AN IMPROVED THEORY OF POLYMER DYNAMICS IN SOLUTION: PROBE DIFFUSION AND VISCOSITY

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SUMMARY: A more complete coupling/scaling theory of polymer dynamics in solution is presented and applied to explain several anomalous properties of probe diffusion and viscosity. Similar properties are found in totally physically and chemically different systems. These similarities strongly support the need of a general approach to these problems as given here.

Introduction

The dynamics of polymers in solutions has been a subject of considerable interest to researchers in the past two decades. In nondilute solutions of high molecular weight polymers, there are a number of problems, which cannot be solved by the model based on reptation motion of polymer chains. These problems summarized more fully in Ref.1 and references cited therein. Here, we consider only the following specific problems[1]

(a) The self-diffusion coefficient follows the stretched-exponential concentration, c, dependence of Phillies[1-3], $D = D_o \exp(-\alpha c^u M^\gamma)$.

(b) The solution viscosity, η, is described well by $\eta = \eta_o \exp(\alpha' c^{u'} M^{\gamma'})$.

(c) The field autocorrelation function, $g^{(1)}(t)$, obtained by quasielastic light scattering spectroscopy (QELSS) fits well to the stretched exponential function $g^{(1)}(t) = \exp[-(t/\tau)^\beta]$, where $0 \leq \beta < 1$.

(d) The time τ in (c) has also a stretched exponential concentration dependence like D in (a) and the dependence, $\tau \propto q^{-2/\beta}$, on the scattering vector q.

(e) Recently, Streletzky and Phillies[2,3] (SP) studied the diffusion of monodisperse spheres in aqueous 1 MDa hydroxypropylcellulose (HPC) by QELSS. They found the form $g^{(1)}(t)=A_f \exp[-(t/\tau_f)^{\beta_f}]+(1-A_f)\exp[-(t/\tau_s)^{\beta_s}]$, henceforth referred to as Eq(e), gives a better fit to the data than $g^{(1)}(t) = A_o \exp[-(t/\tau)^\beta]$ in (c). Here A_f, the amplitude of the "fast mode", lies within the bounds, $0 \leq A_f \leq 1$. We add a subscript s to the quantities τ and β of the "slow mode" of SP in order to avoid confusion with notations used here.

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In 1996, based on the coupling model, Phillies and I[1)] published a coupling/scaling model of polymer dynamics in solution to explain these problems successfully. This model starts with a $g^{(1)}(t)$ in (*c*), which is now superseded by (*e*). The ultimate purpose of this paper is to improve the extant theory[1)] of polymer dynamics in solution and its application to probe diffusion experiment[1-3)], to be consistent with the more recently found experimental fact (*e*)[2,3)]. Nevertheless, we give also a brief review of the properties of polymer solutions that are observed also in several seemingly unrelated systems by QELSS. The striking similarity of the observed properties, particularly the anomalous ones, in apparently totally unrelated systems is an important fact that indicates a general approach to these problems is not only preferable but also necessary, and bolsters the significance of the coupling model approach[4-8)]. In this work, we restrict the discussion to properties (*c*)-(*e*) that are shared by other systems.

An Improved Theory

Properties (*c*) and (*e*), foremost for the purpose of this work, for spherical probe diffusion in aqueous HPC is discussed first. For HPC of 60, 100, 300 and 1000 kDa, Phillies, et al[1)]. successfully fitted the data by $g^{(1)}(t) = A_o \exp[-(t/\tau)^{\beta}]$. Later, studying 1 MDa HPC more carefully, SP found that the form given by Eq.(*e*) due to Nyström, et al.[9-11)] gives a superior fit to the data. Nyström and coworkers actually proposed Eq(*e*) with β_f=1 in the form of $g^{(1)}(t)=A_f\exp[-(t/\tau_f)]+(1-A_f)\exp[-(t/\tau_s)^{\beta_s}]$, and found it applicable to various hydrophobically associating water-soluble polymers. This form, henceforth referred to as Eq(*N*), is motivated by the coupling model[4-8)] results for a *single* mode of relaxation or diffusion having non-cooperative motion with correlation function $\phi(t)$ described by $\phi(t)=\exp[-(t/\tau_o)]$ at short times $t<t_c$ (Eq.1) and slowed-down cooperative motion with $\phi(t)$ described by $\phi(t)=\exp[-(t/\tau^*)^{1-n}]$ for $t>t_c$ (Eq.2). The crossover time t_c depends on the interaction strength. The origin of the coupling model (CM) is the nonlinear Hamiltonian dynamics (chaos) due to anharmonic potentials of interaction and is supported by results of simple models[6)]. The most successful result of the CM is the relation $\tau^* = [t_c^{-n}\tau_o]^{1/(1-n)}$ (Eq.3), which connects the difficult to be understood τ, because of many-body effects of cooperative relaxation, to the transparent τ_o, which is devoid of such effects. It is worthwhile to emphasize that the CM as stated applies to the diffusion correlation function $\phi(t)$ and not immediately to $g^{(1)}(t)$. The steps that lead us from $\phi(t)$ to $g^{(1)}(t)$ was given in Refs.7 and 8. Here, we briefly describe them with slight change of notations to suit the present context. The complex frequency dependent diffusion constant $D(\omega)=(c_o^2/6)\mathrm{Re}(i\omega/\phi^*(\omega))$ is obtained from the Fourier transform of $\phi(t)$ defined by $\phi^*(\omega)=i\omega\int_0^\infty \phi(t)e^{-i\omega t}dt$. The length c_0 can be the radius R of the spherical probes. From known properties of the Fourier transform of $\exp[-(t/\tau_o)]$ and $\exp[-(t/\tau^*)^{1-n}]$, we can immediately deduce the following conclusions. At high frequencies satisfying $\omega >> (t_c)^{-1}$, $D(\omega)=D_S=c_o^2/6\tau_o$, the short time diffusion constant (Regime I). There is an intermediate frequency region approximately defined by $(t_c)^{-1}\leq\omega\leq(\langle\tau^*\rangle)^{-1}$ within which $D(\omega)\propto\omega^n$ (Regime II). At low frequencies such that $\omega<<(\langle\tau^*\rangle)^{-1}$, $D(\omega)=D_L$, the long time diffusion constant (Regime III). Here $\langle\tau^*\rangle$ is the average correlation time of the stretched exponential function, $\langle\tau^*\rangle=\int_0^\infty \exp-(t/\tau^*)^{1-n}dt=[\Gamma(1/(1-n))/(1-n)]\tau^*$ where Γ is the gamma function. The real part of this generalized complex diffusion constant continues to be related to the velocity autocorrelation function by a Fourier transform $\mathrm{Re}\,D(\omega)=\int_0^\infty \cos\omega t\langle v(t)v(0)\rangle dt$. It has been shown that the time-dependent mean-squared displacement can be calculated from $D(\omega)$ according to $\langle\Delta r^2(t)\rangle=(12/\pi)\int_0^\infty \mathrm{Re}\,D(\omega)(1-\cos\omega t)\omega^{-2}d\omega$. The results are given by $\langle r^2(t)\rangle=c_o^2(t/\tau_o)\equiv 6D_S t$, for $t<t_c$ (Regime I, from Eq.1), $\langle r^2(t)\rangle=c_o^2(t/\tau^*)^{1-n}$, for $t_c<t<<\langle\tau^*\rangle$ (Regime II, from Eq.2), and $\langle r^2(t)\rangle=c_o^2 t/\langle\tau^*\rangle\equiv 6D_L t$, for $t\geq\langle\tau^*\rangle$ (Regime III, also from Eq.2). At the start of Regime III, i.e. when t is equal to $\langle\tau^*\rangle$, $\langle r^2(\langle\tau\rangle)\rangle=c_o^2$ and $D_L=\langle r^2(\langle\tau^*\rangle)\rangle/6\langle\tau^*\rangle$. We have also $D_S=\langle r^2(\langle\tau^*\rangle)\rangle/6\tau_o$. Thus the length c_0 is fixed by the value of $\langle\Delta r^2(t)\rangle$ at $t=\langle\tau^*\rangle$. These results for $\langle\Delta r^2(t)\rangle$ are not exact. More quantitatively exact results obtained by numerical procedure can be found in Refs.7 and 8.

The self intermediate scattering function $f(q,t)=\exp[-q^2\langle\Delta r^2(t)\rangle/6]$ can be identified with $g^{(1)}(t)$ if the light scattering is incoherent. Hence, from $\langle\Delta r^2(t)\rangle$ we obtain,

($t<t_c$, Regime I, from Eq.1): $g^{(1)}(t)=\exp[-D_S q^2 t]\equiv\exp[-(c_o^2/6)q^2 t/\tau_o]\equiv\exp[-(t/\hat{\tau}_o)]$,
where $\hat{\tau}_o=6c_o^{-2}q^{-2}\tau_o$.

($t_c<t<<\langle\tau^*\rangle$, Regime II, from Eq.2): $g^{(1)}(t)=\exp[-(c_o^2/6)q^2(t/\tau^*)^{1-n}]\equiv\exp[-(t/\tau)^{1-n}]$,
where $\tau=[t_c^{-n}6c_o^{-2}q^{-2}\tau_o]^{1/(1-n)}\propto q^{-2/(1-n)}$.

($t\geq\langle\tau^*\rangle$, Regime III, also from Eq.2): $g^{(1)}(t)=\exp(-t/\tau_L)$, where $\tau_L=D_L^{-1}q^{-2}$.

The following figure shows the QELSS data of SP[2,3] for 189 nm diameter spheres in 1MDa HPC solution at various concentrations.

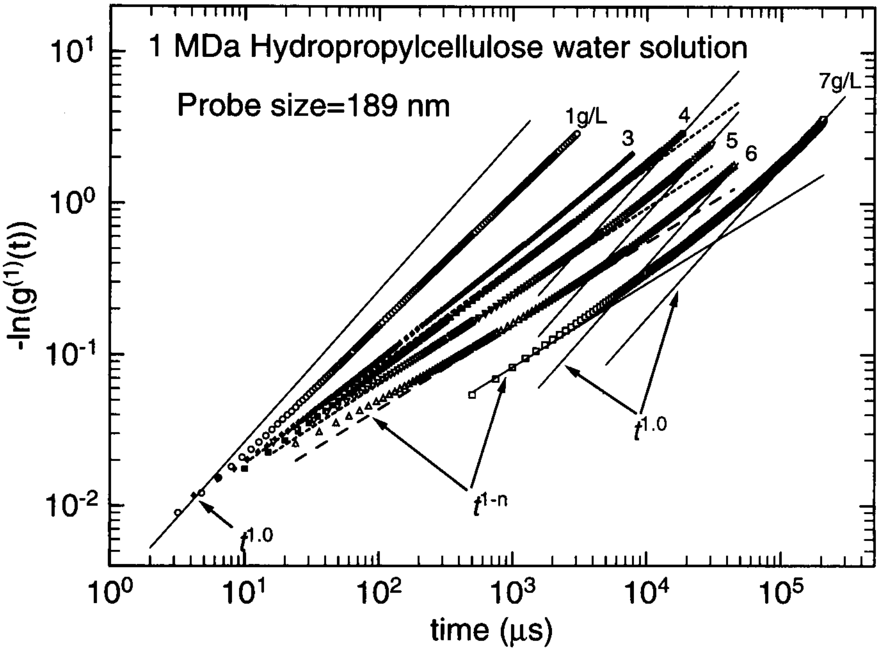

Fig.1: Plot of $-\ln(g^{(1)}(t))$ versus $\log t$ of 189 nm probe in aqueous HPC solutions (after Ref.2).

In this plot of $-\ln(g^{(1)}(t))$ versus $\log t$, Regime II and Regime III correspond to the regions where the data are proportional to t^{1-n} and $t^{1.0}$ respectively. The crossover from Regime II to Regime III is indicated by the neighborhood where the two straight lines intersect. The correlator used by SP to collect data cannot be extended to times much shorter than 10 μs. Although there is some weak indication that there is a crossover from Regime I to Regime II at a $t_c \approx 10$ μs, this result must be considered as tentative at this time. The results shown in Fig.1 are typical of spheres with diameter larger than the radius of gyration, R_g, of the polymer. The 1MDa polymer has $2R_g$=210 nm. In the original version of the theory[1], the decay $g^{(1)}(t)=\exp[-(t/\tau)^{1-n}]$ in Regime II is emphasized, neglecting the other two regimes. Also, at the time of writing down the theory, most the data are fitted well by $g^{(1)}(t)=\exp[-(t/\tau)^{1-n}]$. The decay in regime I is usually negligible because the condition $t_c \ll \hat{\tau}_o$ holds in the studies[1-3]. Regime III where $g^{(1)}(t) = \exp(-t/\tau_L)$ was subsequently found by SP[2]. The neglect of Regime III, the tail end of the decay of $g^{(1)}(t)$, does not affect the validity of the results in Ref.1 when applied to the decay $g^{(1)}(t)=\exp[-(t/\tau)^{1-n}]$ in Regime II. These include the dispersion $\exp[-(t/\tau)^{1-n}]$, the $q^{-2/(1-n)}$-dependence of τ, and the results of the coupling/scaling analysis of the concentration dependence of the probe diffusion coefficient D and η (i.e., Eqs.27 and 36 in Ref.1). It is important to note that the decay $g^{(1)}(t)=\exp[-(t/\tau)^{1-n}]$ in Regime II and $g^{(1)}(t)=\exp(-t/\tau_L)$ in Regime III comes from one and the same diffusion correlation function, $\phi(t)=\exp[-(t/\tau^*)^{1-n}]$, for $t>t_c$ (Eq.2) of the CM. The quantitatively more exact solution to $g^{(1)}(t)$ shows the actual crossover from Regime II to Regime III is not sharp[7,8)] when n is large, a behavior which is shown by the data in Fig.1 from SP[2,3)] at higher concentrations of 6 and 7 g/L. This explains why SP can fit their $g^{(1)}(t)$ data of large probes with $g^{(1)}(t)=A_f\exp[-(t/\tau_f)^{\beta_f}]+(1-A_f)\exp[-(t/\tau_s)^{\beta_s}]$, which has the abundance of four parameters. The τ_f, β_f and τ_s in their equation for large probes are to be identified with respectively τ, $(1-n)$ and τ_L here. Their β for large probes is close to unity (see Table 1 of Ref.2), consistent with our $g^{(1)}(t)=\exp(-t/\tau_L)$. However, in spite of the good fit, one should not interpret $A_f\exp[-(t/\tau_f)^{\beta_f}]+(1-A_f)\exp[-(t/\tau_s)^{\beta_s}]$ as two separate modes. It is fine to apply the coupling/scaling analysis (i.e. Eq.27 of Ref.1) to the concentration dependence of τ_f in $A_f\exp[-(t/\tau_f)^{\beta_f}]$, but definitely not to τ in the "slow mode" $(1-A_f)\exp[-(t/\tau_s)^{\beta_s}]$ as SP did[2,3)] on data of large 189 and 455 nm probes in 1MDa HPC solutions. As expected, SP found that coupling/scaling result works for their "fast mode", i.e., β_c calculated from the concentration dependence of τ_f agrees with β_η calculated from the concentration c dependence of η, β_f from the time dependence, and β_q from the q-dependence, q^{-2/β_q} of τ_f. This is because β_c, β_η, β_f and β_q are all approximately equal to $(1-n)$: i.e., $\beta_c\approx\beta_\eta\approx\beta_f\approx\beta_q\approx(1-n)$ for the "fast mode" (see Table 1 in Ref.3). β_c, β_η, β_f and β_q all fall with increasing c. This trend is consistent with the CM expectation of an increase of the coupling parameter n with increasing c. In the spirit of the present improved theory, one should not applied the coupling/scaling analysis to the "slow mode" of SP. Therefore, it is unsurprising that β_c calculated[3)] from the "slow mode" does not agree with β_s and β_q. It is clear that $\beta_s=1$ from the time dependence of this "slow mode". From $\tau_L=[6q^{-2}\langle\tau^*\rangle/\langle r^2(\langle\tau^*\rangle)\rangle]$, τ_L is proportional to $(q^{-2}\tau)$. Whence, for the "slow mode" we have $\beta_q=1$, but β_c being the same as that of the "fast mode" is less than unity. The results of the "slow mode" of large probes are summarized as $1\cong\beta_s=\beta_q>\beta_c\approx\beta_\eta$, in agreement with experiment (see Table 1 in Ref.3). For small probes with diameter less than the hydrodynamic radius R_h, we agree with SP that the probe motion is coupled to the internal chain modes. The results of the previous and the current version of the coupling/scaling theory are obtained when a single mode dominates the diffusion of the probe. This is a good approximation for large probes with d comparable or larger than $2R_g$ when the terminal chain mode determines the probe diffusion, the self-diffusion and the viscosity. However, for small probe, the plurality of internal chain modes that determine its motion makes the results not immediately applicable. In the context of the SP analysis of $g^{(1)}(t)$ using $A_f\exp[-(t/\tau_f)^{\beta_f}]+(1-A_f)\exp[-(t/\tau_s)^{\beta_s}]$, the many internal modes with different length and time scales introduce a distribution of relaxation times into the time dependence of the "fast mode", which is the cause of β_f being smaller than unity and even less than β_η. The modes within the "fast modes" are uncoupled and hence their coupling parameters are all zero. For these reasons, one should not apply the coupling/scaling analysis to the "fast mode" of small probes to obtain β_c. It is unsurprising that the coupling/scaling analysis fails as found by SP (see Table 1 in Ref.3). The "slow mode" is determined principally by an internal chain mode with length-scale compatible with the diameter of the small probe. This internal chain mode can have a nonzero coupling parameter n_s and this explain why the coupling/scaling analysis works and $\beta_c \approx \beta_f \approx \beta_q \approx (1-n_s)$ (see Table 1 in Ref.3). However, since n_s is less than coupling parameter of the terminal mode, n, the result $\beta_c \approx \beta_f \approx \beta_q \geq \beta_\eta$ follows, as also found experimentally (see Table 1 in Ref.3).

Generality of the Properties

Some anomalous properties (*a*)-(*e*) observed in polymer solutions by QELSS are found in several unrelated systems. Here, we give a brief summary of these findings.

(i) Pulse field gradient and QELSS studies of aqueous solutions of a hydrophobically associating polymer (hydrophobically end-capped poly(oxyethylene)urethane)9) have found the self-diffusion coefficient has the stretched exponential concentration dependence of (*a*), the time dependence of (*e*), $g^{(1)}(t)=A_f\exp[-(t/\tau_f)]+(1-A_f)\exp[-(t/\tau_s)^{\beta_s}]$, and the q-dependence of (*d*), $\tau_S \propto q^{-2/\beta}$. Similar results are found also in aqueous solutions of associating diblock and triblock copolymer10,11), aqueous mixtures of oppositely charged and hydrophobically modified polyelectrolytes and other systems.

(ii) QELSS study of thermoreversible gelling solutions12), and in particular the 3% and 7% aqueous solutions of gelatin13) has observed at 45°C a fast exponential decay at short times less than t_c~50 μsec and the t-dependence of (*c*), $g^{(1)}(t)=\exp[-(t/\tau)^{\beta}]$, at longer times with the q-dependence of (*d*), $\tau \propto q^{-2/\beta}$.

(iii) QELSS and neutron spin-echo measurements in dense microemulsion$^{14)}$ (water, oil and surfactant) have observed the t-dependence of (c), $g^{(1)}(t)=\exp[-(t/\tau)^{\beta}]$, with the q-dependence of (d), $\tau \propto q^{-2/\beta}$.

(iv) QELSS study of interpenetrated polymer cluster solution$^{15,16)}$ have found a fast exponential decay at short times, and the t-dependence of (c), $g^{(1)}(t)=\exp[-(t/\tau)^{\beta}]$, at longer times with the q-dependence of (d), $\tau \propto q^{-2/\beta}$.

(v) QELSS measurements of concentrated suspensions of "hard-sphere" colloidal particles$^{17)}$ have found a fast exponential decay at short times, a crossover to $g^{(1)}(t)=\exp[-(t/\tau)^{\beta}]$ at t_c~1 msec with τ having the q-dependence of (d), $\tau \propto q^{-2/\beta}$, and another crossover at a longer time of the order of $\langle\tau\rangle$ to $g^{(1)}(t)=\exp(-t/\tau_L)$.

Conclusion

The improvement of the theory of dynamics of polymer in solutions brings it to a better agreement with the more recent experimental data of Streletzky and Phillies. The remarkably similar properties found in other unrelated systems show the effects are general and so is the explanation.Thus far, only the coupling model can explain these general properties.

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