

# Do Tube Models Yield Consistent Predictions for the Relaxation Time and Apparent Plateau Modulus of Entangled Linear Polymers?

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**ABSTRACT:** We show that state-of-the-art tube models overestimate the influence of contour length fluctuations (CLF) on the apparent plateau modulus of entangled flexible polymers. The observed inconsistency between the molecular weight dependence of the relaxation time and plateau modulus questions some of the underlying physics and suggests, in particular, that the CLF-based explanation for the zero-shear viscosity vs molecular weight scaling law is not entirely satisfactory.

## Introduction

The tube model developed by Doi and Edwards<sup>1</sup> has become a cornerstone of polymer physics. It is based on the “reptation” concept introduced by de Gennes,<sup>2</sup> which depicts complex topological constraints as a mean-field tube effect restricting the motion of a linear test chain to a 1D curvilinear diffusion. After Doi and Edwards published three seminal papers,<sup>3</sup> Graessley<sup>4</sup> immediately extracted the essential physics regarding chain diffusion and linear viscoelasticity (LVE) and compared them with experiments.<sup>5,6</sup> The most notable discrepancy between the theoretical predictions and experimental results for linear polymers was the molecular weight (MW) dependence of the zero-shear viscosity  $\eta_0$ . While pure reptation predicts  $\eta_0$  and  $\tau_d$ , the terminal relaxation time, to scale as  $Z^3$ , the cube of the number of entanglements, experiments consistently show a higher exponent, usually 3.4. This discrepancy was soon recognized as a serious flaw of the original model and prompted Doi to introduce a fundamental modification<sup>7</sup> by allowing springlike motions of the test chain inside the tube, usually referred to as contour length fluctuations (CLF), to speed up relaxation and reduce the stress level:

$$\eta_0^{(F)} = \eta_0^{(NF)} [1 - \mu(1/Z)^{1/2}]^3 \quad (1)$$

$$G_{app}^{0(F)} = G_{app}^{0(NF)} [1 - \mu(1/Z)^{1/2}] \quad (2)$$

$$\tau_d^{(F)} = \tau_d^{(NF)} [1 - \mu(1/Z)^{1/2}]^2 \cong \eta_0^{(F)} / G_{app}^{0(F)} \quad (3)$$

where superscripts (F) and (NF) stand for “with fluctuations” and “without fluctuations”,  $G_{app}^0$  is the apparent plateau modulus, and  $\mu$  is a universal numerical prefactor. Doi derived  $\mu = 1.47$  from variational principles. With such a high value, fluctuations have significant effects up to  $Z = 200$  because the inverse square root dependence decays slowly. In the same range, eqs 1 and 2 predict  $\eta_0$  to scale as  $Z^{3.4}$  and  $G_{app}^0$  as  $Z^{0.4/3}$  with a smooth transition to  $\eta_0 \propto Z^3$  and  $G_{app}^0 \propto Z^0$  beyond  $Z =$

200.<sup>8</sup> A few years after Doi’s publication, Colby, Fetters, and Graessley<sup>9</sup> measured  $\eta_0$  of quasi-monodisperse polybutadiene over an exceptionally wide range of  $Z$  values (0.5–8000) and seemed to validate the predicted transition at high  $Z$ . Rubinstein proposed the “Repton” model,<sup>10</sup> which qualitatively agreed with Doi’s conclusions. More recently, Milner and McLeish<sup>11</sup> have combined dynamically diluted fluctuations with reptation to yield an accurate  $Z$ -scaling for  $\eta_0$ . Therefore, the 3.4 scaling issue seems to be settled in favor of CLF domination. Very recently, Likhtman and McLeish<sup>12</sup> have published a quantitative theory for LVE of linear entangled polymers (LM theory), which self-consistently combines reptation with CLF and constraint release (CR). The predicted  $Z$  dependence of the dimensionless  $G_{app}^{0(F)} / G_{app}^{0(NF)}$  and the dimensionless  $\tau_d^{(F)} / \tau_d^{(NF)}$  is consistent with eqs 2 and 3, although it is more complex since additional negative powers of  $Z$  show up in the equations. However, the  $Z^{-1/2}$  term dominates, and the dependence is essentially the same as that predicted by Doi, with a numerical factor  $\mu$  even higher than Doi’s, i.e., 1.69.

Obviously, the validity of Doi’s explanation for the observed  $\eta_0$  scaling crucially depends on the magnitude of the numerical factor  $\mu$  in eqs 1–3. Even though  $\mu = 1.47$  generates the right scaling for  $\eta_0$  over a wide range of  $Z$ , it does not imply this is the real contribution of CLF. First, Needs<sup>13</sup> and des Cloizeaux<sup>14</sup> have argued that the effect of CLF on  $\eta_0$  should not be as large as predicted by Doi. They obtained  $\mu = 0.3$  and 0.7 by numerical and analytical methods, respectively. Furthermore, different dynamic modes simultaneously influence the terminal relaxation time  $\tau_d$ . Since it is impossible to distinguish their respective contributions from simple measurements of  $\eta_0$ , the value of  $\mu$  in eq 1 cannot be validated experimentally. On the other hand, the  $Z$  dependence of  $G_{app}^0$  of eq 2 does offer an opportunity to evaluate the prefactor  $\mu$ , which, surprisingly, has not been exploited so far.

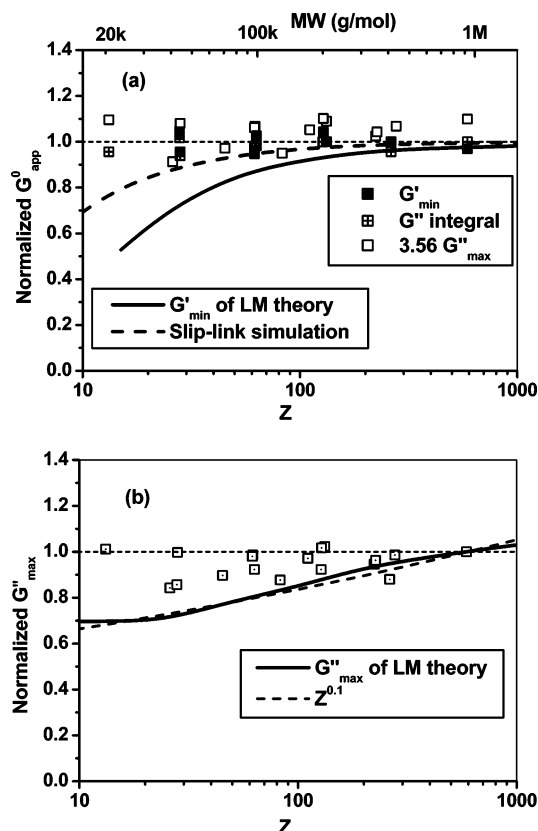
The objective of the present paper is to show that certain predictions of CLF-based tube models, namely the  $Z$  dependence of  $\tau_d$  and  $G_{app}^0$ , are inconsistent and therefore question some of the underlying physics. The predictions of the LM theory,<sup>12</sup> i.e., the state-of-the-art tube theory for LVE of linear polymers, have been compared with an extensive set of accurate experimental data covering a wide range of  $Z$  values. This provides interesting clues about the validity and consistency of eqs 1–3.

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**Figure 1.** (a)  $G'_{app}$  vs  $Z$  or MW:  $G'_{app}$  normalized by  $G'_N = 1.15$  MPa. Solid line represents predicted  $G'_{min}$  by the LM theory; Dashed line represents results of slip-link simulation (ref 30). (b)  $G''_{max}$  vs  $Z$ :  $G''_{max}$  normalized by 0.35 MPa. Solid line represents predicted  $G''_{max}$  by the LM theory. Dashed line corresponds to the slope  $Z^{0.1}$ .

## Results and Discussion

Three accepted methods are described in the literature for the determination of  $G'_{app}$ . First, the plateau modulus can be obtained as the value of  $G'$  at the angular frequency  $\omega_{min}$  where  $G''$  reaches a minimum.<sup>6,8</sup> Second, on the basis of the Kronig–Kramers relation,  $G'_{app}$  can be calculated by integration over the terminal relaxation peak as<sup>6</sup>

$$G'_{app} = \frac{2}{\pi} \int_{-\infty}^{+\infty} G''(\omega) d \ln \omega \quad (4)$$

The third method, developed by Raju et al.,<sup>15</sup> is based on the so-called “universal terminal relaxation spectrum”, i.e., the empirical observation that the terminal peak of well-entangled monodisperse polymer species has a universal shape, when properly scaled. Hence, for sufficiently narrow-distributed long chains, the ratio of the plateau modulus to the maximum of  $G''$  at the terminal peak is a universal proportionality constant, which Raju et al. found to be equal to 3.56. The methods based on  $\omega_{min}$  and  $G''_{max}$  only involve a straightforward reading of mastercurve data, while the method based on the terminal peak integration is more delicate to use because, in some cases, it requires a careful extrapolation of the terminal peak at the high-frequency side in order to properly remove the contributions of the Rouse motions.<sup>16</sup> As shown below, all three methods give very consistent results.

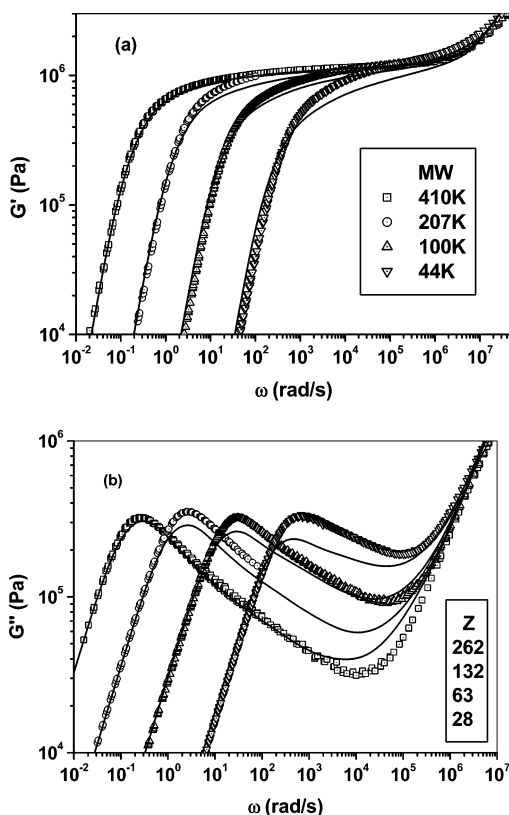
We have applied the three methods described above to a large set of rheological data published in the past 30 years for quasi-monodisperse polybutadiene (PBD), polyisoprene (PI), and polystyrene (PS). Among those polymers, PBD is unique as it has a very small molecular weight between entanglements  $M_e \sim 1600$  g/mol, and hence, a wide range of  $Z$  values can be covered experimentally (up to 600).

The  $G'_{app}$  values for PBD<sup>9,15,17–20</sup> are plotted in reduced form ( $G'_{app}/G'_N$ ) as a function of  $Z$  and MW in Figure 1a, and the molecular characteristics as well as the plateau modulus are also listed in Table 1. We choose  $G'_N = 1.15$  MPa according to Fetters<sup>21</sup> and in agreement with our data for high MW samples. To convert MW to  $Z$ , we take  $M_e = 1570$  g/mol according to  $G'_N = 4\rho RT/5M_e$ .<sup>8</sup> No clear  $Z$  dependence of the reduced  $G'_{app}$  is observed for  $Z > 20$ . For lower  $Z$  values, the data are less accurate because of the strong disturbance of the terminal relaxation by the high-frequency Rouse-like relaxation. All the reduced data are located between 0.9 and 1.1. Considering that the data come from different groups and a 5% random error due to sample loading is unavoidable, the consistency of the data is in fact quite remarkable. We do not exclude the possibility that a very weak dependence of  $G'_{app}$  on  $Z$  is hidden within the experimental uncertainty of 10%. However, this uncertainty does not preclude a comparison with predictions of

**Table 1.** Molecular Characteristics and Apparent Plateau Moduli  $G'_{app}$  (MPa) Estimated by Different Methods for PBD

| sample <sup>a</sup> | min method <sup>b</sup> | integral method <sup>c</sup> | max method <sup>d</sup> | $G''_{max}$ (MPa) | $M_w/M_n$ | $M_w$ (kg/mol) | ref        |
|---------------------|-------------------------|------------------------------|-------------------------|-------------------|-----------|----------------|------------|
| L200                |                         |                              | 1.15                    | 0.323             | <1.05     | 200            | 15 (25 °C) |
| L350                |                         |                              | 1.18                    | 0.331             | <1.05     | 350            |            |
| 41L                 |                         |                              | 1.05                    | 0.305             | 1.04      | 41             | 17 (25 °C) |
| 98L                 |                         |                              | 1.23                    | 0.345             | 1.03      | 985            |            |
| 174L                |                         |                              | 1.21                    | 0.34              | 1.04      | 174            |            |
| 435L                |                         |                              | 1.23                    | 0.345             | 1.03      | 435            |            |
| B1                  |                         |                              | 1.12                    | 0.314             | <1.1      | 71             | 9 (25 °C)  |
| B2                  |                         |                              | 1.09                    | 0.307             | <1.1      | 130            |            |
| B3                  |                         |                              | 1.20                    | 0.337             | <1.1      | 355            |            |
| B4                  |                         |                              | 1.26                    | 0.355             | <1.1      | 925            |            |
| B4                  | $\sim 1.15^e$           | 1.15                         | 1.26                    | 0.355             | <1.1      | 925            | 18 (25 °C) |
| PBD21               |                         | 1.10                         | 1.26                    | 0.354             | <1.1      | 21             | 19 (28 °C) |
| PBD41               | 1.10                    | 1.08                         | 1.24                    | 0.349             | <1.1      | 44             |            |
| PBD97               | 1.09                    | 1.12                         | 1.22                    | 0.343             | <1.1      | 97             |            |
| PBD201              | 1.20                    | 1.15                         | 1.27                    | 0.356             | 1.27      | 201            |            |
| 44K                 | 1.20                    | 1.17                         | 1.19                    | 0.333             | 1.01      | 44             | 20 (40 °C) |
| 100K                | 1.18                    | 1.13                         | 1.15                    | 0.323             | 1.01      | 99             |            |
| 207K                | 1.15                    | 1.15                         | 1.25                    | 0.352             | 1.01      | 208            |            |
| 410K                | 1.15                    | 1.10                         | 1.15                    | 0.323             | 1.01      | 412            |            |
| average             | $1.15 \pm 0.05$         | $1.13 \pm 0.03$              | $1.18 \pm 0.07$         | $0.33 \pm 0.02$   |           |                |            |

<sup>a</sup> Codes in original references. <sup>b</sup> Estimated by using “minimum” method:  $G'_{app} = G'(\omega)_{G''-\text{minimum}}$ . <sup>c</sup> Estimated by using “integral” method:  $G'_{app} = (2/\pi) \int_{-\infty}^{+\infty} G''(\omega) d \ln \omega$ . <sup>d</sup> Estimated by using “maximum” method:  $G'_{app} = 3.56 G''_{max}$ . <sup>e</sup>  $G'$  value at highest attainable frequency.

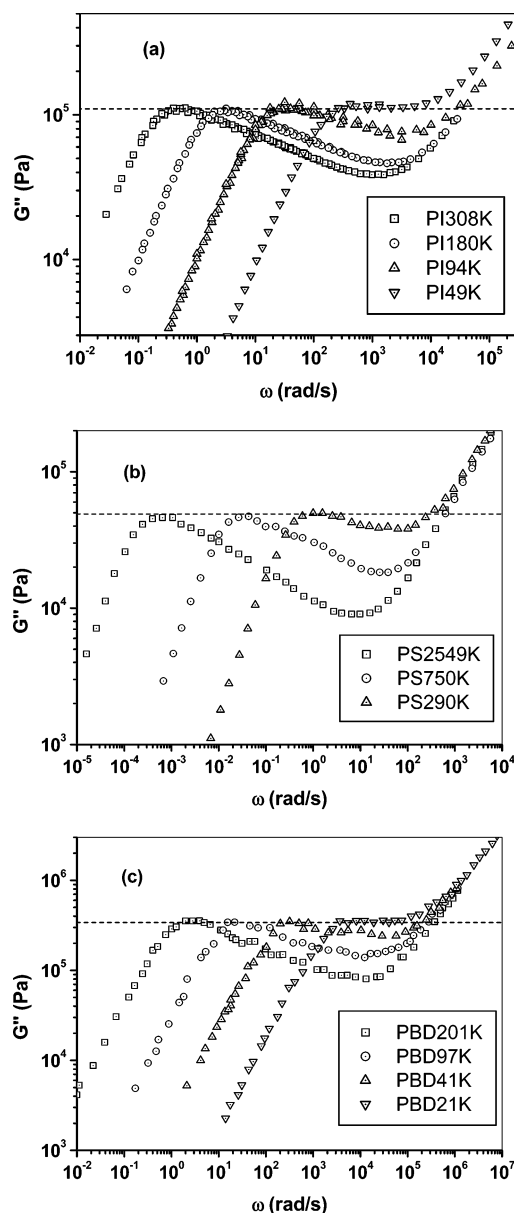


**Figure 2.** Cross-check between the relaxation time and relaxation modulus: comparison between theoretical predictions (lines) by the LM theory and experimental data (points) for monodisperse PBDs of ref 20.

the LM theory, since the latter predicts a much stronger dependence on  $Z$ , as the solid curve shows in Figure 1a. Predictions for  $G_{app}^0$  are taken as the  $G'_{min}$  at the frequency where loss modulus  $G''$  has a minimum and obtained according to ref 12, with the constraint release parameter  $c_v = 1$ .

The maximum of the loss modulus terminal peak,  $G''_{max}$ , which for monodisperse polymers is essentially indistinguishable from the  $G'-G''$  crossover, is reasonably free from disturbance from the high-frequency Rouse-like relaxation.<sup>15,16</sup> Therefore, comparing the experimental and predicted dependence of  $G''_{max}$  vs  $Z$  provides a stronger test. This comparison is presented in Figure 1b. All data and predictions by the LM theory (with  $c_v = 1$ ) have been reduced by  $G''_{max}$  of the highest MW sample ( $=0.35$  MPa). The same discrepancy between the experimental results and the predictions is observed as for  $G_{app}^0$ . The predicted slope<sup>8,12</sup> is very close to  $Z^{0.1}$  represented by the dashed line. This slope is consistent with eq 2, considering that there is a proportionality between  $G''_{max}$  and  $G_{app}^0$ .<sup>15,16</sup>

The above results suggest that the value of  $\mu$  in eq 2 is overestimated by Doi<sup>7</sup> and the LM theory or that the  $Z^{-1/2}$  scaling may be incorrect for  $G_{app}^0$ . It is therefore important to cross-check the consistency of the  $Z$  dependence predicted by CLF tube models for the relaxation time and modulus. To this end, we use a set of accurate LVE data for linear PBD (from 44 to 410 kg/mol) published by Wang et al.<sup>20</sup> and presented in Figure 2. The quality of the data is reflected by the very narrow distribution of the samples (polydispersity about 1.01) and the excellent overlap of the high-frequency Rouse-like relaxation for all samples. For comparison with the LM theory, only two basic parameters must be defined, the entanglement modulus  $G_e = 5/4 G_N^0$  and the equilibration time of a segment between



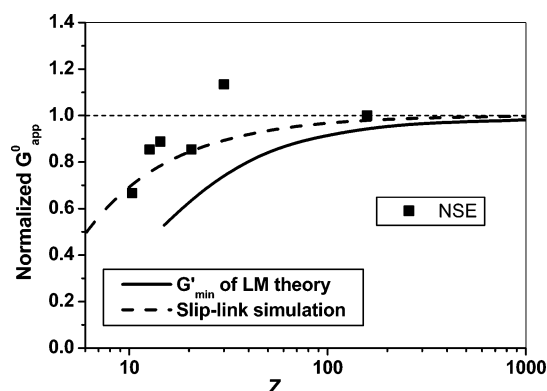
**Figure 3.**  $G''$  terminal relaxation peaks for (a) PI of ref 22, (b) PS of ref 23, and (c) PBD of ref 19.

entanglements  $\tau_e$ ;  $\tau_e$  is the only free fitting parameter. We use  $G_e = 1.45$  MPa based on  $G_N^0 = 1.15$  MPa<sup>21</sup> and  $\tau_e = 2.5 \times 10^{-7}$  s for master curves at 40 °C. The corresponding monomeric friction coefficient  $\xi$  is  $0.8 \times 10^{-7}$  g/s,<sup>8</sup> which compares very well with values reported by Ferry<sup>6</sup> and Colby<sup>9</sup> for linear PBD. The comparison between the experimental results and predictions in Figure 2 is striking. While the agreement is excellent for the terminal relaxation times, significant vertical deviations are observed at intermediate frequencies for all samples but the highest MW. Clearly, the LM theory incorporates the  $Z$  dependence of the fast relaxation processes adequately for the time scale but overestimates their contribution on stress relaxation, which is consistent with the  $G_{app}^0$  and  $G''_{max}$  results presented above. Almost constant  $G''_{max}$  within an uncertainty of 5% is also observed for other polymer species, i.e., PI<sup>22</sup> and PS,<sup>23</sup> as well as for PBD data from another group<sup>19</sup> (see Figure 3). All the above discrepancies indicate an overestimation of CLF effects on the relaxation modulus, which is also a possible reason why the LM model and, similarly, the Milner–McLeish model<sup>11</sup> need a 20–30% larger  $G_N^0$  than the accepted literature value

**Table 2. Tube Diameters from NSE Spectrum and Reduced  $G_{\text{app}}^0$  for Polyethylenes<sup>25</sup>**

| $M_w$<br>(kg/mol) | $\alpha_{\text{(diluted)}}$<br>(nm) | $G_{\text{app}}^0$ <sup>a</sup> | $\alpha_{\text{(CLF)}}$ <sup>a</sup><br>(nm) | $G_{\text{app}}^0$ (CLF) | Z    |
|-------------------|-------------------------------------|---------------------------------|--|--------------------------|------|
| 12.4              | 6.0                                 | 0.67                            | 4.45   | 1.14                     | 10.3 |
| 15.2              | 5.3                                 | 0.85                            | 4.25   | 1.25                     | 12.7 |
| 17.2              | 5.2                                 | 0.89                            | 4.45   | 1.14                     | 14.3 |
| 24.7              | 5.3                                 | 0.85                            | 4.7  | 1.02                     | 20.6 |
| 36                | 4.6                                 | 1.13                            | 4.25   | 1.25                     | 30   |
| 190               | 4.9                                 | 1                               | 4.75   | 1                        | 158  |

<sup>a</sup> Calculated by using  $\alpha^2 = N_e b^2 = (M_e/M_0)b^2 \propto 1/G_N^0$ .

**Figure 4.**  $G_{\text{app}}^0$  vs  $Z$ .  $G_{\text{app}}^0$  extracted from neutron spin echo (NSE) data of ref 25. The theoretical predictions are same as in Figure 1a.

for agreement with experimental data in the  $Z$  range below 200.<sup>12,24</sup>

An apparent overestimation of CLF on the stress level by the LM theory can also be inferred from recent neutron spin echo (NSE) experiments. Wischniewski et al.<sup>25</sup> present a series of NSE spectroscopy data for polyethylene melts with different MWs between 12 and 190 kg/mol. Raw tube diameters  $\alpha$  are obtained by fitting the single-chain dynamic-structure factor with a pure reptation model. Wischniewski et al. correct the diameters by fitting the structure factor instead with a reptation + CLF model, and the two sets of tube diameters as  $\alpha_{\text{(diluted)}}$  and  $\alpha_{\text{(CLF)}}$  are given in Table 2. In the corresponding Figure 3 in ref 25, it can be observed that the *all* corrected tube diameters of lower MW samples are smaller than that of the highest MW sample (190 kg/mol). This could imply an overcorrection. An alternative interpretation of their results would be to consider that the wider tube diameters reflect an overall dilution effect resulting from CLF, CR, and possibly other fast relaxation processes. Lower MW samples hence have wider tube diameters  $\alpha_{\text{(diluted)}}$ , which are related to the high-MW limit  $\alpha_{\text{(undiluted)}}$  and the reduced  $G_{\text{app}}^0$  in the following way:<sup>1,8</sup>

$$\frac{\alpha_{\text{(undiluted)}}^2}{\alpha_{\text{(diluted)}}^2} = \frac{M_e^{\text{(undiluted)}}}{M_e^{\text{(diluted)}}} = \frac{G_{\text{app}}^0}{G_N^0} \quad (5)$$

We convert the observed raw tube diameters into  $G_{\text{app}}^0/G_N^0$  according to eq 5 by considering the diameter of the highest MW sample ( $Z \sim 160$ ) as the undiluted limit value. The results are reported in Table 2 and are plotted as a function of  $Z$  in Figure 4, where we take  $M_e = 1200$  g/mol corresponding to the  $G_N^0 = 2.0$  MPa<sup>16,26,27</sup> to convert MW into  $Z$ . The reduced  $G_{\text{app}}^0$  are compared with the predictions by the LM theory, and again, the influence of CLF seems to be overestimated by the theory.

Considering the limits of tube models,<sup>28</sup> different groups<sup>28–30</sup> recently made attempts to simulate the dynamics of entangled

polymers with slip-link models. Masubuchi et al.<sup>30</sup> suggest a simple dependence of  $G_{\text{app}}^0$  on  $Z$ , which is apparently confirmed by their slip-link simulations:

$$G_{\text{app}}^0 \propto 1 - \frac{3}{Z} \quad (6)$$

The simulation should automatically contain reptation and faster processes, e.g. CLF and CR, as well as so-called “dangling ends” effects. Predictions by eq 6 are also presented in Figures 1a and 4 as dashed lines. Simulation results by Masubuchi et al. show that  $G_{\text{app}}^0$  reaches an asymptotic value at  $Z$  around 30, as opposed to about 200 for CLF tube models. This is in good agreement with both rheological data and the NSE-based evidence discussed above.

## Conclusion

In conclusion, both experimental data and slip-link simulations indicate a weaker dependence of  $G_{\text{app}}^0$  vs  $Z$  than predicted by state-of-the-art tube models, which reveals an inconsistency between the MW dependence of the relaxation time and modulus in CLF tube models. A possible explanation could be an overestimation of the CLF effect, as it is quantified by the numerical factor  $\mu$  in eqs 1–3. Over the years, a wide range of theoretical estimations have been published, ranging from 0.3 to 1.69.<sup>7,10–14</sup> A value around 0.7 would roughly capture the experimental  $Z$  dependence of  $G_{\text{app}}^0$  in Figures 1 and 4 but would not yield the required  $\eta_0 \propto Z^{3.4}$  scaling. As a consequence, the mystical 3.4 power problem might not be entirely solved after all.

Watanabe<sup>31</sup> has commented that the agreement between the observed  $\eta_0$  scaling and the prediction of CLF tube models<sup>7,11,12</sup> should not be construed as an indication that there are no contributions from other dynamic modes, e.g., constraint release (CR). Graessley and others<sup>32–35</sup> have shown that CR contributes to the nonreptative scaling behavior of the self-diffusion coefficient  $D_s \sim Z^{-2.3}$  at low  $Z$  although Lodge has argued that CLF is in fact the origin.<sup>36</sup> Recently, Wang<sup>37</sup> has clarified the situation for  $D_s$  in favor of a CR-only origin. A logical deduction would be that CR should contribute to the  $Z$  scaling for  $\eta_0$  as well as CLF, as already proposed in the literature.<sup>31,37–39</sup> However, the CR and CLF contributions to the  $\eta_0$  scaling are so subtle that there are no unambiguous results from experiments on binary mixtures so far.<sup>17,39–41</sup> It should be noted that a rigorous treatment of CR is a formidable task due to the intrinsic “many-body” nature of the problem.

A related problem is that CLF effects are probably polymer-specific and correlate with chain stiffness.<sup>42,43</sup> To resolve the remaining inconsistencies, well-designed experiments (in particular those combining rheological measurements with other characterization techniques) and multiscale computer simulations<sup>44</sup> are as much in need as additional theoretical developments. A successful self-consistent theory should be able to predict rheology, diffusion, and structure factor at the same time.<sup>28</sup>

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