Comment on "Relating Chain Conformations to Extensional Stress in Entangled Polymer Melts"

Based on nonequilibrium molecular dynamics simulations of entangled polymer melts, a recent Letter [1] claims that the rising extensional stress is *quantitatively* consistent with the decreasing entropy of chains at the equilibrium entanglement length. We point out that quite the opposite is true: the intrachain entropic stress arising from individual entanglement strands agrees with the total "macroscopic" stress under only very limited conditions.

We repeated the simulations of uniaxial extension for the $N = 500$ and $k_{\mathrm{bend}} = 1.5$ system, using the same approach employed in Ref. [1], i.e., integrating the SLLOD equations of motion [2] with the generalized Kraynik-Reinelt boundary conditions [3,4]. The inverse Langevin function L^{-1} [5], originally derived for freely jointed chains, might be used to estimate the entropic extensional stress in the large-strain limit:

$$\Sigma_e(n) = \frac{\rho k_B T}{C_n} \left\langle \frac{r(n)}{nb} L^{-1}\left(\frac{r(n)}{nb}\right) P_2(\cos\theta_n) \right\rangle, \qquad (1)$$

where n is the number of bonds within a coarse-grained segment, b is the bond length, and the characteristic ratio $C_n = \langle r^2(n) \rangle_0 / nb^2$ is approximately equal to C_∞ at $n = N_e$. Reference [1] used a similar equation. However, Eq. (1), in its present form, does not work for the semiflexible chain model considered here: the maximum extension limit nb can be exceeded in simulation for an *individual* strand, particularly for small n and large deformation, because of the "soft" nature of the FENE bonds. In passing, we note that Ref. [1] did not distinguish the Legendre function $P_2(\cos\theta_n)$ and the nematic order parameter, i.e., $\langle P_2(\cos\theta_n) \rangle$, in their Eq. (1), which is misleading.

Figure 1 shows the evolution of tensile stress Σ and entropic tensile stress $\Sigma_e(N_e)$ during a continuous extension simulation at $\mathrm{Wi}_R = 25$, where $\Sigma_e(N_e)$ is evaluated according to the Hookean spring law and Eq. (1) of Ref. [1]. Regardless of the method, the entropic tensile stress at the entanglement length scale is substantially lower than the total stress Σ at relatively small strains. This trend is true for all the other rates we examined, ranging from $\mathrm{Wi}_R = 0.5$ to 50. Unlike the case of large deformation, there should be no ambiguity in calculating the classical intrachain entropic stress [6] in the small-strain limit. The discrepancy between $\Sigma_e(N_e)$ and Σ at relatively small strains clearly suggests that there is more to the story than the simple picture Ref. [1] paints. Generally speaking, "quantitative" agreement between the entanglement strand entropic stress $\Sigma_e(N_e)$ and the total stress can be found only in a very limited range of ϵ_H, even if $\Sigma_e(N_e)$ is computed through Eq. (1) of Ref. [1]. In fact, the steady-state data in Fig. 4 of Ref. [1] indicate a lack of quantitative agreement at tensile stress higher than 0.1. Lastly, while the variation of the potential energy of the FENE bonds is indeed small even at high extension rates in these simulations, the bending energy does change substantially (inset of Fig. 1) when the polymer coil is unraveled at large strains ($\epsilon_H \gg 1$) and high rates. This is a direct violation of the assumption of purely entropic stress.

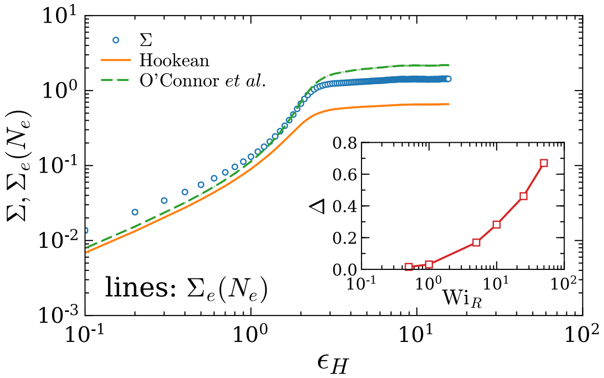

FIG. 1. Evolution of tensile stress Σ and entropic tensile stress $\Sigma_e(N_e)$ as a function of Hencky strain ϵ_H for $N = 500$ and $k_{\mathrm{bend}} = 1.5$ at Rouse Weissenberg number $\mathrm{Wi}_R = 25$. The (orange) solid line and (green) dashed line represent the entropic stresses $\Sigma_e(N_e)$ evaluated according to the Hookean spring law and Eq. (1) of Ref. [1], respectively. The inset shows the relative change bond bending potential $\Delta = (\langle U_{\mathrm{bend}} \rangle_0 - \langle U_{\mathrm{bend}} \rangle_{\mathrm{steady}}) / \langle U_{\mathrm{bend}} \rangle_0$ in steady state as a function of Wi_R.

In summary, we show that the central result of Ref. [1] is premature: analysis of the full simulation trajectory reveals that the total extensional stress and the intrachain entropic stress at the equilibrium entanglement length generally does not agree with each other quantitatively, especially at relatively small deformation. Furthermore, in light of the ongoing debate about the origin of stress in entangled polymer melts in the recent literature [7–11], the conclusion of Ref. [1], which is based on an incomplete and questionable analysis of a limited range of the simulation trajectory, is particularly unconvincing.

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