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Partial Draining and Universality of Dilute Solution Polymer Dynamics: Comparison of Theory and Experiment

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ABSTRACT: Previous renormalization group calculations predict that the conventional Flory ratios P/P_0 and Φ/Φ_0 are not universal functions of excluded volume alone in dilute solutions because of a partial draining effect (finite hydrodynamic interactions) that splits the scaling functions into a family of curves. The theory also predicts that the ratio $\alpha_\eta^3/\alpha_S^2\alpha_H = (\Phi/\Phi_0)/(P/P_0)$ is almost independent of draining and is more nearly a universal function of excluded volume (i.e., the expansion factor α_S). These predictions are tested here against experimental data for polystyrene, poly(α-methylstyrene), and polyisobutylene, a sequence that is interpreted as having increasing relative nondraining behavior. Support is found for the predicted near universality of $\alpha_\eta^3/\alpha_S^2\alpha_H$ for polystyrene and poly(α-methylstyrene), and the qualitative trends for P/P_0 and Φ/Φ_0 are consistent with the partial draining interpretation. Procedures are outlined for more quantitative tests of the theory.

Introduction

Attempts at describing the polymer, solvent, temperature, and molecular weight (M) dependences of the exponent a in the Mark–Houwink expression[1]

$$[\eta] = KM^a \qquad (1)$$

for the intrinsic viscosity have contributed greatly to the development of theoretical models of polymer structure and dynamics. For instance, Kuhn[2] introduced the random flight model, the excluded volume concept, and the impermeable sphere hydrodynamic model of the polymer coil in the process of attempting to explain an empirical relation of the type of (1). Kuhn,[2] Debye and Bueche,[3] and Kirkwood and Riseman[4] introduced the more microscopic pearl-necklace hydrodynamic model of polymers to rationalize the variation of a as due to partial "draining" of the fluid through the polymer coil. Flory and Fox[5a] showed that the *predominant* mechanism for the observed variation of the Mark–Houwink exponent is the excluded volume interaction. They, however, did not discount the possibility that partial draining produces a secondary effect.

The classic argument for estimating the Mark–Houwink exponent a is given by Kuhn, who modeled the polymer chain by an impermeable sphere whose radius is on the order of the end-to-end vector distance $\langle R^2\rangle^{1/2}$. Combining this model of the polymer chain with Einstein's theory of the hydrodynamics of hard spheres leads to the prediction[2,5]

$$a = d\nu - 1 \qquad (2)$$

for polymers in d dimensions (Kuhn uses $d = 3$), where ν is defined by the molecular weight (M) dependence of the radius of gyration R_G:

$$R_G \propto M^\nu \qquad (3)$$

Kuhn gives $\nu = {}^1/_2$ for random coils and presents a rough estimate of ν for chains with excluded volume using simple geometric arguments. Flory gave the first credible calculation of ν as a function of excluded volume (called the crossover dependence) by inserting his mean-field theory for $\langle R^2\rangle$ into the Kuhn impermeable sphere model.[5]

Ever since the introduction of the Flory–Kuhn impermeable sphere model, it has been recognized that some polymer–solvent systems conform well to (1) and (2), while others are observed to have a Mark–Houwink exponent consistently *lower* than the scaling prediction. This occurs despite the fact that the power law form (1) is found to hold for more than 2 decades in molecular weight[6] where the observed a shows no apparent increase over this region.[7] A similar effect is found for the hydrodynamic radius R_H. Naive scaling yields the good solvent limit behavior

$$R_H \propto M^\nu \qquad (4)$$

but in *some* polymer–good solvent systems R_H also exhibits too small an exponent.

Berry[8a] was the first to pursue seriously the idea that draining through the coil periphery in *swollen* chains could explain the discrepancy between the Flory–Kuhn impermeable sphere model and observed exponents for hydrodynamic properties of polymers in dilute solutions. (Recall that Debye[3] and Kirkwood and Riseman[4] had earlier attributed the entire variation of the exponent a to draining.) Berry proposed that the scaling functions for the intrinsic viscosity $[\eta]$ as a function of excluded volume should split into a *family of curves* that are dependent on the draining parameter. While Berry claimed experimental support for this effect, alternative explanations were suggested for the data,[9,10] and the role of partial draining on polymer transport properties has remained a controversial issue.

We have performed a series of renormalization group calculations, using models and theoretical methods of increasing sophistication, to study the combined effects of partial draining and excluded volume.[11-14] The simplest calculations[11,12] use simple double-sum approximations to the Kirkwood–Riseman equations for polymer dynamics in the rigid chain approximation along with equilibrium averages and renormalization group (RG) techniques to

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evaluate the dynamical properties. This approach supports the view that an expanded coil in good solvents provides a greater possibility for the solvent to flow through the chain periphery, leading to $[\eta]$ and R_H that may scale with smaller than naively anticipated exponents. Further second-order in ϵ ($\epsilon = 4 - d$) RG dynamical calculations within the Kirkwood–Riseman[13] and Rouse–Zimm[14] models are in accord with the predictions from the double-sum formulas, aside from small differences in the values of the coefficients analogous to K in (1). An important prediction of these theories is that in good solvents the dimensionless ratio of expansion coefficients $\alpha_\eta^3/\alpha_S^2\alpha_H$ is nearly universal, independent of polymer and solvent and of whether the limiting good solvent dynamical molecular weight exponents agree or depart significantly from naive scaling predictions. (See below and ref 12.) Here the Flory expansion factors are defined as the usual[10] dimensionless ratios with respect to Θ solvent values, e.g.

$$\alpha_\eta^3 = [\eta]/[\eta]_0 \qquad (5)$$

where $[\eta]_0$ designates the Θ solvent value of $[\eta]$. A check of the universality of the ratio $\alpha_\eta^3/\alpha_S^2\alpha_H$ and of the nonuniversality of $P/P_0 = \alpha_H/\alpha_S$ and of $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_S^3$ provides important tests of the theory, and it is the purpose of this paper to make this type of comparison. Unfortunately, it is rare that all three quantities $[\eta]$, R_G^2, and R_H have been determined for the same polymer samples in both θ and good solvents. Consequently, the present test can only be of a preliminary nature.

Comparison between Theory and Experiment

We begin by reviewing the relevant theoretical calculations of ref 11 and 12. While a variety of RG calculations have been made for R_H of increasing levels of sophistication, our only nontrivial calculations for $[\eta]$ in both good and Θ solvents are those obtained by using the simple double-sum approximations. These double-sum calculations are perhaps less accurate than exact calculations with the Rouse–Zimm or Kirkwood–Riseman models, but there are several additional possible sources of discrepancy between theory and experiment that may be more important than the approximations inherent in the double-sum calculations. Some of these difficulties are as follows:

(1) First of all, the double-sum calculations in ref 11 and 12 employ the popular preaveraging approximation for the Oseen tensor as well as other approximations. The preaveraging corrections differ between good and Θ solvents.[13] Other technical limitations of these calculations are reviewed by Wang et al.[13]

(2) The absolute magnitude of Θ solvent polymer properties is known to be affected by the presence of residual interactions that exist at the Θ point.[15] A reasonable approximation[16] is generated by assuming that expansion factors are independent of these residual interactions, but the data discussed below involve different solvents to provide Θ and good solution values, and there are almost certainly corrections resulting from differences in the effects of the residual interactions in these solvents. For instance, the Θ temperature properties of poly(α-methylstyrene) (PαMS) seem to be more sensitive to the nature of the Θ solvent[17,18] than are the Θ solution properties of polystyrene (PS).[19,20]

(3) Although the Rouse–Zimm and Kirkwood–Riseman models are, in principle, more accurate hydrodynamic models than the simple double-sum models, higher order ϵ expansion calculations (at least to order ϵ^3) are necessary to obtain a formal accuracy from the dynamical renormalization group calculations which are equivalent to that of the double-sum treatment. Thus, the ϵ expansion errors may outweigh the approximations inherent in the double-sum formulas. In addition, the Rouse–Zimm model itself is known to be incomplete in the neglect of microscopic phenomena such as dynamical fluctuations in the solvent velocity, and the implications of generalizations of the Rouse–Zimm model are currently unknown.

A. Summary of Relevant Theory. Despite the limitations of the available theoretical calculations, we can test the qualitative predictions of the near universality of $\alpha_\eta^3/\alpha_S^2\alpha_H$ and the nonuniversality of P/P_0 and Φ/Φ_0. Calculations of Wang et al.[12] [see their (19) and (31)] to first order in ϵ yield

$$\alpha_\eta^3/\alpha_S^2\alpha_H = (1 + 0.075\lambda\lambda_\xi)[1 - (13/192)\lambda] \times [1 - (13/96)\lambda]/\{(1 + 0.224\lambda\lambda_\xi)[1 - (13/64)\lambda]\} \qquad (6a)$$

$$\lambda = (32z/3)/(1 + 32z/3), \quad \lambda_\xi = \xi/(1 + \xi) \qquad (6b)$$

where z is to be interpreted empirically as the Fixman excluded volume parameter and where ξ is proportional to the conventional draining parameter h characterizing the strength of the hydrodynamic interactions.[10] Specifically, these interactions are defined in three dimensions as

$$z = (3/2\pi l^2)^{3/2}\beta_2 n^{1/2} \qquad (7a)$$

$$\xi \propto h = [\hat{\zeta}/(12\pi^3)^{1/2}\eta_s l]n^{1/2} \qquad (7b)$$

where n is the polymerization index, β_2 is the binary cluster integral, η_s is the solvent viscosity, $\hat{\zeta}/6\pi\eta_s l$ is the reduced monomer friction coefficient, and l is a Kuhn segment length. The results[12] in (6) provide improved estimates of the coefficients 0.224 and 0.075 over earlier calculations.[11] Recent order ϵ^2 dynamical RG calculations[13] indicate that ξ is dependent on z (on excluded volume) and that the $^1/_2$ exponent for n in (7b) is reduced as solvent quality increases as a natural consequence of a diminishing average chain density within the polymer coil upon chain expansion. (The $^1/_2$ exponent in (7b) appears only in the Kirkwood–Riseman theory when preaveraging is used,[13] but the differences are unimportant here.)

Certain dimensionless ratios are predicted to approach universal limits in the nondraining good solvent limit, and the RG theory enables the calculation of these ratios within the ϵ-expansion method. The "fixed points" of the RG theory merely correspond to limiting situations where dimensionless properties become insensitive to variation of the dimensionless interaction parameters. The large z and ξ limit of (6) corresponds to λ and $\lambda_\xi \rightarrow 1$, and this implies that $\alpha_\eta^3/\alpha_S^2\alpha_H$ approaches

$$\alpha_\eta^3/\alpha_S^2\alpha_H = 0.888 \qquad \text{for } d = 3,\ z,\ \xi \gg 1 \qquad (8a)$$

Douglas and Freed[21,22] employ $d = 3$ perturbation calculations and RG theory to provide the alternative derivation of

$$\alpha_\eta^3/\alpha_S^2\alpha_H = 0.894 \qquad \text{for } d = 3,\ z,\ \xi \gg 1 \qquad (8b)$$

(The nondraining limit should not be interpreted as involving a complete absence of draining but just a relative insensitivity to the draining interaction; see ref 23.) If good solvent, nondraining limit values are designated with an asterisk, the individual ratios of P^*/P_0 and Φ^*/Φ_0 of ref 21 and 12 are quite consistent, giving

$$P^*/P_0 = 0.998 \text{ (ref 21)} \qquad (8c)$$

$$P^*/P_0 = 0.999 \text{ (ref 12)} \qquad (8d)$$

$$\Phi^*/\Phi_0 = 0.892 \text{ (ref 21)} \qquad (8e)$$

$$\Phi^*/\Phi_0 = 0.886 \text{ (ref 12)} \qquad (8f)$$

Recent Monte Carlo simulations of these ratios by Rey et al.[24a] yield

$$P^*/P_0 = 0.94 \tag{8g}$$

$$\Phi^*/\Phi_0 = 0.87 \tag{8h}$$

Rey et al. also summarize other experimental and theoretical values (see also ref 11, 12, and 21). Baumgärtner and Schäfer[24b] provide an approximate ϵ-expansion calculation in which they use the Borel resummed value[25] $\nu = 0.588$ in their calculations to estimate

$$P^*/P_0 = 0.94 \tag{8i}$$

from a double-sum type approximation in the nondraining limit.

The full scaling functions for P/P_0 and for Φ/Φ_0 become rather complicated in the crossover regions of both z and ξ finite and nonzero. When $z > 1$ and ξ is not too large or too small, P/P_0 and Φ/Φ_0 are dominated by the leading behavior:[11-13]

$$P/P_0 \propto \lambda_\xi \alpha_S^{\lambda_\xi - 1} \tag{9a}$$

$$\Phi/\Phi_0 \propto \lambda_\xi \alpha_S^{\lambda_\xi - 1} \tag{9b}$$

where slowly varying prefactors in λ and λ_ξ are neglected. [See (14), (19), and (31) of ref 12 and (5.1), (5.2), and (8.2) of ref 11 for details.] Recent order ϵ^2 dynamical RG calculations[13] produce the same leading behavior as in (9). All these calculations present the qualitative conclution that P/P_0 and Φ/Φ_0 do not necessarily level off at constant values for large α_S if ξ is also not large. Instead, plots of P/P_0 and Φ/Φ_0 versus α_S produce a family of curves having the nondraining limit ($\xi \to \infty$) as an upper bound. The nondraining limit calculations of Wang et al.[12] yield

$$P/P_0 = \{(1 + 0.075\lambda)[1 - (13/192)\lambda]\}^{-1}, \quad \xi \to \infty \tag{10a}$$

$$\Phi/\Phi_0 = [1 - (13/96)\lambda]/\{[1 - (13/64)\lambda](1 + 0.224\lambda)\}, \quad \xi \to \infty \tag{10b}$$

while rather similar results are found by Douglas and Freed[21,22] using $d = 3$ perturbation calculations in conjunction with RG theory. RG predictions[11,12,21,22] of the dependence of α_S on λ may be used with (10) to determine P/P_0 and Φ/Φ_0 as parameter-free functions of α_S in the nondraining limit. This type of scaling function is presented below in our comparisons with experiment.

B. Experimental Data Sources. Reference 12 provides a preliminary comparison of the partial draining theory and experiment in which the excluded volume dependence of the phenomenological hydrodynamic interaction parameter ξ is determined as a function of excluded volume for polystyrene (PS) in cyclohexane. Wang et al.[12] explain that a quantitative test of the theory requires the experimental determination and the theoretical calculation of many properties. Since the required data are unavailable and the theory is still somewhat incomplete, we focus here on some gross qualitative aspects of the partial draining phenomenon that can be understood with the available data and theory. One point is the relative constancy of $\alpha_\eta^3/\alpha_S^2\alpha_H$. In addition, the fact that Φ/Φ_0 and P/P_0 are not universal functions of excluded volume[39] is in direct conflict with the classical two-parameter type hydrodynamic models.[10] This section shows that the qualitative trends in the available data are consistent with the draining interpretation, and a discussion is provided below of the types of data necessary for a quantitative test of the theory. Reference 12 gives more theoretical details and the RG predictions for Φ/Φ_0 as a function of α_S and the excluded volume dependent hydrodynamic interaction ξ.

Table I
Constants for Use in Eq 8 for Polystyrene

	cyclohexane, 35 °C	toluene, 35 °C
$\bar{V}_2$, cm^3/g	0.928	0.919
ρ, g/cm^3	0.7644	0.8530
η_s, P	7.67×10^{-3}	4.93×10^{-3}

We now compare the theoretical predictions of subsection A above with available data for polyisobutylene (PIB), poly(α-methylstyrene) (PαMS), and PS. The PS data are those of Roovers and Toporowski[26] and Varma et al.[27] in cyclohexane at 35 °C (Θ) and in toluene at 35 °C (good solvent), and one set of the data is from Fukuda et al.[28] in Decalin at 20.4 °C (Θ) and in benzene at 30 °C (good solvent). The PαMS data are those of Noda et al.[17,18,29] in cyclohexane at 34.5 °C (Θ) and in toluene at 25 °C (good solvent). Data for PIB are taken from Matsumoto et al.[30] PIB is interpreted as conforming to the nondraining limit in good solvents, whereas PS is interpreted as having a relatively strong partial draining effect since it has considerably lower good solvent limit exponents for $[\eta]$ and R_H. PαMS is intermediate in draining character to PIB and PS. Further discussion and explanation for our statements concerning the degree of partial draining are given below. A more complete comparison between experiment and theory might consider several additional polymer–solvent systems and might vary the temperature to achieve Θ and good solvent situations by using the same polymer and solvent as discussed below. Nevertheless, the current data suffice for a preliminary test of our theoretical predictions.

C. Universality of $\alpha_\eta^3/\alpha_S^2\alpha_H$. The intrinsic friction coefficient $[f] = 6\pi R_H$ is obtained from the sedimentation coefficient s_0^0 through the standard expression

$$[f] = M_w(1 - \bar{V}_2\rho)/s_0^0 N_A \eta_s \tag{11}$$

where $\bar{V}_2$ is the polymer specific volume and ρ the solvent density as presented in Table I. The PS data for $[f]$ are reproduced in Table II. The six required measurements are only available for two of Roovers' samples, PS800f2 and PS1000f2. Two more complete sets of data can be obtained by calculating the missing $[f]_0$ for samples C6bb and C7bb by using[26]

$$[f]_0 = 4.22 \times 10^{-8} M_w^{0.5} \tag{12a}$$

The resultant ratios for $\alpha_\eta^3/\alpha_S^2\alpha_H$ are listed in the last column of Table II.

A check on the consistency of the values of $\alpha_\eta^3/\alpha_S^2\alpha_H$ is provided by calculating all the Θ solvent data from the empirical relations

$$R_{G,0}^2 = 0.079 M_w \ (\text{Å}^2) \tag{12b}$$

$$[\eta]_0 = 8.3 \times 10^{-2} M_w^{0.5} \tag{12c}$$

together with (12a). It is found that the computed values of $\alpha_\eta^3/\alpha_S^2\alpha_H$ lie between 0.85 and 0.88. Similar values (within 5%) are found by use of empirical $R_{G,0}^2$ and $[\eta]_0$ values of Berry[8a,19] or of Yamamoto et al.[31] or the $[f]_0$ data of Mulderije.[32] Estimates of $\alpha_\eta^3/\alpha_S^2\alpha_H$ from the data of Varma et al.[27] and Kurata et al.[28,33,34] are also presented in the last column of Table II. Although the scatter is somewhat larger, the average value of $\alpha_\eta^3/\alpha_S^2\alpha_H$ of 0.85 is in satisfactory agreement with the predictions of (8). The constancy of $\alpha_\eta^3/\alpha_S^2\alpha_H$ is, of course, no surprise, but a test of the theory comes from comparing PS and PαMS, since these polymers are interpreted below as displaying different degrees of partial draining in good solvents.

The PαMS data of Noda et al.[17,18,29] is reproduced in Table III and provides four samples for which all six re-

Table II
Dilute Solution Properties of Polystyrene

		Θ solvent			good solvent			
sample	$10^{-5}M_w$	$R_{G,0}$, Å	$[\eta]_0$, cm^3/g	$10^5[f]_0$	$R_{G,0}$, Å	$[\eta]$, cm^3/g	$10^5[f]$	$\alpha_\eta^3/\alpha_S^2\alpha_H$
C6bb[a]	2.75	146	41.4	(2.21)[b]	204	91.8	2.83	0.89
PS800f2[a]	6.75	229	68.4	3.46	329	171	4.93	0.85
C7bb[a]	8.6	255	77.6	(3.91)[b]	385	213	5.64	0.83
PS1000f2[a]	17.0	377	124.5 (?)	5.31	594	361	8.25	0.75 (?)
0.238[c]	2.38	141	40.9	2.09[d]	200	87.0	2.53[d]	0.87
0.426[c]	4.26	190	52.8	2.75[d]	278	127	3.47[d]	0.89
1.21[c]	12.1	322	92.0	4.65[d]	513	260	6.31[d]	0.82
3.85[c]	38.5	575	165	8.59[d]	998	600	11.9[d]	0.87
5.47[c]	54.7	692	195	10.1[d]	1230	760	14.7[d]	0.85
FF33[e]	24.2	436	123	6.31[d]	791	521	9.9_7[d]	0.81

[a] Reference 26. [b] Calculated with eq 12a. [c] Reference 27. [d] Calculated with $[f] = 6\pi R_H$. [e] References 28, 33, and 34.

Table III
Dilute Solution Properties of Poly(α-methylstyrene)[a]

		Θ solvent			good solvent			
sample	$10^{-5}M_w$	$R_{G,0}$, Å	$[\eta]_0$, cm^3/g	$10^5[f]_0$	$R_{G,0}$, Å	$[\eta]$, cm^3/g	$10^5[f]$	$\alpha_\eta^3/\alpha_S^2\alpha_H$
PαS-4	2.04	(131)[b]	33.6	1.78	178	$62._1$	2.25	0.78_5
PαS-6	4.4_4	(193)[b]	42.0	2.60	270	$104._2$	3.49	0.87
PαS-9	11.9	324	81.1	3.8_7	480	$242._4$	6.04	0.88
PαS-12	18.2	396	98.5	5.2_1	630	$317._5$	7.81	0.85
PαS-13	33.0	523	130	7.0_3	856	465	10.9	0.86
PαS-14	74.7	786	206	$10._6$	1370	940	16.5	0.97

[a] References 17, 18, and 29. [b] Calculated with eq 13a.

quired quantities are available. These give the ratio $\alpha_\eta^3/\alpha_S^2\alpha_H$ of 0.88, 0.85, 0.86, and 0.97 for samples 9, 12, 13, and 14, respectively. The molecular weight of sample 14 (7.47×10^6) makes it more susceptible to experimental errors in clarifying the solution[35] and perhaps explains the anomalous values for this sample. Use of the empirical Θ solvent relation[17]

$$R_{G,0}^2 = 8.4 \times 10^{-18} M_w \text{ (cm}^2) \tag{13a}$$

enables values of $\alpha_\eta^3/\alpha_S^2\alpha_H$ to be obtained for samples 4 and 6 of 0.78_5 and 0.87, respectively. A measure of the accuracy of the data is provided by comparing the empirically determined ratios with ones for which only $R_{G,0}^2$ is computed as well as with ones for which all Θ solvent data are computed by using[18,29]

$$[\eta]_0 = 7.3 \times 10^{-2} M_w^{0.5} \tag{13b}$$

$$[f]_0 = 3.90 \times 10^{-8} M_w^{0.5} \tag{13c}$$

for PαMS. The results are presented in Table IV along with those for one sample of Cowie et al.[36] for which all three good solvent measurements are available. The agreement between the different determinations of $\alpha_\eta^3/\alpha_S^2\alpha_H$ is again quite satisfactory.

Table IV
Ratio $\alpha_\eta^3/\alpha_S^2\alpha_H$ Calculated for Poly(α-methylstyrene)

		$\alpha_\eta^3/\alpha_S^2\alpha_H$	
sample	$10^{-5}M_w$	*a*	*b*
5[c]	4.8	0.91	0.87
PαS-4	2.04	0.78	0.79
PαS-6	4.44	0.87	0.81
PαS-9	11.9	0.83	0.93
PαS-12	18.2	0.83	0.84
PαS-13	33.0	0.87	0.86
PαS-14	74.7	0.99	1.03

[a] Only $R_{G,0}$ calculated with eq 13a. [b] $R_{G,0}$, $[\eta]_0$, and $[f]_0$ calculated with eq 13a, 13b, and 13c. [c] Data of ref 36; other data of Noda et al.[17,18,29]

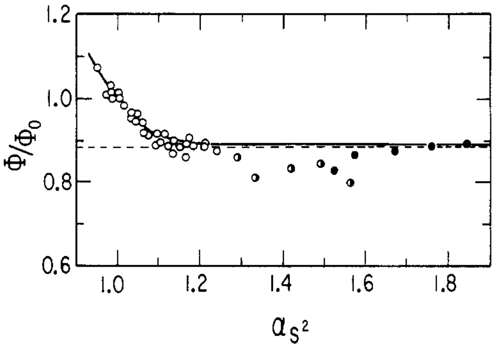

Figure 1. Ratio Φ/Φ_0 for polyisobutylene as a function of the radius of gyration expansion factor α_S. Data are taken from ref 30: (○) in isoamyl valerate at various temperatures; (◑) in *n*-heptane at 25 °C; (●) in cyclohexane at 25 °C. The solid line is the long-chain nondraining limit RG prediction[21] (see also ref 12), and the horizontal dashed line designates the nondraining good solvent limit of the RG theory (equations 8e and 8f). The text discusses possible reasons for the minimum in the experimental data.

The essential point in this subsection is the reasonable constancy of $\alpha_\eta^3/\alpha_S^2\alpha_H$ between PS and PαMS. An average of the empirical values of $\alpha_\eta^3/\alpha_S^2\alpha_H$ gives 0.87 and agrees with the theoretical predictions in (8), but both the experimental and theoretical values are subject to the 5% or so uncertainties described above. The data, therefore, support the predicted universality of $\alpha_\eta^3/\alpha_S^2\alpha_H$ and, in particular, the predictions of RG theory. Data on PIB for $[f]$ would complete this test of the theory, but unfortunately they are currently unavailable. Other data for PIB are discussed in the next section to show that this polymer corresponds closely to the theoretical expectations of the nondraining limit. Thus, [see (8c) and (8d)] we predict that the good solvent limit P^*/P_0 for PIB should be very close to unity for arbitrary $\alpha_S \geq 1$. Taking $P^*/P_0 = 1$ and the empirical estimate $\Phi^*/\Phi_0 \approx 0.9$ from Figure 1 leads to the value $\alpha_\eta^3/\alpha_S^2\alpha_H \approx 0.9$, which is consistent with the above estimates. It is desirable to check these predictions more precisely with more rigorous dynamical RG theory.

The observed universality of $\alpha_\eta^3/\alpha_S^2\alpha_H$ supports the general theoretical predictions and enables further analysis of the draining dependence of the good solvent limit P^*/P_0

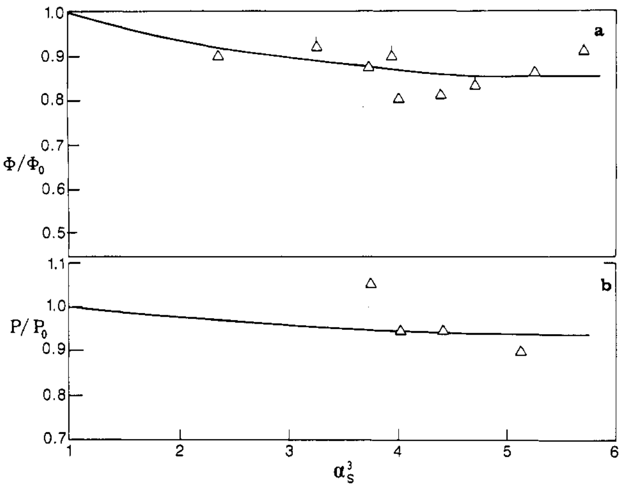

Figure 2. (a) Ratio Φ/Φ_0 for poly(α-methylstyrene) as a function of $\alpha_S{}^3$: triangles, data of ref 17, 18, and 29; (△) Θ solvent cyclohexane; (△) Θ solvent Decalin. (b) Ratio P/P_0 for poly(α-methylstyrene) as a function of $\alpha_S{}^3$. Symbols are as in Figure 2a.

and Φ^*/Φ_0 to deduce the empirical variation of an excluded volume dependent effective draining parameter on the traditional Fixman excluded volume parameter z. The empirical draining parameter for PS in cyclohexane at temperatures above Θ has been shown[12] to drop rapidly from an indeterminately large value at about $z = 1$, and then it appears to level off to a constant z-independent value for large z. The results are consistent with a crude model of nondraining coils for $z < 1$, with the partial draining chain breaking up into some kind of impermeable, molecular weight independent "hydrodynamic blobs". More theory is required to assess the validity of this qualitative picture and to determine why this effect appears to arise only for some polymer–solvent systems.

D. The Flory Ratios P/P_0 and Φ/Φ_0. Next we consider the same data presented for the ratios P/P_0 and Φ/Φ_0 as a function of the expansion factor α_S. It is useful to begin by establishing the nondraining limit behavior as a reference. Figure 1 compares Φ/Φ_0 for PIB in various solvents by using the precise experimental data of Matsumoto et al.[30] The dashed line presents the asymptotic limit from (8a), while the solid line provides the theoretical prediction of the nondraining limit crossover function for Φ/Φ_0 as given in (10b). The good agreement between the PIB data and the nondraining crossover theory is mirrored in similar agreement for polychloroprene[37] (PC; see the comparison in ref 21). It is this type of agreement that leads us to consider PIB and PC to be relatively nondraining in good solvents. Unfortunately, comparable precise data for P/P_0 are not available for PIB and PC.

Figures 2 and 3 present a collection of data[6,17,18,20,26–29,33,34,38] for P/P_0 and Φ/Φ_0 for PαMS and PS in various solvents. The data points exhibit considerably more scatter than those in Figure 1, so that only rather qualitative comparisons between theory and experiment can be made. The scatter in the data is, however, an *anticipated consequence of partial draining* where there are families of curves for different draining strengths (for different solvents) such that the nondraining limit crossover curve for Φ/Φ_0 in Figure 1 is only an upper bound [see (9)]. The Φ/Φ_0 crossover data points for PαMS lie intermediate between the nondraining PIB data in Figure 1 and the main trend of the PS data in Figure 3a. We interpret this as indication that PαMS is intermediate between PIB and PS in its sensitivity to partial draining in good solvents. The slight reduction of P/P_0 from unity in Figure 2b is also consistent with a mild extent of partial draining. The data in Figure 3 for PS present the extreme case of strong partial draining. P/P_0 and Φ/Φ_0 both exhibit a more pronounced dip for PS than do the corresponding data for PαMS. This trend is in accord with theoretical expectations.[11–14]

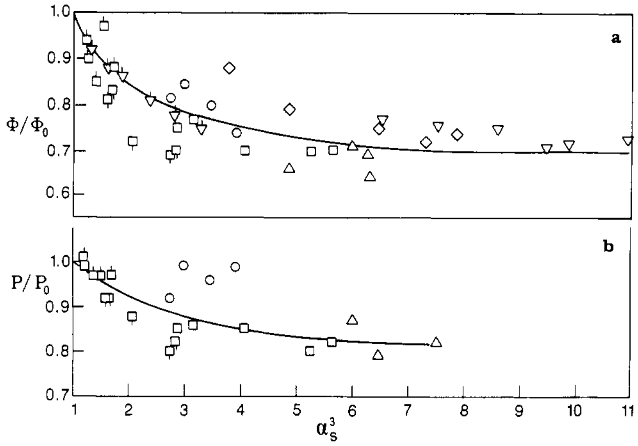

Figure 3. (a) Ratio Φ/Φ_0 for PS as a function of $\alpha_S{}^3$ for PS: (○) data for ref 26; (△) data of ref 28, 33, and 34; data of ref 27 are for □ in toluene, □̩ in butanone, □̍ in cyclohexane at 44.5 °C; (▽) data of ref 6; (◇) data of ref 20; (▽̍) data of ref 38. (b) Ratio P/P_0 for PS as a function of $\alpha_S{}^3$. Symbols are as in Figure 3a. Reference 39 presents an earlier indication that Φ/Φ_0 does not form a single composite curve.

A qualitative signature of partial draining is a nonmonotonicity in P/P_0 and Φ/Φ_0 as a function of α_S for a fixed polymer–solvent system at fixed temperature where only the molecular weight is varied. Equation 7 implies that ξ increases with molecular weight even though there is some uncertainty in the precise rate of increase (see ref 13). Relatively short chains can induce the P/P_0 and Φ/Φ_0 curves to also exhibit some characteristics of partially draining chains, but an increase of α_S through increasing molecular weight also increases ξ and consequently the tendency to nondraining behavior. Thus, if α_S is varied through changes in molecular weight at fixed temperature, the transition from short to longer chains can make the P/P_0 and Φ/Φ_0 curves have a rapid decrease for small α_S [see (9a) and Figure 3], followed by an increase toward the nondraining limiting curves of (10) (see Figure 1). This can produce a minimum in the curves.

The individual ratios P/P_0 and Φ/Φ_0 are certainly not universal functions of α_S, and the trends displayed by the experimental data are consistent with the qualitative predictions of the partial draining theory. More precise and controlled data for carefully prepared monodisperse polymers are needed for a quantitative test of the RG theory of partial draining. The data presented in Figure 1 are representative of the precision required.

Discussion

An examination of the available experimental data for $\alpha_\eta{}^3/\alpha_S{}^2\alpha_H$ supports the RG prediction that this ratio is nearly universal, and indeed quantitative agreement is found between the experimental data and RG calculations based on the somewhat simplified double-sum approximation to the hydrodynamic theory. Comparison is limited here to poly(α-methylstyrene) and polystyrene, and further tests of the theory should be made through measurements of $[f]$ in several solvents for polyisobutylene and poly(chloroprene) as this series of polymers appears to cover a significant range of partial draining to nondraining limits.

Further support is provided for the Flory ratios P/P_0 and Φ/Φ_0 not being universal functions of the expansion factor α_S for all polymer–solvent systems. This important observation is quite independent of our theoretical interpretation, although the trends found for these scaling functions are indeed consistent with the expectations of our partial draining theory where the "nonuniversality" is simply a consequence of the presence of multiple (i.e., two) interactions controlling polymer dynamics in dilute good solutions.

Several other dimensionless ratios may be formed by combining dynamical and equilibrium dilute solution polymer properties. Two additional examples are the Δ and Π ratios defined in ref 21, which involve dimensionless combinations of the second virial coefficient, $[\eta]$, and $[f]$. Comparison between RG calculations[21] and experiment exhibits excellent agreement for Π versus α_S, and the availability of similar data for $[f]$ would enable the testing of the RG predictions for Δ and a completion of this testing of the nondraining limit theory. Then the comparison should be further enlarged to include chains with differing branching architecture as this enlarges the class of dimensionless ratios that may be used to test the theory.[21,22]

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Registry No. PS, 9003-53-6; PIB, 9003-27-4; PαMS, 25014-31-7.

References and Notes

(1) (a) Mark, H. *Der feste Köper Hirzel*; Liepzig, 1938; p 103. Houwink, R. *J. Prakt. Chem.* **1940**, *155*, 241. (c) A useful list of references and a review of early theoretical and experimental studies of polymer hydrodynamics is given in: Ewart, R. W. *Adv. Colloid Sci.* **1946**, *2*, 197.
(2) (a) Kuhn, W. *Kolloid Z.* **1933**, *62*, 269; **1934**, *68*, 2. (b) Kuhn, W.; Kuhn, H. *Helv. Chim. Acta* **1943**, *26*, 1394.
(3) (a) Debye, P.; Bueche, A. M. *J. Chem. Phys.* **1948**, *16*, 573. (b) Debye, P. *Phys. Rev.* **1947**, *71*, 486.
(4) Kirkwood, J. G.; Riseman, J. *J. Chem.* Phys. **1948**, *16*, 565.
(5) (a) Flory, P. J.; Fox, T. G. *J. Phys. Colloid Chem.* **1949**, *53*, 197. (b) Flory, P. J.; Fox, T. G. *J. Am. Chem. Soc.* **1951**, *73*, 1904. (c) See also: de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(6) (a) Miyaki, Y.; Einaga, Y.; Fujuita, H. *Macromolecules* **1978**, *11*, 1180. (b) See also: Flory, P. J. *J. Am. Chem. Soc.* **1943**, 65, 372, and ref 1c.
(7) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2103.
(8) (a) Berry, G. C. *J. Chem. Phys.* **1967**, *46*, 1338. (b) See also: Kringbaum, W. B.; Carpenter, D. K. *J. Phys. Chem.* **1955**, *59*, 1166, and ref 18 and 39.
(9) Yamakawa, H. *J. Chem. Phys.* **1968**, *48*, 2103. (b) Tanaka, G.; Imai, S.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2639. See also ref 37. In analyzing his experimental data, Berry[8a] assumes the binary cluster integral β_2 of the two-parameter theory[10] to have the dependence $\beta \propto (1 - \Theta/T)$, with T the absolute temperature and Θ the Θ temperature. References 9 and 10 suggest that the curve splitting, which Berry attributes to draining, is a consequence of the inadequacy of this assumption for β_2 over a large temperature range. Reference 37 amplifies this argument and states that Berry's interpretation of draining in his hydrodynamic data should be taken as tentative until the temperature dependence of β_2 is verified. Later work by Miyaki and Fujita unambiguously establishes a splitting pattern in the scaling curves for Φ/Φ_0 as a function of α_{S^2} that is independent of assumptions regarding the temperature dependence of β_2. Thus, the present paper is a further amplification of this basic observation by Miyaki and Fujita[39] using recent RG computations and a compilation of available data.
(10) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971; p 379.
(11) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 2354.
(12) Wang, S. Q.; Douglas, J. F.; Freed, K. F. *Macromolecules* **1985**, *18*, 2464. The calculations of this reference contain two different parameters $\lambda_\xi = \xi/(1 + \xi)$ in the evaluation of α_H and α_η to different levels of approximation. Equations 6 and 9 equate these two parameters because general renormalization group arguments dictate that there be a single hydrodynamic scaling variable ξ, and this is found in the more sophisticated computations in ref 13.
(13) (a) Wang, S. Q.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1986**, *85*, 3674; (b) **1987**, *87*, 1346.
(14) Wang, S. Q.; Freed, K. F. *J. Chem. Phys.* **1986**, *85*, 6210; **1987**, *86*, 3021.
(15) (a) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 5293; (b) *J. Chem. Phys.* **1987**, *87*, 3089.
(16) Douglas, J. F.; Cherayil, B. J.; Freed, K. F. *Macromolecules* **1985**, *18*, 2455.
(17) Kato, T.; Miyaso, K.; Noda, I.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 777.
(18) Noda, I.; Mizutani, K.; Kato, T.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 787.
(19) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(20) Utiyama, H.; Utsumi, S.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1978**, *11*, 506.
(21) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 2344; **1985**, *18*, 201.
(22) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley-Interscience: New York, 1987.
(23) Mulderije, J. J. H.; Jalink, H. L. *Macromolecules* **1987**, *20*, 1152.
(24) (a) Rey, A.; Freire, J. J.; de la Torre, J. G. *Macromolecules* **1987**, *20*, 342. (b) Schäfer, L.; Baumgärtner, A. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*, 1431.
(25) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. B* **1980**, *21*, 3976.
(26) Roovers, J.; Toporowski, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907.
(27) Varma, B. K.; Fujita, Y.; Takahashi, M.; Nose, T. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1781.
(28) Fukuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(29) Noda, I.; Mizutani, K.; Kato, T. *Macromolecules* **1977**, *10*, 618.
(30) Matsumoto, T.; Nishioka, N.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 23.
(31) Yamamoto, A.; Fuji, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 799.
(32) Mulderije, J. J. H. *Macromolecules* **1980**, *13*, 1207.
(33) Tsunashima, Y.; Nemoto, N.; Kurata, M. *Macromolecules* **1983**, *16*, 1184.
(34) Nemoto, N.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1984**, *17*, 425.
(35) Berry, G. C., private communication.
(36) (a) Cowie, J. M. G.; Bywater, S. *J. Polym. Sci., Part C* **1970**, *30*, 85. (b) Cowie, J. M. G.; Worsfold, D. J.; Bywater, S. *Polymer* **1967**, *8*, 105. This work obtains $R_G^2 = 1.75 \times 10^{-6} M_w^{1.38}$ (Å^2) in the good solvent toluene. These high values for R_G^2 are responsible for the very low values of Φ/Φ_0 in Figure 2a, and therefore these data are disregarded in the discussion.
(37) Norisuye, T.; Kawahara, K.; Teramoto, A.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4330, 4339.
(38) Suzuki, H. *Br. Polym. J.* **1982**, *14*, 137.
(39) Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.