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Osmotic Second Virial Coefficient and Two-Parameter Theories

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ABSTRACT: Literature data on polystyrene in toluene show that the molecular weight dependence of the interpenetration function, Ψ, does not follow the dependence on chain expansion factor, α_s, that would be predicted by two-parameter theory for Gaussian chains; there is an increase of Ψ at low molecular weight which can be explained by the non-Gaussian dependence of chain dimensions on M caused by local chain stiffness. A different kind of deviation from two-parameter theory is seen under Θ-solvent conditions: for polystyrene in cyclohexane at the Θ-temperature, second virial coefficients at low M do not vanish and can be rationalized as due to three-body interactions within the overlap region of two polymers.

Small Molecular Weights in Good Solvents

Interactions in dilute solutions of flexible high polymers are often discussed in terms of the interpenetration function,[1] Ψ. This dimensionless quantity is defined in relation to the osmotic second virial coefficient, A_2 (for two identical chains), by

$$\Psi = (A_2M^2/4\pi^{3/2}N_A\langle S^2\rangle^{3/2}) \quad (1)$$

where M is the polymer molar weight, $\langle S^2\rangle$ the mean square radius of gyration, and N_A Avogadro's number. Several approximate expressions[2] have been derived for Ψ as a function of the excluded volume parameter.

$$z = \left(\frac{3}{2\pi a^2}\right)^{3/2}\beta n^{1/2} \quad (2)$$

Here β is the binary cluster integral and n the number of statistically independent segments of effective bond length, a. The so-called two-parameter theories[3] based on the Gaussian chain model involve the only combinations na^2 and $n^2\beta$, where n is proportional to M.

It is well-known that z cannot be determined directly by experiment. However, the experimentally accessible expansion coefficient, α_s, for the rms radius of gyration can also be expressed as a function of z. Therefore, a plot of $\Psi(z)$ vs. $\alpha_s(z)$ eliminates z and provides a valuable test for two-parameter theories. As is the case for $\Psi(z)$, several theoretical approximations are available[4–7] for α_s as a function of z. It is important to find self-consistent pairs of functions $\Psi(z)$ and $\alpha_s(z)$. Though several papers[8–13] deal with this test of the two-parameter theories, it appears helpful to add further comments.

As one example, the treatments according to Kurata et al.,[14] Yamakawa,[15] and Yamakawa and Tanaka[16] give the relations

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04z)^{0.45} \quad (3a)$$

$$\Psi = 0.547[1 - (1 + 3.903z/\alpha_s^3)^{-0.468}] \quad (3b)$$

These equations, like other combinations, yield reasonable agreement with many experimental results[9,10] but only under certain circumstances, as will be seen below. We do not suggest that they should necessarily be preferred to other such combinations.

Apart from numerical differences, all but two[17a,b] of the approximate theories of Ψ yield monotonically increasing functions of z. In the limit of high z, they attain constant values. This behavior has been confirmed only by experiments with relatively high molecular weight samples, in which the excluded volume parameter, $z(\alpha_s)$, was varied by *changing the temperature*.[9,10,18] An example, Figure 1 represents such measurements by Berry[18] with different polystyrene (PS) samples in *trans*-decalin.

In good solvents, a limiting plateau value is also found experimentally for high molecular weights.[18–23] According to eq 3b, the limiting value is 0.547, which is significantly larger than any experimental data, available in the high z range. However, more recent theoretical predictions, 0.231 by Oono and Freed[24] and 0.268 by Witten and Schäfer[25], are in closer agreement with experiment. The crucial point here is that the shape of $\Psi(\alpha_s)$ is completely different from that of Figure 1. This is seen in Figure 2, which represents Ψ isothermally over a wide range of α_s^3 for PS in the good solvent toluene and employs several sets of literature data.[21–23,26] In this case, z is varied at constant β by *changing the molecular weight*.

This behavior has already been mentioned by Miyaki[19] et al. We offer further evidence from small-angle neutron scattering experiments[21,27] with four very low molecular weight PS samples in toluene-d_8 and cyclohexane-d_{12}. These provide us with the complete set of data necessary to calculate Ψ and α_s essentially down to the limit $\alpha_s \to 1$. For the other literature data,[22,23,26] $\langle S^2\rangle$ values for unperturbed PS were calculated with the equation of Benoit

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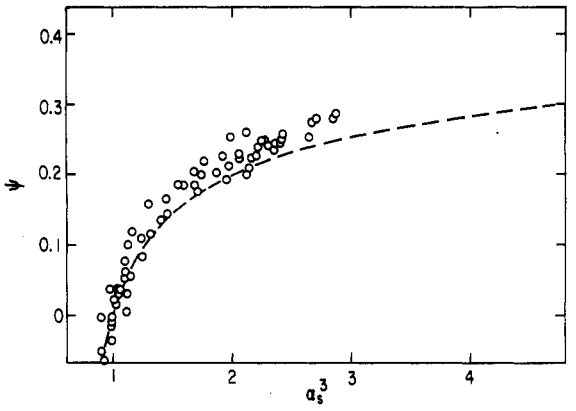

Figure 1. Plot of Ψ vs. α_s^3 from Berry's data[18] for PS in *trans*-decalin. All samples have molecular weights larger than 5×10^5. The dashed curve is calculated with eq 3a and 3b.

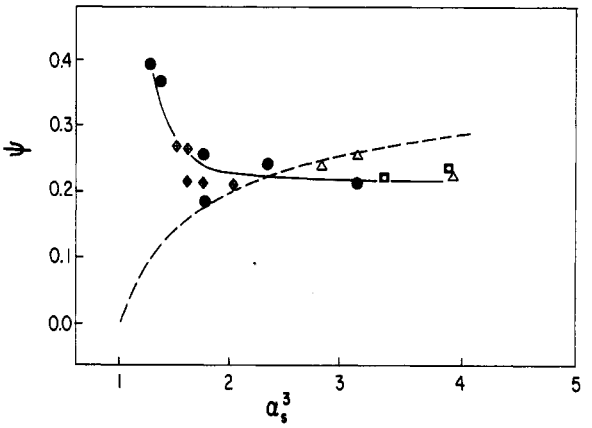

Figure 2. Literature data of Ψ vs. α_s^3 for PS in toluene: (●) ref 21, (△) ref 22, (◇) ref 26, and (□) ref 33. The expansion factor α_s is modified by changing the molecular weight. The drawn line serves as a guide for the eye.

and Doty[28] for wormlike chains, with 2.9 nm as the Kuhn length and 450 g/(mol nm) as the mass per unit length.[21]

In order to give a qualitative interpretation of the behavior of Ψ, we now consider the molecular weight dependence of the second virial coefficient of PS in toluene. If molecular weights are lower than about 10^4, the experimentally determined expansion coefficient, α_s, approaches unity.[27] The two-parameter theories, being based on Gaussian chains, require that when $\alpha_s = 1$, the quantities z, Ψ and A_2 should approach 0. However, the experimental behavior is quite different, as is shown in Figure 3, which again represents literature data[27,29] for PS in toluene.

A proper comparison between theory and experiment at low M should be based on non-Gaussian models. Here we make use of the excluded volume calculations by Yamakawa and Stockmayer[30] for wormlike chains. These authors calculated the effects of chain stiffness on the single contact term in the cluster series for the expansion factor and on the double-contact term in the series for A_2, and they assumed that the effect of stiffness on higher terms could be scaled according to the number of contacts. The result is that Kz replaces $1.333z$ in the equation for α_s and Qz replaces $2.866z$ in the equation for Ψ, where K and Q are functions of contour length available from Table I and eq 96 and 119 of ref 30. Applying this scheme to eq 3, we now have

$$\alpha_s = 0.541 + 0.459[1 + 4.53Kz]^{0.45} \quad (3a')$$

$$\Psi = 0.638Q[1 + 1.3623Q(z/\alpha_s^3)^{-0.468}] \quad (3b')$$

The excluded volume parameter, z, was calculated by eq

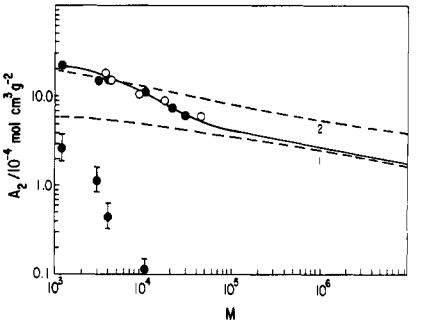

Figure 3. Second virial coefficient of PS in toluene (●) ref 27 and (○) ref 29. Dashed curves: theory of Yamakawa and Stockmayer[30] with $\beta = 1.6$ nm (1) and with $\beta = 5.2$ nm (2). The drawn curve represents experimental results according to ref 27. Second virial coefficient in cyclohexane at $T = 35$ °C: ⊗ with error bars.

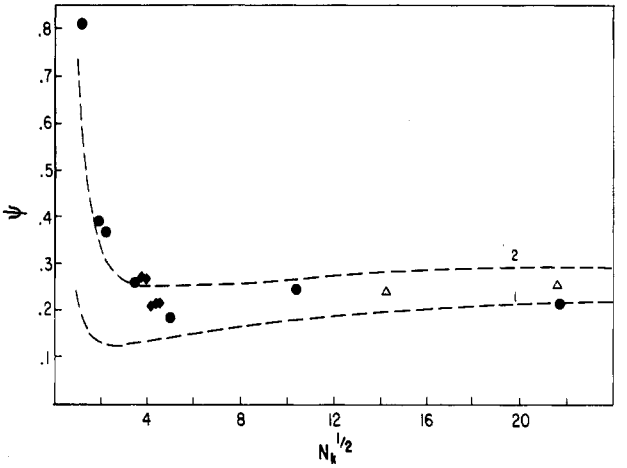

Figure 4. Literature data for Ψ plotted against $N_k^{1/2}$ for PS in toluene; symbols as in Figure 2; the dashed curves correspond to those of Figure 3. Here $N_k = n$ is the number of Kuhn segments.

2, where a and n become the Kuhn length and the number of Kuhn segments, respectively, both estimated according to ref 21. The binary cluster integral, β, was treated as a fitting parameter. Calculations were carried out with two different values for β.

The results of the procedure just described are represented in Figures 3 and 4. Whereas the value $\beta = 1.6$ nm^3 provides good agreement in the high molecular weight range, a considerably higher value of $\beta = 5.2$ nm^3 has to be assumed in order to achieve agreement in the low molecular weight range. However, the main feature of the calculations is an increase of Ψ with decreasing molecular weight in both cases (Figure 4). This can *only* be achieved by applying a theory which takes chain stiffness into account. In the low molecular weight range, stiffness causes an increase of the exponent of $\langle S^2 \rangle$ toward the value for rods. At the same time, A_2 should assume a plateau value.[31] Therefore, we must have the following limiting behavior

$$\Psi \sim A_2 M^2/\langle S^2 \rangle^{3/2} \sim M^{-1} \text{ (low } M\text{, good solvent)} \quad (4)$$

It thus appears that the interpenetration function is of only limited use in good solvent systems.

Small Molecular Weights under Θ-Conditions

Light scattering experiments were performed on four low-M PS samples in cyclohexane at 35 °C. All experiments were carried out on a Sofica light-scattering apparatus at a wavelength of 436 nm. For each sample, at least eight different concentrations were measured. Prior to use,

cyclohexane was distilled over Na wire. To remove dust, each solution was filtered through a Millipore filter (0.05 μm). No angular dependence could be detected, and an average value of Kc/R_θ was calculated from measurements at angles of 60°, 90°, and 120°.

Values of A_2 were estimated by applying a quadratic fit to the concentration dependence of Kc/R_θ. Alternatively, $(Kc/R_\theta)^{1/2}$ was fit according to Berry,[18] leading to somewhat higher A_2 values. Because of the large experimental uncertainty (perhaps 50%) in A_2, we do not put great emphasis on the absolute values, but the dependence on molecular weight is evident enough.

As shown in Figure 3, all four PS samples exhibit a non-zero value for A_2 which increases significantly with decreasing molecular weight. Such behavior was predicted probably for the first time by Orofino and Flory,[32] who used a model of polymeric coils with Gaussian segment distributions around their centers of mass. By taking into account three-body interactions within the overlap region of two neighboring polymers, they arrived at the relationship

$$A_2 = (16\pi/3^{3/2})(N_A\langle S^2\rangle^{3/2}/M^2)\ \ln\ [1 + X_1(\pi^{1/2}/4) + X_2(\pi^{1/2}3^{3/2}/32)] \quad (5)$$

Here X_1 and X_2 are defined as

$$X_1 = (1/4)(3/\pi)^{3/2}(v^2/V_1N_A)(M^2/\langle S^2\rangle^{3/2})\ [(1/2) - \chi_1] \quad (6a)$$

$$X_2 = 3(3^{1/2}/2\pi)^3(v^3/V_1N_A^2)(M^3/\langle S^2\rangle^3)\ [(1/3) - \chi_2] \quad (6b)$$

where v is the partial specific volume of the polymer, V_1 the molar volume of the solvent, and χ_1 and χ_2 the interaction parameters characteristic of the polymer–solvent pair. As pointed out by Orofino and Flory, for high molecular weight samples in a good solvent, the influence of X_2 on eq 5 becomes negligible because $M^3/\langle S^2\rangle^3$ is small in comparison to $M^2/\langle S^2\rangle^{3/2}$; see eq 6a and 6b. In a Θ-solvent, however, χ_1 approaches $^1/_2$ and X_1 diminishes, but not X_2. If χ_2 is, as normally expected, considerably less than $^1/_3$, the term X_2 will become significant at low molecular weights. Here the segment density within the overlap region increases, enhancing the number of contacts among three segments. This type of contact, which is not taken into account by χ_1, decreases the mutual interpenetration and leads to a nonvanishing second virial coefficient.

At the Θ-temperature, $X_1 = 0$, and at low M the effect of chain stiffness will be to limit the three-segment term to the initial one in the expansion of the logarithm in eq 5. Under these conditions, we therefore have

$$A_2 \sim M/\langle S^2\rangle^{3/2} \sim M^p \quad (\text{low } M,\ T = \Theta) \quad (7)$$

In the range $10^3 < M < 10^4$, the wormlike model with the aforementioned parameters gives an exponent of about $\nu = 0.7$ for $\langle S^2\rangle^{1/2}$, so that in eq 7 we get $p = -1.1$, in adequate agreement with the cyclohexane data of Figure 3.

Conclusions

(i) If the molecular weight is high enough, i.e., $M > 10^5$ in the case of PS, mutually consistent relationships for $\Psi(z)$ and $\alpha_s(z)$ based on two-parameter theories can in principle reproduce experimental results.

(ii) When z is modified by the molecular weight, curves of $\Psi(z)$ have a different shape from those obtained when z is modified by the temperature. Maximum values in plots of Ψ vs. α_s^3 deduced from experimental data[11,13] are due to superposition of these two shapes. For this reason, representations of $\Psi(\alpha_s)$ where α_s is determined as a function of M should not be combined with plots where α_s is determined as a function of temperature.

(iii) Two-parameter theories fail to describe completely the experimental behavior of short chains in both good and Θ-solvents. However, a qualitatively correct interpretation is made possible if some third parameter is used: under good solvent conditions this can be achieved by taking into account chain stiffness and under Θ-conditions by introducing a three-segment interaction parameter.

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