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Reply to the Comment 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 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 $g_1(\tau_e)$ give 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 than 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 the inner ones (75-625). Monomers between position (1) and (75) start to move faster in the observed time frame then the middle part of the chain. This faster Rouse-relaxation at the chain ends is neglected in the reptation model, but effects $S(k,t)$ 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 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 between 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 $N_e^{PEB-2} \approx 160$ derived from a tube diameter of $d_T^{PEB-2} = 47\mathring{A}$ appears to be in good agreement with $N_{e,p}^{PEB-2} = 140$. 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.

REFERENCES

[1] M. Pütz, K. Kremer, G. S. Grest, Euro. Phys. Lett **49**,735 (2000).
[2] P. Schleger *et al.*, Phys. Rev. Lett. **81**, 124 (1998).
[3] for an overview see: B. Ewen, D. Richter, Adv. Pol. Sci. **134**,3 (1997)
[4] L. J. Fetters, Macromolecules **32**, 6847 (1999)
[5] R. Faller, Dissertation, University of Mainz (2000), http://archimed.uni-mainz.de
[6] D. C. Morse, Macromolecules **31**, 7030 (1998); **31**, 7044 (1998)

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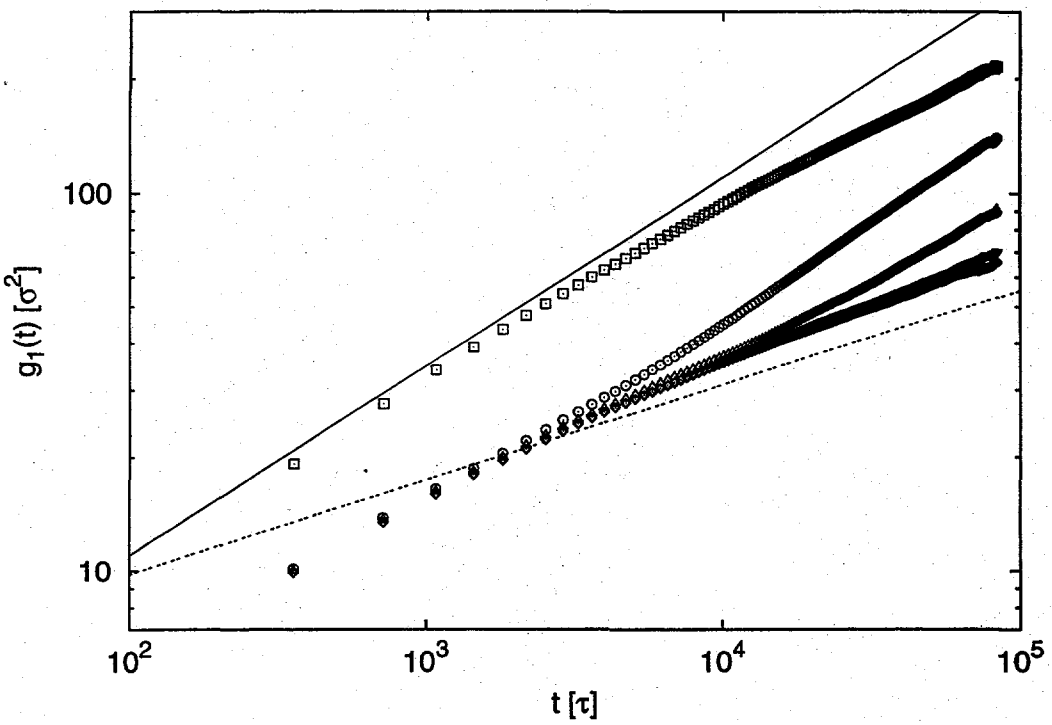

Fig. 1. – Mean-square displacements ($g_1(t)$) for different monomers of a $N = 700$ unit chain: Monomers 1/700 [□], monomers 25/675 [○], monomers 50/650 [△], monomers 75/650 [▽] and monomers 100-600 [◇]. The straight lines show some power law behaviors to guide the eye: $t^{1/2}$ (continuous) and $t^{1/4}$ (dashed).

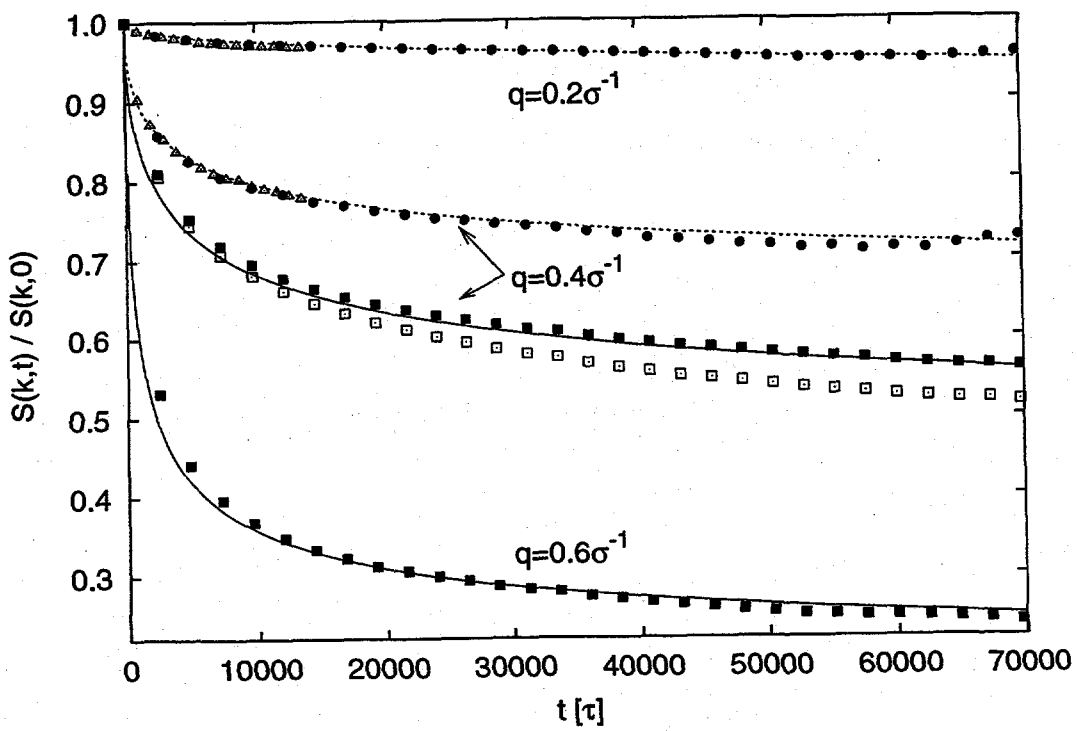

Fig. 2. – $S(k,t)$ for different chain lengths : $N = 10000$ [$\triangle$], $N = 2000$ [$\bullet$] and $N = 700$ [$\square$] and the centered subchain of length 550 of the same $N = 700$ chains [$\blacksquare$]. Continuous curves are simultaneous fits to the $N = 2000$ data corresponding to $d_T = 9.6\sigma$.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