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Relating Chain Conformations to Extensional Stress In Entangled Polymer Melts

Thomas C. O'Connor,^{1,*} Nicolas J. Alvarez,^{2,†} and Mark O. Robbins^{1,‡}

¹*Department of Physics and Astronomy, Johns Hopkins University*

²*Department of Chemical and Biological Engineering, Drexel University*

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Nonlinear extensional flows are common in polymer processing but remain challenging theoretically because dramatic stretching of chains deforms the entanglement network far from equilibrium. Here, we present coarse-grained simulations of extensional flows in entangled polymer melts for Rouse-Weissenberg numbers $Wi_R = 0.06$ –52 and Hencky strains $\epsilon \geq 6$. Simulations reproduce experimental trends in extensional viscosity with time, rate and molecular weight. Studies of molecular structure reveal an elongation and thinning of the confining tube with increasing Wi_R . The rising stress is quantitatively consistent with the decreasing entropy of chains at the equilibrium entanglement length. Molecular weight dependent trends in viscosity are related to a crossover from the Newtonian limit to a high rate limit that scales differently with chain length.

The development of an accurate molecular model for polymer dynamics in complex flows has been the focus of intense research for more than 50 years. The tube model [1] has been incredibly successful in describing the dynamics of polymers in terms of entanglements with other chains that form a temporary confining tube that hinders diffusion. It captures the linear response of chemically distinct melts in terms of a universal function of the number of entanglements per chain Z and a material specific entanglement time τ_e and stress scale G_e [2]. However a growing number of experiments show new physics must be incorporated to understand strongly nonlinear flows that are relevant to industrial applications. A striking example is that melts with identical Z and linear response can show opposite trends in strong elongational flows, with viscosity rising or falling with increasing rate [3–7].

A number of attempts have been made to generalize the tube model based on different hypotheses about molecular mechanisms, including convective constraint release under shear [8], segmental stretch [9, 10], inter-chain pressure [11], formation and destruction of “slip-links” [12–15], and friction reduction in elongational flows [7, 16–18]. To date, no generalization of the tube model has been able to predict behavior in strong elongational flows [3, 5–7] and experiments have not provided direct measures of changes in chain conformation. It remains unclear how the confining tube changes in nonlinear flows, how chain conformations affect dissipation and what role chemistry [19], Z , chain length, and the equilibrium entanglement length N_e play in determining the molecular mechanisms underlying nonlinear behavior.

Molecular dynamics (MD) simulations are an ideal platform for relating macroscopic response to molecular structure [20, 21], but it has been difficult to simulate strong elongational flows at sufficiently large strains to reach steady state [22–24]. In this paper we use a recently developed technique [25, 26] to overcome this barrier. The simulations capture experimental trends in both the transient and steady state nonlinear viscosity of melts with different Z and entanglement length N_e

[7, 19]. Trends in viscosity with rate, Z and N_e are explained as a cross-over from the Newtonian limit to a high rate limit for aligned chains. A simple scaling law for the high rate behavior is derived and verified. The observed macroscopic response is shown to arise from changes in chain statistics that can be described as alignment and contraction of a confining tube with increasing strain rate. Surprisingly, changes in segment orientation only depend on the degree of entanglement Z , while chain stretching at high rates only depends upon the equilibrium entanglement length N_e . For all rates and melts, the steady-state stress is quantitatively related to changes in chain entropy over segments of length N_e .

Polymers are modeled with the well-studied Kremer-Grest bead-spring model [27] using LAMMPS [28]. All beads interact with a truncated Lennard-Jones (LJ) potential and results are presented in reduced LJ units. Linear chains of N beads are bound together with a FENE potential with mean bond length $b \approx 0.96$. To vary tube model parameters, the chain stiffness is controlled by a bond bending potential $k_{bend}(1 - \cos \alpha)$, where α is the angle between successive bonds. For the melt labeled M1, $k_{bend} = 1.5$ and there are $N_e \approx 28$ beads per rheological entanglement length [29]. For melt M2, $k_{bend} = 0.75$ and $N_e \approx 51$ [29].

Melts with M chains are equilibrated at temperature $T = 1$ and density $\rho = 0.85$ with standard methods [30]. M1 melts have $M = 1640$, $N = 112$; $M = 1094$, $N = 168$; $M = 734$, $N = 250$; or $M = 368$, $N = 500$, corresponding to $Z \approx 4, 6, 9$ or 18, respectively. M2 melts have $M=918$, $N=200$; $M=354$, $N=300$ or $M=405$, $N=450$, corresponding to $Z \approx 4, 6$ or 9, respectively. Melts are deformed at constant Hencky strain rate $\dot{\epsilon} \equiv \partial \ln \Lambda / \partial t$ with Λ the stretch along the z-axis. Since polymers are nearly incompressible, the two perpendicular directions contract by $1/\sqrt{\Lambda}$. Flow is maintained by integrating the SLLD equations of motion, and Generalized Kraynik-Reinelt boundary conditions are used to prevent the simulation box from becoming too small in the perpendicular directions [25, 26]. As shown in Supplemental Ma-

terial (SM) Fig. S1, simulations reproduce the time-dependent evolution of viscosity that is observed in experiments, while achieving strains that are not currently experimentally accessible. The steady-state extensional stress $\sigma_{ex} = \sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy})$ and chain statistics are obtained by averaging simulation data over the strain interval $\epsilon \in [5.5, 6.0]$.

Experiments typically plot dynamic viscosity data in reduced units based on tube theory to facilitate comparison between different melts [7, 19, 31]. Times are scaled by the entanglement time τ_e and the viscosity by $G_e \tau_R$, where the Rouse time $\tau_R = \tau_e Z^2$ is the characteristic time for a stretched chain to relax to its equilibrium contour length and $G_e = \rho k_B T / N_e$ is the entanglement modulus. A dimensionless measure of flow rate is the Rouse-Weissenberg number $Wi_R = \dot{\epsilon} \tau_R$. Previous studies have measured $\tau_e \approx 1.98 \times 10^3$ and 6×10^3 for M1 and M2 melts, respectively [29, 32, 33].

Figure 1(a) shows the rate dependence of the steady state viscosity $\eta_{ex} \equiv \sigma_{ex} / \dot{\epsilon}$ normalized by the value in the Newtonian limit η_{ex}^N . Data for M1 and M2 melts are shown alongside experimental results for polystyrene (PS) at similar Z . The significant difference between results for M1 and M2 melts at any common value of Z is consistent with the deviations from tube theory found in past experiments [7]. Although Z is not enough to determine the nonlinear response, all melts show common trends with increasing Z . For both simulations and experiments, the longest chains begin to shear-thin at the lowest Wi_R and show the largest drop in viscosity. The decrease is almost an order of magnitude for M1 and PS at $Z = 18$ and 21, respectively. As Z decreases, the onset of shear thinning moves to larger Wi_R and the decrease in η_{ex} decreases. Indeed shorter chains show some initial shear thickening for all systems [4, 7, 18].

Simulations allow us to directly correlate these changes in macroscopic response with changes in molecular structure. Snapshots in Fig. S2 show chains evolve from nearly equilibrium random coils at $Wi_R \ll 1$ to nearly straight configurations by $Wi_R = 51.5$. This evolving orientational order can be described by the nematic order parameter $P_2(n) = \frac{1}{2} \langle 3 \cos^2 \theta_n - 1 \rangle$, where $\langle \rangle$ indicates an ensemble average and θ_n is the angle between the extension axis and the vector $\vec{R}(n)$ between beads separated by n bonds. As shown in Fig. 2, $P_2(n) = 0$ for randomly oriented chains at low Wi_R and approaches unity at high Wi_R , corresponding to complete alignment. Alignment occurs first at the full chain length ($N - 1$ bonds) and affects smaller n as Wi_R increases. The rate where $P_2(N - 1)$ approaches unity coincides with the onset of a decrease in η_{ex} / η_N . Both changes imply that deformation is faster than the longest relaxation time, the disentanglement time τ_d for chains to escape their tubes.[34, 35] As shown in Fig. S3, $P_2(N - 1) \approx 0.3$ for $\dot{\epsilon} \tau_d = 1$ and saturates near unity for $\dot{\epsilon} \tau_d \gtrsim 5$.

Alignment at the entanglement scale starts at larger

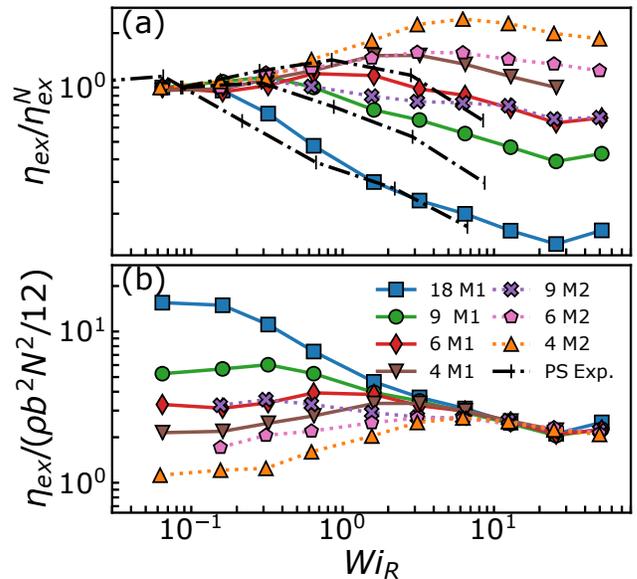


FIG. 1. (a) Ratio of steady state viscosity η_{ex} to Newtonian viscosity vs. Wi_R from simulations of M1 and M2 melts at the indicated Z and experiments on PS at $Z = 7.5$ [4], 10 [18], and 21 [7] (top to bottom). (b) Simulation data from panel (a) renormalized by the formula for the asymptotic drag on straight chains. Results for all chains collapse at large Wi_R .

Wi_R . In the low rate regime ($Wi_R \leq 1$), $P_2(N_e)$ is the same for different melts at the same Z . By $Wi_R = 1$, $P_2(N_e)$ exceeds 0.5 for all melts, and the results collapse on to a common curve for $Wi_R \gg 1$. For $\dot{\epsilon} \tau_d > 1$ chains are deformed faster than they can escape their tubes. For $Wi_R > 1$ the tube is being deformed and aligned along the extension direction faster than chains can relax to their equilibrium length along the tube. As a result, segments are stretched and aligned at shorter and shorter scales as Wi_R increases.

A measure of straightening is provided by $R(n)$ the root mean squared (rms) length of $\vec{R}(n)$. This must be less than the contour length between beads nb , where the bond length b remains essentially unchanged at the highest Wi_R considered here. The fraction of the fully extended length $R(n)/nb$ is shown in Fig. 3. At $Wi_R = 0.06$ chains have a near equilibrium conformation. The ratio $R_{eq}(n)/nb$ decreases slowly with increasing n at small n because k_{bend} makes the chain fairly straight. The behavior changes above the Kuhn length $\ell_K \equiv bC_\infty$, where the chain stiffness constant C_∞ is 2.8 and 2.2 for M1 and M2, respectively [32]. At larger n , chains are random coils and $R_{eq}(n)/nb = \sqrt{C_\infty/n}$ (black solid line in Fig. 3). For $Wi_R = 0.06$ short chains follow the equilibrium behavior at all n . For the longer chains shown, there is a slight straightening and reduced rate of decrease in $R(n)/nb$ at large n because $\dot{\epsilon} \tau_d \sim 1$.

The scale at which there is significant straightening

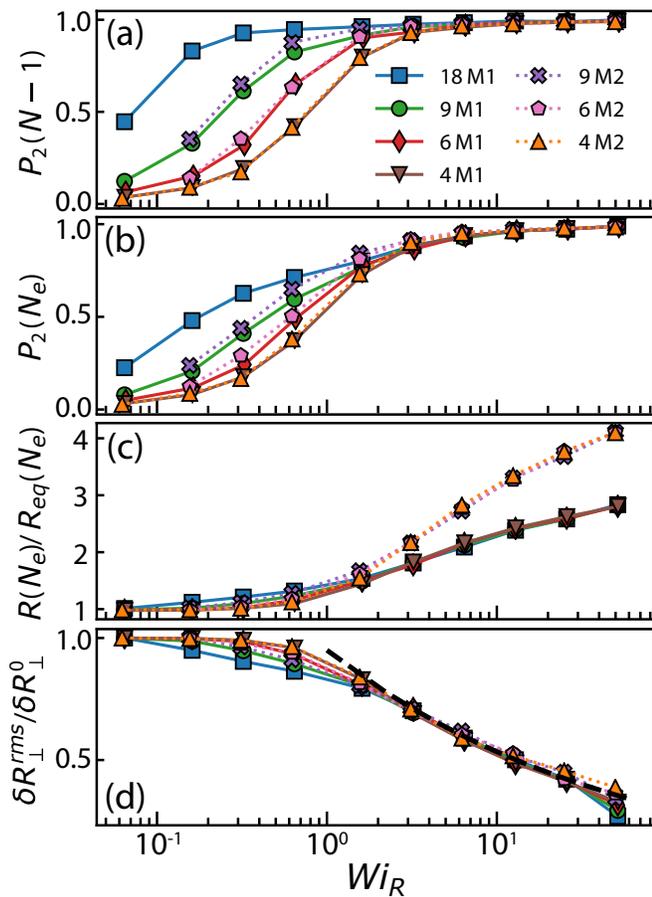


FIG. 2. (a) Orientational order at the end-end scale $P_2(N-1)$ vs. Wi_R for M1 and M2 melts at the values of Z indicated in the legend. (b) Orientational order at the scale of equilibrium entanglements. (c) Measure of tube elongation given by stretch of tube segments of length N_e . (d) Measure of decrease in tube radius given by change in rms deviation of monomers from the line between endpoints of segments of length N_e . A black dashed line indicates $\sim Wi_R^{-1/4}$ scaling.

decreases from N to N_e as Wi_R increases towards unity. For $Wi_R > 1$ the behavior is qualitatively different, with $R(n)/nb$ saturating at large n . Saturation starts near N_e for $Wi_R = 1.61$ and moves to smaller n as Wi_R increases. These results are exactly as expected from the snapshots in Fig. S2. Flow increases the length of chains and reduces fluctuations around their end-end vector.

The changes in $R(n)$ imply changes in the conformation of the tube confining each chain. In equilibrium the tube has a radius of order $R_{eq}(N_e)$ and is a random walk at larger scales with a Kuhn length of order $R_{eq}(N_e)$. Under elongation, Fig. 2 shows that the tube stretches and narrows. The increase in tube length per N_e can be measured by calculating the ratio $R(N_e)/R_{eq}(N_e)$. As shown in Fig. 2c, the tube length remains nearly constant as Wi_R increases to unity and then rises rapidly. Results for each melt collapse on to a common curve and

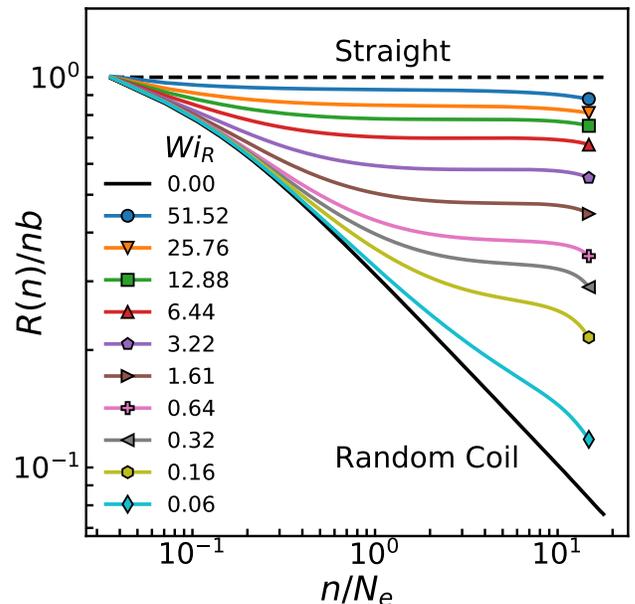


FIG. 3. Ratio of rms length to contour length $R(n)/nb$ as a function of n for a $Z = 18$ M1 melt at the indicated Wi_R . The solid black line corresponds to the equilibrium coil structure with $R(n)/n \sim (C_\infty/n)^{1/2}$ for n larger than C_∞ . Flow straightens chains at scales larger than N_e for $Wi_R < 1$. For $Wi_R > 1$, the chain becomes straight on progressively smaller scales. The small drop at large n indicates that chains are less aligned within an entanglement or two from their ends.

at large Wi_R approach the maximum possible stretch $\lambda_{max} = N_e b / R_{eq}(N_e) = 3.16$ and 4.8 for M1 and M2, respectively.

To characterize the change in tube diameter we consider segments of length N_e and evaluate the maximum rms fluctuation δR_\perp in the plane perpendicular to the end-end vector. Only the central 20% of each segment is included because the fluctuation goes to zero at the ends of each segment (see SM Sec. D). As for the tube length, the tube radius begins to change rapidly for $Wi_R > 1$ (although there is a small change for the longest chains when $\dot{\epsilon}\tau_d > 1$). The fractional change in tube radius at $Wi_R > 1$ is nearly the same for all Z and both melts. In all cases δR_\perp is of order b at the largest Wi_R , corresponding to a nearly straight chain.

Short segments are able to retain a nearly equilibrium conformation up to higher Wi_R . Since the relaxation time scales as n^2 , one may expect that the relaxed length $n_{rel}(Wi_R)$ scales as $Wi_R^{-1/2}$. The length of the corresponding random walk should set the tube radius, leading to a prediction that $\delta R_\perp \propto Wi_R^{-1/4}$ until the radius approaches the bond length. The tube length should grow as the number of segments of length n_{rel} times the rms length of each, implying $R(N_e)/R_{eq}(N_e) \propto (N_e/n_{rel})(n_{rel}/N_e)^{1/2} \propto N_e^{1/2} Wi_R^{1/4}$ until it saturates at

λ_{max} . The scaling range is not large enough to accurately test these scaling exponents, but the thick dashed line in Fig. 2(d) shows that the decrease in δR_{\perp} is consistent with a $-1/4$ power law [11] [36].

The alignment of chains by flow implies a reduction in their entropy that contributes to the steady-state stress σ_{ex} . While there is also an energetic contribution, it is much smaller because there is almost no stretching of chain backbones at the highest Wi_R considered here. One can calculate the stress due to the entropic force $\vec{F}(n)$ of segments of length n stretched to $\vec{R}(n)$. The density of such segments is ρ/n , where ρ is the monomer density. The stress tensor $\sigma_{ij} = (\rho/n) \langle F_i(n) R_j(n) \rangle$ where i and j are cartesian coordinates [37]. Since the force is directed radially, the extensional stress is $\sigma_{ex} = (\rho/n) \langle R(n) F(n) P_2(n) \rangle$. Inserting the standard result for the force on a random chain yields

$$\sigma_{ex}^{ent}(n) = \frac{\rho k_B T}{C_{\infty}} \left\langle \frac{R(n)}{nb} L^{-1} \left(\frac{R(n)}{nb} \right) P_2(n) \right\rangle \quad (1)$$

where the inverse Langevin function L^{-1} accounts for the nonlinear reduction in entropy as segments approach full extension [1, 37].

In the Newtonian limit, the tube model relates the stress to the change in entropy of segments with length $n \sim N_e$. A network of entanglements is assumed to carry the stress at larger scales [1]. It is not clear whether the same n should be used in Eq. 1 for the highly aligned states at large Wi_R . However, $\sigma_{ex}^{ent}(n)$ is insensitive to n at large Wi_R because of the plateau in $R(n)/nb$ (Fig. 3). Figure 4 plots the total measured steady-state stress versus $\sigma_{ex}^{ent}(N_e)$ for all simulated liquids in steady state. The two quantities are in excellent agreement for all melts and over three orders of magnitude in reduced stress. Deviations only become significant at the largest Wi_R where the chains are nearing complete alignment and Eq. 1 becomes singular.

To obtain the viscosity in the large Wi_R limit we equate the macroscopic rate of dissipation per unit volume $\eta_{ex} \dot{\epsilon}^2$ to the microscopic dissipation. Since chains are nearly fully extended, we consider a single straight chain in an extensional uniaxial flow. The entire chain must have the same average velocity, so the mean velocity Δv of its monomers relative to their neighbors grows linearly with distance x from the chain center as $\Delta v = \dot{\epsilon} x$. If there is a linear drag force with drag coefficient ζ , each monomer dissipates energy at a rate $\zeta \Delta v^2$. Averaging the dissipation over x gives a dissipation per monomer of $\langle \zeta \Delta v^2 \rangle = \zeta b^2 N^2 \dot{\epsilon}^2 / 12$ and thus $\eta_{ex} = \rho \zeta b^2 N^2 / 12$. In general, ζ will depend upon the chemical structure and interactions of the chain backbone.

Figure 1(b) shows η_{ex} normalized by $\rho b^2 N^2 / 12$. Results for both models and all chain lengths collapse onto a universal curve at large Wi_R whose limiting value corresponds to ζ . Note that M1 and M2 are expected to have nearly the same ζ because they have identical monomer

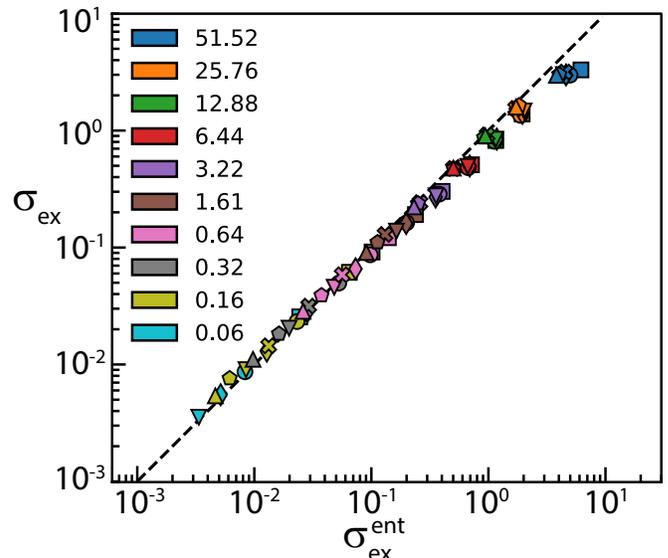


FIG. 4. Comparison of steady state stress from simulations σ_{ex} to the entropic stress from Eq. 1. Colors correspond to the values of Wi_R in the legend and symbols indicate the melt. M1 at $Z = 18$ (squares), 9 (circles), 6 (diamonds), and 4 (down triangles). M2 at $Z = 9$ (X), 6 (pentagons), 4 (up triangles).

masses, bond lengths and interchain interactions. The main difference is that M2 is more rigid and this becomes irrelevant for aligned chains. The derived value of $\zeta \approx 2$ is consistent with the viscosity of short chains.

The above results explain many experimental observations on the nonlinear response of polymers under strong elongational flow and relate them to changes in chain conformation. At all Wi_R the stress is quantitatively described by the entropic forces associated with chain straightening on segments of length N_e . This entropic stress is balanced by drag forces that also depend on chain conformation and scale with different powers of Z at low and high Wi_R .

For small Wi_R , chains remain close to Gaussian random walks. As predicted by the tube model and shown in Fig. S6 [34], $\eta_{ex} \sim \eta_N$ and scales as $G_e \tau_e Z^x \propto \zeta_N N_e Z^x$ where $x \approx 3.4$ for well entangled chains and ζ_N is the monomer drag in the Newtonian limit. At high rates, chains are straight and η_{ex} rises as ζN^2 . The ratio between the Newtonian and high-rate viscosity scales as $\sim Z^{1.4} \frac{\zeta_N}{N_e \zeta}$. The Z dependence explains why the amount of extension rate thinning increases with chain length in both experiments [3, 4, 7] and simulations (Fig. 1). The thinning of long chains can be fit to a power law with a Z dependent exponent over about one decade in rate.

Chemistry enters through N_e and the drag coefficients. Rate thickening may be observed at small Z for melts like M2 with small $\frac{\zeta_N}{N_e \zeta}$. The increased stiffness of M1 chains, decreases N_e and increases the amount of thinning. Di-

luting with short chains increases N_e , which may be part of the reason solutions show less shear thinning [7, 16–18]. There is also evidence that solutions suppress changes in drag because solvent molecules are less aligned by flow [7, 16–18]. Changes in monomer drag with alignment as Wi_R increases are small in our systems because the monomers are spherical. Large effects may be expected for polymers with large and rigid side groups.

Many recent methods identify entanglements with contacts between the primitive paths of polymers [38–40]. These methods suggest that there are no entanglements between the highly aligned chains at large Wi_R [12–15]. However, our measured chain statistics show that chains are highly confined at large Wi_R and the volume of the tube associated with the length and radius in Fig. 2 decreases as Wi_R rises. Studies of chain relaxation will play an important role in unraveling the relationship between entanglements and the confining tube at high rate.

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* toconnor@jhu.edu

† nja49@drexel.edu

‡ mr@jhu.edu

- [1] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Vol. 73 (Oxford University Press, 1988).
- [2] A. E. Likhtman and T. C. B. McLeish, *Macromolecules* **35**, 6332 (2002).
- [3] A. Bach, K. Almdal, H. K. Rasmussen, and O. Hassager, *Society* **36**, 5174 (2003).
- [4] J. K. Nielsen, H. K. Rasmussen, O. Hassager, and G. H. McKinley, *Journal of Rheology* **50**, 453 (2006).
- [5] Q. Huang, N. J. Alvarez, Y. Matsumiya, H. K. Rasmussen, H. Watanabe, and O. Hassager, *ACS Macro Letters* **2**, 741 (2013).
- [6] Q. Huang, O. Mednova, H. K. Rasmussen, N. J. Alvarez, A. L. Skov, K. Almdal, and O. Hassager, *Macromolecules* **46**, 5026 (2013).
- [7] S. L. Wingstrand, N. J. Alvarez, Q. Huang, and O. Hassager, *Physical Review Letters* **115**, 1 (2015).
- [8] G. Marrucci, *Journal of Non-Newtonian Fluid Mechanics* **62**, 279 (1996).
- [9] D. W. Mead, D. Yavich, and L. G. Leal, *Rheologica Acta* **34**, 360 (1995).
- [10] D. W. Mead, R. G. Larson, and M. Doi, *Macromolecules* **31**, 7895 (1998).
- [11] G. Marrucci and G. Ianniruberto, *Macromolecules* **37**, 3934 (2004).
- [12] A. E. Likhtman, *Macromolecules* **38**, 6128 (2005).
- [13] C. Baig, V. G. Mavrantzas, and M. Kröger, *Macromolecules* **43**, 6886 (2010).
- [14] M. Andreev, R. N. Khaliullin, R. J. A. Steenbakkers, and J. D. Schieber, *Journal of Rheology* **57**, 535 (2013).
- [15] G. Ianniruberto and G. Marrucci, *Journal of Rheology* **58**, 89 (2014).
- [16] G. Ianniruberto, A. Brasiello, and G. Marrucci, *Macromolecules* **45**, 8058 (2012).
- [17] T. Yaoita, T. Isaki, Y. Masubuchi, H. Watanabe, G. Ianniruberto, and G. Marrucci, *Macromolecules*, 1 (2012).
- [18] S. Costanzo, Q. Huang, G. Ianniruberto, G. Marrucci, O. Hassager, and D. Vlassopoulos, *Macromolecules* **49**, 3925 (2016).
- [19] T. Sridhar, M. Acharya, D. A. Nguyen, and P. K. Bhattacharjee, *Macromolecules* **47** (2013), 10.1021/ma401213r.
- [20] A. E. Likhtman, S. K. Sukumaran, and J. Ramirez, *Macromolecules* **40**, 6748 (2007).
- [21] J. Cao and A. E. Likhtman, *ACS Macro Letters* **4**, 1376 (2015).
- [22] W.-S. Xu, J.-M. Y. Carrillo, C. N. Lam, B. G. Sumpter, and Y. Wang, *ACS Macro Letters*, 190 (2018).
- [23] M. Kroger, C. Luap, and R. Muller, *Macromolecules* **30**, 526 (1997).
- [24] P. J. Daivis, M. L. Matin, and B. D. Todd, *Journal of Non-Newtonian Fluid Mechanics* **111**, 1 (2003).
- [25] M. Dobson, *The Journal of Chemical Physics* **141**, 184103 (2014), arXiv:1408.7078.
- [26] D. A. Nicholson and G. C. Rutledge, *Journal of Chemical Physics* **145** (2016), 10.1063/1.4972894.
- [27] K. Kremer and G. S. Grest, *The Journal of Chemical Physics* **92**, 5057 (1990).
- [28] S. Plimpton, *Journal of Computational Physics* **117**, 1 (1995).
- [29] L. A. Moreira, G. Zhang, F. Müller, T. Stuehn, and K. Kremer, *Macromolecular Theory and Simulations* **24**, 419 (2015).
- [30] R. Auhl, R. Everaers, G. S. Grest, K. Kremer, and S. J. Plimpton, *The Journal of Chemical Physics* **119**, 12718 (2003).
- [31] J. Dealy and R. Larson, “Structure and rheology of molten polymers: From structure to flow behavior and back again,” (2006).
- [32] H.-P. Hsu and K. Kremer, *The Journal of Chemical Physics* **144**, 154907 (2016), arXiv:1604.00245.
- [33] T. Ge, M. O. Robbins, D. Perahia, and G. S. Grest, *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **90**, 1 (2014), arXiv:1407.3198.
- [34] M. Doi, *Journal of Polymer Science: Polymer Physics Edition* **21**, 667 (1983).
- [35] J. X. Hou, C. Svaneborg, R. Everaers, and G. S. Grest, *Physical Review Letters* **105**, 1 (2010), arXiv:1002.2146.
- [36] Marrucci and Ianniruberto proposed a theory predicting $\delta R_{\perp} \propto Wi_R^{-1/4}$ based on an inter-chain tube pressure. However, the dynamics of their theory predicts a cross-over to this scaling controlled by τ_d . This cannot describe our data which shows δR_{\perp} only depends on τ_R for $Wi_R > 1$.
- [37] M. Rubinstein and R. H. Colby, *Polymer Physics*, Vol. 23 (Oxford university press New York, 2003).
- [38] R. Everaers, S. K. Sukumaran, G. S. Grest, C. Svaneborg, A. Sivasubramanian, and K. Kremer, *Science* **303**, 823 (2004).
- [39] M. Kröger, *Computer Physics Communications* **168**, 209 (2005).
- [40] C. Tzoumanekas and D. N. Theodorou, *Macromolecules* **39**, 4592 (2006), arXiv:0602555 [cond-mat].