

Nonmonotonic Stress Overshoot in Entangled Polymer Melts under Two-step Shear

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Electronic Supplementary Information

Abstract Shear stress overshoot in entangled polymer rheology is a hallmark of transient dynamics, but its microscopic origin remains under debate. Using molecular dynamics simulations, we investigate a two-step shear protocol consisting of successive startup shears separated by a waiting period, with the first shear interrupted before the overshoot. In the homogeneous flow, the GLaMM theory captures the stress response during the first shear, but fails to reproduce the nonmonotonic dependence of the second stress overshoot ($\sigma_{2\max}$) on the waiting time. Contrary to the prediction of a nonmonotonic normal stress component σ_{yy} during the waiting period, our simulations show that σ_{yy} , like the tube segment orientation (S_{xy}), the contour length of the primitive chain (L), and the entanglement number per chain (Z), relaxes monotonically toward equilibrium. At the strain corresponding to $\sigma_{2\max}$, both the tube segment orientation and the entanglement number per chain exhibit a nonmonotonic dependence on the waiting time that closely mirrors the behavior of $\sigma_{2\max}$, indicating that both factors play significant roles in governing $\sigma_{2\max}$. Our findings are consistent with the interpretation of Ianniruberto and Marrucci [ACS Macro. Lett. 2014, 3, 552] for orientation effects and with the viewpoint of Wang *et al.* [Macromolecules 2013, 46, 3147] for entanglement effects, although the two explanations are rooted in distinct physical pictures. These results provide new insights into the stress responses of entanglement polymer fluids and underscore the need for a more unified theoretical framework.

Keywords Entangled polymer rheology; Molecular dynamics simulation; Tube model; Disentanglement

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INTRODUCTION

Entanglement interactions, arising from the uncrossability of polymer chain backbones, play a central role in the nonlinear rheology of entangled polymer fluids (melts or concentrated solutions). A characteristic feature is the stress overshoot observed in the startup shear on the equilibrium sample, where the shear stress first increases to a maximum before decaying to a steady state. A widely accepted interpretation of stress overshoot is based on the Doi–Edwards (DE) tube model,^[1–3] which attributes stress overshoot to the nonmonotonic tube segment orientation. Because polymer fluids often experience multiple flow histories, researchers have extensively investigated the two-step shear,^[4–8] which is traditionally defined as a startup shear applied after a waiting period following steady flow. In such cases, the height of the second stress overshoot $\sigma_{2\max}$ pro-

gressively recovers toward the value observed in the first shear, but only after waiting times comparable to or even much longer than the equilibrium disengagement time τ_{d0} . This behavior is commonly explained in terms of disentanglement in the first shear and subsequent re-entanglement during the waiting period. However, the DE tube model maintains the entanglement number per chain unchanged both during and after the first shear.^[9] Therefore, the microscopic mechanism underlying stress overshoot during two-step shear is not yet fully understood.

To further test the tube model, Wang *et al.*^[10] designed a more complex experiment: the first shear was applied at the Rouse–Weissenberg number $Wi_R = \dot{\gamma}\tau_R = 0.09$ ($\dot{\gamma}$ and τ_R are the shear rate and the Rouse time, respectively) with a strain $\gamma = 1.5$ (before the stress overshoot rather than to steady flow), and then the second shear was imposed at a higher $Wi_R = 5.25$ after a waiting time t_w . The DE tube model assumes that the primitive chain follows Rouse dynamics,^[11] so that the chains are oriented but hardly stretched in the first shear. Accordingly, both chain orientation and entanglement density (if they

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change) should relax monotonically toward equilibrium during the waiting period, implying that $\sigma_{2\max}$ should increase monotonically with t_w .^[12] However, Wang *et al.*^[10] found $\sigma_{2\max}$ initially decreased with increasing t_w and then gradually recovered the value observed in a startup shear from equilibrium. Because of this discrepancy, they^[10,12] proposed that the nonmonotonic $\sigma_{2\max}$ arises from additional damage to the entanglement network of polymer fluids during the waiting period, and regarded this as evidence of force imbalance.^[13] Consequently, they suggested that the force arising from strongly localized intermolecular interactions is missing from the tube model.

Subsequently, Graham *et al.*^[14,15] applied the Rolie-Poly (RP) theory^[16] (based on standard tube model concepts) to propose an alternative explanation. During the waiting period, the shear stress σ_{xy} relaxed monotonically toward equilibrium, while the normal stress component σ_{yy} initially decreased for a short duration around the Rouse time τ_R before gradually recovering toward equilibrium. This short-time reduction was attributed to the Rouse dynamics of the primitive chain. Consequently, the nonmonotonic behavior of $\sigma_{2\max}$ was interpreted as the delayed relaxation of the normal stress. From a numerical perspective, the solution of constitutive equations depends on the initial conditions. At equilibrium, all the stress components vanish. However, the nonmonotonic evolution of σ_{yy} during the waiting period leads to multiple possible initial values for the second shear, which ultimately results in the observed nonmonotonic $\sigma_{2\max}$. Thus, Graham *et al.*^[14,15] argued that the tube model can account for nonmonotonic $\sigma_{2\max}$ without the need to introduce a new mechanism.

In contrast to the above interpretations, Ianniruberto and Marrucci^[17] used the integral equation of the DE tube model, which only accounts for the tube segment orientation function and memory function, and reproduced the nonmonotonic behavior of $\sigma_{2\max}$. Because the stress overshoot arises from the tube segment orientation, the memory effect of the tube segment orientation during the waiting period alters both the height and position of the tube segment orientation in the second shear, thereby altering the stress overshoot in the second shear. Furthermore, they argued that the interpretation of stress overshoot in the second shear, followed by steady flow, as a distinctive mark of disentanglement, is mostly a misconception.

The central issue regarding $\sigma_{2\max}$ is the factor dominates its behavior. Fundamentally, this reflects the controversy over the physical picture of entangled polymer fluids. Notably, the protocol of Wang *et al.*^[10] can be viewed as probing the stress responses of two limiting sample states: a fully equilibrated sample (when the first shear rate is zero) and a fully flowing sample (after a sufficiently long first shear). Each case reveals how entanglement density, polymer chain orientation, and stretching distinctly contribute to the stress overshoot. Molecular dynamics (MD) simulations can directly trace stresses and chain conformations, making them a powerful tool for testing competing interpretations of two-step shear. However, relaxation simulations of highly entangled polymer fluids are extremely time-consuming. Moreover, resolving the debate over the nonmonotonic behavior of $\sigma_{2\max}$ requires fur-

ther theoretical calculations and entanglement analysis.

In this context, our previous studies have investigated the nonlinear rheological behavior of polymer melts. During the startup shear,^[18] the steady-state shear rate-shear stress relationship was found to deviate from the predictions of the GLaMM theory^[19] (the most refined tube model) due to the shear banding. After shear cessation,^[20] the retraction time of the stretched primitive chain exceeded its Rouse time. Notably, applying a second shear after cessation of the first reproduces the two-step shear protocol. More recently, a novel entanglement analysis method, FT-PPA^[21] (Frenet-Trihedron-based Primitive Path Analysis), was proposed by one of the present authors and collaborators, which can reproduce the functionality of the widely used Z1/Z1+ code^[22,23] and provides additional analytical results.^[24] Both the results and the method can help address the key challenges explored in the two-step shear.

In this study, we performed MD simulations to investigate the rheological properties of highly entangled polymer melts. We aim to elucidate the mechanism governing the nonmonotonic behavior of $\sigma_{2\max}$ and provide new insights into the polymer dynamics of entangled fluids. First, we validated the linear viscoelastic response within the tube model framework. We then analyzed the stress response in the startup shear and successfully reproduced the nonmonotonic behavior of the second stress overshoot $\sigma_{2\max}$ by following the two-step shear protocol used in the experiments. Finally, we discussed the evolution of key physical quantities, including the normal stress component σ_{yy} , the tube segment orientation S_{xy} , the contour length of primitive chain L , and the entanglement number per chain Z . All these quantities relax monotonically toward equilibrium during the waiting period, but both S_{xy} and Z exhibit nonmonotonic behavior coinciding with the second stress overshoot $\sigma_{2\max}$. These correlations suggest that both the chain orientation and the entanglement density contribute to the stress response, and future theoretical developments should explicitly account for entanglement dynamics.

SIMULATION MODEL AND METHOD

We employed the Kremer–Grest (KG) model^[25] to simulate entangled polymer melts at a monomer density of $0.85\sigma^{-3}$, with chain length $N=300$. The monomers interact *via* a truncated and shifted 12-6 Lennard-Jones (LJ) potential,

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] \Theta(r_c - r) \quad (1)$$

where r , ϵ , σ , and $r_c = 2^{1/6}\sigma$ are the separation distance between monomers, the energy parameter, the monomer diameter, and the cutoff distance, respectively. $\Theta(x)$ is the Heaviside step function ($\Theta(x)=0$ for $x < 0$, and $\Theta(x)=1$ for $x \geq 0$). The constant $1/4$ is included to shift the potential so that it vanishes smoothly at r_c , thereby ensuring energy continuity. Monomers are connected *via* the finitely extensible nonlinear elastic (FENE) potential,

$$U_{\text{FENE}}(r) = -0.5kr_0^2 \ln \left[1 - (r/r_0)^2 \right] \quad (2)$$

where the spring constant $k = 30\epsilon/\sigma^2$, and the fully stretched bond length is $r_0 = 1.5\sigma$. To increase the entanglement density with the same chain length,^[26] a bending potential is incorpo-

rated,

$$U_{\text{bend}}(r) = k_b (1 - \cos\theta) \quad (3)$$

where θ represents the angle between two subsequent bonds and the bending parameter $k_b = 2.0\epsilon$. In this work, length, energy, and time are nondimensionalized by the monomer diameter (σ), energy parameter (ϵ), and the LJ timescale [$\tau = (m\sigma^2/\epsilon)^{0.5}$], respectively. The monomer mass (m) is set to 1. The dissipative particle dynamics (DPD) thermostat controls the temperature to $k_B T/\epsilon = 1$. The simulation box is set to $L_x = L_y = 6R_{g0}$ and $L_z = 4R_{g0}$, where x , y , and z refer to the flow, gradient, and vorticity directions, respectively. $R_{g0} = 12.7$ is the equilibrium root-mean-square radius of gyration.

To obtain the initial configurations, we employed the double-bridging-MD hybrid algorithm,^[27] which swapped bonds on two different chains, grafting the end of one chain onto the other chain and *vice versa*. All simulations were performed on the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) platform.^[28] The reported data were averaged over eight independent samples, and the integration time step (Δt) was 0.005.

Following the protocol of Wang *et al.*,^[10] we considered three rheological protocols (Fig. 1).

(a) Equilibrium: the sample freely evolves without shear and is used to obtain the linear relaxation modulus $G(t)$.

(b) Startup shear: the sample is sheared with a variable Rouse–Weissenberg number Wi_R , evolving from a quiescent state to a steady flow. The corresponding stress evolution is

shown schematically in Fig. 1(d1), with the stress overshoot labeled as σ_{Emax} .

(c) Two-step shear: the sample is first sheared to $\gamma = 1.5$ at $Wi_{R1} = 0.07$ or 2.85, then allowed to relax for a waiting time t_w , followed by a second shear at $Wi_{R2} = 2.85$. We separately analyzed the dynamics during the waiting period (c1) and the subsequent second shear stage (c2). The corresponding stress evolution is shown schematically in Fig. 1(d2), where the stress overshoot in the second shear is labelled as $\sigma_{2\text{max}}$.

Unlike rheological experiments, it is more computationally efficient to characterize the system through the relaxation modulus $G(t)$ rather than by small-amplitude oscillatory shear. First, the linear relaxation modulus is given by the stress autocorrelation function of the shear stress σ_{xy} ^[29] that is $G(t) = \langle \sigma_{xy}(t)\sigma_{xy}(0) \rangle$. The shear stress can be obtained from the Irving–Kirkwood formula, $\sigma_{xy} = [\sum m_i v_{ix} v_{iy} + \sum F_{ix} r_{iy}]/V$, where F_{ix} is the x -component of the total force acting on the monomer i located at r_i and V is the system volume. Subsequently, the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ were obtained by applying a Fourier transform to the linear relaxation modulus. Finally, using RepTate software,^[30] the storage and loss moduli were fitted with the Likhtman–McLeish (LM) theory^[31], and we obtained the entanglement number per chain, Z , the plateau modulus, G_e , the relaxation time of a tube segment, τ_e , the Rouse time, $\tau_R (= \tau_e Z^2)$, and the disengaged time $\tau_{d0} (= 3Z\tau_R[1 - 3.38/Z^{0.5} + 4.17/Z - 1.55/Z^{1.5}])$ are 14, 0.064, 409, 8.0×10^4 , and 1.2×10^6 , respectively. Therefore, the entanglement number per chain of our system is comparable to that of the experimental system studied by Wang *et al.*^[10]

RESULTS AND DISCUSSION

Linear Viscoelasticity

As shown in Fig. 2, the linear relaxation modulus $G(t)$ (black line) exhibits the characteristics of entangled polymer fluids. For $t < \tau_e$, polymer chains first undergo Rouse dynamics, and hence, $G(t)$ follows a power decay with time, $G(t) \sim t^{-0.5}$. In the intermediate regime ($\tau_e < t < \tau_{d0}$), the chains move into the tube regime, leading to a plateau in $G(t)$. For $t > \tau_{d0}$, the chains disengage from the tube and $G(t)$ decays further as the system relaxes. The storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ (red points) reflect the same underlying tube-model physics. At low frequencies, the chains are fully relaxed, and the system behaves as a Maxwell fluid, yielding $G'(\omega) \sim \omega^2$ and $G''(\omega) \sim \omega$. At high frequencies (short time scale), the Rouse dynamic delivers a scaling with an exponent of 0.5 for both $G'(\omega)$ and $G''(\omega)$ versus ω , which is consistent with the exponent in $G(t) \sim t^{-0.5}$. These results confirm the well-equilibrated status of the sample.

It should be noted that in experiments,^[32,33] the relaxation times τ_e and τ_{d0} are often obtained from the inverse of the high- and low-frequency crossovers of $G'(\omega)$ and $G''(\omega)$, respectively, while the plateau modulus G_e is determined from the value of $G'(\omega)$ at the minimum of $G''(\omega)$. Alternatively, the characteristic parameters of the system can be obtained by fitting the moduli with the Baumgaertel–Schausberger–Winter empirical model. In our previous study,^[18] the relaxation time was obtained using the time correlation functions of the unit end-to-end vector. Although the characteristic parameters obtained from different definitions do not differ in order

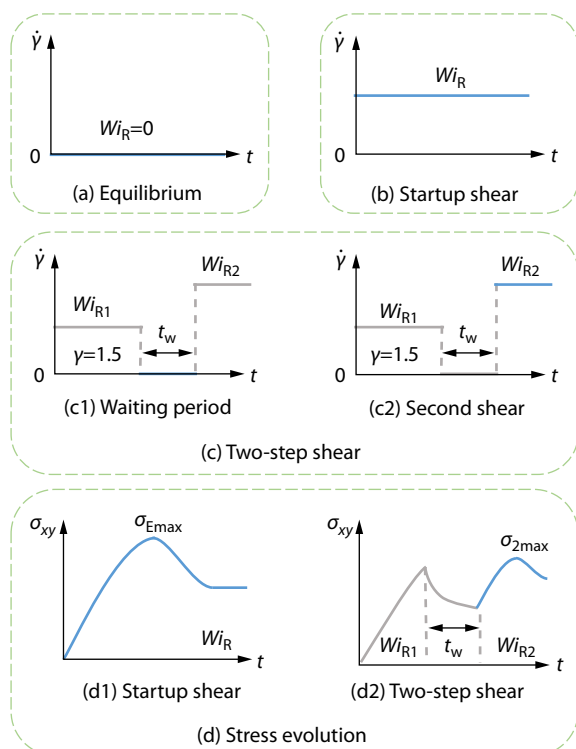


Fig. 1 Schematic illustration of the three protocols used in this work: (a) equilibrium, (b) startup shear, and (c) two-step shear. The blue line indicates the interest stage in each protocol. (d) Schematic illustration of the stress evolution under the startup shear and the two-step shear.

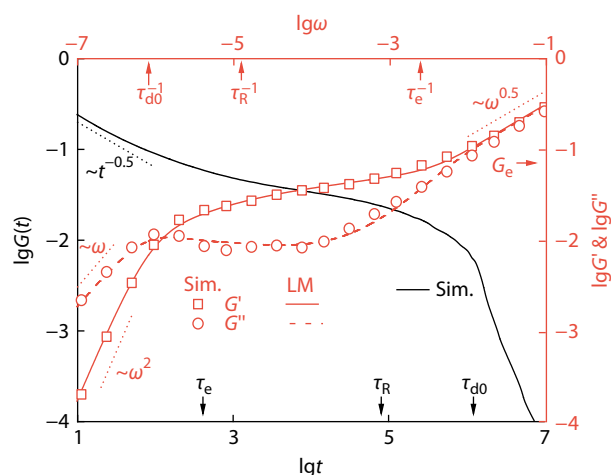


Fig. 2 Simulation results for linear relaxation modulus $G(t)$ (left and bottom axes) and its Fourier transforms (right and top axes): storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$. Red lines represent fits to the LM theory. For clarity, the fitting characteristic parameters are indicated: the plateau modulus G_e , the relaxation time of a tube segment τ_e , the Rouse time τ_R , and the disengaged time τ_{d0} .

of magnitude, to obtain the GLaMM theory^[19] predictions of the stress response of polymer fluids under different flow histories, the characteristic parameters G_e , τ_e , and Z are extracted from the LM theory^[31] fitting in this study. This choice is made because the analysis should be performed within the framework of the tube model, in which both the LM^[31] and GLaMM^[19] theories are formulated based on the curvilinear coordinates of the tube segment.

Startup Shear and Two-step Shear

Before discussing the stress response under the two-step shear, Fig. 3 shows the transient shear viscosity $\eta(t) = \sigma_{xy}(t)/\dot{\gamma}$ as a function of time under the startup shear, where the black line is the linear viscoelastic envelope (LVE) $\eta_{LVE} = \int G(t)dt$. At a short time (small strain), both the simulation (solid lines) and the GLaMM theory (dashed lines) results of $\eta(t)$ nearly coincide with the LVE for all shear rates, because the system satisfies the Boltzmann

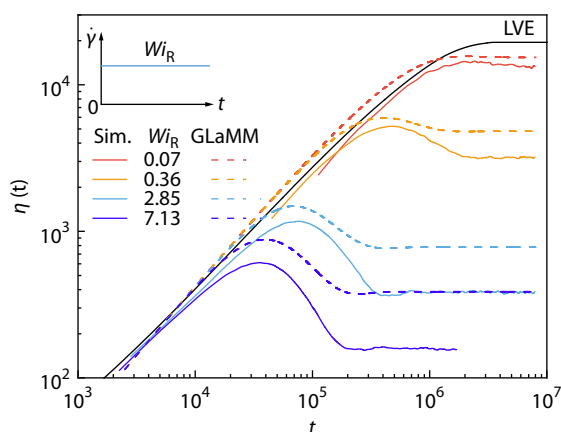


Fig. 3 Transient shear viscosity $\eta(t)$ as a function of time t under the startup shear with varying Wi_R . The solid lines, the dashed lines, and the black line represent simulation results, GLaMM predictions, and linear viscoelastic envelope (LVE), respectively.

superposition principle.^[34] For the lowest $Wi_R=0.07$, where the polymer chains are barely stretched, the GLaMM theory (red) accurately captures the simulation results over the entire time range. In the range of $Wi_R=0.36$ – 7.13 , a stress overshoot occurs and becomes pronounced as the shear rate ($\dot{\gamma} = Wi_R/\tau_R$ with the Rouse time τ_R) increases. In the framework of the tube model,^[35] this overshoot is attributed to the excessive orientation of the tube segments, and its growth is further associated with chain stretching. The GLaMM theory captures the stress response well before the overshoot but deviates significantly afterward. This stems from the assumption of homogeneous shear flow in the GLaMM theory. Our previous study^[18] on the same system revealed that the shear banding occurs sometime after the overshoot when $Wi_R > 0.71$ (defined as $Wi_R > 1.0$ in Ref. [18]), where the sample splits into two layers of differing shear rates. Furthermore, in the range of 0.36 – 7.20 , the steady-state shear stress from simulations^[18] remains nearly constant, whereas the theoretical prediction from the GLaMM theory increases monotonically. In other words, the flow state changes the stress response.

To compare with the tube model, Wang *et al.*^[10,12] performed the two-step shear under the condition of homogeneous shear flow. Specifically, the shear rate remains uniform along the gradient direction, resulting in homogeneous deformation. However, under certain conditions, the system can split into two layers with different local shear rates along the gradient direction, leading to nonhomogeneous deformation^[18], commonly referred to as shear banding. According to Ref. [18], the simulations always maintain a homogeneous shear flow at $Wi_R=0.07$; even at $Wi_R=2.85$, the flow field remains homogeneous as long as the strain $\gamma \leq 5$ ($t \leq 1.4 \times 10^5$). Thus, we adopted a two-stage shear protocol: the sample was first sheared to $\gamma=1.5$ at $Wi_{R1}=0.07$ or 2.85 , and then relaxed for a waiting time t_w , followed by a second shear at $Wi_{R2}=2.85$. The simulation stress in the first shear (startup shear) was in close agreement with the GLaMM theory predictions (see Fig. 3). Therefore, the GLaMM theory is also expected to predict the stress overshoot σ_{2max} in the second shear.

Fig. 4(a) shows the stress overshoot in the second stage σ_{2max} relative to σ_{Emax} as a function of waiting time t_w . σ_{Emax} denotes the stress overshoot obtained by directly applying $Wi_R=2.85$ to an equilibrium sample, that is, the overshoot in Fig. 3. For comparison, we also include Wang *et al.*'s experimental results^[10] for polybutadiene solutions with $Z=18$. Because of the precision of the stress calculations, the simulation data (red) displayed a quasi-plateau around the minimum of σ_{2max} . Nevertheless, both the simulation and the experiment exhibit the same nonmonotonic trend: σ_{2max} first decreases and then increases with increasing t_w , with the minimum σ_{2max} reaching approximately 94% of σ_{Emax} . This consistency indicates the effectiveness of the simulation. We note that because of the different definitions of the Rouse time (Wang *et al.* used $\tau_{d0} = 3Z\tau_R$ relative to ours $\tau_{d0} = 3Z\tau_R[1 - 3.38/Z^{0.5} + 4.17/Z - 1.55/Z^{1.5}]$), our σ_{2max} is still lower than σ_{Emax} within $15\tau_R$ (about $1\tau_{d0}$), and the time corresponding to the minimum also differs from the experiment. When the time scale is normalized by the disengaged time τ_{d0} , the simulation and experimental results nearly converge slightly beyond the minimum (see Fig. S1 in the electronic supplementary, ESI). Additionally, the GLaMM theory^[19] is a multimode

model, and the RP theory^[16] is its simplified single-mode version. At low shear rates, the stress involves multiple modes, whereas at high shear rates, it is dominated by the longest mode. Therefore, Fig. 4(a) differs from the simulation, whereas Fig. 4(b) (high shear rate) agrees well with the simulation. Finally, the GLaMM theory prediction (red dash) $\sigma_{2\max}/\sigma_{E\max}=0.96$ agrees well with the simulation at $t_w=0$, but the theory predicts an imperceptible minimum around the Rouse time τ_R . This is because the primitive chain follows the Rouse dynamics and thus undergoes little stretching at $Wi_R=0.07$. The influence of the strain γ of the first shear on $\sigma_{2\max}$ is shown in Fig. S2 (in ESI). At $\gamma=1.0$, the stress minimum still appears with an amplitude (the difference in $\sigma_{2\max}$ between $t_w=0$ and $t_w=t_{\min}$) comparable to that at $\gamma=1.5$. However, at $\gamma=2.5$, the minimum becomes much less pronounced. The latter is consistent with experimental findings,^[4–8] that is, the stress minimum disappears when the first shear directly reaches the steady state.

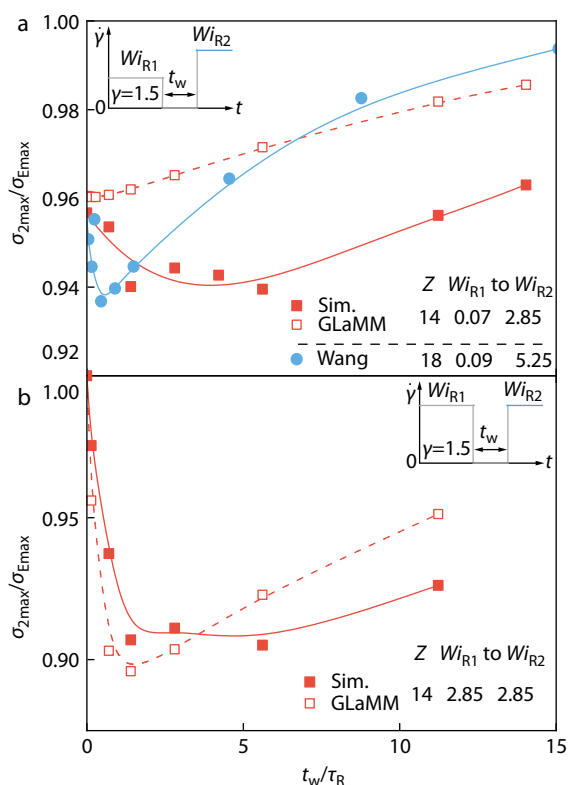


Fig. 4 Stress overshoot in the second shear $\sigma_{2\max}$ as a function of waiting time t_w for a two-step shear from (a) $Wi_{R1}=0.07$ to $Wi_{R2}=2.85$ and (b) $Wi_{R1}=2.85$ to $Wi_{R2}=2.85$. $\sigma_{E\max}=0.0415$ denotes the stress overshoot under the startup shear with $Wi_R=2.85$. Solid squares, open squares, and solid circles represent simulation results, GLaMM predictions, and experiment results, respectively.

To further examine the influence of chain stretching or shear rate, the rate of the first shear Wi_{R1} was increased to 2.8. As shown in Fig. 4(b), the GLaMM theory predicts a distinct minimum around the Rouse time τ_R as the contour length of the primitive chain retracts back to equilibrium near the Rouse time. We observed that the theoretical prediction aligns well with the simulation results, although there is a lack

of corresponding experimental data for comparison. Analyzing these discrepancies is essential for a better understanding of the mechanisms underlying the stress response in two-step shear.

Mechanism of Nonmonotonic $\sigma_{2\max}$ versus Waiting Time

First, we examined the prediction of Graham *et al.*^[14,15] for the normal stress component σ_{yy} . Rotational rheometers can measure the first normal stress difference $N_1 = \sigma_{xx} - \sigma_{yy}$, but they cannot directly access the normal stress components σ_{xx} and σ_{yy} . In contrast, MD simulations calculate all components of the stress tensor. Fig. 5 shows the stress component σ_{yy} as a function of waiting time t_w following shear cessation at a strain of $\gamma=1.5$. As explained by Graham *et al.*,^[14] the Rouse dynamics of the primitive chains lead to a minimum in σ_{yy} around the Rouse time τ_R . However, this minimum is almost indiscernible at a lower shear rate $Wi_R=0.07$ (red dash), whereas it becomes pronounced at a higher shear rate of $Wi_R=2.85$ (blue dash). Consequently, under the condition of $Wi_{R1}=2.85$, the GLaMM theory predicts a stronger nonmonotonicity in $\sigma_{2\max}$ (see Fig. 4b). In contrast, the simulation results (solid lines) do not exhibit such a pronounced minimum, but instead relax monotonically toward equilibrium. This suggests that the stretching of the primitive chain persists for times much longer than the Rouse time, and the nonmonotonic behavior of $\sigma_{2\max}$ is not related to the evolution of the normal stress σ_{yy} during the waiting period.

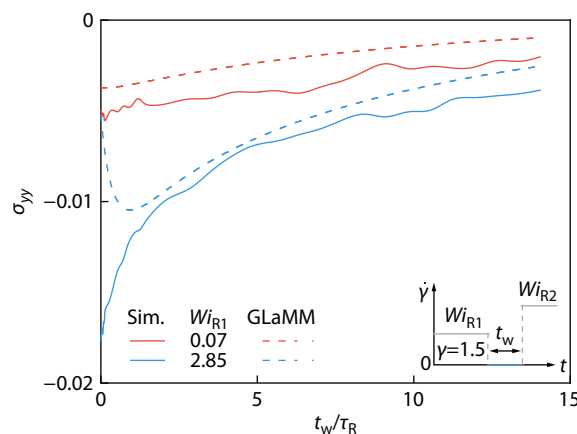


Fig. 5 Normal stress component σ_{yy} as a function of waiting time t_w during the waiting period. Solid and dashed lines are simulation results and GLaMM predictions, respectively.

Within the framework of the tube model, the shear stress in polymer fluids is a function of both the chain stretching and the orientation. To further analyze chain orientation and stretching, we followed the physical picture of the tube model and divided the chain into segment blobs, each consisting of 20 (about entanglement length N_e) monomers. The tube segment vector $\mathbf{R}$ is defined as the line connecting the centers of mass of two sequential blobs. The tube segment orientation is defined as $S_{xy} = \langle R_x R_y / R^2 \rangle$, and the contour length is then given by $L = |\sum \mathbf{R}|$. The shear stress σ_{xy} is taken as the orientational part multiplied by the stretching factor,^[35,36]

$$\sigma_{xy} \sim S_{xy} (L/L_0)^2 \quad (4)$$

where S_{xy} , L , and L_0 ($=85.6$) are the tube segment orientation, the

contour length of the primitive chain, and the equilibrium contour length, respectively. At a relatively small Wi_R , the overshoot of σ_{xy} is most likely governed by the behavior of S_{xy} , which reaches a maximum at a strain (γ is about 2).

As proposed by Ianniruberto and Marrucci^[17] (see the schematic in Fig. 6a), during the waiting period after the first shear, part of the tube segments within the primitive chains relax (black blocks), while the remaining segments retain their orientation (blue block). In the subsequent second shear, the blue block undergoes further orientation, whereas the black blocks reorient from a relaxed state. The combined contributions from these two parts determine the overall tube segment orientation S_{xy} . The ratio between the black and blue blocks depends on t_w , which leads to a nonmonotonic variation in S_{xy} with t_w . In other words, the nonmonotonicity of σ_{2max} reflects the memory effect of entangled polymer fluids. Fig. 6(b) shows the evolution of S_{xy} during the second shear. The strain (symbols) corresponding to the orientation overshoot increases with the waiting time t_w and eventually γ approaches 2. This indicates that chain orientation monotonically relaxes toward equilibrium during the waiting period after the first shear (see Fig. S3 in ESI). Importantly, Fig. 6(b) also reveals that the height of the orientation overshoot first decreases and then increases with increasing t_w . This implies that the nonmonotonic behavior of σ_{2max} may be related to the orientation of the tube segment.

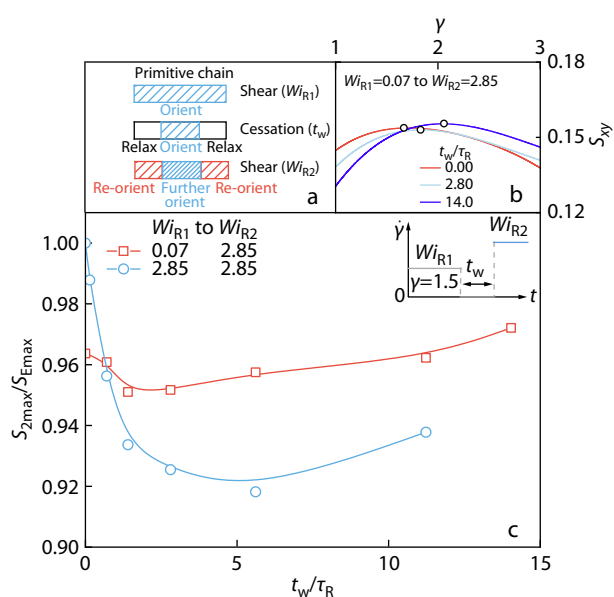


Fig. 6 (a) Schematic illustration of the evolution of tube segment orientation under the two-step shear; (b) Tube segment orientation S_{xy} in the second shear as a function of strain γ for varying waiting time t_w , with symbols indicating the overshoot; (c) Tube segment orientation S_{2max} evaluated at stress overshoot σ_{2max} as a function of t_w . $S_{Emax}=0.158$ corresponds to the tube segment orientation at the stress overshoot under the startup shear with $Wi_R=2.85$.

Owing to chain stretching, the strain corresponding to the orientation overshoot is smaller than that of the stress overshoot σ_{2max} . Therefore, we focus on the tube segment orientation S_{2max} evaluated at the strain corresponding to σ_{2max} . Fig. 6(c) presents the evolution of S_{2max}/S_{Emax} with t_w , where

S_{Emax} denotes the tube segment orientation at the stress overshoot under the startup shear $Wi_R=2.85$. Figs. 4 and 6(c) show similar trends between S_{2max}/S_{Emax} and $\sigma_{2max}/\sigma_{Emax}$. Specifically, both ratios are approximately 0.96 at $t_w=0$, and reach a minimum of about 95% for $Wi_{R1}=0.07$ to $Wi_{R2}=2.85$ (Fig. 4a); whereas for $Wi_{R1}=2.85$ to $Wi_{R2}=2.85$ (Fig. 4b), the minimum decreases to about 90%. This close correspondence suggests that the evolution of the orientation function is strongly correlated with the stress overshoot response in the two-step shear. Furthermore, our simulations support the interpretation proposed by Ianniruberto and Marrucci^[17], that is, the non-monotonicity of σ_{2max} originates from the memory effect of the tube segment orientation.

S_{2max} exhibits a similar nonmonotonic trend to σ_{2max} , but Eq. (4) indicates that chain stretching also contributes to the stress response. Meanwhile, the physical picture presented in Fig. 6(a) is, in principle, applicable to other physical quantities as well, including the contour length and the entanglement number per chain. Because the chain is barely stretched at $Wi_R=0.07$, we first focus on the evolution of the contour length during the waiting period for the first shear at $Wi_{R1}=2.85$, as shown in Fig. 7. The monotonic recovery of L toward equilibrium is consistent with the monotonic increase in σ_{yy} (see Fig. 5). Moreover, the relaxation of the contour length follows a two-step process: the first stage occurs in the order of τ_R , consistent with the chain retraction time scale for a chain executing Rouse dynamics in a smooth tube, and the second stage is a slower relaxation on a significantly longer time scale of about $10\tau_R$, suggesting that there may be additional friction forces impeding chain relaxation and suppressing the non-monotonicity in σ_{yy} .

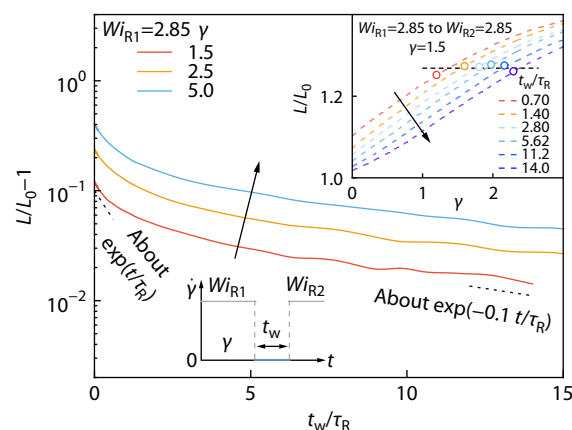


Fig. 7 Normalised contour length of the primitive chain L/L_0 as a function of waiting time t_w during the waiting period for $Wi_{R1}=2.85$. The inset shows L/L_0 in the second shear as a function of strain γ for varying waiting time t_w , with symbols indicating the values at the strains corresponding to σ_{2max} . The equilibrium contour length $L_0=85.6$.

Furthermore, the inset of Fig. 7 shows the evolution of L/L_0 in the second shear, where the symbols indicate the values at the strains corresponding to σ_{2max} . Although L/L_0 at a fixed strain decreases with the waiting time t_w , the symbol heights are nearly identical, with differences of less than 2%, indicating that the contour length of the primitive chain at the stress overshoot is essentially independent of t_w . According to Eq.

(4), the stress overshoot $\sigma_{E_{\max}}$ in the startup shear and the stress overshoot $\sigma_{2\max}$ in the second shear of the two-step shear can be expressed as:

$$\frac{\sigma_{2\max}}{\sigma_{E_{\max}}} \sim \frac{S_{2\max}}{S_{E_{\max}}} \left(\frac{L_{2\max}}{L_{E_{\max}}} \right)^2 \quad (5)$$

where $L_{E_{\max}}$ and $L_{2\max}$ correspond to the contour length at the stress overshoot under the startup shear and the two-step shear, respectively. For the two-step shear with $Wi_{R1}=2.85$ to $Wi_{R2}=2.85$, at waiting time around $5\tau_R$, both $\sigma_{2\max}/\sigma_{E_{\max}}$ and $S_{2\max}/S_{E_{\max}}$ decrease to about 90%, while $L_{E_{\max}}/L_{2\max}$ remains close to 99%. Therefore, the nonmonotonic variation in $\sigma_{2\max}$ is most likely governed by the behavior of S_{xy} .

Finally, we do not exclude the possibility that chain disentanglement plays a role in the stress response. The entanglement number per chain Z is not directly measurable in experiments and is typically inferred indirectly from the mechanical response. In this study, we adopt a recently developed entanglement analysis method from our previous study.^[21] Our method involves two main steps: generating smooth primitive paths (PPs) and subsequently analyzing their geometry via the Frenet trihedron. Specifically, following an energy minimization adapted from Ref. [37], we fixed the chain ends, disabled intrachain excluded-volume and bending potentials, retained interchain interactions and FENE bonds, and cooled the temperature toward $T=0$. This yields PPs with characteristic sharp bends at entanglement points, where paths are in mutual contact. These features are quantified using the Frenet trihedron, which captures the local curvature and torsion in a 3D space. At equilibrium, we determined the entanglement number per chain $Z_F=20$ for chain length $N=300$. Notably, Z_F differs from $Z=14$ predicted by the LM theory because of the different definitions of entanglement used in the two approaches. Nevertheless, existing theories do not define entanglements from a microscopic perspective, and the entanglement numbers obtained from different analysis methods should correlate positively with the actual entanglements.

Fig. 8(a) shows the entanglement number per chain Z_F after a strain of 1.5 at varying shear rates. Polymer chains undergo orientation and stretching under shear, facilitating interchain sliding and disentanglement. A higher shear rate intensifies this process, resulting in a lower Z_F at $t_w=0$. However, Z_F increases monotonically toward its equilibrium value $Z_F=20$. In other words, from the perspective of the entanglement number per chain, no further damage to the entanglement network occurs during the waiting period. The monotonic growth of Z_F reflects the concurrent monotonic recovery of stress (Fig. 5), chain orientation (Fig. 6b), and chain stretching (Fig. 7) toward equilibrium. Similar to the inset of Fig. 7, the inset of Fig. 8(a) presents the evolution of $Z_F/Z_F=20$ in the second shear, and the symbols also indicate the values $Z_{2\max}$ at the strains corresponding to $\sigma_{2\max}$; the heights of $Z_{2\max}$ exhibit a nonmonotonic dependence on t_w , which contrasts with the nearly unchanged trend observed in the inset of Fig. 7.

As shown in Fig. 8(b), $Z_{2\max}/Z_{E_{\max}}$ exhibits a minimum that decreases with increasing Wi_{R1} , and $Z_{E_{\max}}$ corresponds to the entanglement number per chain at the stress overshoot under the startup shear with $Wi_R=2.85$. Notably, Fig. 8(b) shows a minimum and a trend similar to those observed in Figs. 4

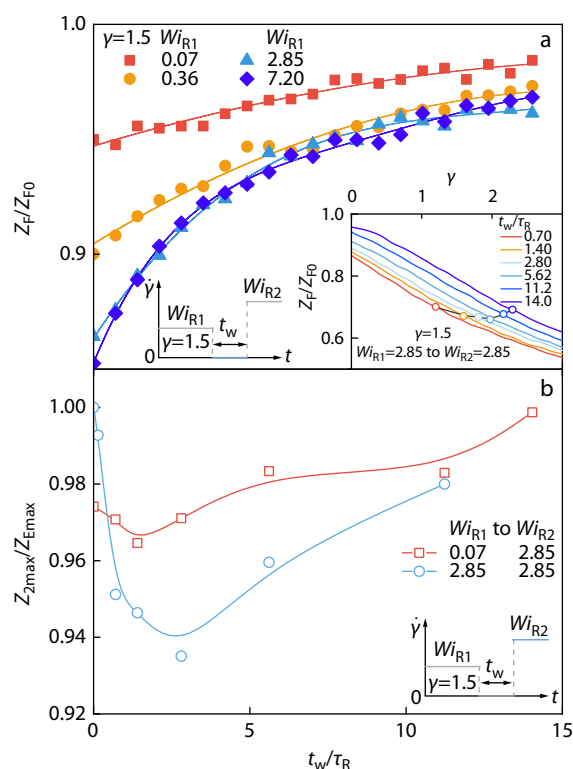


Fig. 8 (a) Normalised entanglement number per chain Z_F/Z_{F0} as a function of waiting time t_w during the waiting period. The inset shows Z_F/Z_{F0} in the second shear as a function of strain γ for varying waiting time t_w , with symbols indicating the values at the strains corresponding to $\sigma_{2\max}$. (b) Entanglement number per chain $Z_{2\max}$ evaluated at stress overshoot $\sigma_{2\max}$ as a function of t_w . $Z_{E_{\max}}=13.86$ corresponds to the entanglement number per chain at the stress overshoot under the startup shear with $Wi_R=2.85$.

(stress $\sigma_{2\max}$) and 6(b) (orientation $S_{2\max}$). For example, for the two-step shear with $Wi_{R1}=2.85$ to $Wi_{R2}=2.85$, at waiting time around $5\tau_R$, $Z_{2\max}/Z_{E_{\max}}$, $\sigma_{2\max}/\sigma_{E_{\max}}$, $S_{2\max}/S_{E_{\max}}$ all decrease to approximately 90%. This similarity suggests that the entanglement density also contributes to the stress response. It should be noted that during the waiting period, the entanglement gradually recovers toward equilibrium. Therefore, as shown in the inset of Fig. 8(a), at the onset of the second shear, $Z_F(t_w=0\tau_R)$ is smaller than $Z_F(t_w=2.85\tau_R)$, but at the second stress overshoot, $Z_F(t_w=0\tau_R)$ is larger than $Z_F(t_w=2.85\tau_R)$. This phenomenon suggests that the strength of entanglement may be related to the entanglement topology. Although the entanglement number per chain increases with waiting time, polymer chains require a longer time to form complex entanglement structures, and only after this process is completed can the system be considered fully equilibrated. This may explain why the recovery of the stress overshoot in the second shear following the steady state occurs over a timescale longer than the orientational relaxation time. Starting from an ordered structure, simulations require a very long time to reach equilibrium in entangled polymer melts, which motivates the use of the double-bridging-MD hybrid algorithm^[27] for rapid equilibration. Finally, this nonmonotonic variation in entanglement strength may, to some extent, reflect the idea of Wang *et al.*^[10] regarding further damage to

the entanglement network. A promising direction for future work is to further quantify the degree of spatial correlation between the entanglements.

CONCLUSIONS AND OUTLOOK

In summary, we investigated the stress overshoot during the second shear in a two-step shear protocol applied to entangled polymer melts. We first calculated the linear relaxation modulus $G(t)$ using the stress autocorrelation function, from which the corresponding storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ were obtained. We then determined the characteristic relaxation times in the tube model by fitting these moduli using Likhtman–McLeish theory. Finally, these relaxation times were used to generate the GLaMM theory predictions of the shear stress response in the two-step shear protocol. In homogeneous flow, we reproduced the experimentally observed non-monotonic behavior of the stress overshoot $\sigma_{2\max}$ in the second shear, where $\sigma_{2\max}$ first decreases and then increases with increasing waiting time between the two shear steps. Although the GLaMM theory captures the stress response during the first shear, it fails to describe the nonmonotonic behavior of $\sigma_{2\max}$ in the second shear. Furthermore, during the waiting period, the normal stress component σ_{yy} does not exhibit the nonmonotonic evolution predicted by the GLaMM theory but instead relaxes monotonically toward equilibrium. Correspondingly, the tube segment orientation, the contour length of the primitive chain, and the entanglement number per chain also exhibited monotonic relaxation to equilibrium. At the strain corresponding to $\sigma_{2\max}$, the contour length of the primitive chain is nearly independent of the waiting time, indicating that the contribution of chain stretching to the stress remains nearly constant. In contrast, both the tube segment orientation and entanglement number per chain exhibit a nonmonotonic dependence on the waiting time, similar to the behavior of $\sigma_{2\max}$. Although the two explanations from Ianniruberto and Marrucci^[17] and Wang *et al.*^[10] are rooted in distinct physical pictures, our results suggest that both orientation and entanglement contribute comparably to the stress response in the second shear.

In general, the stress overshoot starting from an equilibrium state is attributed to the tube segment orientation, whereas that starting from a steady flow state followed by a waiting period is attributed to entanglement recovery. From the perspective of the present methodology, the former corresponds to a first shear of zero duration, whereas the latter corresponds to a first shear of infinite duration. The two-step shear protocol examined in this study naturally falls between these two limiting cases. Therefore, it is reasonable to infer that the contribution of entanglements to the stress response increases with the duration of the first shear. Within the present study, the evolutions of orientation and entanglement with waiting time are very similar, so the entanglement contribution can be effectively incorporated into the orientation effect. However, as the duration of the first shear continues to increase, the entanglements are expected to become the dominant factor. However, the DE theory assumes a fixed entanglement number per chain, and the GLaMM theory predicts an increase in entanglements at $W_R > 1$.^[9] This contradiction has motivated researchers to incorporate disentanglement and re-entanglement kinetics into the existing theory.

Dolata and Olmsted^[38] recently proposed a constitutive model that describes polymer disentanglement under flow and discussed the entanglement kinetics under steady shear flow using MD simulation. In the future, theoretical and computational efforts should focus on the influence of flow history on transient shear processes, which is critical for advancing and refining our understanding of entangled polymer fluid dynamics.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3481-9>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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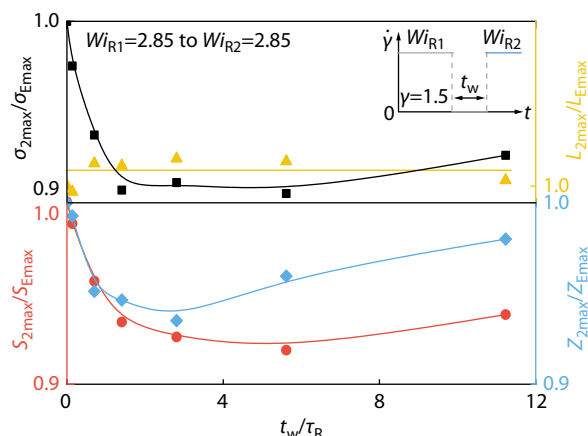
Graphical Abstract

Nonmonotonic Stress Overshoot in Entangled Polymer Melts under Two-step Shear

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Molecular dynamics simulations uncover the microscopic origin of the second stress overshoot $\sigma_{2\max}$ in two-step shear. The nonmonotonic $\sigma_{2\max}$ results from coupled variations of tube orientation and entanglement number, highlighting the need for a unified theoretical framework.



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