



Reply to the Comment by A. Wischnewski and D. Richter on "What is the entanglement length in a polymer melt?"

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Reply to the Comment by A. Wischnewski and D. Richter on “What is the entanglement length in a polymer melt?”

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In their comment on our paper [1], Wischnewski and Richter provide new Neutron Spin Echo (NSE) data on longer PEB-2 polymer chains than in their recent publication [2]. They find that finite-chain-length effects are rather small going from $M_w = 36000$ to $M_w = 190000$. In contrast, our simulations showed rather strong finite-size effects in the dynamic structure factor $S(k, t)$ going from $N = 700$ to $N = 10000$ chains. The issue can be resolved by properly mapping their new data to the simulation. Such a mapping is ambiguous since a unique definition of the entanglement length does not exist. The definition using the plateau modulus gives an entanglement length of $N_{e,p} = 72$ for our bead-spring model as does a scaling analysis of the diffusion constant D [1]. Defining N_e by the crossover point of the monomer displacements, $g_1(t)$, from initial Rouse to local reptation regime, which is the concept used in the original reptation model, we obtain $N_e = 32$. Since $g_1(\tau_e)$ should be closely related to the tube diameter, d_T , we anticipated that d_T measured from $S(k, t)$ and $g_1(\tau_e)$ gives the same number. Apparently a good mapping to experiments is only obtained if one uses the model-independent $N_{e,p}$ value. Using $N_{e,p}$ to map polyethylen onto our model a molecular weight of $M_w = 36000$ would correspond to $N = 1150$, which is twice as large as the mapping proposed in the Comment based on $N_e = 35$. In fig. 2 we show additional simulation data for $N = 2000$ and we find that the $S(k, t)$ data are indistinguishable from the $N = 10000$ results. Hence the transitional range, where finite-chain-length effects become negligible, is consistent with the PEB-2 NSE data. In the Comment it is proposed to use the exact result for the long time decay of the reptation structure function since $kR_g/2\pi \simeq 1$. Doing so improves the quality of the fits significantly and gives slightly larger values for d_T than before ($d_T(2000) = 9.6\sigma$ and $d_T(700) = 12.9\sigma$, $N = 150$ was used for the fits as we argue below). However, the overall finite-size behavior of $d_T(N)$ is not altered. To understand these finite-size effects, we calculated $g_1(t)$ as a function of the monomer position along the chain for $N = 700$. It can be seen from fig. 1 that in the initial time regime the outer monomers (1/700) move twice as fast as the inner ones (75-625). Monomers between position (1) and (75) start to move faster in the observed time frame than in the middle part of the chain. This faster Rouse relaxation at the chain ends is neglected in the reptation model, but affects $S(k, t)$ as well. The magnitude of this effect may be estimated by recalculating $S(k, t)$ for a subchain of inner monomers where the first and the last 75 monomers are not taken into account. In fig. 2 we can see that doing so increases $S(k, t)$ by about 10% (at $t = 70000\tau$). In addition to this direct consequence of the fast end-relaxation, one might also consider that the chain ends do not contribute to the entanglements of neighboring chains and therefore the effective tube diameter is increased

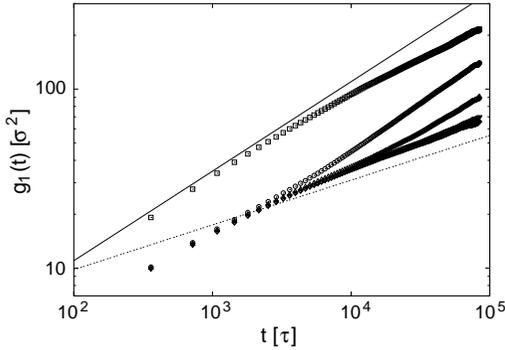


Fig. 1

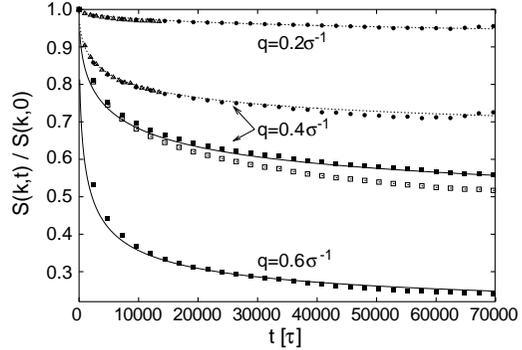


Fig. 2

Fig. 1 – Mean-square displacements ($g_1(t)$) for different monomers of an $N = 700$ unit chain: \square : Monomers 1/700, \circ : monomers 25/675, \triangle : monomers 50/650, ∇ : monomers 75/625 and \diamond : monomers 100-600. The straight lines show some power law behaviors to guide the eye: $t^{1/2}$, continuous line and $t^{1/4}$, dashed line.

Fig. 2 – $S(k, t)$ for different chain lengths: $N = 10000$ (\triangle), $N = 2000$ (\bullet) and $N = 700$ (\square) and the centered subchain of length 550 of the same $N = 700$ chains (\blacksquare). Continuous curves are simultaneous fits to the $N = 2000$ data corresponding to $d_T = 9.6\sigma$. The dotted curve is a simultaneous fit to the $N = 700$, 550 monomer subchain with a tube diameter of $d_T = 12.9\sigma$.

for shorter chains. A first approximation is to reduce the effective chain density by a factor $(1 - 2\frac{75}{N})$ and use a scaling relation of the form $d_T \propto \rho^{-a}$, where $1 \leq a \leq 2$ [3,4]. For $N = 700$ and $N = 2000$ this leads to a difference in the tube diameter of 8% to 17%, which is to be compared to the 34% difference of the fit values.

Both direct and indirect effect of the fast end-relaxation together can explain from 50% to 70% of the difference in $S(k, t)$ between $N = 700$ and $N = 2000$ though not all of it. However, the $N = 700$ chains are certainly at the limit where the reptation formula for $S(k, t)$ (given in [1]) is applicable, since $k = 0.4$ probes distances almost equal to the radius of gyration of the chains and for $q = 0.6$ the product of $kd/6 < 1$. Hence the quality of our fits with just one parameter, d_T , is surprisingly good.

What remains to be addressed is the fact that the NSE value for $N_e^{\text{PEB-2}} \approx 160$ derived from a tube diameter of $d_T^{\text{PEB-2}} = 47 \text{ \AA}$ appears to be in good agreement with $N_{e,p}^{\text{PEB-2}} = 140$. First we note that a subchain of PEB-2 with 160 carbons is not Gaussian due to the finite-chain stiffness, thus using the relation $d_T^2 = R_e^2$ involves an additional approximation. Further our results show that the relation of the two quantities d_T and $N_{e,p}$ is rather complex. Recent simulation results [5] on dense semi-flexible chains and theoretical work on semi-flexible chains in semi-dilute solution [6] support this. Thus we are inclined to believe the very good agreement might be fortuitous for the particular $N_e(d_T)$ mapping chosen.

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