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# Probe Dynamics Constraints on Theoretical Models for Polymer Dynamics

George D. J. Phillies\*

*Department of Physics, Worcester Polytechnic Institute, Worcester, MA 01609*

Measurements of diffusion and driven motion by probe particles in polymer solutions constrain theoretical models of polymer solution dynamics. In this paper, motions of large, intermediate (smaller than a polymer chain, larger than a solvent molecule), and small (solvent, ion) probes through polymer solutions and viscous small-molecule solvents are analyzed. The resulting constraints limit the physical models that can plausibly be used to describe polymer motion and separately limit the mathematical structures that might be used to obtain quantitative predictions from those models. A transition in small-molecule mobility through polymer solutions, at polymer concentrations near 400 g/L, is explained in terms of the size of a solvent molecule relative to the gaps between pairs of chain segments on adjacent polymer molecules.

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## I. INTRODUCTION

A wide range of experimental methods, including rheometry, light scattering spectroscopy, centrifugal sedimentation, and dielectric relaxation, have been used to study how polymer molecules move in non-dilute solution. The specific interest here is probe dynamics, in which one observes the passive (diffusive) or forced (driven by external forces) movements of mesoscopic objects through polymer solutions.

The following analysis reflects two entirely separate topics, namely physical models for polymer dynamics and mathematical structures for representing those models. Physical models identify the forces that dominate polymer dynamics. A search of the literature finds models that are based on the primacy of hydrodynamic interactions<sup>1</sup> and quite different models that assume the primacy of chain crossing constraints (entanglements)<sup>2</sup>. Mathematical structures take one from the forces to quantitative predictions of solution behavior. Different mathematical structures lead to different mathematical forms, such as power laws or stretched exponentials, that describe how transport coefficients depend on polymer concentration and molecular weight.

Physical models and mathematical structures appear to be fundamentally independent. As it happens, most models that are based on the primacy of hydrodynamic interactions do lead via the Altenberger-Dahler Positive-Function Renormalization Group<sup>3</sup> to stretched-exponential functional forms<sup>1</sup>. The archetypical models based on the primacy of chain crossing constraints do often obtain scaling (power law) behavior<sup>2</sup>. However, there is no obvious reason why hydrodynamic models must lead to stretched exponentials, or why entanglement models must lead to power laws. Indeed, the Langevin-Rondelez treatment<sup>4</sup> of probe centrifugation is an entanglement model, but it obtains a stretched-exponential concentration dependence. The Langevin-Rondelez treatment thus shows that entanglement models are not obliged to predict scaling behavior.

How has probe diffusion been measured? Probe diffusion techniques fall into three major categories, viz., techniques (e. g., fluorescence recovery after photobleaching<sup>5</sup>, fluorescence correlation spectroscopy<sup>6</sup>) that give a long-time diffusion coefficient, (ii) techniques (e. g., quasielastic light scattering spectroscopy (QELSS), inelastic neutron scattering) that measure the intermediate structure factor  $g^{(1)}(q, t)$ <sup>7</sup>, and (iii) one-particle<sup>8,9</sup> and two-particle<sup>10</sup> tracking techniques that measure directly various displacement distribution functions. This list of experimental techniques is representative, not complete, but many other techniques fall into these same three categories.

In general, category (ii) methods do not measure the mean-square particle displacement  $\langle x(t)^2 \rangle$ . The quantity measured directly by QELSS is  $S(q, t)$ , the intensity-intensity time correlation function, or "spectrum". There are indeed assertions in the literature that  $S(q, t)$  is related to particle displacements by

$$S(q, t) = A \exp(-q^2 \langle x(t)^2 \rangle) + B. \quad (1)$$

Here  $q$  is the magnitude of the scattering vector,  $x$  is the component of the displacement parallel to  $\mathbf{q}$  of a representative particle during a time interval  $t$ , the brackets  $\langle \dots \rangle$  denote an average over particles, and  $A$  and  $B$  are constants determined by the details of the experimental apparatus. Assertions supporting eq 1 all appear to pass through a common branch point, namely Chapter 5 of Berne and Pecora's monograph<sup>7</sup> on light scattering spectroscopy. Berne and Pecora's entirely correct analysis, summarizing a near-century of research on Brownian motion and the Langevin equation, refers exclusively to dilute probe particles in simple Newtonian fluids. On time scales of interest here,

polymer solutions are viscoelastic, not Newtonian. Derivations from the Langevin equation leading to equation 1 thus do not pertain to probes in polymer solutions.

The actual relationship between  $S(q, t)$  and particle displacements passes through the dynamic structure factor  $g^{(1)}(q, t)$ , which is related to  $S(q, t)$  by

$$S(q, t) = A |g^{(1)}(q, t)|^2 + B. \quad (2)$$

For dilute probe particles in a complex fluid, the relationship between  $g^{(1)}(q, t)$  and particle motions is determined by the displacement distribution function  $P(x, t)$ . This distribution function gives the probability that a particle will have a displacement  $x$  during time interval  $t$ . The relationship between  $g^{(1)}(q, t)$  and  $P(x, t)$  is

$$g^{(1)}(q, t) = \int dx P(x, t) \exp(iqx). \quad (3)$$

For dilute monodisperse probes in a simple Newtonian fluid, the Langevin equation leads to the conclusion that  $P(x, t)$  is a Gaussian in  $x$ . The shape of a Gaussian  $P(x, t)$  is entirely determined by its second moment  $\langle x(t)^2 \rangle$ . Equations 2 and 3 then do lead to equation 1.

For an arbitrary  $P(x, t)$ , an extended analysis shows that  $g^{(1)}(q, t)$  and therefore  $S(q, t)$  are determined by all higher moments  $\langle x(t)^{2n} \rangle$  of  $P(x, t)$ . An exponential series expansion for  $g^{(1)}(q, t)$  opens<sup>11</sup>

$$g^{(1)}(q, t) = N \exp \left( -\frac{1}{2} q^2 \langle X(t)^2 \rangle + \frac{1}{24} q^4 (\langle X(t)^4 \rangle - 3 \langle X(t)^2 \rangle^2) - \mathcal{O}(q^6) \right). \quad (4)$$

The higher-order ( $n \geq 2$ ) terms are important even for a system as simple as a mixture of small and large dilute probes in a Newtonian solvent. The higher-order terms have a direct consequence: With increasing time,  $S(q, t)$  and  $\exp(-q^2 \langle x(t)^2 \rangle)$  progressively diverge from each other, readily by an order of magnitude or more. An example of this divergence is shown in Ref. 17, Figure 4.1b, which shows  $g^{(1)}(q, t)$  and  $\log(S(q, t))$  as calculated for a bidisperse mixture of dilute probes. In the notional spectrum used to generate the Figure, the notional concentrations of the two sizes of probes have been set so that both relaxations are easily seen by the reader. Once the spectral mode corresponding to the smaller particles decays, the time dependence of  $S(q, t)$  is due only to the larger particles, so  $\log(S(q, t))$  does not match  $-q^2 \langle x(t)^2 \rangle$ . The divergence occurs because the small particles continue to move at long times, so they still contribute to the monotonic increase in  $\langle x(t)^2 \rangle$  with increasing  $t$ . However, with increasing  $t$  the initial and current positions of the small particles become uncorrelated, so at large  $t$  the small particles cease to contribute to the time dependence of  $S(q, t)$ . The result is that eq 1 is incorrect, except for the special case of monodisperse probes in a Newtonian solvent.

How can an experimentalist tell if eq 1 is correct in her system, so that  $\langle x(t)^2 \rangle$  can be inferred from  $S(q, t)$ ? Fortunately, Doob's theorem<sup>12</sup> answers this question. Whenever eq. 1 is valid, Doob's theorem mathematically guarantees that (i)  $S(q, t)$  relaxes as a single exponential, (ii) eq 1 is correct, and (iii)  $\langle x(t)^2 \rangle = 2Dt$ ,  $D$  being a time-independent constant. Conversely, if one finds experimentally that  $S(q, t)$  is not a single exponential, Doob's theorem guarantees that  $S(q, t)$  is not determined by and cannot be used to calculate  $\langle x(t)^2 \rangle$  over a range of times. The error in using a non-exponential  $S(q, t)$  to calculate  $\langle x(t)^2 \rangle$  via eq 1 becomes large with increasing  $t$ .

Particle tracking methods actually measure  $P(x, t)$  directly. How does  $P(x, t)$  behave for probes in viscoelastic fluids? Note, for example, studies by Apgar, et al.<sup>8</sup> and Tseng and Wirtz<sup>9</sup>. These workers obtained  $P(x, t)$  for probes in polymer solutions. They demonstrated experimentally that  $P(x, t)$  in their systems is not a Gaussian in  $x$ . Correspondingly, they showed by direct measurement that the so-called 'Gaussian approximation' for  $P(x, t)$  is incorrect for probes in complex fluids. Derivations of eq 1 are based on the Gaussian approximation and therefore are wrong for probes in polymer solutions.

The Langevin model predicts a Gaussian form for  $P(x, t)$ . Why is this derivation invalid for the systems studied by Apgar, et al.<sup>8</sup> and Tseng and Wirtz<sup>9</sup>? The answer is that the Langevin model implicitly assumes that the motions of a Brownian particle are driven by a random thermal force having correlation time zero, and a drag force determined by the current velocity of the particle. However, no simple fluid is perfectly Newtonian, and certainly polymer solutions are not. Real liquids have a memory. As a result, the 'random' thermal force on a Brownian particle in a polymer solution has correlations that last for extended periods of time, while the drag force on the same particle is determined by the particle's motions over the same extended periods of time. Above some frequency, larger for probes in simple liquids than for probes in polymer solutions, real systems do not satisfy the assumptions in the Langevin equation, so the Langevin equation does not predict  $P(x, t)$  for probes in polymer solutions. Recourse must instead be had to the Mori-Zwanzig formalism<sup>13</sup>. Correspondingly, as explained in ref. 11,  $S(q, t)$  is only determined by  $\langle x(t)^2 \rangle$  at the very short times at which the decay of  $S(q, t)$  is linear in  $t$  to within experimental error.

Probe dynamics has also been studied by observing the response of probes to external forces. Measurements of driven probe motion are the only true microrheological measurements: They determine the response of the fluid to

an external force that is applied on a microscopic distance scale. At least four major experimental methods employ driven probes. In order of decreasing size though not necessarily importance of their literatures, note electrophoresis, ultracentrifugal sedimentation, magnetic tweezers, and optical tweezers. As generally implemented, the first two of these study large displacements at long times, while with the latter two the magnitude and frequency of the applied force can be separately controlled by the experimenter.

Microrheological fluid responses are not always the same as the macrorheological response determined with a conventional rheometer. For example, Schmidt, et al.<sup>14</sup> observed 4.5  $\mu\text{m}$  probes in protein solutions for frequencies 0.003-6 Hz. They found that the dynamic moduli  $G'(\omega)$  and  $G''(\omega)$  as measured with a microscopic rheometer are in general less than the corresponding moduli determined with a classical instrument. Their measurements have implications for the interpretation of observations of particle diffusion. It might be found that dynamic moduli calculated using a particular passive microscopic method happen to agree with dynamic moduli measured with a classical macroscopic instrument. This finding does not validate the passive microscopic method as a rheological technique, because Schmidt, et al. show that the true true dynamic moduli found on microscopic length scales do not agree with true dynamic moduli measured classically, and, therefore, a microscopic method that happened to report on occasion the macroscopic moduli would not be reporting the moduli on the time and distance scales that it appeared to be probing. Indeed, a primary motivation for studies of optical probe diffusion was non-Stokes-Einsteinian diffusion, the widespread finding that particles diffuse through polymer solutions more rapidly than would have been expected from the measured viscosity<sup>15</sup>.

The potential utility of electrophoresis as a path to understanding driven probe motion in complex systems has been amply demonstrated by studies of electrophoresis in crosslinked gels, as systematically reviewed by Viovy<sup>16</sup>. The literature on electrophoresis through solutions of neutral polymers is very large, but has largely not been approached from the polymer physics standpoint seen in Viovy's review. Electrophoretic mobilities of charged species through neutral polymer solutions are conventionally used to infer the properties of the charged migrating species. The discussion here calls for the inverse analysis, using the electrophoretic mobility of known probes to infer properties of the neutral polymer solutions being used as support media, as has previously been proposed in Ref. 17.

The following sections treat the phenomenology of probe diffusion and driven probe motions. The constraints that these observations place on possible models for polymer dynamics are discussed. Some constraints are not consistent with every current model for polymer motion in non-dilute solution. The discussion begins with the largest probe particles and works down to small-molecule motions.

## II. LARGE PROBES

There are extensive literatures on diffusion and driven motion by large, primarily spherical probes. Diffusion studies include experiments leading to a single diffusion coefficient  $D_s$  and QELSS studies finding multimodal relaxations. In works identifying a single diffusion coefficient, the concentration dependence of  $D_s$  almost always<sup>15</sup> follows a single stretched exponential

$$D_s = D_{s0} \exp(-\alpha c^\nu) \quad (5)$$

in  $c$ , over the entire observed range of matrix concentrations. Here  $D_{s0}$  is the low-concentration limit of  $D_s(c)$ , and  $\alpha$  and  $\nu$  are a scaling prefactor and scaling exponent, respectively. For example, Phillies, et al.<sup>18</sup> used QELSS to measure  $D_s$  for 41 and 460 nm polystyrene spheres in 8 aqueous dextrans,  $10 \leq M_w \leq 542$  kDa, at matrix concentrations up to 250 g/L. Fifteen of the sixteen sphere-polymer combinations follow eq. 5; the 41 nm spheres in solutions of the 542 kDa material have a single sharp change in  $\nu$  above a crossover concentration. In this same system,  $\alpha \sim M^{0.84}$ , while with increasing  $M$  one finds that  $\nu$  decreases from 1.0 to 0.6.

There are two rare exceptions to a stretched-exponential concentration dependence, which may be described as plateau behavior and as re-entrant behavior. In plateau behavior,  $D_s(c)$  is independent of  $c$  at matrix concentrations near zero. A stretched-exponential concentration dependence appears above a crossover concentration. In re-entrant behavior,  $D_s(c)$  deviates from stretched-exponential behavior over a narrow concentration range, but returns toward the stretched exponential at larger  $c$ . Yang and Jamieson<sup>19</sup> used QELSS to examine 120, 210, and 350 nm diameter spheres diffusing through aqueous 110, 140, 450, and 850 kDa hydroxypropylcelluloses. They found plateau behavior. Won, et al.<sup>20</sup> found re-entrant behavior for the diffusion of 200 nm polystyrene spheres through 1300 kDa polyvinylmethylether: toluene.

In interpreting QELSS spectra in terms of a single probe diffusion coefficient, several control experiments are needed. Scattering must be attributable to the probes. Either scattering by the polymer solution must be negligible relative to scattering by the probes, or polymer scattering must be removed from  $S(q, t)$  via spectral subtraction at the field correlation function level. Probe aggregation must be controlled, as by addition of surfactant, validated for example

by demonstrating that  $D$  ceases to change when more surfactant is added. Spectra must be clearly unimodal and near-exponential, validated by measurement of the spectrum to extended times and confirmation that the second cumulant is neither large nor markedly concentration-dependent. The QELSS papers cited here satisfy these conditions.

Given the interest in alternative mathematical structures, it is reasonable to search for instances in which  $D_s$  of large probes in non-dilute polymer solutions shows scaling-law ( $D_s \sim c^x$  or  $D_s \sim M^y$ ) behavior<sup>15</sup>. No such instances are found, other than the physically trivial outcome that any plot of  $\log(D_s(c))$  against  $\log(c)$  must have locally-valid power-law tangent lines. Models that predict concentration scaling laws for large probes diffusing in non-dilute solutions are thus rejected by experiment. A sound general model of polymer dynamics should instead predict that  $D_s$  usually has a stretched-exponential concentration dependence, and should predict the observed molecular weight dependences of  $\alpha$  and  $\nu$ .

The concentration dependence of  $D_s$  can be compared with the concentration dependence of the solution viscosity  $\eta$ . For large spheres, spheres that are larger than any distance scale in solution, it might be proposed that  $D_s$  should be determined by  $\eta$ , so that  $D_s\eta$  is independent of  $c$ . The constancy of  $D_s\eta$  is termed Stokes-Einsteinian behavior, because it would be found if the Stokes-Einstein equation

$$D_s = \frac{k_B T}{6\pi\eta a} \quad (6)$$

were applicable. Here  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $a$  is the sphere radius. It might further be proposed that Stokes-Einstein behavior would only be found for diffusion over particular distance scales, distances shorter or longer than some distance scale established by solution features and the probe size.

Some caution is needed because Stokes' law refers to particles moving in a straight line at constant speed. The hydrodynamic drag on a particle performing irregular motion in a Newtonian fluid is given not by Stokes' Law but by the Boussinesq equation<sup>21,22</sup>

$$-F(t) = \xi u(t) + \frac{1}{2}m_0\dot{u}(t) + \alpha_B\pi^{-1/2} \int_0^t ds(t-s)^{-1/2}\dot{u}(s) \quad (7)$$

Here  $F(t)$  is the force on a sphere of radius  $a$  that moves at velocity  $u(t)$ ,  $\xi$  is the Stokes' Law drag coefficient of the particle, all motion is along the same axis,  $m_0 = 4\pi a^3\rho/3$  is the mass of fluid displaced by the particle,  $\rho$  is the density of the surrounding fluid, and

$$\alpha_B = \xi a(\rho/\eta)^{1/2}, \quad (8)$$

where  $\eta$  is the liquid viscosity. The Boussinesq equation includes a memory kernel  $(t-s)^{-1/2}$ , so that the drag force at time  $t$  depends on the particle's acceleration  $\dot{u}(s)$  at all earlier times  $s$ . Eq 7 is very different from Stokes' law. Indeed, a significant concern in statistical mechanics, four decades ago, was whether a sphere subject to a Boussinesq equation drag force rather than a Stokes' Law drag force diffuses as predicted by eq. 6. For spheres diffusing through a Newtonian solvent, the required affirmation was supplied, e. g., by Chow and Hermans<sup>21</sup>.

For large spheres, the phenomenological relationship between  $D_s$  and  $\eta$  is complex. There are indeed systems in which  $D_s\eta$  is substantially independent from  $c$  and  $M$ , so that  $D_s\eta$  in concentrated polymer solutions is close to its value for probes in pure solvent. For example, Brown and Rymden<sup>23</sup> report on 160 nm radius stearic-acid-coated silica spheres in polymethylmethacrylate solutions, using polymers with molecular weights in the range 101-445 kDa. With the largest polymer,  $D_s$  and  $\eta$  each change by nearly 1000-fold as the polymer concentration is increased. Diffusion remains Stokes-Einsteinian;  $D_s\eta/D_{s0}\eta_0 = 1$  for all polymers and polymer concentrations. Also, log-log plots of  $D_s$  and  $\eta$  against  $c$  for these systems show that  $D_s$  and  $\eta$  consistently lie on smooth curves of monotonically increasing slope, not on the straight lines corresponding to scaling behavior.

However, there are other systems in which  $D_s\eta/D_{s0}\eta_0 \approx 1$  is only found for solutions of low molecular weight polymers or at very low concentration, for example, aqueous non-neutralized polyacrylic acid as studied with QELSS by Lin and Phillies<sup>24</sup>, aqueous polyethylene oxide as studied with QELSS by Ullmann, et al.<sup>25</sup>, and hyaluronic acid solutions as examined by De Smedt, et al.<sup>26</sup>. De Smedt, et al.'s measurements were done with fluorescence recovery after photobleaching, and correspond to diffusive motion over distances larger than any length scales in the system. At elevated polymer concentrations, probes in these studies consistently diffused more rapidly (in some cases, much more rapidly) than would be expected from the solution viscosity.

Corresponding to these and many other<sup>17</sup> experimental results, a valid model of probe diffusion should not predict that Stokes-Einsteinian behavior is automatically found for large probes in polymer solutions. Models predicting that Stokes-Einsteinian behavior is automatic for large probes are rejected by experiment. From the range of different behaviors observed for  $D_s\eta$  as a function of  $c$  and  $M$ , a sound model must allow effectively for the manifestation of specific chemical effects.

Light scattering spectra obtained by Delfino, et al.<sup>27</sup>, Bremmell and Dunstan<sup>28</sup>, and Streletzky and Phillies<sup>29</sup>, among others, find multimodal probe spectra, in which  $S(q, t)$  of probes in polymer solutions is not described by a single diffusion coefficient. Spectra measured at a single  $q$  correspond to diffusion over a fixed set of distances, so that small-time behavior corresponds to short-lived modes, while long-time behavior corresponds to transient long-lived modes. For fixed  $q$ , the short- and long-lived modes are necessarily relaxed by particle motions over the same distances.

Delfino, et al., examined 14, 47, and 102 nm radius polystyrene latex spheres diffusing in 700 kDa carboxymethylcellulose at concentrations  $0 - 17c^*$ . The two larger spheres have radii larger than the radius of gyration  $R_g$  of the matrix polymer. Spectra were found to be adequately characterized as a sum of one or two pure exponentials, and thus could correspond to one or two true diffusion coefficients. Most spectra were bimodal. Delfino, et al., propose interpreting their spectra in terms of cage-confined (short-distance) and longer distance motions. This general interpretation might be verified by examining spectra at large or small  $q$ ; the reported experiments correspond directly to multiple time scales for motions on the same length scale  $q^{-1}$ . Because the modes are pure exponentials, they can be proposed to correspond two separate motional processes, each with a  $\langle x(t)^2 \rangle$  that increases linearly in time. The rapid process is weakly  $c$ -dependent,  $D_p$  decreasing by no more than an order of magnitude over the observed concentrations. The slow process decreases exponentially in  $c$ , decreasing for the larger spheres by 3-4 orders of magnitude over the observed range of concentrations. For the slow mode of the two larger spheres and concentrations  $c > c^*$ ,  $D_s\eta/D_{s0}\eta_0 \gg 1$ . The ratio  $D_s\eta/D_{s0}\eta_0$  has a maximum and then decreases (but not to less than 2 or 3) with increasing  $c$ . Delfino, et al.'s results for large spheres and long times at elevated matrix concentrations show neither scaling ( $c^{-x}$ ) nor Stokes-Einsteinian ( $D_p\eta/D_{p0}\eta_0 \approx 1$ ) behavior. The theoretical models corresponding to these observations must be able to predict two diffusive modes, corresponding to simultaneous particle motions over the same range of distances at very different rates.

Extensive measurements of probe size effects were made by Streletzky and Phillies<sup>29</sup>, who examined 14-455 nm diameter polystyrene spheres diffusing in 1 MDa hydroxypropylcellulose. Spectra were bimodal, in the form of a sum of stretched exponentials in time. Mode parameters showed distinctive small and large probe behaviors, the division between small and large probes occurring for probes between 40 and 60 nm in diameter. The accuracy in determining the transition radius was limited by the number of different-size probes that were studied. Hydroxypropylcellulose solutions appear to have a longest length scale  $R_t \approx 50$  nm that is, approximately, the size of a complete polymer chain.  $R_t$  depends at most weakly on matrix concentration. One could reasonably infer that whole-matrix-chain motion becomes central to probe diffusion.

Experimental studies of driven probe motion provide fresh constraints on possible models for polymer dynamics. Large-probe motion in the form of centrifugal sedimentation through polymer solutions was examined a half-century ago by Laurent and collaborators<sup>30-32</sup>. Note also more recent work by Tong and Ye<sup>33-35</sup>. Laurent, et al.<sup>32</sup> obtained the sedimentation coefficient  $s$  of 11 globular colloids, diameters 4.7-365 nm in 1.5 MDa hyaluronic acid. Measurements at different rotor speeds, corresponding to a fifty-fold change in sedimentation speed, obtained the same  $s$ ; these measurements were clearly obtained in the linear-response regime. In our notation, Laurent, et al. reported

$$s/s_0 = \exp(-kac^{1/2}), \quad (9)$$

$a$  being the probe radius. Sedimentation measurements also yield the probe's diffusion coefficient; the effects of the matrix polymer on  $s$  and on  $D_s$  were found experimentally to be the same.

From eq. 9,  $s/s_0$  depends on probe radius, even for very large probes. Eq. 9 corresponds to non-Stokesian behavior, in that the same solution has a differential effect on retarding the motion of small and large probes. Referring to implications of eq. 9, Laurent, et al.<sup>32</sup> wrote "...it will be shown that this sieving effect can be used for the separation of various compounds that would otherwise sediment together in the ultracentrifuge...". The sieving effect is the factor of  $a$  on the rhs of eq. 9. Laurent, et al.'s proposal that polymer solutions can enhance biochemical separations by serving as sieves came to fruition a half-century later: Polymer solutions are widely used as support media in capillary electrophoresis. Laurent and Persson<sup>30</sup> also measured solution viscosities. Contrary to any expectation that the solution viscosity determines the sedimentation rate of large probes, matrix polymers are more effective at increasing  $\eta$  than at reducing  $s$ .

Driven probe motion in polymer solutions has also been studied with capillary electrophoresis. The observed experimental quantity is the electrophoretic mobility  $\mu$ , obtained from an elution time, typically the minutes needed to travel centimeters down a capillary. Capillary electrophoresis thus observes probe motion on time and distance scales that are extremely long relative to polymer molecule time and length scales. Representative electrophoretic studies of  $\mu(c, M)$  are reported by Barron, et al.<sup>36</sup> and Heller<sup>37,38</sup>. Most measurements were made in a low-electric-field linear regime, but it is also practical experimentally<sup>39</sup> to enter a non-linear transport regime in which  $\mu$  itself depends on  $E$ . It should be emphasized that the electrophoresing probes are DNA restriction fragments, each species in a probe mixture being virtually perfectly monodisperse.

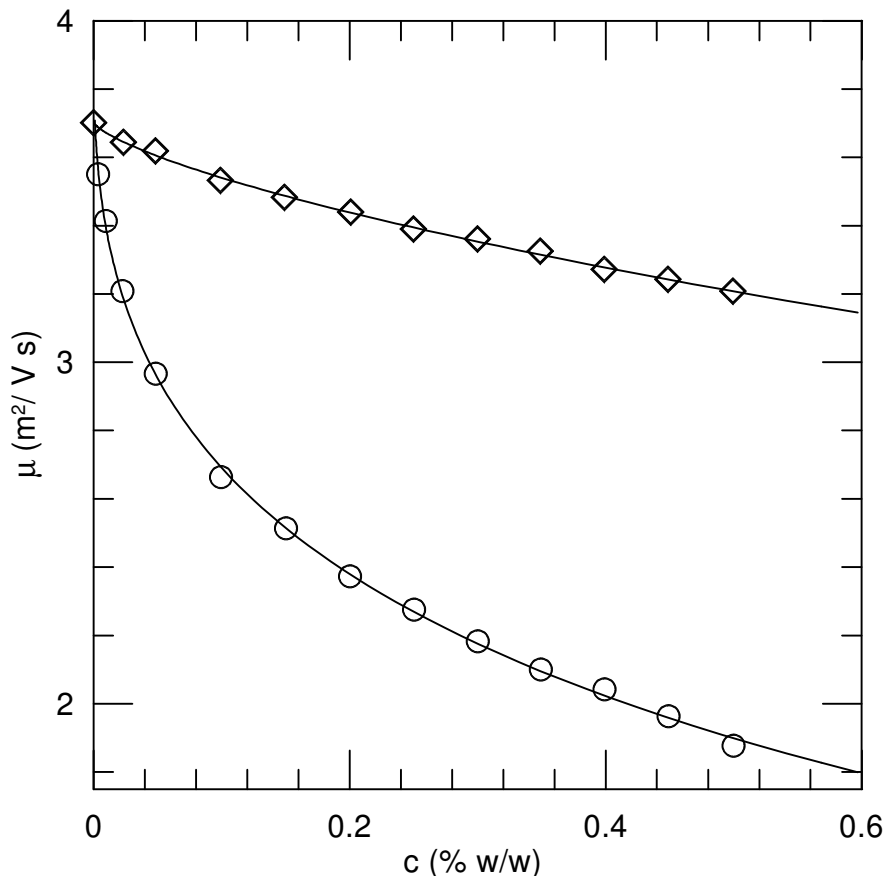


FIG. 1: Electrophoretic mobility  $\mu$  of (◇) 72 and (○) 23130 base pair restriction fragments in 300 kDa hydroxypropylcellulose, showing the stretched-exponential concentration dependence of  $\mu$ . Measurements as reported by Barron, et al.<sup>36</sup>; stretched exponential fits are from Phillies<sup>17</sup>.

How does  $\mu$  depend on matrix concentration, matrix molecular weight, or probe size? Because capillary zone electrophoresis is not widely recognized as revealing aspects of the dynamics of its neutral polymer support medium, it appears worthwhile to show a few representative measurements. Figures 1 and 2 show  $\mu$  as functions of  $c$  and  $M$ . The original data are from Barron, et al.<sup>36</sup>. The original authors also measured  $\eta(c)$  and inferred from it an overlap concentration  $c^*$ . Functional fits are from Phillies<sup>17</sup>. Figure 1 shows representative determinations of  $\mu$  as a function of concentration for one matrix polymer. The electrophoretic measurements cover both  $c < c^*$  and  $c > c^*$ , in this Figure mostly the former. There is no change in the functional form of  $\mu(c)$  at or near  $c^*$ , either in these measurements or in the similar measurements made by Barron, et al., on a half-dozen other polymers, some of which extended to appreciably larger  $c/c^*$  than the measurements shown here. A single stretched exponential, using the same parameters for concentrations below  $c^*$  and for concentrations above  $c^*$ , provides an accurate description of  $\mu(c)$  at all concentrations. Unfortunately, in analytic applications of electrophoresis there is less interest in measuring  $\mu$  in concentrated polymer solutions, so in Barron, et al.'s experiments on a range of polymers (which were intended to develop analytical applications)  $\mu(c)$  was never measured even up to  $c/c^* \approx 10$ . Figure 2 shows representative measurements of  $\mu$  as a function of probe size. For these probe molecules,  $\mu$  follows a stretched exponential in probe size, up to a sharp crossover. For probes larger than the crossover size,  $\mu$  follows a weak power law in probe size. Even on these very large time and distance scales,  $\mu/\mu_0$  ( $\mu_0$  being the probe mobility in pure solvent) continues to depend on probe size. There is no indication of a transition to Stokes-type ( $\mu/\mu_0$  independent from probe size) behavior.

Extensive video microscopy studies<sup>40</sup> have been made of electrophoresing large DNAs, revealing the variety of configurations<sup>41</sup>, e.g., "J", "U", "W", adopted by DNAs as they move. Of particular interest are videos of (artificial<sup>42</sup>) star DNAs, which show that DNA stars advance end-of-arms first, star core last<sup>43</sup>. These measurements appear to be made in the low-field linear regime, implying via the linear-response theorem that the observed *teuthidic* (squidlike) migration mechanism is continuous with the migration mechanism used by star polymers as they diffuse. Teuthidic migration does not resemble hypothesized arm-retraction mechanisms.

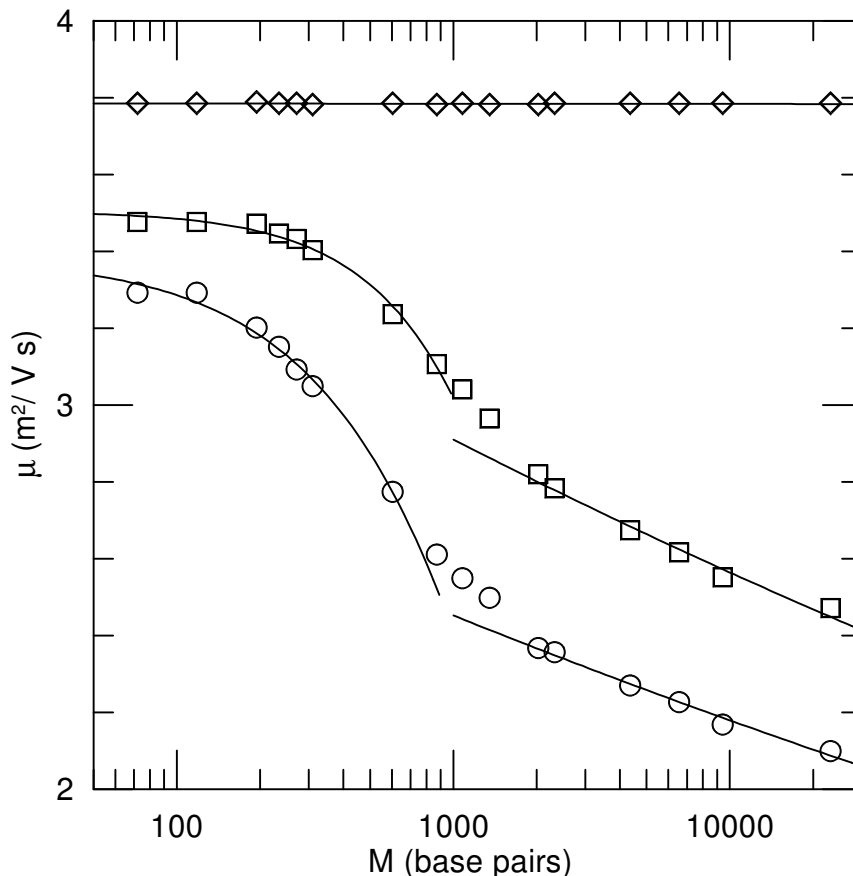


FIG. 2: Electrophoretic mobility  $\mu$  of DNA restriction fragments of various sizes in 1.14 MDa polyacrylamide at concentrations 0.5 (circles) and 0.2(squares) % w/w and in pure solvent (diamonds), showing the smaller-probe stretched-exponential regime, transition, and large-probe power-law regime. Restriction fragment molecular weights are quoted in number  $M$  of base pairs. In pure solvent,  $\mu$  is independent of probe size. Measurements as reported by Barron, et al.<sup>36</sup>; stretched exponential and power-law fits are from Phillis<sup>17</sup>.

Figures 1 and 2 are representative of a much larger body of data<sup>17</sup>. Their implications for models of polymer dynamics include: The model should show that  $\mu(c)$  for a given system follows a single analytic form with constant parameters over a wide range of  $c$ . Conversely, any treatment that assumes one model of polymer dynamics applies below  $c^*$  and a different model applies above  $c^*$  must explain why the transition between the two models is entirely invisible, so that the same function and parameters describes  $\mu(c)$  in both concentration regimes. The model also should account for the observed transition from linear ( $\mu \sim E^0$ ) to nonlinear ( $\mu \sim E^x$ ) behavior with increasing applied field  $E$ , and should explain the observed migration modes of star polymers.

### III. PROBES HAVING INTERMEDIATE SIZES

We now turn to intermediate size probes, probes that are appreciably larger than a solvent molecule but substantially smaller in radius than a matrix chain. A substantial study of intermediate size probes was made by Bu and Russo<sup>44</sup>. These workers used FRAP to measure  $D_s$  of fluorescein (0.5 nm), dextrans having hydrodynamic radii 1.3, 1.7, 2.8, 4.5, 5.8, 8.8, 13.3, and 17.9 nm, and 55 nm polystyrene spheres. The matrix polymer was 300 kDa dextran observed at concentrations up to 38 g/L and viscosities as large as  $\eta(c)/\eta_0 \approx 5 \cdot 10^3$ . Bu and Russo found that  $D_s$  of these probes accurately follows the Langevin-Rondelez equation<sup>4</sup>

$$\frac{D_s}{D_{s0}} = \frac{\eta_0}{\eta} + \exp(-(a/\xi_L)^\delta). \quad (10)$$



Here  $\xi_L \sim c^{-x}$  is a scaling length and  $a$  is the probe radius. Bu and Russo report  $x \approx 0.87$  and  $\delta$  slightly larger than 0.6.

The smallest and largest of Bu and Russo's probes are entirely rigid.  $D_s$  for the intermediate-size and somewhat-flexible dextrans lies on the lines for  $D_s(a)$  generated from eq. 10 and agreeing with the rigid probe results, so in terms of eq. 10 it appears that the chain flexibility of dextrans does not have a substantial effect on  $D_s(c, a)$ . For the largest probe at the highest concentration studied,  $a/\xi_L > 10$ , but  $D_s$  is still more than twice what would be expected from the solution  $\eta$ . Eq. 10 is clearly not a scaling law in  $c$ ; sound theoretical models for  $D_s(c)$  of intermediate-size probes should therefore not predict a scaling law.

Even for fluorescein,  $D_s$  decreases modestly with increasing matrix  $c$ . Models that predict  $D_s$  of small probes is determined by the solvent viscosity rather than the solution viscosity, the addition of polymer having no significant effect, therefore appear to be discouraged by experiment. Finally, the  $a$  and  $c$ -dependences found by Bu and Russo lie on smooth curves having constant parameters, with no indication that their results pass through multiple concentration or probe size regimes between which probe transport properties change significantly. Models that predict multiple regimes must explain quantitatively why any crossovers between regimes – which may be broad rather than sharp – are not apparent in the smooth curves.

Bu and Russo limited their experiments to relatively small polymer concentrations. Mustafa, et al.,<sup>45</sup> measured  $D_s$  of the small probe fluorescein in aqueous hydroxy propylcellulose at polymer concentrations up to 0.7 polymer weight fraction. For this probe,  $D_s(c)$  followed a single exponential in  $c$  through all concentrations studied. There are no indications of a concentration range in which  $D_s$  follows a scaling law in  $c$ . There are no indications of multiple concentration regimes between which matrix dynamics change qualitatively. Bu and Russo also measured  $D_s$  for probes in a series of different matrix polymers. Matrix molecular weights ranged from 60 kDa to 1 MDa. Just as  $D_s$  of small probes is affected by changing the matrix concentration, so also is  $D_s$  affected by changing the matrix molecular weight. Fluorescein is not much affected by the change in matrix  $M$ , but the 2.8 and 8.8 nm dextran probes diffuse more slowly as matrix  $M$  is increased.

#### IV. SMALL MOLECULES

Solvent motions are substantially perturbed by the dissolution of polymer chains. The solution viscosity increases. Short-range interactions between polymer molecules and neighboring solvent molecules may be present. As discussed in detail below, at elevated polymer concentration polymers exert a sieving effect on solvent motions, so that solvent flows can no longer be modeled with continuum hydrodynamics.

A sensible starting point for understanding how polymers affect small-molecule motions is provided by the effect of solvent viscosity  $\eta_s$  on the tracer diffusion coefficient  $D_s$  and electrical conductivity  $\lambda$  of ions and small molecules in mixed small-molecule solutions. Electrical conductivity studies began in a far earlier era in physical chemistry, but substantially refer to the same physical parameter also studied by electrophoresis, namely the rate of motion of charged particles through a liquid when acted upon by an electrical field. Results of Green<sup>46</sup>, Stokes and Stokes<sup>47</sup>, Hiss and Cussler<sup>48</sup>, and others<sup>49</sup> lead to a uniform phenomenology. In mixed solvents having  $\eta_s < 5$  cP,  $\lambda$  and  $D_s$  both scale as  $\eta_s^{-1}$ . There is then a sharp transition to a high-viscosity regime. The exact location of the transition depends on the solvent family being studied, but is near 5 cP. In small-molecule mixtures more viscous than the transition limit, conductivity and diffusion scale with viscosity as  $\eta_s^{-a}$  for  $a \approx 2/3$ .

For  $D_s$  of small probes, the effect of adding polymer to the solution is quite different from the effect of adding small-molecule solutes to the solution. The transition near 5 cP, first described a century ago by Green, is not seen in polymer solutions. A systematic re-examination of published results, e.g., refs. 50-52, finds for polymer solutions that  $D_s$  falls into two phenomenological regimes, separated by a transition in the range 350-500 g/L.

Representative measurements exhibiting the transition appear in Fig. 3. The points show self-diffusion coefficients for toluene in toluene:polystyrene mixtures as the polystyrene concentration is increased from dilute solution nearly to the melt. At concentrations below 450-500 g/L,  $D_s$  clearly fits well to a simple exponential  $D_{s0} \exp(-\alpha c)$ . Models that propose that  $D_s$  of solvent molecules is unaffected by adding polymer are rejected by experiment. At higher concentrations,  $D_s$  falls much more rapidly with increasing concentration, namely as a stretched exponential  $D_{s0} \exp(-\alpha c^\nu)$  with  $\nu > 1$ . The boundary between the two regimes is sharp, with no indication of a bridge regime in which  $D_s(c)$  is not described by the exponential or by the stretched exponential. The futility of attempting to describe the small-molecule  $D_s(c)$  with a scaling law form is revealed in the Figure by the dashed line, which shows a local best fit  $D_s \sim c^{-1.61}$ . Over a modest range of concentrations, the power law provides a tangent curve to the measurements. However, the curve is convex rather than concave; the power law is incorrect as to sign in its second derivative  $d^2 \log D_s / dc^2$ . Once again, phenomenology leads to a constraint, namely that under accessible conditions one must obtain exponential and stretched-exponential dependences of  $D_s$  of small probes on the matrix polymer concentration. An explanation for the transition with implications for theoretical modeling is supplied in the

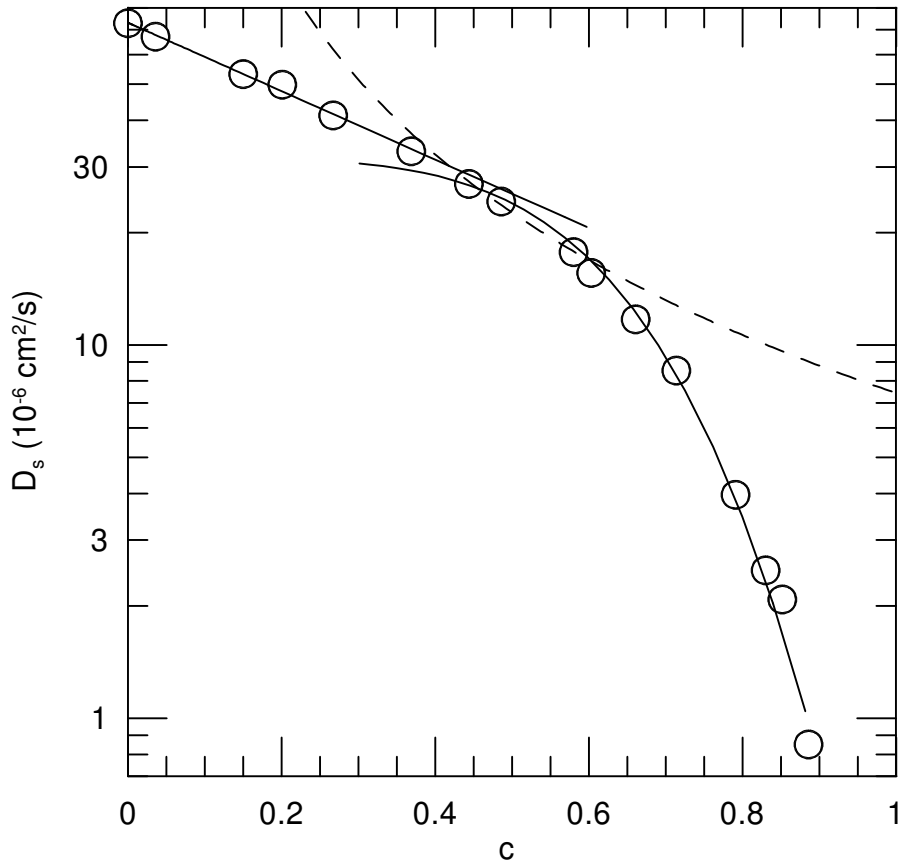


FIG. 3: Self-diffusion coefficient of toluene in solutions of 270 kDa polystyrene at 115 C, showing measurements (circles) of Pickup and Blum<sup>51</sup>, simple and stretched-exponential fits (solid lines) from Phillis<sup>17</sup>, and a power-law fit (dashes). Concentration units are polymer weight fraction.

#### Discussion.

An entirely different effect of added polymer on solvent self-diffusion is described by von Meerwall, et al.<sup>53</sup> These authors identify several systems in which the addition of polymer increases  $D_s$ . Seemingly, a relatively flexible polymer can act to plasticize a highly viscous solvent. Krahn and Lodge<sup>54</sup> used oscillatory electric birefringence to demonstrate that this plasticizing effect, as manifested in solvent rotation times, corresponds to a short-range (1-2 solvent diameters) interaction of the polymer with nearby solvent molecules.

### V. DISCUSSION

In the above, experimental observations on driven and diffusive motion of probe particles have been presented. Experiment imposes a long list of specific constraints on models for probe motion. One general constraint is found: The mathematical structure associated with a valid model for probe diffusion should lead naturally to exponential or stretched-exponential concentration dependences. Until the nonlinear driven transport regime is entered (Figure 2, lower right part of graph), mathematical structures that predict scaling (power-law) concentration dependences for the probe diffusion coefficient and probe mobility are inconsistent with experiment.

As a terminal aside, a mechanical model that leads to the phenomenological regimes observed for solvent self-diffusion, as seen in Figure 3, is now presented. The model is seen graphically as Figure 4. The central issue for the model is the relationship between the size of a typical solvent molecule and the perpendicular distance  $\xi$  between pairs of adjoining polymers. In the Figure, the circles A, B, and C represent polymers of radius  $r$  seen in cross-section; the lengths of the polymers extend perpendicular to the page. The hexagon represents a solvent molecule; its size is  $R$ . Circles A and B correspond to a near-melt situation. Circles A and C show a typical distance  $\xi$  between polymer chains in concentrated solution. At the concentration at which the typical center-to-center distance between two

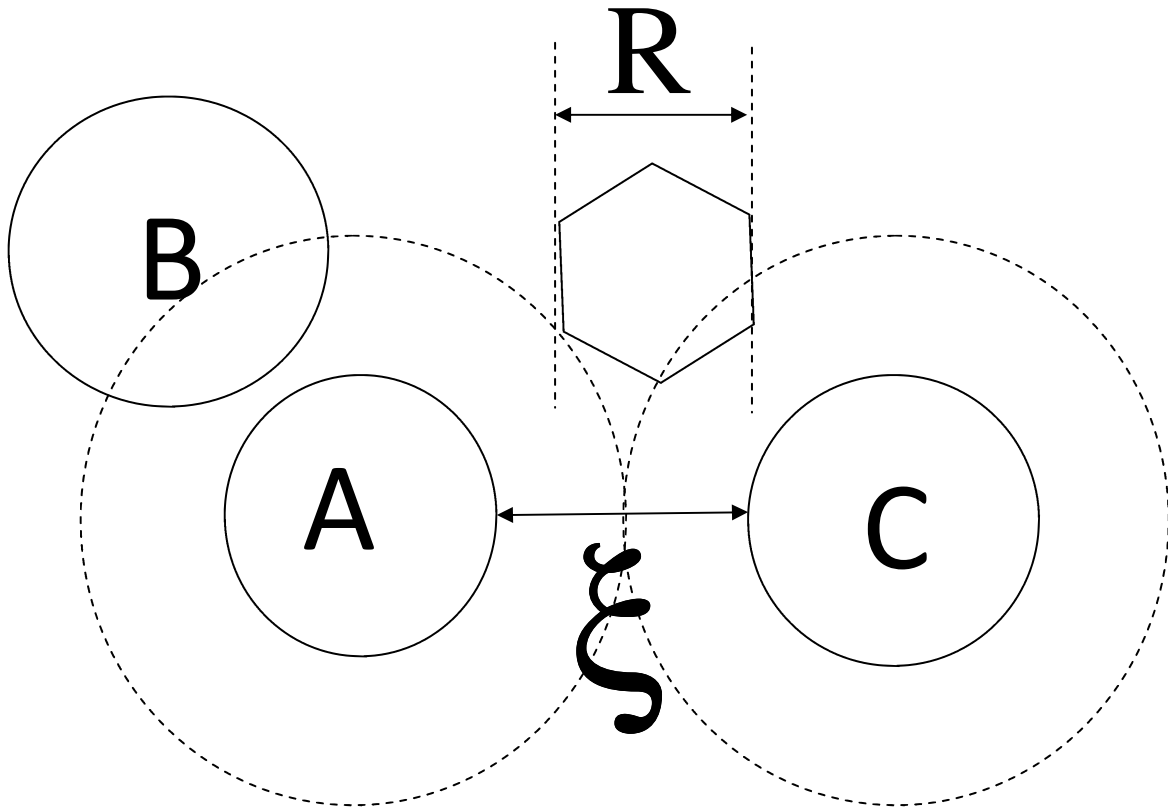


FIG. 4: The low-high matrix concentration transition for solvent diffusion. Circles A, B, and C are polymer chains, radius  $r$ , seen in cross-section. The hexagon of size  $R$  is a probe molecule. Circles A and B show a near-melt density. Circles A and C represent a concentration at which the size of a solvent molecule is comparable with the distance between polymers. Dashed circles are radius  $r + R/2$ , as treated in the text.

polymer chains is less than  $2r + R$ , the typical gap between polymer chains is less than the size of a solvent molecule, solvent molecules can no longer pass freely between chains, and it is no longer appropriate to approximate the solvent as a continuum Newtonian fluid. Recognizing that the critical ratio between  $R$  and  $\xi$  is unknown, only crude estimates of this transition concentration are possible. The figure shows a cross-section of two very long polymer chains, so the chain concentration in volume fraction units is  $\approx r^2/(r + R/2)^2$ . Mindful that  $r$  is somewhat larger than  $R/2$ , and that the circles are highly simplified approximations to molecular cross-sections,  $\xi$  matches a solvent molecule size for polymer volume fractions near  $1/3$ , which is close to the 350-500 g/L of the observed boundary. The concentration at which  $2r + R$  is a typical distance between polymer lines of centers lies approximately in the concentration regime in which  $D_s(c)$  changes its functional dependence on  $c$ .

What implication does this crossover have for theory? For hydrodynamic calculations using the Kirkwood-Riseman picture, the space between a typical pair of polymer beads is generally taken to be filled with a solvent, a Newtonian fluid of some known viscosity  $\eta_s$ . A typical pair of beads, not a nearest-neighbor pair of beads as seen in the Figure, has the two beads on two different polymer chains separated by several or many times a polymer radius of gyration. Above the crossover, the space between most pairs of polymer beads, most pairs of beads in the solution being separated from each other by far more than the distances seen in Figure 4, is filled not with Newtonian solvent but with the non-Newtonian polymeric liquid formed by the other chains in solution. Replacing the Newtonian solvent with a non-Newtonian fluid is reasonably expected to modify the hydrodynamic interaction tensors, with consequences for the ensuing hydrodynamic calculations.

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\* Electronic address: [phillies@wpi.edu](mailto:phillies@wpi.edu)

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