Macromolecules **2002,** *35,* 7414−7418

Self-Consistency of Hydrodynamic Models for the Zero-Shear Viscosity and the Self-Diffusion Coefficient[†]

George D. J. Phillies[‡]

Department of Physics and Associated Biochemistry Faculty, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Received March 11, 2002; Revised Manuscript Received June 14, 2002

ABSTRACT: The hydrodynamic model treatments of the zero-shear viscosity η and the self-diffusion coefficient D_s of polymers in nondilute solution are shown to be self-consistent. Hydrodynamic models for polymer dynamics in nondilute solution postulate that interchain hydrodynamic interactions dominate other interchain forces. These models predict concentration dependences of η, D_s, and other transport coefficients. Previously published predictions of η and D_s include a single hitherto-undetermined physical parameter, whose value is here obtained from the concentration dependence of η. When this parameter is supplied to the self-diffusion calculation, the concentration dependence of D_s is entirely determined with no adjustable parameters. Comparison is made with the literature. The model prediction for D_s is in excellent agreement with data on solutions of linear and three-armed star polymers covering a full range of polymer concentrations and homologous polymers spanning nearly 4 orders of magnitude in polymer molecular weight.

Introduction

For dilute polymer solutions, theoretical treatments based on the Kirkwood−Riseman[1] model give a general description of transport behavior. Fujita[2] has enumerated issues for which the current theory of dilute polymer solutions remains in need of improvement. In nondilute solutions, interchain polymer−polymer interactions are significant and polymer transport coefficients depend on concentration. A variety of very different models[3] predict these concentration dependences. The models differ both in the predicted mathematical forms for the concentration dependences of the transport coefficients and also in their assumptions as to the predominant forces between polymers in solution. A complete treatment of polymer dynamics in nondilute solution remains a significant theoretical challenge.

Models for polymer dynamics in nondilute solution may be categorized by their treatment of fundamental forces in solution. A useful categorization is as follows:

(i) Models in which the dominant forces are solvent-mediated hydrodynamic interactions.[4,5]

(ii) Models in which the dominant forces are excluded-volume effects that prevent chains from interpenetrating.[6,7]

(iii) Models in which the properties of some subunits depend on polymer concentration, such as heavy-bead[3] and cryptocrystallite[8] models.

(iv) Models of nondilute solutions that refer to general properties of collective systems without invoking mechanical details, such as the Ngai coupling model.[9]

It should be emphasized that these models are not all mutually inconsistent. For example, the Ngai coupling picture does not embody a specific underlying dynamics. It might describe systems in which chain crossing constraints dominate or systems in which hydrodynamic forces dominate. If bead properties depend on concentration, that dependence could arise from, e.g., hydrodynamic interactions or from chain-crossing constraints.

In some models, the dominance of some forces over others only occurs in certain concentration ranges. Hydrodynamic and excluded-volume forces exist in almost all solutions: So long as there is solvent, there will be some solvent- mediated (hydrodynamic) interactions. Chains cannot interpenetrate at any concentration. How, then, might one force or the other dominate?

Hydrodynamic interactions have no thermodynamic consequences: chains may approach each other whether there are hydrodynamic interactions or not. Nearby chains only attempt to interpenetrate if their Brownian displacements are not the same. In the hydrodynamic models, short-range hydrodynamic interactions cause Brownian displacements of nearby chains to become very highly correlated. Such correlations suppress dynamic but not static effects of excluded volume forces; by this mechanism, hydrodynamic effects might suppress entanglement constraints.

In many entanglement models, hydrodynamic interactions are often neglected because they are said to be screened. That is, it is proposed[7] that the totality of many-body hydrodynamic interactions replaces the long range ($1/r$) Oseen tensor with a short-range ($\exp(-\kappa r)/r$) screened hydrodynamic interaction. At large distances, hydrodynamic interactions can then be neglected. Rationales for screening include resummations of long-range interaction tensors or appeals by analogy with Debye screening to a proposal that long-range forces are screened in statistical mechanics.

Extensive resummations of hydrodynamic interactions have been made by Altenberger et al.,[10] Freed and Perico,[11] and Beenakker et al.[12] Altenberger and collaborators demonstrate that hydrodynamic screening arises for moving particles in the presence of fixed obstacles but that screening does not arise in systems containing steady flows and mobile macroparticles.[10] Freed and Perico[11] similarly conclude that hydrodynamic flows through polymer solutions are not screened

---

[†] The partial support of this work by the National Science Foundation under Grant DMR94-23702 is gratefully acknowledged.

[‡] E-mail: phillies@wpi.edu.

10.1021/ma020376s CCC: $22.00

when chains do not encounter topological constraints. Similarly, Beenakker and Mazur[12] resummed the longest-range (ring) diagrams for interacting spheres in solution, showing that resummation renormalizes the strength of the hydrodynamic interactions but does not lead to screening; the long-range nature of the mobility tensor is unchanged. While numerical coefficients differ between spheres and polymer coils, the range and directional dependences of the sphere−sphere and polymer−polymer hydrodynamic interactions are the same, so Beenakker's calculations refer equally well to polymer solutions.

Analogies between hydrodynamics and other long-range forces are sometimes proposed to lead to an expectation of hydrodynamic screening. However, there are two long-range forces, namely electrostatics and gravity. Newtonian gravity is not screened on any distance scale. Electrostatic forces are only screened in electroneutral systems. Supposed analogies between hydrodynamics and other long-range forces thus does not lead to an automatic conclusion that hydrodynamic interactions are screened.

In addition to differences in assumptions as to the dominant forces, models vary as to the mathematical form for the concentration dependence of transport coefficients. Some forms are assumed directly; other forms are implicit in the mathematical structure. Three important categories of form are as follows:

(i) In particular, at lower concentrations, a common assertion[13] is that transport coefficients have pseudovirial expansions with coefficients given by cluster-integral averages[14]. For example, for neutral polymers the viscosity is formally expanded

$$\eta(c) = \eta_o(1 + [\eta]c + k_H([\eta]c)^2 + ...) \tag{1}$$

Here η_o, $[\eta]$, and k_H are the solvent viscosity, the intrinsic viscosity, and the Huggins constant, respectively. A demonstration of series convergence is usually omitted. Interactions between chains include long-range parts, so convergence is not necessarily trivial.

(ii) In some models, polymer transport coefficients are taken to have power-law behavior; i.e., they are taken to depend on polymer molecular weight M and concentration c as

$$D_s(c), \sim M^{\gamma} c^{-x} \tag{2}$$

for the self-diffusion coefficient, with γ and x being scaling exponents. For polymer melts, derivations leading to power-law behavior and a numerical value for γ have been given[6]. More commonly, power-law behavior is assumed, with theoretical efforts focusing on obtaining the postulated scaling exponents.

(iii) In yet other models,[4,17] polymer transport coefficients are taken to follow a stretched exponential

$$D_s(c) = D_o \exp(-\alpha c^{\nu}) \tag{3}$$

in polymer concentration, the form being for the self-diffusion coefficient with $D_o = \lim_{c\to 0} D_s$. Here ν is a scaling exponent, and D_o and α are scaling prefactors. Derivations of this form for particular values of ν based on effective-medium arguments[17] or on renormalization-group methods[4] have been given. The renormalization group model[4] includes physical interpretations for α and ν with predictions for ν and for the molecular weight dependence of α.

For nondilute solutions, there is not uniform agreement as to the nature of polymer dynamics in solution. The objective of this paper is to examine the internal consistency of calculations within the hydrodynamic model and not to debate the relative merits of the hydrodynamic, reptation, cryptocrystallite, or other models of polymer solution dynamics. One however notes that Lodge et al.[15] observe "...only extremely high-molecular-weight polystyrenes would be sufficiently entangled in semidilute solutions to be constrained to reptate.... This rough calculation suggests that it is very unlikely that reptation is significant for linear polymers in the semidilute regime..." and concludes "As argued in the text, it is unlikely that reptation is significant in the semidilute regime, whereas in entangled melts it is often the dominant mode." In these remarks, Lodge is referring to a semidilute regime that is "overlapping" yet "unentangled", and offers quantitative reasoning indicating that most polymer solution data in the literature refers to this regime.

Contrariwise, it is sometimes proposed that the semidilute regime should be defined as the regime in which entanglements and reptation dominate, making the success of the reptation model for semidilute solutions a tautalogy. However, Lodge et al.'s review implies that this definition of "semidilute" excludes most though not all polymer solutions that have been studied experimentally.

This author has presented[4,5] a series of calculations of the concentration dependence of polymer solution transport coefficients. In the 1998 paper,[4] polymer self-diffusion was treated; in the 2002 paper,[5] a general approach to calculating the low-shear viscosity of nondilute polymer solutions is given. In each paper, hydrodynamic interaction tensors describing forces between a series of polymer chains are obtained. Ensemble averages over these tensors then lead to pseudovirial series such as that seen in eq 1.

For the self-diffusion calculation,[4] where the first three terms of the concentration expansion were found, the Altenberger−Dahler[16] positive function renormalization group (PFRG) method was used to extrapolate the series expansion to elevated polymer concentrations. This extrapolation yields eq 3 with explicit forms and phsyical interpretations for α and ν. Only the long-range part of the hydrodynamic interaction tensors was available, so numerical evaluation of ref 4's expression for α required supplying a short-range cutoff length a_D. This length could not readily be calculated, but the molecular weight dependence of α was obtained. More recently, a corresponding calculation of $\eta(c)$ has been performed,[5] leading to an expression for the Huggins coefficient k_H that includes a corresponding length a_η. Because k_H is known experimentally, the viscosity calculation determines a_η.

This paper examines if the calculations of η and D_s are consistent. The following section of the paper describes the calculations of $\eta(c)$ and the resulting value for a_η. A subsequent part of the calculation describes the calculation of D_s in terms of the radius of gyration R_g, the hydrodynamic radius R_h, and a cutoff length a_D. The lengths R_g and R_h follow from static light scattering and photon correlation spectoscopy, respectively; the length a_η is obtained with viscometry experiments. The final section combines these results to compute α and compare with the literature.

Viscosity

As presented in ref 5, in the hydrodynamic model the viscosity is obtained by considering a solution of polymer molecules subjected to an imposed shearing flow. As consequences of the applied shear, the polymers translate, rotate, and exert hydrodynamic forces on each other. Energy is dissipated because polymer beads move with respect to the solvent, the dissipation rate being

$$P = \langle \sum_{j=1}^{N_c} \sum_{i=1}^{N} f_{ij}(\mathbf{v}_{ij} - \mathbf{u}_{ij})^2 \rangle \tag{4}$$

Here the sum is over the N beads on each of N_c chains, f_{ij} is a bead drag coefficient, $\mathbf{v}_{ij}$ is the velocity of bead i of chain j, and $\mathbf{u}_{ij}$ is the velocity that the fluid would have had at the location of bead i of chain j if that one bead were absent.

The solvent flow at $\mathbf{u}_{ij}(\mathbf{r})$ includes the initial shear field at the location $\mathbf{r}$ of bead i of chain j. When the initial shear field acts on a chain, that chain is induced to translate and rotate. The velocity of its individual beads cannot in general match the solvent velocity at every point, so the polymer through its motions with respect to the solvent exerts forces on the solvent. The forces induce additional "scattered" flows in the solvent, flows that are rescattered by other polymer chains *ad infinitum*. All flows scattered by chains, pairs of chains, ..., etc., terminating in an induced flow at $\mathbf{r}$ are included in $\mathbf{u}_{ij}$, except that the flow induced by a bead does not directly act on the bead that created it.

The actual calculation of $\mathbf{u}$ follows from (i) division of bead motions into whole-body translation, chain rotation, and chain internal modes describing bead motions relative to whole-body motion, (ii) identification of $f_{ij}(\mathbf{u}_{ij} - \mathbf{v}_{ij})$ as the force on bead ij, (iii) the small-inertia approximation that the total force and total torque on each chain both approximately vanish, this approximation determining the chain whole-body motion, (iv) computation of solvent flows induced by each chain's low-frequency motions with respect to the solvent motions, (v) Taylor-series expansions of expressions for the induced flows in powers of the distances between beads and chain centers of mass, and (vi) ensemble averages over possible chain conformations. This calculation is described in ref 5.

The viscosity is obtained from eq 4 by substituting for the solvent and bead velocities, collecting terms that involve the same number of scattering events or number of distinct chains, and comparing with the power dissipation per unit volume written as

$$P = \eta(c)\left(\frac{\partial V_y}{\partial x}\right)^2, \tag{5}$$

in terms of the shear $\partial V_y/\partial x$.

The hydrodynamic approach to computing P is subject to three mathematical challenges. The first two challenges arise from the long- and short-range behaviors of the hydrodynamic interactions. The third challenge is the relationship between the velocity shear implicit in eq 6, below, and the shear appearing in eq 5. First, at long range the hydrodynamic interaction tensors for the induced flows and induced bead velocities depend on interchain distances as r^{-2} or r^{-3}, potentially leading to difficulties with the convergence at long range of ensemble averages over chain positions. This convergence issue was first noted by Saito[18]. In ref 5, the convergence issue is removed by using a sinusoidal-imposed velocity field

$$\mathbf{u}^{(0)} = u_o \sin(kx)\hat{\mathbf{j}} \tag{6}$$

the long-wavelength $k \to 0$ limit finally being taken at constant ku_o. A sinusoidal applied shear leads to properly convergent integrals for P, even in the long-wavelength limit, without creating any need to take into account the applied forces at the boundaries of the system.

Second, the series expansions used in ref 5 to compute the scattered flow fields and the induced translational and rotational velocities are not entirely appropriate at small interchain distances. Chains can interpenetrate. When two chains are more-or-less entirely interpenetrated, strong short-range hydrodynamic interactions not included in the published calculation should bring the velocity of the second chain into approximate agreement with the velocity of the first chain and its entrained solvent, causing two interpenetrated chains to move at approximately the same velocity. The second chain's contribution to the frictional dissipation and the scattered hydrodynamic flow field is thereby greatly reduced when the two chains are overlapped, This reduction was incorporated into the approximate calculation of ref 5 by supplying a nominal short-range cutoff a_η. No cutoff of this sort is required to compute the intrinsic viscosity, because only one chain is involved.

Third, in interpreting eq 5, the shear rate $\partial V_y/\partial x$ is the phenomenological shear rate. This rate includes not only the imposed shear field of eq 6 but also the shear due to all scattered flow fields. The various shears must be totalled to determine $\partial V_y/\partial x$.

As shown in ref 5, on combining the above considerations, one finds

$$[\eta]_t = \frac{13 F_o S^2}{30 \eta_o} \tag{7}$$

for the intrinsic viscosity. For the Huggins coefficient, the same approach gives[5]

$$k_H = \frac{88 - 240\pi - 384\pi^2}{169} + \frac{225[\eta]_t}{4394\pi {a_\eta}^3} \tag{8}$$

Experimentally,[19] $k_H \approx 0.3 - 0.6$. Identifying $[\eta]_t$ with the measured $[\eta] \approx 2.5\bar{v}$ and $\bar{v} = 4\pi R_g^3/3$, one finds

$$a_\eta \approx 0.18 R_g \tag{9}$$

The actual a_η is not very sensitive to which value of k_H is inserted into eq 8.

Self-Diffusion Coefficient

The hydrodynamic model has also been used to calculate the concentration dependence of the self-diffusion coefficient of polymers in solution.[4] In this calculation, a single moving polymer chain in an initially stationary liquid is viewed as creating a flow field in the fluid. The flow field is scattered and re-scattered by the other chains, just as in the viscosity problem the applied shear field is scattered and rescattered. In the self-diffusion problem, the scattered field finally acts back on the initial chain. On the average, the backscattered flow field retards the motion of the first chain. This multiple scattering model leads to a series expansion for the hydrodynamic interactions between two, three, ..., etc. polymer chains.

Ensemble averages over the resulting hydrodynamic interaction tensors result in a pseudovirial expansion for D_s. One obtains

$$D = D_o(1 + \alpha_D c + \beta c^2 + \mathcal{O}(c^3)) \qquad (10)$$

with α_D given by

$$\alpha_D = -\frac{9}{16}\frac{R_h^{\ 2}}{R_g a_D}\frac{4\pi R_g^{\ 3}}{3}\frac{N_A}{M} \qquad (11)$$

At the level of approximation of ref 4, β is quite small, so on extending the series to elevated concentrations the Altenberger−Dahler positive function renormalization group method[16] gives

$$D_s(c) = D_o \exp(-\alpha_D c^{\nu}) \qquad (12)$$

R_h and R_g are the chain hydrodynamic radius and mean-square radius of gyration, N_A is Avogadro's number, M is the chain molecular weight, and a_D is a short-range cutoff distance reasonably expected to be approximately equal to a_η. The concentration c is scaled to unit reference concentration relative to the scaling law $R_g^{\ 2} \sim c^{-x}$ for the concentration dependence of the radius of gyration.

For 1.27 MDa polystyrene in benzene, measurements of Adam and Delsanti[20] give $R_g \approx 62$ nm and $R_h \approx 38$ nm. From the above, $a_\eta \approx 0.18 R_g$. Identifying a_η with a_D, one finds $\alpha_D = 0.56$ for solutions of 1.27 MDa polystyrene. Noting R_g/a_D is reasonably expected to be relatively independent of M, α_D should depend on polymer molecular weight as $R^3/M \sim M^{0.8}$.

Experimental Test of Model Prediction

To determine α_D, a systematic analysis was made[21] of virtually the entirety of the published literature on self-diffusion by random-coil linear chains and three-armed star polymers, including experiments using pulsed-field gradient nuclear magnetic resonance, optically tagged polymers, forced Rayleigh scattering, and fluorescence recovery after photobleaching. For each polymer:solvent combination and polymer molecular weight, nonlinear least-squares methods were used to fit the experimental $D_s(c)$ measurements to eq 3. In every case, the concentration dependence of D_s was described well by a stretched exponential.

As a practical matter, to obtain reasonably accurate fits to eq 3, one must have the conditions that D_s varies over a substantial range, that it was measured adequately accurately, and that it was measured at concentrations sufficiently low that $D_s(c) \approx D_o$. A small number of data sets that did not meet all of these criteria, usually because they only include data at elevated concentrations, are excluded here from further consideration. In addition, a few series of measurements are repeated in subsequent papers by the same core authors, as parts of more extensive series of measurements. Such data are included in the following only once.

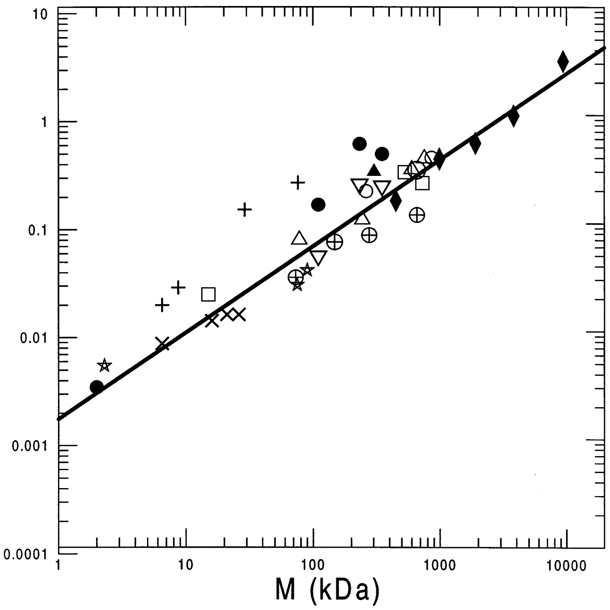

Figure 1. Line giving the hydrodynamic model prediction for α_D, eq 3, based on eq 11, literature values for R_g and R_h,[20] and a lower cutoff length a_D determined from a hydrodynamic model for the viscosity[5] and known values for the Huggins constant. Points represent fits of eq 3 to the experimental literature on polymer self-diffusion, including (●) polystyrene:CCl_4,[22,23,24] (▽) polystyrene:C_6D_6,[22,23,24] (○) polystyrene:cyclopentane,[25] (□) poly(dimethylsiloxane):toluene,[26,27] (△) polystyrene:benzene,[28] (+) three-armed polybutadiene:CCl_4,[30] (⊕) poly(ethylene oxide):water,[31] (☆) polybutadiene:CCl_4,[30] (×) three-armed polybutadiene:CCl_4,[30] (♦) xanthan:water,[32] and (▲) polyisoprene:CCl_4.[29]

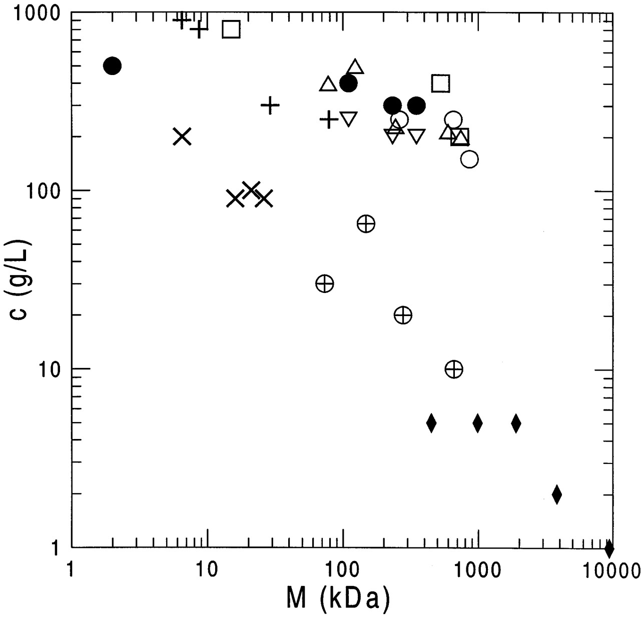

Figure 2. Range of quantitative validity of the hydrodynamic model for polymer self-diffusion. Each point represents the largest polymer concentration at which a polymer of specified molecular weight was studied in one of refs 22−32, leading to a point in Figure 1. Symbols are as in Figure 1.

These determinations of α from the literature[22−29] appear in Figure 1. Figure 1 represents polymers with molecular weights in the range 2 to 1 × 10^4 kDa. Polymer concentrations in individual series of measurements often extended out to several hundred grams per liter. The solid line in Figure 1 represents the prediction of the previous sections for α_D. The numerical prediction

$\alpha_D = 0.56$ for 1.27 MDa polystyrene in benzene was used to fix an intercept. The dependence $\alpha_D \sim R^3/M \sim M^{0.8}$ was used to extrapolate this prediction to other molecular weights.

There are no free parameters in the solid line. Within the approximations noted above and in refs 4 and 5, there is no way to change either the slope of the line or its vertical position in the graph. From Figure 1, within the scatter in measurements of α_D there is excellent agreement between the predicted value of α_D and experiment.

Figure 2 shows the range of polymer concentrations and molecular weights for which this agreement has been found. Points in the figure indicate—for each molecular weight of each polymer studied—the highest concentration at which $D_s(c)$ was observed. In almost all cases, the concentration cutoffs are in the original experimental papers, with no indication that the predicted behavior did not continue to larger polymer concentrations.

The hydrodynamic model treatments of viscosity[5] and self- diffusion[4] are thus shown to be mutually consistent and to agree with experiment. The hydrodynamic model treatment of polymer self-diffusion and a parameter obtained from viscosity measurements predict quantitatively the parameter α that determines the concentration dependence of D_s. Good agreement is found between this prediction and the published experimental literature on self-diffusion by linear and three-armed star polymers.

References and Notes

(1) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(2) Fujita, H. *Macromolecules* **1988**, *21*, 179.
(3) Skolnick, J.; Kolinski, A. *Adv. Chem. Phys.* **1989**, *78*, 223.
(4) Phillies, G. D. J. *Macromolecules* **1998**, *31*, 2317.
(5) Phillies, G. D. J.*J. Chem. Phys.* **2002**, *116*, 5857.
(6) de Gennes, P.-G., *Scaling Concepts in Polymer Physics*; Cornell UP: Ithaca, NY, 1979.
(7) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*, Clarendon Press: Oxford, England, 1986.
(8) Rouse, P. E., Jr. *J. Chem. Phys.* **1998**, *108*, 4628.
(9) Ngai, K. L.; Phillies, G. D. J. *J. Chem. Phys.* **1996**, *105*, 8385.
(10) Altenberger, A. R.; Tirrell, M.; Dahler, J. S. *J. Chem. Phys.* **1986**, *84*, 5122; Altenberger, A. R.; Dahler, J. S.; Tirrell, M. *Macromolecules* **1988**, *21*, 464.
(11) Freed, K. F.; Perico, A. *Macromolecules* **1981**, *14*, 1290.
(12) Beenakker, C. W. J.; Mazur, P. *Phys. Lett*, **1983**, *98*, 22; *Physica A*, **1984**, *126*, 349; *Physica A* **1984**, *128*, 48.
(13) Altenberger, A. R.; Deutch, J. M. *J. Chem. Phys.* **1972**, *59*, 894.
(14) For a detailed explication, note: Phillies, G. D. J. *Elementary Lectures in Statistical Mechanics*; Springer-Verlag: New York, 2000; in particular, Lectures 28−30.
(15) Lodge, T. P.; Rotstein, N. A.; Prager, S. *Adv. Chem. Phys.* **1990**, *79*, 1.
(16) Altenberger, A. R.; Dahler, J. S. *J. Chem. Phys.* **1996**, *54*, 6242.
(17) Adler, R. S.; Freed, K. H. *J. Chem. Phys.* **19080**, *72*, 4186.
(18) N. Saito, *J. Phys. Soc. Jpn.* **1952**, *7*, 447.
(19) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(20) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(21) Phillies, G. D. J. "Self-and Tracer Diffusion of Polymer Molecules in Solution", submitted for publication.
(22) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.
(23) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1981**, *14*, 1334.
(24) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1984**, *17*, 431.
(25) Deschamps, H.; Leger, L. *Macromolecules* **1986**, *19*, 2760.
(26) Giebel, L.; Benmouna, M.; Borsali, R.; Fischer, E. W. *Macromolecules* **1993**, *26*, 2433.
(27) Skirda, V. D.; Sundukov, A. I.; Maklakov, A. I.; Zgadzai, O. E.; Gafrurov, I. R.; Vasiljev, G. I. *Polymer* **1988**, *29*, 1294.
(28) Leger, L.; Hervet, H.; Rondelez, R. *Macromolecules* **1981**, *14*, 1732.
(29) Xuexin, C.; Zhongde, X.; von Meerwall, E.; Seung, N.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1984**, *17*, 1343.
(30) von Meerwall, E. D.; Tomich, D. H.; Grigsby, J.; Pennisi, R. W.; Fetters, L. J.; Hadjichristidis, N. *Macromolecules* **1983**, *16*, 1715.
(31) Brown, W.; Stilbs, P.; Johnsen, R. M. *J. Polym. Sci., Polym. Phys.* **1983**, *21*, 1029.
(32) Tinland, B.; Maret, G.; Rinaudo, M. *Macromolecules* **1990**, *23*, 596.

MA020376S