Competition between Hydrodynamic Screening ("Draining") and Excluded Volume Interactions in an Isolated Polymer Chain

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ABSTRACT: A remaining challenge in the theory of polymer solution dynamics is associated with establishing a relation between the macroscopic hydrodynamic properties of polymer solutions and the molecular structure of the polymer and solvent. This problem is unsolved even for the simplest case of polymer solutions at "infinite dilution". Recent studies have focused on technical problems such as the "preaveraging" approximation, ϵ-expansion truncation errors, and the influence of ternary excluded volume interactions which limit the accuracy of analytic calculations. The present paper examines the role of polymer excluded volume in altering intramolecular hydrodynamic interactions and the possible significance of dynamic chain flexibility on hydrodynamic polymer solution properties. This investigation is aided by analysis of our previous renormalization group (RG) computations and simple exactly solvable models. We also examine experimental trends for the variation of the polymer hydrodynamic interaction with solvent and the variation of the translational friction of small molecules with molecular size.

1. Introduction

Much of our theoretical understanding of polymer solutions derives from efforts to explain the molecular weight, temperature, and solvent dependence of the intrinsic viscosity and translational diffusion coefficient. For example, the anomalous viscosities of certain "colloids", in part, suggested the existence of polymers.[1] Onsager deduced the "coiled" shape of solvated polymer chains from deviations between Staudinger's viscosity measurements and his calculations of the intrinsic viscosity of rod polymer solutions.[2] The coil picture of a dissolved polymer, developed by Kuhn[3] and others,[4] evolved into the classical random walk and Brownian motion models of polymer chain configurations. Early modeling of polymer hydrodynamics in solution was based on the recognition that the solvent is "more or less entrapped" within the domain occupied by the polymer.[3-5] Thus, Kuhn[3] introduced the "impermeable sphere model" in which the polymer and solvent are assumed to move together as a collective body whose mean dimensions are those of the random coil.[3] The random coil and impermeable sphere models have been extremely fruitful in polymer science applications.

The observation of a universal Mark-Houwink relation[6] between the intrinsic viscosity $[\eta]$ and molecular weight M,

$$[\eta] \sim M^a \tag{1.1}$$

stimulated the introduction of the presumably more molecularly faithful pearl-necklace ("bead") polymer models[7-9] with extensions that included hydrodynamic interactions.[10,11] When hydrodynamic interactions are strong ("nondraining" limit), the pearl-necklace models reduce to the "impermeable sphere model", while for weak hydrodynamic interactions ("free-draining" limit), the Staudinger law ($a = 1$) is recovered.[7-9] On the other hand, Flory and Fox[5] interpreted the variation of a in terms of the impermeable sphere model and polymer chain swelling.[3] The success of the Flory-Fox model has largely dominated the theoretical interpretation of the variations in a with solvent, and there has been relatively little interest in descriptions based on variable hydrodynamic interactions. The incorporation of excluded volume interactions into the nondraining limit pearl-necklace model has brought a convergence between the impermeable sphere and pearl-necklace approaches. The strong hydrodynamic interaction limit of the Kirkwood-Riseman (KR) and Rouse-Zimm (RZ) models is now standard for describing polymers in dilute solutions.[12]

Increasingly accurate measurements of the hydrodynamic properties of dilute polymer solutions, however, display apparent deviations from pearl-necklace model predictions. Deviations are found even in Θ solutions where excluded volume interactions are supposed to be absent. Fixman summarizes the conflict between observations for the ratio of the hydrodynamic radius and the radius of gyration and predictions from conventional hydrodynamic theories.[13] Miyake and Fujita[14] discuss experimental data for $[\eta]$ which are difficult to reconcile with the simple nondraining chain models (see below). Recently, Freed et al.[15a] compiled further experimental data for the intrinsic viscosity and diffusion coefficient for a variety of polymers and solvents and compared these observations to renormalization group (RG) calculations using a continuum formulation of the pearl-necklace model with variable hydrodynamic and excluded volume interactions. The study of Freed et al. indicated that polymer solution hydrodynamic properties are *not* universal functions of excluded volume, as the simple nondraining pearl-necklace models would imply, and Freed et al. suggest that "draining" (i.e., intramolecular hydrodynamic interactions of intermediate strength) could be part of the explanation for measured deviations between theory and experiment. These observations amplify earlier work by Berry,[16] Douglas and Freed,[17] and Wang et al.[18], which interpret the "nonuniversality" of $[\eta]$ in terms of variable "draining".

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The "draining" interpretation for the nonuniversality of the scaling curves of hydrodynamic solution properties has recently been challenged by Horita et al.[15b] They argue that the "impermeable sphere" model is a sufficient approximation (i.e., there is no necessity to consider variable hydrodynamic interaction), although the description of excluded volume interactions in even nominally flexible polymers must be modified to account for *chain stiffness*. They have also made the important observation that the "splitting" seen in the data of Miyake and Fujita[14] is probably due to an inaccurate estimation of Θ point properties in forming dimensionless ratios with corresponding properties measured in good solvents. Indeed, the new and corrected data for polystyrene (PS) in various solvents strongly support their supposition that $[\eta]$ is a universal function of excluded volume, as measured by expansion of the chain radius of gyration.

The claim for a "universal" dependence of $[\eta]$ and other hydrodynamic solution properties on excluded volume, however, becomes problematic when different polymers are compared. Details of the chain structure evidently have relevant consequences for the observed hydrodynamic solution properties. Wang et al.[18] illustrate this nonuniversality with literature data for $[\eta]$ and radii of gyration for polyisobutylene (PIB) and PS in various solvents (see Figures 2 and 3 of ref 18). The PS data cited by Wang et al. are consistent to within experimental uncertainty with the new PS data obtained by Horita et al.,[15b] and there are no complications associated with the definition of "unperturbed" polymer solution properties. The excluded volume dependence of these two polymers, when examined over a large range of chain expansion, is seen to exhibit *qualitatively different* variations. This observation has nothing to do with the choice of model scaling variables to describe the excluded volume interaction.

The nonuniversality $[\eta]$ as a function of excluded volume needs to be understood as a first step in describing the concentration dependence of semidilute solution hydrodynamic properties because the hydrodynamic virial coefficient $[\eta]$ naturally defines the concentration variable for the hydrodynamic properties of more concentrated polymer solutions. Weill and des Cloizeaux[19] have suggested a simple "spatial crossover" model to rationalize the observed different excluded volume dependence of hydrodynamic and static (e.g., radius of gyration) solution properties. However, this physically appealing model predicts that hydrodynamic solution properties are *unique* functions of excluded volume (again echoing the "impermeable sphere" model). The observed *nonuniversal* dependence of $[\eta]$ on excluded volume indicates that the problem is more subtle, and a more refined model is needed.

Before concentrating on the influence of variable hydrodynamic interactions on the properties of dilute polymer solutions, we briefly mention other factors which should contribute to an improved hydrodynamic polymer solution theory. Preaveraged Kirkwood–Riseman theory[10] calculations for the hydrodynamic radius of flexible polymers at the Θ point imply that ternary interactions can contribute significantly to hydrodynamic polymer solution properties.[20] Lattice Monte Carlo simulations of the preaveraged Kirkwood–Riseman hydrodynamic theory also exhibit similar deviations of Θ chain dimensions from those expected from simple random walk statistics.[21] Berry has estimated the ternary interactions from osmotic third virial coefficient measurements at Θ conditions and finds that a significant part of the observed deviations of the translational friction coefficient from KR theory predictions can be rationalized on the basis of ternary interactions.[22] The influence of ternary interactions should *diminish* upon chain expansion, but the theoretical description of this effect is technically difficult.[23] In addition, Fixman emphasizes that chain rigidity affects dilute solution hydrodynamic properties, and this effect appears to persist in the long-chain limit.[24] More microscopic models of local chain dynamics would be useful to explore this phenomenon.

The Kirkwood–Riseman (KR) and Rouse–Zimm (RZ) models belong to a hierarchy of hydrodynamic models involving a variety of purely mathematical and physical approximations. Simulation methods have allowed a close examination of the rather severe "preaveraging" approximation. Zimm[25] and de la Torre and Freire[26] provide estimates of the configurational preaveraging errors associated with the friction coefficient and intrinsic viscosity for the rigid-body KR theory, placing the error on the order of 15%. Fixman's estimate of the preaveraging error for the friction coefficient is somewhat smaller (7%) for chains which are not rigid[27] (see ref 13), which suggests that *dynamic chain flexibility* is a relevant variable (see below) to describe chain friction. Second-order renormalization group (RG) calculations (perturbative expansions in $\epsilon = 4 - d$, where d is the spatial dimension) for the KR model yield configurational preaveraging errors (d = 3) on the order 25% for Gaussian chains and on the order 16% for swollen flexible chains.[28] The treatment of the excluded volume dependence for the preaveraging corrections introduces serious complications into quantitative analytical calculations of hydrodynamic properties. Monte Carlo calculations by de la Torre et al. further indicate that preaveraging corrections are dependent on chain architecture.[29] An understanding of preaveraging corrections and other factors mentioned above is necessary for computing the absolute magnitudes of the intrinsic viscosity $[\eta]$ and the translational diffusion coefficient f of dilute polymer solutions. However, these factors are not expected to affect the qualitative scaling of hydrodynamic properties with molecular weight as in (1.1).

Section 2 presents a comparison of lowest order RG computations with KR, RZ, and Debye–Bueche model predictions. All these models illustrate the competition between excluded volume and hydrodynamic interactions in determining chain friction. Limitations of current hydrodynamic models as well as recent "mode-coupling" theory results are also discussed. Section 3 examines the observed nonuniversality of the ratio of the hydrodynamic radius and the chain radius of gyration, and these results are interpreted in terms of an idealized "liquid droplet model" of flexible polymers in solution. We also discuss measurements of the friction coefficient for small molecules and low molecular weight polymers, as well as recent efforts to understand observed deviations from simple hydrodynamic theories.

2. Variable Hydrodynamic Interactions in Dilute Polymer Solutions

A. Decrease of Hydrodynamic Friction with Chain Swelling. The magnitude of the polymer–polymer hydrodynamic interactions depends strongly on the chain configuration. More compact chains exhibit stronger hydrodynamic interactions than extended chains. For instance, the KR theory in three dimensions shows that hydrodynamic interactions within a rodlike polymer are very weak and are dominated by the "free-draining" contribution.[30] The translational friction coefficient in the free-draining limit equals $f = n\zeta$, where n is the number of segments in a chain and ζ is the friction coefficient per segment. The rod polymer friction coefficient in three dimensions has logarithmic corrections in n arising from the weak hydrodynamic interactions. In contrast, a three-dimensional random coil (idealized by a random walk configuration) exhibits strong hydrodynamic interactions that lead to a friction coefficient which scales[10,11] as $f \propto n^{1/2}$. The chain friction thus corresponds to that of an "effective sphere" having dimensions on the order of the chain radius of gyration. As the spatial dimension approaches $d = 4$ and the random coil monomer density decreases, the random coil hydrodynamic interactions decrease. The friction of a random coil in $d = 4$ scales with chain length like a rod polymer in $d = 3$ dimensions. Swelling of a flexible polymer affects the magnitude of the hydrodynamic interactions in a manner similar to the change induced by an increase of the spatial dimension since the coil density is likewise reduced by an increase of d. Thus, we observe a general principle: Hydrodynamic interactions diminish as bodies become more extended (e.g., swelling) and increase as bodies become more compact. Next, we specifically illustrate this effect by use of dynamical RG calculations for the friction coefficient f. The discussion begins with the KR model since this approximation yields exact solutions that provide guidance in situations where exact analytic treatment is not currently possible.

The calculation of the translational friction coefficient f for flexible chains with the KR model and RG theory[28] involves a pair of dimensionless interaction parameters, z_2 and z_H, corresponding to excluded volume and hydrodynamic interactions, respectively. z_2 is the standard "Fixman parameter" of the two-parameter model, and z_H is proportional to the conventional h interaction parameter of the KR and RZ models (see below). Previous RG calculations[28] for the crossover description of polymer solution hydrodynamic properties are presented in a nonstandard notation convenient to these calculations, but these results are reexpressed below in a notation which can be more readily compared with previous calculations based on alternative methods. This notational transcription should make the results more accessible.

The friction coefficient f for a flexible polymer with excluded volume, for example, can be expressed directly in terms of z_2 and z_H,[28]

$$f_{RG}/\eta_s = [2d/(d-1)](2\pi\langle \mathbf{R}^2\rangle/d)^{(d-2)/2}A(\phi,z_2,z_H) + O(\epsilon^2) \tag{2.1}$$

where the prefactor $A(\phi,z_2,z_H)$ is given by

$$A(\phi,z_2,z_H) = A_0(\phi)u_H(z_2,z_H), \qquad A_0(\phi) = \pi(1-\phi^2) \tag{2.2}$$

$$u_H(z_2,z_H) = u_H{}^*(z_2)[z_H/u_H{}^*(z_2)](1 + z_2/u_2{}^*)^\sigma/\{1 + [z_H/u_H{}^*(z_2)](1 + z_2/u_2{}^*)^\sigma\} \tag{2.3}$$

$$u_H{}^*(z_2) = (\epsilon/2)(3/4)[(z_2/u_2{}^*)/(1 + z_2/u_2{}^*)]/[1 - (1 + z_2/u_2{}^*)^{-3/4}] \tag{2.4}$$

$$\phi = \epsilon/2, \qquad \sigma = -1/4 + O(\epsilon) \tag{2.5}$$

$$u_2{}^* = (\epsilon/8) + O(\epsilon^2), \qquad u_H{}^*(z_2 \to \infty) = 3\epsilon/8 + O(\epsilon^2),$$

$$u_H{}^*(z_2 \to 0^+) = (\epsilon/2) + O(\epsilon^2) \tag{2.6}$$

where $\langle \mathbf{R}^2\rangle$ is the mean-square end-to end distance, d is the spatial dimension ($2 \leq d < 4$), and η_s is the solvent viscosity. Equations 2.1–2.6 correspond to the exact first order in ϵ dynamical RG calculations for the KR model.[28] A simple scaling behavior is obtained from (2.1) in the Gaussian "nondraining" limit ($z_2 \to 0^+$, $z_H \to \infty$),

$$f_{RG}(z_2 \to 0^+, z_H \to \infty)/\eta_s = [2d/(d-1)](2\pi\langle \mathbf{R}^2\rangle/d)^{(d-2)/2}A_0(\phi)\phi \tag{2.7a}$$

whereas an *exact* preaveraged KR theory (no ϵ-expansion) calculation for f produces the slightly different prefactor[32,33]

$$A_{KR}(\phi) = 2(1-\phi)\sin(\pi\phi/2)\Gamma^2(1-\phi/2)/\Gamma(2-\phi) \tag{2.7b}$$

where Γ is the gamma function. Similarly, the first order in ϵ dynamical RG calculation[28b] for the intrinsic viscosity $[\eta]$ can be expressed in terms of the friction coefficient and the radius of gyration $\langle S^2\rangle^{1/2}$ as

$$[\eta] = (2N_A/M\eta_s)f_{RG}(z_2,z_H)(\langle S^2\rangle/d) + O(\epsilon^2) \tag{2.8a}$$

Equation 2.8a justifies the Weill–des Cloizeaux approximation[19] $[\eta] \propto f\langle S^2\rangle$ to order ϵ in the dynamical RG theory. It is also readily shown that the average rotational friction coefficient f_R equals[10]

$$f_R = (2/d)f_{RG}(z_2,z_H)\langle S^2\rangle + O(\epsilon^2) \tag{2.8b}$$

The RG estimate of $A_0(\phi)$ in (2.2) differs from the exact value in (2.7b) by less than 2% over the range ($2 < d < 4$).[33] On the other hand, application of the RG method of Oono et al.[34,35] to the preaveraged KR theory for Gaussian chains leads to an alternative estimate,

$$f_{Oono}/\eta_s = [2d/(d-1)](2\pi\langle \mathbf{R}^2\rangle/d)^{(d-2)/2}[(4\pi/3)e^{\epsilon/12}\epsilon] + O(\epsilon^2) \tag{2.9}$$

The ϵ-expansion error in the calculation of Oono et al. is a substantial 27% in $d = 3$. Hence, this comparison with the exactly solvable preaveraged KR theory argues against the re-exponentiation method employed by Oono and coworkers (see Appendix D of ref 31). The variable z_H has been introduced into eq 2.1 to minimize such ϵ-expansion errors,[28] leading to the improved RG estimate (2.2).

The conventional hydrodynamic interaction variables h and h^* of the KR[10] and Rouse–Zimm[11] (RZ) theories are directly related to z_H and the RG theory parameter $u^*{}_H$ by

$$h = 2^{-\phi}(1+\phi)z_H/2, \qquad h^* = 2^{-\phi}(1+\phi)u^*{}_H/2 \tag{2.10a}$$

$$h = (d/2\pi l^2)^{(d-2)/2}\beta_H n^\phi, \quad \beta_H = (\zeta/2\pi d\eta_s)(d-1)2^{-\phi}/(d-2) \tag{2.10b}$$

$$h(d{=}3) = (12\pi^3)^{-1/2}(\zeta/\eta_s l)n^{1/2} \tag{2.10c}$$

where η_s is the solvent viscosity. The Gaussian chain "hydrodynamic fixed-point" $h_\theta{}^*$ [see (2.4) and (2.10a)] takes a simple form when expressed in terms of the "hydrodynamic crossover exponent" ϕ,

$$h_\theta{}^* = 2^{-\phi}(1+\phi)(\phi/2), \qquad h_\theta{}^*(d{=}3) = 3/2^{7/2} = 0.26516... \tag{2.10d}$$

where ϕ is defined by the scaling of h with chain length in (2.10b). This scaling becomes altered when excluded volume interactions are included in the KR or RZ models (see below).

Some particular limits for the RG result (2.1) establish connections with the classical KR and RZ theories.[10,11] Equations 2.1 and 2.8 also describe to order ϵ the translational friction and intrinsic viscosity in the RZ model with inclusion of the excluded volume interactions, so there is no need to distinguish these models in our discussion here.[36,37] Osaki's RZ model estimate,[38] $h^*(d{=}3;\text{Osaki}) = 1/4$, corresponds to the leading-order contribution of h_θ^* in (2.10d),

$$h_\theta^* = \epsilon/4 + O(\epsilon^2), \qquad h_\theta^*(d{=}3) \approx 1/4 \qquad (2.11)$$

A simple generalization of Osaki's calculation to the bead-spring model in d-dimensions gives $h^*(\text{Osaki}) = \epsilon/4$ for Gaussian chains and accords with (2.11). Upon passage to the limit of vanishing excluded volume ($z_2 \to 0^+$), the first-order RG computation in (2.1) recovers the original KR estimate of f,[10]

$$f(h,z_2{=}0) = n\zeta/(1 + h/h_\theta^*), \qquad d = 3 \qquad (2.12a)$$

$$f(h\to\infty,z_2{=}0) = 5.11\ \langle \mathbf{R}^2\rangle_0^{1/2} \qquad (2.12b)$$

Equation 2.1 does not invoke the preaveraging approximation because this approximation affects the friction coefficient only at *second oder* in ϵ.[28] The important parameters, the hydrodynamic crossover exponent ϕ [see (2.10)] and the hydrodynamic fixed-point h^*, are also affected by preaveraging only at second order in ϵ. The magnitude of the preaveraging error in h^* governs the magnitude of preaveraging corrections to hydrodynamic properties.[28]

The variable combination $\xi = z_H(1 + z_2/u_2^*)^{-1/4}$ in (2.3) is the natural generalization of the hydrodynamic interaction parameter h arising in the description of Gaussian chains ($z_2 = 0$). This variable clearly decreases with chain swelling [$z_2 \geq O(1)$] for a fixed value of h. In the long-chain limit the swollen-chain hydrodynamic interaction ξ exhibits the asymptotic scaling

$$\xi \sim n^{\hat\phi}, \qquad \hat\phi = 3\epsilon/8 + O(\epsilon^2) \qquad (2.13)$$

where $\hat\phi$ denotes the "hydrodynamic crossover exponent" for self-avoiding chains. The hydrodynamic interaction parameter ξ inevitably becomes large for fixed monomer friction, large polymer excluded volume interaction, and sufficiently long chain lengths. However, in the absence of a means to estimate the molecular friction, it is entirely unclear how long a "sufficiently long" chain must be. This is the basic observation which motivates much of the investigation below.

A simple scaling analysis of the Kirkwood–Riseman integral equation yields the hydrodynamic crossover exponent as

$$\hat\phi = 1 - (d-2)\nu \qquad (2.14)$$

since the Oseen tensor scales with distance R as $R^{-(d-2)}$ and the average chain radius scales as $\langle \mathbf{R}^2\rangle \sim n^{2\nu}$. Using the RG relation $2\nu = 1 + \epsilon/8 + O(\epsilon^2)$ in eq 2.14 recovers eq 2.13 to order ϵ. Equation 2.14 is conjectured to be *exact* for the chain length dependence of the hydrodynamic interaction for self-avoiding chains in the *preaveraged* KR and RZ models. Explicit calculation[28] shows that (2.14) is not exact for the KR model in the absence of preaveraging, however.

Even the simple Debye–Bueche theory[39] predicts decreased hydrodynamic interactions (diminished "shielding") with chain swelling. A brief discussion of this model serves to illustrate further the university of this effect. The friction coefficient f_{DB} in the Debye–Bueche model is calculated as

$$f_{DB} = 6\pi\eta_s R_s g(\delta^2) \qquad (2.15a)$$

where R_s is a measured of the average chain dimensions, $R_s \sim O(\langle \mathbf{R}^2\rangle^{1/2})$ and the scaling function $g(\delta^2)$ is specified by Debye and Bueche.[39] They define the "shielding parameter" δ as

$$\delta^2 = (R_s/L_p)^2 \qquad (2.16a)$$

where the invese square "penetration depth" L_p is taken as proportional to the average monomer density $\hat\rho \sim M/\langle \mathbf{R}^2\rangle^{3/2}$ and the monomer friction coefficient so that

$$L_p^{-2} \sim \hat\rho(\zeta/\eta_s) \qquad (2.16b)$$

The strong shielding ($\delta \gg 1$) limit of (2.15a) reduces f to the "impermeable sphere" model of Kuhn[3]

$$f_{DB}(\delta \gg 1) \sim 6\pi\eta_s R_s + O(\delta^{-2}) \qquad (2.15b)$$

and for "weak shielding" f_{DB} approaches the limiting behavior,

$$f_{DB}(\delta \ll 1) \sim n\zeta + O(\delta^2) \qquad (2.15c)$$

The "weak shielding" and "strong shielding" limits (2.15b) and (2.15c) correspond to the "free-draining" and "non-draining" regimes in the bead models ($h < h^*$ and $h \gtrsim O(1)$, respectively). Debye and Bueche[39] note that by adjusting R_s to conform to the nondraining KR theory, the Debye–Bueche theory yields a scaling function virtually coincident with the Kirkwood–Riseman prediction for Gaussian chains (see eq 2.1) where we take $\delta^2 \propto h$. Since the mean chain dimensions scale in good solvents as $\langle \mathbf{R}^2\rangle \sim n^{2\nu}$ and the segmental density scales as $\hat\rho \sim M/\langle \mathbf{R}^2\rangle^{d/2}$, eq 2.16 implies that the Debye–Bueche shielding parameter δ^2 scales with chain length as ($d = 3$)

$$\delta^2 \sim (\zeta/\eta_s)n^{\hat\phi}, \qquad \hat\phi = 1 - \nu \approx 7/17, \qquad \nu(d{=}3) \approx 10/17 = 0.5882... \qquad (2.17)$$

This corresponds to the leading-order KR approximation for $\hat\phi$ [see (2.14)].

In summary, first-order dynamical RG theory predicts that chain expansion diminishes the extent of the hydrodynamic interactions in the KR and RZ bead models, and this reduction leads to a *diminished* "hydrodynamic crossover exponent" $\hat\phi$. This general principle is also explicit in the simpler Debye–Bueche "porous sphere" model.[39,40]

B. An Alternate View of "Draining". Shiwa and Oono have recently introduced an alternative model of the "draining effect" in dilute polymer solutions.[41] These authors, in effect, consider the viscosity η_e in the Oseen hydrodynamic contribution to the molecular friction as a free parameter reflecting the "local viscosity" of the solvent which is perturbed in the proximity of the polymer chain. This "internal viscosity"[42] theory variant is motivated by the mathematical observation that the hydrodynamic interactions between the polymeric beads are suppressed by taking the $\eta_s \to \infty$ limit (independent of the true solvent viscosity), so that the friction on the polymer chain can be formally made to approach the free-draining scaling $f \sim n\zeta$. Shiwa and Oono[41] do not accept the possibility that the free-draining limit can be approached in the absence of this local viscosity ansatz. In fact, the free-draining scaling is readily obtained[43] in the bead model of a polymer chain by simply taking the beads to be small relative to the bond length. The crossover from "free-draining" to "non-free-draining" polymer hydrodynamics is just as natural in these bead models as the variation of the excluded volume interaction through adjustment of bead size. Near $d = 4$ dimensions the hydrodynamic interactions are weak, as in the case of the rod polymer in $d = 3$, so that the treatment of the free-draining theory as a physically appropriate limit is especially justifiable within ϵ-expansion perturbation theory. In the next section we discuss experimental evidence consistent with the existence of partial draining.

Although the general idea of a "mode coupling" between polymer and solvent motions is well founded,[44] the implementation of this idea is weak in the calculations of Shiwa and Oono.[41] Accepting for the moment a variable "local viscosity" η_e, we are naturally led to theoretical estimates of polymer hydrodynamic properties in terms of viscosity ratio $\lambda_0 = \eta_e/\eta_s$, the "mode-coupling" parameter of Shiwa and Oono. This ad hoc modification of the conventional hydrodynamic modeling actually leads to rather modest changes in the hydrodynamic formalism whose validity is easily checked experimentally. An exercise in dimensional analysis (see Appendix A) shows that the introduction of λ_0 simply amounts to a rescaling of the bare monomer friction coefficient,

$$\zeta(\lambda_0) = \lambda_0^{-4/(d-2)}\zeta(\lambda_0{=}1), \qquad \lambda_0 = \eta_e/\eta_s \tag{2.18a}$$

which to order ϵ becomes

$$\zeta(\lambda_0) = (\lambda_0)^{-2}\zeta(\lambda_0{=}1) + O(\epsilon) \tag{2.18b}$$

The introduction of λ_0 likewise has simple implications for the intrinsic viscosity $[\eta]$ and the translational friction f,

$$[\eta(\lambda_0)] = \lambda_0^{-2}[\eta(\lambda_0{=}1)] + O(\epsilon) \tag{2.19a}$$

$$f(\lambda_0) = \lambda_0^{-2}f(\lambda_0{=}1) + O(\epsilon) \tag{2.19b}$$

Evidently, the "mode-coupling" parameter cancels in the ratio $[\eta]/f$, and the conventional hydrodynamic theory (with $\eta = \eta_e$) is recovered with a rescaled friction ζ. It is true that this cancellation does not occur for the ratio of f to the chain radius of gyration, thereby leading to "nonuniversality". Consistency of this approach would require a *unique* value of λ_0 for a given polymer–solvent system in comparison of eq 2.19 and other hydrodynamic properties to experiment. We would be very surprised if this procedure led to consistent estimates of λ_0. In our opinion, the introduction of the parameter λ_0 by Shiwa and Oono is simply not commensurate with the sophistication of their starting hydrodynamic model. The method would be more palatable if a self-consistent means of calculating λ_0 were provided, since otherwise the hydrodynamic properties become theoretically indeterminate in magnitude. Some further comments of their dynamical RG calculations are given in Appendix A. The following subsection investigates an alternative "internal viscosity" model suggested to us by some comments made by Fixman on the nature of friction in polymer chains.

C. Other Limitations of Current Hydrodynamic Models. Recent studies indicate inadequacies in treating the solvent as a continuum which mediates the polymer–polymer hydrodynamic interactions as if the chain were a macroscopic object. Stepto et al.[45] argue that elaborate generalizations of continuum hydrodynamic models are not justified given the crudeness of the continuum hypothesis, and they argue that emphasis should rather be placed on understanding the variations of hydrodynamic parameters, such as the bead friction coefficient ζ, in terms of molecular parameters emerging from the simpler available hydrodynamic models.

Inconsistencies are known to arise in applying bead models to small-molecule fluids, and attempts to improve upon these hydrodynamic models are given in a series of papers by Zwanzig and co-workers[46] and by Wolynes and Deutch.[47] These authors suggest that a "slip" boundary condition should be applied to the beads rather than a "stick" boundary condition. It is of historical interest that Onsager[2] originally suggested the need for employing "slip" boundary conditions to polymer chains, while Burgers provided a rough estimate of the rod friction coefficient with boundary conditions intermediate between "slip" and "stick".[48] Extensive experimental evidence on small molecules indicates that "slip" boundary conditions provide a better idealization in computing molecular friction coefficients from hydrodynamic models.[49] Mode-coupling calculations by Masters and Madden[50] demonstrate a relation between hydrodynamic boundary conditions ("slip" and "stick") and the pair potential and thus provide a theoretical basis for interpreting molecular transport properties in terms of mixed boundary conditions. Computed transport properties of slender bodies are very sensitive to hydrodynamic boundary conditions, and this may be important in interpreting molecular variations of the "bead" friction coefficient.[2,48] Evidently, the details of the polymer–solvent interaction can significantly affect the magnitude of the molecular friction coefficient. Observed variations in the "bead" friction coefficient with solvent for a given polymer (see below) accord with this expectation.[45]

Although we can relate the model parameters z_2 and h of the KR model to simulations for hydrodynamic properties of polymer solutions based on the bead model, the comparison of the KR theory to experiment is problematic because of the many idealizations implicit in this model (modeling chain segments by "beads", the rigid-body approximation, etc.). Moreover, the dynamical RG calculations are rather crude at the present stage. Basically, all hydrodynamic models of polymer friction coefficient are equivalent to $O(\epsilon)$, and preaveraging does not even enter for the friction coefficient f until second order.[28] Third-order calculations in ϵ are the minimal necessary for determining the predominant excluded volume contributions required to evaluate prefactors for f. The ϵ-expansions are generally asymptotic, and the meaning of high-order calculations is questionable, even if it were feasible to perform them.

The greatest difficulties lie with the *configurational preaveraging* approximation.[25–29] Gaussian chains exhibit large fluctuations in the friction coefficient arising from large size fluctuations of the chains.[51] The KR and Debye–Bueche theories implicitly assume that the friction is governed by "typical" (most probable) chain configurations. Rarer more or less compact configurations, having lower or much higher friction, respectively, can give a disproportionate contribution to the *average* friction. These friction fluctuations limit the accuracy of the mean-field "preaveraging" calculations of KR[10] and Debye–Bueche.[39] The magnitude of the fluctuation errors is strongly dependent on polymer excluded volume,[28,51] a natural consequence of the fact that increased chain expansion reduces the hydrodynamic screening within the chain. A quantitative theory describing the excluded volume dependence of the preaveraging corrections is required for a reasonably accurate theory of the hydrodynamics of polymers in dilute solution. Such an analytic theory does not yet exist.

3. Molecular Friction in Polymers and Small Molecules

A. Hydrodynamic Interaction in Low Molecular Weight Polymers. A comparison of the Kirkwood formula (2.12) for the translational friction coefficient to the diffusion coefficient data of normal alkanes[52] in a variety of solvents indicates an experimental range in which the "free-draining" contribution ($f \sim n\zeta$) to the friction f predominates. However, if the analysis of these polymer–solvent systems takes the assumption of a Stokes friction $\zeta = 6\pi\eta a$ where the bead size a is on the order of a (–CH$_2$–) van der Waals radius ($\approx$2 Å), then the "free-draining" friction is predicted to be significantly smaller (by roughly a factor of 3) than observed for n-alkanes in various solvents (benzene, decalin, tetralin, n-heptane, CCl$_4$). Moreover, the experimental estimates of ζ obtained by equating $f = n\zeta$ to the observed friction show a variation with solvent. Hence, the detailed polymer–solvent hydrodynamic interactions influence the magnitude of ζ. Debye and Bueche[39] long ago indicated the inadequacy of applying Stokes law to the single monomer to estimate ζ in the KR theory.

Stepto et al.[45] present a series of studies on how the solvent and chain length affect the friction coefficient of polymers. Their work considers a homologous series of carefully prepared low molecular weight polymers in a variety of solvents. The most complete studies involve poly(methylene) in the solvents CCl$_4$, benzene, tetralin, quinoline, and decalin. An approach to the "nondraining" limiting behavior is observed at low molecular weights where the friction coefficient ζ is *defined* empirically from the Kirkwood expression (2.12). Stepto et al.[45] observed that this empirical ζ is smaller for solvents having a larger molar volume or higher viscosity. It is evidently difficult to rationalize these observations in terms of a simple hydrodynamic model of friction, and we return to these questions in the next subsection.

B. "Nonuniversality" in Macroscopic Hydrodynamics. Nonuniversality is also observed in the relation between translational friction and object "size" for macroscopic objects, and simple exactly solvable models provide important insights into the corresponding nonuniversal relation observed between polymer friction f and polymer size $\langle \mathbf{R}^2 \rangle^{1/2}$. To illustrate this point, we recall the well-known expression for the friction on a macroscopic spherical droplet with viscosity η_{droplet} and radius R moving in a liquid of viscosity η_s,[53–55]

$$f = (4\pi\eta_s)R[1 + (1/2)z_\eta/(1 + z_\eta)], \qquad z_\eta = \eta_{\text{droplet}}/\eta_s \quad (3.1)$$

(Considerations of surface tension limit the validity of this relation to a range of droplet sizes[56]). The friction experienced by the droplet is seen to depend on the "relative fluidity" z_η between the inside and the outside of the droplet. The Stokes law relation $f = 6\pi\eta_s R$ between the friction and droplet radius emerges only in the limit of a very viscous droplet ($z_\eta \rightarrow \infty$) relative to the solvent medium. Otherwise, the friction is reduced from the "rigid sphere" limit value by the internal circulations within the droplet which are induced by its motion.

Fixman has discussed the nonuniversality of the observed relation between f and $\langle \mathbf{R}^2 \rangle_0^{1/2}$ in flexible polymers and noted that ... "the polymer chain behaves more like an oil drop with a limited amount of internal circulation"....[57] Fixman also suggests that large fluctuations in chain configurations could produce a situation in which the polymer diffuses like an effective sphere with varying degrees of "solvent slippage".[13] A theoretical treatment for a sphere of radius R with a variable tangential surface friction ζ_s again leads to the crossover form of (3.1), where z_η is replaced by the dimensionless "slip parameter" $(\zeta_s/3\eta_s)R$. Although the magnitude of the friction coefficient depends on z_η or the surface friction, some regularity appears in the range of values for the friction versus radius R relation. The proportionality factor for the sphere friction lies in the range 4π and 6π for $d = 3$. This situation is apparently similar to that for polymers in dilute solution.

C. "Liquid Droplet Model" for Polymers. We now adopt an idealized "liquid droplet model" for a polymer chain and compare this model to both the KR theory and experimental data. The model is meant to be only illustrative for the present. Taking the size of a polymer "droplet" to be equal to the chain radius of gyration $\langle S^2 \rangle^{1/2}$ gives a simple estimate of the friction coefficient f of a polymer chain in a dilute solution,

$$f(\text{droplet}) = 4\pi\eta_s\langle S^2 \rangle^{1/2}[1 + (1/2)z_\eta/(1 + z_\eta)] \quad (3.2)$$

The parameter z_η measures the chain mobility relative to that of solvent. It is possible to invent specific models for z_η (e.g., the ratio of monomer to solvent viscosities), but the crudeness of the model does not warrant developing such details presently. Thus, we pass on to a discussion of limiting behaviors from this model, where z_η is an unspecified measure of the relative mobility of the chain segments and the solvent molecules.

When $z_\eta \rightarrow 0^+$, the friction coefficient f(droplet) in (2.11a) reduces to a simple scaling with the radius,

$$f(\text{droplet}) = 4\pi\eta_s\langle S^2 \rangle^{1/2} \equiv 12.57\eta_s\langle S^2 \rangle^{1/2} \quad (3.3a)$$

which is compared to the first-order RG estimate [see (2.12)],

$$f_{\text{RG}}(\text{preaveraged}) = 12.53\eta_s\langle S^2 \rangle^{1/2} \quad (3.3b)$$

Equation 3.3 also corresponds to the original Kirkwood estimate[10] of f. The analog of the prefactor in (3.3) from the preaveraged KR (see eq 2.7) and the Rouse–Zimm[11] theories is 12.74, which is less than a 2% discrepancy. The droplet model represents the ideal random coil as comparable to a bubble having low viscosity relative to the surrounding medium ($z_\eta \approx 0$). Increasing the viscosity of the droplet leads to a larger friction coefficient and to a *range* of values for f which can be compared with observations on real polymers. The polymer droplet model, for example, provides an estimate for the range of values obtained for the ratio ρ of the hydrodynamic radius R_{H} ($f \equiv 6\pi\eta_s R_{\text{H}}$) to the radius of gyration as

$$\rho \equiv \langle S^2 \rangle^{1/2}/R_{\text{H}} = (3/2)/[1 + (1/2)z_\eta/(1 + z_\eta)] \quad (3.4)$$

The polymer droplet model then indicates that ρ lies in the interval (1, 3/2) as z_η ranges from 0 to ∞. Experimental measurements of ρ for Θ solutions cluster in the range (1.16, 1.3).[58] The KR double-sum estimate[10] of $\rho = 8/3\pi^{1/2} \approx 1.50$ lies at the upper end of this range. The representative experimental value $\rho \approx 1.2$ corresponds to $z_\eta \approx 1$ and thus to a similar mobility for both the solvent and chain. Thus, there seems to be some merit to Fixman's suggestion that the internal chain viscosity might be responsible for some of the observed nonuniversality in experimental friction coefficients. The idealized model of a polymer chain as an "oil drop" is probably more faithful to reality than treating the polymer as an effective hard sphere.

The polymer droplet model also gives reasonable estimates for the observed intrinsic viscosity range. Taylor[59] calculates the intrinsic viscosity of a spherical droplet, and his result can also be expressed in terms of the relative fluidity z_η,

$$[\eta] = [1 + (3/2)z_\eta/(1 + z_\eta)](N_A V/M) \tag{3.5}$$

where V is the particle's average volume, M is its molecular weight, and N_A is Avogadro's number. The factor $(N_A V/M)$ is replaced by unity when volume fraction concentration units are employed. Taking the spherical polymer droplet volume as $V = 4\pi\ \langle S^2\rangle^{3/2}/3$ and $\langle S^2\rangle \approx \langle \mathbf{R}^2\rangle/6$ implies that (2.13) is converted to

$$[\eta] = \Phi(z_\eta)\langle \mathbf{R}^2\rangle^{3/2}/M \tag{3.6a}$$

$$\Phi(z_\eta) = [1 + (3/2)z_\eta/(1 + z_\eta)](4\pi/3)6^{-3/2}N_A \tag{3.6b}$$

The polymer droplet model yields a Flory constant $\Phi(z_\eta)$ in (3.6c) which lies in the interval $(1.72 \times 10^{23}, 4.29 \times 10^{23})$. A value of $z_\eta \approx 0.5 \sim O(1)$ yields an estimate of Φ which equals the commonly cited value $\Phi_0 = 2.58 \times 10^{23}$ for Θ point solutions of high molecular weight flexible polymers.[60] This choice of z_η is qualitatively consistent with the polymer droplet estimate of z_η from f data.

For completeness we also mention the leading concentration virial k_D for the cooperative diffusion coefficient of a liquid droplet with a short-range attractive ("sticking") interaction,

$$k_D = 4(\psi/\psi^*) - [1 + (3/2)z_\eta/(1 + z_\eta)] \tag{3.7a}$$

which was recently estimated by Kholodenko and Douglas.[61] The ratio (ψ/ψ^*) is a dimensionless osmotic second virial coefficient, which ranges between unity in a "good solvent" and zero in a Θ solvent, and k_D reduces to 3/2 for a hard sphere suspension in a good solvent. Now if we take the polymer droplet to have the same viscosity as the surrounding medium ($z_\eta \approx 1$), as suggested from the previous estimates, we have

$$k_D(z_\eta \approx 1) = 4(\psi/\psi^*) - 7/4 \tag{3.7b}$$

which ranges from 9/4 in a good solvent to −7/4 in a Θ solvent. These predictions seem consistent with measurements on flexible polymer solutions.[62,63] We mention that RG calculations by Oono et al.[64] predict that $k_D = 0$ for θ point polymer solutions, in conflict with observations.[62,63] The main point of introducing the droplet model is to illustrate the qualitative dependence of polymer hydrodynamic properties on the relative mobility of the solvent and the polymer "droplets".

D. Recent Attempts To Estimate the Stokes Friction of Molecules. The problem of estimating ζ from molecular parameters is not restricted to polymers. Careful experiments attempting to relate ζ to molecular size have been available since the 1930s. Kuhn and Kuhn,[65] for example, note that the translation friction coefficients of small molecules (N_2, O_2, CO_2) are about two-thirds the value predicted by using the Stokes law for spheres having their respective van der Waals radii, a commonly observed phenomenon which is consistent with arguments mentioned above for a "slip" boundary condition. More recent molecular dynamics studies by Alder et al.[66] for hard sphere fluids and experimental studies of Parkhurst and Jonas[67] give friction coefficients of small molecules which correspond to a mixed "slip–stick" boundary condition. Much of the data apparently conform to the "slip" extreme.

There are many interesting rationalizations for the variation of the proportionality constant between the translational friction and the radius of a small molecule. Glasstone et al.[68a] and Sutherland[68b] emphasize the differences between the dynamical motions of diffusing particles moving through a fluid of smaller particles and their diffusion through a fluid of particles having comparable dimensions. These arguments provide a crude account of variations from "slip-like" to "stick-like" diffusion of small molecules. Zwanzig and Harrison[69] discuss variations of hydrodynamic boundary conditions in terms of the efficiency for momentum transport by small molecules to the surrounding fluid. The efficiency of the momentum transport is affected by a coupling of solute and solvent motions and the effective bead size is interpreted as being analogous to a scattering length.[69,70] Mode-coupling calculations[50] have elaborated upon the role of the solute–solvent pair interactions in determining the effective hydrodynamic boundary conditions. All these arguments are very interesting, but the ultimate goal of making molecular predictions for the translational friction coefficient remains elusive. Perhaps the most challenging finding to be explained by theory is the observation of *negative intrinsic viscosities* in short alkanes and other polymers in various solvents.[49c]

Pastor and Karplus[71] review various models for estimating ζ for small molecules, and they introduce a remarkably simple "effective accessible surface area" (ASA) model for estimating molecular friction. The ASA model computes the molecular friction coefficient as $\zeta = 6\pi\sigma_{\mathrm{ASA}}$, where the effective radius σ_{ASA} is defined in terms of the "molecular surface area" A_e as $\sigma_{\mathrm{ASA}} = (A_e/4\pi)^{1/2}$. (Appendix B summarizes recent work by Hubbard and Douglas[70] which provides some theoretical justification for the ASA model.) This ASA method cleverly accounts for the granularity of the solvent by considering the area exposed to the solvent to define A_e. Smaller solvent molecules encounter a larger area of the diffusing molecule than larger solvent molecules. Numerical methods for estimating A_e, given molecular dimensions of the solute, have been developed to compute A_e for proteins.[72] These methods have been adapted by Pastor and Karplus[71] and by Venable and Pastor[73] for estimating the molecular friction coefficients, and reasonable translational diffusion coefficients are obtained from this geometrical argument—an interpretation of the friction coefficient variations which is quite distinct from the slip hypothesis.

Reliable estimates of ζ are necessary in extending the Rouse–Zimm model to describe the dynamics of complicated protein and polymer molecules[74a] and, of course, in making molecular predictions of the friction coefficient for long polymers. Work is currently in progress to refine the hydrodynamic description of the monomer subunits within a generalized Rouse–Zimm type model of protein and polymer dynamics.[74] Recent parameter-free tests of the generalized Rouse model for united atom models of alkane dynamics[74b] pave the way for improving the polymer hydrodynamic theory to a point where predictive estimates of molecular friction should be possible.

4. Conclusion

Attempts at describing the polymer, solvent, temperature, and molecular weight dependence of the intrinsic viscosity have stimulated the development of many of our fundamental models for polymer structure and dynamics. Aspects of polymer dynamics remain unexplained and remain active areas of research. One such outstanding problem involves providing a description of the degree to which solvent "penetrates" through the polymer coil as the chain dimensions swell with increased excluded volume interactions. This "partial draining" phenomenon is important not only for the intrinsic viscosity at infinite dilution but it is also basic to treating dynamical polymer properties at semidilute concentrations.

Hydrodynamic properties of polymer solutions reflect a delicate interplay between hydrodynamic and excluded volume interactions. Hydrodynamic interactions generally weaken with chain expansion, and this phenomenon can be appreciated by considering the extreme cases of rodlike polymers in $d = 3$ dimensions and random coils in $d = 4$ dimensions. In each of these examples the hydrodynamic interactions are weak because of the low monomer density. Indeed, renormalization group theory shows that these dimensions are "critical" for these structures, so that only weak logarithmic corrections to the ideal "free-draining" theory are obtained. The ϵ-perturbative theory is naturally developed about these critical dimensions where the hydrodynamic interactions are weak. Random coil polymers in $d = 3$ dimensions, on the other hand, exhibit significant hydrodynamic interactions ("screening") and behave roughly as "impermeable spheres" having dimensions on the order of the chain radius of gyration.

Swollen coils exhibit a degree of "screening" intermediate between random coil and rodlike polymers. The decrease of hydrodynamic interactions with swelling in flexible polymers is illustrated with the idealized Kirkwood–Riseman[10] and Debye–Bueche[39] hydrodynamic models. Excluded volume interactions in the cited KR model calculations are modeled by the two-parameter theory in conjunction with dynamical renormalization group methods, and the calculations are restricted to leading order in ϵ-perturbation theory.[28] Despite the limitations of these model calculations, a consistent picture of decreased hydrodynamic screening with chain swelling is found, demonstrating the universality of the effect.

Fixman[13a,27] has recently suggested that the dynamic flexibility of the chain could be important for the hydrodynamic properties of polymer solutions. We examine this possibility using a very simple "liquid droplet model" of polymer chains in solution. Comparison of this model to observations on polymer solutions leads to surprising agreement, suggesting that the influence of dynamic chain flexibility on solution properties deserves further serious consideration.

These observations on the polymer liquid drop model also suggest that the preaveraging approximation of the KR theory might have a *physical* as well as a mathematical interpretation. The deviations from the preaveraged KR theory are associated with rare chain configurations with high friction which give a disproportionate weight to the true average friction.[51] Increased chain mobility allows these rare configurations to quickly relax, thereby making the mean-field "preaveraging" approximation a better approximation.[51] Indeed, the second-order ϵ-expansion calculation of chain friction in the (dynamically flexible chain) Rouse–Zimm model by Wang et al. leads to *no preaveraging error*.[28b] This result, whose physical significance was previously unclear to us, is contrasted with the large preaveraging error predicted by the rigid-body KR theory for the friction coefficient of a random coil.[28a] The extent of the "preaveraging error" could well depend on the degree of dynamic chain rigidity—a very interesting possibility.

Although there is evidence of a crossover between "free-draining" and "nondraining" hydrodynamic limits (see Appendix C) in the friction coefficient of dilute polymer solutions,[52] it is difficult to realistically estimate hydrodynamic parameters such as the monomer friction[52] ζ and the binary cluster integral[60] β_2 from molecular information. In response to this fundamental problem we examine hydrodynamic data for low molecular weight polymers and small-molecule tracer particles to outline some of the theoretical issues which require resolution before prediction of hydrodynamic solution properties in terms of molecular parameters is possible. Further careful studies for the variation of the monomer friction coefficient in solution are necessary to refine the hydrodynamic modeling of polymer solutions. The detailed modeling of chain dynamics with the generalized Rouse–Zimm model seems to provide an obvious place to begin.[74a] An increased understanding of the nature of chain friction in the dilute regime is also essential in developing a more realistic description of polymer solutions at higher concentrations. Recent studies of polymer friction in solution[74c] provide invaluable information which should be useful for improving hydrodynamic modeling of polymer solutions, and further theoretical developments based on this information are needed.

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Appendix A. Rescaling the Mode-Coupling Parameter

The analogy with treatments of critical dynamics has led Oono and Freed[75] and Oono[76] to suggest a kinetic model of polymer dynamics described by the equations

$$\frac{\partial c(\tau,t)}{\partial t} = -\zeta_0^{-1}\frac{\delta H\{c\}}{\delta c(\tau,t)} + \lambda_0\int \mathrm{d}\mathbf{r}\,\mathbf{u}(\mathbf{r},t)\,\delta[\mathbf{r}-\mathbf{c}(\tau,t)] + f_c(\tau,t) \tag{A.1}$$

$$\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} = \mathbf{T}\cdot\left[\eta_{\mathrm{e}}\nabla^2\mathbf{u}(\mathbf{r},t) - \lambda_0\int \mathrm{d}\tau\,\frac{\delta H\{c\}}{\delta \mathbf{c}(\tau,t)}\delta[\mathbf{r}-\mathbf{c}(\tau,t)] + f_{\mathbf{u}}\right] \tag{A.2}$$

where $\mathbf{c}(\tau,\mathrm{t})$ designates the position at time t for the polymer segment at a contour distance τ along the continuous chain of length N_0, $\mathbf{u}(\mathbf{r},\mathrm{t})$ is the solvent velocity field at the spatial position r, ζ_0 is the bare friction coefficient per unit chain length, η_e is the "local" solvent viscosity, the f's are Gaussian random forces that are provided below, and H is the Edwards continuous chain Hamiltonian,

$$H\{c\} = \frac{1}{2}\int_0^{N_0}\mathrm{d}\tau\left[\frac{\mathrm{d}\mathbf{c}(\tau)}{\mathrm{d}\tau}\right]^2 + \frac{\upsilon_0}{2}\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\sigma\,\delta[\mathbf{c}(\tau)-\mathbf{c}(\sigma)] \tag{A.3}$$

with υ_0 the bare excluded volume parameter. The solution is assumed to be incompressible, and T in eq A.2 operates on the transverse part of the vector field. (A compressible fluid has additional longitudinal hydrodynamic interactions.[77]) The units in A.1–A.3 are scaled to remove dimensional quantities, such as the Kuhn segment length. We now shown that the "mode-coupling" parameter λ_0, appended by Shiwa and Oono[41] to the kinetic equations A.1–A.3, is a similar removable scale parameter.

It is clear that the limit $\lambda_0 \to 0^+$ eliminates the frictional coupling to the solvent velocity field $\mathbf{u}(\mathbf{r},t)$ and thereby recovers the "free-draining" limit and that λ_0 is constrained to be positive to ensure positive frictional forces.[41] Shiwa and Oono deduced these results from their RG computations but these results follow directly from the kinetic equations (A.1) and (A.2). We next consider a set of scale transformations of the kinetic equations,

$$\mathbf{c}(\tau,t) = \lambda_0^{2/(d-2)}\mathbf{c}'(\tau',t') \tag{A.4}$$

$$t = \lambda_0^{4/(d-2)}t' \tag{A.5}$$

$$\zeta_0 = \lambda_0^{-4/(d-2)}\zeta_0' \tag{A.6}$$

$$\mathbf{u}(\mathbf{r},t) = \lambda_0^{-d/(d-2)}\mathbf{u}'(\mathbf{r}',t') \tag{A.7}$$

$$\mathbf{r} = \lambda_0^{2/(d-2)}\mathbf{r}' \tag{A.8}$$

$$\tau = \lambda_0^{4/(d-2)}\tau' \tag{A.9}$$

$$v_0 = \lambda_0^{2(d-6)/(d-2)}v_0' \tag{A.10}$$

which converts eqs A.1 and A.2 to identical forms in terms of the primed variables, except that λ_0 is now absent. The transformation A.4–A.10 also preserves the spectrum of the random forces such that

$$f'_{\mathbf{c}'}(\tau',t') = \lambda_0^{2/(d-2)}f_{\mathbf{c}}(\tau,t) \tag{A.11}$$

$$f'_{\mathbf{u}'}(\mathbf{r}',t') = f_{\mathbf{u}}(\mathbf{r},t) \tag{A.12}$$

has the original spectrum

$$\langle f'_{\mathbf{c}'}(\tau',t')f'_{\mathbf{c}'}(\sigma',s')\rangle = 2\zeta_0^{-1}\mathbf{I}\delta(\tau'-\sigma')\delta(\tau'-s') \tag{A.13}$$

$$\langle f'_{\mathbf{u}'}(\mathbf{r}',t')f_{\mathbf{u}'}(\mathbf{p}',s')\rangle = -2\eta_e\nabla^2\mathbf{I}\delta(\mathbf{r}'-\mathbf{p}')\delta(t'-s') \tag{A.14}$$

in the scaled variables, where $\mathbf{I}$ is the unit tensor. This completes the proof that the Shiwa–Oono parameter λ_0 is a (RG "irrelevant") scale factor.

The above situation is directly analogous to the well-known fact in φ^4 field theories that the parameter b, which multiplies the square gradient term in the free energy functional, can be removed by a scale transformation and so the parameter b introduces no new physics. Of course, we require $b > 0$ just as $\lambda_0 > 0$ is necessary in the Shiwa–Oono theory.

Apart from the quantitative limitations of the dynamical RG calculation scheme, we respond to some misleading statements by Oono and Kohmoto.[34,35] These authors retain only a portion of the second order in ϵ contributions to their hydrodynamic properties,[23] and they concluded on the basis of these *faulty* calculations that the KR theory for the friction coefficient f is unaffected by preaveraging. Such a conclusion is in stark contrast to the 13% preaveraging error estimated by Zimm in his simulations of f based on the KR model.[25] A correct second order in ϵ RG calculation[28] yields a large preaveraging error for f in the KR RG theory. Equation 2.9 demonstrates the large (27%) ϵ-expansion error incurred by applying the re-exponentiation methods of Oono et al. to the exactly solvable preaveraged KR theory.[23] Since Oono and coworkers apply the same re-exponentiation method in all their dynamical RG calculations, it would evidently be a mistake to identify experimental agreement of these crude calculations with an improved physical description of polymer solution hydrodynamics. Oono and Kohmoto[34,35] further make incorrect statements that the KR theory for Gaussian chain hydrodynamic properties *does not depend on hydrodynamic interactions* despite mathematical proofs to the contrary based on the exactly solvable preaveraging KR model. They also state that the dimensionless interactions (z_2, h) have "no direct microscopic meaning" and that all theories expressed in these variables are "conceptually wrong". We feel some obligation to respond to these statements condemning all conventional calculations of the hydrodynamic properties of polymer solutions (see Appendix D).

Appendix B. Comment on the Effective Surface Analogy

The success of the "accessible surface model" can be understood, in part, from recent calculations by Hubbard and Douglas[70] which show that the translational friction f on a body of arbitrary shape undergoing Brownian motion is *approximated* by

$$f \approx 6\pi\eta_s C \tag{B.1}$$

where C is the capacity of the body. The units of C are chosen so that a sphere of radius R has the capacity $C = R$. Equation B.1 thus reduces for a sphere to Stokes law. The derivation of (B.1) assumes angular preaveraging which is a minor approximation $O(1\%)$ relative to configurational preaveraging which leads to errors on the order of 10% for random coil polymers.

Although the analytic calculation of C is much easier than that for the friction coefficient f, the calculation of C is not a trivial matter. There are simple approximations for C, however, which are applicable provided the body is not too elongated or flattened. A perturbative calculation[78] of C of an ellipsoid in terms of a spherical harmonic expansion about the spherical limit yields a simple approximation,[79]

$$C \approx (A/4\pi)^{1/2} \quad \text{(Russell approximation)} \tag{B.2}$$

where A is the surface area of the particle. This approximation is discussed by Russell,[79] but is probably has a much earlier origin. Rayleigh[80] develops a similar perturbative expansion for an elliptic disk and arrives at an approximation for the capacity of flat bodies,

$$C(\text{flat}) \approx (2/\pi)(A/\pi)^{1/2} \quad \text{(Rayleigh approximation)} \tag{B.3}$$

Equation B.3 is constructed so that equality is obtained for the circular disk. The combination of (B.1) and (B.2) yields the basic relation of the "effective surface model",

$$f \approx 6\pi\eta_s(A/4\pi)^{1/2} \tag{B.4}$$

A leading-order perturbative calculation of f by Brenner[81] employs an expansion about the sphere limit and also produces (B.4) to leading order in perturbation theory. The combination of (B.1) and (B.3) should provide useful estimates of f for platelet-shaped objects (e.g., membranes).

We also mention that C is proportional to the Smoluchowski rate constant k_s for diffusion-limited reactions.[82] Since k_s is a primary parameter in many biological processes, substantial efforts have been made to develop efficient Brownian dynamics algorithms for calculating C.[83] These programs can be applied directly to the calculation of C for arbitrarily-shaped objects,[45] making relation B.1 very useful.

Appendix C. "Ginzburg Criterion" for Hydrodynamic Interaction

The terms "draining" and "nondraining" are often used rather loosely to indicate the regimes where hydrodynamic interactions are weak and strong, respectively. However, confusion occurs when the terms are interpreted literally. "Nondraining" certainly does not imply that the solvent field is entirely excluded from the interior coil, and this point has recently been emphasized by Mulderije and Jalink.[84]

The crossover function (2.1) allows for a precise specification of the "draining" and "nondraining" regimes in terms of the dimensionless hydrodynamic interaction z_H (or h). The "weak coupling" or "draining" regime for Gaussian chains is limited to the interaction range [radius of convergence in (2.2)],

$$h \le h^* \approx \epsilon/4 \quad (\text{"draining" regime}) \tag{C.1}$$

which is an analog of the Ginzburg criterion for describing the breakdown of mean-field theory in phase-separating systems.[85] There is also a condition for "strong coupling" or "nondraining",

$$h \ge 10h^* \quad (\text{"nondraining" regime}) \tag{C.2}$$

The condition $h \sim 10h^*$ in (C.2) means that the dimensionless crossover function u_H has approached 90% of its asymptotic "fixed-point" value [see (2.3)].

The corresponding criteria for delineating "poor" and "good" solvent regimes are given by Douglas and Freed[86,87] and Dudowicz et al.[88] These regimes are simply specified in terms of the excluded volume interaction z_2,

$$|z_2| < u_2^* \quad (\text{"poor" solvent}) \tag{C.3}$$

$$|z_2| \ge 10u_2^* \quad (\text{"good" solvent}) \tag{C.4}$$

Dudowicz et al.[88] also discuss the corresponding critical phenomena problem of specifying the magnitude of the reduced temperature $\tau = (T - T_c)/T$ at which mean-field theory becomes inaccurate ("weak coupling regime") and the onset of the critical regime ("strong coupling regime") where nonclassical critical scaling of scattering properties is exhibited. The mathematical criteria describing the "weak coupling", "crossover", and "strong coupling" regimes are of the same form in these and many other problems.

Appendix D. Physical Interpretation and Determination of *h* and *z*₂

Large-scale hydrodynamic solution properties may be calculated from the KR and RZ theories in conjunction with the two-parameter model of excluded volume. The hydrodynamic properties emerge as functions of the radius of gyration $\langle S^2\rangle^{1/2}$, and the hydrodynamic h and excluded volume z_2 variables (see eqs 2.1 and 2.8). We discuss the physical interpretation of these variables.

The hydrodynamic interaction variable h is the dimensionless ratio of the total friction $f \sim n\zeta$ from the chain elements, when separated to great distances, to the friction of a sphere[70] having the same average dimensions as the polymer chain,

$$2^\phi h = n\zeta/f_{\text{sphere}}, \qquad \phi = \epsilon/2 \tag{D.1}$$

$$f_{\text{sphere}} \equiv [d/(d-1)]H(d)\eta_s\bar{R}^{d-2}, \qquad H(d) = 4\pi^{d/2}/\Gamma(d/2-1) \tag{D.2}$$

Equation D.2 corresponds to Stokes law for an "effective sphere" having the average chain dimensions R defined as

$$\bar{R}^{-(d-2)} \equiv \langle|\mathbf{R}|^{-(d-2)}\rangle_0 = [(d/2\langle\mathbf{R}^2\rangle_0]^{(d-2)/2}/\Gamma(d/2) \tag{D.3}$$

The configurational averages correspond to Gaussian chains. Other choices of the average radius are possible (differing by a constant of proportionality), but this does not alter the physical definition of h or related parameters. For example, Kirkwood[10] denotes the variable $2^\phi h$ by X, and other convenient choices (see eq 2.10) are possible.

The excluded volume interaction z_2 also has a direct physical interpretation. The excluded volume between the independent segments equals $(n^2\beta_2/2)$ when the segments are dilute, where β_2 is the binary cluster integral familiar from the theory of nonideal gases. Similarly, the "average volume" of an effective chain sphere V_{sphere} is well defined,

$$V_{\text{sphere}} \equiv [\pi^{d/2}/\Gamma(1+d/2)]\ \langle|\mathbf{R}|^d\rangle_0 \tag{D.4}$$

The dimensionless excluded volume parameter z_2 is just the ratio of these volumes,

$$z_2 = B(d)n^2\beta_2/2V_{\text{sphere}} = (d/2\pi l^2)^{d/2}\beta_2 n^\phi \tag{D.5a}$$

$$B(d) = \Gamma(1+d)/\Gamma^2(1+d/2) \tag{D.5b}$$

Both h and z_2 are represented in terms of well-defined physical variables. Descriptions of real polymer chains, however, involve many complications. The application of hydrodynamics to segments on the scale of a monomer is questionable, and many-body interactions renormalize[20] the binary cluster integral β_2 in (D.5) so that direct molecular estimation of these parameters becomes problematic.

The direct physical significance of z_2 and h can also be appreciated by relating these parameters to measured properties of polymer solutions. Dynamic light scattering methods allow the determination of the chain diffusion coefficient and thus the chain friction $f_{\text{polymer}} = 6\pi\eta_s R_H$, and the radius of gyration $\langle S^2\rangle^{1/2}$ can be determined from static scattering measurements. We then form the ratio corresponding to (D.1) for Gaussian chains, but with the total polymer friction f_{polymer} replacing $n\zeta$,

$$2^\phi\Psi_H \equiv f_{\text{polymer}}/f_{\text{sphere}} \tag{D.6a}$$

where f_{sphere} is defined in (D.2). The definition (D.6a) implies

$$\Psi_H = h + O(h^2), \qquad h \lesssim h^* \tag{D.6b}$$

corresponding to weak hydrodynamic interactions.

The renormalization group (RG) method involves the study of functions such as (D.6b) under variation of the argument h. The existence of a RG fixed point ensures the existence of the limit $\Psi_H(h \rightarrow \infty) = \Psi_H^* = h^*$ [see (2.10)], and the RG method guides the resummation of the perturbative series of the form (D.6b), so that the correct limiting behavior is obtained for $h \rightarrow 0^+$ and $h \rightarrow \infty$. To first order in ϵ the calculation of Ψ_H amounts to a simple Euler transform of the leading-order correction to (D.6b),

$$\Psi_H = h^*(h/h^*)/(1 + h/h^*) + O(\epsilon^2), \qquad z_2 = 0 \quad \text{(D.7)}$$

recovering the original Kirkwood approximation[10] eq (2.12) in $d = 3$.

The description of polymer excluded volume is entirely analogous. The "penetration function" Ψ is defined as the ratio of the observed osmotic second virial coefficient A_2M^2 divided by an average volume V_{sphere}. If we define the dimensionless virial coefficient such that $\Psi \propto A_2M^2/V_{\text{sphere}}$ and $\Psi = z_2 + O(z_2^2)$, then the RG analysis is identical to the hydrodynamic analog of (D.7) and yields[86]

$$\Psi(z_2) = \Psi^*(z_2/u_2^*)/(1 + z_2/u_2^*) + O(\epsilon^2) \quad \text{(D.8a)}$$

$$\Psi^* = u_2^* = \epsilon/8 + O(\epsilon^2) \quad \text{(D.8b)}$$

The second-order estimate of Ψ^* equals[86,87]

$$\Psi^* = \epsilon/8 + (77/12 + 4 \ln 2)(\epsilon/8)^2 + O(\epsilon^3), \qquad \Psi^*(d{=}3) = 0.269 \quad \text{(D.8c)}$$

Equation D.8 provides a direct means of estimating the dimensionless excluded volume interaction z_2 from the measured osmotic penetration function Ψ. This and higher order estimates are limited by the accuracy of computing the functional dependence Ψ on excluded volume and the faithfulness of the continuous Gaussian chain model to describe real polymers. The two-parameter model is obviously inappropriate for low molecular weight and stiff polymers.[15b,89]

Once the functional dependence of $\Psi(z_2)$ is fixed by RG methods or other resummation techniques (e.g., Borel resummation) and these results are checked against lattice two-parameter model calculations where the z_2 parameter is exactly prescribed in terms of the walk length and the lattice cell volume, then a direct inference of z_2 values from Ψ measurements is possible. (See Yamakawa[60] and the more recent discussion by Freed[85] for details.) The excluded volume interaction is certainly a physically meaningful quantity if determined with appropriate caution. This task is evidently much more difficult for hydrodynamic properties where there are two parameters z_2 and h to determine.

We finally note that the RG theory predicts a simple relation between the "hydrodynamic penetration function" Ψ_H and the "osmotic penetration function" Ψ in the limit of strong hydrodynamic interaction—a limit often assumed in comparisons with experiment. From (2.4), (2.10a), and (D.8) we obtain the closed relation

$$\Psi_H(\text{nondraining}) = h^* = (3\epsilon/16)(\Psi/\Psi^*)/[1 - (1 - \Psi/\Psi^*)^{3/4}] + O(\epsilon^2) \quad \text{(D.9a)}$$

which has the limiting Θ solvent and good solvent values

$$\Psi_H(\text{nondraining};z_2{=}0) = h_\Theta^* = 0.25 \quad \text{(D.9b)}$$

$$\Psi_H(\text{nondraining};z_2{\rightarrow}\infty) = h^*(\text{good solvent}) = 3/16 \approx 0.19 \quad \text{(D.9c)}$$

Equation D.9 gives the variation of h^* with excluded volume which should be useful in comparisons of the Rouse–Zimm model with excluded volume to experiments in "good" and "marginal" solvents. Of course, h^* in (D.9a) is *not equivalent* to the adjustable parameter h^*_{emp} obtained by fitting the Gaussian chain theory to experiments on dilute polymer solutions in good solvents. It is possible, however, to relate h^*_{emp} to h^* in the leading-order ϵ-expansion ("nondraining" limit),

$$h^*_{\text{emp}} = h^*/[\langle S^2\rangle/\langle S^2\rangle_0]^{(d-2)/2} + O(\epsilon^2) \quad \text{(D.10)}$$

where h^* is given by (D.9) and the zero subscript denotes a Θ point property. Equation D.10 specifies the commonly cited parameter h^*_{emp} in terms of radius of gyration and second virial coefficient data. We also note that (D.10) is independent of branching architecture (linear, ring, star). Osaki et al.[90] fit dilute polymer solution data in "good" and "marginal" (see Appendix C) solvents to the Gaussian chain RZ model and they find

$$h^*_{\text{emp}} \approx (0.21 \pm 0.02)/([\eta]/[\eta]_0)^{1/3} \quad \text{(D.11)}$$

in qualitative accord with the good solvent estimate of h^* in (D.9c) and (D.10) since

$$[\eta]/[\eta]_0 \approx [\langle S^2\rangle/\langle S^2\rangle_0]^{d/2} \quad \text{(D.12)}$$

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