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Brownian Motion of Colloidal Spheres in Aqueous PEO Solutions

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ABSTRACT: The Brownian motion of colloidal spheres in aqueous poly(ethylene oxide) (PEO) solutions ranging in concentration from 0.2 to 15 wt % is measured with diffusing wave spectroscopy over more than 6 decades of time. The measured colloidal sphere mean-squared displacements are shown to satisfy the generalized Stokes–Einstein relation that relates the particle mean-squared displacement to the polymer solution shear modulus as the microrheological creep compliance calculated from the colloidal sphere Brownian motion was found to agree with that measured by mechanical rheometry. The microrheological zero shear viscosity concentration dependence for the entangled solution regime, $\eta \sim c^{4.7}$, is in agreement with that reported by others from mechanical rheometry measurements on polymer–good solvent solutions and is stronger than the tube model prediction, $\eta \sim c^{3.9}$. Essentially the entire deviation between the predicted and measured entangled solution regime zero shear viscosity concentration dependence is accounted for in the difference between the predicted, $\tau \sim c^{1.6}$, and measured, $\tau \sim c^{2.3}$, terminal relaxation time concentration dependence as the predicted, $G \sim c^{2.3}$, and measured, $G \sim c^{2.4}$, plateau modulus scaling at the terminal relaxation time are in excellent agreement. A power-law viscoelastic “plateau” region is observed to persist to frequencies of at least 10^5 s^{-1} , thereby extending knowledge of polymer solution dynamics by nearly 3 decades of frequency. Interestingly, the high-frequency shear modulus was found to scale as $G \sim c^{4.5}$, not as $G \sim c^{2.3}$.

Introduction

The use of colloidal sphere thermal or Brownian motion as an experimental probe of soft matter dynamics is gaining increasing interest.^{1–7} This primarily owes to using so-called microrheological techniques to probe the viscoelastic response of fluids through application of very small strains over a much wider frequency range than allowed by conventional mechanical rheometry techniques. Passive microrheological techniques monitor the thermal fluctuations of micron size probe particles with the dynamical properties of the suspending matrix being inferred from the temporal evolution of the probe particles’ mean-squared displacements, $\langle \Delta r^2(t) \rangle$. This thermal or Brownian particle motion is typically measured with light scattering or optical microscopy techniques.

The ability of microrheological techniques to extract the rheological parameters of complex fluids may however be limited due to (i) the presence of local heterogeneities in these complex systems, (ii) the possible perturbation of the local rheological properties brought about by the probe particles themselves (i.e., the formation of a depletion layer or a layer of strongly adsorbed polymer on the colloidal sphere), and (iii) the influence of longitudinal dynamical modes. The influence of matrix heterogeneities can be investigated via optical microscopy-based single and multiple particle tracking methods since the motion of individual particles will vary if heterogeneities are important.^{7–9} The influence of the particles on the matrix can be eliminated by cross-correlating the motion of two particles, thereby isolating the bulk dynamical properties from the local ones.⁷

Schnurr and co-workers and more recently Levine and Lubensky have discussed the effect of the longitudinal modes on Brownian motion.^{6,8,9} These authors provide an estimate for the characteristic frequency, below which the longitudinal modes may affect the extracted viscoelastic modulus (transverse modes) of a solvent swollen polymer network. This viscous coupling frequency, ω_c , is basically an estimate of the frequency above which solvent and network motions are coupled in a two-fluid model.^{6,8,9} If this characteristic frequency is lower than the lowest frequency probed in the diffusing wave spectroscopy measurements, then the network and solvent will remain coupled for the entire frequency range under investigation, and longitudinal modes should not significantly affect the observed thermal motion. For the poly(ethylene oxide) (PEO) solutions studied here an upper bound for this frequency is estimated to be on the order of 1 s^{-1} for a $1 \mu\text{m}$ diameter sphere undergoing thermal motion in a 10 wt % aqueous PEO solution. Since this is essentially the lowest frequency that is probed here, longitudinal modes should not play a significant role in the reported studies. The time scale below which inertial effects will influence the probe dynamics can also be determined quantitatively.^{6,8–10} This inertial time scale is on the order of 10^{-6} – 10^{-5} s for the polymer solutions and colloidal sphere sizes considered in this study.

Recently, microrheological techniques have been applied to wormlike micelle gels and solutions,^{10–12} associating polymer solutions,^{13–16} polymer gels,^{17,18} and triblock copolymer micellar solutions and soft crystals.¹⁹ These previous investigations indicate that a detailed study of spherical probe Brownian motion in simple flexible polymer solutions would provide an excellent means for interpreting Brownian motion in the more structurally complex systems—especially an investigation of the effect of polymer concentration on the observed Brownian motion. Although some flexible polymer solutions

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have been investigated in limited detail previously, these earlier studies have not considered a wide range of polymer concentrations and have essentially been used to demonstrate the microrheology approach (i.e., the agreement between the viscoelastic properties determined from microrheology and mechanical rheometry).^{1–7,20–22} This study reports a detailed investigation of colloidal sphere Brownian motion in aqueous poly(ethylene oxide) (PEO) solutions as a model flexible polymer system. Aqueous PEO solutions have been chosen primarily because it is very easy to disperse the required optical probes in these systems and that they behave as good solvent systems at room temperature. Therefore, the osmotic modulus for the system should be very high, thus diminishing the influence, if any, of concentration fluctuation induced longitudinal modes on the Brownian motion. Previous mechanical rheometry measurements indicate that aqueous PEO solutions exhibit the concentration, molecular weight, and temperature dependencies expected for polymer solutions under good solvent conditions.²³ Good solvent behavior has also been determined from static light scattering measurements.²⁴

It should be noted that the work reported here is distinctly different from the rich literature on tracer sphere diffusion in polymer solutions where the primary objective is the determination of the tracer sphere diffusion coefficient, D , via conventional dynamic light scattering techniques and thereby the zero shear viscosity of the polymer solution, η , via the Stokes–Einstein relationship $D = kT/6\pi\eta a$.^{25–35} These earlier investigations were focused on determining whether the zero shear viscosity determined from probe sphere diffusion measurements agreed with independently determined values. If the two independently measured zero shear viscosity values agreed with one another, the probe diffusion was said to satisfy the Stokes–Einstein relation. While some investigators have observed such agreement, a significant number have also observed positive deviations (larger spherical probe diffusivity than expected) as well as negative deviations (smaller spherical probe diffusivity than expected) from the Stokes–Einstein relation. It has been recently noted that one potential difficulty with these investigations is the fact that the zero shear viscosity was oftentimes determined from capillary viscometry where the shear rates can be quite large in reality, thereby potentially negating the validity of the comparison.²⁸ In contrast, the measurements of colloidal sphere Brownian motion in polymer solutions described here utilize diffusing wave spectroscopy to monitor the colloidal sphere motion for time scales ranging from 10^{-6} to a few seconds at very high spatial resolution. These measurements demonstrate the role played by solution elasticity at short times for sufficiently concentrated solutions as manifested by subdiffusive colloidal sphere motion as well as the long time diffusive motion extensively investigated before.^{25–35} This behavior can be described by a generalized Stokes–Einstein relation (GSER), $\tilde{D}(s) = kT/6\pi s \tilde{\eta}(s) a$, where \sim denotes a Laplace transformed quantity, s is the frequency, and $\tilde{\eta}(s)$ is the complex viscosity associated with viscoelastic fluids.³ It can be shown that colloidal sphere Brownian motion, as manifested by the mean-squared displacement, is directly proportional to the creep compliance, $J(t)$, when the GSER is satisfied:²¹

$$\langle \Delta r^2(t) \rangle = \frac{kT}{\pi a} J(t) \quad (1)$$

Therefore, agreement between the optically determined microrheological creep and mechanically measured creep indicates that the GSER is satisfied. Also, successful scaling of the measured mean-squared displacements with polymer solution dynamical behavior also indicates the validity of the GSER. This scaling is based on the predicted thermal motion of a colloidal sphere in a single relaxation time Maxwell fluid¹⁰

$$\langle \Delta r^2(t) \rangle = \frac{kT}{\pi a G} (t/\tau + 1) = \frac{kT}{\pi a} (t/\eta + 1/G) \quad (2)$$

where G is the plateau modulus and τ is the terminal relaxation time. Therefore, at long times the mean-squared displacement should scale with respect to the terminal relaxation time and plateau modulus. Both the agreement of microrheology and mechanical rheology as well as the above scaling are demonstrated here. In addition, the microrheological zero shear viscosity and plateau modulus are shown to exhibit the same concentration dependence found from mechanical rheometry studies of polymer–good solvent systems. Finally, a new high-frequency shear modulus concentration dependence is demonstrated for the first time to the best of the authors' knowledge.

Materials and Methods

Materials. Poly(ethylene oxide) (PEO, $M_w = 333\,000$ g/mol) was obtained from Polymer Source (Montreal, Quebec, Canada). Dust-free PEO aqueous solutions were prepared with deionized water that had been filtered through a $0.02\,\mu\text{m}$ syringe filter (Whatman-Anotop 25, Whatman, Scarborough, ME). Polystyrene latex spheres bearing sulfate surface groups ranging in size from 0.195 to $1.55\,\mu\text{m}$ in diameter were utilized as optical probes (Duke Scientific, Palo Alto, CA). The optical probes were dispersed in the PEO solutions at ~ 1 vol % to ensure the strong multiple scattering required for diffusing wave spectroscopy measurements. All of the samples were examined with optical microscopy to ensure that the optical probes were not aggregated prior to further investigation. The samples were maintained at $40\,^\circ\text{C}$ for 3 days and then transferred to flat-sided 2 and 10 mm thick spectrophotometric cells for diffusing wave spectroscopy measurements (Spectrocell, Orelan, PA).

Diffusing Wave Spectroscopy. Transmission mode diffusing wave spectroscopy in the point-point geometry (DWS) was utilized to monitor the mean-squared displacement of the polystyrene latex spheres.^{36,37} The beam from a diode pumped solid state (DPSS) Nd:YAG laser operating at a wavelength of $532\,\text{nm}$ in vacuo was incident upon a flat scattering cell, containing the polymer solution and polystyrene latex spheres. An ALV SI/SIPD photon detector (Langen, Germany) collected the multiply scattered light via a single mode optical fiber. To ensure the point–point geometry, the single mode optical fiber was coupled to a gradient refractive index (GRIN) lens with a very narrow angle of acceptance (Flextronics Photonics Wave Optics, Hillsboro, OR). The output from the ALV SI/SIPD photon detector was fed to an ALV fast digital correlator (Langen, Germany) operating in the cross-correlation mode. The measured intensity autocorrelation function was converted into the electric field autocorrelation function using the Siegert relationship.

The electric field autocorrelation function obtained from a DWS measurement can be related to the mean-squared displacement through³⁷

$$g_1(t) = \int_0^\infty P(s) \exp\left[-\frac{1}{3} k_0^2 \langle \Delta r^2(t) \rangle \frac{s}{J^*}\right] ds \quad (3)$$

where $g_1(t)$ is the electric field autocorrelation function, $P(s)$ is the path length distribution function which is determined by the experimental geometry, k_0 is the incident wave vector,

$\langle \Delta r^2(t) \rangle$ is the particle mean-squared displacement, and l^* is the distance over which light becomes completely randomized. The mean-squared displacement of the probe spheres was extracted pointwise from the electric field autocorrelation function from eq 2 via a bisection root searching algorithm for the case of the point-point transmission path length distribution function.³⁷ For the case of standard dynamic light scattering (i.e., single photon scattering) the length scale over which particle motion is probed can be adjusted by varying the scattering angle; in DWS the length scale over which the motion is probed is adjusted by varying the cell thickness L with thicker cells providing access to smaller time scales. Most importantly, owing to the multiple scattering nature of DWS, the technique is capable of resolving angstrom-scale particle motions and thereby much higher frequency dynamic processes than conventional dynamic light scattering.

Mechanical Rheometry. The polymer solution rheological properties were measured with a stress-controlled rheometer (DSR II, Rheometrics, Piscataway, NJ). A 40 mm cone and plate geometry was utilized for all the measurements. The sample temperature was kept fixed at 25 °C throughout the measurements. A custom-made vapor trap was used to minimize evaporation effects. Both the dynamic oscillatory and transient creep experiments were carried out using small stresses so that the samples were always well within the linear viscoelastic region where mechanical properties are independent of the applied stress. The linear viscoelastic region was determined for each polymer concentration from a stress sweep experiment.

Results and Discussion

The main objective of this experimental study was to probe both the high- and low-frequency dynamical behavior of aqueous PEO solutions over a wide concentration range via measurements of colloidal sphere Brownian motion with diffusing wave spectroscopy. The 333 000 g/mol PEO considered is estimated to have a radius of gyration, R_g , of ~ 36 nm and a hydrodynamic radius, R_H , of ~ 21 nm.²⁴ On the basis of the above estimate of R_g , the overlap concentration is expected to occur at ~ 0.3 wt %. Zero shear viscosity mechanical measurements indicate that the transition to the entangled regime occurs at a polymer concentration of 1.75 wt %. To study the behavior in a concentration range that ranges from the unentangled to the entangled regimes, eight aqueous PEO solutions were prepared in which the concentration was varied from 0.2 to 15 wt %.

Colloidal Sphere Brownian Motion in Aqueous PEO Solutions. The mean-squared displacement of 0.966 μm diameter polystyrene latex spheres in aqueous PEO solutions with concentrations ranging from 0.2 to 15 wt % is shown in Figure 1. The probe size is much larger than all relevant length scales present in the solutions (i.e., R_g and the correlation length ξ for the case of semidilute solutions which are defined as solutions whose concentrations are greater than the overlap concentration). The observed polystyrene latex sphere Brownian motion is intimately related to both the structure and dynamics of the suspending medium. A readily observable feature is the shift of mean-squared displacement time traces to longer times with increasing PEO concentrations (i.e., decreasing probe motion with increasing PEO concentration). This is expected as the solution viscosity and elasticity increase with increasing PEO concentration. While the polystyrene latex sphere mean-squared displacement for the three lowest PEO concentration solutions, 0.2, 0.5, and 1.0 wt %, are somewhat similar to that found for polystyrene latex spheres diffusing in water, they do exhibit slightly

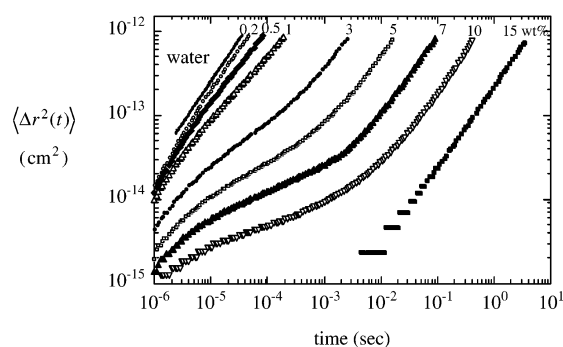


Figure 1. Colloidal sphere Brownian motion in aqueous PEO solutions. The mean-squared displacement of 0.966 μm diameter polystyrene spheres diffusing in aqueous PEO solutions of the following concentrations: (○) 0.2, (◆) 0.5, (△) 1, (●) 3, (□) 5, (▲) 7, (▽) 10, and (■) 15 wt % (increasing from left to right). Probe motion was measured by diffusing wave spectroscopy in 2 and 10 mm cells (except for the 15 wt % case for which only a 2 mm cell was considered). The probe sphere concentration was 1 vol %.

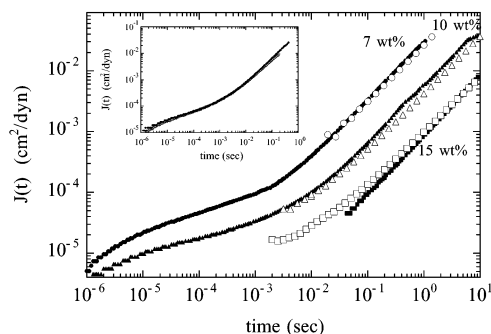


Figure 2. Comparing the microrheology and mechanical rheometry of aqueous PEO solutions. The creep compliance of three representative aqueous PEO solutions (7, 10, and 15 wt %) as measured by microrheology and mechanical rheometry is shown. Open symbols denote mechanical measurements, and closed symbols denote diffusing wave spectroscopy measurements. Unfortunately, the available mechanical rheometers did not offer enough sensitivity to accurately determine the creep compliance of less concentrated solutions. The sphere diameter used in the microrheology measurements is 0.966 μm in all cases. Inset: the microrheological creep compliance determined for five different sized polystyrene spheres undergoing Brownian motion in a 7 wt % aqueous PEO solution. The sphere diameters are as follows: (▽) 0.195, (●) 0.511, (△) 0.739, (■) 0.966, and (□) 1.55 μm .

subdiffusive behavior (especially the 1 wt % solution) that increases with increasing PEO concentration. A distinct elastic region in the mean-squared displacement is apparent for PEO concentrations exceeding the measured entanglement concentration of 1.75 wt % (i.e., concentrations ≥ 3 wt %). It should be noted that the data for the 15 wt % solution are only presented for a 2 mm cell as sufficient PEO of the same batch was not available to prepare a 10 mm sample.

Comparison of Microrheology and Mechanical Rheometry. To form a basis for comparison with the rheological parameters extracted from microrheology measurements, standard mechanical creep compliance measurements were conducted. A direct comparison of the creep compliances obtained from mechanical rheometry and microrheology for three representative PEO solutions (7, 10, and 15 wt %) demonstrates that the agreement between the two techniques is excellent (see Figure 2), thereby confirming the observations of previous investigators.^{1-4,20-22} This agreement confirms the

validity of the GSER and indicates that the polymer solution near the sphere surface must not be significantly altered as the no slip/continuum assumption inherent to the GSER must be satisfied. Therefore, there is a conclusive body of evidence that microrheology methods can successfully determine the bulk rheological properties of semidilute polymer solutions under good solvent conditions if the probe sphere is much larger than the solution correlation length ξ while failing for the case of correlation lengths that are relatively large in comparison with the probe size such as those present in DNA solutions.³⁸ These observations are in agreement with those found for tracer sphere diffusion in polymer solutions where the Stokes–Einstein relation is satisfied for the case of good solvent systems,^{26,32} albeit the current study indicates that this agreement holds over longer time (frequency) ranges. Interestingly, tracer sphere diffusion studies indicate that the Stokes–Einstein relation is not satisfied for Θ and marginal solvent systems.^{26,29} Future studies aim to determine whether this is also true for the microrheology measurements described here.

The close agreement between the creep compliance extracted from both microrheology and mechanical rheometry measurements indicates that any influence of longitudinal modes on Brownian motion in aqueous PEO solutions is minimal at most. This can be further demonstrated by examining the effect of polystyrene latex sphere size on the measured creep compliance. Variations in probe sphere size change the characteristic longitudinal mode frequency below which longitudinal modes are predicted to affect the extracted rheological parameters.^{6,8,9} If longitudinal modes do not play a significant role, the recovered creep compliance should be independent of sphere size. The Brownian motion of polystyrene latex spheres ranging in diameter from 0.195 to 1.55 μm in 7 wt % PEO solutions was investigated (Note: these polystyrene latex sphere sizes are much larger than the correlation length, ξ , of the solution, which is on the order of a few nanometers.) The measured creep compliance is shown to be independent of polystyrene latex sphere size in the inset of Figure 2, also confirming the observations of others.^{15,22} These observations demonstrate that the Stokes–Einstein relationship is obeyed, the investigated polystyrene latex sphere size range is insensitive to the underlying microstructure of the PEO solutions, and longitudinal modes do not significantly affect colloidal sphere Brownian motion in aqueous PEO solutions.

Microrheology of Aqueous PEO Solutions from Colloidal Sphere Brownian Motion. The most straightforward viscoelastic parameter to determine from the measured mean-squared displacements is the zero shear viscosity. The zero shear viscosity, η , is simply determined from the slope, $kT\pi\eta a$, of the long time diffusive region of the mean-squared displacement. The measured microrheological zero shear viscosities are shown in Figure 3. It is readily apparent that at sufficiently large concentrations a power law regime exists with $\eta \sim c^{4.7}$. This observation is in excellent agreement with recent mechanical measurements of aqueous PEO solutions that yielded $\eta \sim c^{4.8,23}$ This is also in good agreement with the zero shear viscosity of polystyrene–toluene solutions,³⁹ $\eta \sim c^{4.55}$, and polybutadiene–phenyloctane solutions,⁴⁰ $\eta \sim c^{4.7}$, thereby confirming the good solvent character of the PEO–water system. These observations, along with the above-noted

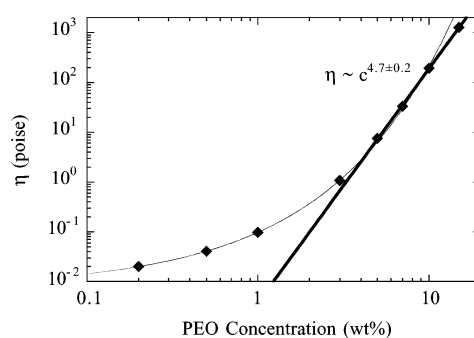


Figure 3. Aqueous PEO solution viscosity determined from colloidal sphere Brownian motion. The viscosity was determined from the long time or diffusive regime of the mean-squared displacement measurements (see text). The observed concentration scaling, $\eta \sim c^{4.7}$, is essentially that found recently via mechanical rheometry measurements, $\eta \sim c^{4.8,23}$. The exponent of 4.7 is larger than the predicted value of 3.9.⁴⁴ The curve corresponds to a stretched exponential proposed by Phillies and co-workers.^{41–43}

strong correspondence between microrheological and mechanical measurements of the creep compliance, indicate that the Stokes–Einstein relationship is satisfied for colloidal spheres diffusing in aqueous PEO solutions. The curve in Figure 3 corresponds to the stretched exponential fit of the zero shear viscosity concentration dependence proposed by Phillies and Peczak.⁴¹ The near tangency of the high-concentration power law and the stretched exponential representation denotes the location of the “solution”-like to “melt”-like transition proposed by Phillies and co-workers.^{42,43} The reptation description of polymer solution dynamics would attribute the observed strong viscosity concentration dependence to the onset of entanglement or topological effects.^{44,45} The measured zero shear viscosity concentration dependence, $\eta \sim c^{4.7}$, does not correspond with the predicted scaling $\eta \sim c^{3.9}$ of the reptation or tube model of polymer–good solvent dynamics.⁴⁴ However, it should be noted that some studies have found essentially this predicted scaling, a classic example being that of Adam and Delsanti, $\eta \sim c^{4.1,46}$

The determination of the terminal relaxation time or plateau modulus is more problematic. For the case of a single relaxation time Maxwell fluid the latter quantity is readily discerned from the plateau of the mean-squared displacement as apparent in eq 2. Unfortunately, there is not an observable distinct plateau in any of the mean-squared displacement time traces presented in Figure 1, thereby negating any simple determination of this quantity. However, further examination of eq 2 indicates that the intercept of the extrapolation of the elastic plateau region with the extrapolation of the diffusive (or viscous) region occurs at the terminal relaxation time for the case of a single relaxation time Maxwell fluid. As shown in Figure 4, analogous extrapolations of the viscoelastic and diffusive regions present in the measured mean-squared displacements can also determine a terminal relaxation time for the aqueous PEO solutions under study. The viscoelastic region is characterized by subdiffusive behavior with $\langle \Delta r^2(t) \rangle \sim t^\alpha$, where $\alpha = 0.25, 0.31, 0.40, 0.52, 0.75$, and 0.85 for 10, 7, 5, 3, 1, and 0.5 wt % aqueous PEO solutions, respectively. The decreasing value of α with increasing polymer concentration is indicative of the concomitant increase in elasticity. The slow increase in the mean-squared displacement in the viscoelastic

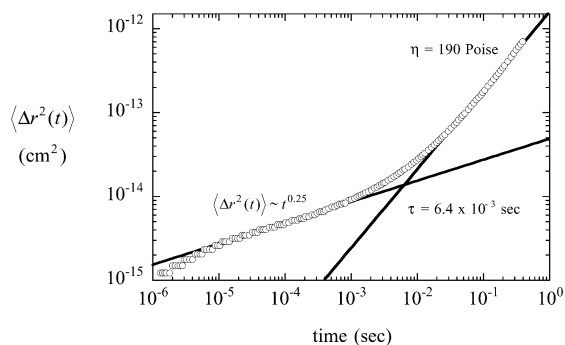


Figure 4. Determining viscoelastic parameters from colloidal sphere Brownian motion. The terminal relaxation time is estimated from the intercept of the diffusive regime and viscoelastic regime fits as shown. The method is exact for the case of a single relaxation time Maxwell fluid.¹⁰ In this case, a 10 wt % aqueous PEO solution, the viscoelastic regime exhibited time scaling of $t^{0.25}$. The exponent of the viscoelastic regime was observed to decrease with increasing concentration, thereby reflecting the increasing role of elasticity with increasing polymer concentration.

regime indicates that the stress relaxation modulus is slowly decreasing during this time period. This slow, subdiffusive increase in the mean-squared displacement is consistent with recent mechanical measurements of the creep compliance of aqueous PEO solutions.²³ This is a result of the multiple relaxation modes operating in the reptation region. The current study indicates that the degree of temporal variation in the “plateau” modulus increases with decreasing concentration as also observed in the above referenced creep compliance study²³ and in the viscoelastic spectra for polybutadiene–phenyloctane solutions reported by Colby and co-workers.⁴⁰ It should be noted that the viscoelastic regime is shown to persist up to frequencies of 10^5 s^{-1} in the current study—a gain of nearly 3 decades in frequency space owing to the use of diffusing wave spectroscopy. The nonexistence of a distinct plateau region may primarily be a result of the decreasing strength of chain confinement with decreasing concentration, thereby enhancing the effects of nonreptation stress relaxation mechanisms such as constraint release and tube length fluctuations.

An examination of the mean-squared displacement time traces in Figure 1 indicates that the temporal extent of the viscoelastic regime, an indication of the terminal relaxation time, increases with increasing polymer concentration. The concentration dependence of the graphically determined terminal relaxation times shown in Figure 5 more quantitatively supports this observation. One should also note the ability of diffusing wave spectroscopy measurements of colloidal sphere Brownian motion to easily access very small terminal relaxation times. Analogous to the previously considered zero shear viscosity concentration dependence (see Figure 3), there is a distinct high concentration power law behavior $\tau \sim c^{2.3}$ that deviates from the tube model prediction of $\tau \sim c^{1.6}$.⁴⁴ This deviation in terminal relaxation time concentration dependence essentially accounts for all of the observed deviation in the zero shear viscosity concentration dependence as the plateau modulus, G , concentration dependence derived from the experimentally determined zero shear viscosity and terminal relaxation time concentration dependence, $G \sim \eta/\tau \sim c^{2.4}$, is essentially the predicted concentration scaling $G \sim c^{2.3}$.⁴⁴ This correspondence is reassuring in that the plateau

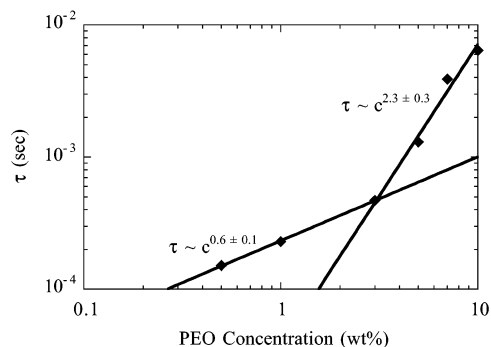


Figure 5. Aqueous PEO solution terminal relaxation times determined from colloidal sphere Brownian motion. The microrheologically determined terminal relaxation times, τ , exhibit two regimes—entangled and unentangled solutions. The observed entangled solution concentration dependence, $\tau \sim c^{2.3}$, yields a larger exponent than the predicted value of 1.6.⁴⁴ The observed concentration dependence of the terminal relaxation time essentially accounts for the increased viscosity concentration dependence also observed.

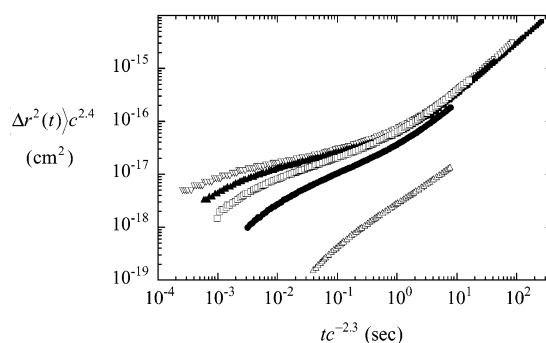


Figure 6. Long time scaling of colloidal sphere Brownian motion in entangled polymer solutions. The mean-squared displacement of $0.966 \mu\text{m}$ polystyrene spheres in aqueous PEO solutions is scaled with respect to the measured terminal time concentration dependence and the predicted plateau modulus concentration dependence ($G \sim \eta/\tau \sim c^{2.4}$, see text). The aqueous PEO solution concentrations are as follows: (Δ) 1, (\bullet) 3, (\square) 5, (\blacktriangle) 7, (∇) 10, and (\blacksquare) 15 wt %. Note the strong deviation of the 1 wt % solution from the scaling found for the others, thereby indicating its unentangled nature.

modulus concentration dependence is derived from polymer solution microstructural arguments that are well understood experimentally and theoretically. The terminal relaxation time concentration dependence discrepancy indicates that our current understanding of the friction/hydrodynamic interaction physics underlying polymer solution dynamics is still lacking. As noted in the discussion of the zero shear viscosity concentration dependence, this might owe to the influence of tube length fluctuations and constraint release.

Upon examination of eq 2, it is apparent that the long time colloidal particle mean-squared displacement can be scaled with respect to the terminal relaxation time and the plateau modulus.¹⁰ Already it has been demonstrated that the terminal relaxation time scales as $\tau \sim c^{2.3}$, while the plateau modulus scaling at the terminal relaxation time can be found from $G \sim \eta/\tau \sim c^{2.4}$. Therefore, a plot of $\langle \Delta r^2(t) \rangle c^{2.4}$ vs $tc^{-2.3}$ should yield the correct scaling at long times as is confirmed in Figure 6 for solutions concentrations ≥ 5 wt % with the 3 wt % solution exhibiting nearly entangled behavior. In fact, the predicted entanglement concentration, c_e , is $c_e = c^* [N_e(1)]^{0.76}$, where $N_e(1)$, the number of monomers in an entanglement length in the melt, is 15 for PEO and

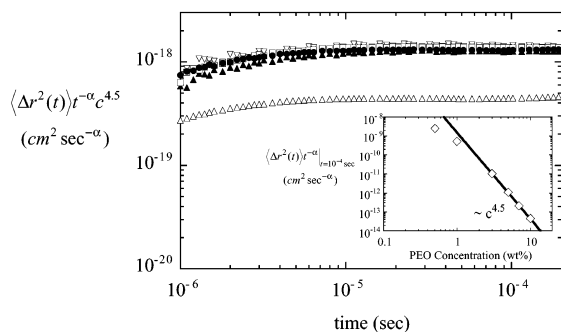


Figure 7. Short time scaling of colloidal sphere Brownian motion in entangled polymer solutions. The mean-squared displacement of 0.966 μm diameter polystyrene spheres in aqueous PEO solutions is scaled with respect to the measured viscoelastic region time dependence and the concentration dependence of this rescaled viscoelastic regime (see text). The lack of an apparent concentration dependent entanglement onset time indicates the persistence of inertial effects. The aqueous PEO solution concentrations are as follows: (Δ) 1, (\bullet) 3, (\square) 5, (\blacktriangle) 7, and (∇) 10 wt %. Inset: the concentration dependence of the temporally isolated viscoelastic region, $\langle \Delta r^2(t) \rangle t^{-\alpha}|_{t=10^{-4} \text{ s}} \sim c^{4.5}$.

therefore $c_e \approx 2.3$ wt %, close to the measured value of 1.75 wt %, corroborating the observations in Figure 6.⁴⁴ The lowest concentration considered in Figure 6, 1 wt %, definitely corresponds to an unentangled polymer solution, leading to the failure of the rescaling. The successful scaling of the higher concentration solutions indicates that the zero shear viscosity and terminal relaxation time concentration dependence determined from colloidal sphere thermal motion measurements provides a good description of the aqueous PEO solution microrheology.

Examination of the very short time dynamics are a bit more problematic in that the influence of inertial effects on colloidal sphere Brownian motion may obscure the location of the entanglement time as this time is much shorter than the terminal relaxation time.⁴⁴ This is most easily illustrated by isolating the viscoelastic region via multiplying the mean-squared displacement by $t^{-\alpha}$, $\langle \Delta r^2(t) \rangle t^{-\alpha}$, which yields a long-lived plateau region indicative of the viscoelastic regime lifetime. The concentration dependence of $\langle \Delta r^2(t) \rangle t^{-\alpha}$ in the plateau region can then be determined, $\langle \Delta r^2(t) \rangle t^{-\alpha}|_{t=10^{-4} \text{ s}} \sim c^{4.5}$ (see inset to Figure 7). Finally, rescaling the mean-squared displacement with respect to both time and concentration successfully collapses short time polystyrene latex sphere Brownian motion in entangled polymer solutions onto a master curve (see Figure 7). This scaling implies that the high-frequency shear modulus concentration dependence is $c^{4.5}$, not $c^{2.3}$, thereby indicating demonstrably different physics than expected. To the authors' best knowledge, this is the first time such a high-frequency shear modulus concentration scaling has been observed. The onset of the viscoelastic regime appears to be essentially independent of polymer concentration, which leads one to believe that the onset of entanglements is somewhat obscured by persistent inertial effects. While decreasing sphere size would reduce the inertial effects, sufficient sphere size must be maintained such that the polymer solution is still essentially a continuum on the length scale of the sphere. At most, one might access one more decade in time by decreasing the sphere size from 1 to 0.1 μm diameter.

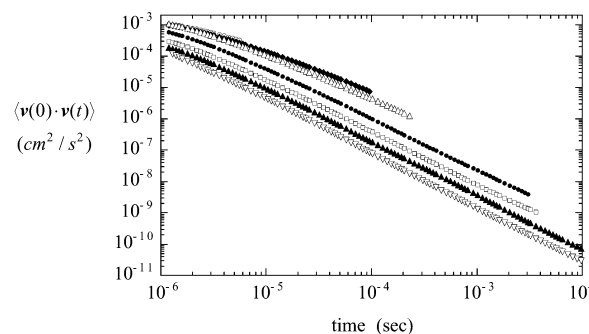


Figure 8. Velocity autocorrelation functions of colloidal Brownian motion in aqueous PEO solutions. The velocity autocorrelation function of 0.966 μm diameter polystyrene spheres diffusing in aqueous PEO solutions of the following concentrations: (\circ) 0.2, (\blacklozenge) 0.5, (Δ) 1, (\bullet) 3, (\square) 5, (\blacktriangle) 7, and (∇) 10 (increasing from top to bottom). The velocity autocorrelation functions were calculated from a mean-squared displacement fit of the data in Figure 1 and the use of eq 4.

Probe Velocity Autocorrelation Functions. A more detailed understanding of probe motion in an entangled polymer solution can be obtained through extraction of the probe velocity autocorrelation function, $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$. The velocity autocorrelation function is calculated from the following expression

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = -\frac{dD(t)}{dt} = -\frac{d}{dt} \frac{\langle \Delta r^2(t) \rangle}{6t} \quad (4)$$

where the experimental mean-squared displacement data have been locally smoothed for presentation purposes (i.e., to account for the correlator resolution). Qualitatively, the velocity autocorrelation function can be associated with the dissipation of the microsphere motion due to its interaction with the polymer mesh. The measured velocity autocorrelation functions exhibit long time tails that decay algebraically (i.e., $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \approx t^{-\alpha}$), as shown in Figure 8. Once again, there is a distinct change in behavior with the onset of entanglements (i.e., concentrations ≥ 3 wt %). Spherical colloidal particles diffusing in purely viscous fluids exhibit velocity autocorrelation functions that decay algebraically as $t^{-3/2}$. This nonexponential decay is simply a result of hydrodynamics—not viscoelasticity.^{47–49} This hydrodynamic memory is a result of the vorticity engendered by the particle motion, thereby enhancing the persistence of the particle's motion. Spherical colloidal particles diffusing in complex fluids are potentially subject to substantially stronger memory effects, owing to the viscoelastic nature of the suspending medium and substantially longer terminal relaxation times. It is apparent that the magnitude of α increases with increasing solution elasticity (i.e., polymer concentration) with $|\alpha|$ increasing from 1.61 to 1.73 as the polymer concentration increases from 3 to 10 wt %. Therefore, the velocity autocorrelation decay rate is greater than that found for a purely viscous fluid. The increasingly elastic nature of the suspending medium acts directly against the probe motion, thereby increasing the rate at which the probe motion is decorrelated in comparison with a simple viscous fluid. Xu and co-workers observed a similar value of $|\alpha| = 1.75$ for the long-time tail of probes diffusing in actin solutions.²¹ Since the velocity autocorrelation function of a colloidal sphere diffusing in a single relaxation time Maxwell fluid exhibits a long-time tail decaying as $|\alpha| = 2$,^{10,50} it is apparent that the

decay rates found here, $1.5 \leq |\alpha| \leq 2$, are indicative of the multiple relaxation processes underlying the dynamical properties of polymer solutions. For instance, colloidal sphere Brownian motion in CTAB/KBr wormlike micelles conforms very well to Maxwellian dynamics,¹⁰ and the corresponding velocity autocorrelation functions exhibit $|\alpha|$ values of ~ 1.95 —nearly perfectly Maxwellian.⁵⁰

Summary

Colloidal sphere Brownian motion in aqueous poly(ethylene oxide) solutions ranging in concentration from 0.2 to 15 wt % was shown to satisfy the generalized Stokes–Einstein relation that relates the particle mean-squared displacement to the polymer solution shear modulus as the microrheological creep compliances inferred from the colloidal sphere Brownian motion were found to agree with those found by mechanical rheometry. In addition, the creep compliance was found to be independent of polystyrene latex sphere size for diameters ranging from 0.195 to 1.55 μm . Therefore, microrheology can be used to determine the viscoelastic moduli of good solvent polymer solutions when the probe size is much larger than the solution correlation length. The viscoelastic region was observed to persist to frequencies of at least 10^5 s^{-1} , thereby extending knowledge of polymer solution dynamics by nearly 3 decades of frequency. Interestingly, the high-frequency shear modulus was found to scale as $c^{4.5}$. An examination of the long time dynamics yielded the concentration dependence of the zero shear viscosity, terminal relaxation time, and by extension the plateau modulus at the terminal relaxation time. The zero shear viscosity concentration dependence is similar to that found by others from mechanical rheometry measurements on polymer–good solvent solutions and is larger than the tube model prediction. The entire deviation between the predicted and measured zero shear viscosity concentration dependence is essentially accounted for by the observed terminal relaxation time concentration dependence discrepancy. This failure is indicative of the inability of current theories to properly describe the friction/hydrodynamic interaction physics underlying polymer solution dynamics. The measured colloidal sphere velocity autocorrelation functions in entangled polymer solutions exhibited long time algebraic tails whose decay rates increased with increasing concentration and were more rapid than those expected for colloidal sphere Brownian motion in viscous liquids, owing to the increasing elasticity of the polymer solutions. The observed decay rates were intermediate to those expected for a simple viscous fluid and a single relaxation time Maxwell fluid, thereby illustrating the fact that multiple relaxation processes underlie the observed colloidal sphere Brownian motion.

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