Derivation of the Universal Scaling Equation of the Hydrodynamic Scaling Model via Renormalization Group Analysis†

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ABSTRACT: The Altenberger−Dahler positive-function renormalization group (PFRG) method is shown to yield the universal scaling equation $D_s = D_o \exp(-\alpha c^\nu)$ of the hydrodynamic scaling model for polymer self-diffusion. Here D_o is the bare polymer self-diffusion coefficient at some low concentration, c is the (potentially high) polymer concentration, and ν and α are a scaling coefficient and scaling prefactor, respectively. To integrate the Lie equations of motion of the PFRG and obtain the universal scaling equation, the Kirkwood−Risemann model for polymer hydrodynamics is extended analytically to determine leading terms of the chain−chain and (for the first time) chain−chain−chain translation−translation hydrodynamic interaction tensors $\mathbf{b}_{ij}^{(2)}$, $\mathbf{b}_{ijl}^{(3)}$, $\mathbf{T}_{ij}^{(2)}$, $\mathbf{T}_{ijl}^{(3)}$, and $\mathbf{T}_{ijkl}^{(4)}$, as well as many of their translational−rotational and rotational−rotational analogues.

Introduction

This paper presents a derivation of the universal scaling equation[1]

$$D_s = D_o \exp(-\alpha c^\nu) \tag{1}$$

for polymer self-diffusion. This equation ascribes to D_s a stretched-exponential dependence on polymer concentration c. Here D_o is the diffusion coefficient of a dilute polymer chain, and ν and α are a scaling exponent and prefactor, respectively. Phenomenologically,[2] the scaling coefficients ν and α both depend on polymer molecular weight M and solvent quality; in particular, $\alpha \sim M^{0.9\pm0.1}$.

The derivation here is based on applying the Altenberger−Dahler[3] positive-function renormalization group technique to a multichain extension of the Kirkwood−Riseman model[4] of polymer chain dynamics. As a necessary preliminary, I for the first time obtain expressions for the three- and four-chain hydrodynamic translation/rotation coupling tensors, and take a required ensemble averages over them. It is then shown (culminating in eq 70 below) that the universal scaling equation for polymer self-diffusion follows naturally from the Altenberger−Dahler positive-function renormalization group technique, as an approximant correct to a certain order in the hydrodynamic coupling parameter.

The motivation for this calculation arises from considerations on the experimental literature on dynamics of dilute and nondilute polymer solutions. In 1986, I demonstrated[1] that the bulk of the extant literature on polymer self-diffusion is consistent to high accuracy with eq 1. Examination of the literature on polymer solution viscosity η,[5,6] centrifugation coefficient s,[5] rotational diffusion coefficient D_r,[5] and dielectric relaxation time τ_r[7] finds that a stretched-exponential form with various numerical prefactors and exponents also describes η, s, D_r, and τ_r. (In a few systems,[8−10] at large c and M, the transport coefficients go over from stretched-exponential to power-law dependences on polymer concentration and molecular weight. Under careful examination, this transition in the functional form of the concentration dependence is[9,10] analytic, both η and $d\eta/dc$ being continuous at a sharp transition concentration c^+.)

An analytic derivation[11] of the stretched-exponential form for D_s and an analytic-numerical calculation[12,13] of α and ν without any free parameters have previously been presented. The earlier derivation was based on the hydrodynamic scaling model of polymer dynamics, whose major assumptions have been discussed in detail previously.[11] In summary, the model relies on three major physical assumptions, namely that, (i) in solution, polymer chains contract with increasing concentration, as seen experimentally,[14] (ii) a self-similarity assumption permits bootstrapping the calculation from low to high concentration, and (iii) in solution, polymer motions are dominated by hydrodynamic interactions between polymer chains.

Assumption iii marks the core physical difference between hydrodynamic scaling and many other models of polymer solution dynamics. In many though not all[15,16] other treatments of nondilute polymer solutions, it is assumed that topological constraints ("entanglements") between polymer chains are their dominant physical interaction, chain−chain hydrodynamic interactions serving largely to dress a bare monomer diffusion coefficient. In contrast, the hydrodynamic scaling model takes hydrodynamic interactions to be dominant, with chain crossing constraints making only second-order corrections. The objective of this paper is to replace the self-similarity assumption with a renormalization group expansion. It is not the purpose of this paper to contrast the merits of these very different physical assumptions about polymer dynamics. The above remarks are meant only to remind readers that the following calculation is informed by the hydrodynamic-scaling and not the widely used topological-chain-crossing-constraint image of polymer dynamics.

In previous derivations,[11−13] the validity of the self-similarity approximation was not explicitly demonstrated. In principle, it should be possible to validate (or disprove) this approximation with appropriate dia-

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grammatic and analytic expansions. In this paper, an alternative approach to advancing from low to high concentration is pursued, namely the use of a renormalization group expansion.

The work here has three parts, namely, (i) computation of hydrodynamic interaction tensors, (ii) ensemble average over the hydrodynamic interaction tensors, and (iii) demonstration and application of the positive-function renormalization group. An aside shows a privileged position for stretched exponentials within the PFRG. A final section discusses our results and compares them with experiment.

Multichain Hydrodynamic Interaction Tensors

The evaluation of two- and three-chain hydrodynamic interaction tensors is based on the Kirkwood−Riseman model[4] for polymers and their dynamics. In this model, a polymer chain is treated as a string of frictional points, or *beads*, the links between the frictional points being the *bonds*. In addition to the bonds, the beads interact with each other via hydrodynamic forces. In the original model, the beads were polymer monomer units, and the bonds were the actual chemical bonds linking the monomers. In many more modern models, the beads are abstracted statistical segments of a polymer chain, and the bonds linking the beads are an averaged representation of the behavior of a series of covalent bonds. This paper requires a well-defined distance of closest approach for two beads and therefore remains with the Kirkwood−Riseman physical interpretation of the bead.

The original[4] Kirkwood−Riseman model referred to the dynamics of a single polymer chain. The model was used to compute a polymer chain's diffusion coefficient and intrinsic viscosity. Interactions between different polymer chains were ignored, so the original Kirkwood−Riseman model is limited to computing dilute-solution limits for physical parameters.

In this paper, the Kirkwood−Riseman description of polymer hydrodynamics is extended to describe hydrodynamic interactions between two, three, or four polymer chains. The chain-chain interaction is a statistical average over a sum of bead−bead interchain hydrodynamic interactions. Our calculational procedure has a simple physical description as a multiple-scattering treatment of fluid motion. A first chain has initial translational and rotational velocities $\mathbf{V}^{(1)}$ and $\Omega^{(1)}$. The chain's beads move with respect to the solvent, creating a solvent flow field. The flow field acts on a nearby polymer chain, which attempts to conform to the solvent flow by translating and rotating. However, the nearby chain is unable—so long as it remains intact—to conform in all of its parts to the imposed solvent movements. The nearby chain therefore moves with respect to, and thus applies an additional force on, the solvent. The additional force creates a further (rescattered) solvent flow field that in turn acts on further polymer chains. The calculation proceeds iteratively, with rescattered flow fields impinging on additional polymer chains.

We have previously[12,13] reported a highly simplified form of this calculation, limited to couplings between the translational motions or the rotational motions of two nearby chains. These calculations focused on the ability of a chain to hinder the translation or rotation of a neighboring chain. Reference 13 explored alternative descriptions of bead−bead hydrodynamic interactions, supplementing the long-range Oseen interaction tensor with the shorter-range Rotne−Prager interaction and higher order correction terms. The higher order hydrodynamic interactions between pairs of beads make limited contributions to the chain−chain hydrodynamic interaction tensor. In contrast to these earlier calculations, the computation here (i) describes interactions between three or four chains, (ii) includes translation−rotation and rotation−translation cross-couplings, and (iii) presents a systematic approach for extending the calculation to incorporate additional chains and shorter range corrections.

This section obtains leading terms (in R^{-1}) for the two-, three-, and four-chain hydrodynamic interaction tensors $\mathbf{T}$ and $\mathbf{b}$ defined below. The notation follows Phillies and Kirkitelos.[13] The hydrodynamic interactions proceed from chain to chain by multiple scattering, chains in a scattering series being numbered 1, 2, 3, ..., etc., beginning with the initial chain. The same physical chain may appear repeatedly in a series but is given a fresh number at each appearance. The vector extending from the center of mass of polymer i to the center of mass of polymer $i + 1$ is denoted $\mathbf{R}_i$; the vector $\mathbf{r}_j$ gives the location of a chain bead j. A field vector $\mathbf{r}$ specifies a point in space with respect to the current scattering polymer. The vector from the center of mass of a chain to a bead i of that chain is $\mathbf{s}_i$; a field variable $\mathbf{s}$ denotes a vector from a chain center of mass to a nearby point at which chain beads might be located.

A chain i has center-of-mass velocity $\mathbf{V}^{(i)}$ and whole-chain rotational velocity (with respect to the center of mass) $\Omega^{(i)}$. For a chain containing M beads, $\mathbf{V}^{(i)} = \mathrm{M}^{-1} \sum_{j=1}^{M} \partial \mathbf{r}_j / \partial t$. The velocity of bead j may then be written

$$\frac{\partial \mathbf{r}_j}{\partial t} = \mathbf{V}^{(i)} + \Omega^{(i)} \times \mathbf{s}_j + \dot{\mathbf{D}}_j \tag{2}$$

where $\mathbf{D}_j$ represents the sum of internal coordinates describing bead i's location, $\dot{\mathbf{D}}_j$ being the part of the bead's velocity arising from the time dependence of the chain's internal coordinates. The internal coordinates describe short-time motions that are neglected in the following. Each chain i has a true drag coefficient f_{oi} and corresponding hydrodynamic radius R_{hi}; the chain radius of gyration is R_{gi}.

Hydrodynamic interactions between entire chains are formally described by self- and cross-interaction tensors $\mathbf{b}_{il}$ and $\mathbf{T}_{ij}$ and their multichain analogues. In particular, if an external force is applied to the beads of a freely floating chain j to give the chain a uniform translational velocity $\mathbf{V}^{(1)}$, each of the other N chains i, $i \neq j$, gains an induced velocity determined by $\mathbf{T}$, namely

$$\mathbf{v}_i = [\mathbf{T}_{ij} + \sum_{1=l\neq i,j}^{N} \mathbf{T}_{ilj} + ...]\cdot\mathbf{F}_j \tag{3}$$

$\mathbf{F}_j$ being the total force on chain j, and the ellipsis referring to four-chain and higher hydrodynamic interactions. Furthermore, the induced velocity of the original chain j is affected by the presence of other chains though the tensors $\mathbf{b}$, so that

$$\mathbf{v}_j = [\mathbf{I} + \sum_{1=l\neq i}^{N} \mathbf{b}_{jl} + \sum_{1=l,m\neq i,l\neq m}^{N} \mathbf{b}_{jlm} + ...]\cdot\mathbf{F}_j \tag{4}$$

Similar tensors describe the translation induced in a chain by applying a torque to the same or a neighboring

chain and the rotation induced in a chain by applying a force or torque to that chain or a neighboring chain.

The motion of polymer beads and polymer chains is determined by the three major forces acting on each bead, namely the hydrodynamic force coupling the motions of nearby polymer beads, the excluded-volume force forbidding polymer beads to overlap, and the bond-coupling force linking together the neighboring beads on a polymer chain.

Hydrodynamic forces appear because each bead has a frictional interaction with the solvent. If bead j moves with respect to the solvent, it applies to the solvent a force $\mathbf{F}_j = f_j(\mathbf{v}_j - \mathbf{u}(\mathbf{r}_j))$, with $\mathbf{u}$ being the unperturbed solvent velocity and $\mathbf{v}_j = \partial\mathbf{r}_j/\partial t$. Here f_j is a bead drag coefficient, which may be written $f_j = 6\,\pi\eta a_o$, η being the solvent viscosity and a_o being the bead's effective hydrodynamic radius. The force exerted on the solvent by a moving bead causes the solvent to move, producing an induced current $\mathbf{u}^{(i)}(\mathbf{r})$ responsible for the hydrodynamic interactions that couple the motions of neighboring beads. To lowest order in a_o, the induced current is described by the Oseen tensor $\mathbf{T}$

$$\mathbf{u}^{(i)}(\mathbf{r}) = \mathbf{T}\cdot\mathbf{F}_j \equiv \frac{3a_o}{4r}(\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}})\cdot\mathbf{v}_j, \tag{5}$$

in which $\mathbf{I}$ is the identity tensor, $\mathbf{r}$ is the vector from the point where the force was applied to the point of interest, $r = |\mathbf{r}|$, and $\hat{\mathbf{r}} = \mathbf{r}/r$ is the unit vector corresponding to $\mathbf{r}$. The Oseen tensor is the leading term in a power series (in a_o/r) description of $\mathbf{u}^{(i)}(\mathbf{r})$.

We only treat explicitly scattering events in which the induced current created by a bead of one chain acts on a bead of some second chain. There are also intrachain hydrodynamic interactions. These interactions tend to entrain solvent within each polymer chain, so that in a moving polymer the velocity of a bead with respect to neighboring solvent molecules is almost always less than the velocity of that bead with respect to distant regions of the solvent. A chain moving with velocity $\mathbf{V}^{(i)}$ applies a net force $f_{oi}\mathbf{V}^{(i)}$ to the solvent, f_{oi} being the true drag coefficient of the chain. Entrainment substantially reduces f_{oi} relative to the sum of the drag coefficients f_i that individual chain beads would have if they were isolated from each other; f_{oi} of an M-bead chain is much less than Mf_i. Similarly, because the following treatment neglects intrachain hydrodynamic interactions, the computed chain−chain and chain−chain−chain hydrodynamic interactions will overestimate the real interaction.

The bead−bead excluded volume force prevents pairs of beads from overlapping with each other; two beads may never approach more closely than $2a_o$. This requirement is implicit in the development of the Rotne−Proger and higher order corrections, which describe the hydrodynamic coupling between two beads of hydrodynamic radius a_o separated by a region of solvent. If the beads could interpenetrate, there could be no flow of solvent in the space along the line of centers, a condition not accounted for in the underlying derivation of the Oseen and other bead−bead hydrodynamic interaction tensors. Also, if there were no distance of closest approach, several of the integrals treated in the next section would be divergent, a nonphysical outcome.

The bond interactions determine the stiffness of the chain. In this calculation, these interactions are reduced to fixing the radius of gyration and hydrodynamic radius of each chain.

The calculation invokes one further physical principle. Chain motion is highly overdamped. A chain's inertia and moment of inertia are both therefore negligible, so on the time scales of interest here the total force $\mathbf{F} = m\mathbf{a}$ on a chain becomes $\mathbf{F} = 0$, and a similar scheme is observed for the torque. For a given chain, a sum over all beads in the chain gives the zero-net-force condition

$$\sum_{i=1}^{M}\mathbf{F}_i = 0 \tag{6}$$

and the zero-net-torque condition

$$\sum_{i=1}^{M}\mathbf{s}_i \times \mathbf{F}_i = 0 \tag{7}$$

The calculation of the $\mathbf{b}$ and $\mathbf{T}$ tensors begins with a polymer chain 1 that has velocity $\mathbf{V}^{(1)}$ and angular velocity $\Omega^{(1)}$ with respect to the unperturbed (hence, stationary) solvent. A bead i of that chain has initial velocity $\mathbf{v}_i^{(1)} = \mathbf{V}^{(1)} + \mathbf{s}_i \times \Omega^{(1)}$ with respect to the solvent, and applies to the solvent a force $\mathbf{F}_i = f_i\mathbf{v}_i^{(1)}$. The Oseen tensor shows that the induced fluid flow $\mathbf{u}^{(1)}(\mathbf{r})$ due to the entirety of chain 1 is

$$\mathbf{u}^{(1)}(\mathbf{r}) = \sum_{i=1}^{M}\mathbf{T}(\mathbf{r} - \mathbf{s}_i)\cdot f_i\mathbf{v}_i^{(1)} \tag{8}$$

A series of replacements are now made. The set of bead positions $\{\mathbf{s}_i\}$ is replaced by a field variable $\mathbf{s}$ and a bead distribution function $g(s)$, centered on the center of mass of the polymer, which gives the ensemble average density of beads at a point a distance s from the center of mass, and which satisfies $\int \mathrm{d}s\, g(s)s^2 = R_g^2$. There is considerable evidence that a typical polymer chain configuration is not spherically symmetric. However, the ensemble average includes each arrangement of beads in all possible orientations, so after an ensemble average $g(s)$ is only a function of $s = |\mathbf{s}|$. If eq 9 below were taken to higher order in s/r, greater care in the treatment of $g(s)$ would be required. The sum of drag coefficients f_i of the individual beads is replaced as explained above by the chain drag coefficient f_o. A MacLaurin series expansion for the Oseen tensor is $\mathbf{T}(\mathbf{r} - \mathbf{s}_i) = \mathbf{T}(\mathbf{r}) - (\mathbf{s}_i\cdot\nabla)\mathbf{T}(\mathbf{r})$ plus higher order (order s^2 or higher) terms, namely

$$\mathbf{T}(\mathbf{r} - \mathbf{s}) \cong \frac{1}{8\pi\eta}\left[\frac{\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{r} - \hat{\mathbf{r}}\frac{\mathbf{s}\cdot(\mathbf{I} - 3\hat{\mathbf{r}}\hat{\mathbf{r}})}{r^2} - \frac{\mathbf{s}\hat{\mathbf{r}}}{r^2} + \frac{\mathbf{s}\cdot\hat{\mathbf{r}}}{r^2}\mathbf{I}\right] + O\left(\left(\frac{s}{r}\right)^2\right), \tag{9}$$

$\mathbf{s}\hat{\mathbf{r}}$ being the dyadic product of $\mathbf{s}$ and $\hat{\mathbf{r}}$. One finds

$$\mathbf{u}^{(1)} = f_o\int \mathrm{d}\mathbf{s}\, g(s)\left\{\frac{1}{8\pi\eta}\left[\frac{\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}}}{r} - \hat{\mathbf{r}}\frac{\mathbf{s}\cdot(\mathbf{I} - 3\hat{\mathbf{r}}\hat{\mathbf{r}})}{r^2} - \frac{\mathbf{s}\hat{\mathbf{r}}}{r^2} + \frac{\mathbf{s}\cdot\hat{\mathbf{r}}}{r^2}\mathbf{I}\right]\right\}\cdot\{\mathbf{V}^{(1)} + \Omega^{(1)} \times \mathbf{s}\} \tag{10}$$

Noting that $\int$ ds $g(s)\mathbf{s}\cdot\hat{\mathbf{r}}\Omega \times \mathbf{s} = (R_g^2/3)\Omega \times \hat{\mathbf{r}}$, that here $f_o = 6\pi\eta R_{h1}$, and that terms odd in $\mathbf{s}$ vanish under integration over $\mathbf{s}$,

$$\mathbf{u}^{(1)}(\mathbf{r}) = \frac{3}{4}\frac{R_{h1}}{r}[\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}}]\cdot\mathbf{V}^{(1)} + \frac{1}{2}\frac{R_{h1}R_{g1}{}^2}{r^2}(\Omega^{(1)} \times \hat{\mathbf{r}}) \quad (11)$$

The above equation describes the longest-range parts of the solvent flow created by a polymer with translational velocity $\mathbf{V}^{(1)}$ and rotational velocity $\Omega^{(1)}$. Expansion of $\mathbf{T}$ to higher order in $\mathbf{s}\cdot\nabla$ would give terms of higher order in $(R_g/r)^2$.

The remainder of the calculation is iterative. The fluid flow $\mathbf{u}$ causes the next chain to translate and rotate, thereby inducing a further fluid flow, etc. In particular the solvent flow $\mathbf{u}^{(1)}(\mathbf{r})$ acts on chain 2, inducing in that chain translational and angular rotational velocities $\mathbf{V}^{(2)}$ and $\Omega^{(2)}$. The velocities of chain 2 are obtained by applying the zero-net-force and zero-net-torque conditions, eqs 6 and 7. At each consequent scattering step, a solvent flow $\mathbf{u}^{(n)}$ acts on chain $n + 1$ and gives that chain − via the zero-force and zero-torque conditions − velocities $\mathbf{V}^{(n+1)}$ and $\Omega^{(n+1)}$.

The force due to $\mathbf{u}^{(1)}(\mathbf{r})$ on a single bead, taking into account the motions of the whole chain in response to the forces on all of its beads and neglecting higher frequency internal mode relaxations, is $\mathbf{F}_i^{(2)} = f_i(\mathbf{u}^{(1)}(\mathbf{r}) - \mathbf{V}^{(2)} - \Omega^{(2)} \times \mathbf{s}_i)$. Expanding $\mathbf{u}^{(1)}(\mathbf{r})$ in powers of $\mathbf{s}\cdot\nabla$ around $\mathbf{r} = \mathbf{R}_1$, the zero-force condition is

$$f_o \int \mathrm{d}\mathbf{s}\; g(s)[\mathbf{u}^{(1)}(\mathbf{R}_1) + (\mathbf{s}\cdot\nabla)\mathbf{u}^{(1)}(\mathbf{R}_1) - \mathbf{V}^{(2)} - \Omega^{(2)} \times \mathbf{s}] = 0 \quad (12)$$

Eliminating terms odd in $\mathbf{s}$, as these integrate to zero, eq 12 shows

$$\mathbf{V}^{(2)} = \mathbf{u}^{(1)}(\mathbf{R}_1) \quad (13)$$

An argument identical save for labels applies at each further scattering step. In general, to lowest order in s, one has $\mathbf{V}^{(n+1)} = \mathbf{u}^{(n)}(\mathbf{R}_n)$.

To obtain the angular velocity of chain 2, the zero-torque condition is applied as

$$\sum_{i=1}^{M} f_i[\mathbf{s}_i \times \mathbf{u}^{(1)}(\mathbf{r}_i) - \mathbf{s}_i \times \mathbf{V}^{(2)} - \mathbf{s}_i \times (\Omega^{(2)} \times \mathbf{s}_i)] = 0 \quad (14)$$

Replacing the sum over a specific set of bead positions with an average over the bead density and eliminating terms that integrate to zero because they are odd in $\mathbf{s}$

$$\frac{2}{3} f_o \langle R_{g2}{}^2 \rangle \Omega^{(2)} = f_o \int \mathrm{d}\mathbf{s}\; g(s)\mathbf{s} \times (\mathbf{s}\cdot\nabla_{\mathbf{R}})\mathbf{u}^{(1)}(\mathbf{R}) \quad (15)$$

the subscript on ∇ specifying the coordinate appearing in its derivatives.

One next applies the auxiliary results $\mathbf{s}\cdot\nabla_r(1/r^n) = -n\mathbf{s}\cdot\mathbf{r}/r^{n+2}$ and $\mathbf{s}\cdot\nabla_r(\hat{\mathbf{r}}) = \mathbf{s}\cdot[(\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}})]/r$, and notes that the spherical averages over $g(s)$ give $\langle(\mathbf{s}\cdot\mathbf{a})(\mathbf{s} \times \mathbf{b})\rangle = {}^1/_3 R_g^2(\mathbf{a} \times \mathbf{b})$; $\langle(\mathbf{s}\cdot\mathbf{a})(\mathbf{s} \times (\mathbf{b} \times \mathbf{a}))\rangle = {}^1/_3 R_g{}^2\mathbf{b} \times [\mathbf{I} - 3\mathbf{a}\mathbf{a}]$; $\langle\mathbf{s}(\mathbf{b}\cdot\mathbf{s})\rangle = R_g{}^2\mathbf{b}/3$; and $\langle\mathbf{s} \times (\mathbf{b} \times \mathbf{s})\rangle = {}^2/_3 R_g^2\mathbf{b}$. Reducing eq 15, for a polymer chain at $\mathbf{R}_1$ one finds

$$\Omega(2) = -\frac{3}{4}\frac{R_{h1}}{R_1^2}[\hat{\mathbf{R}}_1 \times \mathbf{V}^{(1)}] - \frac{1}{4}\frac{R_{h1}R_{g1}{}^2}{R_1^3}\Omega^{(1)}\cdot[\mathbf{I} - 3\hat{\mathbf{R}}_1\hat{\mathbf{R}}_1] \quad (16)$$

Equations 11, 13, and 16 give the fluid flow near chain 2, and the translational and rotational response of chain 2 to the imposed flow. Note the fundamental physical difference between $(\mathbf{V}^{(1)}, \Omega^{(1)})$ and $(\mathbf{V}^{(2)}, \Omega^{(2)})$. The former pair of velocities were externally imposed, while the latter pair are a consequence of solvent flow through chain 2. Equations 13 and 16 display translational and rotational cross-coupling effects. If polymer 1 is caused either to translate but not rotate, or to rotate but not translate, polymer 2 both translates and rotates.

The solvent flow $\mathbf{u}^{(1)}$ is now scattered by chain 2, creating an additional flow $\mathbf{u}^{(2)}(\mathbf{r})$. The effect of chain 2 is the sum of the contributions of chain 2's beads, namely

$$\mathbf{u}^{(2)}(\mathbf{r}) = \sum_{j=1}^{M} \mathbf{T}(\mathbf{r} - \mathbf{s}_j)\cdot f_j[\mathbf{v}_j(\mathbf{s}_j) - \mathbf{u}^{(1)}(\mathbf{R}_1 + \mathbf{s}_j)] \quad (17)$$

The vectors $\mathbf{r}$ and $\mathbf{s}$ are now measured from the center of mass of chain 2.

Replacing the $\mathbf{s}_j$ with the field variable $\mathbf{s}$ and replacing the specific bead configuration with the radial distribution function $g(s)$, expanding $\mathbf{T}$ and $\mathbf{u}$ in powers of $\mathbf{s}\cdot\nabla$, eliminating terms that vanish via reflection symmetry for $\mathbf{s}$, and applying the generalized form of eq 13, the general result

$$\mathbf{u}^{(n+1)}(\mathbf{r}) = \frac{f_o}{8\pi\eta}\int \mathrm{d}\mathbf{s}\; \frac{g(s)}{r^2}[-\hat{\mathbf{r}}\mathbf{s}\cdot[\mathbf{I} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}] - \mathbf{s}\hat{\mathbf{r}} + (\mathbf{s}\cdot\hat{\mathbf{r}})\mathbf{I}]\cdot[\Omega^{(n+1)} \times \mathbf{s} - \mathbf{s}\cdot\nabla[\mathbf{u}^{(n)}]] \quad (18)$$

follows.

Applying the forms $\langle(\mathbf{s}\cdot\mathbf{a})(\mathbf{s}\cdot\mathbf{b})\rangle = {}^1/_3 R_g{}^2\mathbf{a}\cdot\mathbf{b}$, $\langle(\mathbf{s}\cdot\mathbf{a})(\mathbf{b} \times \mathbf{s})\rangle = {}^1/_3 R_g{}^2\mathbf{b} \times \mathbf{a}$, $\langle(\mathbf{s}\mathbf{a}\cdot(\mathbf{b} \times \mathbf{s})\rangle = {}^1/_3 R_g{}^2\mathbf{a} \times \mathbf{b}$; and $\langle\mathbf{s}\mathbf{a}\cdot(\mathbf{b} \times \mathbf{s})\rangle = {}^1/_3 R_g^2(\mathbf{a} \times \mathbf{b})$ for averages over $g(s)$, one has

$$\mathbf{u}^{(n+1)}(\mathbf{r}) = \frac{R_{h,n+1}R_{g,n+1}{}^2}{4r^2} \times [2(\Omega^{(n+1)} \times \hat{\mathbf{r}}) - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\cdot[(\hat{\mathbf{r}}\cdot\nabla_{\mathbf{R}})\mathbf{u}^{(n)}(\mathbf{R}_n)] + \nabla_{\mathbf{R}}(\hat{\mathbf{r}}\cdot\mathbf{u}^{(n)}(\mathbf{R}_n)) - \hat{\mathbf{r}}\cdot\nabla_{\mathbf{R}}(\mathbf{u}^{(n)}(\mathbf{R}_n))] \quad (19)$$

The derivatives $\nabla_{\mathbf{R}}$ are taken with respect to the coordinate location $\mathbf{R}$ of chain $n + 1$, not with respect to the field vector $\mathbf{r}$ connecting the center of mass of chain $n + 1$ with the location at which $\mathbf{u}^{(n+1)}(\mathbf{r})$ is being calculated.

Choosing $n = 1$, taking $\Omega^{(2)}$ from eq 16, and obtaining $\hat{\mathbf{r}}\cdot\nabla_R\hat{\mathbf{R}}$ and $\hat{\mathbf{r}}\cdot\nabla_R R^{-m}$ from the above, one obtains after a

long series of rearrangements

$$\mathbf{u}^{(2)}(\mathbf{r}) = -\frac{9}{16}\frac{R_{h1}R_{h2}R_{g2}{}^2}{R_1{}^2 r^2}[(1-3(\hat{\mathbf{r}}\cdot\hat{\mathbf{R}}_1)^2]\hat{\mathbf{r}}(\hat{\mathbf{R}}_1\cdot\mathbf{V}^{(1)}) + \frac{3}{8}\frac{R_{h1}{}^2R_{h2}{}^2R_{g1}{}^2R_{g2}{}^2}{R_1{}^3 r^2}\times[\hat{\mathbf{r}}\times\Omega^{(1)} - (\hat{\mathbf{r}}\times\hat{\mathbf{R}}_1)\hat{\mathbf{R}}_1\cdot\Omega^{(1)} + \hat{\mathbf{r}}\cdot\hat{\mathbf{R}}_1(\Omega^{(1)}\times\hat{\mathbf{R}}_1) - \hat{\mathbf{r}}\cdot(\Omega^{(1)}\times\hat{\mathbf{R}}_1)\hat{\mathbf{R}}_1\cdot(\mathbf{I}-3\hat{\mathbf{r}}\hat{\mathbf{r}})] \quad (20)$$

for the current scattered by chain 2.

From the generalization following eq 13, $\mathbf{V}^{(3)} = \mathbf{u}^{(2)}(\mathbf{R}_2)$. To obtain $\Omega^{(3)}$, one uses the zero torque condition, which for the nth scattering event (here $n = 2$) is

$$\sum_{i=1}^{M} f_i[\mathbf{s}_i\times\mathbf{u}^{(n)}(\mathbf{r}_i) - \mathbf{s}_i\times\mathbf{V}^{(n+1)} - \mathbf{s}_i\times(\Omega^{(n+1)}\times\mathbf{s}_i)] = 0 \quad (21)$$

To lowest order in $\mathbf{s}$, integration provides

$$\frac{2}{3}R_{g,n+1}^2\Omega^{(n+1)} = \int \mathrm{d}\mathbf{s}\, g(s)\mathbf{s}\times(\mathbf{s}\cdot\nabla)\mathbf{u}^{(n)}(\mathbf{r}_n) \quad (22)$$

However, expansion of the $\mathbf{s}$ in Cartesian coordinates gives a rearrangement of the right-hand side as an integral over s^2 and a constant independent of s, leading to

$$\Omega^{(n+1)} = \frac{1}{2}(\nabla\times\mathbf{u}^{(n)}) \quad (23)$$

to order $O(s^2)$ only.

If one sets $n = 2$, substitutes it in eq 23, and uses identities $\nabla_r\times\hat{\mathbf{r}} = 0$, $\nabla_r\times[(\hat{\mathbf{r}}\cdot\hat{\mathbf{R}})^2\hat{\mathbf{r}}/r^3] = [2(\hat{\mathbf{r}}\cdot\hat{\mathbf{R}})(\hat{\mathbf{R}}\times\hat{\mathbf{r}})/r^3$, $\nabla_r\times(\mathbf{r}\times\mathbf{a})/r^3 = (\mathbf{a}/r^3)\cdot[\mathbf{I}-3\hat{\mathbf{r}}\hat{\mathbf{r}}]$, $\nabla_r\times(\mathbf{r}\cdot\mathbf{a})\mathbf{b}/r^3 = [\mathbf{a}\cdot(\mathbf{I}-3\hat{\mathbf{r}}\hat{\mathbf{r}})\times\mathbf{b}]/r^3$, and $\nabla_r\times[(\hat{\mathbf{r}}\cdot\mathbf{a})(\mathbf{b}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}}]/r^2 = (\mathbf{b}\cdot\hat{\mathbf{r}})\mathbf{a}\times\hat{\mathbf{r}}/r^3 + (\mathbf{a}\cdot\hat{\mathbf{r}})\mathbf{b}\times\hat{\mathbf{r}}/r^3$, the angular velocity of the third chain is seen to be

$$\Omega^{(3)} = \frac{27}{16}\frac{R_{h1}R_{h2}R_{g2}^2\hat{\mathbf{R}}_1\cdot\mathbf{V}^{(1)}}{R_1^2R_2^3}\hat{\mathbf{R}}_2\cdot\hat{\mathbf{R}}_1(\hat{\mathbf{R}}_1\times\hat{\mathbf{R}}_2) + \frac{9}{16}\frac{R_{h1}R_{h2}R_{g1}^2R_{g2}^2}{R_1^3R_2^3}\times[\Omega^{(1)}(1-2(\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2)^2) - \hat{\mathbf{R}}_1\,\Omega^{(1)}\cdot[\mathbf{I}-2\hat{\mathbf{R}}_2\hat{\mathbf{R}}_2]\cdot\hat{\mathbf{R}}_1 - \hat{\mathbf{R}}_2\,\Omega^{(1)}\cdot[\mathbf{I}-\hat{\mathbf{R}}_1\hat{\mathbf{R}}_1]\cdot\hat{\mathbf{R}}_2] \quad (24)$$

In an obvious check, if $\mathbf{R}_1$, $\mathbf{R}_2$, and $\Omega^{(1)}$ are parallel, then $\Omega^{(3)}$ vanishes. The second chain simply rotates with the solvent circulation and does not perturb the circulation $\nabla\times\mathbf{u}$ at the location of the third chain.

A further iteractive cycle gives the solvent flow at a fourth chain. Applying eq 19 with $n = 2$, the above expressions for $\mathbf{u}^{(2)}$ and $\Omega^{(3)}$ give $\mathbf{u}^{(3)}$. Our further work only requires the contribution to $\mathbf{u}^{(3)}$ from linear translation by the first bead, namely

$$\mathbf{u}^{(3)}(\mathbf{r}) = \frac{27}{64}\frac{R_{h1}R_{h2}R_{h3}R_{g2}{}^2R_{g3}{}^2}{R_1{}^2R_2{}^3r^2}\times[(1-3(\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2)^2)(1-3(\hat{\mathbf{R}}_2\cdot\hat{\mathbf{r}})^2) - 6(\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2)(\hat{\mathbf{R}}_2\cdot\hat{\mathbf{r}})\hat{\mathbf{r}}\cdot[\mathbf{I}-\hat{\mathbf{R}}_2\hat{\mathbf{R}}_2]\cdot\hat{\mathbf{R}}_1]\hat{\mathbf{r}}(\hat{\mathbf{R}}_1\cdot\mathbf{V}^{(1)}) \quad (25)$$

As shown above, $\mathbf{V}^{(4)} = \mathbf{u}^{(3)}(\mathbf{R}_3)$.

The $\mathbf{T}$ and $\mathbf{b}$ tensors follow from eqs 3 and 4 and the $\mathbf{V}^{(n)}$ and $\Omega^{(n)}$. In particular, $\mathbf{T}_{ij}$, $\mathbf{T}_{ilj}$, and $\mathbf{T}_{ilmj}$ are given by the terms of $\mathbf{V}^{(2)}$, $\mathbf{V}^{(3)}$, and $\mathbf{V}^{(4)}$ that are proportional to $\mathbf{V}^{(1)}$, on requiring that the first and last particles in each scattering series be distinct, by factoring out an $f_{o1}\mathbf{V}^{(1)}$ from the $\mathbf{V}^{(n)}$. From eq 11

$$\mathbf{T}_{21} = \frac{1}{f_{o1}}\frac{3}{4}\frac{R_{h1}}{R_1}[\mathbf{I}+\hat{\mathbf{R}}_1\hat{\mathbf{R}}_1] \quad (26)$$

Equation 20 leads to the conclusion

$$\mathbf{T}_{321} = -\frac{1}{f_{o1}}\frac{9}{16}\frac{R_{h1}R_{h2}R_{g2}{}^2}{R_1{}^2R_2{}^2}[(1-3(\hat{\mathbf{R}}_2\cdot\hat{\mathbf{R}}_1)^2]\hat{\mathbf{R}}_2\hat{\mathbf{R}}_1 \quad (27)$$

$$\mathbf{T}_{4321} = \frac{1}{f_{o1}}\frac{27}{64}\frac{R_{h1}R_{h2}R_{h3}R_{g2}{}^2R_{g3}{}^2}{R_1{}^2R_2{}^3R_3{}^2}\times[\{(1-3(\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2)^2)(1-3(\hat{\mathbf{R}}_2\cdot\hat{\mathbf{R}}_3)^2) - 6(\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2)(\hat{\mathbf{R}}_2\cdot\hat{\mathbf{R}}_3)\hat{\mathbf{R}}_3\cdot[\mathbf{I}-\hat{\mathbf{R}}_2\hat{\mathbf{R}}_2]\cdot\hat{\mathbf{R}}_1\}\hat{\mathbf{R}}_3\hat{\mathbf{R}}_1] \quad (28)$$

Similarly, $\mathbf{b}_{il}$ and $\mathbf{b}_{ikl}$ follow from $\mathbf{V}^{(3)}$ and $\mathbf{V}^{(4)}$, respectively, on requiring that the first and last particles in the scattering series are the same, and then factoring out an $f_{o1}\mathbf{V}^{(1)}$. In particular

$$\mathbf{b}_{12} = -\frac{1}{f_{01}}\frac{9}{8}\frac{R_{h1}R_{h2}R_{g2}{}^2}{R_1{}^4}\hat{\mathbf{R}}_1\hat{\mathbf{R}}_1 \quad (29)$$

in agreement with the slightly different methods of the previous papers.[12,13] For the three point function one has

$$\mathbf{b}_{321} = \frac{1}{f_{01}}\mathbf{T}_{4321}|_{(\mathbf{R}_3=-\mathbf{R}_2-\mathbf{R}_1)} \quad (30)$$

These forms for the chain−chain $\mathbf{T}$ and $\mathbf{b}$ tensors may be compared to the corresponding tensors found, e.g., by Mazur and van Saarloos,[17] for hydrodynamic interactions between hard spheres having stick boundary conditions. The numerical coefficients are different, but for each corresponding pair of tensors both the angular and radial dependences are the same for spheres as for chains.

In addition to the tensors linking translation to translation, there are also tensors analogous to $\mathbf{T}$ and $\mathbf{b}$ that link a force or torque on the first chain to a rotation or translation of the final chain of the scattering sequence. In each case, to extract the terms corresponding to induced translation or rotation of the final chain, one examines the expression for $\mathbf{V}^{(n)}$ or $\Omega^{(n)}$, respectively, for $n > 1$. To extract terms corresponding to motion caused by translation or rotation, respectively, of the first chain, one isolates those components of the $\mathbf{V}^{(n)}$ (or $\Omega^{(n)}$, respectively) that depend on $\mathbf{V}^{(1)}$ or $\Omega^{(1)}$, respectively. Tensors $\mathbf{T}$ always refer to scattering series in which the first and last chains of the series are distinct; tensors $\mathbf{b}$ refer to scattering series in which the first and last chains of the series are the same.

Ensemble Average of the Hydrodynamic Interaction Tensors

The ultimate objective of this section is to obtain the leading coefficients B_2 and B_3 in a pseudovirial expan-

sion of the chain self-diffusion coefficient

$$D_s = D_o(1 + B_2c + B_3c^2) \tag{31}$$

The self-diffusion coefficient is also given by a generalized Einstein relation as

$$D_s = \frac{k_BT}{3}\,\mathrm{Tr}\,\frac{1}{N}\langle\sum_{i=1}^{N}\mu_{ii}\rangle \tag{32}$$

the Trace operator being taken with respect to the 3 Cartesian coordinates, and the brackets $\langle\cdots\rangle$ denoting an ensemble average. Here the mobility is

$$\mu_{ii} = \frac{\mathbf{I}}{f_{oi}} + \sum_{l=1}^{N}\mathbf{b}_{il} + \sum_{l,m=1}^{N}\mathbf{b}_{ilm} + \ldots \tag{33}$$

the **b** tensors vanishing whenever two or more of their indices are equal.

The ensemble average of eq 32 is written in terms of the N-particle potential energy U_N and chain center-of-mass coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, ..., and relative coordinates $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. We introduce n-chain distribution functions $g^{(n)}(\mathbf{r}_{12}, \ldots, \mathbf{r}_{1n})$ where, e.g.

$$cg^{(2)}(\mathbf{r}_{12}) = \frac{N\int \mathrm{d}\mathbf{r}_{13}\ldots\mathrm{d}\mathbf{r}_{1N}\exp(-\beta U_N)}{\int \mathrm{d}\mathbf{r}_{12}\ldots\mathrm{d}\mathbf{r}_{1N}\exp(-\beta U_N)} \tag{34}$$

$c = N/V$ here being the chain number concentration. In terms of the chain distribution functions, the self-diffusion coefficient may be written

$$D_s = \frac{k_BT}{f_o}\Big[1 + \frac{f_o}{3}\,\mathrm{Tr}\{c\int_V \mathrm{d}\mathbf{r}_{12}\,\mathbf{b}_{12}\,g^{(2)}(\mathbf{r}_{12}) + c^2\int_V \mathrm{d}\mathbf{r}_{12}\,\mathrm{d}\mathbf{r}_{13}\,\mathbf{b}_{123}\,g^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13})\}\Big] \tag{35}$$

Equations 31, 35, and 29 show that B_2 is

$$B_2 = \frac{1}{3}\mathrm{Trace}\left\{c\int_V \mathrm{d}\mathbf{r}_{12}\left(-\frac{9}{8}\frac{R_{h1}R_{h2}{R_{g2}}^2}{R^4}\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12}\right)g^{(2)}(r_{12})\right\} \tag{36}$$

Evaluation of B_2 requires an expression for $g^{(2)}(r_{12})$. It would be possible to use elaborated forms based on depths of correlation holes[14] or degrees of chain penetration at concentrations above and below the thermodynamic overlap concentration. For simplicity, $g^{(2)}(r_{12})$ is taken to be flat, with the constraint that r_{12} initially arose as a distance between pairs of beads and therefore can never be smaller than the bead-bead contact distance $2a_o$.

Integration then provides

$$B_2 = -\frac{9}{16}\frac{R_{h1}R_{h2}}{a_oR_g}\left(\frac{4\pi}{3}{R_g}^3\right) \tag{37}$$

as found previously in ref 12.

The corresponding calculation of B_3 was performed numerically via Monte Carlo methods. The chains were again allowed to interpenetrate, subject to the constraints that r_{12}, r_{13}, and r_{23} must each remain larger than $2a_o$. Because chains can interpenetrate with solvent and other chains, while spheres do not, results differ substantially from the corresponding calculation[18] for hard spheres. With spheres, $g^{(2)}(r_{12})$ has a power series expansion in concentration, so the integral over $\mathbf{b}(\mathbf{r}_{12})$ that is analogous to eq 36 yields not only a contribution to B_2 but also contributions to B_3 and the higher B_i. In contrast, with the system here and our approximation for $g^{(2)}(\mathbf{r}_{12})$, $\mathbf{b}(\mathbf{r}_{12})$ only contributes to B_2.

The third pseudovirial coefficient is

$$B_3 = \frac{9}{64}\frac{R_{h1}R_{h2}R_{h3}{R_{g2}}^2{R_{g3}}^2}{a_o}\left\{\int_2^\infty r^2\,\mathrm{d}r\int_2^\infty s^2\,\mathrm{d}s\int_{4\pi}\mathrm{d}\Omega_r\,\mathrm{d}\Omega_s\,\frac{g^{(2)}(r_{23})}{r^2\,r_{23}^3\,s^2}\times \mathrm{Tr}[f(\Omega_r, \Omega_s)]\right\} \tag{38}$$

In the term in braces, r, r_{23}, and s are dimensionless distances in units with $a_o = 1$, $g^{(2)}(r_{23})$ serves to exclude states in which the distance between particles 2 and 3 is less than 2, and $[f(\Omega_r, \Omega_s)]$ is the bracketed function of unit vectors of eq 28 with the constraint $\mathbf{R}_3 = -\mathbf{R}_1 - \mathbf{R}_2$.

Because $\mathbf{b}_{123}$ depends strongly on the interparticle distances, separate numerical integrations were made for cases in which at least one of the particles was in each of a series of nonoverlapping spherical shells. We took 2×10^8 samples in each shell. On integration and rearrangement, one finds

$$B_3 = 9.321\times10^{-4}\frac{R_{h1}R_{h2}R_{h3}}{a_oR_{g2}R_{g3}}\frac{4\pi{R_{g2}}^3}{3}\frac{4\pi{R_{g3}}^3}{3} \tag{39}$$

The two factors of volume in B_3 can be combined with the corresponding factors of concentration c to yield effective volume fraction units $\phi = 4\pi{R_g}^3c/3$.

For later purposes representative numerical values for B_2 and B_3 are required. Necessary quantitative data on polymer chain sizes are taken from Adam and Delsanti[20]: For a 1.27×10^6 Da polystyrene in benzene, their work provides $R_g = 621$ Å, and (taking $\eta = 0.6$ cP) $R_h = 380$ Å. The distance of closest approach $2a_o$ of two polystyrene chains is certainly not less than 7 Å; a more detailed treatment of chain statistics may suggest a larger value. Substituting in eqs 37 and 38, and choosing concentration units to be g/L, one obtains and

$$B_2 = -18 \tag{40}$$

$$B_3 = 8.5\times10^{-3} \tag{41}$$

With different concentration units, B_2 and B_3 would have different numerical values. As remarked above, neglect of intramolecular hydrodynamic interactions leads to a substantial overestimate of $|B_2|$; empirically, $B_2 \approx -1$ for chains of this molecular weight.

Positive-Function Renormalization Group

The calculation in this section employs the Altenberger−Dahler positive-function renormalization group (PFRG),[3,19] as developed from Shirkov's general treatment of renormalization group analysis based on functional self-similarity.[21−23] As noted by these authors, one can identify a variety of paths to applying renor-

malization group analysis. In high-energy physics, renormalization group methods originally arose from difficulties associated with cutoff wavelengths and the removal of infinities in series expansions. In statistical mechanics, renormalization group analysis arose from processes such as block renormalization, in which self-similarity over wavelength is used for example to eliminate insignificant fine detail from a description of critical fluctuations. More generally, in a wide variety of physical cases,[23] renormalization group analysis is an efficient tool for extending the regime of validity of low-order power series expansions. The work here is most directly based on the last of these uses for the renormalization group: we are not considering systems with divergences or systems with a multiplicity of short but unimportant length scales; we have available a low-order series expansion that would be tedious to extend to very high order.

Previous derivations[11,12] of the universal scaling equation also invoked a self-similarity approximation. In the earlier work on polymer dynamics, concentration increments δc were taken to increase the concentration-dependent drag coefficient $f(c)$ of a polymer chain by amounts $\alpha(c)\delta c$; the self-similarity assumption was that $\alpha(c)$ is linearly proportional to the drag coefficient f at the current concentration c. The mathematical form of the universal scaling equation was fixed by this self-similarity approximation. While the procedures of Shirkov,[21−23] and Altenberger and Dahler[3,19] also invoke functional self-similarity, the self-similarity process in their procedures is far more general than is the bootstrapping process of refs 11 and 12.

Since the Altenberger−Dahler approach is not widely used, we first will outline the physical arguments leading to the method and then apply it. Physically, one begins with the observation that, e.g., for a solution many properties A (such as the osmotic pressure or the self-diffusion coefficent) can at low concentration be expressed accurately with a few terms of a pseudovirial series such as

$$A = a_0 + a_1 c' + \frac{1}{2} a_2 c'^2 \tag{42}$$

Here c' is the concentration in physical units. The a_i variables are pseudovirial coefficients. For $i > 0$ the a_i variables are determined by the strength of the interactions between the solute molecules. A is therefore a function of two parameters, namely the concentration c and a solute coupling parameter R. (Cases in which there are several independent coupling parameters, e.g., a Lennard−Jones potential, are included by interpreting R as a vector.) In one writes $A = A(c, R)$, the limit $A(c, 0) = a_0$ corresponds to an ideal solution; if the solute molecules are noninteracting, $R = 0$ and $a_i = 0$ for $i > 0$. Equation 42 thus implicitly includes both the dependence of A on c and the dependence of A (through the a_i) on R.

It is convenient in the following to use explicitly dimensionless units for a concentration c. By introducing a standard reference concentration c_r having physical units, one may write $c = c'/c_r$ and

$$A = a_0 + (a_1 c_r)c^1 + \left(\frac{1}{2} a_2 c_r^2\right)c^2 \tag{43}$$

for c in dimensionless units.

Equations 42 and 43 are truncated series, which become inaccurate if c is increased sufficiently. One approach to extending eq 42 to higher concentration is to compute additional coefficients a_i, for example via cluster diagrams. The Altenberger−Dahler PFRG method instead extends eq 42 by replacing the bare coupling parameter R with an effective coupling parameter $\bar{R}(c, R)$, while retaining eq 42 (including the implicit functional dependence of the a_i on R) for A. The renormalization-group aspect of the calculation is used to determine $\bar{R}(c, R)$.

The calculation has five parts, the first three of which closely follow Altenberger and Dahler's treatment[3] of the equation of state of a hard-sphere fluid. First, constraints on A are used to determine functional requirements—which turn out to be group properties—for the effective coupling parameter $\bar{R}$. Second, at low concentration $\bar{R} = R$; the group properties of $\bar{R}$ determine a set of Lie differential equations and infinitesimal generators for the dependence of A and $\bar{R}$ on c. Third, for the case $A \equiv D_s$ the calculations of the two previous sections determine the first three a_i, their dependence on R, and hence the Lie equations and group generators for $\bar{R}$ and D_s. Fourth, numerical integration provides the concentration dependence of D_s at elevated c for objects of given bare R. Finally, applying the results of Daoud et al.[14] on chain contraction at elevated c leads to the universal scaling equation for polymer self-diffusion, as an approximant valid to a specific order in the coupling parameter $\bar{R}$.

As the first part of the derivation, we are doing a transformation with respect to an initial concentration c_o in physical units. It is convenient to introduce a normalized $\tilde{A}$ as

$$\tilde{A}(c', R) = A(c', R)/A(c_o, R) \tag{44}$$

The constraint on $\tilde{A}$ is now introduced, namely that $\tilde{A}$ is positive definite ($\tilde{A} > 0$). With this constraint $\tilde{A}$ may always be put in the form

$$\tilde{A}(c', R) = \exp\left(\int_{c_o}^{c'} \mathrm{d}s\, L(s, R)\right) \tag{45}$$

where

$$L(s, R) = \frac{\partial}{\partial s} \ln(\tilde{A}(s, R)) \tag{46}$$

Equation 45 is the positive function (PF) constraint of the positive function renormalization group.

By incorporation into eq 45 of an intermediate concentration z in physical concentration units, one has

$$\tilde{A}(c', R) = \exp\left(\int_{c_o}^{z} \mathrm{d}s\, L(s, R)\right) \exp\left(\int_{z}^{c'} \mathrm{d}s\, L(s, R)\right) \tag{47}$$

Note that the physical reference concentration c_o is arbitrary, so the above three equations will remain true for any physical choice of c_o. It is mathematically highly convenient to choose the thusfar arbitrary reference concentration c_r to equal c_o, so that the initial concentration is $c = 1$ in dimensionless units. Unless elsewise specified, we use dimensionless units throughout the following. With a change of variables $y = s/z$, eq 47 becomes in dimensionless units

$$\tilde{A}(c, R) = \tilde{A}(z, R)[\exp\left(\int_1^{c/z} \mathrm{d}y\, L(yz, R)\right)]^z \tag{48}$$

Equation 48 is now in a form that naturally admits of renormalization. Suppose in the integrand that the coupling parameter R can be replaced by an effective coupling parameter $\bar{R}$ having the property

$$L(yz, R) = L(y, \bar{R}(z, R)) \tag{49}$$

According to this form, the value of L at some elevated concentration yz can be replaced with L at some lower concentration y via the expedient of replacing R with the appropriate effective coupling parameter $\bar{R}$; also, $\bar{R}(1, R) = R$. The replacement of R with $\bar{R}$ is physically analogous to the self-similarity assumption of previous derivations[11−13] of the hydrodynamic scaling model, in which the bare drag coefficient f_o of each chain was repeatedly replaced with the drag coefficient f of the chain at each elevated concentration c.

On inserting the effective coupling parameter $\bar{R}$ into eq 48, one may write a renormalized form for $\tilde{A}$, namely

$$\frac{\tilde{A}(c, R)}{\tilde{A}(z, R)} = \left[\tilde{A}\left(\frac{c}{z}, \bar{R}(z, R)\right)\right]^z \tag{50}$$

This equation is numerically renormalized in the sense that $\tilde{A}(c, R)/\tilde{A}(z, R) = 1$ for $c = z$. Equation 50 only follows from eqs 45 and 48 because we are using dimensionless concentration units with $c_r = c_o$. With a different choice of c_r, eq 48 would still be correct, but would not imply eq 50. Renormalization group behavior is exhibited in the sense that eqs 48 and 50 define a group operation in which changes in the independent variable c can be replaced by changes in an (effective) coupling parameter R.

Equation 50 may also be written

$$\tilde{A}(cz, R) = \tilde{A}(z, R)[\tilde{A}(c, \bar{R}(z, R)]^z \tag{51}$$

By inspection of its left-hand side, eq 51 is symmetric under exchange of c and z, which imposes severe constraints on the functional form of $\bar{R}$. As shown by ref 3, Appendix 1, in order for the above equation to be true $\bar{R}$ must satisfy

$$\bar{R}(c, R) = \bar{R}(c/z, \bar{R}(z, R)) \tag{52}$$

The above equation concludes the first part of the derivation. The constraint that A is a positive definite function of a variable c and parameter R, and the hypothesis that R can be replaced with an effective coupling parameter $\bar{R}$ that allows A to be renormalized (as per eq 50), lead to a functional equation for $\bar{R}$.

As the second part of the derivation, eqs 50 and 52 also yield differential equations for $\bar{R}$. At the reference physical concentration c_o no renormalization is needed, so $\bar{R}(c_o, R) \equiv \bar{R}(1, R) = R$, which is the needed boundary condition for the integration. Specifically, beginning from eq 50, taking a derivative with respect to c, setting $c = z$, and applying (as follows from eq 50) the renormalization $\tilde{A}(1, \bar{R}(z, R)) = 1$, one obtains

$$\frac{\partial \ln \tilde{A}(z, R)}{\partial z} = \left.\frac{\partial \tilde{A}(u, \bar{R}(z, R))}{\partial u}\right|_{u=1} \equiv \gamma(\bar{R}(z, R)) \tag{53}$$

where $u = c/z$. Equation 53 defines the differential generator γ. Setting $z = 1$, one also finds

$$\left.\frac{\partial \ln \tilde{A}(z, R)}{\partial z}\right|_{z=1} \equiv \gamma(R) \tag{54}$$

On the other hand, the derivative of $\bar{R}$ with respect to z may be obtained from eq 52 via a derivative with respect to c and again setting $c = z$, which gives

$$\frac{\partial \bar{R}(z, R)}{\partial \ln z} = \left.\frac{\partial \bar{R}(u, \bar{R}(z, R))}{\partial u}\right|_{u=1} \equiv \beta(\bar{R}(z, R)), \tag{55}$$

which defines β. Alternatively, the derivative may be obtained from eq 53 via a derivative of γ with respect to z, giving

$$\frac{\partial \bar{R}(z, R)}{\partial z} = \frac{(\tilde{A}''(z, R)/\tilde{A}(z, R)) - (\tilde{A}'(z, R)/\tilde{A}(z, R))^2}{(\partial\gamma(\bar{R}(z, R))/\partial \bar{R}(z, R))} \tag{56}$$

where $\tilde{A}''(z, R) = \partial^2\tilde{A}(z, R)/\partial z^2$ and $\tilde{A}'(z, R) = \partial\tilde{A}(z, R)/\partial z$. Evaluating eqs 55 and 56 at $z = 1$ provides

$$\beta(R) = \frac{(\tilde{A}''(1, R)/\tilde{A}(1, R)) - (\tilde{A}'(1, R)/\tilde{A}(1, R))^2}{(\partial\gamma(R)/\partial R)} \tag{57}$$

for β, as a function of R rather than $\bar{R}$, at the initial concentration.

The forms for $\beta(\bar{R})$ and $\gamma(\bar{R})$ provide infinitesimal generators for Lie equations for the concentration dependences of $\tilde{A}$ and $\bar{R}$. A variety of procedures for integrating these equations are available. This paper follows Altenberger and Dahler,[3,19] who approximate $\tilde{A}$ with its low-order series expansion, eq 42. Since the required inputs are $\tilde{A}$ and its derivatives at $z = 1$, and the series expansion for $\tilde{A}$ should be good near $z = 1$ for reasonable choices of the initial concentration (in physical units) c_o, this approximation is not very demanding. Indeed, for the hard-sphere gas Altenberger and Dahler[3] used the third-order virial expansion as the input to a PFRG computation of the pressure P. Choosing $c_o = 0.16$ in volume fraction units (which is well within the range in which the third order series is nearly exact), Altenberger and Dahler's PFRG prediction of P agrees with Monte Carlo calculations of P for $\phi \leq 0.5$, and is indistinguishable from the eight-term virial expansion for P for $\phi \leq 0.62$.

As the third part of the derivation, the above procedure is applied to the self-diffusion problem to obtain the Lie equation and the generators γ and β for the specific case $A \equiv D_s$.

D_s depends on the concentration and the chain radii R_g and R_h. For simplicity, we represent R_h and R_g as a single radius $\tilde{R}$ (in physical units) and treat numerical factors later. [This replacement of R_h and R_g with a single effective radius $\tilde{R}$ is not entirely trivial. For sodium polystyrene sulfonate at different ionic strengths, Pietzsch et al.[24] show that R_h and R_g have independent dependences on I, so that between 2 and 4000 mM NaCl, R_g of 780 kDa NaPSS changes 2.5-fold, while R_h changes by no more than 40%. Treating R_g and R_h as a single radius $\tilde{R}$ is therefore a potential oversimplification.]

Identifying c as the concentration variable, and introducing a dimensionless $R = \tilde{R}/R_o$ as a dimensionless coupling parameter, with R_o as the reference state radius at $c = 1$, eq 31 becomes

$$D_s = D_o(1 + \bar{a}R^4c + \bar{b}R^7c^2) \tag{58}$$

with $D_o = k_BT/f_o$. All dependence on the now-dimensionless R appears explicitly. From eqs 37 and 39 the

first two pseudovirial coefficients of eq 58 would be written

$$\bar{a} = -\frac{9}{16}\frac{4\pi}{3a_o}R_o^4 c_r \tag{59}$$

$$\bar{b} = \frac{9.321 \times 10^{-4}}{a_o}\left(\frac{4\pi}{3}\right)^2 R_o^7 c_r^2 \tag{60}$$

Just as c_r is the physical concentration c_o at which the renormalization transformation is first applied, so also R_o is the physical chain radius at the physical concentration $c_r = c_o$ (or $c = 1$ in dimensionless units) prior to any renormalization. At physical concentration c_o, $c = R = 1$. At this c and R, eq 58 gives the two-term pseudovirial value for D_s at $c' = c_r$.

Equation 58 differs from expressions obtained by Altenberger and Dahler[3,19] in one substantial respect. Their variables analogous to c and R consistently enter their equations analogous to eq 58 as a product (cR), so their c^n term depends on the nth power of the coupling parameter. In this paper, each series expansion term has a nontrivial dependence on R, and each pseudovirial coefficient has a nontrivial functional dependence on R_o.

Following ref 3, D_s is replaced with the $\tilde{D}_s$ normalized by $D_s(1) = D_o(1 + \bar{a}R^4 + \bar{b}R^7)$; $\tilde{D}_s$ replaces $\tilde{A}$ henceforth. If one applies $1/(1 - x) - > 1 + x + x^2 + ...$ to move all dependence on R to the numerator and truncates at the $O(R^7)$ to which the hydrodynamics are complete

$$\tilde{D}_s = 1 + \bar{a}R^4(c - 1) + \bar{b}R^7(c^2 - 1) \tag{61}$$

If eq 54 is applied

$$\gamma(R) = \bar{a}R^4 + 2\bar{b}R^7 \tag{62}$$

The infinitesimal generator $\beta(R)$ is determined by $\tilde{D}_s(c)$ and its derivatives, namely $\tilde{D}_s(1) = 1$, $\tilde{D}'_s(1) = \bar{a}R^4 + 2\bar{b}R^7$, and $\tilde{D}''_s(1) = 2\bar{b}R^7$, as well as $\partial\gamma(R)/\partial R = 4\bar{a}R^3 + 14\bar{b}R^6$. The generator $\gamma(R)$ is only known to $O(R^7)$, so its derivative $\partial\gamma(R)/\partial R$ and quantities derived from the derivative are only known to $O(R^6)$. [If one were to assume from the structure of the hydrodynamic calculation that the next term of $\tilde{D}_s$ is $O(R^{10})$, then one would effectively know $\partial\gamma/\partial R$ to $O(R^7)$.]

After truncation of the individual terms at the highest valid orders in the coupling parameter R

$$\beta(R) = \frac{2\bar{b}R^7 - (\bar{a}R^4 + 2\bar{b}R^7)^2}{4\bar{a}R^3 + 14\bar{b}R^6} \cong \left(\frac{\bar{b}R^7}{2\bar{a}R^3}\right) \tag{63}$$

The final approximation follows because only the first term of the numerator has the allowed order R^7 or lower in R, while (noting $\bar{a} >> \bar{b}$, expanding the denominator in powers of $\bar{b}/\bar{a}$, and doing a geometric series expansion of the denominator) only the first term of the denominator leads to a term $\sim\partial\gamma/\partial R$ of order R^6 or lower. If one allowed that the numerator and denominator were actually correct to orders 8 and 7 in R, respectively, an additional term $-\bar{a}R^5/4$ of the expansion would appear on the rhs of eq 63.

Equation 63 provides $\partial\bar{R}(z, R)/\partial z$, but only at $z = 1$ at which $\bar{R} = R$. We now follow Altenberger and Dahler, who used the approximation that the dependence of $\partial\bar{R}(c, R)/\partial c$ on $\bar{R}$ for $c \neq 1$ is reasonably represented by the dependence of $\beta(R)$ on R at $c = 1$ by replacing R with $\bar{R}$. With this approximation that $\partial R/\partial \ln c \equiv \beta(R)$

$$\frac{\partial\bar{R}}{\partial \ln c} \cong \frac{\bar{b}\,\bar{R}^4}{2\bar{a}} \tag{64}$$

Taking $\bar{R}^4$ to the lhs, and noting that $\bar{R}(c)|_{c=1} = 1$, one finds that an integral with respect to $\ln c$ gives

$$\bar{R} = \left[1 - \frac{3}{2}\frac{\bar{b}}{\bar{a}}\ln(c)\right]^{-1/3} \tag{65}$$

Finally, from eq 54

$$D_s(c) = D_s(1)\exp[\int_1^c \mathrm{d}x\ \gamma(x)] \tag{66}$$

Substitution of eq 62 into eq 66 gives the Positive-Function Renormalization Group extrapolation for D_s

$$D_s(c) = D_s(1)\exp[\int_1^c \mathrm{d}x\ (\bar{a}\,\bar{R}^4 + 2\bar{b}\,\bar{R}^7)] \tag{67}$$

in which $\bar{R} \equiv \bar{R}(x)$ is the concentration-dependent quantity approximated by eq 65.

At this point, having developed the generators β and γ, it would in principle be possible to analyze the fixed points and structure of the renormalization group form for D_s. This calculation confines itself to making an extrpolation from the fixed point at the origin. There is some phenomenological evidence that in the corresponding to theory, not developed here, for the concentration and molecular weight dependence of the viscosity, that an analysis of fixed points may be of greater importance. In particular, for large-M polymers as elevated c, the concentration dependence of the viscosity goes over from a stretched-exponential to a power-law form,[8] η and its concentration derivative being continuous at the transition,[9] suggestive of effects that might be encountered if the theoretical description of the viscosity had a second interesting fixed point.

As the fourth part of the derivation, eq 66 is used to obtain $D_s(c)$. Equation 65 supplies $\bar{R}$ as a function of concentration, permitting numerical integration of eq 65. Note that $\bar{a}$ and $\bar{b}$ have opposite signs, so $\bar{R}(c)$ of eq 65 is not ill-behaved for $c > 1$. (For $c < 1$, eq 65 can be ill-behaved, so eqs 65 and 67 are suspect if used to extrapolate to concentrations $c < 1$. Numerical values for $\bar{a}$ and $\bar{b}$ were obtained above. Because the very simple calculation of the previous section did not include intrachain hydrodynamic interactions, these values are both substantial overestimates. However, the same physical simplifications were made in calculating B_2 and in calculating B_3, so the relative values of B_2 and B_3 should be adequate for a qualitative examination of $D_s(c)$.

Figure 1 shows the PFRG prediction for the concentration dependence of D_s/D_o, based on numerical integration of eqs 67 and 65. For the numerical integration, $\bar{a}$ and $\bar{b}$ were taken from eqs 59 and 60, using eq 40 to supply a numerical value for the factor $-3\pi R^4/4a_o$ of $\bar{a}$ in eq 59 and, similarly, for $\bar{b}$, and choosing $c_r = 0.01$ in the physical units of eqs 40 and 41. The PFRG-calculated D_s is sensibly independent of one's choice of physical reference concentration c_o so long as $D_s(c_o)$ is close to unity. Figure 1 clearly demonstrates that D_s has very nearly a simple exponential dependence on the chain concentration c over more than two magnitudes of decay of D_s, even though eqs 67 and 65 have complicated dependences on c.

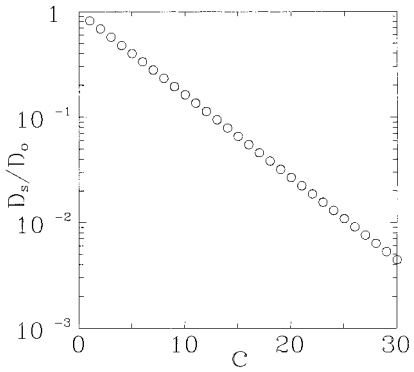

Figure 1. PFRG prediction of the self-diffusion coefficient of polymer chains in nondilute solution. Note the simple-exponential behavior of D_s for chains of constant bare radius R. Concentration units are as per eqs 40 and 41.

Fifth and last, in the integration the bare chain radius R_o was taken to be a constant, while the effective chain radius R is c-dependent. The calculation above refers to chains whose bare, physical radii are independent of c. However, Daoud et al.[14] have shown that real polymer chains in solution contract with increasing polymer concentration, namely with good accuracy as

$$R_g^2(c) = R_{g0}^2 c^{-x} \tag{68}$$

where R_{g0} is the radius at the reference concentration c_o with c in dimensionless units. Experiment and theory concur[14] that $x \approx 1/4$. Equation 68 does not apply to very low-molecular-weight chains and is replaced with a near-linear form at very small c. The renormalization calculation above requires R_o only at the single concentration $c = 1$ and requires R only for $c \geq 1$, so the difficulty that the power-law form of eq 68 at $c \geq 1$ is replaced for $c < 1$ by an unspecified concentration dependence of R_g does not appear to change the following considerations on $D_s(c)$ for $c \geq 1$.

The renormalization group transformation given above may be generalized to treat chains whose physical radii are concentration-dependent in accord with eq 68. To take into account this chain contraction, and construct $D_s(c)$ for real chains, one repeats the calculation of D_s afresh for each final c, each time using the bare R_o corresponding to the final concentration. The concentration dependences of $\bar{R}$ and R_o are physically independent. R_o is the actual size of a chain at the final concentration c, but $\bar{R}$ is a concentration-dependent effective radius, introduced so as to extend the range of validity of the low-order series for D_s.

The effect of chain concentration on $D_s(c)$ may be obtained analytically, without numerical integration, if one is willing to make a slightly cruder approximation for $\gamma(R)$ and $D_s(c)$ than seen above. In the above, $\bar{R}$ followed eq 65, while D_s follows eq 67; the combination of these two equations was integrated numerically. Numerically, $\bar{b}/\bar{a} << 1$; by using the cruder approximation $\bar{b}/\bar{a} \approx 0$ (which is equivalent to truncating the hydrodynamics at $O(R^4)$ rather than the $O(R^7)$ seen above), the numerical integration may instead be performed analytically. Under the new approximation, eqs 65 and 67 become $R = 1$ and $D_s(c) = D_s(1) \exp(R^4\, dx)$. Displaying explicitly the dependence of $\bar{a}$ on the physical chain radius R_g, under the newer and cruder approximation one may integrate eq 67 analytically to find

$$D_s = D_o \exp(-aR_g^4 c^1) \tag{69}$$

for some constant a. Use of eq 68 for the c-dependence of the physical radius leads to the universal scaling equation of the hydrodynamic scaling model

$$D_s = D_o \exp(-aR_o^4 c^{1-2x}) \tag{70}$$

Equation 70 has been derived previously by other means.[11] Earlier references[11] had identified the universal scaling equation as an approximant. From the preceding analysis, this equation is here seen to be the $O(R^4)$ approximant to a more precise form for $D_s(c)$. The identification here of the universal scaling equation as an $O(R^4)$ approximant is consistent with previous derivations of this equation, which included only the two- chain, lowest-order-in-s terms that lead to the $O(R^4)$ approximant for the chain-chain hydrodynamic interaction tensor $\mathbf{b}_{il}$.

Aside: the Stretched Exponential Is an Invariant of the Positive-Function Renormalization Group

With respect to the rational question as to whether the stretched-exponential form is an artifactual consequence of approximations in the above derivation, we now show that the stretched exponential occupies a privileged position. Consider a system property whose true functional form is a stretched exponential

$$A = \exp(\alpha c^{\nu'} R^{\nu}) \tag{71}$$

and whose normalized form for unit reference concentration is

$$\tilde{A}(c, R) = \exp(\alpha R^{\nu}(c^{\nu'} - 1)) \tag{72}$$

As noted in ref 3, if the exact form for $\tilde{A}$ is known, then no approximations are required to compute γ, β, or $\bar{R}$ for any c or R.

We now show that applying the PFRG to eq 72 always recovers the original form for $\tilde{A}$. The infinitesimal generator γ follows from eq 54, namely

$$\gamma(\bar{R}) = \nu'\alpha c \nu'^{-1} R^{\nu} \tag{73}$$

The normalized function satisfies $\tilde{A}(1, R) = 1$, while its derivatives are $\tilde{A}'(1, R) = \nu'\alpha R^{\nu} \equiv \gamma$ and $\tilde{A}''(1, R) = \nu'(\nu' - 1)\alpha R^{\nu} + \nu'^2\alpha^2 R^{2\nu}$. Also, $\partial\gamma/\partial R = \alpha\nu'\nu R^{\nu-1}$, so eq 57 gives

$$\beta = \frac{\nu' - 1}{\nu} R \tag{74}$$

as an exact result.

Replacing β with its derivative form via eq 55 and integrating

$$\int_1^c \frac{1}{\bar{R}} \frac{\partial \bar{R}}{\partial \ln c} d\ln c = \int_1^c d\ln c \, \frac{\nu' - 1}{\nu} \tag{75}$$

so

$$\bar{R}(c) = \bar{R}(1) c^{(\nu'-1)/\nu} \tag{76}$$

Furthermore, eq 53 shows

$$\tilde{A}(c) = \tilde{A}(1) \exp[\int_1^c \gamma(\bar{R})\, dc] \tag{77}$$

If eq 73 is applied for γ and eq 76 for the implicit concentration dependence of $\bar{R}$, integrating gives

$$\tilde{A}(c) = \tilde{A}(1) \exp[\alpha R^{\nu}(c^{\nu'} - 1)] \tag{78}$$

which is the same as the original eq 72.

Q.E.D., the stretched exponential in concentration and coupling parameter is invariant under the positive-function renormalization group transformation. No step of the proof required $\nu \neq 1$ or $\nu' \neq 1$, so invariance is also demonstrated for simple-exponential dependences on c and R.

Discussion

Here we have shown that the Altenberger−Dahler[3] positive-function renormalization group method and a low-concentration series expansion for the self-diffusion cofficient of a polymer chain lead directly to the universal scaling equation as an approximant for the concentration dependence of the polymer self-diffusion coefficient. A detailed numerical expression for $D_s(c)$ awaits refinements in the calculation of the chain-chain hydrodynamic interaction tensors.

This is not the first use of the PFRG to treat dynamic properties of solutions. Altenberger and Dahler[19] have previously used the method, together with known results for the second and third pseudovirial coefficients for the viscosity η of a hard sphere suspension, to compute $\eta(c)$ numerically for hard spheres in a continuum solvent and volume fractions up to 0.6. This paper treats D_s rather than η; unlike ref 19, it was here necessary to compute B_2 and B_3 rather than taking them from the literature.

The physical nature of the coupling parameter $\bar{R}$ in this calculation is somewhat different than in many other renormalization group treatments. Typically one introduces a bare coupling parameter q_o. Iteration of the renormalization process replaces the bare q_o with a dressed coupling parameter q. The dressed q is physically observable, but the bare q_o is not. In contrast, here the bare radius R_o is experimentally observable, while the dressed radius $\bar{R}$ is an effective coupling constant, not the physical size of the chain at some elevated concentration.

How is a dressed radius $\bar{R}$ to be interpreted? Physically, instead of asking what happens to D_s if the volume fraction is increased by increasing N, we could imagine asking what happens to D_s if the volume fraction is increased by increasing the radius of each of a fixed number of particles. If one thinks of $\bar{R}$ as simply a coupling constant for interparticle interactions, this procedure appears transparent. For example, if instead of $\bar{R}$ the field variable were the charge q on a partially charged spherical polyelectrolyte, one could imagine that instead of changing interparticle interaction strengths by changing the concentration, one could change the interparticle interactions by changing q as could be done by changing the solution pH. Unless one encountered a phase transition, the responses of the system to variations in q or c should be equally continuous and integrable.

Because in our case the field variable is the chain radius, potential complications arise. For example, consider the ensemble that describes a suspension of hard spheres. As a sphere radius R is increased, the list of allowed states of the ensemble (allowed lists of particle positions) changes by shrinking, because states in which particles overlap are not allowed, while increasing R causes hitherto nonoverlapping particles to begin to overlap. The renormalization procedure described above does not appear to capture completely correctly the loss of allowed states attendant to an increase in R. However, this difficulty appears to be most serious for volume-excluding potentials. In the present system, polymer chains are free to overlap, with only overlaps of pairs of polymer beads being forbidden. Until quite high concentrations are reached, increasing R should only have a modest effect on the list of allowed states of a polymer system.

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