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Reconciliation of the Molecular Weight Dependence of Diffusion and Viscosity in Entangled Polymers

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New measurements of chain self-diffusion (D) in highly entangled hydrogenated polybutadiene solutions and melts indicate that $D \sim M^{-2.3\pm0.1}$, where M is the molecular weight. Although these results contradict the widespread belief that in melts $D \sim M^{-2.0}$, we demonstrate that in fact the literature data for seven different polymers are consistent with $D \sim M^{-2.28\pm0.05}$. This result largely removes a recalcitrant discrepancy between the M exponents for D and the viscosity. Important implications for theoretical approaches are also noted.

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The reptation model is the cornerstone for our current understanding of the dynamics of entangled flexible polymers [1,2]. It is able to capture in a qualitative way, and in many cases a nearly quantitative way, an impressive variety of experimental phenomena concerning the rheological and diffusion properties of linear and branched chains [3]. Nevertheless, there are several persistent discrepancies between the predictions of reptation and the reported experimental results that constitute an important challenge to the model. It is the intent of this Letter to demonstrate that two of these discrepancies may now be resolved.

The fundamental assumption of the reptation model is that the topological restrictions presented by intertwined neighboring chains constrain a given chain to diffuse along its own contour. At a given instant in time, t', the entanglement constraints around a test chain define a tube along which the chain executes a one-dimensional random walk. As either chain end departs from this tube, it executes a three-dimensional random walk, which ultimately randomizes the conformation of the chain relative to that prevailing at t'. Similarly, when a chain end diffuses further into the original tube, that portion of the tube is relaxed. Stress relaxation in this model is equivalent to a loss of orientational memory, and thus the viscosity (the integral over the stress relaxation modulus) is determined by the time to escape completely from the tube, τ_1. During this interval the chain center of mass also moves an rms distance proportional to the chain radius of gyration, R_g, and thus the diffusivity (D) and viscosity (η) are intimately related. Specifically, the model predicts that τ_1, and therefore η, scales with molecular weight, M as [2]

$$\eta \sim \tau_1 \sim M^3, \tag{1}$$

whereas experimentally $\eta \sim M^{3.4\pm0.2}$ for a wide range of different polymer materials and up to numbers of entanglements per chain, M/M_e [4], approaching several hundred [3,5]. Concurrently, D is predicted to scale as

$$D \sim \frac{R_g^2}{\tau_1} \sim M^{-2}. \tag{2}$$

This M dependence has been reported to be consistent with experimental results for melts of various polymers [2,3,6], including polystyrene (PS) [7–11], polyethylene (PE) [12–18], and hydrogenated polybutadiene (hPB) [19–23]. The difficulty thus presented is, if additional modes of motion change the M dependence of τ_1 and η, up to and beyond 10^2 entanglements per chain, why do they not influence the M dependence of D, which is also related to τ_1? This apparent inconsistency between the η and D exponents has long been recognized [24], and has even been termed "...one of the biggest remaining mysteries in polymer physics" [25]. It is important to note that although it certainly presents a severe challenge to reptation, it also is problematic for any model, as it implies a significantly different M dependence between chain rotation and translation.

The original reptation model was formulated for an unattached chain trapped in a cross-linked network [1]. In polymer liquids the surrounding chains that constitute the entanglements are also free to diffuse and relax stress. Consequently there will be some finite rate of tube erosion at any point along the tube, not just the ends; this inherently interchain process is termed "constraint release" (CR), and has been considered by many authors [3,26]. Doi first noted that random fluctuations of the position of the test chain ends within the tube, even with the chain center of mass fixed, would erase some tube segments [27]. As the spatial extent of such "contour length fluctuations" (CLF) should scale approximately with $\sqrt{M}$, this intrachain mechanism could enhance the M exponent for η by about 0.5. Milner and McLeish have recently developed a more complete version of CLF that gives an exponent ca. 3.4 for τ_1 [28]. Both CR and CLF accelerate the escape from the tube, and consequently reduce η and increase D. This is the right direction to bring theory into better agreement with experiment, but to date there has not been a self-consistent treatment of both CR and CLF that describes the viscoelastic properties and the diffusivity simultaneously. Other nonreptative models have also been proposed, and, in particular, the polymer-mode-coupling (PMC) theory of Schweizer and co-workers is able to reconcile the differing exponents for η and D, and the apparently nonuniversal character of the crossover to the high M exponents anticipated by reptation [29–31].

Measurements of D in concentrated solutions and gels have generally produced M exponents in the vicinity of -2.4 to -2.5, and clearly stronger than -2 [32–38]. These exponents reflect data extending up to 10^2 entanglements per chain, and are therefore not easily dismissed as a crossover effect associated with the transition from unentangled to entangled behavior. The viscosity of well-entangled solutions, however, follows $\eta \sim M^{3.4}$ just as in the melt [5,39]. These results raise the possibility of a fundamental difference between the dynamics of entangled chains in the melt and in the solution, which is not anticipated by reptation theory (but which can be accommodated within the PMC framework [29–31]). However, the solution results are free of the inconsistency between the η and D exponents; in this light it is the M exponent of D in the melt that is most puzzling.

We recently undertook a thorough examination of the M and volume fraction (ϕ) dependences of D and η for a series of hPB in n-alkane solvents, in an attempt to gain further insight into these issues [40,41]. This system was chosen because the low value of M_e (ca. 950 g/mol) yields well-entangled solutions even for a rather modest ϕ, and because the low glass transition temperature minimizes any ϕ or M dependence to the segmental dynamics, which would otherwise complicate the analysis. We found that $\eta \sim M^{3.4}$ for all entangled solutions, consistent with previous results, and we also found that $D \sim M^{-2.4\pm0.1}$ for concentrated solutions, in agreement with the results for PS [33–35]. However, our data indicated that $D \sim M^{-2.4}$ *even in the melt* [40,41], in apparent disagreement with several other groups. Consequently, we have collected all of the reported values of self-diffusion for entangled hPB melts [18,20–23], and they are plotted as a function of M in Fig. 1. (We restrict attention to $M/M_e > 2.5$, to correspond to the regime for which $\eta \sim M^{3.4}$.) A least squares fit to a power law gives the indicated straight line: $D \sim M^{-2.30\pm0.05}$. The quoted uncertainty is determined by linear regression with a greater than 95% confidence interval. We thus conclude that, contrary to widespread belief [2,3,6], the experimental scaling law for entangled hPB melt diffusion is not $D \sim M^{-2.0}$. Previous workers have successfully interpreted their data in terms of a high M asymptotic exponent of -2.0, combined with CR contributions at lower M/M_e [22,23]. This viewpoint has been bolstered by extensive tracer diffusion measurements in high M matrices [9–11,19] which indicate that (a) self-diffusion is faster than tracer diffusion in a high M matrix, and that (b) the resulting tracer diffusivities scale as $M^{-2.0}$. We are not arguing against, or even contradicting, this approach; rather, we simply ask whether self-diffusion can be well represented by a single power law in M, and if so, what is the associated exponent? (It is exactly this direct approach that yields the value 3.4 for η.) The importance of the result in Fig. 1 is that it largely reconciles the two issues above, at least for this polymer. First, the M exponents for D and η are consistent within the combined experimental uncertainty, and therefore the processes that reduce τ_1 relative to the bare reptation prediction appear in both quantities. Second, there is no need to invoke different dynamic modes of motion for solutions and melts.

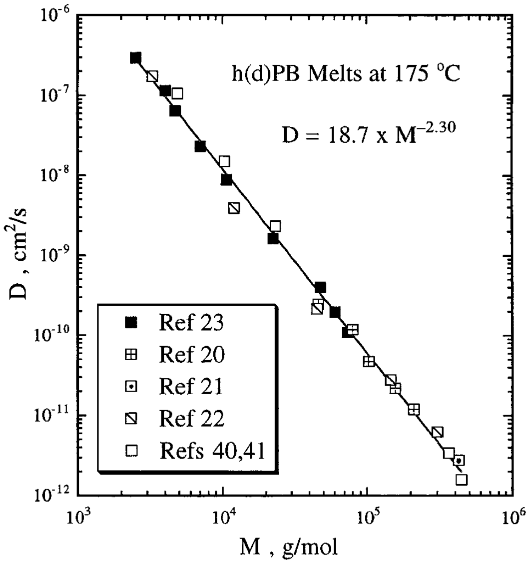

FIG. 1. Melt self-diffusion data for hydrogenated (or deuterated) polybutadiene samples adjusted to 175 °C, as a function of molecular weight.

The data in Fig. 1 require additional comments. First, they were acquired at different temperatures (125 °C [20,21], 140 °C [40,41], 170 °C [22], and 175 °C [23]), and have been reduced to 175 °C by the known T dependence of D for hPB over this measurement range [23,40,41]. Second, the self-diffusion data were determined by several techniques: pulsed-field gradient NMR [23,40,41], infrared microdensitometry [22], small-angle neutron scattering [20], and forward recoil spectrometry [21,40,41]. Third, the reduction to a master curve is remarkable, given the previous two points and the difficulties in determining accurate M values for polymers that are not soluble in organic solvents at modest temperatures. Fourth, the data have been corrected for the M dependence of the segmental friction, following the careful analysis of Pearson *et al.* [23]. Fifth, we have treated each pair of reported values (D, M) as equally reliable, i.e., any systematic errors among the different research groups or measurement techniques are viewed as random errors in the global fit. It is conceivable that a more detailed parsing of the data might conclude that some points are more reliable than others, but at this time we have no basis for doing so, and furthermore the resulting exponent is rather insensitive to the exclusion of any small subset of the data (e.g., if our own data [40,41] were excluded the exponent would become -2.26).

The M dependence of D may be more fairly revealed by plotting DM^2 vs M/M_e, as shown in Fig. 2; in this format any deviations from the predicted M^{-2} are more clearly exposed. The data are shown with error bars, which we estimate conservatively as $\pm 10\%$ for M and $\pm 30\%$ for D. There is a distinct trend to lower values as M/M_e increases, but there is some indication that the data level off beyond $M/M_e \approx 10^2$. In this plot we also show the asymptotic, high M reptation prediction for D as a horizontal line,

$$k_D \equiv DM^2 = \left(\frac{2G_N R_g^2}{45M}\right)\left(\frac{\rho RT}{G_N}\right)^2\left(\frac{M_c}{\eta(M_c)}\right). \quad (3)$$

This expression was developed by Graessley [42] in order to replace model parameters with experimental observables: G_N is the plateau modulus, ρ is the density, and M_c is the critical molecular weight for the crossover to entanglement effects in η [5]. However, there is still uncertainty of up to $\pm 50\%$ in the resulting value of k_D, due primarily to the last term on the right-hand side of Eq. (3). Nevertheless, it is clear that the data are converging upon the reptation prediction at high M, and that the degrees of motional freedom neglected in the strict reptation model enhance the mobility. The dashed line in Fig. 2 represents the prediction of the strict reptation model for D, but based on experimentally determined (viscosity-based) longest relaxation time τ_1 [2],

$$D = \frac{2R_g^2}{\pi^2 \tau_1} = \frac{G_N R_g^2}{6\eta}. \quad (4)$$

Here $R_g^2 = 2 \times 10^{-17}$ M (cm^2), $G_N = 2.3 \times 10^7$ dyn/cm^2, and $\eta = 3.43 \times 10^{-13} M^{3.42}$ (poise) [23,40,41,43]. This comparison confirms that the experimental M dependences of D and η are fully consistent within the experimental uncertainties.

Melt self-diffusion data exist for many other entangled chemical systems: PE [12–18], polyisoprene (PI) [44], PS [7–11], polybutadiene (PB) [44], polyethyleneoxide (PEO) [45], polydimethylsiloxane (PDMS) [45], and polymethylstyrene (PMS) [9]. PE is, in fact, structurally very similar to hPB, and if the PE data were simply superposed on the hPB data in Fig. 1, the scatter would increase but the M exponent remains essentially the same. The hPB data are to be preferred, because the PE samples are relatively polydisperse. For each of the other polymers the data for $M/M_e > 2.5$ were fit to a power law in M. (Data for any $M < 5000$ were also excluded, to minimize friction factor effects.) The exponents ranged from ca. -2.0 for PI [44] to -2.4 for PEO [45] and PMS [9]. These power laws were used to estimate $D(M = 10M_e)$, a reference point which fell within the range of each data set. All these data, plus those from Fig. 1, are collected as a master plot of $D/D(10M_e)$ vs M/M_e in Fig. 3. The fit gives an exponent of -2.28 ± 0.05 (95% confidence). These results demonstrate that entangled polymer melt self-diffusion coefficients universally scale with an exponent significantly stronger than -2.0. A fit to the non-hPB data gives an exponent of -2.17, raising the possibility of a nonuniversal response; however, the range of the independent variable is much smaller for these polymers. A crossover to -2.0 at higher M/M_e is suggested but not established definitively by these data; such a crossover might also be nonuniversal. Finally, extensive measurements of tracer diffusion in high M matrices for PS and hPB are certainly supportive of an asymptotic -2.0 exponent.

Deutsch and Madden simulated the motion of unattached chains in a cage of fixed obstacles [46]. They found $D \sim M^{-2.4}$ and $\tau_1 \sim M^{3.4}$, a result which at the time was rather puzzling [46], but now we may consider to be in

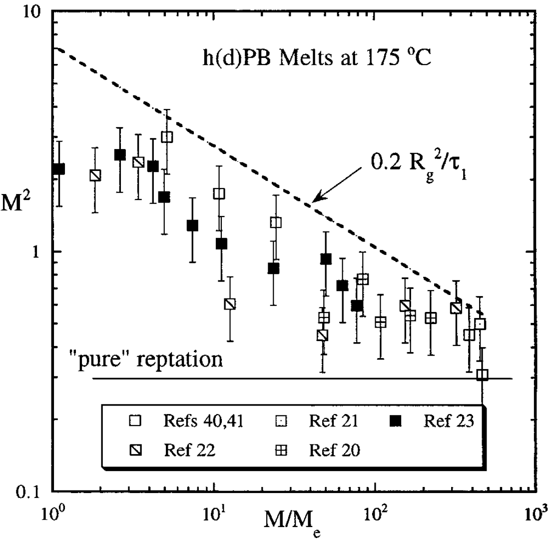

FIG. 2. Data from Fig. 1 replotted as DM^2. The horizontal line represents the prediction of the bare reptation model, and the dashed line the prediction utilizing the experimentally determined longest relaxation time, as discussed in the text.

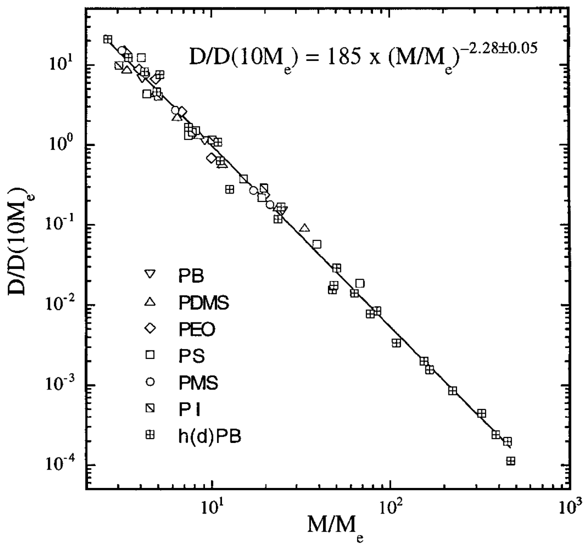

FIG. 3. Data from Fig. 1, combined with data for six other polymers from the literature, along with the global power law fit.

agreement with experiments. More recently Reiter also found similar scaling laws: $D \sim M^{-2.4}$ and $\tau_1 \sim M^{3.5}$ [47]. Rubinstein proposed an elegant discretized version of reptation, the "repton" model, which gives $\tau_1 \sim M^{3.4}$ [25], and $D \sim M^{-2.4}$ when evaluated in three dimensions [46,48]. Collectively, these results suggest that accounting for CLF modes correctly could be sufficient to reproduce the experimental scaling relations, as there are no CR processes in these simulations. A recent extension of the Milner-McLeish [28] treatment of fluctuations also generates diffusion exponents close to -2.4 [49], which supports this contention. On the other hand, the extensive tracer diffusion data clearly demonstrate that D decreases as the matrix molecular weight is increased [9–11,18], which cannot be accounted for by CLF. Consequently, an appropriately self-consistent incorporation of *both* CLF and CR into reptation theory is essential. The PMC theory is fully capable of reproducing the effects of both CLF and CR, in the framework of a more fundamental but possibly less transparent liquid state theory [29–31]. Both reptation and PMC theory require a crossover to $D \sim M^{-2}$ at high M, but as yet, the data do not extend to sufficiently large M/M_e to establish this crossover beyond doubt. Interestingly, an alternative model for cooperative dynamics of fractal objects anticipates the correct finite M/M_e exponents, but explicitly rejects a crossover to the reptation exponents at higher M/M_e [50]. Measurements to significantly higher M/M_e would therefore clearly be interesting, albeit extremely challenging. The available data imply a persistent slight discrepancy between solution and melt exponents, and between melt exponents for *h*PB and other polymers; both issues bear further investigation.

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