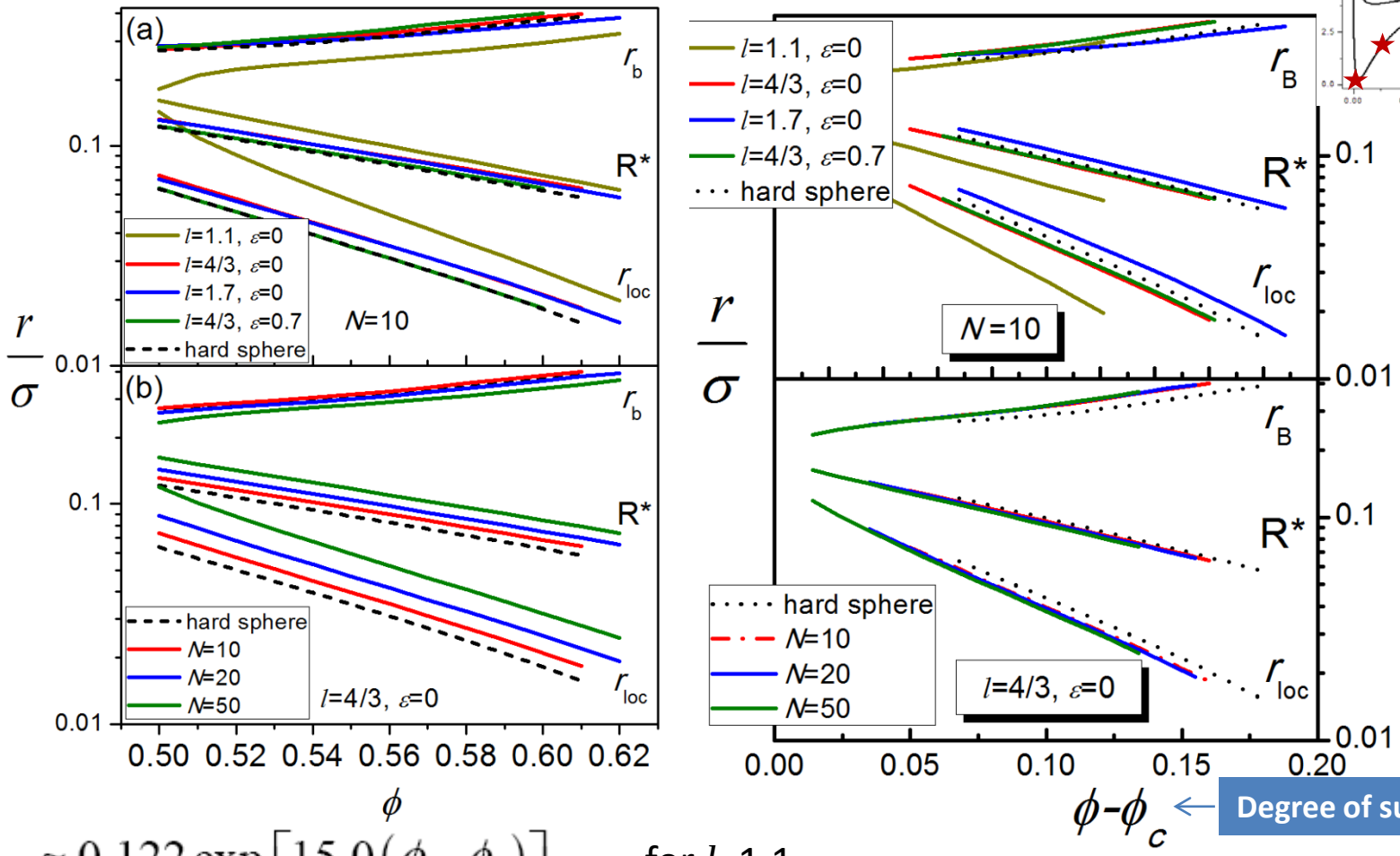


- Critical volume fraction increases with chain length
- Critical volume fraction varies with rigidity significantly for long chains
- Critical length scale is a weak function of chain length and rigidity, but depends markedly on bond length

Unique role of bond length

Local length scales





Degree of supercooling

$$r_{loc} \approx 0.122 \exp\left[15.0(\phi-\phi_c)\right] \quad \text{for } l=1.1$$

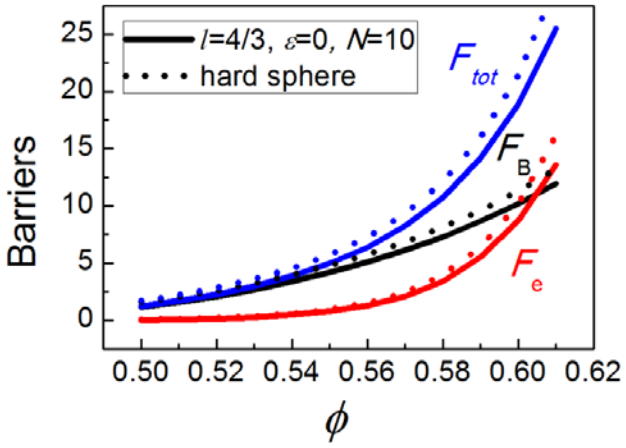
$$\approx 0.139 \exp\left[-12.6(\phi-\phi_c)\right] \quad \text{for } l=4/3$$

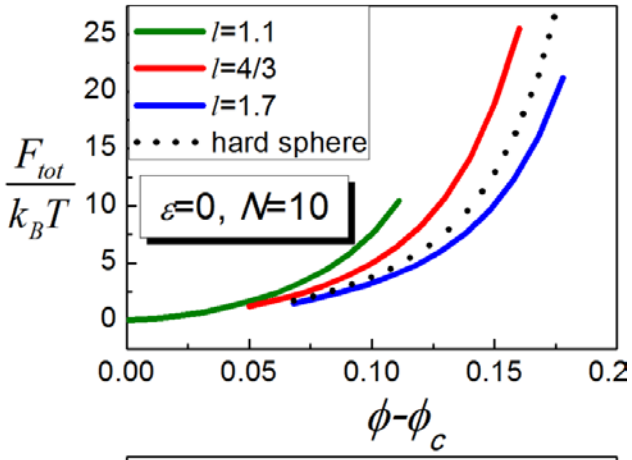
$$\approx 0.168 \exp\left[-12.4(\phi-\phi_c)\right] \quad \text{for } l=1.7$$

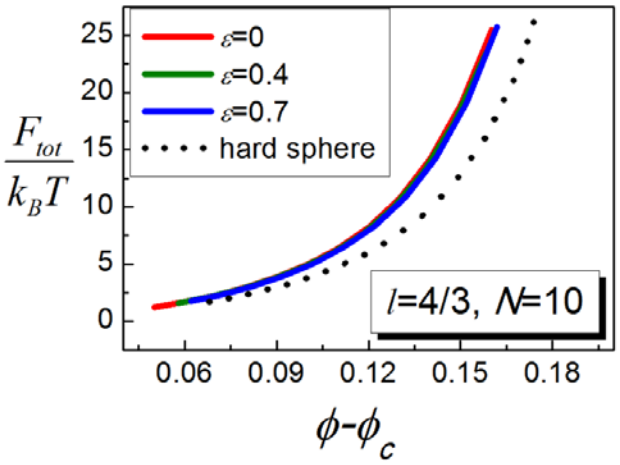
Unique role of bond length in determining the local length scales

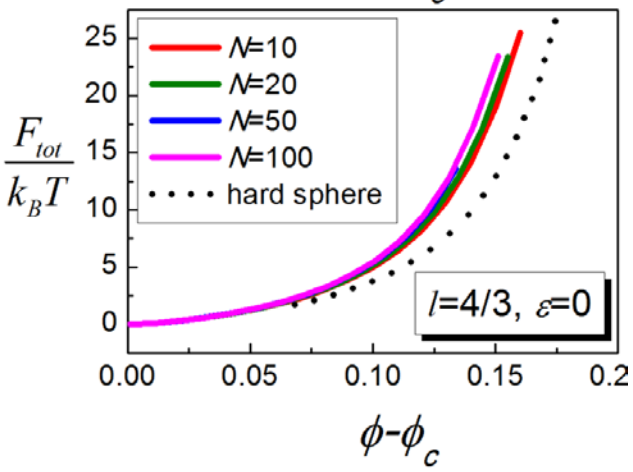
Barrier and hopping time

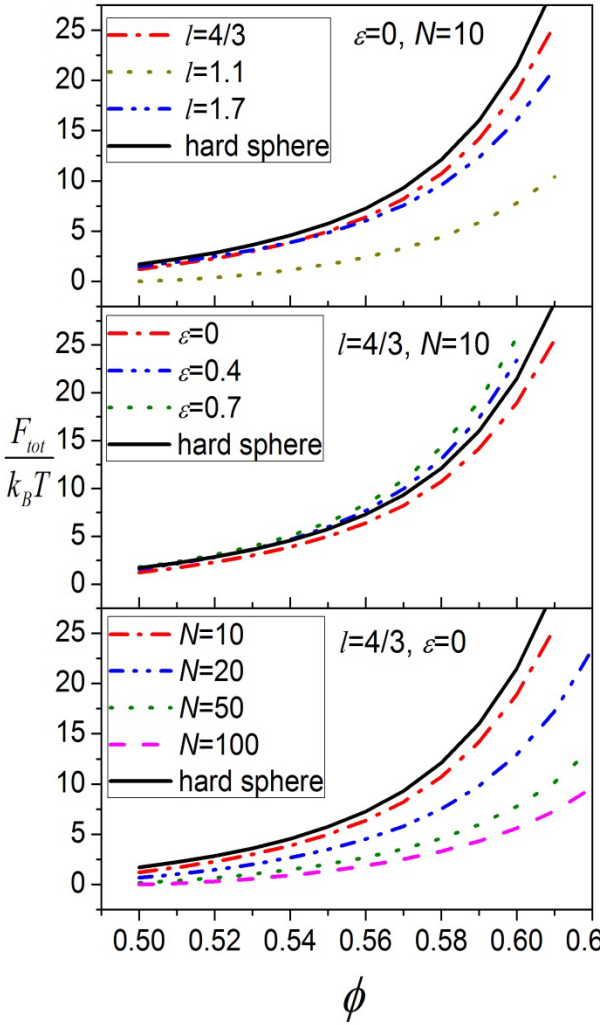
nonmonotonicity











Unique role of bond length in determining the barriers

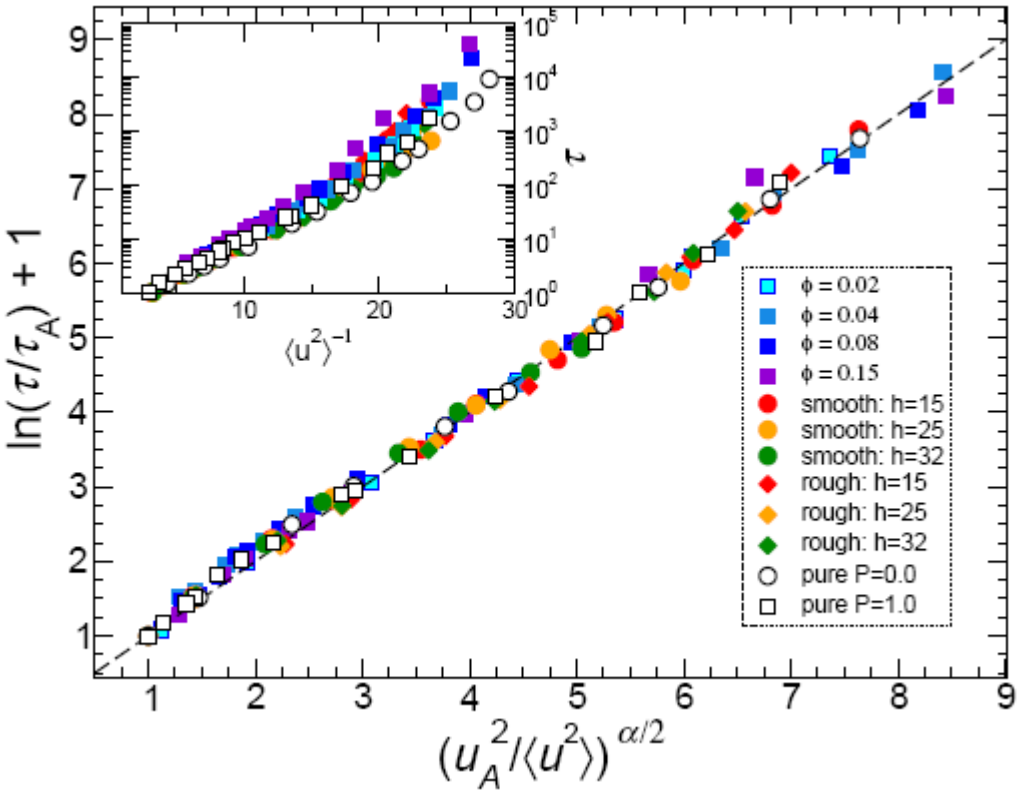
Universal relationship …

$$\tau_\alpha \propto \exp\left(u_0^2 / \langle u^2 \rangle\right)$$

$$\tau_\alpha \propto \exp\left(a^2/2\langle u^2\rangle + \delta^2/8\langle u^2\rangle^2\right)$$

$$\tau_\alpha \propto \exp\left[\left(u_0^2/\langle u^2\rangle\right)^{\alpha/2}\right]$$

The Debye-Waller factor $\langle u^2 \rangle$



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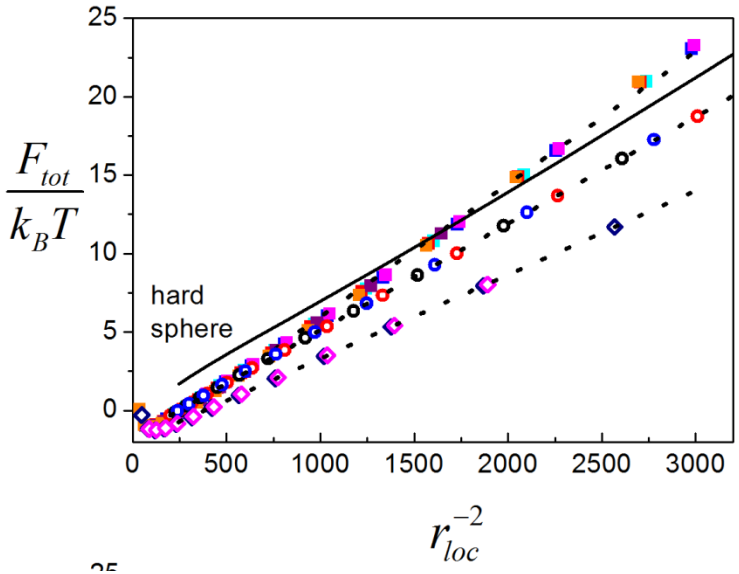
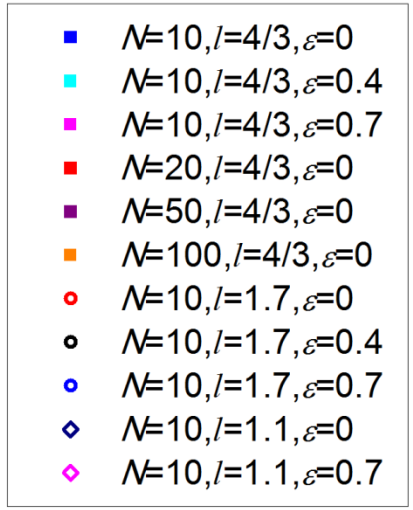
Universal relationship …

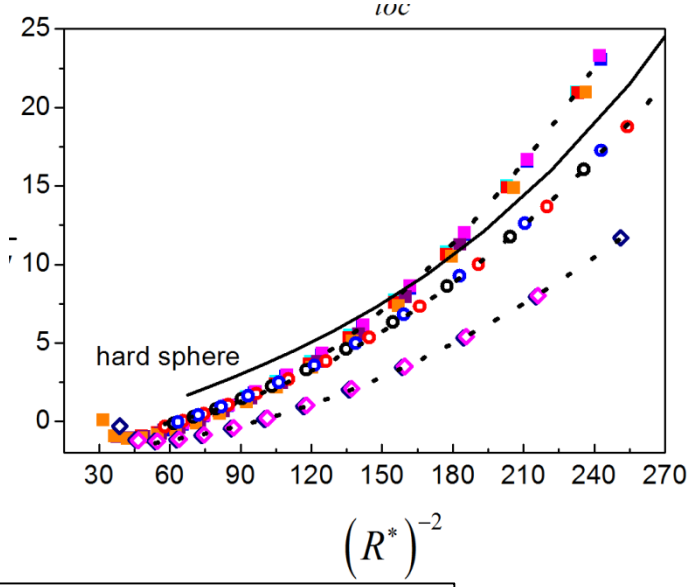
$$\tau_\alpha = \tau(\phi)\exp\left(F_{tot}/k_BT\right)$$

$$\tau(\phi)/\tau_0 = 2\pi g(\sigma)k_BT/\sigma^2\sqrt{K_0K_B} \qquad \tau_0 = \sigma^2\zeta_0/k_BT$$

$$\tau_\alpha \propto \exp\left[\left(u_0^2/\langle u^2\rangle\right)^{\alpha/2}\right]$$







Unique role of bond length in the universal relationship between localization length and relaxation time.

nonmonotonicity

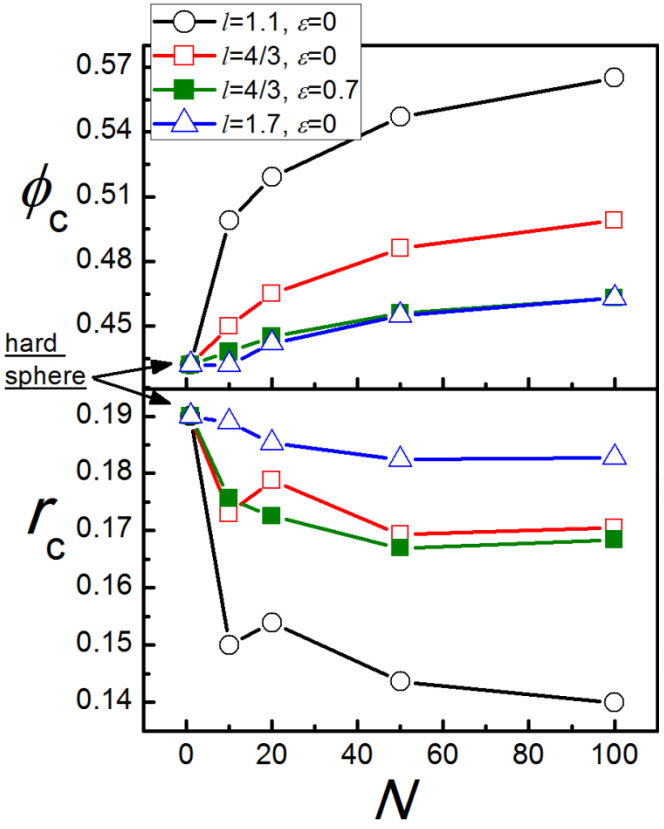
Conclusion

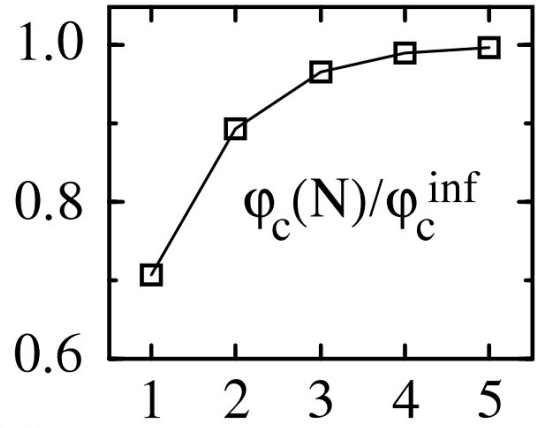
- Colloidal polymer is a promising model system to study glassy behavior of chain “molecules”.
- The influence of chain length and rigidity on the local length scale and activated barrier is encoded in the critical volume fraction.
- In contrast, bond length plays a special role in determining the behavior of localization length and dynamic barrier.
- We find nonmonotonic dependences of structure factor, barrier height and the universal relationship on the bond length.

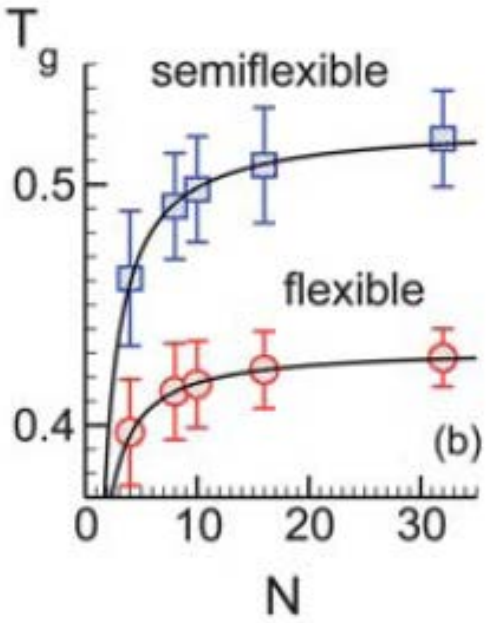
Outline

- Backgroud
- The basics of the NLE theory
- The unique role of bond length in colloidal polymer glass
- Outlook

Simulation as the input



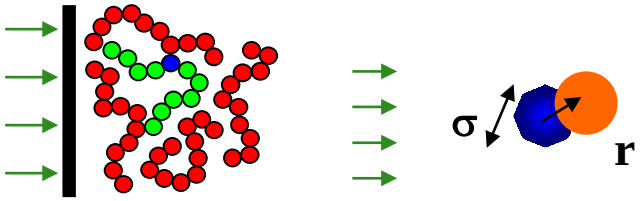




Possible reasons for the discrepancy:

1. density-controlled vs temperature-controlled
2. incomplete consideration of intrachain excluded-volume interaction

Mechanical response and Active glass



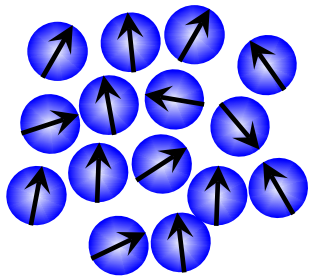
τ : Applied Stress

External force on segment $\propto \sigma^2\tau$

Instantaneous Mechanical work ~ $-\tau\Delta V \propto -\sigma^2\tau r$

$$F_{dyn}(r;\tau) = F_{dyn}(r;\tau=0) - c\sigma^2\tau r$$

Structural correlations NOT affected by stress



Brownian motion + driven by propelling force

Modified structural correlations by simulation + the stress effect?

Acknowledgment

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danke
謝謝
ngiyabonga
teşekkür ederim
спасибо
dank je
thank you
gracias
tapadh leat
mochchakkeram
bedankt
dziękuje
go raibh maith agat
obrigado
sukriya
kop khun krap
arigato
dakujem
grazie
terima kasih
merci