On dynamic scaling theories of polymer solutions at nonzero concentrations

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A scaling theory is presented for the translational diffusion coefficient of a tagged chain and for the specific viscosity of polymer solutions at nonzero concentration. The derivations employ the full diffusion equation including unaveraged hydrodynamic interactions for the dynamical motion of continuous Gaussian coils with excluded volume. The effects of screened excluded volume and hydrodynamic interactions at nonzero polymer concentrations are introduced through an effective excluded volume strength, $v(c)$, and draining strength, $h(c)$, c being the monomer concentration. For $c[\eta] \lesssim O(1)$, $[\eta]$ is the intrinsic viscosity, the hydrodynamics of the polymer solution is treated using effective medium arguments, resulting in exponential forms for $v(c)$ and $h(c)$ (e.g., $h(c) = h(0)\exp[\text{constant } c[\eta]]$). Towards the concentrated end of the semidilute regime, $c[\eta] \gtrsim O(1)$, a bloblike picture of chain dynamics is seen to appear. An application of the results derived herein is also presented for polyelectrolyte solutions at nonzero concentrations in the presence of added salt.

I. INTRODUCTION

The application of scaling arguments to polymer solutions provides a useful tool to discuss the asymptotic long chain properties of various quantities. These arguments have been successfully used to derive the power law dependence of both equilibrium[1-9,17] and dynamic[10-17] solution parameters as a function of the number of monomers per chain N, the monomer concentration c, etc., when N is "sufficiently" large. They have also recently shed some light on the behavior of polyelectrolytes.[17]

Although a "rigorous" justification of scaling exists only in the case of static properties, where a full renormalization group treatment is possible,[1,2] Komas and Freed[9] and Adler and Freed[16] (henceforth referred to as KF and AF, respectively) demonstrate that the scaling functions, upon which scaling theories are based, follow from a simple dimensional analysis of the polymer free energy functional and of the dynamical equations of motion when the presence of certain cutoff dependencies is ignored. These scaling relations explicitly contain all dimensional quantities. They, therefore, enable the derivation of the exponents in the power law dependence of, for example, the translational diffusion coefficient D as a function of N when combined with interdimensional scaling arguments. We find that $D \propto N^{-\nu_d}$, where $\nu_d = 3/(d+2)$, $d = 1, \ldots, 4$, is the Flory exponent in agreement with the *assumption* of de Gennes.[10]

In contrast to the equilibrium properties of a polymer solution for which scaling behavior is well documented experimentally, the characterization of transport coefficients has proven to be a rather subtle issue both experimentally and theoretically.[19-23] Several reasons for these complications include the following:

(i) Short wavelength cutoffs usually enter as irrelevant variables in scaling theories, although it is known that such cutoffs introduce corrections to the critical indices in the case of critical phenomena. The extent to which these alter static properties can be estimated using renormalization group arguments. The effect of these cutoffs on dynamical properties have not as yet been assessed.

(ii) Dynamical experiments,[19] to date, for the hydrodynamic radius of a single chain $R_h \propto D^{-1}$ have not been performed in a truly asymptotic regime as a result of the inverse distance dependence of the hydrodynamic interactions. Akcasu et al.[21] and Weill and des Cloiseaux[22] have accounted for the observed molecular weight dependence of R_h within the context of the blob model.[15] Physically, their arguments that hydrodynamic properties, dependent on $\langle |R_i - R_j|^{-1} \rangle$, require much longer chains to become asymptotic than equilibrium properties. The latter probe long wavelength behavior, e.g., the radius of gyration with averages like $\langle |R_i - R_j|^2 \rangle$. (Here R_i denotes the position of the ith segment and the average is over the configurational distribution of a chain.)

(iii) The transition from the pseudogel to the regime in which entanglements are fully developed has not been satisfactorily described. The reptation model, proposed by de Gennes,[10] and the more quantitative tube model of Doi and Edwards[24] are positive steps in gaining an understanding of the entanglement regime. However, these theories predict that the polymer viscosity $\propto N^3$ as opposed to the experimentally observed $N^{3,4}$ dependence.[23]

(iv) It appears that scaling theories are only capable of expressing certain homogeneity relations and power law dependencies.

Recently, Odijk[17] has applied scaling arguments to the behavior of polyelectrolyte solutions. In the presence of added salt, the condensation of counterions along a polyion results in a renormalized, salt concentration-dependent Kuhn length and excluded volume strength.[25,26] Odijk has evaluated the scaling behavior of various equilibrium properties (e.g., mean square end to end

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distance, $\langle R^2 \rangle$), and the intrinsic viscosity $[\eta]$ with considerable agreement with experiment.

In this paper the dynamical scaling theory proposed by AF is extended to nonzero concentrations. The latter consider continuous Gaussian chains with excluded volume. It is in the asymptotic long chain limit, in which the chain may be regarded as a continuous space curve, that simple scaling functions are obeyed. In addition, the full polymer diffusion equation without preaveraging of the Oseen tensor is employed. The arguments presented below deal primarily with the behavior of the specific viscosity, $\eta_{sp}(c)$, where c is the polymer concentration. The important features of the present work are as follows:

(i) The transition from nondraining to free-draining behavior is taken to depend only on a single "renormalized" draining strength, $h(c)$, in Θ solvents. For good solvents, we likewise include a renormalized excluded volume parameter, $v(c)$, thereby characterizing a polymer by the set $\{h(c), v(c)\}$.

(ii) Effective medium arguments are used to give expressions for $h(c)$ and $v(c)$. The resulting scaling functions are, therefore, found *not* to involve simple power law behavior. It is shown, for example, that there exists a concentration regime over which $\eta_{sp}(c)$ increases exponentially with c in agreement with the empirical Martin equation.[23] This concentration regime involves values of c for which $h \exp(-k_H[\eta]c) \gg 1$ where h is proportional to the draining parameter and k_H is the Huggins coefficient. Thus the exponential form persists well into the semidilute region for long chains.

(iii) In the higher concentration regime the scaling functions are shown to exhibit "blob" behavior in accordance with the so-called blob model introduced by Daoud.[3]

(iv) The recent work of Odijk[17] for polyelectrolytes is extended to nonzero concentrations of polymer in the case of added salt. The onset of entanglements are *not* explicitly treated. Therefore, we are restricted to concentrations below which macroscopic manifestations of the latter occurs.

The transformations used to obtain scaling relations at nonzero polymer concentration is addressed in the next section. These are then applied to the correlation function expression for the specific viscosity resulting in a scaling form for $\eta_{sp}(c)$. As a matter of convenience, Θ and good solvents are considered separately in Sec. III, where the concepts of a renormalized draining parameter, $h(c)$, and excluded volume, $v(c)$ are introduced. Effective medium arguments are used to give explicit expressions for $h(c)$ and $v(c)$, which are expected to be valid for $c[\eta] \lesssim O(1)$. The arguments of Sec. III are then used to obtain a scaling relation for the translational diffusion coefficient of a tagged chain in Sec. IV. Section V deals with the behavior of $v(c)$ and $h(c)$ in the higher concentration regime, and draws a connection between the scaling procedure presented here and the so-called blob model. An extension of Odijk's scaling arguments for polyelectrolytes in the presence of added salt and at nonzero polymer concentration is treated in Sec. VI.

II. DYNAMICAL SCALING AT FINITE CONCENTRATION: THE SPECIFIC VISCOSITY

Dynamical scaling relations at nonzero concentration follow from a simple extension of the ideas set forth in AF and KF.[9,16] We require a knowledge of the n chain free energy and time evolution operator for continuous Gaussian coils with excluded volume. The former is given by

$$(k_B T)^{-1} F[\{\mathbf{R}_\alpha\}, L, l, v] = \frac{3}{2l} \sum_{\alpha=1}^{n} \int_0^L ds \left| \frac{\partial}{\partial s} \mathbf{R}_\alpha(s) \right|^2$$
$$+ \frac{v}{2l^2} \sum_{\substack{\alpha, \beta=1 \\ \alpha \neq \beta}}^{n} \int_0^L ds \int_0^L ds_0 \delta[\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s_0)] , \qquad (2.1)$$

where $\mathbf{R}_\alpha(s)$ denotes the position vector from an arbitrary origin to a point at a contour length s measured along chain α, L denotes the extended length of an individual chain, l is the Kuhn length, v is the excluded volume strength, and $k_B T$ is the temperature in units of energy.

The corresponding evolution operator in the diffusion approximation is

$$\Lambda = \sum_{\alpha, \beta=1}^{n} \int_0^L ds \int_0^L ds_0 \left[\frac{\delta}{\delta \mathbf{R}_\alpha(s)} - \frac{1}{k_B T} \frac{\delta}{\delta \mathbf{R}_\alpha(s)} F[\{\mathbf{R}_\beta\}, L, l, v] \right]$$
$$\times \left[\frac{k_B T l}{\zeta} l \delta(s - s_0) \delta_{\alpha\beta} + \frac{k_B T}{\eta_0} \mathbf{T}[\mathbf{R}_\alpha(s) - \mathbf{R}_\beta(s_0)] \right] \cdot \frac{\delta}{\delta \mathbf{R}_\beta(s_0)}$$
$$(2.2)$$

where ζ/l denotes the friction coefficient per unit length of chain,

$$\frac{1}{\eta_0} \mathbf{T}[\mathbf{x}] = \frac{1}{8\pi\eta_0 |\mathbf{x}|} \left[\mathbf{I} + \frac{\mathbf{x}\mathbf{x}}{|\mathbf{x}|^2} \right] \qquad (2.3)$$

is the Oseen tensor, and η_0 is the solvent viscosity. As remarked by AF, the Oseen tensor Eq. (2.3) is taken as the fundamental source of hydrodynamic interactions, although the arguments presented are equally valid for an appropriate d dimension hydrodynamic interaction tensor. The results for $d = 3$ are the same in either approach.

As the viscosity and diffusion coefficient can be evaluated from correlation function expressions, the notation for the correlation functions is introduced. The configurational, two-time correlation function is calculated according to

$$\langle A(t)B(0) \rangle \equiv \int \prod_{\alpha=1}^{n} \mathfrak{D}[\mathbf{R}_\beta(s)] \exp \left\{ -\frac{1}{k_B T} F[\{\mathbf{R}_\beta\}, L, l, v] \right\} B[\{\mathbf{R}_\beta\}]$$
$$\times e^{t\Lambda} A[\{\mathbf{R}_\beta\}] \bigg/ \int \prod_{\alpha=1}^{n} \mathfrak{D}[\mathbf{R}_\alpha(s)] \exp \left\{ -\frac{1}{k_B T} F[\{\mathbf{R}_\alpha\}, L, l, v] \right\} ,$$
$$(2.4)$$

for A and B arbitrary. $A(t) = e^{t\Lambda} A$ denotes the time evolution of A. Following KF we introduce a *simple change in variables*,

$$\mathbf{R}_\alpha'(s') \equiv \frac{b^{1/2}}{l} \mathbf{R}_\alpha(s), \quad b > 0, \text{ any } \alpha \qquad (2.5a)$$

$$s' \equiv \frac{b}{l} s . \qquad (2.5b)$$

In addition to Eq. (2.5), t must also be rescaled. However, as opposed to using Eq. (2.6) in AF, it is convenient to define

$$t' \equiv \frac{k_B T}{\zeta l^2} b^2 t . \qquad (2.6)$$

Substitution of Eqs. (2.5)–(2.6) into the expressions for the free energy, and the time evolution operator,[27] Eqs. (2.1) and (2.2), respectively, results in the following homogeneity relations,

$$F[\{\mathbf{R}_\alpha\}, L, l, v] = F[\{\mathbf{R}'_\alpha\}, Nb, 1, vl^{-d}b^{d-4/2}] , \qquad (2.7a)$$

$$t\Lambda\left[\left\{\frac{\delta}{\delta\mathbf{R}_\alpha}\right\}, \{\mathbf{R}_\alpha\}, L, l, v, \frac{k_B Tl}{\zeta}, \frac{k_B T}{\eta_0}\right]$$

$$= t'\Lambda\left[\left\{\frac{\delta}{\delta\mathbf{R}'_\alpha}\right\}, \{\mathbf{R}'_\alpha\}, Nb, 1, vl^{-d}b^{d-4/2}, 1, \frac{\zeta}{\eta_0 l}b^{-1/2}\right] , \qquad (2.7b)$$

where $N = L/l$ and d is the dimensionality of the system under consideration. Equations (2.5)–(2.7) enable the derivation of "exact" scaling functions (exact within the context of the dynamical and equilibrium model behavior with the neglect of small cutoff corrections) for various equilibrium and transport properties of the solution.

Linear response theory predicts that the specific viscosity, η_{sp}, may be written as[28]

$$\eta_{sp}(c) = \frac{1}{k_B T \eta_0 V} \int_0^\infty dt \langle J(t) J(0) \rangle , \qquad (2.8)$$

where V is the system volume. $J(t)$ is the momentum flux tensor

$$J(t) = -\sum_{\alpha=1}^n \int_0^L ds\, \mathbf{R}_{\alpha x}(s, t)$$

$$\times \frac{\delta}{\delta R_{\alpha y}(s, t)} F[\{\mathbf{R}_\beta\}, L, l, v] . \qquad (2.9)$$

Applying the variable transformations (2.5)–(2.6) to Eqs. (2.8) and (2.9) and noting the homogeneity relations, (2.7), yields a scaling function for $\eta_{sp}(c)$,

$$\eta_{sp}(c) = \frac{\zeta l^2 b^{-2}}{\eta_0 V} f\left(n, Nb, vl^{-d}b^{d-4/2}, \frac{\zeta}{\eta_0 l}b^{-1/2}, Vb^{d/2}l^{-d}\right) . \qquad (2.10)$$

In order that (2.10) exist in the thermodynamic limit, $n \to \infty$, $V \to \infty$, $n/V \to c N_A/M$, M being the molecular weight of a chain and N_A Avogadro's number, f must exhibit an overall proportionality to n. Furthermore, other factors of n and $Vb^{d/2}l^{-d}$ combine as $n/V(b^{1/2}l^{-1})^d = c N_A/M(b^{1/2}l^{-1})^d$. Therefore, Eq. (2.10) reduces to

$$\frac{\eta_{sp}(c)}{c} = \frac{\zeta l^2 N_A N^2}{M\eta_0} \hat{f}_\eta\left(c/c_0^*, \frac{\zeta}{\eta_0 l}N^{1/2}, vl^{-3}N^{1/2}\right) , \qquad (2.11)$$

for the choice $b = N^{-1}$, $d = 3$ and the definition

$$c_0^* \equiv M/N_A(N^{1/2}l)^3 . \qquad (2.12)$$

We recognize the characteristic concentration c_0^* at which chains begin to interpenetrate in a Θ solvent and the appearance of the draining parameter (apart from a numerical factor)

$$h \equiv \frac{\zeta}{\eta_0 l}N^{1/2} , \qquad (2.13)$$

which measures the strength of the hydrodynamic interactions at infinite dilution.

III. REPRESENTATION IN TERMS OF RENORMALIZED PARAMETERS: THE EFFECTIVE MEDIUM ASSUMPTION

In the arguments to follow, it is convenient to first consider Θ solvents in which only hydrodynamic interactions are screened in the case of Gaussian coils. The generalization to include excluded volume interactions is then fairly straightforward.

A. $\eta_{sp}(c)$ for Θ solvents

Setting $v = 0$ in the expression for $\eta_{sp}(c)$, Eq. (2.11), yields

$$\frac{\eta_{sp}(c)}{c} = \frac{N^2 N_A \zeta l^2}{M\eta_0}\hat{f}_\eta\left(\frac{c}{c_0^*}, h, 0\right) . \qquad (3.1)$$

At infinite dilution, $c \to 0$, the only relevant variable is the draining parameter $h = (\zeta/\eta_0 l)N^{1/2}$. In the limit as $N \to \infty$, or $h \to \infty$, AF have shown that the self-friction ζ becomes irrelevant. This implies that $\hat{f}_\eta$ must obey the power law,

$$\hat{f}_\zeta(0, x, 0) \propto x^y , \qquad (3.2)$$

where y is determined by the requirement that $\eta_{sp}(0) = c[\eta]$ be independent of ζ. The appropriate choice is $y = -1$ giving

$$[\eta] = a_\eta \frac{N_A N^{3/2} l^3}{M} = a_\eta/c_0^*, a_\eta = \text{constant} . \qquad (3.3)$$

Equation (3.3) is the usual Rouse–Zimm result[18] and, furthermore, indicates the interchangeability of c_0^* and $[\eta]$ in Θ solvents (apart from an unknown constant). The coefficient a_η is not given by scaling theory, but is well known from Rouse–Zimm theory ($a_\eta = \pi^{3/2}(0.586)/4\sqrt{3}$). $c[\eta]$ has been used widely as a scaling variable in polymer solution theory,[23] and the above analysis shows that it emerges in the asymptotic, $N \to \infty$, long chain limit.

As the concentration is increased, hydrodynamic screening sets in and, therefore, h is no longer the only relevant variable. Instead we expect that h is replaced by a concentration dependent draining strength, $h(c)$, such that

$$\frac{\eta_{sp}(c)}{c} = \frac{N^2 N_A \zeta l^2}{M\eta_0}f_\eta(h(c)) .$$

Comparing this expression to Eq. (3.1) leads to the assertion that

$$\frac{\eta_{sp}(c)}{c} = \frac{N^2 N_A \zeta l^2}{M\eta_0}f_\eta(h\,g(c[\eta])) , \qquad (3.4)$$

where the dimensional equivalence of c_0^* and $[\eta]$ have been used, $c_0^* = a_\eta/[\eta]$. Equation (3.4), thus, defines a draining strength

$$h(c) \equiv h\,g(c[\eta]) = \frac{\zeta}{\eta_0 l}N^{1/2}g(c[\eta]) , \qquad (3.5)$$

in terms of a new concentration dependent function, $g(c[\eta])$. Note that (3.5) describes the total dimensionless strength of the hydrodynamic interactions. As Freed and Edwards[29] have shown, the averaged Oseen tensor, Eq. (2.3), dramatically changes its functional form for $c \gtrsim c_0^*$.

The problem is now reduced to the determination of a function of a single variable. At $c = 0$, we require $h(0) = h$ or equivalently, $g(0) = 1$. On the other hand, the specific viscosity reduces to the Rouse result[18] as $c \to \infty$, when the effects that produce entanglements are ignored, $\eta_{sp}(\infty) \propto N^2 N_A \zeta l^2 c / M \eta_0$. The latter result follows from Eq. (3.4) provided that $g(\infty) = 0$, then it gives

$$\eta_{sp}(\infty) = \frac{c N_A N^2 l^2 \zeta}{M \eta_0} f_\eta(0) . \qquad (3.6)$$

These considerations, therefore, provide a set of boundary conditions for $g(c[\eta])$,

$$g(0) = 1 , \qquad g(\infty) = 0 . \qquad (3.7)$$

A specific form for g may be obtained by invoking effective medium arguments.[29] An approach is used similar to that employed by Brinkman.[30] We can regard $h(c)$ as specifying the draining strength for a single chain in the effective medium produced by the solvent plus all the other chains. The addition of more polymers δc to the solution alters the draining parameter $h(c)$ to $h(c)g(\delta c[\eta])$ in order to account for the hydrodynamic screening in the "effective" solvent. However, this new solution is equivalent to a solution which is already at concentration $\bar{c} = c + \delta c$. Consequently, the two draining parameters are related to one another as follows:

$$h(\bar{c}) = h(c + \delta c) = h(c)g(\delta c[\eta]) \qquad (3.8a)$$

or

$$g((c + \delta c)[\eta]) = g(c[\eta])g(\delta c[\eta]) \qquad (3.8b)$$

Equation (3.8b) is well known in statistical mechanics[31] as relating the equilibrium statistics between two weakly coupled systems. For continuous arguments, Eq. (3.8b) has the unique solution

$$g(c[\eta]) \exp(-\alpha[\eta]c) , \quad \alpha = \text{constant} . \qquad (3.9)$$

The boundary conditions, Eq. (3.7), applied to (3.9) result in the choice $\alpha > 0$. Substitution of the expression for $g(c[\eta])$ into (3.4) yields

$$\frac{\eta_{sp}(c)}{c} = \frac{N_A N^2 \zeta l^2}{M \eta_0} f_\eta[h \exp(-\alpha[\eta]c)] . \qquad (3.10)$$

For sufficiently long chains and/or at sufficiently low concentrations the condition $h \exp(-\alpha[\eta]c) \gg 1$ is satisfied. In this asymptotic regime the behavior of $f_\eta(x)$ is given by Eq. (3.2) with $y = -1$. Thus,

$$\eta_{sp}(c) = c[\eta] \exp(\alpha[\eta]c), \quad h \exp(-\alpha[\eta]c) \gg 1 . \qquad (3.11)$$

Such behavior as displayed in Eq. (3.11) is indeed observed experimentally (before the onset of entanglements) and is known as the empirical Martin equation.[23] Furthermore, Eq. (3.11) is an example of a nonpower law dependence obtained from scaling arguments (i.e., for $c[\eta] \lesssim O(1)$, $\eta_{sp}(c)$ will not exhibit a behavior such as $\eta_{sp}(c) \propto c^x$, $x \neq 0$).

As exact determination of α in terms of a solution property follows from the above expression for $\eta_{sp}(c)$. At small concentrations, expansion of the exponential gives

$$\eta_{sp}(c) = c[\eta](1 + c[\eta]\alpha + O(c^2)) .$$

Experimentally, the Huggins coefficient, k_H, is defined

by the expansion

$$\eta_{sp}(c)\big|_{exp} = c[\eta](1 + c[\eta]k_H + O(c^2)) ,$$

from which we identify $\alpha = k_H$, or

$$\frac{\eta_{sp}(c)}{c} = \frac{N_A N^2 \zeta l^2}{M \eta_0} f_\eta(h(c)) , \qquad (3.12a)$$

$$h(c) = \frac{\zeta}{\eta_0 l} N^{1/2} \exp(-k_H[\eta]c) . \qquad (3.12b)$$

B. $\eta_{sp}(c)$ for good solvents

In good solvents hydrodynamic and excluded volume interactions are screened. In analogy to part A, we expect that both h and v are renormalized. Therefore, we write Eq. (2.11) as $(d = 3$ again)

$$\frac{\eta_{sp}(c)}{c} = \frac{N^2 N_A \zeta l^2}{M \eta_0} f_\eta\left(\frac{\zeta}{\eta_0 l} N^{1/2}\right.$$
$$\left. \times g_1\left(\frac{c}{c_0^*}, vl^{-3}N^{1/2}\right), vl^{-3}N^{1/2} g_2\left(\frac{c}{c_0^*}, vl^{-3}N^{1/2}\right)\right). \quad (3.13)$$

This particular decomposition displays both intermolecular and intramolecular excluded volume; the former by the screening functions g_1 and g_2, and the latter by the explicit $vl^{-3}N^{1/2}$ dependence.

As noted by de Gennes, the demarcation between dilute and semidilute behavior in good solvents occurs at a characteristic concentration,

$$c^* \sim M/N^{3\nu} , \quad \nu \simeq 0.6 \text{ as } N \to \infty ,$$

which reflects the perturbed chain dimensions. Following KF, we, therefore, invoke the power law form

$$g_i = \bar{g}_i\left(\frac{c}{c_0^*}(vl^{-3}N^{1/2})^x\right) , \quad i = 1, 2 , \quad vl^{-3}N^{1/2} \gg 1 , \quad (3.14)$$

with the requirement that $N^{1/2(1+x)} = N^{-1+3\nu}$ or $x = 3(2\nu - 1)$, thereby introducing the characteristic concentration

$$c^* = M/N_A N^{3\nu} l^3 (vl^{-3})^{3(2\nu-1)} . \qquad (3.15)$$

In good solvent (3.13) then reduces to

$$\frac{\eta_{sp}(c)}{c} = \frac{N_A N^2 \zeta l^2}{M \eta_0} f_\eta\left(\frac{\zeta}{\eta_0 l} N^{1/2} \bar{g}_1\left(\frac{c}{c^*}\right), vl^{-3}N^{1/2} \bar{g}_2\left(\frac{c}{c^*}\right)\right) \qquad (3.16)$$

as a consequence of Eqs. (3.14)–(3.15).

We may again choose $\bar{g}_1(0) = \bar{g}_2(0) = 1$ in order to recover our previous results at infinite dilution,

$$[\eta] = \frac{N_A N^4 \zeta l^2}{M \eta_0} f_\eta\left(\frac{\zeta}{\eta_0 l} N^{1/2}, vl^{-3}N^{1/2}\right) , \qquad (3.17)$$

for which only intramolecular interactions are important. Once more the irrelevance of the self-friction ζ for long chains at infinite dilution results in

$$f_\eta(x, y) = \frac{1}{x} f_\eta'(y), x \gg 1 . \qquad (3.18)$$

For large excluded volume, $vl^{-3}N^{1/2} \gg 1$, AF show that

$$f_\eta'(y) \propto y^{3(2\nu-1)} , \quad y \gg 1 . \qquad (3.19)$$

Combining these two asymptotic forms with (3.17) reproduces the expression for $[\eta]$ given by AF,

$$[\eta] = a_\eta' \frac{N_A}{M} l^3 N^{3\nu} (vl^{-3})^{3(2\nu-1)} = a_\eta'/c^* , \qquad (3.20)$$

where $(\zeta/\eta_0 l)N^{1/2} \gg 1$, $v l^{-3} N^{1/2} \gg 1$, and a_η' is a number which cannot be determined by pure scaling arguments. The interchangeability of c^* and $[\eta]$ as scaling variables is again displayed.

Specific forms for the $\tilde{g}_i(c/c^*)$ are obtained using the same effective medium arguments leading to (3.9),

$$g_i(c[\eta]) = \exp(-\alpha_i c[\eta]), \qquad \tilde{g}_i(c/c^*) \equiv g_i(c[\eta]) . \quad (3.21)$$

The requirement at very high concentrations, that $\eta_{sp}(\infty)$ $\propto c N^2 N_A \zeta l^2/M\eta_0$ indicates that $\alpha_i > 0$. Equation (3.16), therefore, reduces to

$$\frac{\eta_{sp}(c)}{c} = \frac{N_A N^2 l^2 \zeta}{M\eta_0} f_\eta\left(\frac{\zeta}{\eta_0 l}N^{1/2}\exp(-\alpha_1 c[\eta]),\right.$$
$$\left. v l^{-3} N^{1/2} \exp(-\alpha_2 c[\eta])\right) . \quad (3.22)$$

Making use of Eqs. (3.18) and (3.19) enables the elimination of one of the α_i in terms of the Huggins' coefficient in good solvents. Thus, for $(\zeta/\eta_0 l)N^{1/2}$ $\times \exp(-\alpha_1 c[\eta]) \gg 1$, $v l^{-3} N^{1/2} \exp(-\alpha_2 c[\eta]) \gg 1$, we have

$$\eta_{sp}(c) = c[\eta] \exp\{c[\eta](\alpha_1 - 3(2\nu - 1)\alpha_2)\} , \quad (3.23)$$

which suggests that

$$k_H = \alpha_1 - 3(2\nu - 1)\alpha_2 . \quad (3.24)$$

k_H involves contribution from both hydrodynamic and excluded volume screening. Again the scaling theory cannot provide values of k_H in (3.24) or α in (3.11); a detailed theory is needed. Calculations of k_H for Θ and good solvents has been given.[32] k_H drops by a factor of roughly two in going from Θ to good solvents, while $[\eta]$ increases. Hence, when the viscosity expansion factor, α_η^3, obeys $\alpha_\eta^3 < 2$, $k_H[\eta]c$ is larger for Θ solutions, but for $\alpha_\eta^3 > 2$ the reverse is true.

Before proceeding, several important points should be discussed:

(i) The exponential forms (3.11) and (3.23) have well defined ranges of validity (i.e., $h(c) \gg 1$, $v(c)N^{1/2}l^{-3} \gg 1$). At higher concentrations and/or for shorter chains the behavior of $\eta_{sp}(c)$ requires a knowledge of the functional dependence of f_η.

(ii) The expression for $[\eta]$, Eq. (3.20) is valid only for very long chains. Dynamical experiments, to date, have not attained the asymptotic limit for which Eq. (3.20) is applicable. Therefore, it is reasonable that the expression given for $[\eta]$ above be replaced by that given by the blob model calculations of Akcasu et al., and Weill and des Cloizeaux[21] to approximately correct for nonasymptotic behavior.

(iii) The work of Daoud et al.,[3] suggests that in the semidilute regime, $c[\eta] \gtrsim 1$, a chain behaves as a Gaussian coil consisting of blobs, each blob of dimension

$$\xi(c) = l\left(\frac{N_A l^3 c}{M_A}\right)^{\nu/1-3\nu}(v l^{-3})^{(2\nu-1)/(1-3\nu)} , \quad (3.25)$$

M_A being the mass of a monomer. Within the blob strong excluded volume and hydrodynamic interactions persist. Although the exponential form for $g_i(c[\eta])$ Eq. (3.21), is expected to be valid far into the semidilute region, a smooth transition to bloblike behavior should

occur for the higher concentration region $c[\eta] \gtrsim O(1)$. In the latter regime, the effective medium arguments employed earlier are, presumably, no longer valid. This transitional behavior is considered further in Sec. V.

(iv) The theory, as elucidated thus far, is incapable of adequately describing the onset of entanglements.

IV. TRANSLATIONAL DIFFUSION COEFFICIENT FOR A TAGGED CHAIN

A scaling relation for the translational diffusion coefficient D is readily obtained from linear response theory as a correlation function expression,[33]

$$D(c) = \frac{1}{3} \int_0^\infty dt\langle \mathbf{V}_\alpha(t) \cdot \mathbf{V}_\alpha(0)\rangle , \quad (4.1)$$

where $\mathbf{V}_\alpha(t)$ is the center of mass velocity of the tagged chain α,

$$\mathbf{V}_\alpha(t) = \frac{1}{L} \int_0^L ds \frac{\partial}{\partial t}\mathbf{R}_\alpha(s, t) . \quad (4.2)$$

Applying the transformations (2.5)–(2.6) to (4.1) and (4.2), and requiring that the thermodynamic limit exists, results in the following scaling relation for $D(c)$:

$$D(c) = \frac{k_B T}{\zeta N} f\left(\frac{\zeta}{\eta_0 l}N^{1/2}, v l^{-3} N^{1/2}, c/c_0^*\right) , \quad (4.3)$$

where the selection $b = N^{-1}$ is made.

In Θ solvents, $v = 0$, the draining parameter, $h = (\zeta/\eta_0 l)N^{1/2}$, and the reduced concentration $c/c_0^* \propto c[\eta]$ are expected to combine according to Eq. (3.12b). We find that $D(c)$ is then given by

$$D(c) = \frac{k_B T}{\zeta N} f_D(h \exp(-k_H'[\eta]c) , \quad (4.4)$$

which displays the Rouse behavior, $D(\infty) \propto k_B T/\zeta N$, when entanglement effects are ignored. The requirements that $D(c)$ be independent of ζ for $h \exp(-k_H'c[\eta]) \gg 1$ results in the asymptotic behavior

$$D(c) = a_D \frac{k_B T}{\eta_0 l}N^{-1/2}\exp(-k_H'[\eta]c) , \quad a_D = \text{constant} . \quad (4.5)$$

At $c = 0$, the Rouse–Zimm result,

$$D(0) = a_D \frac{k_B T}{\eta_0 l}N^{-1/2} \quad (4.6)$$

is recovered. If hydrodynamic screening for D were determined by the same effective draining parameter $h(c)$, as for $\eta_{sp}(c)$, then k_H' would equal k_H. However, this is not a requirement of the arguments presented thus far.

In good solvents, $v l^{-3} N^{1/2} \gg 1$, an expression for $D(c)$ is obtained in analogy to (3.22),

$$D(c) = \frac{k_B T}{N\zeta} f_D(h \exp(-\alpha_1'c[\eta]), v l^{-3} N^{1/2}\exp(-\alpha_2'[\eta]c) \quad (4.7)$$

The scaling function $f_D(x, y)$ displays asymptotic dependences on x and y that reflect the irrelevance of ζ as $c \to 0$ and the perturbed chain dimensions,

$$f_D(x, y) = x f_D'(y) , \quad x \gg 1 , \quad (4.8a)$$

$$f'_D(y) \propto y^{-(2\nu-1)} \ , \quad y \gg 1 \ . \tag{4.8b}$$

Consequently, $D(c)$ is given by

$$D(c) = a'_D (k_B T/\eta_0 l) N^{-\nu} (vl^{-3})^{-(2\nu-1)} \exp\{-c[\eta](\alpha'_1 - (2\nu-1)\alpha'_2)\},$$

$$a'_D = \text{constant}, \quad h \exp(-\alpha'_1[\eta]c) \gg 1,$$

$$vl^{-3}N^{1/2} \exp(\alpha'_2[\eta]c) \gg 1 \ . \tag{4.9}$$

Expanding the exponential in Eq. (4.9) leads to an identification of the second virial correction $\overline{k}_H$ to $D(c)$,

$$\overline{k}_H = \alpha'_1 - (2\nu-1)\alpha'_2 \ , \tag{4.10}$$

which follows from

$$D(c)\big|_{\text{exp}} = D(0)(1 - \overline{k}_H c[\eta] + O(c^2)) \ . $$

V. SCALING RELATIONS FOR $h \exp(-k_H c[\eta]) \gg 1$ IN GOOD SOLVENTS

As discussed earlier, the blob model contends that in the semidilute regime, $c[\eta] \gtrsim 1$, a chain displays Gaussian behavior characterized by an effective segment whose dimension is given by the screening length $\xi(c)$, Eq. (3.25). Within a distance scale $\sim \xi(c)$, a coil experiences strong excluded volume and hydrodynamic interactions. Such a transition to blob behavior indicates an apparent breakdown in the effective medium arguments leading to the exponential forms

$$g_i(c[\eta]) = \exp(-\alpha_i[\eta]c) \ , \quad i = 1, 2 \ ,$$

which are expected to be valid for $h \exp(-\alpha_i[\eta]c) \ll 1$. In the latter regime, the polymer solution is characterized by a uniform distribution of spherical objects of volume $\sim N^{3\nu}l^3 \propto [\eta]/M$. However, for $h \exp(-\alpha_i[\eta]c) \gg 1$, the only relevant distance scale is $\xi(c)$, which is not expressed in the exponential form for $g_i(c[\eta])$. We must, therefore, invoke a new type of behavior for the $g_i(c[\eta])$ in the higher concentration regime.

Arguments presented up to now have incorporated the effects of nonzero concentrations through the renormalized parameters,

$$h(c) = (\zeta/\eta_0 l)N^{1/2}g_1(c[\eta]) \ ,$$

and

$$v(c)l^{-3}N^{1/2} = vl^{-3}N^{1/2}g_2(c[\eta]) \ .$$

In the lower concentration range the validity of effective medium arguments suggest the behavior

$$\ln g_i(c[\eta]) = \alpha_i c[\eta] + O((c[\eta])^2), \quad c[\eta] \lesssim O(1) \tag{5.1}$$

On the other hand, for higher concentrations, $c[\eta] \gtrsim O(1)$, the effective excluded volume and draining strengths no longer depend on the number of monomers, N, per chain. Thus, we require a power law dependence

$$g_i(c[\eta]) = a_{g_i}(c[\eta])^x, \quad a_{g_i} = \text{constant} \ , \tag{5.2}$$

where x is chosen such that $N^{1/2}(c[\eta])^x$, the effective number of monomers, $n(c)$, experiencing strong excluded volume and hydrodynamic interactions, be independent of N. This condition yields $x = \frac{1}{2}(1 - 3\nu)^{-1}$ or

$$h(c) = a_{g_1}(\zeta/\eta_0 l)(c N_A l^3/M_A)^{1/2(1-3\nu)}$$

$$\times (vl^{-3})^{(3/2)(2\nu-1)/(1-3\nu)}, \quad c[\eta] \gg 1 \tag{5.3a}$$

$$v(c)l^{-3}N^{1/2} = a_{g_2}vl^{-3}(c N_A l^3/M_A)^{1/2(1-3\nu)}$$

$$\times (vl^{-3})^{(3/2)(2\nu-1)/(1-3\nu)} , \tag{5.3b}$$

suggesting that $n(c)$ is given by

$$n(c) = (c N_A l^3/M_A)^{(1-3\nu)^{-1}}(vl^{-3})^{3(2\nu-1)/(1-3\nu)} \ . \tag{5.4}$$

This value differs (in the v dependence) from the number of monomers in a blob given by Daoud.

For sufficiently large values of $n(c)$, Eqs. (3.18), (3.19), and (4.8) are applicable resulting in

$$\eta_{\text{sp}}(c) \propto \frac{c N^2 N_A}{M}\xi^3(c), \ n^{1/2}(c)\frac{\zeta}{\eta_0 l} \gg 1, \ n^{1/2}(c)vl^{-3} \gg 1, \tag{5.5a}$$

$$D(c) \propto \frac{k_B T}{N\eta_0 \xi(c)} \ , \tag{5.5b}$$

where $\xi(c)$ is the screening length, Eq. (3.25). It is of interest to see whether such a bloblike region of chain behavior can be distinguished experimentally before the onset of the entanglement regime.

VI. APPLICATION TO POLYELECTROLYTES

In polyelectrolyte solutions the elementary charges q_e situated along a polyion, introduce a large degree of local stiffness into the configurational behavior of the chain. Consequently, the polyion exhibits rodlike behavior as opposed to the random coil behavior of its nonionic counterpart. The addition of salt effectively reduces the range of correlations along the polyion due to counterion condensation. Odijk and Houwaart[25] and Skolnick and Fixman[26] have shown that in the latter case the polyion is well represented as a Gaussian coil with excluded volume (for sufficiently long chains). In the former the effective Kuhn length l_{eff} and excluded volume strength v_{eff} are approximately given as

$$l_{\text{eff}} \simeq l + \frac{1}{8Q\kappa^2} \tag{6.1a}$$

$$v_{\text{eff}} \simeq 32\pi l_{\text{eff}}^2 \kappa^{-1} \tag{6.1b}$$

where the parameters entering Eq. (6.1) are defined as follows:

(i) l is the Kuhn length in the absence of the charges q_e.

(ii)
$$Q = q_e^2/D(k_B T) \tag{6.2}$$

is the Bjerrum length. D is the dielectric constant of the solvent.

(iii)
$$\kappa^{-1} = (8\pi Q n)^{-1/2} \tag{6.3}$$

is the Debye–Hückel screening length, and n is the concentration of added monovalent salt. The ranges of validity of (6.1) are discussed in detail by Odijk.[17,25]

The polyion of contour length L and effective Kuhn length l_{eff} has

$$N_{\text{eff}} = L/l_{\text{eff}} \tag{6.4}$$

statistical segments associated with it. If each statistical segment consists of p elementary charges, then

(6.4) is equally written as

$$L = (N_{eff}\,p)(l_{eff}/p) \equiv N_q A \,, \tag{6.5}$$

where $N_q = N_{eff}\,p$ is the total number of charges on the polyions and A is the average distance between elementary charges.[34] N_q is an invariant quantity proportional to its molecular weight, M. Thus we have

$$M = m_q N_q = m_q L/A \,, \tag{6.6}$$

m_q being the mass of the segment containing the charge q_e.

In terms of the relations (6.1)–(6.6), Odijk has successfully discussed both equilibrium properties of a polyelectrolyte solution and the intrinsic viscosity. Here we are interested in obtaining scaling relations for both the specific viscosity and translational self-diffusion coefficient in polyelectrolytes utilizing the ideas developed in Secs. II–IV.

In order to proceed, the parameters v and l entering Eqs. (2.1)–(2.2) are replaced by v_{eff} and l_{eff}, Eq. (6.1). η_0 is still taken as the viscosity of the solvent. We expect, however, that the self-friction ζ must be suitably renormalized, although it is not clear whether this distinction is experimentally detectable. From Eq. (6.1a), an estimate of the number of unrenormalized segments, n_{eff}, is possible,

$$n_{eff} \simeq l_{eff}/l = 1 + \frac{1}{8Q\kappa^2 l}$$

from which the simplest approximate expression for the renormalized friction coefficient ζ_{eff} is obtained as

$$\zeta_{eff} \simeq \zeta n_{eff} = \zeta\left(1 + \frac{1}{8Q\kappa^2 l}\right). \tag{6.7}$$

This procedure is somewhat speculative in nature, since it is not immediately obvious that such a simple separation is possible. The approximations, (6.1) and (6.7), bear a resemblance to the Born–Oppenheimer approximation. We consider very slow motions of the polymer and assume that reorganization of the counterions is rapid on this time scale. Thus, the net effect of the counterions is considered with these renormalized quantities. It is of considerable interest to test these assumptions.

In terms of these renormalized parameters and Eqs. (3.22) and (4.7), scaling relations for the specific viscosity and translational diffusion coefficient follow immediately (for $c[\bar{\eta}] \lesssim O(1)$),

$$\frac{\eta_{sp}(c)}{c} = \frac{N_A L^2 \zeta(1 + (8Q\kappa^2 l)^{-1})}{M\eta_0} f_\eta\left(\frac{\zeta}{\eta_0 l}L^{1/2}\left(l + \frac{1}{8Q\kappa^2}\right)^{-1/2}\right)$$

$$\times \exp(-\alpha_1[\bar{\eta}]c),\ \ 4\kappa^{-1}\left(l + \frac{1}{8Q\kappa^2}\right)^{-3/2}L^{1/2}\exp(-\alpha_2[\bar{\eta}]c)\bigg), \tag{6.8}$$

$$D(c) = \frac{k_B T l}{\zeta L}f_D\left(\frac{\zeta}{\eta_0 l}L^{1/2}\left(l + \frac{1}{8Q\kappa^2}\right)^{-1/2}\exp(-\alpha_1'[\bar{\eta}]c),\right.$$

$$\left.4\kappa^{-1}\left(l + \frac{1}{8Q\kappa^2}\right)^{-3/2}L^{1/2}\exp(-\alpha_2'[\bar{\eta}]c)\right) \tag{6.9}$$

and $[\bar{\eta}]$ is the intrinsic viscosity for a polyion with strong

excluded volume, which follows from Eq. (3.20) as

$$[\bar{\eta}] = a_\eta'\frac{N_A}{M}L^{3\nu}(4\kappa^{-1})^{3(2\nu-1)}\left(l + \frac{1}{8Q\kappa^2}\right)^{3(5/2-4\nu)},$$

$$4\kappa^{-1}\left(l + \frac{1}{8Q\kappa^2}\right)L^{1/2} \gg 1 \,. \tag{6.10}$$

It should be noted that the coefficients α_1, α_2, α_η, etc., are universal numbers independent of whether the solution consists of polyelectrolyte or neutral polymers. The distinction between neutral polymer and polyion enters only through the effective strength parameters, Kuhn lengths, etc.

The situation corresponding to strong, but partially screened, hydrodynamic and excluded volume interactions,

$$\frac{\zeta}{\eta_0 l}L^{1/2}\left(l + \frac{1}{8Q\kappa^2}\right)^{-1/2}\exp(-\alpha_1[\bar{\eta}]c) \gg 1, \text{ (and for } \alpha_i \to \alpha_i')$$

$$\tag{6.11a}$$

$$4\kappa^{-1}\left(l + \frac{1}{8Q\kappa^2}\right)^{-3/2}L^{1/2}\exp(-\alpha_2[\bar{\eta}]c) \gg 1 \,, \tag{6.11b}$$

results in scaling forms for $\eta_{sp}(c)$ and $D(c)$ analogous to (3.23) and (4.9), respectively,

$$\eta_{sp}(c) = c[\bar{\eta}]\exp\{c[\bar{\eta}](\alpha_1 - 3(2\nu - 1)\alpha_2)\} \,, \tag{6.12}$$

$$D(c) = a_D'\frac{k_B T}{\eta_0}L^{-\nu}(4\kappa^{-1})^{-(2\nu-1)}\left(l + \frac{1}{8Q\kappa^2}\right)^{3\nu-1}$$

$$\times \exp\{c[\bar{\eta}](\alpha_1' - (2\nu - 1)\alpha_2')\} \,. \tag{6.13}$$

VII. CONCLUSION

The dynamical scaling theory proposed by Adler and Freed has been extended to nonzero polymer concentrations. The derivations are presented for continuous Gaussian coils with excluded volume whose dynamical behavior is described by the Kirkwood diffusion equation.

The central feature presented herein is the renormalization of the draining and excluded volume strengths at nonzero polymer concentrations. These renormalized parameters reflect the effects of screening in two ways:

(i) The coherence length associated with hydrodynamic interactions is reduced as the distribution of monomers becomes uniform.

(ii) There is a net cancellation between intra and intermolecular excluded volume interactions.

The screened excluded volume and draining strengths exhibit an exponential decay in concentration, for $h\exp(-k_H[\eta]c) \ll 1$ in marked contrast to the well-known power law dependences typical of scaling theories.

Scaling functions for the specific viscosity and translational diffusion coefficient for a tagged chain are presented in which the aforementioned parameters enter explicitly. It is demonstrated that a sufficiently low concentrations and/or sufficiently long chains, the specific viscosity exhibits the behavior $\eta_{sp}(c) = [\eta]c$ $\times \exp(k_H[\eta]c)$ in agreement with the empirical Martin equation. These considerations allow a natural extension to nonzero concentrations of Odijk's scaling argu-

ments for polyelectrolytes with added salt. The dynamical equations are somewhat speculative here.

The extension of scaling far into the semidilute regime, $c[\eta] \gtrsim O(1)$, is discussed. Asymptotic results (i.e., for long chains) are presented for the translational self-diffusion coefficient and the specific viscosity.

Apart from the power law assumptions entering scaling theories, several additional points should be noted for the sake of clarity:

(i) We assume that concentration effects act only to renormalize the draining and excluded volume parameters and, therefore, neglect the onset of entanglements. However, we believe that this is a drawback inherent in the form of the free energy given by Eq. (2.1) in that chains are regarded as having infinitesimal thickness. The introduction of additional entanglement length scales in an appropriate manner may be sufficient to compensate for these inadequacies.

(ii) The exponential forms $g_i(c[\eta]) = \exp(-\alpha_i c[\eta])$ are obtained from effective medium arguments. Although these forms are expected to be correct at sufficiently low concentrations, $h \exp(-k_H c[\eta]) \ll 1$ the $g_i(c[\eta])$ display a power law dependence for $h \exp(-k_H c[\eta]) \gtrsim 1$, where a polymer displays "bloblike" behavior.

(iii) Arguments have been presented for asymptotic properties $(N \to \infty)$, whereas experiments, to date, are not truly asymptotic. The nonasymptotic behavior of a chain is manifest by ideal intrachain substructures[15,35] which become irrelevant in the $N \to \infty$ limit. An appropriate treatment of these is encompassed in the work of Akcasu et al. and Weill and des Cloiseaux resulting in a corrected form for the intrinsic viscosity, $[\eta]'$. The latter includes corrections due to the nonasymptotic values N and v (i.e., N is neither sufficiently large and/or v is not sufficiently large). A simple improvement to the scaling arguments presented herein would then be the replacement of $[\eta]$ by $[\eta]'$.

ACKNOWLEDGMENTS

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