

## Supporting Information

### Non-Rouse Behavior of Short Ring Polymers in Melts by Molecular Dynamics Simulation

Yedi Li<sup>a, b</sup>, Pu Yao<sup>a, b</sup>, Hongxia Guo<sup>\*, a, b</sup>

<sup>a</sup> Beijing National Laboratory for Molecular Sciences, Joint Laboratory of Polymer  
Sciences and Materials, State Key Laboratory of Polymer Physics and Chemistry,  
Institute of Chemistry Chinese Academy of Sciences, Beijing 100190, China.

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China.

\*Corresponding author. Tel: +86 10 82618124, fax: +86 10 62559373.

E-mail: [hxguo@iccas.ac.cn](mailto:hxguo@iccas.ac.cn)

## A Concise Summary for the Density-fluctuation-based and the Hydrodynamic-interaction-based Mode-coupling theory

Following Ref.1, for the density-fluctuation-based MCT (dMCT), the Laplace form of the center-of-mass velocity autocorrelation function (c.m. VAF) ( $C_{c.m.}(t)$ ) is related to the memory kernel  $\Gamma(t)$ :

$$\mathcal{L}(C_{c.m.}(t)) = v_T^2 N^{-1} / [p + \mathcal{L}(\Gamma(t))], \quad (\text{S1})$$

where  $v_T^2 = k_B T / m$ .  $\Gamma(t)$  from mode-coupling theory is:

$$\Gamma(t) \equiv \frac{\rho v_T^2}{3} \int \frac{d^3 q}{(2\pi)^3} q^2 [\tilde{c}(q)]^2 F(q, t) S(q, t), \quad (\text{S2a})$$

$$\tilde{c}(q) \equiv \frac{1}{\rho} \left( \frac{1}{F(q)} - \frac{1}{S(q)} \right), \quad (\text{S2b})$$

$$F(q, t) \equiv \frac{1}{N} \langle \rho_0(-q, 0) \rho_0(-q, t) \rangle. \quad (\text{S2c})$$

Under the assumptions of Rouse model and random phase approximation, scaling equations of  $F(q, t)$  and  $S(q, t)$  are deduced (not shown) and then the prediction for  $\Gamma(t)$  when  $t$  is shorter than the Rouse time is given as:

$$\Gamma(t) = \frac{\rho v_T^2}{3} \int \frac{d^3 q}{(2\pi)^3} q^2 \varphi(Aq^4 t) \sigma(Aq^4 t) \approx 0.54 (Wt)^{-5/4} \frac{v_T^2}{\rho b^5}. \quad (\text{S3a})$$

$$W = \left( \frac{h_0}{b^2} \right)^2 / t. \quad (\text{S3b})$$

where  $W$  is a time constant determined by the sub-diffusion of the monomer MSD  $h_0 = \frac{1}{6} \langle [r_i(t) - r_i(0)]^2 \rangle$ . Finally, substituting Eq. (S3) into Eq. (S1), we get the theoretical prediction for  $C_{c.m.}(t)$  from dMCT:

$$C_{c.m.}(t) \approx - \frac{(Wt)^{-5/4} b^2 W}{N \rho b^3} \times 0.037. \quad (\text{S4})$$

The hydrodynamic interaction-based MCT (hMCT) predicts that c.m. VAF is quite simple:

$$C_{c.m.}(t) \simeq \frac{1}{3\rho N} \int \frac{dq^3}{N(2\pi)^3} S(q, t) [2C_T(q, t) + C_L(q, t)]. \quad (\text{S5})$$

Here,  $C_T(q, t)$  and  $C_L(q, t)$  are, respectively, the longitudinal and the transverse current correlation functions indicative of the response to external forces. For the Langevin dynamics, the motion equation of polymers takes the frictional term into account so that the transverse current correlation functions also involve the friction term.

When the Langevin friction  $\gamma$  is not too high, one has:

$$\frac{\partial C_T(q,t)}{\partial t} = -\frac{q^2}{\rho} \int_0^t dt' E(t') C_T(t-t') - \gamma C_T(q,t). \quad (S6)$$

$E(t)$  is the shear relaxation modulus independent of  $q$  for the time longer than the monomer time  $t_1$  but shorter than the Rouse time  $t_R$ , which is predicted by the classical Rouse model as:

$$E(t) \simeq \frac{\rho m v_T^2}{\sqrt{2\pi^2 W t}}, \quad t_1 \ll t \ll t_R, \quad (S7)$$

When the time is longer than the Langevin relaxation time  $\gamma^{-1}$ , applying a Laplace transform and an inverse Laplace transform,  $C_T(q,t)$  is:

$$C_T(q,t) = -\frac{A v_T^2}{\gamma \bar{\gamma}^2} q^4 C_1(A q^4 \bar{\gamma}^{-2} t), \quad (S8a)$$

$$\bar{\gamma} = \frac{\pi b^2 W \gamma}{12 v_T^2}, \quad (S8b)$$

$$\mathcal{L}(C_1(t)) = C_1(p) = -\frac{\sqrt{2p}}{\sqrt{2p+1}}, \quad (S8c)$$

$$C_1(y) = \frac{1}{\sqrt{2\pi y}} - \frac{1}{2} \operatorname{erfcx}(\sqrt{y/2}), \quad (S8d)$$

where  $\operatorname{erfcx}(y) = e^{y^2} \frac{2}{\sqrt{\pi}} \int_y^\infty e^{-u^2} du$  is one of the error functions. Under the condition of the small Langevin friction ( corresponding to the dressed friction coefficient  $\bar{\gamma}$  of  $\bar{\gamma} \ll 1$  ) which encompasses the momentum-conserving dynamics, some simplified conditions hold. As regards  $S(q,t)$  of unentangled polymer melts, one should apply the results of the Rouse model, which shows a scaling of the form  $S(q,t) = S(q)\varphi(Aq^4 t)$ . Then, the decay of  $C_{c.m.}(t)$  is dominated by  $C_T(q,t)$ , while the longitudinal component  $C_L(q,t)$  can be negligible and static structure factor  $S(q)$  can take place of the dynamic structure factor. Then, when  $t \gg \gamma^{-1}$  we get:

$$C_{c.m.}(t) = -\frac{b^2 W^2 \bar{\gamma}^{-3}}{4\sqrt{6}\rho b^3 N^{7/2}} f_1(\pi \bar{\gamma}^{-2} W t / (4N^2)), \quad (S9a)$$

$$f_1(y) = \int_0^\infty dx x^6 f(x^2) C_1(y x^4). \quad (S9b)$$

The form factor function  $f(x)$  for Gaussian linear and ring polymers is defined in Eqs. (4) and (5), respectively. The difference of  $f(x)$  only affects the magnitude of c.m.VAF but not the scaling relation. Thus, as Ref. 1 predicts, c.m. VAF of both linear

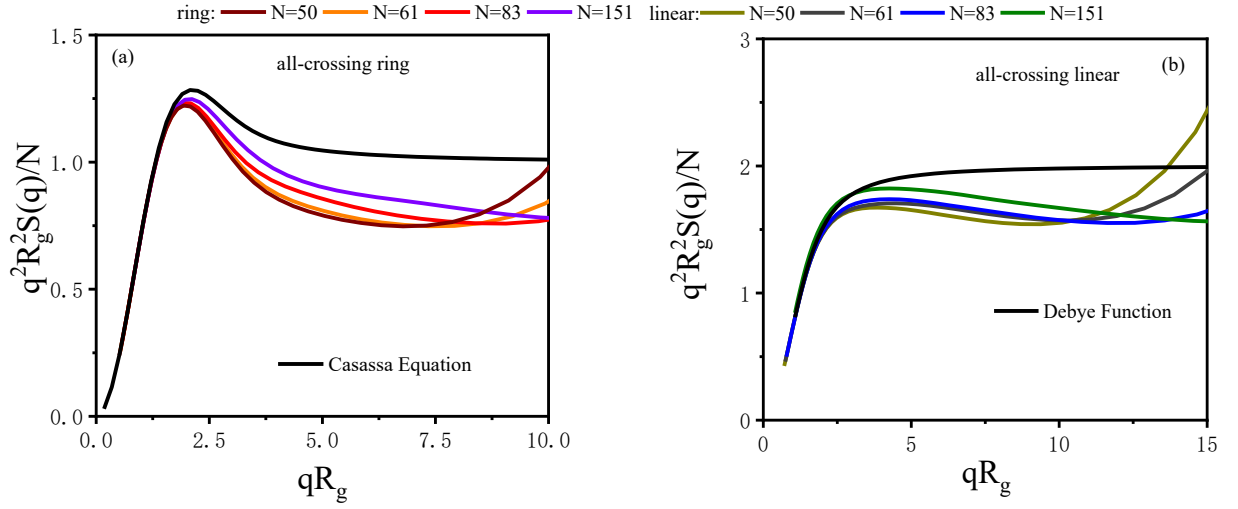
and ring polymer melts with small Langevin friction scales as  $t^{-5/4}$  for short time and  $t^{-3/2}$  for long time. For simplicity, Eq. (S9) can be rewritten as:

$$C_{c.m.}(t) = -Af_1(t\mu), \quad (\text{S10a})$$

$$A = \frac{b^2W^2\bar{\gamma}^{-3}}{4\sqrt{6}\rho b^3N^{7/2}}, \quad (\text{S10b})$$

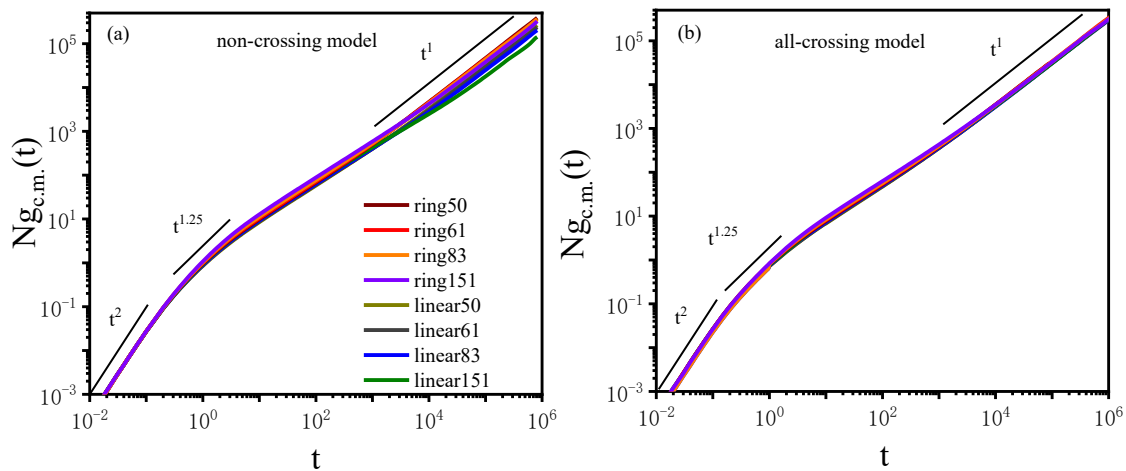
$$\mu = \pi\bar{\gamma}^{-2}W/(4N^2), \quad (\text{S10c})$$

### Static Single-chain Structure Factor of all-crossing polymer chains



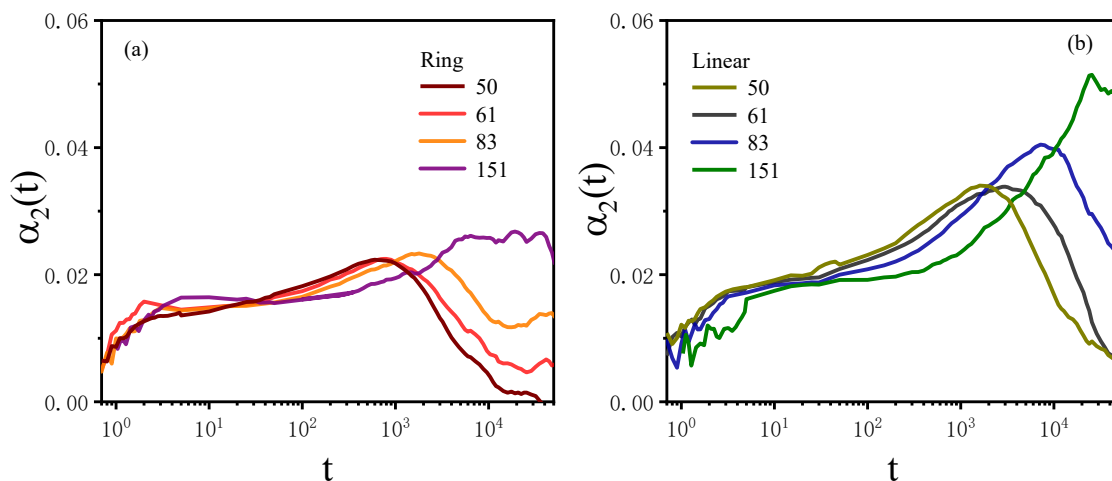
**Figure S1** Kratky representation of  $S(q)R_g^2q^2/N$  versus  $qR_g$  for the all-crossing (a) ring and (b) linear chains with different chain length. Also, Casassa equation and Debye function are shown by black solid curves for comparison.

## Center-of-mass Mean-square Displacement



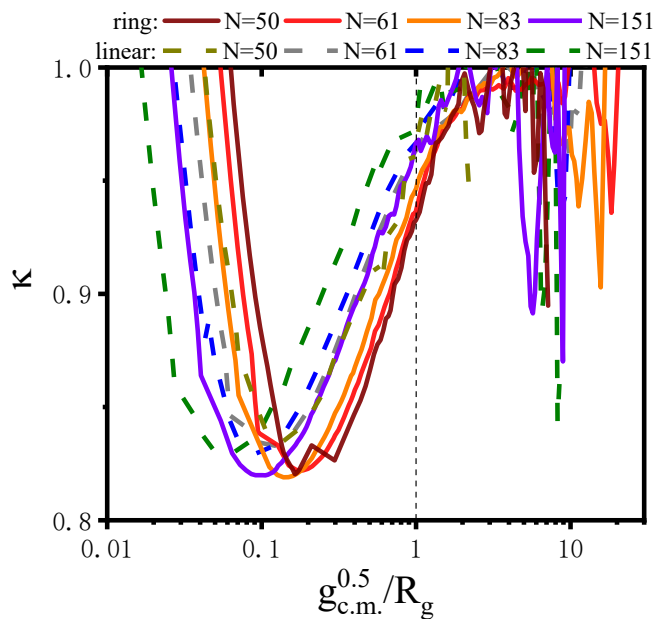
**Figure S2** Center-of-mass mean-square displacement multiplied by the chain length  $N$  for (a) non-crossing and (b) all-crossing ring and linear polymers. Three scaling laws are indicated by straight black lines for comparisons.

## Non-Gaussian Parameter (NGP)



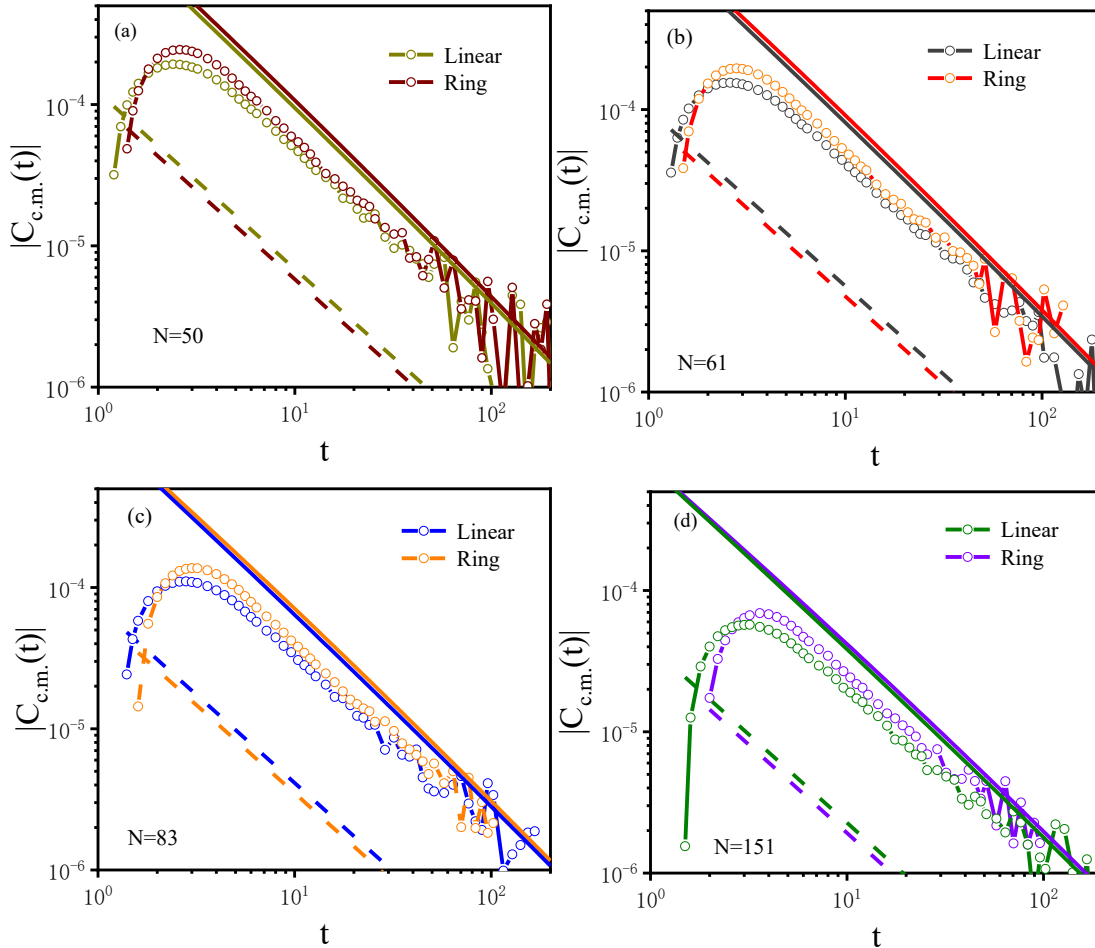
**Figure S3** Non-Gaussianity parameter of center of mass  $\alpha_2(t)$  for non-crossing (a) ring and (b) linear polymer melts.

## The Instantaneous Temporal Exponent



**Figure S4** semi-log plot of the temporal power law scaling exponent  $\kappa$  for the c.m. MSD data versus reduced displacement  $g_{c.m.}(t)^{0.5}/R_g$  for all-crossing ring and linear chains with different chain lengths. The black dashed straight line indicates the displacement that the polymer chain moves over a distance of the radius of gyration.

## The Center-of-mass Velocity Autocorrelation Function



**Figure S5** Comparison of the center-of-mass velocity autocorrelation function between simulation data (line+symbol), prediction by dMCT (eqn.(S4), dash lines) and hMCT (eqn.(S9), solid lines) for linear and ring polymer melts with  $N=50, 61, 83$  and  $151$  with friction constant  $\gamma = 0.5$ .

### References

1. Farago, J.; Meyer, H.; Baschnagel, J.; Semenov, A. N. Mode-coupling approach to polymer diffusion in an unentangled melt. II. The effect of viscoelastic hydrodynamic interactions. *Phys Rev E Stat Nonlin Soft Matter Phys* **2012**, 85 (5 Pt 1), 051807 DOI: 10.1103/PhysRevE.85.051807.