3980 *Macromolecules* **2010**, *43*, 3980–3983
DOI: 10.1021/ma9027849

Macromolecules
NOTE

Comment on "Entangled Polymer Melts: Relation between Plateau Modulus and Stress Autocorrelation Function"

Alexei E. Likhtman*,[†] **and Sathish K. Sukumaran**[‡]

[†]*Department of Mathematics, University of Reading, Whiteknights, Reading RG6 6AX, U.K., and*
[‡]*Graduate School of Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan*

Received December 18, 2009

In their recent paper,[1] Lee and Kremer report results on the stress autocorrelation function for flexible and slightly semiflexible bead−spring model polymers calculated using molecular dynamics (MD) simulations.[2] The flexible and the semiflexible chains consisted of $N = 100$ beads corresponding to about 2 and 4 entanglement segments per chain, respectively. Lee and Kremer concluded that "Plateau values of the SAF compare well with plateau values predicted from the entanglement length evaluated via primitive path analysis (PPA)". In particular, the plateau extracted from the semiflexible system with about 4 entanglements from the stress autocorrelation function (SAF) without invoking any theory or model is in excellent agreement with that from the PPA of considerably longer chains.[3]

This, however, contradicts our recently published results,[4] where we utilized an efficient method for calculating correlation functions on the fly using multiple-τ correlators. We calculated stress autocorrelation functions for a wide range of chain molecular weights and chain stiffnesses and showed that none of them display an unambiguous plateau for the moderate molecular weights accessible to MD simulations. Zhou and Larson,[5] while studying comparable systems using MD, also made a similar point. In light of these, we argued that one has to use a model in order to extract the plateau modulus and demonstrated that the slip-spring model performs creditably, whereas the tube model is not adequate for such mildly entangled systems. Also, we believe that this issue is well-known in experimental rheology, where the plateau modulus is never extracted from any plateau in the linear rheology data, especially for chains with molecular weights below about 10 times the entanglement molecular weight (see, for instance, ref 6, pages 150−152). To illustrate this, in Figure 1 we show experimental data on monodisperse polyisoprene from ref 7 for molecular weights 23 and 226 kg/mol, corresponding to approximately 5 and 47 entanglement segments per chain, respectively. It is clear that neither the linear nor the logarithmic plot allows an unambiguous definition of a plateau for chains with 5 entanglements. Even for chains 10 times as long, the visual definition is, at best, ambiguous. Therefore, we believe that the most reliable method of extracting the plateau is to fit the data to an adequate theory (the horizontal line and the caption in Figure 1).

To further clarify the matter, we simulate exactly the same systems studied by Lee and Kremer[1] but use our correlators to calculate stress autocorrelation functions. We first report results for the flexible chains with $N = 100$. In this case the chains are made of purely repulsive Lennard-Jones beads connected by FENE springs. In Figure 2 the line shows results from ref 1, and the circles with the error bars are our results from ref 4. In order to improve the accuracy and obtain an error estimate, we run 10 independent simulations and average the results. The error bars show standard deviations divided by $\sqrt{10}$. The first point to note is that the results for $G(t)$ with and without using the correlators agree within the statistical error, which is evidently significantly larger if one does not use correlators. In ref 1 around the terminal time, the error bars in the $G(t)$ data seem to be of the same magnitude as the signal itself, making it impossible to draw conclusions about the functional form of $G(t)$. The less noisy results from ref 4 clearly show that there is no visible plateau in either the linear or the logarithmic plots of $G(t)$. Moreover, the slope of $G(t)$ for $N = 100$ is never larger than -0.5 (as was demonstrated in ref 4), which is consistent with pure Rouse theory. Thus, apart from a slightly longer terminal time than that predicted by Rouse theory, there is virtually no information about entanglements in this $G(t)$ signal. Hence, any algorithm that claims to extract a plateau from such data has to be treated with skepticism.

Now we turn our attention to the semiflexible polymer system studied by Lee and Kremer.[1] In addition to the potentials mentioned in the flexible case, the monomers experience a weak bending potential. Following Lee and Kremer,[1] we use for the bending potential

$$U_{\text{bend}} = k_\theta \sum_{i=2}^{N-1} (1 - \cos(\theta_i - \pi)); \quad k_\theta = 1.5 \tag{1}$$

Here θ_i is the angle between two bonds emerging from monomer i. We exercised care to ensure that the parameter values we used were identical to that of Lee and Kremer, but we also use our correlators to calculate the stress autocorrelation functions. Figure 3 shows results for the semiflexible Kremer−Grest model with $N = 100$. This time the error bars were generated using 35 independent simulation runs.

The most glaring feature of Figure 3 is the serious discrepancy between our results and those of Lee and Kremer. It is clear that this discrepancy persists over the entire range of time shown. Even at short times where the statistical errors in both data sets are small, the two results are discernibly different. This suggested a careful examination of all the expressions used in the stress calculation. Below we provide the necessary equations for the evaluation of the instantaneous stress. We calculate this stress using the virial expression

$$\sigma^{\alpha\beta} = -\frac{1}{V}\left(\sum \frac{p_i^\alpha p_i^\beta}{m_i} + \frac{1}{2}\sum_{j\neq i} r_{i,j}^\beta f_{i,j}^\alpha\right) \tag{2}$$

---

*To whom correspondence should be addressed. E-mail: a.likhtman@reading.ac.uk.

where $\mathbf{p}_i$ and m_i are respectively the momentum and mass of particle i. The vector $\mathbf{r}_{i,j}$ is related to the position vectors of particles i and j, $\mathbf{r}_i$ and $\mathbf{r}_j$, through $\mathbf{r}_{i,j} \equiv (\mathbf{r}_i - \mathbf{r}_j)$. The α and β denote spatial components of the respective vectors. This expression is obtained from

$$\sigma^{\alpha\beta} = -\frac{1}{V}\left(\sum \frac{p_i^{\alpha} p_i^{\beta}}{m_i} + \sum r_i^{\beta} f_i^{\alpha}\right) \qquad (3)$$

by writing the force acting on particle i as a sum of contributions due the other particles in the system coupled with $\mathbf{f}_{i,j} = -\mathbf{f}_{j,i}$. Using $\mathbf{f}_{i,j} = -\nabla_{\mathbf{r}_{i,j}} U$ automatically ensures the appropriate behavior under an index exchange and allows one to think of $\mathbf{f}_{i,j}$ as the force exerted by particle j on particle i. For calculating stresses in simulations with periodic boundary conditions, eq 2 is the preferred form.[10]

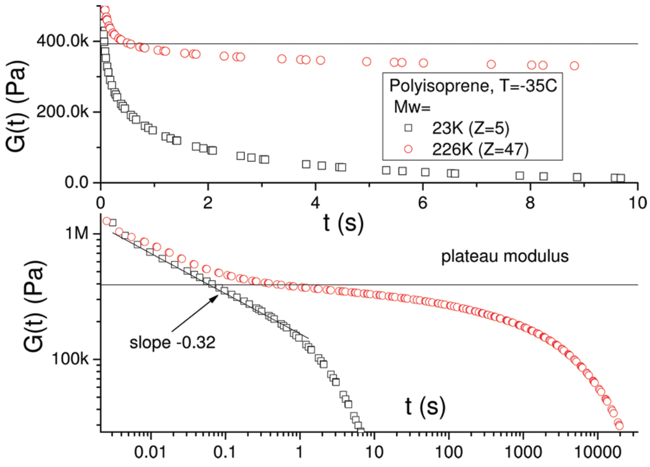

Figure 1. Experimental stress relaxation function of monodisperse polyisoprene for molecular weights 23 kg/mol (squares) and 226 kg/mol (circles) from ref 7, obtained by fitting a set of Maxwell modes to the loss and storage moduli using the Reptate[8] software. The horizontal lines indicate the value of the plateau modulus $G_N^0 = {}^4/_5 G_e$ obtained by using the theory in ref 9.

For the flexible case, our results agree with those of Lee and Kremer. Hence, below we will restrict our attention to the contribution to the stress from the bending potential. The contribution to the force acting on particle i due to the bending potential, $\mathbf{f}_i^{\mathrm{b}}$, can be used in eq 3 to calculate the bending contribution to the instantaneous stress. For the bending potential given in eq 1, this force can be written as $\mathbf{f}_i^{\mathrm{b}} = \mathbf{f}_{i,i-1}^{\mathrm{b}} - \mathbf{f}_{i+1,i}^{\mathrm{b}}$. The force $\mathbf{f}_{i,i-1}^{\mathrm{b}}$ is given by

$$\begin{aligned}\mathbf{f}_{i,i-1}^{\mathrm{b}} &= k_\theta\left[\frac{\mathbf{r}_{i+1,i}}{r_{i+1,i} r_{i,i-1}} - \left(\frac{\mathbf{r}_{i+1,i}\cdot\mathbf{r}_{i,i-1}}{r_{i+1,i}}\right.\right.\\ &\quad\left.\left. + \frac{\mathbf{r}_{i,i-1}\cdot\mathbf{r}_{i-1,i-2}}{r_{i-1,i-2}}\right)\frac{\mathbf{r}_{i,i-1}}{r_{i,i-1}^3} + \frac{\mathbf{r}_{i-1,i-2}}{r_{i,i-1} r_{i-1,i-2}}\right] \qquad (4)\\ &\equiv a_2\mathbf{r}_{i+1,i} + a_3\mathbf{r}_{i,i-1} + a_4\mathbf{r}_{i-1,i-2}\end{aligned}$$

Here, $\mathbf{r}_{i,i-1} \equiv \mathbf{r}_i - \mathbf{r}_{i-1}$ and the absolute value $|\mathbf{r}_{i,i-1}| \equiv r_{i,i-1}$. Note that $\mathbf{f}_{i,i-1}$ depends on the positions of other particles besides i and $i-1$ and hence is not a purely pairwise force. Similarly, $\mathbf{f}_{i+1,i}^{\mathrm{b}}$ is given by

$$\begin{aligned}\mathbf{f}_{i+1,i}^{\mathrm{b}} &= k_\theta\left[\frac{\mathbf{r}_{i+2,i+1}}{r_{i+2,i+1} r_{i+1,i}} - \left(\frac{\mathbf{r}_{i+2,i+1}\cdot\mathbf{r}_{i+1,i}}{r_{i+2,i+1}}\right.\right.\\ &\quad\left.\left. + \frac{\mathbf{r}_{i+1,i}\cdot\mathbf{r}_{i,i-1}}{r_{i,i-1}}\right)\frac{\mathbf{r}_{i+1,i}}{r_{i+1,i}^3} + \frac{\mathbf{r}_{i,i-1}}{r_{i+1,i} r_{i,i-1}}\right] \qquad (5)\\ &\equiv b_1\mathbf{r}_{i+2,i+1} + b_2\mathbf{r}_{i+1,i} + b_3\mathbf{r}_{i,i-1}\end{aligned}$$

Using these expressions to calculate the stress autocorrelation function yielded our data shown in Figure 3. Our results are consistent with those of Zhou and Larson,[5] who used the same form of the potential shown in eq 1 but for $k_\theta = 2.0$, which results in slightly stiffer chain with a smaller entanglement molecular weight. On the other hand, from the expression for $\mathbf{f}_i^{\mathrm{b}}$ discussed

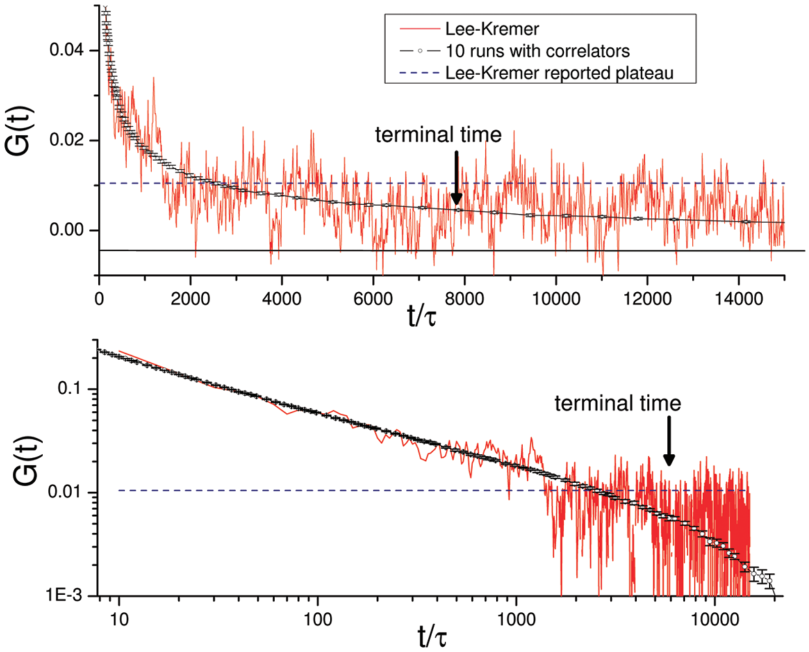

Figure 2. Comparison of simulations of flexible Kremer–Grest chains of length $N = 100$ from ref 1 (line) and from our work[4] (circles with error bars). The dashed horizontal lines indicate the value of the plateau modulus extracted by Lee and Kremer (obtained from the values of $N_{\mathrm{e,SAF}}$ reported in Table 3 of ref 1). The terminal time indicated by an arrow is the relaxation time of the longest Maxwell mode obtained by fitting the $G(t)$ to a set of Maxwell modes.[8]

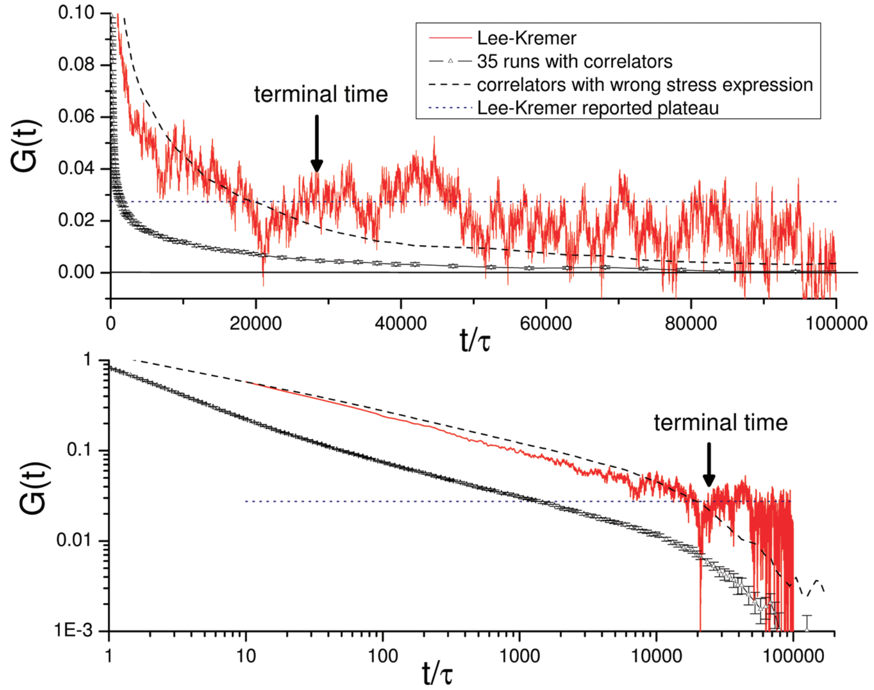

Figure 3. Comparison of the simulations of the slightly semiflexible Kremer−Grest chains of length $N = 100$ from ref 1 (continuous line) and from this work (circles with error bars). The plateau modulus corresponding to the $N_{\mathrm{e,SAF}}$ reportedby Lee and Kremer is indicated by a horizontal dotted line (from Table 3 in ref 1). The dashed line is our attempt at reproducing the incorrect results of Lee and Kremer. The terminal time indicated by an arrow is the relaxation time of the longest Maxwell mode.[8]

above, if we erroneously identify a_i and b_i with the spring constants of the pairwise force acting between corresponding atoms and plug them into eq 2, we get a result almost identical to that of Lee and Kremer and shown as dashed line in Figure 3. Thus, the SAF data in ref 1 contain an accidental error which produced $G(t)$ about 4 times as large in the terminal region, yet the plateau extracted from such data agree to within 10% with the value obtained using the PPA.

The form of the potential most commonly used in the literature to add a bending contribution to the chain Hamiltonian is that given by eq 1. However, motivated by theory, in our earlier work[4] we had chosen a slightly different form of bending potential given by

$$U_{\mathrm{bend}} = \frac{k_{\mathrm{b}}}{2}\sum_{i=2}^{N-1}(\mathbf{r}_{i+1} - 2\mathbf{r}_i + \mathbf{r}_{i-1})^2 \qquad (6)$$

This is equivalent to adding a weak linear attractive force between monomers i and $i + 1$ (spring constant, $4k_{\mathrm{b}}$) and a weak linear repulsive force between monomers i and $i + 2$ (spring constant, k_{b}). The commonly held view (which can be traced to the early days of polymer science) is that, for many macroscopic properties, the exact functional form of the intermolecular potential does not matter as long as the structural properties of the polymer coil are the same. For example, we can use the average square distance between monomers $\langle \mathbf{r}_{i,j}^{\;2}\rangle/|i - j|$ as one measure to quantify the structure. In Figure 4 we show a comparison of both the $G(t)$ and the chain structure between simulations performed with the two potentials given by eqs 1 and 6 for chains of length $N = 100$. The chain structure given by eq 1 with $k_\theta = 1.5$ (the system used by Lee and Kremer) is virtually identical to the structure of chains with bending energy givenby eq 6 with $k_{\mathrm{b}} = 1.5$. What is perhaps more interesting is that the $G(t)$ curves are also very close. However, further work is definitely needed before we can conclude that the commonly held view mentioned earlier is, without exception, true. The example discussed here is just another instance where changes in the details of the potential that do not significantly alter the chain structure appear to also not affect the $G(t)$.

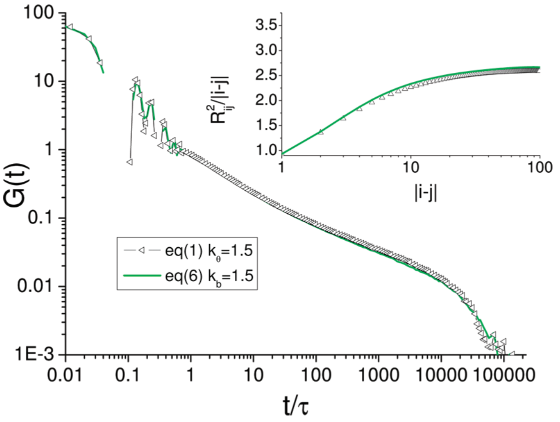

Figure 4. Stress relaxation and average square distance between monomers (inset) obtained from MD simulations with the two forms of bending energy: eq 1 (points) and eq 6 (line).

We conclude that noisy data for stress autocorrelation function can mislead one into believing that a plateau can be discerned in the $G(t)$ data for chains corresponding to about 4 entanglement segments (ref 11 appears to be another example of overinterpretation of noisy $G(t)$ data). However, such a plateau is not expected in any graphical representation from either theory or experiment, and more accurate calculations using multiple-τ correlators indeed confirm this. The only method known to us for extraction of accurate information about entanglements from $G(t)$ is fitting it with some model, such as tube or slip-links. This was recently demonstrated in refs 4 and 12. In addition, we show that two different forms of bending potential that lead to very similar chain structure produce $G(t)$ signals that are also very close.

Acknowledgment. We gratefully acknowledge Prof. Kremer for providing their data shown here in Figures 2 and 3.

References and Notes

(1) Lee, W.; Kremer, K. *Macromolecules* **2009**, *42*, 6270.

(2) Lee and Kremer also discuss a coarse-grained model for bisphenol A−polycarbonate in ref 1, but that is not explicitly under discussion in this work.

(3) Everaers, R.; Sukumaran, S. K.; Grest, G. S.; Svaneborg, C.; Sivasubramanian, A.; Kremer, K. *Science* **2004**, *303*, 823.

(4) Likhtman, A. E.; Sukumaran, S. K.; Ramirez, J. *Macromolecules* **2007**, *40*, 1607.

(5) Zhou, Q.; Larson, R. G. *Macromolecules* **2006**, *39*, 6737.

(6) Dealy, J. M.; Larson, R. G. *Structure and Rheology of Molten Polymers*; Hanser: Munich, 2006.

(7) Auhl, D.; Ramirez, J.; Likhtman, A. E.; Chambon, P.; Fernyhough, C. *J. Rheol.* **2008**, *52*, 801.

(8) Ramirez, J.; Likhtman, A. E. http://reptate.com, **2009**.

(9) Likhtman, A. E.; McLeish, T. C. B. *Macromolecules* **2002**, *35*, 6332.

(10) Theodorou, D. N.; Boone, T. D.; Dodd, L. R.; Mansfield, K. R. *Makromol. Chem., Theory Simul.* **1993**, *2*, 191.

(11) Sen, S.; Kumar, S. K.; Keblinski, P. *Macromolecules* **2005**, *38*, 650.

(12) Sukumaran, S. K.; Likhtman, A. E. *Macromolecules* **2009**, *42*, 4300.