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A time-integrated estimate of the entanglement mass in polymer melts in agreement with the one determined by time-resolved measurements

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We make a critical examination of how the entanglement molecular mass $M_e$ is determined from various measurable quantities. We are guided by reptation theory, where it is assumed that characteristic relaxations abruptly change and become equal to those of a chain moving in a Gaussian tube, as soon as the corresponding length scales surpass the tube diameter $d$ or similarly as soon as the corresponding mass surpasses a critical value. Taking this critical mass as a definition of the “reptational” entanglement mass, we observe that all methods based on time-resolved quantities, such as the single-chain dynamic structure factor $S(q, t)$ and the zero-shear relaxation modulus $G(t)$, give the same result. We observe that such a value differs, beyond error bars, from that obtained from the plateau modulus, which is a time-integrated quantity. We have investigated an alternative definition of entanglement mass in terms of time-integrated quantities and observe that the value of this specific entanglement mass is consistent with that obtained from the time-resolved observables. We comment on possible reasons for the plateau modulus discrepancy.

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I. INTRODUCTION

The existence of a plateau in the shear relaxation modulus $G(t)$ has led people to consider polymer melts as temporary rubbery networks. This naturally led to the definition of the “rubbery” entanglement mass $M_r$ as given in Eq. (3) below. Values of such entanglement masses for a great variety of polymers can be found in the literature. With the advent of reptation theory of Doi, Edwards, and de Gennes, a new concept was introduced in the theory of the dynamics of polymer melts. In reptation theory each polymer is supposed to move in a tube around a Gaussian path in space. The tube only serves one purpose, namely to roughly represent the repulsive interactions with the surrounding chains and to turn the multichain problem into a one-chain problem. The tube therefore very much is a mean field concept. We now have two options: either we try to give a precise definition of the tube in terms of the many-chain configurations, or we simply accept the tube diameter as a new parameter to describe the dynamics of polymer melts. To the best of our knowledge, the first has only been done by Theodorou et al. and Kremer and Everaers. Although very attractive from a conceptual point of view, all such definitions suffer from the problem that no exact relation exists between the tube and experimentally measurable properties of the melt. If one were to find such a relation by performing simulations of one chain in a tube, one would have to introduce new assumptions about the way the moving chain annihilates and creates new parts of the tube at its head and tail. Leaving this for future research, we simply accept the Doi–Edwards–de Gennes assumption of a Gaussian path, rendering the tube diameter as the only new parameter. The assumption of reptation theory is that characteristic relaxations abruptly change and become equal to those of a chain moving in a tube, as soon as the corresponding length scales surpass the tube diameter or similarly as soon as the corresponding mass surpasses a critical value. We take this as our definition of tube diameter and “reptational” entanglement mass $M_{r,r}$, respectively. We feel strengthened in accepting this definition by the fact that, as we will see below, all estimates of the reptational entanglement mass yield consistent values within the given error bars. We furthermore observe that this value differs from the rubbery entanglement mass introduced above. Apparently these two quantities relate to different aspects of the dynamics of polymer melts. There is a very obvious operational difference in the definition of the two types of entanglement mass given above. The reptational entanglement mass has been defined in terms of time-resolved quantities, whereas the rubbery entanglement mass has been defined in terms of a time-integrated quantity. Obviously the latter type of definition has some advantages from an experimental point of view. Therefore we have investigated yet another definition of entanglement mass in terms of time-integrated quantities and observed that the value of this specific entanglement mass coincides with the value of the reptational entanglement mass obtained before. We tend to conclude that the reptational entanglement mass is a bit more fundamental than the rubbery entanglement mass but realize that this is largely a matter of taste.

Relaxation processes in polymer melts occur on an enormous range of time and length scales. It is therefore not surprising that a host of experimental techniques is used to
study their dynamic properties on all relevant time and length scales. Before going into details, we will explain the distinction between time-resolved and time-integrated experiments. Time-resolved experiments measure the dynamics of the system with sufficiently small time resolution to be able to probe a relevant time dependent correlation function before it reaches its long time limit. Examples are neutron spin-echo (NSE) spectroscopy, measuring the coherent dynamic structure factor, proton and deuteron field-cycling NMR relaxometry, probing the Kuhn segment tangent vector correlation function, and NMR field-gradient diffusometry (when applied to relatively short time-scales), probing the mean-squared displacement of Kuhn segments. On the other hand, time-integrated experiments either integrate over a long-time or measure the long-time limit of some correlation function, which amounts to integrating its time derivative. Examples are measurements of the shear viscosity or plateau modulus, both by means of rheometry, and measurements of self-diffusion coefficients, e.g., by means of NMR field-gradient diffusometry, forward recoil spectroscopy, or scanning infrared microscopy.

II. TIME-RESOLVED RESULTS

In this section we will show that from the analysis of different time-resolved results a consistent value for the reptational entanglement mass emerges. We will clarify our point by the example of polyethylene (PE) melts at 450 K. We will refer to experimental work and to the results of molecular dynamics simulations of PE melts at 450 K and density \( \rho = 0.761 \text{ g/cm}^3 \), reported in our previous work.

A. Coherent dynamic structure factor

Richter and co-workers have performed NSE experiments on high molecular weight PE melts. For the single-chain coherent dynamic structure factor, they found very good agreement with the predictions of the reptation model. A simultaneous fit could be made for several values of the wave vector \( q \) using a slightly adapted version of an expression formulated by de Gennes, with the tube diameter \( d \) as the only fit parameter. This allowed them to extract the tube diameter \( d \) very accurately: at a temperature of 509 K, a tube diameter of about 4.6 nm was found.

Although in the original tube model it was assumed that the tube diameter is more or less independent of temperature, in reality this is only approximately true. The conformations are different between 509 and 450 K, leading to different local structures and different tube diameters. In their 1993 paper, Richter et al. investigated the temperature dependence of the tube diameter and found that it increases slowly with temperature. In a range of temperatures, including the two above, \( d \) was found to be proportional to \( \exp[(1.2 \pm 0.2) \times 10^{-3} T] \). Using this formula, one finds a smaller tube diameter, \( d = 4.3 \text{ nm} \), at the lower temperature of 450 K at which we have performed our molecular-dynamics simulations. In these simulations, like in the experiments of Richter, the single-chain coherent dynamic structure factor was found to be in good agreement with the tube model for times larger than the entanglement time (vide infra). A simultaneous fit for several values of \( q \) yielded \( d = 5.4 \text{ nm} \) in the molecular weight range \( M = 8 - 14 \text{ kg/mol} \). These results are in good agreement with those results of Richter et al. which apply to the same range of molecular masses.

The reason for the deviation of \( d \) from its “true” value is the fact that, in the quoted molecular weight range, the chains are still very much influenced by tube contour length fluctuations. Richter et al. have shown that, on correcting for these tube contour length fluctuations, the resulting tube diameter does not significantly depend on the chain length. In other words, the corrected tube diameter is found to be in agreement with the tube diameter of asymptotically long chains \( (d = 4.3 \text{ nm} \text{ at 450 K}) \).

The tube diameter must next be translated to a reptational entanglement mass. To this end we assume that \( d^2 \) equals the average squared end-to-end distance of a (sub)chain with molecular weight \( M = M_{c,r} \), i.e.,

\[ d^2 = R_c^2(M_{c,r}). \]  

(1)

In Fig. 1 we present the average squared end-to-end distance of polyethylene as a function of molecular weight. Circles are data from our simulations, the solid lines are based on the characteristic ratio for very long chains, i.e., \( R_c^2 = C_x N l^2 \), where \( N \) is the number of bonds and \( l \) the bond length. Here we have used \( C_x = 7.3 \) according to experimental measurements in the melt state at a comparable temperature of 440 K. Clearly, the simulation data are converging to these lines from below because the characteristic ratio of relatively short chains is still increasing with chain length. However, the convergence is slower than one would expect for real polyethylene, partly because of finite system size effects, but more importantly because the end-to-end distance is always underestimated in coarse-grained simulations. The average squared end-to-end distance is measured between the center-of-mass positions of the first and last blobs (coarse particles) of a chain, while in an atomistically detailed chain it is measured between the first and last atoms.
Finally, the characteristics of both the short-time and the long-time Rouse mode correlation functions change drastically when $M/k = M_{e,r}$. In our previous work we have
shown that the short-time Rouse-mode correlation function decays according to a stretched exponential. In Fig. 4 we show the stretching exponent $\beta_k$ as a function of $M/k$. After a dip $\beta_k$ stabilizes to a nearly constant value (see dashed lines in Fig. 4). The crossover from the dip to the constant value is very gradual, and we estimate $M_{e,r}$ to be 1.6 ± 0.4 kg/mol. Similarly, for $M/k > M_{e,r}$ the terminal relaxation times scale as predicted by the reptation model, whereas for $M/k < M_{e,r}$ this is certainly not the case [see Fig. 8(b) in Ref. 13].

In Fig. 5 we have summarized the estimates of the reptational entanglement mass. Notice that the values of $M_{e,r}$ from various time-resolved measurements agree within their respective error bars. From the results so far, we estimate $M_{e,r} = 1.6 ± 0.2$ kg/mol. We will now focus on time-integrated measurements.

III. TIME-INTEGRATED RESULTS

In rheological practice, the rubbery entanglement mass is defined in relation to the experimental value of the plateau modulus $G_N^0$, by application of the following equation:

$$G_N^0 = \frac{4}{5} \frac{\rho N_A k_B T}{M_e},$$

where $N_A$ is Avogadro’s number, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $\rho$ is the polymer melt density. Fetters et al. measured the value of the plateau modulus in PE melts at a density of $\rho = 0.768$ g/cm$^3$ and temperature $T = 443$ K, close to the conditions of the molecular-dynamics simulations. Using Eq. (3) (including the prefactor 4/5) they found $M_e = 0.92$ kg/mol. Clearly, the estimates of $M_{e,r}$ from time-resolved measurements are larger than this.

Notice that Eq. (3) uses a rather arbitrary prefactor of 4/5 from the Doi-Edwards model. Using different models, different prefactors may be found. However, the prefactor never exceeds unity. Even when this largest prefactor of 1 is used, the entanglement mass from the plateau modulus ($M_e = 1.15$ kg/mol in that case) is significantly smaller than $M_{e,r}$ (see Fig. 5). We will put forward a possible reason for this discrepancy in the discussion.

There is no straightforward way to extract the reptational entanglement mass from the molecular weight dependence of time-integrated quantities such as the viscosity $\eta$ or the self-diffusion coefficient $D$. The reptation model predicts a transition in the scaling of $D$ from $M^{-1}$ to $M^{-2}$ at the reptational entanglement mass. However, both experiment and simulation have revealed that the molecular weight region in which $D$ scales like $M^{-2}$ (and even faster) clearly starts before $M_{e,r}$. No transition is observed at the molecular weight $M_{e,r}$ itself, not under constant pressure nor under constant density conditions. The reason why the transition does not occur at $M_{e,r}$ is that there are additional molecular relaxation processes besides those in the original reptation model, and that the Kuhn segment density is still increasing in the region where the transition should occur, as was already noticed by Pearson et al. Similarly, the exponent in the scaling of the viscosity $\eta$ has a transition at a molecular weight, which is much larger than $M_{e,r}$. This molecular weight is usually referred to as the critical molecular weight.
$M_e$ [4–5 kg/mol for PE (Ref. 9)]. It is evident that, if one insists on estimating $M_{e,r}$ from time-integrated data, one should aim for combinations of observables which do not rely on the precise mechanism for the polymer motion.

Oostwal and Odijk introduced a dynamic scaling hypothesis, which applies to both semidilute and concentrated solutions and to polymer melts. In the Appendix we have reported. In Fig. 6, $v/\rho N_A$ is plotted against molecular weight. In this scaling, the vertical axis represents the inverse of the molecular weight corresponding to one effective dynamic unit. The low molecular weight data are observed to approach $1/M$ (solid line), confirming that in this regime the individual chains are the dynamic units. At large molecular weights, the data stabilize to a constant value, indicating that in entangled polymer melts the density of dynamic units is independent of the molecular weight. As already mentioned above, application of Eq. (4) to a melt whose dynamics obeys reptation theory yields $v/\rho N_A = 1/M_{e,r}$. In Fig. 6 it is seen that, with increasing molecular weight, $v/\rho N_A$ first goes through a minimum and then quickly approaches $1/M_{e,r}$, where $M_{e,r}$ is equal to the value obtained from time-resolved experiments.

### IV. DISCUSSION AND CONCLUSION

Let us note that the combination of viscosity and self-diffusion coefficient was already investigated by Pearson.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M$ (kg mol$^{-1}$)</th>
<th>$R_e^2$ (nm$^2$)</th>
<th>$\eta$ (Pas)</th>
<th>$D$ (10$^{-10}$ m$^2$ s$^{-1}$)</th>
<th>$\nu$ (nm$^{-3}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>8$H$</em>{16}$</td>
<td>1.12</td>
<td>10.2</td>
<td>0.005</td>
<td>1.8</td>
<td>0.51</td>
</tr>
<tr>
<td>C$<em>{120}$H$</em>{242}$</td>
<td>1.69</td>
<td>16.3</td>
<td>0.011</td>
<td>0.90</td>
<td>0.35</td>
</tr>
<tr>
<td>C$<em>{200}$H$</em>{402}$</td>
<td>2.81</td>
<td>25.3</td>
<td>0.033</td>
<td>0.30</td>
<td>0.23</td>
</tr>
<tr>
<td>C$<em>{400}$H$</em>{802}$</td>
<td>5.61</td>
<td>54.9</td>
<td>0.20</td>
<td>0.084</td>
<td>0.18</td>
</tr>
<tr>
<td>C$<em>{600}$H$</em>{1202}$</td>
<td>8.42</td>
<td>91.8</td>
<td>0.88</td>
<td>0.036</td>
<td>0.20</td>
</tr>
<tr>
<td>C$<em>{800}$H$</em>{1602}$</td>
<td>11.23</td>
<td>132</td>
<td>2.95</td>
<td>0.018</td>
<td>0.23</td>
</tr>
<tr>
<td>C$<em>{1000}$H$</em>{2002}$</td>
<td>14.03</td>
<td>167</td>
<td>5.98</td>
<td>0.011</td>
<td>0.23</td>
</tr>
</tbody>
</table>

$^a$Average squared end-to-end distance, zero shear viscosity, and self-diffusion coefficient are taken from molecular-dynamics simulations, Ref. 13. All these simulations were performed at constant density, $\rho = 0.761$ g cm$^{-3}$. $^b$Density of effective dynamic units making up the temporary network, calculated according to Eq. (4) in the main text.
et al.\textsuperscript{9,10} No attempt was made, however, to derive the entanglement mass from the high molecular weight data. Rather, they used the “rubbery” value based on the plateau modulus to test the reptation theory prediction

\begin{equation}
(\eta D)_{s} = (\eta D)_{r}(M_{w}/M_{e}) \tag{6}
\end{equation}

with the subscript $l$ referring to long chains and $s$ to short chains. As we have reviewed, such a relation is to be expected to hold true on much more general grounds. The fact that a scaling like Eq. (6) holds is, in itself, not a validation of reptation theory.

However, we have shown that the density of effective dynamic units $\nu$ obtained by the combination of viscosity and self-diffusion coefficient [Eq. (4)] becomes a constant for large values of $M$, and that this constant agrees with the value of $M_{c,r}$ obtained by time-resolved experiments, when the outcomes of these experiments are interpreted in terms of the reptation model. This is indeed extra motivation for the validity of the reptation model. As a side result we have validated Eq. (1), which was used by Richter \textit{et al.} to derive the reptational entanglement mass from the measured tube diameter.\textsuperscript{14,22}

An important result is that the reptational entanglement mass $M_{c,r}$, which appears as a parameter in the reptation theory, differs from the usual entanglement mass $M_{e}$, defined through the value of the plateau modulus in Eq. (3) by a factor of about 1.5 (see Fig. 5). As was already noticed by Tanaka \textit{et al.},\textsuperscript{23} $M_{e}$ defined by Eq. (3) is not a pure entanglement parameter, and may therefore not be the same as the reptational entanglement mass. In real polymer melts, the shear relaxation modulus $G(t)$ is not only influenced by entropic contributions, relaxing according to a reptation based spectrum of relaxation times. It is also influenced by various potential contributions from both inter- and intrachain interactions, relaxing on various time scales.\textsuperscript{13} Such contributions are certainly important in polymer melts at the relatively short-time scale where the chain “hits the tube,” i.e., at the entanglement time. As we have seen, an inflection point is still present at the entanglement time. However, the value of the shear relaxation modulus at this time is probably larger than can be accounted for by tube effects alone, which would explain the observed discrepancy. We expect that the ratio of 1.5 between $M_{e,r}$ and $M_{e}$ will not be universal. Different polymer species will have different details of their potential contributions. Therefore, to directly measure the reptational entanglement mass $M_{e,r}$, one needs to measure a physical quantity that is sensitive to density fluctuations occurring in a tube, such as the single-chain coherent dynamic structure factor.\textsuperscript{6}

Such a subtlety was not known to Pearson. In retrospect, deriving $M_{e,r}$ from Pearson’s data we find an $M_{e,r}$ close to 1.7 kg/mol, in agreement with our simulation results and the neutron spin-echo experiments of Richter and co-workers\textsuperscript{6,15} and not with $M_{e}$ obtained from the value of the plateau modulus. More theoretical work will be needed to fully understand the exact relationship between the value of the plateau modulus and the value of $M_{e,r}$ as it occurs in the reptation model.

\section*{ACKNOWLEDGMENTS}

We would like to thank Theo Odijk for bringing Ref. 19 to our attention. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

\section*{APPENDIX: DYNAMIC SCALING HYPOTHESIS}

Suppose we know both the average squared radius of gyration ($R_{g}^{2}$) and the self-diffusion coefficient of a polymer chain. The relation

\begin{equation}
D = \frac{R_{g}^{2}}{6\tau} \tag{A1}
\end{equation}

defines a time scale $\tau$ during which a test chain diffuses over a distance $R_{g}$. The probability of two test chains initially occupying essentially the same domain of size $R_{g}^{3}$ to still overlap at a later time $t$, decays rapidly to zero after a time of order $\tau$. Stated differently, the correlation of the network at time $t$ with the original network at time $t=0$, decays rapidly for $t > \tau$. As a consequence, stresses induced by a small shear strain applied at $t=0$ will quickly disappear at times $t > \tau$. This statement is made operational by assuming that there is really only one time scale involved in both processes, i.e., diffusion and stress relaxation. This leads to the scaling relation introduced previously by de Gennes:\textsuperscript{20}

\begin{equation}
\eta \approx E \tau. \tag{A2}
\end{equation}

We will consider this equation as the definition of $E$, which has the dimension of a modulus, but does not necessarily equal the plateau modulus $G_{N}^{0}$. Still, it has to be interpreted in terms of a temporary elastic network presumed to exist for times shorter than $O(\tau)$. Therefore it can be used to define $\nu$, the effective number of dynamic units per unit volume making up the temporary network:

\begin{equation}
E = k_{B}T \nu. \tag{A3}
\end{equation}

Combining Eqs. (A1)–(A3), we eliminate the unknown time scale $\tau$.

\begin{equation}
\nu \approx \frac{6\eta D}{k_{B}TR_{g}^{2}}. \tag{A4}
\end{equation}

Notice that Bueche derived essentially this formula in a very similar context already in 1952.\textsuperscript{24} Bueche devised a model that used the idea of “entanglement coupling,” in which one chain is dragging another in shear flow. However, as also stressed by Oostwal and Odijk,\textsuperscript{10} Eq. (A4) can be obtained without specifying the detailed dynamics of the surrounding fluctuating network of other chains, nor specifying whether the test chain diffuses in or out of an effective tube, or by any other mechanism. Equation (A4) is therefore valid up to some unknown prefactor of order unity. The prefactor can be fixed by considering well-known limiting cases. For polymer melts, both the Rouse model and the reptation model predict a prefactor of 1 (note that $R_{g}^{2} = R_{g}^{2}/6$).
5 K. Kremer (private communication).