Detailed analysis of Rouse mode and dynamic scattering function of highly entangled polymer melts in equilibrium

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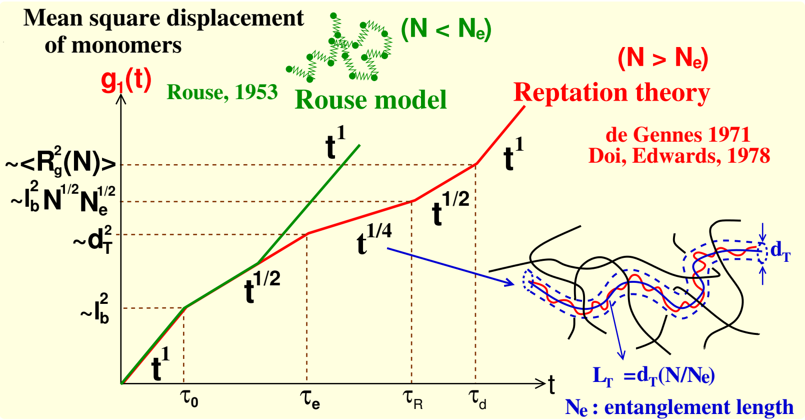
Motivation

Dynamic behavior of polymer chains in a melt:



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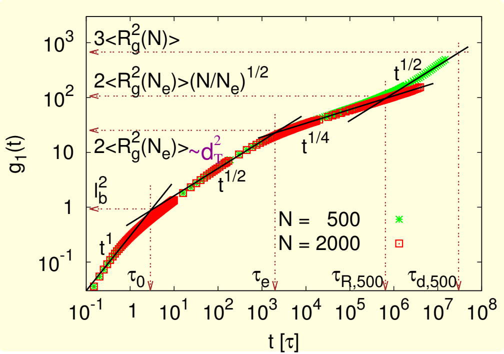


- Characteristic time: $\tau_0 \approx 2.89\tau$
- Entanglement time: $\tau_e \approx \tau_0 N_e^2$
- Rouse time: $\tau_R \approx \tau_0 N^2$
- Disentanglement time:
  $\tau_d \approx \tau_R (N/N_e)^{1.4} \propto N^{3.4}$
- Entanglement length: $N_e \approx 28$
- Tube diameter: $d_T \approx 5.02\sigma$

Bead-spring model

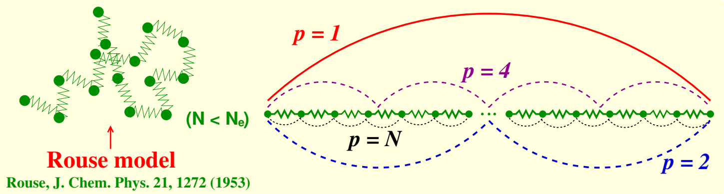
"Static and dynamic properties of large polymer melts in equilibrium"

Hsu & Kremer, J. Chem. Phys. 144, 154907 (2016)

Motivation

Dynamic behavior of polymer chains in a melt:

- Rouse mode analysis: (Gaussian chains, Brownian motion)



excluded volume effect, chain stiffness

topological constraint are all ignored

Trajectory of chains $\{\mathbf{r_i}\} \Rightarrow$ Rouse mode $\mathbf{X}_p(t)$, $p = 0, 1, \ldots, N$

Rouse mode relaxation time $\tau_p = \tau_0(N/p)^2$:

longest relaxation time $p = 1$: $\tau_1 = \tau_R$

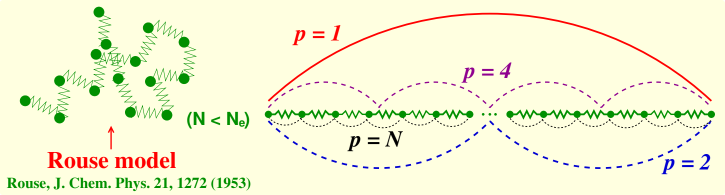
shortest relaxation tine $p = N$: $\tau_N = \tau_0$

$p = 0 \Rightarrow$: motion of center of mass

Motivation

Dynamic behavior of polymer chains in a melt:

- Rouse mode analysis: (Gaussian chains, Brownian motion)



- Dynamic structure factors: coherent and incoherent

Neutron spin echo (NSE) experiment, Mezei, Z. Physik 255, 146 (1972)

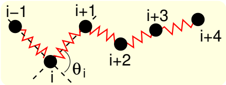
Witschnewski, Richter et al.,

Europhys. Lett. 52, 719 (2000), Phys. Rev. Lett. 88, 058301 (2002), 90, 058302 (2003)

$\Rightarrow$ tube diameter d_T

Bead-spring chains in a melt, $\rho = 0.85$

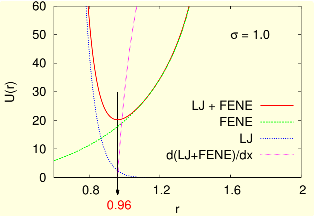
- Lennard-Jones potential: bonded, non-bonded
  (Weeks-Chandler-Andersen (WCA))



$$U_{\rm LJ}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right] & , \; r \le r_{\rm cut} \\ 0 & , \; r > r_{\rm cut} \end{cases}$$

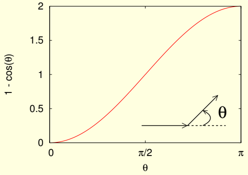
- Finitely Extensible Nonlinear Elastic potential:
  bonded

$$U_{\rm FENE}(r) = \begin{cases} -\frac{k}{2}R_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] & , \; r \le R_0 \\ \infty & , \; r > R_0 \end{cases}$$



- Bending potential:

$$U_{\rm bend}(\theta) = k_\theta(1 - \cos\theta)$$



$r_c = 2^{1/6}\sigma$, $k = 30\varepsilon/\sigma^2$, $R_0 = 1.5\sigma$

Kremer & Grest, JCP, 92, 5057 (1990)

Standard MD with Langevin thermostat

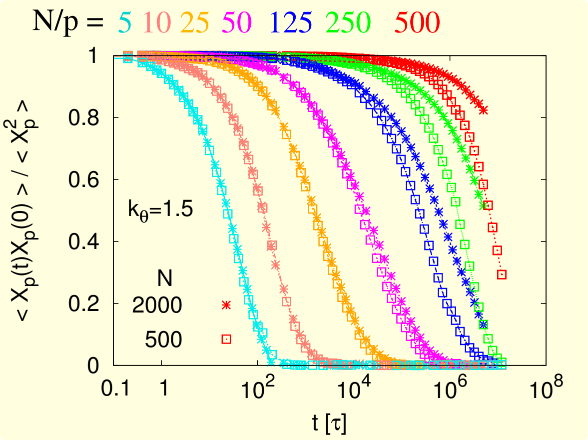
ESPResSo++

Autocorrelation function of Rouse modes

- Rouse modes:

$$\mathbf{X}_p(t) = \left(\frac{2}{N}\right)^{1/2} \sum_{i=1}^{N} \mathbf{r}_i(t) \cos\left[\frac{p\pi}{N}(i-1/2)\right], \quad p = 0, 1, \ldots N-1$$

Kopf, Dünweg, Paul, J. Chem. Phys. 107, 6945 (1997)



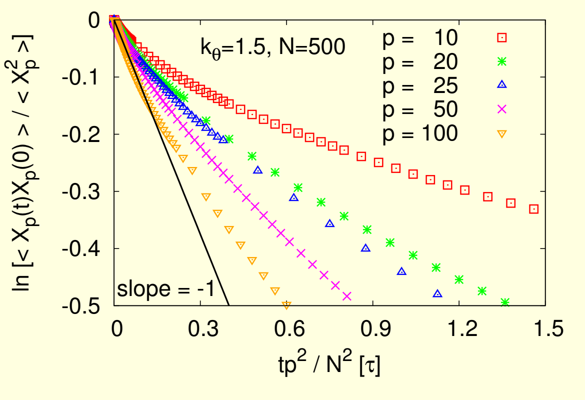
Entanglement length: $N_e \approx 28$

$N/p < N_e$
Rouse behavior

Autocorrelation function of Rouse modes

- Rouse modes: Brownian motion, independent of each other

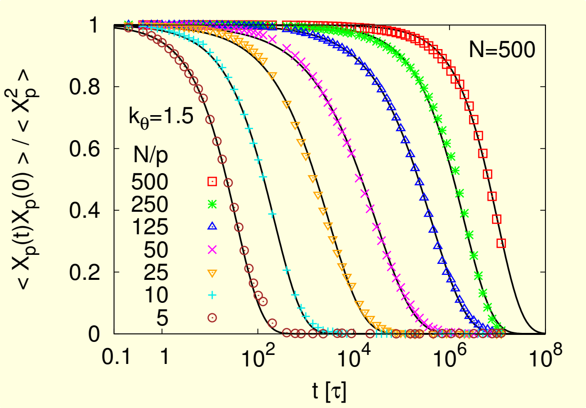
$$\frac{\langle \mathbf{X}_p(t)\mathbf{X}_p(0)\rangle}{\langle \mathbf{X}_p(0)\mathbf{X}_p(0)\rangle} = \exp(-t/\tau_p)\,, \quad \tau_p = \tau_0 \left(\frac{p}{N}\right)^{-2}$$



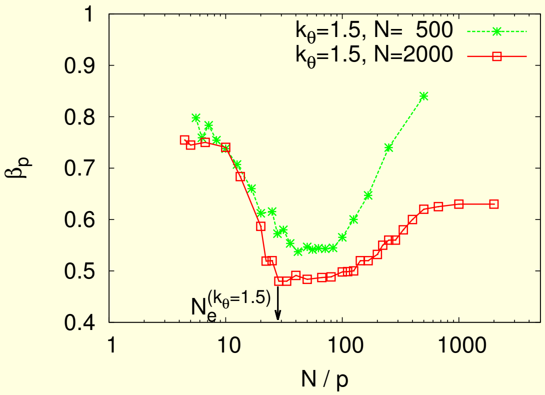
Autocorrelation function of Rouse modes

- Stretched exponential Kohlrausch-Williams-Watts (KWW) function: excluded volume interactions, topological constraints

$$\frac{\langle \mathbf{X}_p(t)\mathbf{X}_p(0)\rangle}{\langle \mathbf{X}_p(0)\mathbf{X}_p(0)\rangle} = \exp[-(t/\tau_p^*)^{\beta_p}]\,, \quad \tau_p^*\,,\beta_p \ : \ \text{fitting parameters}$$



Stretching exponent β_p

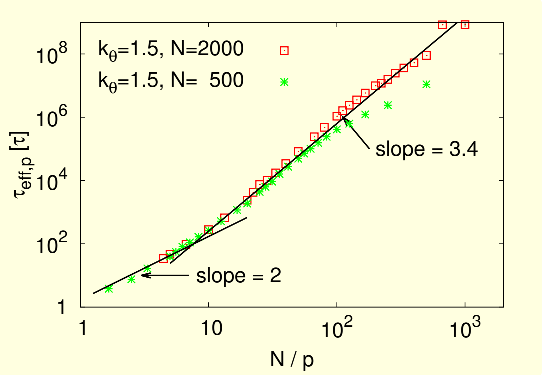


Kinetic constraints $\Rightarrow$ min $.\{\beta_p\}$ at $N/p = N_e \approx 28$

- Chain connectivity, excluded volume effect $N/p < N_e$
- Entanglement effect, topological constraints $N/p > N_e$

Effective Rouse time of mode p, $\tau_{\text{eff},p}$

$$\tau_{\text{eff},p} = \int_0^\infty dt \exp[-(t/\tau_p^*)^{\beta_p}] = \frac{\tau_p^*}{\beta_p}\Gamma(\frac{1}{\beta_p}), \Gamma(x) : \text{Gamma function}$$

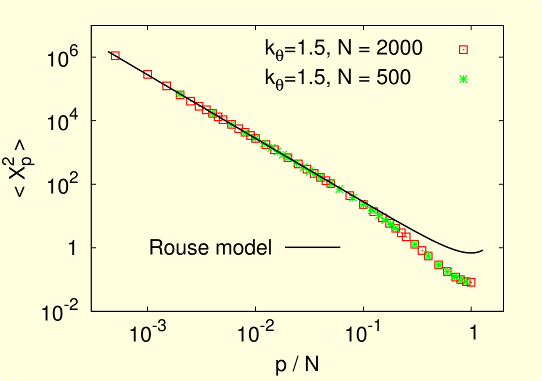


$$\tau_{\text{eff},p} = \begin{cases} (N/p)^2, & N/p < N_e \text{ (Rouse model, } \tau_R \approx N^2) \\ (N/p)^{3.4}, & N/p > N_e \text{ (reptation theory, } \tau_d \approx N^{3.4}) \end{cases}$$

Amplitude of autocorrelation function

- Rouse model: ignore the intrinsic stiffness of chains

$$\langle \mathbf{X}_p^2 \rangle = \langle \mathbf{X}_p(0)\mathbf{X}_p(0) \rangle = b^2 \left[4 \sin^2 \left(\frac{p\pi}{2N} \right) \right]^{-1}$$

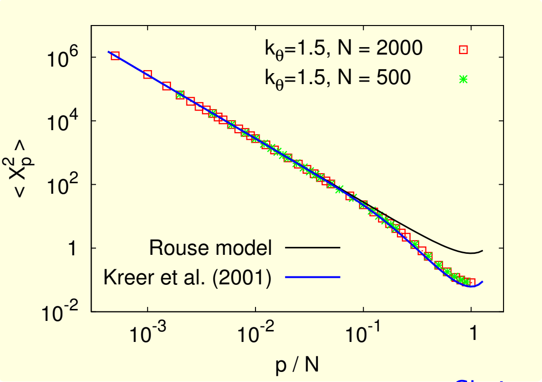


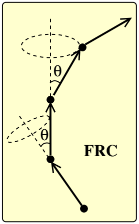
Amplitude of autocorrelation function

- Replacing random walk chains by freely rotating chains:

$$\langle \mathbf{X}_p^2 \rangle = b^2 \left\{ \left[4\sin^2\left(\frac{p\pi}{2N}\right)\right]^{-1} - \left[\frac{1- \mid \langle \cos\theta \rangle \mid^2}{4 \mid \cos\theta \rangle \mid} + 4\sin^2\left(\frac{p\pi}{2N}\right)\right]^{-1} (1+\mathcal{O}(N^{-1}) \right\}$$

Kreer, Baschnagel, Müeller, Binder, Macromolecules 34, 1105 (2001)
(Bond fluctuation model)





Chain stiffness is considered

Dynamic structure factors

- Coherent dynamic structure factor:

$$S_{\mathrm{coh}}(q,t) = \frac{1}{N}\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \exp\{i\vec{q}\cdot[\vec{r}_i(t)-\vec{r}_j(0)]\}\rangle$$

- Incoherent dynamic structure factors:

$$S_{\mathrm{inc}}(q,t) = \frac{1}{N}\langle \sum_{i=1}^{N} \exp\{i\vec{q}\cdot[\vec{r}_i(t)-\vec{r}_i(0)]\}\rangle$$

Dynamic structure factors

- Coherent dynamic structure factor:

$$S_{\mathrm{coh}}(q,t) = \frac{1}{N}\langle\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\{i\vec{q}\cdot[\vec{r}_i(t)-\vec{r}_j(0)]\}\rangle$$

$$\Rightarrow \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\{-\frac{1}{6}q^2\langle[\vec{r}_i(t)-\vec{r}_j(0)]^2\rangle\}$$

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$$\langle[\vec{r}_i(t)-\vec{r}_i(0)]^2\rangle \sim g_1(t)$$

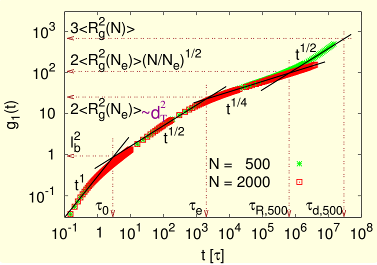
Rouse model: the displacement between monomer positions is Gaussian distributed

Incoherent dynamic structure factors

$$\ln[S_{\rm inc}(q,t)]\,,\; g_1(t) \sim \begin{cases} t^1\,, & t<\tau_0 \\ t^{1/2}\,, & \tau_0<t<\tau_e\,, \quad 2\pi/d_T<q<\ldots \\ t^{1/4}\,, & \tau_e<t<\tau_R\,, \quad 2\pi/R_g(N)<q<2\pi/d_T \\ t^{1/2}\,, & \tau_R<t<\tau_d\,, \quad \ldots<q<2\pi/R_g(N) \\ t^1\,, & t>\tau_d \end{cases}$$

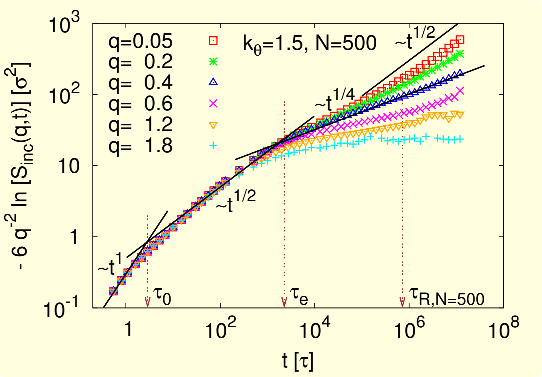
- Mean square displacement of monomers

$$g_1(t) \equiv \frac{1}{(N/2+1)} \sum_{i=N/4}^{3N/4} \left\langle [\vec{r}_i(t)-\vec{r}_i(0)]^2 \right\rangle$$



Incoherent dynamic structure factors

$$\ln[S_{\rm inc}(q,t)]\,,\; g_1(t) \sim \begin{cases} t^1\,, & t < \tau_0 \\ t^{1/2}\,, & \tau_0 < t < \tau_e\,, \quad 2\pi/d_T < q < \ldots \\ t^{1/4}\,, & \tau_e < t < \tau_R\,, \quad 2\pi/R_g(N) < q < 2\pi/d_T \\ t^{1/2}\,, & \tau_R < t < \tau_d\,, \quad \ldots < q < 2\pi/R_g(N) \\ t^1\,, & t > \tau_d \end{cases}$$



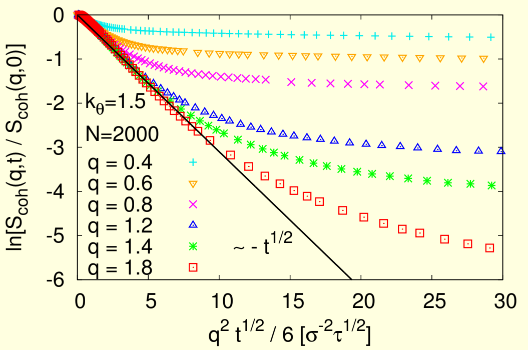
$2\pi/d_T \approx 1.26\sigma^{-1}$

$2\pi/R_g(N) \approx 0.4\sigma^{-1}$

Coherent dynamic structure factors

- For $t < \tau_e$ ($N < N_e$),

$$ln\left[\frac{S_{\rm coh}(q,t)}{S_{\rm coh}(q,0)}\right] = -q^2(Wt)^{1/2}/6 \quad \text{(Rouse model)}$$

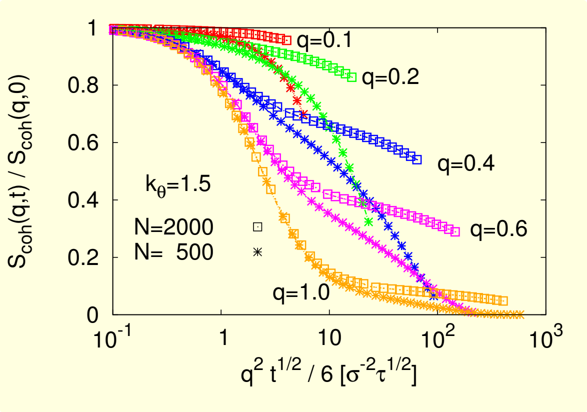


$$\Rightarrow \ln\left[\frac{S_{\rm coh}(q,t)}{S_{\rm coh}(q,0)}\right] \propto q^2 t^{1/2} \text{ for } q > \frac{2\pi}{d_T}$$

Coherent dynamic structure factors

- For $\tau_e \ll t \ll \tau_d$, reptation theory

$$\frac{S_{\mathrm{coh}}(q,t)}{S_{\mathrm{coh}}(q,0)} = 1 - q^2 d^2/36$$



⇒ plateau, first evidence!

$S_{\mathrm{coh}}(q,t)/S_{\mathrm{coh}}(q,t)$ vs. t

In the deep reptation regime:

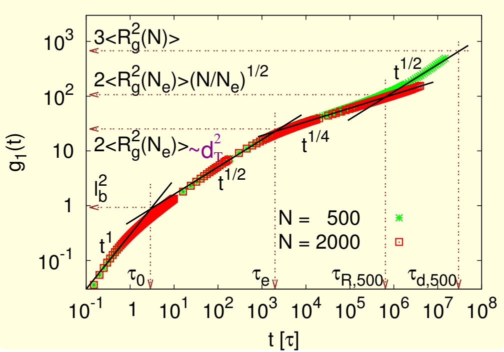
$$\frac{S_{\mathrm{coh}}(q,t)}{S_{\mathrm{coh}}(q,0)} = \left\{ \left[1-\exp\left(-\frac{q^2d^2}{36}\right)\right] f(q^2(Wt)^{1/2}) + \exp\left[-\frac{q^2d^2}{36}\right] \right\} \frac{8}{\pi^2} \sum_{n=1,odd}^{\infty} \frac{\exp[-tn^2/\tau_d]}{p^2}$$

Kremer & Binder, J. Chem. Phys. 81, 6381 (1984).
Pütz, Kremer, & Grest, Europhys. Lett. 49, 735 (2000).

Mean squared displacement of monomers:

$$d \approx \langle R_e^2(N_e)\rangle^{1/2}$$
$$= \sqrt{6}\langle R_g^2(N_e)\rangle^{1/2} = \sqrt{3}d_T$$
$$d_T = 5.02\sigma$$

Hsu & Kremer
J. Chem. Phys. 144, 154907 (2016).



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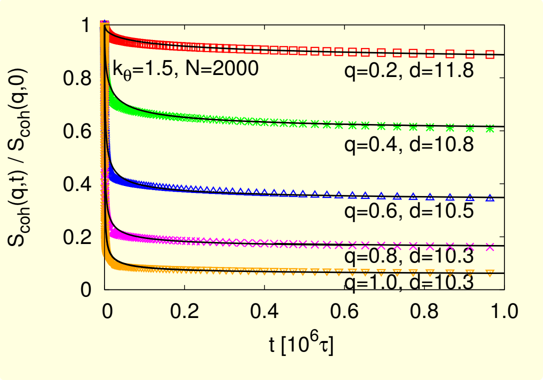

$\Rightarrow$ tube diameter $d_T = d/\sqrt{3} \approx 5.95\sigma$

Conclusion

- Relaxation of $\langle \mathbf{X}_p(t)\mathbf{X}_p(0)\rangle$ is independent of of chain size N for $N/p < N_e$
- Minimum value of the stretching exponent β_p occurs in the vicinity of $N/p \approx N_e$
- The cross-over behavior of the effective relaxation time $\tau_{\mathrm{eff},p}$ of mode p from Rouse regime to reptation regime is verified
- Scaling predictions of coherent $(S_{\mathrm{coh}}(q,t))$ and incoherent $(S_{\mathrm{inh}}(q,t))$ dynamic structure factors are investigated
- The tube diameter d_T extracted from $S_{\mathrm{coh}}(q,t)$ is equivalent to the estimate from the mean square displacement of monomers, $g_1(t)$

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Thank You!