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George D. J. Phillies
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Introduction

This volume presents a systematic analysis of experimental studies on the dynamics of polymers in solution. I cover not only classical methods, e.g., rheology, and more modern techniques, e.g., self-diffusion, optical probe diffusion, but also radically innovative methods not generally recognized as giving information on polymer dynamics, e.g., capillary zone electrophoresis. Actual knowledge comes from experiment. The intent is to allow the data to speak for themselves, not to force them into a particular theoretical model in which they do not fit; freed of the Procrustean bed of model-driven analysis, the data do speak, loudly and clearly.

The *Phenomenology* examines what we actually know about polymer motion in solution. The objective has been to include every significant physical property and experimental method, and what each method shows about polymer motion. The list of methods includes several that have not heretofore been widely recognized as revealing the dynamics of polymer solutions. Undoubtedly there are omissions and oversights, for which I apologize. The reader will note occasional discussions that speak to particular models, but experiment comes first, while comparison with various hypotheses is postponed.

The following dozen chapters demonstrate that the vast majority of measurements on polymer dynamics can be reduced to a very modest number of parameters. These parameters have simple relationships with underlying polymer properties such as polymer molecular weight. The relationships in turn speak to the validity of several possible models for polymer dynamics, models whose validity is also tested by a number of more qualitative observations on how polymers move in solution.

1.1 Plan of the work

What methods are treated here, and in which order are they presented? I begin by considering experiments based on applying forces directly to individual molecules and observing their resulting motions. I then turn to diffusive processes of single molecules or their parts, proceeding from the smallest to the largest mobile units: Solvent motion, segmental dynamics, dielectric relaxation, single-entire-chain diffusion, and optical probe diffusion are examined. In each of these processes, the motions of the object being studied are altered by the presence of other polymer molecules in solution, but each experimental technique corresponds to a single-object correlation function. Finally, experiments measuring collective effects are considered, including results on mutual diffusion and the dynamic structure factor, the polymer slow mode, zero-shear viscosity, and linear and nonlinear viscoelasticity. A short chapter summarizes what has been said. A concluding chapter of analysis and interpretation unifies earlier presentations. Several topics that lie apart from this general arrangement, notably chapters on light scattering and diffusion, and on properties of colloidal systems, are inserted at seemingly convenient places. The discussion of diffusion and methods of measuring it is sensibly placed before the chapters on diffusive properties. Colloidal dynamics are treated prior to considering the dynamic structure factor of polymer solutions. We turn now to short sketches of the later chapters.

We begin with two experimental methods, sedimentation and electrophoresis, that measure the driven motion of polymer chains and colloidal particles. In each method, an external force is applied directly to particular molecules in solution, and particle motion is observed. The forces are buoyancy and the Coulomb force. Light pressure (“optical tweezers”) has also been used to move particles; this method appears in Chapter 9. Chapter 2 presents phenomenology associated with sedimentation by polymers and sedimentation of particulates through polymer solutions. The sedimentation rate of polymers in homogeneous solution, and the sedimentation of particulate probes through polymer solutions, both depend on the polymer concentration and molecular weight and the size of the particulates.

Chapter 3 takes us from one of the oldest techniques for the study of polymer dynamics – sedimentation – to one of the newest – capillary electrophoresis. A primary theme of this chapter is the unity of behavior shown by the electrophoretic mobility over a wide range of concentrations and molecular weights of the polymeric support media. As an experimental method in biochemistry, electrophoresis is almost as old as sedimentation. Discussions of electrophoresis center on how the separation process can be improved. It was recently recognized that one can invoke particular models for polymer dynamics to describe the progress of a separation. However, prior to the discussion in this chapter it does not appear to have been recognized that electrophoretic separations, in addition to separating charged species, are at the same time measuring properties of the support medium.

Chapter 4 presents an extended treatment of scattering techniques and diffusion coefficients. There is a variety of diffusion coefficients, a variety of names that have been assigned to those coefficients, and a need for consistency. Several

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approaches, including the Onsager regression hypothesis, the Langevin equation, and statistico-mechanical averaging over intermacromolecular forces, have been used to compute diffusion coefficients. The emphasis is on colloids, generating results needed in Chapter 10. For a solution of dilute diffusing particles, the relationship between the measured dynamic structure factor $g^{(1)}(q,t)$ and the statistical moments of the probability distribution $P(\Delta r, t)$ for particle displacements Δr is sometimes misunderstood; the relationship is therefore examined at length. Finally, methods for extracting parameters from measurements of $g^{(1)}(q,t)$ are examined. Computational information-theoretic methods confirm what has long been known practically, namely that the number of independent parameters that can be extracted from a light scattering spectrum is quite modest.

The book next turns to dynamic properties determined by motions of single macromolecules. Chapters 5 and 6 consider the smallest molecular motions, namely motions of single solvent molecules and motions of molecular bonds and polymer segments. Until recently, it was assumed that the solvent had the same physical properties in a polymer solution and in the neat liquid. It has now become clear that just as solvents modify polymer properties such as chain radius, so also do polymer molecules modify properties of nearby solvent molecules. The relationship between the small-molecule diffusion coefficient and the solvent viscosity has sometimes been assumed to follow Walden's rule $D \sim T/\eta$, T being the absolute temperature. The experimental literature as developed in Chapter 5 leads to alternative relationships, different for small and large diffusing objects in low and high viscosity simple liquids and in dilute and highly concentrated polymer solutions. The subsequent Chapter 6 on segmental diffusion considers VH light scattering, time-resolved polarization measurements, and NMR as paths to determining how fast chain segments move, each technique being sensitive to motions on its own length scale. A generalized Kramers relation for segment orientation times is found, the relationship plausibly being the one that would have been obtained by Kramers if the phenomenology demonstrated in Chapter 5 had been recognized.

Dielectric relaxation is the primary topic in Chapter 7. Dielectric relaxation affords information on a plethora of different polymer properties, including (for appropriately chosen materials) the average mean-square length of the end-to-end vector $\mathbf{r}$, the relaxation time for end-to-end vector reorientation, the dynamic dielectric and dielectric loss functions $\epsilon'(\omega)$ and $\epsilon''(\omega)$, and cross-correlations between motions of different parts of the same chain. Parametric dependences of these quantities on polymer properties, and several cross-correlations, are noted. Comparison is made with other techniques for measuring polymer chain extent, including static light scattering and elastic neutron scattering.

Single-chain diffusion, the motion of an identified chain through a uniform polymer solution, is treated in Chapter 8. The diffusion coefficients for polymer self-diffusion (the motion of a single probe chain through a solution of substantially identical matrix chains) and tracer diffusion (the diffusion of a single probe chain through a solution of matrix chains that are not the same as the chain of interest) in general depend on the molecular weight P of the probe chain, the concentration c and molecular weight M of the matrix chains, solvent quality, temperature, and other physical variables.

Probe diffusion is the subject of Chapter 9. Probe motion in polymer solutions has long been studied with light scattering spectroscopy. Interest in the method was enhanced by the early observation that the probe diffusion coefficient is often not determined by the solution's shear viscosity. In some systems slow probe modes are seen; these are not the same as the polymer slow modes seen in light scattering from binary polymer : solvent mixtures. More recently, computer and video techniques permit tracking the motion of individual particles, permitting determination of hitherto-inaccessible statistical properties of particle motion. Chapter 9 also considers the few true microrheological studies in which the motion of mesoscopic particles subject to outside forces is examined.

Chapter 10 is nearly unique in a volume on polymer dynamics, namely it assigns to the dynamics of rigid colloidal particles an importance equal to the dynamics of nonrigid polymer coils. There are few precedents for such an assignment. However, polymer and colloid dynamics are governed by the same forces and the same general dynamic equations, so it should not be surprising that polymer and colloid dynamics have many fruitful points of comparison. In particular, any nondilute solution property that qualitatively is exhibited both by colloid and by polymer solutions cannot arise from topological interactions unavailable to colloids.

No location for Chapter 10 was entirely satisfactory. It seemed critical to introduce the concentration dependence of the colloidal mutual diffusion coefficient D_m, in particular the fundamental issue that D_m of diffusing macromolecules cannot meaningfully be represented in terms of a scaling length ξ, before reaching Chapter 11 on the dynamic structure factor. On the other hand, the functions used to represent the zero-shear viscosity and the dynamic moduli of colloidal suspensions are taken from the chapters on zero-shear viscosity and viscoelasticity of polymer solutions, and those chapters were best placed toward the end of the book. Discussions of colloids might have been dispersed throughout chapters on random-coil polymers, but that alternative would have lost the impact of a unified display of properties of colloidal preparations. These contrary needs were resolved by allowing Chapter 10 to invoke results from later chapters.

Finally the book reaches properties that are determined by the collective properties of the dissolved polymers, including the dynamic structure factor, the polymer slow mode, the zero-shear viscosity, and linear and nonlinear viscoelasticity. Chapter 11 treats the dynamic structure factor $S(q, t)$ of polymer solutions as obtained by the scattering of light, neutrons, or other coherent waves. In dilute solution, $S(q,t)$ measures a translational diffusion coefficient; equivalently, it measures a hydrodynamic radius r_H. At large q, $S(q,t)$ reflects polymer internal motions. In not-quite-dilute solutions, the initial relaxation rate K_1 of $S(q,t)$ depends on q and c in simple ways; the observed q-dependence of K_1 has implications for references to hydrodynamic screening hypotheses. At elevated concentration, $S(q,t)$ sometimes shows a very slow relaxational mode. A discussion of polyelectrolytes, which sometimes have spectral slow modes, is included; recent experiments appear to clarify the physical nature of the polyelectrolyte slow modes.

The low-shear viscosity of polymer solutions is considered in Chapter 12. The major effort in the chapter is demonstrating the functional form of the dependence of η on c and M. A large-concentration transition in the functional form of $\eta(c)$ is found for some but certainly not all systems. We finally consider the behavior of the parameters obtained from an accurate functional description of $\eta(c, M)$.

Chapter 13 examines the dependence of viscoelastic behavior, including the storage and loss moduli and shear thinning, on solution properties. Historically, it has been difficult to obtain a simple description of the dependence of G' and G'' on c, M, or other parameters. Traditional reduced-variable methods have been disappointing; experimental results remained confusing. Chapter 13 presents a novel *ansatz* and set of functional forms that describe $G'(\omega)$, $G''(\omega)$, and $\eta(\kappa)$ accurately at all frequencies and shear rates, while reducing measurements to a very small number of parameters. These parameters are found to have simple dependences on c and M, reinforcing the belief that the *ansatz* description has a fundamental basis.

Chapter 14 sketches nonlinear properties of polymer solutions, some classical and some quite modern. Strange behaviors can arise in polymer solutions because the normal stress differences are nonzero, i.e., the diagonal components of the pressure tensor can be unequal. Memory effect properties, such as stress and strain relaxations, and responses to imposing multiple strains, are noted. Finally we consider very recent developments in the study of nonlinear effects, such as shear banding and nonquiescent relaxation following imposition of a sudden strain.

A summary chapter presents briefly what was done in each of the prior chapters. Results from different experimental properties are then united, showing how they are interrelated and drawing additional conclusions that would not have been obvious from a single experimental method.

1.2 Classes of model for comparison with experiment

The approach here is to compare experimental measurements of transport coefficients with functional forms and parametric dependences predicted by models of polymer dynamics. There is a very large number of proposed models. Most models fall into two major phenomenological classes, distinguished by the functional forms they give for the transport coefficients. These phenomenological classes are not the same as theoretical classes categorized by assumptions as to the dominant forces in solution. This section sketches the predictions of these classes in preparation for the comparison.

(1) In *scaling* models (1), the relationship between, e.g., the self-diffusion coefficient and polymer properties is described by power laws such as

$$D_s = D_1 M^{\gamma} c^{-x}, \tag{1.1}$$

where here γ and x are scaling exponents, and D_1 is a scaling prefactor, namely the nominal diffusion coefficient at unit molecular weight and concentration. In some cases, scaling laws are proposed to be true only over some range of their variables, or only to be true asymptotically in some limit. On moving away from the limit, corrections to scaling then arise. Some models of melts derive a scaling law for $D_s(M)$ from model dynamics, and then predict numerical values for γ. For polymer solutions, more typically a scaling-law form is only postulated; the theoretical objective is limited to calculating the exponents.

Many scaling-type models propose a transition in solution behavior between a lower-concentration dilute regime and a higher-concentration nondilute regime. Scaling arguments do not usually supply numerical coefficients, so there is no guarantee that an interesting transition actually occurs at unit value of a hypothesized transition concentration c_t rather than at, say, $2c_t$. Correspondingly, the observation that a transition is found at $2c_t$ rather than c_t is generally in no sense a disproof of a scaling model, because in most cases scaling models do not supply numerical prefactors required for a disproof. (Some level of rationality must be preserved. If a physical model leads to c_t as the transition concentration, and the transition is found at 30–150 c_t, and then only in some systems, one must ask why one should believe that the observed transition is related to the transition in the model.)

Two transition concentrations are often identified in the literature. The first transition concentration is the overlap concentration c^*, formally defined as the concentration $c^* = N/V$ at which $4\pi R_g^3 N/(3V) = 1$. Here N is the number of macromolecules in a solution having volume V and R_g is the macromolecule radius of gyration. In many cases, c^* is obtained from the intrinsic viscosity via $c^* = n/[\eta]$ for some n in the range 1–4. The second transition concentration is the entanglement concentration c_e. In some papers, the entanglement concentration is obtained from a log–log plot of viscosity against concentration by extrapolating an assumed low-concentration linear behavior and an assumed higher-concentration power-law behavior (e.g., c^x for, e.g., $x = 4$) to an intermediate concentration at which the two forms predict the same viscosity, this intermediate concentration being taken to be c_e. In other papers, the entanglement concentration is inferred from the behavior of the viscoelastic moduli, for example, the onset of viscous recovery.

(2) In *exponential* models, the concentration dependence is an exponential or stretched exponential in concentration(2, 3). For self-diffusion, the stretched exponential form is

$$D_s = D_o \exp(-\alpha c^{\nu}). \tag{1.2}$$

Here D_o is the diffusion coefficient in the limit of infinite dilution of the polymer, α is a scaling prefactor, and ν is a scaling exponent; $\nu = 1$ for a simple exponential. If the probe and matrix polymers have unequal molecular weights P and M, an elaborated form of the stretched exponential is

$$D_p = D_o P^{-a} \exp(-\alpha c^{\nu} P^{\gamma} M^{\delta}), \tag{1.3}$$

where a, γ, and δ are additional scaling exponents, D_o now represents the diffusion coefficient in the limit of zero matrix concentration of a hypothetical probe polymer having unit molecular weight, and P^{-a} describes the dependence on probe molecular weight of the diffusion coefficient of a dilute probe molecule.

In derivations leading to stretched-exponential models, functional forms and numerical values for exponents and prefactors are obtained, subject to various approximations(2–5). Some derivations assume that chain motion is adequately approximated by whole-body translation and rotation, which may be appropriate if $P \approx M$, but which is not obviously appropriate if P and M are substantially unequal.

Some exponential models also include a transition concentration, namely a transition between a lower-concentration regime in which some transport coefficients show stretched-exponential concentration dependences and a higher-concentration regime in which the same transport coefficients show power-law concentration dependences(6, 7). This transition concentration is here denoted c^{+}. The lower-concentration regime is the *solutionlike* regime, the higher-concentration regime is the *meltlike* regime. Power-law and exponential forms can both follow from a renormalization-group approach, depending on the location of the supporting fixed point(8). The stretched-exponential form is an invariant of the Altenberger–Dahler (8) positive-function renormalization group(5).

Our analysis will examine whether either of these classes of model describes experiment. While a power law and a stretched exponential both can represent a narrow range of measurements to within experimental error, on a log–log plot a power law is always a straight line, while a stretched exponential is always a smooth curve of nonzero curvature. Neither form can fit well data that are described well by the other form, except in the sense that in real measurements with experimental scatter a data set that is described well by either function is tangentially approximated over a narrow region by the other function.

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1.3 Interpretation of literature experimental results

Phenomenology of Polymer Solution Dynamics presents and systematizes the researches of hundreds of researchers who employed a large number of experimental techniques, including centrifugation, electrophoresis, light scattering spectroscopy, neutron scattering, electrical conductivity, depolarized light scattering, time-resolved polarization, nuclear magnetic resonance, dielectric relaxation, elastic neutron scattering, fluorescence recovery, optical probe diffusion, particle tracking, true microrheology, viscometry, and multiple methods for examining viscoelastic response and shear thinning, among others.

What was done here was to extract the original measurements and provide a uniform phenomenological description. Numerical values for each property were obtained from the literature, rarely from tabulated data but usually by scanning and point-by-point digitization of individual figures in the original papers. A modest obstacle was that some authors report only measurements that have been heavily processed with respect to particular theoretical models, so for a few papers it was impossible to determine the fundamental underlying measurements. A nonlinear least squares fitting program employing the simplex algorithm was then used to fit possible functional forms to measurements, thereby extracting fitting parameters that were studied further(9). Possible functional forms for each property were inferred from the measurements or drawn from the theoretical literature. The quantity minimized by the fitting algorithm was the mean-square difference between the data and the fitting function, expressed as a fraction of the value of the fitting function. This quantity is the appropriate choice for minimization if the error in the measurement is some constant fraction of the value of the quantity being measured. In some cases, one or more potentially free parameters were held constant ("frozen") during the fitting process.

The approach here differs from much valid analysis in the earlier literature. Historically, there has been great interest in reducing variables and superposition plots. A starting point for applying reducing variables is a set of measurements of, for example, the viscosity $\eta(c, M)$ at a series of concentrations c and molecular weights M. With an appropriate choice of molecular-weight-dependent reducing factors a_c and perhaps a_η, a plot of $a_\eta \eta$ against $a_c c$ reduces $\eta(c, M)$ at different M to a single *master curve* for $a_\eta \eta(a_c c)$. When it works, reduction transforms a series of very different curves into a single line. A master curve predicts dynamic properties at concentrations and molecular weights that were not studied.

In this work, we advance from reducing variables to numerical curve fitting. Numerical fitting methods afford strong advantages over reducing variables and superposition plots. Numerical fits reveal weak dependences not readily apparent to the naked eye. Furthermore, reducing variables can only lead to superposition

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plots if the underlying experimental variable has appropriate scaling properties. Numerical fitting can handle parametric dependences far more complex than simple scaling. For example, if the functional form of the concentration dependence depends on the polymer molecular weight, in general no reducing variable can lead to a master plot covering multiple molecular weights. This challenge to reducing variables was long known to be an issue for the viscoelastic functions. As Ferry wrote: *It is evident … that the concentration reduction scheme for the transition zone described … above cannot be applied in the plateau zone, and indeed that no simple method for combining data at different concentrations can exist; … the shapes of the viscoelastic functions change significantly with dilution* (10). Here an alternative method for reducing measurements to a few parameters will be revealed.

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Sedimentation

2.1 Introduction

The importance of sedimentation to the study of macromolecules has been apparent since the early 1920s, when Theodor Svedberg invented the ultracentrifuge and used it to demonstrate that proteins are monodisperse macromolecules and not, as he had originally believed, colloidal aggregates formed from amino acids. The application of sedimentation studies in the analytic ultracentrifuge to determine the molecular weight of polymers is well known. This chapter considers sedimentation in nondilute polymer solutions, including both the sedimentation of polymers in a homogeneous monodisperse preparation and the sedimentation of probe chains and particles through a background ("matrix") polymer.

In a dilute solution, the sedimentation rate of a polymer is characterized by its sedimentation constant s, which is related to other solution properties by

$$s = \frac{M(1 - \bar{v}_2\rho)}{N_A f_s^*}, \tag{2.1}$$

where M is the polymer molecular weight, $\bar{v}_2$ is the polymer's specific volume, ρ is the solvent density, N_A is Avogadro's number, and f_s^* is the drag coefficient for sedimentation.

At elevated concentrations, hydrodynamic and other interactions between sedimenting molecules become important. Two sorts of sedimentation measurement, involving respectively a binary and a ternary system, then suggest themselves. First, s in binary polymer systems may depend on polymer concentration and molecular weight. Second, the sedimentation rate of colloidal particles or probe polymer molecules through a solution of a second polymer, as might occur in ternary systems, may depend on the second polymer's properties.

Polymers at sufficiently large concentrations overlap uniformly. It has been asserted that polymers in a binary solution may be envisioned as an amorphous