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NOTE

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

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Determining the plateau modulus of a polymeric melt out-of-equilibrium by simulation has been a longstanding problem due to the extremely long simulation times required for systems of very long chains. In addition, the data of instantaneous stresses for system sizes accessible to simulations suffer from typical noise, which usually significantly exceeds the signal. In a paper by two of the above authors,[1] an efficient and fast method based on preaveraging of stress autocorrelation data was presented, which reduces the typical noise significantly and thus allows for a better analysis of the data. This was based on the idea that, as done automatically by experiment, very high frequency fluctuations in the (off-diagonal) elements of the stress tensor can be averaged out without any significant loss of information. It was found that signatures of a plateau modulus could be obtained for relatively short chains of about four entanglement lengths N_e, which agree nicely with predictions from a primitive path analysis of much longer chains.[1] In their comment Likthman and Sukumaran criticize this work in two ways. First, they argue that one needs much longer chains to obtain any reliable signature of N_e in the stress autocorrelation function and that one has to use a model-based analysis as i.e. their multiple correlator method and slip-spring model.[2] Second, they argue that the stress data we employ for the semiflexible chains did not take into account the contributions to the off-diagonal stresses from the bond bending potential, which is responsible for the increased stiffness of the chains. As a consequence, the reported signal was too high. As to the second point, we agree that the ESPResSo software[3] used did not account for the bending potential contributions to the off-diagonal elements of the stress tensor. We thank A. Likhtman and S. Sukumaran for pointing this out. In the public CVS version of the open source package ESPResSo[3] this has been corrected.

The first point of their comment actually incorporates two different aspects. It is clear that short chains of a few entanglement weights only cannot be used to determine the entanglement molecular weight of a given polymer. Also, it is clear that in order to determine N_e unambiguously from i.e. the stress autocorrelation function an underlying model for the relaxation curve is needed. Our paper neither disputes this, nor do we in any way indicate that short chains are sufficient to obtain reliable estimates of N_e. The only claim our contribution made was that using the significantly noise-reduced stress autocorrelations function, signatures of entanglements can be obtained, which reasonably agree with predictions of a primitive path analysis from much longer chains. In part, this claim was somewhat too strong due to the missing bending energy contributions in the stress tensor. However, using the preaveraged version of the stress tensor, as tested and explained in ref 1, most probably also the multiple correlator approaches could be improved significantly.

In the literature there are many different investigations based on motion on a segmental level which report significant entanglement effects already for relatively short chains. These studies range from computer simulations through scattering and NMR experiments to local probe techniques.[4−11] Also, conformational analysis based on primitive path methods reveals entanglement effects already at chain lengths of the order of a very few N_e.[12] In an elegant recent experiment[13] the difference between radiation and conformational decay of the first excited state of the tracer molecule FCVJ in a poly(propylene oxide) matrix was studied and linked to the viscosity of the matrix. The onset of entanglements clearly could be observed for chains of only two N_e. In contrast, for rheological experiments usually long polymer chains (more than 10 times the entanglement length or more) are required to detect a plateau region and thus a clear signature of N_e. It is possible that this discrepancy may indicate the fundamental difference between molecular and macroscopic level measurements.[13] Nevertheless, we would expect some signature of entanglement effects in the autocorrelation functions of the stress tensor, even for short chains. To determine this, our approach is especially suited. The stress autocorrelation function (SAF) evaluated by molecular dynamics simulation uses stresses which are "measured" on the scale of molecules. (Although the virial stress is used, the system size is still microscopic.) That is why the SAF was carefully investigated using our time-averaging scheme in the previous paper.[1] First we show how the preaveraging procedure reduces the noise without losing any significant information by comparing rather short simulations of small systems with a much longer simulation of a much larger system, originally performed in a different context. Figure 1 shows the time-dependent moduli $G(t)$, as given in eq 6 of ref 1. The blue line in Figure 1b represents the modulus $G(t)$ averaged over four independent runs of small systems. Very good agreement between the results of the two simulation packages is found.

For the plateau modulus one would expect a signature between the Rouse time of subchains of N_e ($\sim 600\,\tau$) and that of the whole chain of length N. As noted by the comment, there is no clear signature of a plateau after its Rouse time ($\sim 600\tau$). The same conclusion actually holds for the simulations of BPAPC with $N = 20$, taking the corrected pressure tensor for our analysis. It is interesting to note that both cases have about the same chain length in terms of their entanglement length (i.e., $N = 3.6N_{e,PPA}$[15] for the semiflexible model and $N = 4.4N_{e,PPA}$[15] for the BPAPC model). It should however be noted that these chain lengths already are sufficient to predict N_e based on the primitive path analysis within about 15%.[12]

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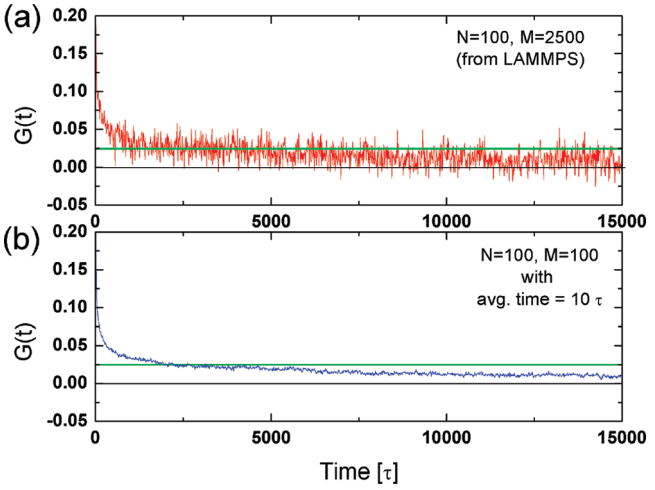

Figure 1. Moduli $G(t)$ of a semiflexible case ($N = 100$). (a) $G(t)$ by LAMMPS[13] with $N = 100$ and $M = 2500$ without any time averaging. Because of the large number of chains, there is relatively little noise. (b) $G(t)$ averaged over four independent runs each with an averaging time of 10τ of $M = 100$ chains of length $N = 100$. We emphasize that the green line is the plateau value based on $N_{e,PPA} = 28$[14] and is not the plateau value as determined by $G(t)$ as indicated in Figures 2 and 3 in the comment.

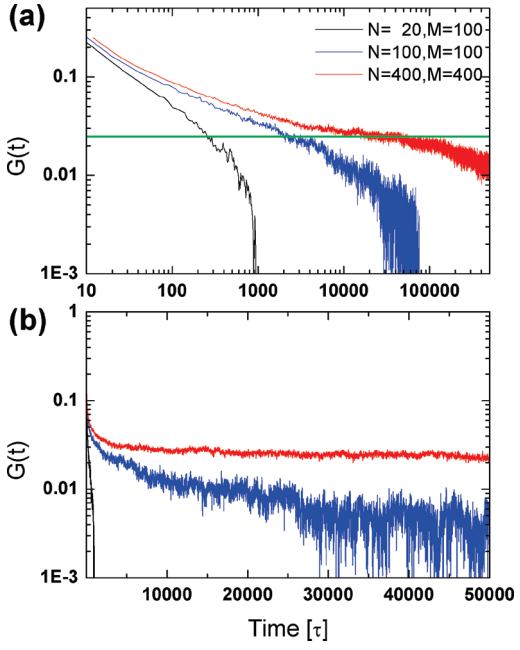

Figure 2. Moduli $G(t)$ of three semiflexible cases ($N = 20$, 100, 400) shown on (a) log−log and (b) log−linear scales. The $N = 400$ case was simulated using the LAMMPS[14] package with $M = 400$. The data from this simulation have not been time averaged. Because of the large number of chains, it has relatively small noise. For the shorter chains $G(t)$ is averaged over four independent runs each with an averaging time of 10τ. The green line is the plateau value which has been calculated using $N_{e,\,PPA} = 28$.[15]

As chain length increases, the plateau region can directly be observed. Figure 2 shows three cases ($N = 20$, 100, 400) for the semiflexible model. As expected for Rouse chains, $G(t)$ for the $N = 20$ case decays continuously before fluctuating about zero for all cases (11 independent runs). For the $N = 400$ case a long plateau region is found. Figure 2a,b shows these data on log−log and log−linear plots. It is however important to mention that already for $N = 100$ we observe clear deviations from Rouse like behavior, as illustrated in the log−linear representation in Figure 2b. As Figure 2a shows, at short times the decay for all systems is the same, indicating the same bead friction. Again the expected plateau modulus is indicated.

Finally, let us turn back to the problem of the missing bending contribution in our original paper. Already almost 20 years ago Fixman[16] argued that the plateau stress should originate from the excluded volume contribution of the pressure tensor rather than the contour stress of the chains. Taking the fact that our previous results indicate reasonable agreement between the predictions of the primitive path analysis and the first indications of entanglement effects in the stress autocorrelation function into account, the question of the reason arises. Since this was the case for both the semiflexible simple Lennard-Jones chains as well as the BPAPC model, this is a problem to follow up on.

In conclusion, our previous results[1] of the stress autocorrelation function for semiflexible and BPAPC systems did not account for the contribution from bending potentials. In the present reply we correct that and checked our results also by a different code.[14] The ESPResSo software[3] has been corrected as well. We would however like to point out the advantages of our approach, which are not affected by the comment of Likhtman and Sukumaran. First, with the time-averaging scheme, the size of the raw data is significantly reduced, and on-the-fly analyses such as computing the stress autocorrelation function are easily performed. The typical strong scattering of the data due to the small system sizes is reduced strongly without losing any essential information. This ansatz is in line with the theoretical models employed in polymer theory as well as the typical experimental procedures. Second, our method allows for one to store raw (time-averaged) data within checkpoint files which reduces the file sizes in terms of IO requirements. This allows for the analysis to be carried out at a later time for any reason. Also, the stored data may be used to perform a related analysis as to avoid an ill-equilibrated starting point such as an abnormal distribution of the end-to-end distance as shown in ref 1.

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