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Influence of Draining and Excluded Volume on the Intrinsic Viscosity of Flexible Polymers

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ABSTRACT: The excluded volume dependence of the intrinsic viscosity $[\eta]$ of linear polymers is calculated with the two-parameter model, the renormalization group method, and the approximate preaveraging-type "double-sum" formula of Tsuda. Our previous calculations treat the excluded volume dependence of $[\eta]$ in the nondraining limit, so the present analysis is designed solely to study the modifications due to draining. The Kirkwood and Tsuda double-sum formulas introduce errors into the absolute magnitudes of hydrodynamic quantities which are shown to be minimized by considering only the *relative* effects of draining and excluded volume through reduced variables such as the expansion coefficient $\alpha_\eta{}^3 = [\eta]/[\eta]_\Theta$, with $[\eta]_\Theta$ the value of the intrinsic viscosity under Θ conditions. The theory is in good agreement with experimental data which we interpret as conforming to the nondraining limit. For partial draining conditions our renormalization group calculations imply that the exponents describing the molecular weight dependence of $[\eta]$ and the hydrodynamic radius R_H in good solvents are sensitive functions of the hydrodynamic interactions. Partial draining experimental data are analyzed by fitting the data with a phenomenological draining parameter that varies smoothly with excluded volume. These results explain why good solvent exponents for $\alpha_\eta{}^3$ and other dynamical properties are often found to be less than that given by naive scaling predictions. A description is provided of how to make more stringent tests of the theory. Regular branched (ring, star, and comb) polymers are also shown to exhibit a similar scaling structure to the linear polymer as a function of draining parameter and excluded volume.

I. Introduction

Following the Kirkwood-Riseman[1] (KR) theory, the majority of dynamic theories of polymers introduce the preaveraging approximation to reduce the complexity in calculating dynamical properties through the substitution of static averages into the dynamical equations. The Kirkwood preaveraging approximation considers the instantaneous velocity field incident on a monomer in the chain due to hydrodynamic disturbances produced by the motion of the other monomers of the chain, and this instantaneous velocity field is replaced by its average in much the same spirit as Hartree's analogous treatment of the motion of electrons in atoms.[2] The inverse distance dependence of both hydrodynamic disturbances and Coulomb interactions highlights the qualitative similarity of these "mean-field-like" approximations.

Recently there has been a growing awareness of some of the practical limitations of the preaveraging theory. In particular Zimm[3,4] uses a rigid-body approximation to obtain a bound of about 13% and 12% on the error involved in the Kirkwood-Riseman preaveraging calculation of the diffusion coefficient and the intrinsic viscosity, respectively, for Gaussian chains. Fixman[5,6] estimates a more conservative value of about 7% for the preaveraging error in the diffusion coefficient. Experiments[7] on the ratio of the hydrodynamic radius and radius of gyration seem to support Zimm's upper bound. This agreement, however, may be fortuitous because it is likely that there is also a substantial contribution from ternary interaction that could very well account for the observed difference between the Fixman estimate and experiment.[8] A combination of these theoretical and experimental analyses indicates that the preaveraging approximation and ternary interactions can each cause an error on the order of 10% in the calculation of dynamical properties. Thus, dynamical observables such as the Flory constants under Θ conditions are not universal but rather are "quasiuniversal" in the sense that they take values in a small range in the vicinity of the value calculated from preaveraged Gaussian statistics. Fixman[6] arrives at the same conclusion based upon different considerations.

The best that can be achieved within the preaveraging approximation is, therefore, an approximate description of the *relative* effect of draining and excluded volume through the introduction of so-called expansion factors such as $\alpha_\eta{}^3 = [\eta]/[\eta]_\Theta$, where $[\eta]$ is the intrinsic viscosity and $[\eta]_\Theta$ is its value in Θ solutions. Comparisons between theory[9,10] and experiment indicate that these reduced variables serve to largely eliminate the preaveraging error, while recent theoretical arguments[8] show that it also minimizes the effects of ternary interactions,[11] polydispersity,[12] and other systematic experimental errors that may arise in the determination of the absolute magnitude of dynamical quantities.

The conventional two-parameter (TP) perturbation theory is only applicable when polymers are very near the Θ point.[1,13] In order to describe polymer properties in the regime of intermediate excluded volume between Gaussian and self-avoiding chain limits, it is necessary to resum this asymptotic perturbation expansion in some systematic manner. Renormalization group (RG) methods accomplish this task and provide predictions that are not restricted to the regime of small interactions.

Polymer dynamics can be studied with renormalization group methods applied to theories with varying levels of sophistication. The most rigorous approach includes corrections due to dynamical fluctuations in the solvent velocity, while the Kirkwood diffusion equation ignores these fluctuations. A more approximate theory is provided by the Kirkwood-Riseman method (see ref 1) in which the polymer is taken to be rigid, thereby enormously simplifying the treatment of the polymer dynamics. All of these approaches, in principle, permit the analysis of polymer dynamics without the use of the preaveraging approximation.

Studies based on this fundamental perspective have been given by Oono and Konmoto[14] (and references therein) with the Kirkwood-Riseman method and by Kawasaki and Shiwa[15] using the full Kirkwood diffusion equation. These calculations, however, have quantitative limitations. For example, the Flory constant P_0 (the zero subscript denoting Gaussian statistics) is calculated by

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Allesandrini and Pesci[16] to second order in ϵ using the preaveraged nondraining limit Kirkwood–Riseman method in conjunction with the renormalization group, and they find an error of about 20% in comparison with the "exact" solution. This inaccuracy of the RG–KR approach does not involve any matter of principle but comes entirely from the truncation of the ϵ-expansion. Hence, the current nonpreaveraging theory can be expected to have errors of a similar magnitude,[17] and this indicates that advances of a practical nature are required within the dynamical renormalization group method scheme before it is the quantitative tool now available for equilibrium properties.[9,10] Elsewhere we shall show how advances presented in this paper enable a large portion of the ϵ-expansion error in the evaluation of P_0 to be eliminated to obtain a more practically useful theory.

The quantitative accuracy of the renormalization group method for equilibrium properties provides an alternative pragmatic approach for evaluating dynamical polymer properties. The preaveraging approximation, in conjunction with our equilibrium RG method, is useful for several reasons: (1) Comparison with experimental data indicates that the preaveraging theory gives a quantitative description of the variation of reduced variables, such as α_η^3, with excluded volume and draining even though the absolute magnitudes of dynamical properties, such as $[\eta]$, are not well predicted. An order of magnitude argument is given in Appendix A to explain the success of this approach. (2) The relatively simple preaveraging theory gives important insight into the analytic structure of the more fundamental nonpreaveraging theory that is still being developed. Preaveraging should not alter the qualitative scaling structure of dynamical properties, so it provides an important reference for the more complicated nonpreaveraging calculations. (3) The simplicity of the preaveraging theory is important in the extension of the RG theory to the calculation of more complicated properties such as the dynamical properties of block copolymers and the hydrodynamic virial coefficients. Mathematical tractability is also an important consideration in the development of a comprehensive preaveraging theory encompassing both dynamical and static properties of lightly branched polymers in both dilute and semidilute solutions. The more fundamental but complicated nonpreaveraging theory is ultimately required to gauge the limitations of the approximate preaveraging theory.

The RG method can be readily applied to the description of excluded volume effects on polymer dynamics within the preaveraging approximation by simply evaluating the equilibrium averages with standard TP perturbation theory in conjunction with RG techniques,[10] since dynamical properties, such as the intrinsic viscosity calculated from the Kirkwood–Riseman (KR) theory (see ref 1), are expressed in terms of the static averages, the mean-square intersegment distance $\langle|\mathbf{r}_{ij}|^2\rangle$ and the mean reciprocal intersegment distance $\langle|\mathbf{r}_{ij}|^{-1}\rangle$. These quantities have been evaluated for d dimensions by Miyake and Freed[18] using RG methods in the crossover regime between the Gaussian and self-avoiding polymer limits.

Our approach is the simplest and most approximate one for treating the dynamical equations with the RG theory. We follow the pragmatic philosophy of Douglas and Freed,[9] who stress the preaveraging model for chain dynamics because of the current lack of a quantitatively reliable nonpreaveraged theory even in simple Gaussian limit. As mentioned before, application of our theory is based upon the hypothesis[19] that the preaveraging theory is sufficient to describe the relative effect of excluded volume in expansion factors. The success or failure of this simple approach should eventually be explained in terms of a more fundamental theory that takes into account the polymer motions and the fluctuations in the hydrodynamics interaction.

In section II we evaluate to first order in ϵ a simplified intermediate draining expression for the excluded volume dependence of the intrinsic viscosity $[\eta]$ using the approximate formula of Tsuda.[20,22] Limiting cases are used to guide aspects of resummation of the ϵ-expansions that are not dictated by the RG. This simple approach remedies certain considerable errors that could arise in the use of the ϵ-expansion truncated to finite order. The intrinsic viscosity is predicted to have a universal dependence on *two variables*, the traditional (empirical) excluded volume parameter z and a phenomenological draining parameter ξ which experiment implies is likewise a function of z. These scaling laws derived for a linear polymer are shown to also apply for flexible uniform regular star polymers.

A similar calculation for the hydrodynamic radius expansion factor α_H is sketched in section IV. The calculation rederives the previous results of Douglas and Freed[9] in a much simplied manner with an improved value of the prefactor coefficient. Since the Tsuda formula[20,22] yields errors in the absolute value of dynamical variables like the Flory constant Φ_0 (see below), we rectify this deficiency by only considering the expansion factor where absolute quantities like Φ_0 cancel. Likewise, it is to be anticipated that other numerical coefficients may incur some numerical inaccuracies due to the Tsuda approximation and may require some slight adjustment in comparisons with experiment. Any such small numerical uncertainties would be of no consequences to our major goal of elucidating the overall combined effects of excluded volume and draining.

Section V compares the theory with experiment to deduce empirically the variation of $\xi(z)$ with z. The results explain the often observed variation of the asymptotic exponents of α_η^3 and α_H from the values obtained by simplistic scaling arguments.

II. Variation of Intrinsic Viscosity with the Hydrodynamic and Excluded Volume Interactions

After introducing the preaveraging approximation, the Kirkwood–Riseman equation of polymer dynamics reduces to solving certain integral equations. One conventional approach of deriving dynamical properties of a dilute polymer solution has been to solve these integral equations directly.[1,23] However, nontrivial analytic solutions for $[\eta]$ can be obtained only in the nondraining limit. In order to have closed-form analytical formulas for dynamical properties in the regime between the free-draining and nondraining limits, it is convenient to resort to the more approximate double-sum formulas of Kirkwood[1] for the friction coefficient f and the intrinsic viscosity $[\eta]$ as given by

$$f = n\hat{\zeta}[\sum_{i=1}^{n}\sum_{j=1}^{n} H_{ij}] \tag{1}$$

$$[\eta] = (N_A\hat{\zeta}/6M\eta_s)\sum_{i=1}^{n}\sum_{j=1}^{n} H_{ij}^{-1}\langle\mathbf{R}_i\cdot\mathbf{R}_j\rangle \tag{2a}$$

where the Zimm matrix is

$$H_{ij} = 1 \qquad \text{for } i = j$$

$$H_{ij} = (\hat{\zeta}/6\pi\eta_s)\langle|\mathbf{R}_i - \mathbf{R}_j|^{-1}\rangle \qquad \text{for } i \neq j \tag{2b}$$

The H_{ij}^{-1} are inverse matrix elements, n is the number of "beads" in the polymer, $\mathbf{R}_i$ represents the position of the ith bead referred to the center of mass of the polymer chain, N_A is the Avogadro number, η_s is the solvent viscosity, $\hat{\zeta}$ is the friction coefficient of a bead, $\langle\ \rangle$ denotes the equilibrium conformational average, and M is the molecular weight of the polymer.

A. Tsuda Approximation. Equation 2 is still not useful for obtaining analytical expressions since it requires the inversion of the hydrodynamic interaction matrix **H**. However, there is a simplified formula for the intrinsic viscosity due to Tsuda involving an orientational preaveraging besides other aproximations (see ref 21). Tsuda's double-sum formula is

$$[\eta] = (N_A\hat{\zeta}/6M\eta_s)[\sum_{i=1}^{n}\langle \mathbf{R}_i^2\rangle]^2/(\sum_{i=1}^{n}\sum_{j=1}^{n}H_{ij}\langle \mathbf{R}_i\cdot\mathbf{R}_j\rangle) \quad (3)$$

where H_{ij} is given in (2b). The use of Kirkwood's eq 1 and Tsuda's formula[20-22] (3) provides a rather crude approximation to the *absolute value* of the Flory constants P_0 and Φ_0, but below we show that the deficiencies of (1) and (3) are not so great when considering the reduced quantities α_H and α_η^3 where the absolute errors involved in P_0 and Φ_0 are removed and only the dependences of α_H and α_η^3 on excluded volume and draining are considered. Elsewhere we present more accurate calculations of the excluded volume dependence of α_η^3 in the nondraining limit.[9,10] The results are shown below to be in close agreement with the nondraining limit of our calculations using Tsuda's formula, indicating that the latter approximation should be adequate for studying draining effects on expansion factors. Perhaps more importantly, we demonstate that both the Tsuda and Kirkwood–Riseman preaveraging calculations for α_η^3 are consistent with available nondraining data where the comparison is made with no adjustable parameters. Moreover, the Tsuda equation enables us to provide a semiquantitative description of draining effects in a good solvent for the first time. This is important because we find that for certain polymer–solvent systems the influence of draining effects rivals that of excluded volume in determining the magnitude of dynamical properties in good solvents.

The symmetry of H_{ij} with respect to the interchange of the labels i and j permits the double sum in (3) to be written as

$$\sum_{i=1}^{n}\sum_{j=1}^{n}H_{ij}\langle \mathbf{R}_i\cdot\mathbf{R}_j\rangle = 2\sum_{i>j=1}^{n}H_{ij}\langle \mathbf{R}_i\cdot\mathbf{R}_j\rangle + \sum_{i=1}^{n}\langle \mathbf{R}_i^2\rangle \quad (4)$$

Combining eq 3 and 4 allows the intrinsic viscosity to be expressed as

$$[\eta] = (N_A\hat{\zeta}/36M\eta_s)(\sum_{i=1}^{n}6\langle \mathbf{R}_i^2\rangle)F \quad (5)$$

where F is given by the double sum

$$F^{-1} = 1 + 2(\sum_{i>j=1}^{n}H_{ij}\langle \mathbf{R}_i\cdot\mathbf{R}_j\rangle)/\sum_{i=1}^{n}\langle \mathbf{R}_i^2\rangle \quad (6)$$

Our task is then to evaluate F^{-1} as a function of draining and excluded volume. The RG calculations of $\langle \mathbf{S}^2\rangle$, $\langle|\mathbf{r}_{ij}|^2\rangle$, and $\langle|\mathbf{r}_{ij}|^{-1}\rangle$ of Miyake and Freed[18] enable us to accomplish this calculation in a straightforward manner. To compute (6), we pass to the continuum limit and change the sums to integrals by setting $i = nx$ and $j = ny$. The integration is evaluated in the region $\{0 \le x \le 1, 0 \le y \le 1\}$, and the calculation is performed to first order in $\epsilon = 4 - d$, where d is the spatial dimensionality.

B. Renormalization Group Approach. There are several parameters that enter naturally into the RG theory[10] to characterize the excluded volume interaction. For example, there is a crossover variable $\zeta \propto M^{1/2}$, which ranges from zero to infinity as the chain changes from a Gaussian to self-avoiding configuration. There is also a parameter Λ that characterizes the excluded volume interactions along the chain—a "blob size".[24] Finally, there are the effective exponents that are evaluated as functions of ϵ and ζ. Since our calculations are performed within the TP model, it is possible to relate Λ and ζ to a representation involving the usual z variable of the TP theory.[10] Hence, we convert to the z form in section IV where comparisons with experiment are made. Those readers most interested in this comparison can skip directly to section IV. The calculations, however, are most conveniently performed in the "blob" representation involving ζ and Λ.

Miyake and Freed[18] have evaluated ($x > y$)

$$\langle|\mathbf{r}|^2\rangle_{x,y} = r_0^2(x - y)\{1 + H(x,y)(\epsilon/8)[\zeta/(1 + \zeta)]\} + \mathcal{O}(\epsilon^2), \qquad x > y \quad (7)$$

$$\langle|\mathbf{r}|^{-1}\rangle_{x,y} = r_1^{-1}(x - y)^{-1/2}\{1 - G(x,y)(\epsilon/8)[\zeta/(1 + \zeta)]\} + \mathcal{O}(\epsilon^2), \qquad x > y \quad (8)$$

where $H(x,y)$ and $G(x,y)$ are defined in Appendix B by (B.2c) and (B.13) and r_0^2 and r_1^{-1} are given by (B.2d) and (B.7), respectively. From these expressions, F^{-1} is calculated in Appendix B to order ϵ as

$$F^{-1} = 1 + \xi_\eta[1 + \epsilon(\ln 2 - 5/8)][1 + (13/96 + 0.089)\epsilon\zeta/(1 + \zeta)](2\pi N/\Lambda)^{-\epsilon\zeta/16(1+\zeta)} + \mathcal{O}(\epsilon^2) \quad (9a)$$

where ξ_η is defined by

$$\xi_\eta = (16/315)(\hat{\zeta}/\pi l\eta_s)(2\pi n)^{1/2} \quad (9b)$$

and N is the chain length $N \propto M$. l is related to the number n of segments in the chain by $nl = N$. The quantity ξ_η is proportional to the usual draining parameter $h = [\hat{\zeta}/(12\pi^3)^{1/2}\eta_s l]n^{1/2}$, with the extra numerical factor absorbed to make the final formulas simpler.

Experiment shows that in good solvents the intrinsic viscosity behaves like $[\eta] \sim N^\delta$ for large N, where δ is an effective exponent that depends on the polymer–solvent system. Hence, we must reexpress (5) and (9a) to have this analytic scaling form in this limit. Our previous treatment of the translational diffusion coefficient imposes the analogous exponential good solvent limit, and the procedure also yields effective exponents depending upon both the excluded volume interaction and draining strength in the crossover region.[9]

This type of power-law-type representation is produced by first expanding the factor $(2\pi N/\Lambda)^{-\epsilon\zeta/16(1+\zeta)}$ in (9) to first order in ϵ to have

$$F^{-1} = (1 + \xi_\eta)\{1 + (13/96 + 0.089)\epsilon\zeta\xi_\eta/(1 + \zeta) \times (1 + \xi_\eta) + (\ln 2 - 5/8)\epsilon\xi_\eta/(1 + \xi_\eta) - [\epsilon\zeta\xi_\eta/16(1 + \zeta)(1 + \xi_\eta)] \ln (2\pi N/\Lambda)\} + \mathcal{O}(\epsilon^2) \quad (10)$$

a form analogous to that arising in the dynamical RG method[16] where there are expansions in hydrodynamic and excluded volume interaction with both placed on an equal footing. In order to obtain the required power-law-type expression, the $\ln (2\pi N/\Lambda)$ terms are reexponentiated as

$$1 - \epsilon\zeta(1 + \zeta)^{-1}\xi_\eta(1 + \xi_\eta)^{-1} \ln (2\pi N/\Lambda) = (2\pi N/\Lambda)^{-(\epsilon/16)[\zeta/(1+\zeta)][\xi_\eta/(1+\xi_\eta)]} + \mathcal{O}(\epsilon^2) \quad (11)$$

This reexponentiation is a legitimate and necessary procedure provided the intrinsic viscosity scales as $[\eta] \sim N^\delta$ with a weaker molecular weight dependence entering through the $\zeta(1 + \zeta)^{-1}$ and $\xi_\eta(1 + \xi_\eta)^{-1}$ factors. The scaling behavior is known to apply in good and Θ solutions, so our procedure in (10) is consistent with these limits. In Appendix C, an alternative expression for the intrinsic viscosity is derived where the above reexponentiation is avoided.

The ϵ-expansion

$$d^{1/2}\Gamma[(d-1)/2]/\Gamma(d/2) = \pi^{1/2}[1 + (\ln 2 - 5/8)\epsilon] + \mathcal{O}(\epsilon^2) \quad (12)$$

is used in (10) to rewrite it in the form

$$F^{-1} = [(1+\xi_\eta)/\pi^{1/2}H(\xi_\eta)][1 + (13/96 + 0.089)\epsilon\zeta\xi_\eta/(1 + \zeta)(1+\xi_\eta)](2\pi N/\Lambda)^{-[2\nu(\zeta)-1]\xi_\eta/(1+\xi_\eta)} + \mathcal{O}(\epsilon^2) \quad (13a)$$

$$H(\xi_\eta) = \Gamma[2 - \epsilon\xi_\eta/2(1+\xi_\eta)]/[4 - \epsilon\xi_\eta/(1 + \xi_\eta)]^{1/2}\Gamma[3/2 - \epsilon\xi_\eta/2(1+\xi_\eta)] \quad (13b)$$

$$2\nu(\zeta) - 1 = \epsilon\zeta/8(1+\zeta) + \mathcal{O}(\epsilon^2)$$

which is consistent with (10) to $\mathcal{O}(\epsilon)$. This rewriting is shown below to be important in making (13) produce the correct Gaussian free-draining chain limit. Often resummations such as (12) are not introduced,[18] leading to $\epsilon \to 1$ values that unfortunately deviate from the known unperturbed limits. We prefer to use this known information in the above fashion which is consistent to the order ϵ of the calculation.

The precedure of reexponentiation in (11) is analogous to that used by Oono and Freed[25] for the crossover regime for equilibrium polymer properties. After correction of exponents to second order, the results of this approach for equilibrium quantities are in good agreement with experiment,[10] providing, perhaps, a major justification for its use. Here we proceed by analogy, given the knowledge that in dynamical RG calculations the parameters ξ and ζ are put on an equal footing, something that the transition from (9)–(13) reintroduces in the preaveraged theory.

The quantity $\sum_{i=1}^{n}\langle\mathbf{R}_i^2\rangle$ in eq 5 is related to the mean-square radius of gyration that is calculated in ref 24 as

$$\sum_{i=1}^{n}\langle\mathbf{R}_i^2\rangle = n\langle S^2\rangle = (n/6)\langle\mathbf{R}^2\rangle_0[1 - 13\epsilon\zeta/96(1+\zeta)](2\pi N/\Lambda)^{[2\nu(\zeta)-1]} + \mathcal{O}(\epsilon^2) \quad (14)$$

$$\langle\mathbf{R}^2\rangle_0 = Nl \equiv nl^2$$

Expressing exponents in (13), (14), and the following equations in terms of $\nu(\zeta)$ enables us later to generalize these effective exponents to second order in ϵ in the manner previously derived for equilibrium properties.[10] Substitution of (13) and (14) into (5) and use of the definition (9b) give

$$[\eta] = (N_\mathrm{A}/M)\langle\mathbf{R}^2\rangle_0^{3/2}[\xi_\eta/(1+\xi_\eta)] \times [35\pi H(\xi_\eta)/104(2)^{1/2}](2\pi N/\Lambda)^{[2\nu(\zeta)-1][1+\xi_\eta/2(1+\xi_\eta)]}[1 - 13\epsilon\zeta/96(1+\zeta)]/[1 + (13/96 + 0.089)\epsilon\zeta\xi_\eta/(1+\zeta)(1 + \xi_\eta)] \quad (15)$$

where $\langle\mathbf{R}^2\rangle_0 = Nl$ is the Gaussian mean-square end-to-end vector distance. As expected,[26] the intrinsic viscosity in (15) has an N-power-law dependence with part of the effective exponent given by $[2\nu(\zeta) - 1][1 + \xi_\eta/2(1 + \xi_\eta)]$. In the large N limit this exponent varies with the excluded volume parameter ζ and the draining parameter ξ_η in a simple way. The prefactor portion contains a much weaker N dependence through the terms in ζ and ξ_η in this coefficient. However, near the Θ point, where ζ is very small, the hydrodynamic interaction contributes negligibly to the important factor $(2\pi N/\Lambda)^{[2\nu(\zeta)-1][1+\xi_\eta/2(1+\xi_\eta)]}$. That is, the limit $\zeta \to 0$ implies that the effective exponent $[2\nu(\zeta) - 1][1 + \xi_\eta/2(1 + \xi_\eta)]$ vanishes for arbitrary draining strengths ξ_η. Equation 15 then reduces to the classical result $[\eta] = N_\mathrm{A}\zeta N^2/36M\eta_\mathrm{s}$ in the limit of free draining and no excluded volume.

C. Nondraining Limit. The nondraining limit $\xi_\eta \to \infty$ of (15) is readily evaluated as

$$[\eta] = (N_\mathrm{A}/M)\langle\mathbf{R}^2\rangle_0^{3/2}(2\pi N/\Lambda)^{(3/2)[2\nu(\zeta)-1]}[35\pi^{3/2}/208(6)^{1/2}] \times [1 - 13\epsilon\zeta/96(1+\zeta)]/[1 + (13/96 + 0.089)\epsilon\zeta/(1+\zeta)] \quad (16a)$$

In the Gaussian limit of $\zeta = 0$, eq 16a reduces to

$$[\eta](\text{nondraining}) = 2.30 \times 10^{23}\langle\mathbf{R}^2\rangle_0^{3/2}/M \quad (16b)$$

which is given previously by Tsuda.[22] The experimental value of the Flory constant Φ_0 ($[\eta]_0 = \Phi_0\langle\mathbf{R}^2\rangle_0^{3/2}/M$) is frequently observed[1,26] to be about 2.5×10^{23}. This is also to be compared with the $\xi_\eta \to \infty$, $\zeta \to 0$ limit of the Kirkwood–Riseman (KR) theory, which yields $\Phi_0(\mathrm{KR}) = 2.87 \times 10^{23}$. Hence, the usual experimental value lies midway between the estimates of Tsuda's formula[22] and the KR theory.[1] Because Tsuda's formula yields an error on the order 10% for Φ_0, we may anticipate that the numerical coefficients like 0.089 in the denominator of (15b) may also require some slight alteration to achieve optimal comparison with experiment. Such adjustments are not made here since our goal is in probing the general ξ_η and ζ dependence implied by (15) and similar expressions.

III. Intrinsic Viscosity Expansion Factor

It is generally convenient to choose the Θ state as a reference point. We consider the expansion factors of dynamical quantities in order to remove errors in the calculation of Φ_0 as well as to eliminate other problems from polydispersity, three-body interactions, etc. The intrinsic viscosity expansion factor α_η^3, for example, is defined as $\alpha_\eta^3 = [\eta]/[\eta]_\Theta$, with $[\eta]_0 = [\eta]|_{\zeta=0}$. From (15) we then have

$$\alpha_\eta^3 = \frac{H(\xi_\eta)\xi_\eta/(1+\xi_\eta)}{H(\xi_0)\xi_0/(1+\xi_0)}(2\pi N/\Lambda)^{[2\nu(\zeta)-1][1+\xi_\eta/2(1+\xi_\eta)]}[1 - 13\zeta/96(1+\zeta)]/[1 + 0.224\zeta\xi_\eta/(1+\zeta)(1+\xi_\eta)] \quad (17)$$

in three dimensions where we allow the phenomenological draining parameter to be a function of the excluded volume interaction parameter and define $\xi_0 = \xi_\eta(\zeta = 0)$. Experimental evidence[1,9] implies that for long chains $\xi_0 \to \infty$; i.e., Gaussian chains are nondraining, and this simplifies (17) to

$$\alpha_\eta^3 = [3^{1/2}H(\xi_\eta)\xi_\eta/(1+\xi_\eta)\Gamma(3/2)] \times (2\pi N/\Lambda)^{[2\nu(\zeta)-1][1+\xi_\eta/2(1+\xi_\eta)]}[1 - 13\zeta/96(1+\zeta)]/[1 + 0.224\zeta\xi_\eta/(1+\zeta)(1+\xi_\eta)] \quad (18)$$

Combining (18) with the definition of the Flory constant and (14) gives the dimensionless ratio ($d = 3$)

$$\Phi(\xi_\eta,\zeta)/\Phi_0 = \alpha_\eta^3/\alpha_{\mathrm{s}^2}{}^3 = [3^{1/2}H(\xi_\eta)\xi_\eta/(1+\xi_\eta)\Gamma(3/2)] \times (2\pi N/\Lambda)^{-[2\nu(\zeta)-1]/2(1+\xi_\eta)}[1 - 13\zeta/96(1+\zeta)]/[1 - 13\zeta/64(1+\zeta)][1 + 0.224\zeta\xi_\eta/(1+\zeta)(1+\xi_\eta)] \quad (19)$$

which reduces in the nondraining limit to

$$\Phi(\xi_\eta \to \infty,\zeta)/\Phi_0 = [1 - 13\zeta/96(1+\zeta)]/[1 - 13\zeta/64(1+\zeta)][1 + 0.224\zeta/(1+\zeta)] \quad (20)$$

In addition the intrinsic viscosity expansion factor of (17) is equal in this limit to

$$\alpha_\eta^3(\xi_\eta \to \infty) = (2\pi N/\Lambda)^{3[2\nu(\zeta)-1]/2}[1 - 13\zeta/96(1+\zeta)]/[1 - 13\zeta/64(1+\zeta)][1 + 0.224\zeta/(1+\zeta)] \quad (21)$$

The self-avoiding limit for $\zeta = \infty$ of (20) provides a lower bound

$$(\Phi^*/\Phi_0)_{\text{nondraining}} = (1 - 13/96)/(1 - 13/64)(1 + 0.224) = 0.886 \quad (22)$$

to Φ/Φ_0 as a function of ζ in the nondraining limit. This good solvent limit for $(\Phi/\Phi_0)_{\text{nondraining}}$ is close to the value of $\Phi^*/\Phi_0 = 0.892$ obtained by Douglas and Freed,[10] who combine the RG theory with the $d = 3$ two-parameter calculation. This close correspondence supports the contention that the Tsuda approximation is useful for the dimensionless ratio Φ/Φ_0.

The simplified Tsuda[22] formula can also be applied to flexible regularly branched polymers.[20] The availability of the general expressions for $\langle|\mathbf{r}_{ij}|^2\rangle$ and $\langle|\mathbf{r}_{ij}|^{-1}\rangle$ for star polymers from the work of Miyake and Freed[18] implies that a similar calculation can be performed to predict the crossover behavior of the intrinsic viscosity for flexible star polymers. In fact, any regularly branched flexible polymer has expressions for $\langle|\mathbf{r}_{ij}|^2\rangle$ and $\langle|\mathbf{r}_{ij}|^{-1}\rangle$ similar to those given by (7) and (8) except for different functional forms for $H(x,y)$ and $G(x,y)$, forms that do not change the scaling structures of the dynamical properties such as $[\eta]$ and R_H. In the Tsuda formula[22] approximation to the intrinsic viscosity, flexible star, comb, and ring polymers all obey the same scaling law as those for linear polymers but with draining parameters dependent on the structure of polymers (e.g., number of arms f in a star polymer, etc.). In particular this implies that, if we assume $\xi_\eta(\zeta = 0,f) \rightarrow \infty$, the intrinsic viscosity expanision factor for a regular star polymer, for example, has a form analogous to (17)

$$\alpha_{\eta,f}{}^3 = ([\eta]/[\eta]_\Theta)_{\text{star}} = \frac{1 + [\epsilon\zeta/8(1 + \zeta)]I(f)}{1 + \{\epsilon\zeta\xi_\eta(f)/8(1 + \zeta)[1 + \xi_\eta(f)]\}J(f)} \{3^{1/2}H(\xi_\eta,f)\xi_\eta(f)/[1 + \xi_\eta(f)]\Gamma(3/2)\}(2\pi N/\Lambda)^{[2\nu(\zeta)-1]\{1+\xi_\eta(f)/2(1+\xi_\eta(f))\}} \quad (23a)$$

where the draining parameter ξ_η is a function of both the number of arms of the star and the molecular weight. $I(f)$ and $J(f)$ are prescribed by double integrals similar to (B.8) given in Appendix B. These terms are obtained in a straightforward manner from the expressions for $\langle|\mathbf{r}_{ij}|^2\rangle$ and $\langle|\mathbf{r}_{ij}|^{-1}\rangle$ of Miyake and Freed[18] in the same way as the homopolymer calculation, *provided* it is assumed as in ref 21 that the viscosity center is coincident with the center of the molecule. More generally if this approximation is not made, the scaling form (23a) still holds except that more complicated expressions arise for $I(f)$, $J(f)$, and $\xi_\eta(f)$. Quite generally from scaling and the RG theory we can generalize (23a) to any regularly branched species (ring, regular comb, regular star) based upon the Tsuda equation (3). This leads to the scaling form

$$\alpha_\eta{}^3(\text{branched}) = F[\xi_\eta(\text{branching parameter}),\zeta] \times (2\pi N/\Lambda)^{[2\nu(\zeta)-1]\{1+\xi_\eta(\text{branch})/2[1+\xi_\eta(\text{branch})]\}} \quad (23b)$$

for which the homopolymer and star expressions are special cases. The calculation of $F[\xi_\eta(\text{branched}),\zeta]$ is straightforward but tedious.

However, even if $\alpha_\eta{}^3$ is calculated with a hypothetically exact theory for the hydrodynamics, the resulting theory cannot be expected to describe highly branched polymers realistically. For rings and stars having $f \geq 6$ the average segment density under Θ conditions is much higher than in the linear polymer,[11] so ternary interactions and perhaps higher body ones must be included into the model. At even higher branching density (say $f = 12$ or 18 arm stars), experiments show that the Gaussian reference state ceases to be meaningful at all, and the segment density of the polymer becomes closer to that of a collapsed polymer than that of the idealized unperturbed linear chain.[11] Roovers[28] has recently obtained evidence that is consistent with "topologically induced contraction" in the hydrodynamic properties of rings. Rather substantial deviations from Gaussian statistics also have been noted for highly branched stars[29] $f \geq \mathcal{O}(10)$. There are very definitely limitations on what can be quantitatively described in these high-density branched systems using the Gaussian chain model.

IV. Hydrodynamic Radius

Besides preaveraging, Kirkwood introduces other approximations (see ref 21) to obtain the well-known approximate expression for the long-time diffusion coefficient[9] of a dilute polymer solution[1]

$$D = (k_B T/n\hat{\zeta})\left(1 + \frac{\hat{\zeta}}{6\pi\eta_s n}\sum_{i\neq j}^{n}\sum_{j=1}^{n}\langle|\mathbf{r}_{ij}|^{-1}\rangle\right) \quad (24)$$

where k_BT is the absolute temperature in energy units. Other quantities assume the same meanings as defined before. Upon substituting (8) into the double-sum portion of (24), we find

$$g \equiv \sum_{\substack{i\neq j \\ i,j=1}}\sum \langle|\mathbf{r}_{ij}|^{-1}\rangle = (2n^2/r_1)\int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\, [1 - \epsilon\zeta G(x,y)/8(1 + \zeta)]/(x - y)^{1/2} = (8n^2/3r_1)[1 + 0.075\epsilon\zeta/(1 + \zeta)] \quad (25)$$

Introducing (25) into (24) gives

$$D = (k_BT/n\hat{\zeta})(1 + g\hat{\zeta}/6\pi n\eta_s) = (k_BT/n\hat{\zeta})\{1 + [2(2\pi n)^{1/2}\hat{\zeta}/9\pi l\eta_s](2\pi N/\Lambda)^{-[2\nu(\zeta)-1]/2}[1 + 0.075\epsilon\zeta/(1 + \zeta)][d^{1/2}\Gamma[(d - 1)/2]/\pi^{1/2}\Gamma(d/2)]\} \quad (26)$$

Based on experimental experience, the diffusion coefficient D is also assumed[9] to obey a global power-law dependence on molecular weight $D \sim N^\theta$ for large N with θ an effective exponent for large N and with a prefactor that is only weakly N dependent. In analogy with (9) we introduce the draining parameter

$$\xi_D = (35/13)\xi_\eta \quad (27a)$$

The difference between ξ_η and ξ_D arises presumably because of the preaveraging and orientational averaging approximations involved in (3) and (24) (see ref 21), since only a single ξ parameter appears when using the dynamical RG approach.[14] Introduction of ϵ-expansions and of (11) and (12) and the use of ξ_D through (27a) convert (26) to

$$D = (k_BT/n\hat{\zeta})\{1 + \xi_D[1 + 0.075\epsilon\zeta/(1 + \zeta)] \times [1 + \epsilon(\ln 2 - 5/8)][1 - (\epsilon/16)\zeta(1 + \zeta)^{-1} \ln (2\pi N/\Lambda)]\} \quad (27b)$$

Exponentiating the ln $(2\pi N/\Lambda)$ term as in (11) transforms (27b) into

$$D(\xi_D,\zeta) = (8/n)^{1/2}(k_BT/9\pi l\eta_s)[(1 + \xi_D)/\xi_D H(\xi_D)] \times (2\pi N/\Lambda)^{-[2\nu(\zeta)-1]\xi_D/2(1+\xi_D)}[1 + 0.075\epsilon\zeta\xi_\eta/(1 + \zeta)(1 + \xi_D)] \quad (27c)$$

where $H(\xi_D)$ is defined in (13b) with ξ_η replaced by ξ_D.

The diffusion coefficient (27c) is the same as obtained previously by Douglas and Freed[9] except that the prefactor in (27c) has been altered. The reason for discrepancy arises because the previous calculation begins from a reexponentiated form of the structure function, while here the analysis proceeds with full ϵ-expansions. It is now understood that the former can lead to small inconsistencies with respect to ϵ-expansions. It is best to evaluate observables from ϵ-expanded distributions and moments and then to use renormalization group considerations and other physically motivated arguments to guide the reexponentiation at the *end* of the calculation. Sometimes exact results, such as the well-known nondraining Gaussian limit in (27c), are helpful in guiding the reexponentiation in a unique way.

The hydrodynamic radius is defined from D and the Stokes–Einstein equation through

$$D = k_B T/6\pi\eta_s R_H \tag{28}$$

Substitution of (27) into (28) yields

$$R_H(\xi_D,\zeta) = (3/4)(Nl/2)^{1/2}[\xi_D H(\xi_D)/(1+\xi_D)] \times [1 + 0.075\epsilon\zeta\xi_D/(1+\zeta)(1+\xi_\eta)]^{-1}(2\pi N/\Lambda)^{[2\nu(\zeta)-1]\xi_D/2(1+\xi_D)} \tag{29}$$

The hydrodynamics radius expansion factor follows from (29) as ($d = 3$)

$$\alpha_H = R_H(\xi_D,\zeta)/R_H(\xi_D,\zeta=0) = [3^{1/2}H(\xi_D)\xi_D/(1+\xi_D)\Gamma(3/2)][1 + 0.075\zeta\xi_D/(1+\zeta) \times (1+\xi_D)]^{-1}(2\pi N/\Lambda)^{[2\nu(\zeta)-1]\xi_D/2(1+\xi_D)} \tag{30}$$

where the assumption $\xi_D(\zeta = 0) = \infty$ is again used.

Experimentalists often present data in terms of the ratio $P/P_0 = \alpha_H/\alpha_{S^2}$ where $\alpha_{S^2} = [\langle S^2\rangle/\langle S^2\rangle_0]^{1/2}$. Combining (30) with (14) yields ($d = 3$)

$$P/P_0 = \alpha_H/\alpha_{S^2} = \{[3^{1/2}H(\xi_D)\xi_D/(1+\xi_D)\Gamma(3/2)]/[1 + 0.075\zeta\xi_D/(1+\zeta)(1+\xi_D)][1 - 13\zeta/192(1+\zeta)]\} \times (2\pi N/\Lambda)^{-[2\nu(\zeta)-1]/2(1+\xi_D)} \tag{31}$$

The nondraining $\xi_D = \infty$ limit of (31) is

$$(P/P_0)_{\text{nondraining}} = \{[1 + 0.075\zeta/(1+\zeta)][1 - 13\zeta/192(1+\zeta)]\}^{-1} \tag{32a}$$

and in good solvents it becomes

$$P^*/P_0 = 0.998 \tag{32b}$$

This is in good agreement with the previous calculations in ref 10, which give $P^*/P_0 = 0.999$, and it corrects the prediction (see (27c) and below) of ref 9 of $P^*/P_0 = 0.929$.

The draining parameter ξ_D enters the expression (27c) for the diffusion coefficient in a similar fashion as in (15) for the viscosity. Draining potentially plays an important role in the description of the dynamical properties of the polymer in good solvents because of the dependence of good solvent exponents for α_η^3 and α_H on ξ. In the next section we analyze some available experimental data to assess the role of draining for polymers in good solvents.

V. Comparison with Experiment and the z Representation

A. Phenomenological Motivation To Consider Draining. It is widely believed that draining is not a significant factor dictating the molecular weight dependence of the intrinsic viscosity and diffusion coefficient. Indeed, there is evidence that this is true for long Gaussian chains and near Gaussian chains ($\alpha_{S^2}{}^2 \leq 1.3$) where a universal relation between data for α_η^3 and $\alpha_{S^2}{}^3$ is found.[30] For larger α_{S^2} no such universal relation is apparent,[30] and at first this discrepancy was ascribed to experimental difficulty.[30] It has long been[31] noted that polystyrene data deviates particularly from the idealized expectation of a nondraining theory.[31,32] More recent data shows that the correlation between α_η^3 and $\alpha_{S^2}{}^2$ for polystyrene in various solvents is solvent-dependent, leading Varma et al.[33] to conclude that α_η^3 and α_H do not seem consistent with the TP model. This conclusion is also reflected in the observed lack of a single universal relation between P/P_0 and α_{S^2} which is described in ref 9.

The calculations of sections III and IV suggest, however, that these discrepancies in good solvents are not due merely to experimental difficulties but rather have an explanation in terms of a draining effect that becomes important as the chain becomes highly expanded. Equations 17 and 30 for intermediate draining and excluded volume interaction indicate that in a good solvent the excluded volume forces and draining effects compete with each other to determine the effective molecular weight exponents for $[\eta]$ and R_H.[34] This effect can qualitatively be understood as being due to an increased penetration (corresponding to decreased ξ_η) of the solvent flow into the expanded coil that thereby decreases the effective hydrodynamic radius of the polymer.[9] (See eq 29.) Hence, in addition to an excluded volume parameter, large-scale dynamical properties like $[\eta]$ and R_H require another coarse grained parameter to reflect the strength of hydrodynamic interactions.

The approximations, inherent in (18) and (30) due to preaveraging and to Tsuda's formula, limit the quantitative accuracy of these predictions. However, we anticipate that the dominant errors are merely of a numerical nature and that these can be remedied by slight adjustment of the numerical prefactors. Part of this is automatically included in considering expansion factors, so that, for instance, numerical errors in determining Φ_0 from Tsuda's formula are eliminated (see Appendix A). Hence, we expect the theory to be of semiquantitative accuracy and sufficient for elucidating the gross combined effects of draining and excluded volume on dynamical polymer quantities.

B. z Representation. The representation of the RG results in terms of the variables N, Λ, and ζ is not the most convenient for comparison between theory and experiment. However, previous papers derive a correspondence[10,24,35] between this representation and that of the TP theory which is familiar to experimentalists. We cite the relations between the excluded volume parameter ζ and $(2\pi N/\Lambda)$ and a parameter $\bar{z}$ akin to the TP theory z variable in which experimental data are usually presented

$$[\epsilon\zeta/(1+\zeta)] \rightarrow \lambda(\bar{z}) \equiv (32\bar{z}/3)/(1 + 32\bar{z}/3); \quad \text{for } \bar{z} < 0.15 \tag{33a}$$

$$(2\pi N/\Lambda)^{[2\nu(\zeta)-1]/2} \rightarrow [1 - \lambda(\bar{z})]^{-1/8} \equiv (1 + 32\bar{z}/3)^{1/8}; \quad \text{for } \bar{z} < 0.15 \tag{33b}$$

$$[\epsilon\zeta/(1+\zeta)] \rightarrow 1; \quad \text{for } \bar{z} > 0.75 \tag{33c}$$

$$(2\pi N/\Lambda)^{[2\nu(\zeta)-1]/2} \rightarrow (6.441\bar{z})^{2\nu-1}; \quad \text{for } \bar{z} > 0.75 \tag{33d}$$

where introducing second-order corrections[36] as described in ref 10 we have $2\nu - 1 = \epsilon/8 + (15/4)(\epsilon/8)^2 + \mathcal{O}(\epsilon^3)$. For example, a generic polymer property Q having the RG form[10,35]

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(2\pi N/\Lambda)^{p[2\nu(\zeta)-1]/2}[1 + a_Q\epsilon\zeta/(1+\zeta)] \tag{34a}$$

with $\langle S^2\rangle_0$ the Θ point radius of gyration, is translated in the $\bar{z}$ representation as

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}[1 - \lambda(\bar{z})]^{-p/8}(1 + a_Q\lambda(\bar{z})); \quad \bar{z} < 0.15 \tag{34b}$$

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(6.441\bar{z})^{p(2\nu-1)}(1 + a_Q); \quad \bar{z} > 0.75 \tag{34c}$$

where $\bar{z}$ is a pure phenomenological variable. Equation

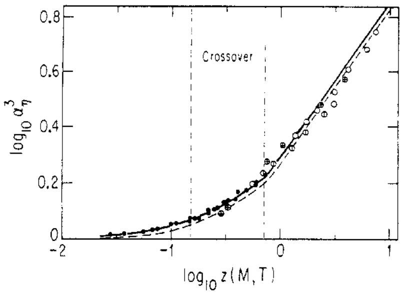

Figure 1. The intrinsic viscosity expansion factor α_η^3 presented as a function of the phenomenological variable z_{emp}. The solid line is from a previous calculation[9] for α_η^3 in the nondraining limit, and the dashed line is the prediction of (35) in the nondraining limit. As discussed in ref 9 and 10, the relation between the theoretical $\bar{z}$ and phenomenological z parameter is fixed by comparing $\alpha_{S^2} = \langle S^2 \rangle / \langle S^2 \rangle_0$ between theory and experiment to determine an overall scale factor. Hence, the theoretical predictions involve no free parameters. The symbols (○) and (⊕) are for polyisobutylene (PIB) in cyclohexane at 25 °C, (⊖) is for PIB in *n*-heptane at 25 °C, and (●) is for PIB in isoamylvalerate (IAV) at various temperatures. The data is reproduced from ref 37 with the new prediction and that of ref, 9 added.

34b has previously been found[10] to be accurate for many properties in the crossover regime $\{0.15 \leq \bar{z} \leq 0.75\}$, so this equation is also used here in that region.

Experiments[10,26b] take z_{emp} to be proportional to $\tau M^{1/2}$ where M is the molecular weight and τ the reduced temperature $\tau = (T - \Theta)/T$ with Θ the theta temperature. The coefficient of proportionality between z_{emp} and $\tau M^{1/2}$ is a polymer–solvent-dependent constant that is uniquely specified by comparing theory and experiment. When Q is taken, for example, as the radius of gyration in (34b) and (34c), this implies $p = 2$ and $a_{S^2} = -13/96 = -0.135$ from (14). The identification between the theoretical $\bar{z}$ and the z_{emp} of Miyaki and Fujita $\bar{z} = 0.906 z_{\mathrm{emp}}$ is found by comparing our expression from (34) for $\alpha_{S^2}{}^2$ with experimental data[37] as displayed in Figure 4 of ref 10. The comparison between theory and experiment is then excellent. Once the overall scale factor in $\bar{z}$ is uniquely determined from the fit to theory of equilibrium properties like α_{S^2}, it becomes possible to estimate ξ (ξ_η or ξ_n) by comparing experimental data for dynamical quantities like α_η and α_{H} with the intermediate draining theory.

First let us write α_η^3 and α_{H} as functions of $\bar{z}$ and ξ. Combining (18), (30), and (33a)–(33c) yields the series of results

$$\alpha_\eta^3 = [3^{1/2} H(\xi_\eta) \lambda_{\xi_\eta} / \Gamma(3/2)](1 + 0.224 \lambda \lambda_{\xi_\eta})^{-1} (1 - 13\lambda/96)(1 - \lambda)^{-1/4 - \lambda_{\xi(\eta)}/8}; \qquad \bar{z} < 0.15 \quad (35a)$$

$$\alpha_{\mathrm{H}} = [3^{1/2} H(\xi_D) \lambda_{\xi_D} / \Gamma(3/2)] \times (1 - \lambda)^{-\lambda_{\xi(D)}/8} (1 + 0.075 \lambda \lambda_{\xi_D})^{-1}; \qquad \bar{z} < 0.15 \quad (36a)$$

where $\lambda_\xi \equiv \xi/(1 + \xi)$, $\lambda \equiv \lambda(\bar{z})$, and

$$\alpha_\eta^3 = [3^{1/2} H(\xi_\eta) \lambda_{\xi_\eta} / \Gamma(3/2)](1 - 13/96) \times (1 + 0.224 \lambda_{\xi_D})^{-1} (6.441 \bar{z})^{0.1836 \lambda_{\xi(\eta)} + 0.3672}; \qquad \bar{z} > 0.75 \quad (35b)$$

$$\alpha_{\mathrm{H}} = [3^{1/2} H(\xi_D) \lambda_{\xi_D} / \Gamma(3/2)] \times (1 + 0.075 \lambda_{\xi_D})^{-1} (6.441 \bar{z})^{0.1836 \lambda_{\xi(D)}}; \qquad \bar{z} > 0.75 \quad (36b)$$

$$\Phi/\Phi_0 = [3^{1/2} H(\xi_\eta) \lambda_{\xi_\eta} / \Gamma(3/2)](1 - \lambda)^{1/8(1+\xi_\eta)} (1 - 13\lambda/96)/(1 - 13\lambda/64)(1 + 0.224 \lambda \lambda_{\xi_\eta}); \qquad \bar{z} < 0.15 \quad (37a)$$

$$\Phi/\Phi_0 = (6.441 \bar{z})^{-0.1836/(1+\xi_\eta)} (1 - 13/96) \times [3^{1/2} H(\xi_\eta) \lambda_{\xi_\eta} / \Gamma(3/2)]/(1 - 13/64)(1 + 0.224 \lambda_{\xi_\eta}); \qquad \bar{z} > 0.75 \quad (37b)$$

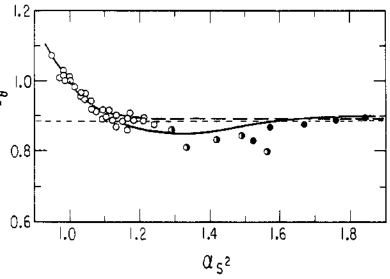

Figure 2. The dimensionless ratio $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_{S^2}{}^3$ as a function of α_{S^2}. (○) is for PIB in IAV at different temperatures (see Figure 1), (◐) is for PIB in *n*-heptane at 25 °C, and (●) is for PIB in cyclohexane at 25° C. The data in the figure is reproduced from Matsumoto et al.[41] with the theoretical predictions superimposed. The solid line is an experimental best fit from the original reference, and the dashed line is our prediction from (35) in the nondraining limit. This type of representation is preferred over that of Figure 1 because it involves a parameter-free theory that is entirely independent of theoretical assumptions regarding the phenomenological dependence of the z variable. The data display a peculiar hump similar to that noted in the case of the penetration function.[10,12]

Equations 35a–37b reduce to the scaling form 34b,c in the nondraining limit.

It is useful to begin by analyzing experimental data for the nondraining limit of the theory. Figure 1 presents eq 35a and 35b for $\log_{10} \alpha_\eta^3$ vs. $\log_{10} z_{\mathrm{emp}}$ along with the experimental data from Miyaki and Fujita[26b] for α_η^3 vs. their z_{emp} variable. The previous nondraining RG prediction[10] fits the data well and appears to be superior to the Tsuda-based expression (35). On the other hand, Figure 2 presents a preferred representation of the data for Φ/Φ_0 where some of the data is identical with that in Figure 1. This type of representation involves no approximations regarding the phenomenological dependence of z_{emp} on τ and M and simply involves the relation of one observable to another. The Tsuda theory compares quite favorably with experiment in this case, and we conclude that the polyisobutylene data is behaving consistently with the nondraining theory. This agreement between theory and experiment in the nondraining limit suggests that the Tsuda theory enables us to provide a semiquantitative description of data exhibiting draining effects.

C. Qualitative Influence of Draining. Sections III and IV employ the assumption that Gaussian and near-Gaussian chains are nondraining so that $\xi \gg 1$ for $T \approx \Theta$. The data in Figure 1 suggest that, in accord with previous observations,[30] this is not always true for $\bar{z} \geq O(1)$, i.e., beyond the onset of the good solvent regime.[10] Nemoto et al.[37] note that the slope of the log α_{H} vs. log z_{emp} data approaches a constant for large coil expansion (large z_{emp}) for polystyrene in *trans*-decalin, and they find asymptotically

$$\alpha_{\mathrm{H}} = 1.27 z_{\mathrm{emp}}{}^{0.1} \qquad (38)$$

The constancy of this exponent[37] is observed for very high molecular weights $M \sim \mathcal{O}(10^7)$. Nemoto et al. find *no indication* of the approach to the nondraining exponent of 0.18 for the particular solvent they consider. The interesting aspect of this observation, when interpreted by our theory, is that it implies that ξ_D in (36b) is approaching a finite constant value $\xi_D(\bar{z} \to \infty) = \xi_\infty$ for large $\bar{z}$. Below intrinsic viscosity data is used to provide additional evidence for this type of behavior.

Because the RG theory cannot describe the functional dependence of $\xi(\bar{z})$ on $\bar{z}$, we utilize experimental data for the intrinsic viscosity to empirically determine this dependence, choosing data that we believe exhibits a very

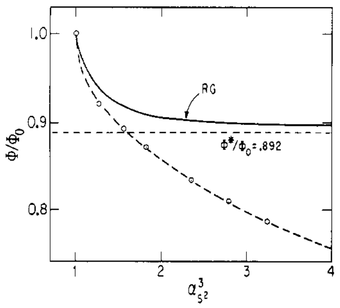

Figure 3. The dimensionless ratio $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_{S^2}^3$ as a function of $\alpha_{S^2}^3$ for polystyrene in cyclohexane. High molecular weight data for polystyrene in cyclohexane are reproduced from Suzuki.[42] These data have a qualitatively different character than the data of Figure 2. The theoretical nondraining curve is based upon a previous prediction from the KR theory in the nondraining limit, but comparison with Figure 2 shows that it differs from the Tsuda expression only to a small amount. We associate the tendency of the curve not to level off for large α_{S^2} as evidence of the draining effect. By adjusting ξ_η as a function of $\bar{z}_{\mathrm{emp}}$ (see Figure 4), we obtain the long dashed curve passing through the data. The real test of the theory involves using the same phenomonolgically determined ξ_η in other dynamical observables to check for self-consistency.

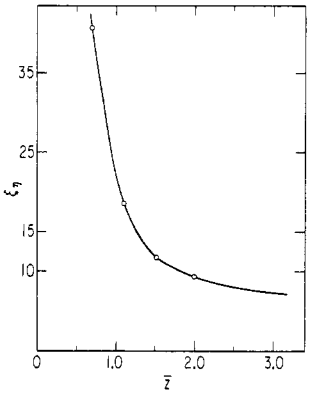

Figure 4. Phenomenological variation of the draining parameter as a function of $\bar{z}$. The value of ξ_η is determined as a function of α_{S^2} in (35) to fit the draining curve data in Figure 3. The relation between α_{S^2} and $\bar{z}$ of (34) then enables the construction of the plot of ξ_η vs. $\bar{z}$. $\xi_\eta(\bar{z})$ seems to level off at large values of $\bar{z}$ to a limit $\xi_\eta(\infty) \simeq 10$. We suspect this trend to be fairly general.

strong draining effect. The most obvious case to study is polystyrene in cyclohexane, a system whose "deviant" dynamical behavior has long been recognized.[31,32] Figure 3 displays data for Φ/Φ_0 for this polymer–solvent system. The curve is obtained from the nondraining KR theory as described in ref 10 and is quite similar to the Tsuda expression (35) (see Figure 2). The data for polystyrene in cyclohexane strongly deviates from the predictions of the nondraining theory, except for $\alpha_{S^2} \simeq 1$, and this deviation is too large to be ascribed to experimental difficulty. The quantity $\xi(\bar{z})$ in (35) is determined to fit the curve that passes through the data, and the resultant semiempirical $\xi(\bar{z})$ is given in Figure 4.

As in the case of the hydrodynamic radius data of Nemoto et al.,[37] the value of ξ_η in Figure 4 appears to be monotonically approaching a constant value ξ_∞ (polystyrene–cyclohexane) which in this case is on the order of 10. Polymer–solvent systems having a limiting ξ_∞ much larger than this are, of course, expected from (35) to exhibit little or no draining effect as in Figure 2.

It is of interest to study additional systems to determine whether $\xi(\bar{z})$ displays a universal variation with polymer- and solvent-dependent parameters in the same way that z_{emp} or $\bar{z}$ depend on simple system parameters, an overall constant factor and the Θ temperature, in addition to the molecular weight and temperature.[10] It would also be interesting to study the factors that apparently make the phenomenological dependence of $\xi(\bar{z})$ vary from solvent to solvent. The agreement with experiment appears to be good, but the available data is too limited to make the most stringent test of the theory which involves taking the function $\xi_\eta(\bar{z})$ obtained from intrinsic viscosity data and inserting it into the theoretical prediction of α_{H} as a function of draining and excluded volume to obtain a parameter-free prediction for α_{H}. It is essential for the comparison with experiment that the data for the hydrodynamic and static properties all be taken under the same polymer–solvent conditions. Unfortunately data of this kind is currently unavailable.

There are some theoretical ambiguities that arise from the preaveraging-type approximations in our calculations that must be eliminated before we can expect a quantitative comparison between theory and experiment when there is substantial draining. For instance, we believe that the difference between ξ_η and ξ_D in our calculations arises solely from the use of different varieties of preaveraging approximations. The relation between ξ_η and ξ_D is very important in comparing theory with experiments. The full KR-RG theory has only a single ξ for all large-scale zero-frequency dynamic properties. Hence, it is probably best to replace ξ_η and ξ_D by a common value ξ until less approximate but more laborious calculations are performed. Thus, although we are confident of the semiquantitative nature of our conclusions regarding draining, some refinement of the theory is clearly necessary before the same level of accuracy is obtained as for static properties.[10]

VI. Conclusion

Using the approximate double-sum formulas of Tsuda[22] and Kirkwood[1] in conjunction with the TP model and renormalization group method, we derive approximate closed-form expressions for the hydrodynamic expansion factors α_η^3 and α_{H} as a function of both draining parameters and excluded volume. A limited comparison of theory with experiment enables the rationalization of the effect of draining. Universality is restricted to the expansion factors and the other reduced variables due to a complicated admixture of hydrodynamic and ternary interactions that make the values of the properties of Θ-point polymers in general nonuniversal.[6,8] The introduction of the expansion factors apparently allows for a good semiquantitative description of dynamical properties in the preaveraging approximation for the data we consider.

Despite the approximate nature of our calculations, comparison of theory and experiment shows that draining effects can semiquantitatively explain the observed "nonuniversality" of dynamical polymer properties in good solvents through the introduction of an empirically determined excluded volume dependent draining parameter $\xi_\eta(\bar{z})$ that varies monotonically from an indeterminantly large value near the Θ point, where the polymer is relatively contracted, to a constant value $\xi_\infty = \xi_\eta(\bar{z} \to \infty)$ in a very good solvent. Thus, the "failure" of the two-parameter theory to describe dynamical properties in good solvents, discussed in the literature, is found to arise due to neglect of a basic interaction parameter characterizing the strength of hydrodynamic interaction. Draining is also expected to be important in semidilute solutions, as evidenced by data showing that equilibrium and dynamical properties of semidilute solutions do not scale with molecular weight in the same fashion. A theoretical analysis of this dependence is necessary before a quantitative theory of the concentration dependence of dynamical observables can be constructed.

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Appendix A. Estimate of the Relative Error in the Preaveraging Approximation

Oono and Kohmoto[14] calculate $[\eta]$ and the friction coefficient $f = k_BT/D$ using the KR-RG method both with and without preaveraging. Their results are analyzed here to compare the two intrinsic viscosity expansion factors for $[\eta]$ and $[\eta]_{\text{pre}}$. The errors involved in the ϵ-expansion in this method are expected to be reduced by considering expansion factors. Elsewhere we will discuss this point in more detail. Without preaveraging the results of ref 14 give

$$\alpha_\eta^{\,3} = \alpha_{S^2}{}^2\alpha_{\mathrm{H}}[1 + 25(\bar{\xi} - \bar{\xi}_0)/24(2\pi)^2] \qquad \text{(A.1a)}$$

where $\alpha_{\mathrm{H}} = f(\xi,\zeta)/f(\xi,\zeta = 0)$ and $\bar{\xi}$ is the dimensionless draining parameter (not to be confused with our variable ξ) defined in Oono and Kohmoto[14] and $\bar{\xi}_0$ its value at Θ point.

The preaveraging approximation on the other hand leads to[14]

$$\alpha_\eta^{\,3}(\text{preaveraging}) = \alpha_{S^2}{}^2\alpha_{\mathrm{H}}[1 + 5(\bar{\xi} - \bar{\xi}_0)/4(2\pi)^2] \qquad \text{(A.1b)}$$

In the good solvent nondraining limit[14] the difference $(\bar{\xi} - \bar{\xi}_0)$ is $(\bar{\xi}^* - \bar{\xi}_0^*)/(2\pi)^2 = -\epsilon/6$ so the ratio

$$\alpha_{\eta\text{pre}}{}^3/\alpha_\eta{}^3 = (1 - 5\epsilon/24)/(1 - 25\epsilon/144) = 1 - 5\epsilon/144 + \mathcal{O}(\epsilon^2) = 0.965; \qquad \epsilon = 1 \qquad \text{(A.2)}$$

determines the relative preaveraging error for α_η for nondraining good solvents. Although the preaveraging approximation gives rise to large deviations for the absolute magnitude of hydrodynamical quantities,[19] the Oono–Kohmoto[14] theory predicts less than a 4% (to order ϵ) error in the relative quantity $\alpha_\eta{}^3$. This supports Stockmayer's hypothesis[19] that the preaveraging errors involved in the calculations of reduced hydrodynamical properties are perhaps small. Our purpose here is to make a qualitative point. The ill-behaved nature of the ϵ-expansion in (A.2) does not allow us presently to be too confident about (A.2) as a quantitative result.

The small preaveraging error in the expansion factors can be rationalized from rather general considerations. We assume that the preaveraging error in the prefactor coefficients a_Q in (34) is of the same magnitude as the error in the calculation of Φ_0, an error on the order, say 10% (see section I). Then, since the prefactor coefficient is generally on the order $a_Q \sim \mathcal{O}(0.1)$ (see ref 9) the overall error is only on the order of 1% for the observable property $\alpha_Q{}^p$. The error predicted by the Oono–Kohmoto theory is thus slightly larger than that provided by a simple order of magnitude argument.

Appendix B. Calculation of *F* from Section III

We carry out the calculation step by step. First, we have

$$\langle \mathbf{R}_i{}^2 \rangle = n^{-1}\sum_{k=1}^{n} \langle |\mathbf{r}_{ik}|^2 \rangle - \langle S^2 \rangle \qquad \text{(B.1a)}$$

$$|\mathbf{r}_{ik}|^2 = |\mathbf{R}_i - \mathbf{R}_k|^2 \qquad \text{(B.1b)}$$

where $\langle S^2 \rangle = n^{-2} \sum_{i>j=1}^{n} \langle |\mathbf{r}_{ij}|^2 \rangle$ with $\langle |\mathbf{r}_{ij}|^2 \rangle$ given by eq 7. Introduction of a continuous variable $x = i/n$ allows the double sums in (B.1) to be written as double integrals

$$\sum_{k=1}^{n} \langle |\mathbf{r}_{ik}|^2 \rangle = n\int_0^x \mathrm{d}y\ \langle |\mathbf{r}|^2 \rangle_{x,y} + n\int_x^1 \mathrm{d}y\ \langle |\mathbf{r}|^2 \rangle_{y,x} = nr_0{}^2[1/2 - x(1 - x) + \epsilon\zeta E(x)/(1 + \zeta)] + \mathcal{O}(\epsilon^2) \qquad \text{(B.2a)}$$

where

$$E(x) = \int_0^x \mathrm{d}y\ (x - y)H(x,y) + \int_x^1 \mathrm{d}y\ (y - x)H(y,x) \qquad \text{(B.2b)}$$

with $H(x,y)$ from Miyake and Freed[18] used here in the nonexponentiated form

$$H(x,y) = \ln (x - y) - 3/2 + (x - y)/2 + y[\ln (x/y)]/(x - y) - (1 - x) \times \{\ln [(1 - x)(1 - y)]\}/(x - y), \qquad x > y \qquad \text{(B.2c)}$$

and

$$r_0{}^2 = Nl(2\pi N/\Lambda)^{2\nu-1} \qquad \text{(B.2d)}$$

The radius of gyration squared $\langle S^2 \rangle$ is known from ref 25 as

$$\langle S^2 \rangle = (r_0{}^2/6)[1 - 13\epsilon\zeta/96(1 + \zeta)] + \mathcal{O}(\epsilon^2) \qquad \text{(B.3)}$$

Substitution of (B.2) and (B.3) into (B.1) yields

$$\langle \mathbf{R}^2(x) \rangle = r_0{}^2[1/3 - x(1 - x) + \epsilon\zeta(13/72 + E(x))/8(1 + \zeta)] \qquad \text{(B.4)}$$

Equations 7 and B.4 enable $\langle \mathbf{R}_i \cdot \mathbf{R}_j \rangle$ to be rewritten as for $i > j$ $(x > y)$

$$\langle \mathbf{R}(x)\cdot\mathbf{R}(y) \rangle = [\langle \mathbf{R}^2(x) \rangle + \langle \mathbf{R}^2(y) \rangle - \langle |\mathbf{r}|^2 \rangle_{x,y}]/2 = (r_0{}^2/2)\{2/3 - 2x + x^2 + y^2 + (\epsilon/8)[E(x) + E(y) + 13/36 - (x - y)H(x,y)]\zeta/(1 + \zeta)\} \qquad \text{(B.5)}$$

Next, the sum $\sum_{i>j=1}^{n} \mathrm{H}_{ij}\langle \mathbf{R}_i \cdot \mathbf{R}_j \rangle$ is likewise expanded up to order ϵ to give

$$\sum_{i>j=1}^{n} H_{ij}\langle \mathbf{R}_i \cdot \mathbf{R}_j \rangle = (n^2\zeta/6\pi\eta_s)\int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\ \langle \mathbf{R}(x)\cdot\mathbf{R}(y) \rangle \langle |\mathbf{r}|^{-1} \rangle_{x,y} = (n^2\hat{\zeta}r_0{}^2/6\pi r_1\eta_s)[26/315 + \epsilon\zeta(I + 13/54)/8(1 + \zeta)] \qquad \text{(B.6)}$$

where $r_1{}^{-1}$ is given by

$$r_1{}^{-1} = (2\pi N/\Lambda)^{-[2\nu(\zeta)-1]/2}(d/2Nl)^{1/2}\Gamma[(d - 1)/2]/\Gamma(d/2) \qquad \text{(B.7)}$$

and I is given by the integral

$$I = \int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\ [E(x) + E(y) - (x - y)H(x,y) - (2/3 - 2x + x^2 + y^2)G(x,y)]/2(x - y)^{1/2} \qquad \text{(B.8)}$$

With eq B.6 and B.3, the definition of F^{-1} of (6) implies

$$F^{-1} = 1 + (52n\hat{\zeta}/315\pi r_1\eta_s)[1 + 13\epsilon\zeta/96(1 + \zeta) + (315/208)(I + 13/54)\epsilon\zeta/(1 + \zeta)] \qquad \text{(B.9)}$$

The definition of a draining parameter from (9b) and the ϵ-expansion (12) convert (B.9) to

$$F^{-1} = 1 + \xi_\eta[1 + (\ln 2 - 5/8)\epsilon](2\pi N/\Lambda)^{-[2\nu(\xi)-1]/2}\{1 + [13/96 + (315/208)(I + 13/54)]\epsilon\zeta/(1 + \zeta)\} \qquad \text{(B.10)}$$

We now turn to the calculation of I of (B.8). The two-dimensional integral I is divided into three parts

$$I = I_1 - I_2 - I_3 \qquad \text{(B.11a)}$$

$$I_1 = \int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\ [E(x) + E(y)]/2(x - y)^{1/2} \qquad \text{(B.11b)}$$

$$I_2 = \int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\ H(x,y)(x - y)^{1/2}/2 \qquad \text{(B.11c)}$$

$$I_3 = \int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\ (2/3 - 2x + x^2 + y^2)G(x,y)/2(x - y)^{1/2} \qquad \text{(B.11d)}$$

Equations B.2b for $E(x)$ and B.2c for $H(x,y)$ enable the former to be evaluated as

$$E(x) = -1 + [x^2 + (1 - x)^2]/4 + [x^3 + (1 - x)^3]/6 - x^2(\ln x)/2 - [(1 - x)^2 \ln (1 - x)]/2 - x(1 - x) \ln [x(1 - x)] = E(1 - x) \quad \text{(B.12a)}$$

Then (B.11b) and (B.11c) are analytically evaluated as

$$I_1 = 2\int_0^1 \mathrm{d}x\, x^{1/2}E(x) = -0.476 \quad \text{(B.12b)}$$

$$I_2 = \int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\, H(x,y)(x - y)^{1/2}/2 = -0.164 \quad \text{(B.12c)}$$

The function $G(x,y)$ in I_3 from Miyake and Freed[18] is used here in the nonexponential form

$$G(x,y) = [\ln (x - y)]/2 + 5/2 + \ln [2/y(1 - x)] + 2\{(1 - x + y)^{1/2} - (2x - y)(y/x)^{1/2} - (1 + x - 2y)[(1 - x)/(1 - y)]^{1/2}\}/(x - y) - (x - y)\{\psi([(x - y)/(4 - 3x - y)]^{1/2},[(x - y)/(1 - y)]^{1/2}) - 1\}/(1 - x) - (x - y)\{\psi([(x - y)/(x + 3y)]^{1/2},[(x - y)/x]^{1/2}) - 1\}/y - (x - y)\{(xy)^{-1/2} + [(1 - x)(1 - y)]^{-1/2}\} \quad \text{(B.13)}$$

where ψ is defined by $\psi(k,\cos \phi) = [E(k,\pi/2) - E(k,\phi)]/k$ and $E(k,\phi)$ is the elliptic integral of the second kind, $E(k,\phi) = \int_0^\phi(1 - k^2 \sin^2 \theta)^{1/2}\, \mathrm{d}\theta$. We list values of the two more complicated integrals involved in the evaluation of I_3 which are calculated numerically as

$$I_{(1)} = \int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\, (2/3 - 2x + x^2 + y^2)[(1 + y - x)^{1/2} - (2x - y)(y/x)^{1/2} - (1 + x - 2y)(1 - x)^{1/2}/(1 - y)^{1/2}]/(x - y)^{3/2} = -0.425$$

$$I_{(2)} = \int_0^1 \mathrm{d}x \int_0^x \mathrm{d}y\, (x - y)^{1/2}\{\psi([(x - y)/(4 - 3x - y)]^{1/2},[(x - y)/(1 - y)]^{1/2}) - 1\}/y = 0.003$$

From (B.11a) we then obtain $I = I_1 - I_2 - I_3 = -0.182$. Therefore, (B.10) can be written

$$F^{-1} = 1 + \xi_\eta[1 + (13/96 + 0.089)\epsilon\zeta/(1 + \zeta)] \times (2\pi N/\Lambda)^{-[2\nu(\zeta)-1]/2}[1 + (\ln 2 - 5/8)\epsilon] + \mathcal{O}(\epsilon^2) \quad \text{(B.14)}$$

which is eq 9.

Appendix C. Alternative Expressions for [η] and R_H

The derivation of the scaling functions for [η] and R_H in sections III and IV invokes an assumption regarding the asymptotic scaling properties of these quantities. This is not necessary but is very convenient. Alternatively, this assumption can be avoided altogether.

Begin by defining the dynamical radius[9] expansion factor

$$\alpha_D^{-1} = \sum_{i,j=1,i\neq j}\langle|\mathbf{r}_{ij}|^{-1}\rangle / \sum_{i,j=1,i\neq j}\langle|\mathbf{r}_{ij}|^{-1}\rangle_0 = [1 + 0.075\epsilon\zeta/(1 + \zeta)](2\pi N/\Lambda)^{-[2\nu(\zeta)-1]/2} \quad \text{(C.1)}$$

The diffusion coefficient is written in terms of using (26) as[9]

$$D = (k_BT/n\hat{\zeta}) \times \{1 + [2(2\pi n)^{1/2}\hat{\zeta}/9\pi l\eta_s]d^{1/2}\Gamma[(d - 1)/2]/\Gamma(d/2)\alpha_D\} \quad \text{(C.2)}$$

Introducing the conventional definition[1] of the draining parameter into (C.2) gives

$$D = (k_BT/n\hat{\zeta})(1 + 8X/3\alpha_D) \quad \text{(C.3)}$$

$$f = n\hat{\zeta}/(1 + 8X/3\alpha_D) \quad \text{(C.4)}$$

where $X = 2^{1/2}h$ [see (9.b)]. Equation C.4 is the same as the one found by Barrett[38] and also resembles the form of the friction coefficient derived as an approximate[19] solution of the Kirkwood integral equation for f. Similarly F^{-1} from (9) can be formally written as

$$F^{-1} = 1 + \xi_\eta[1 + (13/96 + 0.014)\epsilon\zeta/(1 + \zeta)]d^{1/2}\Gamma[(d - 1)/2]/\pi^{1/2}\Gamma(d/2)\alpha_D + \mathcal{O}(\epsilon^2) \quad \text{(C.5)}$$

Finally, substituting (C.4) and (C.5) into (5) yields the alternative form for the intrinsic viscosty in $d = 3$

$$[\eta] = (N_A/6M\eta_s)\langle S^2\rangle n\hat{\zeta}\{1 + 104X[1 + 0.149\zeta/(1 + \zeta)]/105\alpha_D\} = (N_A/6M\eta_s]\langle S^2\rangle f(1 + 8\, X/3\alpha_D)/\{1 + [1 + 0.149\zeta/(1 + \zeta)](104X/105\alpha_D)\} \quad \text{(C.6)}$$

The ratio α_{S^2}/α_D, computed from (C.1) and (14), does not differ appreciably from unity regardless of the excluded volume interaction. Weill and des Cloizeaux[39] use the blob model to argue to the contrary that α_D and α_{S^2} scale with qualitatively different exponents based upon the blob model. Their argument has been used to rationalize the different exponents for $\langle S^2\rangle^{1/2}$ and R_H and is simply not correct although there is some truth to their argument with regard to the sensitivity of radial properties to ternary interactions.[8] This example emphasizes the danger in taking the "poetic" blob model literally as a model of crossover phenomena. The data of Ackasu and Han[40] show that the blob model provides a very poor description of crossover, so that this conclusion about α_{S^2}/α_D should come as no surprise. On the other hand, our expressions for α_η, α_H, and α_{S^2} indicate that the Weill–des Cloizeaux[39] argument $\alpha_\eta^{\,3} \approx \alpha_{S^2}{}^2\alpha_H$ holds to within about 10% (see ref 9). The correction factors to this simple approximation are easily calculated from (35) and (36) or (C.3), (C.6), and (34) for $Q = \langle S^2\rangle$.

Registry No. Polyisobutylene (homopolymer), 9003-27-4; polystyrene (homopolymer), 9003-53-6.

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Second Osmotic Virial Coefficient Revisited. 2. Buildup from Contributions of Inter- and Intramolecular Contacts between Polymer Segments†

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ABSTRACT: The variation of the second osmotic virial coefficient A_2 with the molar mass M of the polymer is interpreted as the result of the thermodynamic inequality of inter- and intramolecular contacts between polymer segments. This inequality can take effect since the coil dimension (and consequently the number of intramolecular contacts) changes with concentration as M becomes larger. A model is presented in which A_2 should depend linearly on $M^{-(a-0.5)}$, where a is the exponent of the viscosity–molecular weight relationship. The evaluation of numerous literature data confirms the present concept and yields a consistent picture for the size of the inter- and intramolecular interaction parameters, their interdependence, and their variation with the thermodynamic quality of the solvent.

Introduction

In practically all cases reported so far, the second osmotic virial coefficient A_2 decreases as the molecular weight M of the polymer is raised isothermally. Recent light scattering investigations[1] with the system *tert*-butyl acetate/polystyrene have however demonstrated that $A_2(M)$ can become an increasing function for sufficiently exothermal conditions. Since this finding contradicts the results of the classical excluded volume theory[2] (according to which lim A_2 for infinite M should be 0), it was postulated[1] that (except for Θ conditions) the volume a given polymer segment excludes for the placement of a second segment depends on its belonging to the same or to a different molecule. In the present contribution this ine-

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