Wave-Vector Dependence of the Initial Decay Rate of Fluctuations in Polymer Solutions

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We present experimental results for the initial decay rate Γ_1 of concentration fluctuations in solutions of linear polymers, for various molecular weights, concentrations, and wave vectors q, in two rather different solvents. We find that under all conditions explored the dimensionless decay rate $6\pi\eta_0\Gamma_1/k_BTq^3$ is a function only of the scaled wave vector $q \xi_H$. Here η_0 is the solvent viscosity, and ξ_H is the length scale defined by $\xi_H^{-1} \equiv \lim_{q \to 0} 6\pi\eta_0\Gamma_1/k_BTq^2$.

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The behavior of long-wavelength fluctuations in polymer solutions has elicited immense interest over a prolonged period of time.¹ Even now the detailed behavior of individual coils in dilute solution remains challenging; recently, however, progress in elucidating the concentration dependence of both static and dynamic properties has been very rapid. It has been shown experimentally that the osmotic susceptibility, which is proportional to the mean squared amplitude of the fluctuations, and the static length scale ξ , which gives their range, exhibit relatively simple crossover behavior with increasing concentration.² Both quantities may be scaled so as to be universal functions of a dimensionless concentration, independent of molecular weight and solvent type. Crossover functions, calculated by use of real-space renormalization-group techniques to study the Edwards model of flexible interacting strings, are in excellent agreement with the experimental results.³⁻⁵ Similar agreement has been obtained for the initial decay rate of fluctuations in the q = 0 limit (q is the wave vector of the fluctuation).^{6,7}

It is the purpose of the present work to examine the behavior of the initial decay rate Γ_1 , at finite q, as a function of molecular weight, concentration, and solvent quality. We find that, to within the accuracy of our data, the reduced decay rate $\Gamma^* = 6\pi \eta_0 \Gamma_1 / k_B T q^3$ is a function only of the single dimensionless variable $q\xi_H$. Here η_0 is the solvent viscosity, Γ_1 is the first cumulant of the autocorrelation function $\langle \delta c(q,\tau) \delta c^*(q,0) \rangle$ describing the temporal behavior of a fluctuation of wave vector q, and ξ_H is a length scale defined by

$$\xi_{H}^{-1} = \lim_{q \to 0} 6\pi \eta_{0} \Gamma_{1} / k_{\rm B} T q^{2}; \tag{1}$$

i.e., ξ_H is related to the mutual diffusion coefficient D by

$$D = k_{\rm B} T / 6\pi \eta_0 \xi_H. \tag{2}$$

Of course D, and thus ξ_H , depend strongly on molecular weight, concentration, and solvent quality. As shown previously,⁶ ξ_H and the static length scale ξ are simply not proportional, except in the zero-concentration limit, and thus relating the dynamic behavior to the static properties remains very challenging.

The polymer system studied was linear synthetic polystyrene dissolved in either the good solvent toluene or the marginal solvent methyl ethyl ketone. The molecular weights ranged from 1.8×10^6 to 26×10^6 , with $M_w/M_n < 1.1$, where M_w and M_n are the weight- and number-average molecular weights, respectively. The samples and sample handling were identical to those employed in our previous studies.² The autocorrelation function of the fluctuations in the intensity of 6328-A-wavelength light scattered at fifteen different scattering angles⁸ (11.5° < θ < 164°) was analyzed to obtain the first cumulant Γ_1 and the reduced second cumulant μ_2/Γ_1^2 . In the small-q limit we found $\mu_2/\Gamma_1^2 \le 0.05$ and for the highest molecular weights at large q we found $\mu_2/\Gamma_1^2 \le 0.3$. The twocumulant expansion provided an excellent representation of the data under all conditions explored.

Figure 1 shows the results for Γ_1/q^2 as a function of qR_G for a sample with $M_w = 26 \times 10^6$ dissolved in toluene. Here R_G is the experimentally determined radius of gyration in the zero-concentration limit. As expected, Γ_1/q^2 becomes independent of q at low qand simply defines the concentration-dependent mutual diffusion coefficient $D = \lim_{q \to 0} \Gamma_1/q^2$. For qR_G > 1, Γ_1/q^2 begins to increase, apparently in proportion to q, for the lowest-concentration solutions. This is expected and has been observed experimentally by other investigators.⁹⁻¹¹ The effect is very similar to that which occurs near a gas-liquid or binary-fluid critical point when one probes the dynamics of fluctuations on a length scale smaller than the correlation length.^{12, 13} In this case the effective q-dependent dif-



FIG. 1. The effective diffusion coefficient Γ_1/q^2 as a function of qR_G for polystyrene ($M_w = 26 \times 10^6$) in the good solvent toluene at various concentrations ranging from the dilute limit into the semidilute regime. The straight line has a slope of 1.

fusion coefficient Γ_1/q^2 becomes proportional to the inverse of the length scale q set by q itself, and Γ_1/q^2 varies very nearly as q. In the polymer system, the fluctuations being probed are the internal modes of an isolated coil in the dilute-solution case. As the figure shows, increasing the concentration causes the crossover to occur at higher q and results in an increasingly broad regime where Γ_1 is proportional to q^2 . This indicates the existence of a concentration-dependent length scale $\tilde{\xi}^{-1}$, such that the scattering probes "internal modes" only for $q > \tilde{\xi}^{-1}$. Very similar behavior is observed for the same polystyrene in the much poorer solvent methyl ethyl ketone, as shown in Fig. 2. Since R_G is smaller in methyl ethyl ketone the crossover to q^3 behavior for the dilute solutions occurs at larger q, and the same trend is evident at all concentrations. Data for lower molecular weights $(10^{-6}M_w = 7.2, 3.8, \text{ and } 1.8)$ shows crossover at increasingly larger q values until, for $M_w = 1.8 \times 10^6$, the crossover to q behavior is barely accessible using light scattering as the probe.

Guided by analogy with critical dynamics, we have explored the extent to which our data support the possibility of a universal q dependence for Γ_1 , by plotting the reduced decay rate Γ^* , defined above, vs $(q \xi_H)^{-1}$. Such a plot is exactly analogous to those used in critical phenomena¹² to display, as a single universal function, decay-rate data for different fluids and fluid mixtures for various values of the scattering wave vector and reduced temperature. Our results for all samples, in both solvents, are shown in Fig. 3, and clearly indi-



FIG. 2. The effective diffusion coefficient Γ_1/q^2 as a function of qR_G for polystyrene $(M_w = 26 \times 10^6)$ in the marginal solvent methyl ethyl ketone at various concentrations.

cate that all our data are consistent with the hypothesis that Γ^* is a function only of $q \xi_H$ and that $\tilde{\xi} = \xi_H$. For the sake of clarity we have plotted only a small fraction of the data (20%); however, all 855 data points fall within the scatter shown in the figure.

Although Fig. 3 represents a considerable simplification for the dynamics of polymer solutions, it should be emphasized that a much less profound level of understanding is involved in our treatment than exists for critical dynamics, because in the polymer case the length scale ξ_H has been extracted from the dynamics, while in critical fluids the dynamics have been relat $ed^{12, 13}$ directly to the static length scale ξ . As we have shown,⁶ for polymer solutions ξ_H and ξ are not strictly proportional, and thus Γ^* cannot be regarded as a function of $q \xi$. It should also be recognized that because of the limitations on the value of q which can be reached through light scattering, we cannot reach large values of $q \xi_H$ in the more concentrated solutions. Nevertheless, given the obvious similarity to critical fluid behavior, it is tempting to plot the Kawasaki result¹³ $\Gamma^* = k_0(x)/x$, where

$$k_0(x) = \frac{3}{4x^2} [1 + x^2 + (x^3 - x^{-1})\tan^{-1}(x)], \quad (3)$$

and this is shown as the solid line in Fig. 3. Here, of course, we have set $x = q \xi_H$. Clearly the large-q limit is not adequately represented by this simple approach, but the overall behavior is qualitatively correct.

There are theoretical predictions^{14, 15} as well as measurements^{10, 16} of Γ_1/q^2 for polymer solutions in the dilute limit with which we may compare the data. Toward this end we have extrapolated our measurements



FIG. 3. The reduced decay rate $\Gamma^* = 6\pi\eta_0\Gamma_1/q^3k_BT$ as a function of the dimensionless wave vector $q\xi_H$. The solid line is the Kawasaki (Ref. 13) result for order-parameter fluctuations near a gas-liquid critical point, $k_0(x)/x$ with $x = q\xi_H$, and is shown for comparison only.

to c = 0 for each sample studied, and Fig. 4 shows the result as a plot of $\Gamma^*(c=0)$ vs qR_H , where R_H , the hydrodynamic radius of an isolated coil, is simply $\xi_H(c=0)$. Experimentally this plot is indistinguishable from Fig. 3 since, as we have emphasized, the scaling shown in Fig. 3 appears to hold for all concentrations from the dilute limit to well into the semidilute regime. The first theoretical result with which we may compare is that of Akcasu and Benmouna,¹⁴ and their predictions are shown as the solid line (preaveraged Oseen tensor) and as the dashed line (nonpreaveraged Oseen tensor) in Fig. 4. In plotting their results, which are expressed in terms of qR_G , as a function of qR_H , we used the theoretical result¹⁰ $R_H/R_G = 0.537$ in good solvents in order to be consistent with their theory. Although the small-q behavior is adequately described, the theory clearly fails to approach the proper high-q limit, for which we find experimentally $\Gamma^*(x \gg 1) = 1.05 \pm 0.06$, and for which the theory gives 1.34 (preaveraged) and 1.49 (nonpreaveraged). A similar trend is clear in the data of Han and Akcasu.¹⁰ The second theoretical result with which we may compare our data is based on a renormalization-group calculation.¹⁵ We again had to relate R_G and R_H , but this time used¹⁵ R_H/R_G = 0.792, again for theoretical consistency. The agreement between theory (dash-dotted line) and experiment is somewhat better, although the nonmonotonicity of the theoretical result could be an artifact due to approximations in the ϵ expansion.¹⁵ We want to emphasize at this point that we used the dimensionless wave vector qR_H , because a plot of Γ^* vs qR_G does not superimpose the data to within experimental accuracy but results in a systematic broadening. This is prob-



FIG. 4. The reduced decay rate Γ^* extrapolated to zero concentration as a function of the scaled wave vector qR_H . R_H is the experimentally determined hydrodynamic radius. The lines are theoretical predictions by Akcasu and Benmouna (Ref. 14) (solid and broken lines) and Lee, Baldwin, and Oono (Ref. 15) (dash-dotted line).

ably related to the fact that the hydrodynamic radius does not assume its asymptotic dependence on molecular weight nearly as soon as does the radius of gyration.^{17, 18}

We conclude that to within experimental accuracy the wave-vector dependence of the reduced initial decay rate of concentration fluctuations is a universal function of $q\xi_H$. The concentration range covered reaches from the dilute limit into the semidilute regime for various molecular weights and two different solvents. The comparison with theory cannot be regarded as satisfactory. Although only a single length scale, i.e., the dynamic correlation length ξ_H , is necessary for the interpretation of all our dynamic data, the serious question of the relationship⁶ between ξ_H and the static correlation length ξ certainly requires further theoretical investigation, as does the detailed shape of the autocorrelation function at finite q.

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