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Microscopic Theory of Concentration Scaling in Entangled Polymer Solutions and Melts

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ABSTRACT: The microscopic polymer mode coupling theory of entangled solution and melt dynamics is combined with equilibrium integral equation methods and a theory for the Rouse/entangled crossover to make predictions for the concentration and statistical segment length dependences of transport properties. Both Θ and good solvents are treated, and analytic scaling laws are derived for the crossover chain lengths, plateau modulus, diffusion constant, terminal relaxation time, and shear viscosity. The physical origin of the concentration and segment length scaling behavior is a direct connection between dynamics and equilibrium conformational and intermolecular correlations. The predictions appear to be consistent with most, but not all, of the existing data in solutions and melts. Comparisons with phenomenological reptation and entanglement scaling ideas, and a nonreptation correlated cluster dynamics approach, are made. Similarities and differences between the various theories are identified.

1. Introduction

Long-chain polymer fluids exhibit extraordinary dynamics as a consequence of the combined constraints of backbone connectivity and uncrossability due to excluded-volume forces.[1-3] This phenomenon is attributed to chain "entanglements", the physical nature of which remains elusive despite many theoretical studies.[4-12] The phenomenological reptation/tube theory[2,3] postulates an anisotropic curvilinear diffusive motion as being the dominant mechanism for "disentanglement" and has been quite successful in explaining many of the distinctive experimental features.[11] However, significant discrepancies still exist, and this approach makes no statement about what an entanglement is, why it occurs, or what is the nature of the fluctuating forces in a viscoelastic polymer fluid. More recently, alternative dynamical theories have been developed.[12-21] For flexible macromolecules, the polymer mode-coupling (PMC) approach[15-20] is unique in that it attempts a microscopic description of chain motion at the level of the fluctuating intermolecular forces. Direct connections between the slow polymer dynamics, and single- and many-chain equilibrium structural features, have been identified. Most recently, the PMC theory has been generalized to numerically treat the crossover from Rouse to mode-coupled dynamics,[18,19] thereby allowing quantitative calculations and detailed comparisons with experiments and simulations to be carried out.

A full understanding of the crossover from unentangled Rouse dynamics to slow entangled dynamics remains a difficult theoretical problem. We have recently investigated[22] this issue using a microscopic statistical dynamical approach[15] which does not rely on resolving the controversial question of what mechanism of motion dominates long time entangled polymer dynamics.[11,12,23-25] In the course of this study,[22] we have developed the necessary theoretical tools to analytically establish the predictions of PMC theory[15-19] for the solution concentration and melt statistical segment length dependences of the zero frequency transport properties of highly entangled chains. This is the subject of the present report.

There exists a significant body of experimental data concerning the concentration dependence of viscoelastic properties.[1,11] Definite trends exist, often of a power law or scaling form (at fixed segmental friction constant), although a fundamental understanding remains controversial.[4-6,26] Our present emphasis is on deriving qualitative relationships, so numerical prefactors, although calculable, are ignored. Our primary result is the discovery of a direct connection between the concentration and statistical segment length scaling of the dynamical and elastic properties of entangled chain fluids and their equilibrium conformational and intermolecular correlations. These predictions appear to be consistent with most, but not all, of the existing data in melts and solutions.

The remainder of the paper is structured as follows. In section 2 the basic model, dynamical crossover theory, and the relevant equilibrium properties are summarized. By combining these results and prior PMC theory analysis, new analytic predictions are derived in section 3 for the concentration and segment length dependences of the zero frequency transport properties in the long-chain limit. Comparisons with experiment and prior theories are the subject of section 4. Prior published results of polymer mode-coupling theory[15-19] and related topics[22,27] that are required for our present analysis are quoted without derivation. The reader interested solely in our transport coefficient predictions may skip directly to section 3.

2. Model, Equilibrium Properties, and Dynamical Crossover

Evaluation of the concentration dependence of the predictions of PMC theory requires a theory of the equilibrium properties which quantify the fluctuating force memory functions. Evaluation of the shear viscosity also requires a theory for the plateau modulus.

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These aspects have been recently discussed,[22] so here we briefly summarize the results needed as input to our new analyzes in section 3.

A. Model and Equilibrium Properties. We consider the simplest possible structural model of three-dimensional polymer fluids which is consistent with use of Rouse and related dynamical theories: Gaussian chains composed of N statistical segments of length σ which interact intermolecularly via pair-decomposable hard-core repulsions of diameter d. An "aspect ratio" can be defined as $\Gamma = \sigma/d$. The compressible fluid is characterized by a reduced density ϱd^3, where ϱ is the segment number density. Solvent quality ("Θ" or "good") enters only *indirectly* via the dependence of chain dimensions on solution density. Very short time dynamics is described by the Rouse model[1-3] characterized by a "bare" system-specific friction constant, ζ_o, which describes (irreversible) dynamics on the subsegment length scale and serves to set the elementary time scale.

For our present purposes, the key collective and interchain equilibrium properties that enter the statistical dynamical theory are as follows: $\hat{S}(0)$, the zero wavevector value of the static collective structure factor (proportional to the isothermal compressibility), which is related to the density−density screening length, ξ_ρ, as $\hat{S}(0) = 12(\xi_\rho/\sigma)^2$, and $g(d)$, the "contact value" of the chain-averaged *inter*molecular site−site pair correlation (radial distribution) function. The strength of the equilibrium interchain hard-core forces enters via a dimensionless quantity ψ given by[15,22]

$$\psi = \rho d^3 (d/\sigma)^3 g^2(d) \hat{S}(0) \tag{2.1}$$

Physically, ψ is proportional to the segmental-scale equilibrium mean square total force exerted by the surrounding polymers on a tagged chain.

The equilibrium properties described above can be most simply computed using the Gaussian string polymer reference interaction site model (PRISM) integral equation theory.[22,27,28] In the calculation of all equilibrium properties, we employ the limiting large N values since they describe the intrinsic (N-independent) behavior relevant to experiments. In specific applications we set $d = \sigma$ since this is the simplest choice and leads to predictions for ξ_ρ and the osmotic pressure which are in agreement with experiments.[22] However, an important caveat is that such a choice means all chemical structural information is contained in only one local length scale, a simplification that may have nontrivial limitations.

The string PRISM model predictions have been obtained numerically for reduced densities of experimental relevance.[22] To a good approximation, very simple scaling laws are found

$$\xi_\rho \propto (\rho\sigma^2)^{-1}, \quad g(\sigma) \propto \psi \propto \rho\sigma^3 \tag{2.2}$$

The screening length has the form of an inverse "segment length on an equal volume basis", or "packing length" which is equal to the molecular volume per mean square end-to-end distance, as recently discussed in a variety of equilibrium and dynamic contexts.[26-31] Equation 2.2 holds for the quantity ψ up to meltlike reduced densities of $\rho\sigma^3 = 1$. However, there are two important caveats which should be mentioned. The simple relations of eq 2.2 are not "exact", so small system-specific deviations may occur.[22] Corrections due to nonuniversal local chain structure (e.g., a nonunity aspect ratio) may also be significant and are presently under study.

It is important to determine what string PRISM theory predicts for well-understood equilibrium properties. Using eq 2.2, the density dependence of the screening length is predicted to be of a power law form: $\xi_\rho \propto \rho^{-1}$ for Θ solvents, and $\xi_\rho \propto \rho^{-3/4}$ for good solvents. In obtaining these results, we have assumed Θ solvent implies the statistical segment length is ρ-independent, while good solvent conformational behavior is described using the blob scaling[2] or field theoretic[3] prediction for the semidilute concentration regime that $\sigma \propto \rho^{-1/8}$. As an important caveat, we note that direct experimental tests of these conformational scaling laws are surprisingly few. Moreover, the question of whether chain dimensions saturate in concentrated good solutions or continue to contract up to melt densities is not clear from existing neutron scattering studies.[32] Recent self-consistent PRISM analysis[33] suggests nonnegligible variation of chain dimensions up to melt densities is possible. Thus, there may be some nonuniversality of the σ versus ρ relation which would modify our predictions. The osmotic pressure is predicted to be[22] $\beta\Pi \propto \xi_\rho^{-3} \propto \rho^3$ ($\rho^{9/4}$) for Θ (good) solutions. These string PRISM results agree with the scaling and field theoretic work[2,3] for the screening length and osmotic pressure, which in turn are in excellent accord with experiments.

B. Crossover and Plateau Modulus Predictions. For very short times, the nonMarkovian excluded-volume friction and elastic effects predicted by PMC theory are not important and the chains obey Rouse dynamics. The crossover from Rouse to slower dynamics (reptation, mode-coupled, or some other mechanism) occurs at a characteristic time τ_c and has recently been studied[22] in detail based on the so-called "renormalized Rouse" (RR) theory formulated at the level of the bare hard-core fluctuating forces.[15] This approach is used to estimate the breakdown of Rouse dynamics and does not presume what the nature of the entangled long-time motions are. For long chains the characteristic crossover time and length scale, r_c, from Rouse to entangled dynamics are given by[17,22]

$$\tau_c \propto \sigma^2 \beta\zeta_o/\psi^4$$

$$r_c^{\,2} \propto \sqrt{\tau_c/\beta\zeta_o} \propto \sigma^2\psi^{-2} \tag{2.3}$$

which are system-specific and density-dependent, but N-independent. In the reptation picture, r_c is identified with the "tube diameter".

A plateau shear modulus is determined as follows.[22] The breakdown of RR theory is assumed to signal the onset of entanglement effects and the emergence of a plateau modulus. Thus, the plateau modulus is estimated as the value of the stress relaxation modulus predicted by Rouse theory at the crossover time.

$$G_N \cong G_{\mathrm{Rouse}}(t=\tau_c) \propto \rho k_B T \psi^2 \tag{2.4}$$

$$N_e \propto \psi^{-2}$$

An "entanglement degree of polymerization" is defined by the classical rubber elasticity relation $G_N \equiv \rho k_B T/N_e$.

As shown in previous work,[22] explicit dynamical crossover predictions follow immediately from employing the equilibrium results quoted in section 2A. The shear stress plateau modulus, crossover time, length scale, and entanglement degree of polymerization are given by[17,18,22]

$$\tau_c \propto \tau_0(\rho\sigma^3)^{-4}$$

$$G_N \propto (\rho\sigma^2)^3 \propto \xi_\rho^{-3}$$

$$r_c \propto \xi_\rho \propto 1/\rho\sigma^2 \qquad N_e \propto (\rho\sigma^3)^{-2} \tag{2.5}$$

where $\tau_0 = \beta\sigma^2\zeta_0$ is the elementary "jump time" of the bare Rouse model. For polymer solutions, we obtain the following density scaling predictions for Θ solvents

$$G_N \propto \rho^3, \quad r_c \propto \rho^{-1}, \quad N_e \propto \rho^{-2} \tag{2.6}$$

and for good solvents

$$G_n \propto \rho^{9/4}, \quad r_c \propto \rho^{-3/4}, \quad N_e \propto \rho^{-5/4} \tag{2.7}$$

The predicted power law dependence of the plateau modulus and entanglement degree of polymerization on chain segment length and liquid density in terms of the invariant "inverse packing length" variable $\rho\sigma^2$ are in complete agreement with a recent comprehensive melt experimental study.[26]

The above predictions also appear to be quantitatively invariant to the question of whether the density screening length is larger or smaller than the dynamic crossover length.[22] Hence, eqs 2.5–2.7 apply for all densities well above the semidilute crossover. This feature seems to be in qualitative accord with the experimental conclusion that only one type of scaling behavior is seen for the elastic properties of a particular material.[34] However, as mentioned in section 2A, our results are sensitive to the (possibly nonuniversal) dependence of chain dimensions on polymer concentration (for which there are few direct measurements), and possibly also local non-Gaussian chain stiffness. Moreover, hydrodynamic interactions have been ignored.

It should be pointed out that there exists many disparate theoretical ideas, based on various ansatzes of what constitutes an entanglement, which make predictions for some of the above properties.[4-12] Relations such as $r_c \propto \xi_\rho$ have been proposed by several workers based on "packing arguments" and/or a "one-parameter" scaling ansatz.[2,6,8,10] Alternative "mean field" arguments[3-5] and a "two-parameter" scaling ansatz[4] have also been suggested and result in different predictions. Detailed discussions of the various theoretical ideas can be found in the literature.[4,11,12,22,26]

3. Concentration and Segment Length Scaling Predictions for Entangled Fluids

We now combine the dynamical crossover and string PRISM equilibrium results with the analytic polymer mode-coupling approach for entangled chain polymer fluids.[15,17] Our goal is to establish the concentration and segment-length scaling predictions of PMC theory for the low-frequency transport properties in the asymptotic large N limit. Finite N fluctuations effects, which are relevant to experimental systems, require rather complicated numerical analysis[18,19] and will be not considered here.

A. Polymer Mode-Coupling Theory. The large N analytic predictions of the polymer mode-coupling theory as a function of equilibrium structural properties have been discussed at length elsewhere.[15-17] The self-diffusion constant, or tracer diffusion constant in a frozen matrix, is predicted to be

$$D/\zeta_0 \propto \rho\sigma^3\hat{S}(0)\psi^{-1}N^{-2} \propto g^{-2}(\sigma)N^{-2} \tag{3.1}$$

Polymer mode-coupling theory *predicts* (not assumes) from first principles the emergence of a plateau shear modulus when the collective dynamical feedback effects become manifest.[15-18] In the terminal relaxation regime, the stress relaxes exponentially with a characteristic time τ_D. This terminal or longest relaxation time is proportional to the zero frequency part of the viscoelastic memory function[15] and is given by

$$\tau_D \propto \tau_0(\rho\hat{S}(0))^{-1}\psi N^3 \propto \tau_0 g^2(\sigma)N^3 \tag{3.2}$$

where $\tau_0 = \beta\sigma^2\zeta_0$. The shear viscosity is predicted to be

$$\eta \propto G_N\tau_D \propto \rho\psi^2 g^2(\sigma)N^3\zeta_0 \tag{3.3}$$

Both eqs 3.2 and 3.3 are based on the validity of the Markov limit (time scale separation between single chain and fluctuating intermolecular force relaxation times), which is valid in the large N limit within the simplest PMC approach.[15]

Finally, the product $D\eta$ is an especially interesting quantity since the poorly understood concentration-dependent segmental friction constant cancels out. Combining eqs 3.1 and 3.3 yields

$$D\eta \propto \rho\psi^2 N \tag{3.4}$$

B. Concentration and Segment-Length Scaling Predictions. We now combine the equilibrium string model and dynamical crossover results, discussed in section 2, with the large N PMC results of section 3A, to obtain concentration and segment-length dependence predictions for highly entangled fluids.

Equations 2.2 and 3.1 yield for the self-diffusion constant, or tracer diffusion constant in a frozen matrix,

$$D/\zeta_0 \propto (\rho\sigma^3)^{-2}N^{-2} \propto N_D/N^2 \tag{3.5}$$

The final proportionality defines a critical degree of polymerization, N_D. Comparison of eq 3.5 with eq 2.5 shows that N_D is predicted to obey the same reduced concentration scaling law as N_e. At fixed (local) segmental friction constant, the polymer concentration scaling predictions are

$$D \propto \rho^{-2} \propto N_D, \quad \Theta$$

$$\propto \rho^{-5/4} \propto N_D, \quad \text{good} \tag{3.6}$$

By combining eqs 2.2 and 3.2, the terminal relaxation time is given by

$$\tau_D \propto \tau_0(\rho\sigma^3)^2 N^3 \propto (N/N_\tau)\tau_R \tag{3.7}$$

where $\tau_R \propto N^2$ is the Rouse time. Thus, with regard to the concentration dependence eq 3.7 predicts the terminal relaxation time scales with polymer concentration in the same qualitative manner as the inverse diffusion constant D^{-1}. The final proportionality defines a crossover degree of polymerization, N_τ, from Rouse behavior to entangled dynamics, which obeys the same reduced concentration scaling law as N_D and N_e. Note that this feature is a prediction, not an assumption. Combining eqs 3.7 and 2.4 yields the shear viscosity

$$\eta \propto \rho^5\sigma^{12}N^3\zeta_0 \propto \eta_{\text{Rouse}}(N/N_\eta)^2 \tag{3.8}$$

The final proportionality defines a crossover degree of polymerization for the shear viscosity, N_η, which again is predicted to obey the same concentration scaling law as all the other crossover N values. The shear viscosity concentration scaling laws are

$$\eta/\zeta_0 \propto N^3\rho^5 \propto (\rho/\rho^*)^5\sqrt{N}, \quad \Theta$$
$$\propto N^3\rho^{3.5} \propto (\rho/\rho^*)^{3.5}N^{1/5}, \quad \text{good} \qquad (3.9)$$

where the standard Flory values are employed for the semidilute overlap density: $\rho^* \propto N^{-1/2}$ and $N^{-4/5}$ for Θ and good solvents, respectively. Note that perfect scaling in terms of the reduced concentration variable ρ/ρ^* is not predicted, but the N-dependent deviation is very weak for the good solvent case.

Combining eqs 3.5 and 3.8 yields the product $D\eta$ as

$$\begin{aligned} D\eta &\propto \rho^3\sigma^6 N \\ &\propto \rho^3, \quad \Theta \\ &\propto \rho^{2.25}, \quad \text{good} \end{aligned} \qquad (3.10)$$

Note that the invariant packing length, $\rho\sigma^2$, again enters as the crucial material parameter.

All the above PMC theory results have employed the renormalized Rouse approximation for the projected fluctuating force memory function dynamics.[15] This scheme leads to asymptotic N scaling laws identical to the reptation/tube theory. However, one problem in comparing the viscoelastic predictions with experiment is that the N^3 scaling is never seen, but rather a N^z law with $z = 3.5 \pm 0.2$ is observed for both the shear viscosity and longest relaxation time.[1-3] Within the microscopic PMC approach there are several possible origins for this "anomaly", including finite N fluctuation corrections associated with the frequency dependence of the fluctuating force memory functions.[18,19]

To illustrate the interplay between the N and concentration scaling behaviors, we consider the original suggested source of this anomaly.[15] Since the viscoelastic memory function is sensitive to longer wavelength $kR_g \leq 1$ force fluctuations, it was argued that a more appropriate approximation for the projected dynamics might be the full propagator in the spirit of self-consistent mode-coupling theories (but we do not claim this idea is the only possible mechanism for enhanced exponents). In physical terms, this corresponds to the idea that the viscoelastic or "entanglement" forces that create the shear stress plateau do not fully relax until the polymer chain has diffused a distance of order its radius of gyration. This assumption results in an extra factor of $N^{1/2}$ in the terminal relaxation time[15] with the result

$$\tau_D/\tau_0 \propto g^2(\sigma)[\rho\sigma^3\hat{S}(0)]^{-1}N^{7/2} \propto (\rho\sigma^3)^3N^{7/2} \qquad (3.11)$$

The enhanced N scaling also leads to an enhanced reduced concentration dependence of the terminal time and shear viscosity via one extra factor of reduced polymer density

$$\eta/\zeta_0 \propto G_N g^2(\sigma)[\rho\sigma^3\hat{S}(0)]^{-1}N^{7/2} \propto (\rho\sigma^2)^3(\rho\sigma^3)^3N^{7/2}$$
$$\propto \rho^6 \propto (\rho/\rho^*)^6\sqrt{N}, \Theta$$
$$\propto \rho^{4.125} \propto (\rho/\rho^*)^{4.125}N^{1/5}, \text{good} \qquad (3.12)$$

Under the assumption that the diffusion constant is still given by eq 3.5, the crossover values of N for the terminal relaxation time and shear viscosity exhibit a slightly stronger dependence on polymer concentration than N_D or N_e. Equation 3.10 is changed to $D\eta \propto \rho^4$ (Θ solvent) and $\rho^{2.875}$ (good solvent).

4. Discussion

Many measurements of the concentration dependence of the shear viscosity of various polymer species have been performed and are often reported in the apparent scaling form $\eta/\zeta_0 \propto \rho^\Delta$. Pearson has nicely summarized the situation for the apparent exponent as[11] $\Delta = 3.5-4$ for good solvents and often larger for Θ solvents $\Delta \simeq 4-6$. For example, recent experiments by Adam find an exponent of 5.14 for polystyrene in the Θ solvent cyclohexane in the semidilute regime.[36] Colby et al.[34] examined polybutadiene in good and Θ solvents. Solvent quality was found to produce very little difference in concentration scaling, with a $\Delta \simeq 4.7-4.8$ found in the roughly 1-10% polymer volume fraction region ("semidilute"), and $\Delta \simeq 3.6$ in the 10-100% "concentrated" regime. Our theoretical predictions of eqs 3.9-3.12 are broadly consistent with the experimental measurements that seem to exhibit a degree of nonuniversality according to polymer and investigator.

Most recently, an interesting experimental study of the viscoelastic properties of semidilute good solutions of polystyrene, polybutadiene, and polyisoprene was published by Raspaud et al.[37] All three systems followed a common concentration scaling law for the viscosity with an exponent of $\Delta = 4.6-4.7$. However, strict scaling was found to fail in the sense that the reduced concentration variable, which collapses equilibrium properties for different polymer systems onto a universal curve, does not lead to superposition of the shear elastic modulus or viscosity.

Theoretical understanding is somewhat unsettled since a variety of distinct ideas have been advanced and different predictions made. Consider first the reptation-based approaches with extra scaling assumptions appended to describe the concentration dependence.

The simplest "mean field" reptation approach, argued by Brochard and de Gennes[35] to be valid for Θ solvents or concentrated solutions in general, predicts $\eta \propto N^3\rho^{3.5}$ and a concentration scaling of $\tau_D \propto \rho^{1.5}$. On the other hand, the single-parameter scaling assumption that $r_c \propto \xi_\rho$ in the semidilute good solvent regime yields a concentration scaling exponent of $\Delta = 3.75$ (based on the Flory exponent for a self-avoiding walk) and 6.0 for Θ solvents; the corresponding longest relaxation time concentration scaling is predicted to be $\tau_D \propto \rho^{1.5}$ (ρ^3) for good (Θ) solutions.[2,12] If a $N^{3.5}$ molecular weight scaling is phenomenologically employed in conjunction with a scaling ansatz, then the above viscosity exponents are modified to $\Delta \simeq 4.4$ and 6.8, respectively.

Yet another scaling-based suggestion has been made by Adam for semidilute Θ solvents: $\Delta = 5$ if the hydrodynamic screening length is the relevant length scale, and $\Delta = 3.5$ if the tube diameter or "entanglement length" is the relevant length scale.[36]

Most recently, a "two-parameter scaling" ansatz has been proposed by Colby and Rubinstien.[4] It postulates that an entanglement is due to a collective effect of a fixed number of binary intermolecular contacts. Under the assumption that $r_c \gg \xi_\rho$ in semidilute Θ solvent, these workers predict the tube diameter scales $r_c \propto \rho^{-2/3}$ and the plateau modulus scales as $\rho^{7/3}$. In good solvents, this approach reduces to the one-parameter scaling idea, but in Θ solvents it predicts viscosity exponents of $\Delta \simeq 4.67$ and 5.3 for N^3 and $N^{3.5}$ chain-length scaling, respectively. In terms of the reduced concentration variable, these results can be cast in the form $\eta \propto (\rho/\rho^*)^{3.75}$ for good solvents (de Gennes result) and $\eta \propto (\rho/\rho^*)^{14/3}N^{2/3}$ for Θ solvents (based on the N^3 reptation scaling and the semidilute crossover density computed using the classic Flory exponents). Comparison of these results with our predictions in the reduced concentration form of eq 3.9 shows small differences in the density and N exponents, although these might be difficult to distinguish within typical experimental error.

Douglas and Hubbard[12] recently proposed a nonreptation semiempirical model for entangled polymer dynamics based on many-chain, "correlated cluster" motions. Nonreptation scaling laws are predicted for both the concentration and N dependence of transport coefficients. For concentrated solutions of ideal random walk chains they find $\eta \propto (\rho N)^{10/3}$. These workers also propose a packing model to estimate the shear plateau modulus and various crossover degrees of polymerization. For concentrated solutions, the scaling laws $G_N \propto \rho^2$ and $N_e \propto \rho^{-1}$ are derived. The concentration dependences of the transport coefficients are also predicted to depend on solvent quality (via an effective chain fractal dimension) and to differ in the semidilute and concentrated states. In entangled semidilute Θ solutions, the shear viscosity is predicted to scale with a higher concentration exponent as $\eta \propto N^{10/3}\rho^{17/3}$.

Summarizing the situation for η and τ_D, it appears that the predictions of our microscopic theory and the phenomenological scaling plus reptation approaches are in rather close (but not exact) agreement for the good solvent case. Our prediction that the crossover degree of polymerization for the plateau modulus, shear viscosity, and diffusion constant obey the qualitatively same (or nearly so) concentration scaling law seems to be supported by experiments.[11] However, significant differences among all the approaches exist for Θ solvents, where, unfortunately, there is the least amount of data. Our predicted concentration scaling exponents for shear viscosity fall in between the one- and two-parameter scaling values for Θ solutions. With the possible exception of the correlated cluster model,[12] it appears that no satisfactory explanation exists for the different concentration scaling of the polybutadiene shear viscosity in the semidilute and concentrated regimes.[34] However, the generality of the latter behavior is unclear. More viscosity, plateau modulus, *and* chain dimension data on various polymer solutions over a wide concentration range are desirable before definitive conclusions can be safely drawn.

A convincing explanation of the "nonstrict scaling" behavior observed by Raspaud et al.[37] is also lacking. Within our theory, use of a simple coarse-grained Gaussian string model seems well justified in semidilute solution but may be less accurate under concentrated and melt conditions. In addition, the simplifying choice of $\sigma = d$ (aspect ratio of unity) may not be adequate. Work is in progress to address this question by employing PRISM theory for more realistic semiflexible chain models to investigate the influence of local non-Gaussian chain statistics and a nonunity aspect ratio on our equilibrium and viscoelastic predictions.[38]

For the diffusion constant at fixed segmental friction, the reptation-based approaches predict $D \propto \rho^{-\delta}N^{-2}$, where the exponent $\delta = 1.5$ ("mean field" argument), $^7/_4$ (good solvent/scaling), and 3 (Θ solvent/scaling).[11] Comparison with eq 3.6 shows the PMC theory predicts significantly smaller exponents relative to the reptation/scaling theory, while the "mean field" reptation exponent is intermediate between our good and Θ solvent values. We are unaware of diffusion constant concentration dependence predictions based on the two-parameter scaling ansatz.[4] The dynamically correlated cluster model predicts $D \propto \rho^{-4/3}N^{-7/3}$ for concentrated ideal solutions, and $D \propto \rho^{-8/3}N^{-7/3}$ for entangled semidilute solutions.[12]

We also note that the reptation approaches predict the product $D\eta \propto \rho^{\theta}$ where $\theta = 2$ (mean field and good solvent scaling approach) and 3 (Θ solvent/scaling). These exponents are in close accord with the PMC predictions of eq 3.10. For Θ solvents (ideal chain statistics), the dynamically correlated cluster model[12] predicts $\theta = 2$ and 3 for the concentrated and semidilute solution regimes, respectively.

It would seem the concentration scaling of the diffusion constant might be a good question to study experimentally since the various theoretical models of entangled polymer dynamics make significantly different predictions. Unfortunately, experimental data over a wide range of solution concentrations (reduced to a local isofriction form) seem considerably more scarce for diffusion than for viscoelastic properties. The work of Nemoto et al.[39] in semidilute and concentrated good solutions finds $D \propto \rho^{-1.5}$, in reasonable accord with the predictions of eq 3.6. However, other workers have reported considerably higher effective exponents under semidilute conditions.[11,39] Moreover, under most solution (and also gel) conditions, the $D \propto N^{-2}$ scaling is not observed; higher effective exponents in the range of 2.3–3 have been reported.[11,39] This behavior is not well understood and complicates comparison of theory and experiment for the concentration dependence question.

Finally, we note that Phillies has argued that hydrodynamic interactions dominate much of polymer solution dynamics, and the concentration dependences of transport properties obey stretched exponential laws.[40] This non-power-law scaling approach is completely different from our analysis, and also reptation/scaling and alternative entanglement theories, so comparisons cannot be easily made.

In conclusion, we have constructed what we believe to be the first microscopic theory at the level of the fluctuating hard-core forces of the concentration, solvent quality, and chain conformation dependences of the transport properties of highly entangled linear chain fluids. A key aspect is the prediction of analytic PRISM theory that the dynamically relevant equilibrium properties depend in a power law fashion on reduced density.[22] Our results for the concentration scaling exponents appear to be in reasonable accord with most, but not all, of the existing data. For fixed concentration (e.g., melt), we have also presented scaling laws for the polymer-specific segment-length dependences in terms of the invariant "packing length" $(\rho\sigma^2)^{-1}$. This aspect is perhaps experimentally testable as has been recently successfully carried out for the plateau shear modulus.[26]

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