laxation. That is, it asserts orientational autocorrelation functions are insensitive to local molecular details. In partial contrast, the modified Hall–Helfand models give a "molecular" explanation of a portion of the local relaxation, embodied in the parameters κ_0 and κ_1, and a "hydrodynamic" description of the long-wavelength relaxation process embodied in the parameters α and μ; thus the MHH expression is a hybrid description of the system. On the other hand, as pointed out above, the "hydrodynamic" explanation given by the damped diffusion model can also be viewed as an approximate resummation of the "molecular" explanation given by a generalized diffusion and loss model.

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Molecular Weight Dependence of the Second Virial Coefficient for Linear Flexible Polymers in Good Solvents

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It is well established experimentally that the second virial coefficient A_2 for a linear flexible polymer in a good solvent decreases with an increase in the polymer's molecular weight M. This decrease is usually represented on a log–log graph by a straight line; i.e.

$$\log A_2 = K - b \log M \qquad (1)$$

where K and b are constants. Reported values of b are in the range 0.2–0.3. However, in some studies[1–4] where A_2 was determined over a very wide range of M, it was found that plots of $\log A_2$ against $\log M$ were not linear but followed a convex-downward curve with an asymptotic slope of −0.20, as shown schematically by line A in Figure 1a and by typical data[4] in Figure 1b. Mathematically, the behavior of this curve is expressed by

$$\mathrm{d} \log A_2/\mathrm{d} \log M < 0 \qquad (\text{approaches } -0.2 \text{ as } M \rightarrow \infty) \qquad (2)$$

$$\mathrm{d}^2 \log A_2/(\mathrm{d} \log M)^2 > 0 \qquad (3)$$

The penetration function Ψ is defined by[5]

$$\Psi \equiv A_2 M^2/(4\pi^{3/2} N_{\mathrm{A}} \langle S^2 \rangle^{3/2}) \qquad (4)$$

where N_{A} is the Avogadro constant and $\langle S^2 \rangle$ the mean-square radius of gyration of the polymer in the solvent considered. Differentiation of eq 4 with respect to M gives

$$\mathrm{d} \log \Psi/\mathrm{d} \log M = \mathrm{d} \log A_2/\mathrm{d} \log M + 2 - (3/2)\, \mathrm{d} \log \langle S^2 \rangle/\mathrm{d} \log M$$

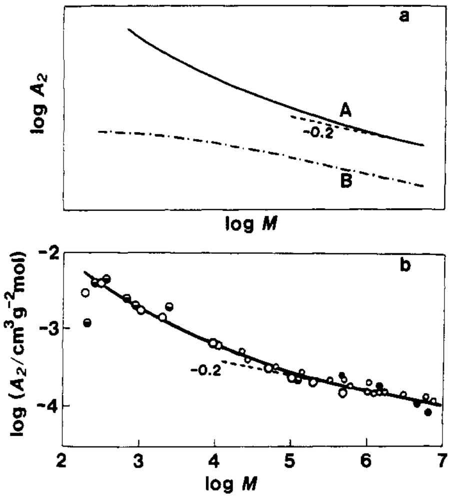

Figure 1. (a) Schematic representation of $\log A_2$ vs. $\log M$ curves for a linear flexible polymer in a good solvent. Line A, experiment; line B, prediction from current theories. (b) Plot of $\log A_2$ vs. $\log M$ for poly(methyl methacrylate) in acetone, a good solvent:[4] (◯) Kirste and Wunderlich (*Z. Phys. Chem.* **1968**, *N58*, 133); (●) Cantow and Schulz (*Z. Phys. Chem.* **1954**, *N2*, 117); (○) Schulz and Craubner (*Z. Electrochem.* **1959**, *63*, 301); (◒) Springer et al. (*Z. Electrochem.* **1965**, *69*, 494).

Much experimental evidence is now available for the fact that $\langle S^2 \rangle$ of a linear flexible polymer in a good solvent varies in proportion to $M^{1.2}$ at sufficiently high M. Thus, the above relation may be written

$$\mathrm{d} \log \Psi/\mathrm{d} \log M = \mathrm{d} \log A_2/\mathrm{d} \log M + 0.2 \qquad (5)$$

Hence

$$\mathrm{d}^2 \log \Psi/(\mathrm{d} \log M)^2 = \mathrm{d}^2 \log A_2/(\mathrm{d} \log M)^2 \qquad (6)$$

When combined with eq 2 and 3, these relations yield

$$\mathrm{d} \log \Psi/\mathrm{d} \log M < 0 \qquad (\text{approaches zero as } M \rightarrow \infty) \qquad (7)$$

$$\mathrm{d}^2 \log \Psi/(\mathrm{d} \log M)^2 > 0 \qquad (8)$$

For $\langle S^2 \rangle \propto M^{1.2}$ the radius expansion factor α_S ($\alpha_S{}^2 \equiv \langle S^2 \rangle/\langle S^2 \rangle_\Theta$, with $\langle S^2 \rangle_\Theta$ the value of $\langle S^2 \rangle$ in the unperturbed state) varies in proportion to $M^{0.1}$, since, as is well-known, $\langle S^2 \rangle_\Theta$ depends linearly on M. Thus, it can be shown that eq 7 and 8 are equivalent to

$$\mathrm{d}\Psi/\mathrm{d}\alpha_S < 0 \qquad (\text{approaches zero as } \alpha_S \rightarrow \infty) \qquad (9)$$

$$\mathrm{d}^2\Psi/(\mathrm{d}\alpha_S)^2 > 0 \qquad (10)$$

provided that α_S is not close to unity.

From eq 9 and 10 it follows that plots of Ψ against α_S for a linear flexible polymer in a good solvent should follow a concave-downward curve as line A′ in Figure 2; i.e., as α_S increases from unity, Ψ should *decrease* monotonically to a certain asymptotic value with a convex-downward curvature. Previous measurements of A_2, which were mostly restricted to relatively small values of α_S, failed to reveal this type of α_S dependence of Ψ, but our recent studies on poly(hydroxybutyrate) in trifluoroethanol[2] and polystyrene in benzene[3] demonstrated it clearly, since they were extended to the values of α_S much larger than those attained before.

The molecular weight dependence of A_2 for linear flexible polymers has been formulated by many authors, previously by two-parameter methods[5] and lately more

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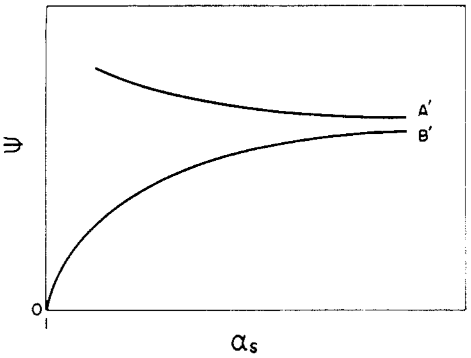

Figure 2. Schematic representation of Ψ vs. α_S plots for a linear flexible polymer in a good solvent: line A′, from eq 9 and 10; line B′, from two-parameter or renormalization-group theories.

elaborate renormalization-group methods.[6,7] Except for a calculation by Gobush et al.,[8] the proposed theories predict in common that Ψ is a universal function of α_S which starts from zero at $\alpha_S = 1$ and *increases* monotonically to a certain limiting value with an increase in α_S, as schematically shown by line B′ in Figure 2; Gobush et al.'s calculation shows Ψ to decrease with increasing α_S after passing through a broad maximum at $\alpha_S \sim 1.5$.

What is important in Figure 2 is the opposite curvatures of lines A′ and B′. This discrepancy indicates that any current A_2 theories except Gobush et al.'s are inconsistent with the above-mentioned experimental findings on linear flexible polymers in good solvents. Though quite serious, it does not seem to have been pointed out in previous publications.

Douglas and Freed[9] attributed the observed decreases in Ψ at large α_S to increasing polydispersity of the polymer samples of higher molecular weight and also to the improper account of the third virial coefficient in determining A_2 from light scattering data. However, as can be understood from the above analysis, it is legitimate to interpret the observed fact as the consequence of the convex-downward curvature of measured log A_2 vs. log M plots (see Figure 1). It can be shown that if line B' in Figure 2 holds for a linear flexible polymer in a good solvent, we should observe for such a system a log A_2 vs. log M plot of the type illustrated by line B in Figure 1a. However, as noted above, no actual data consistent with the curvature of this line have ever been reported.

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Communications to the Editor

Concentration Dependence of the Diffusion Coefficient and the Longest Relaxation Time of Polymer Chains in Solution

The concentration dependence of the long-time dynamical behavior of polymer chains as measured by the diffusion constant D and the longest relaxation time τ_1 provides an insightful means of examining the effect of inter- and intrachain interactions in concentrated polymer solutions and melts and of testing theoretical representations of these interactions and the physical models upon which they are built. The effect of the volume occupied by the chain and the resulting entanglement of the chain with itself and with other chains on dynamical behavior have been difficult to treat theoretically and to characterize experimentally. The Doi–Edwards[1] and de Gennes[2] models of concentrated polymer systems view the segmental motion of entangled chains as reptation of the polymer chain along its contour within a "tube" formed by neighboring chains. As pointed out by Wesson, Noh, Kitano, and Yu[3] (hereafter WNKY), the Doi–Edwards model predicts that D lacks a simple power-law dependence upon concentration c. Scaling laws as developed by de Gennes provide another theoretical approach to the concentration dependence of D, which is predicted to be the −1.75 power in a good solvent and the −3 power in a Θ-solvent or its concentration equivalent. Both of these approaches invoke several concentration regions with different predicted behavior.

In the experimental area, it has been equally difficult to characterize the concentration dependence of dynamical behavior. Recently, WNKY have reported[3] measurements of D as a function of concentration for labeled polystyrenes with molecular weights from 32 000 to 360 000. They examined their data in the context of the Doi–Edwards theory and scaling predictions and found that their results did not fit the predictions of the Doi–Edwards theory as formulated by Graessley.[4] Nor did they find the simple power-law dependences of D on c over wide concentration ranges predicted by scaling theory. Their results showed a power-law dependence of D upon c which became greater than −1.75 at weight fractions greater than 0.2 and approached −13 at the highest concentration studied. Overall they reported that the concentration profile of D was best represented as a smooth curve.

Recent NMR studies by von Meerwall, Amis, and Ferry[5] (hereafter MAF) on diffusion in polystyrene solutions showed similar results. They measured the diffusion constant of polystyrene from a concentration below overlap to concentrations above the onset of entanglement and again failed to observe the power-law dependences of D upon c predicted by scaling laws. However, if the concentration dependence of D due to free volume was factored out, the remaining concentration dependence appeared to agree with scaling theory at sufficiently high concentrations.

At the same time that WNKY reported their findings, we reported the results of Monte Carlo simulations of the dynamic and equilibrium properties of many-chain systems.[6] The concentration dependence of the long-time relaxation behavior of our lattice models is represented reasonably well by a simple free volume model and an