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On the Theory of the Second Virial Coefficient for Polymer Chains

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ABSTRACT: The theory of the second virial coefficient A_2 for flexible polymers is reconsidered in order to explain two observations inconsistent with the two-parameter theory prediction. One is the decrease in the interpenetration function Ψ with increasing molecular weight M in good solvents even in the ordinary range of M in which the unperturbed mean-square radius of gyration is proportional to M. The other is the nonvanishing of A_2 for small M at the Θ temperature. It is shown that the first observation may be explained by considering effects of chain stiffness on Ψ and also on the expansion factor α_S, which remain rather large even in the range of M above, although vanishingly small for very large M, according to the Yamakawa–Stockmayer–Shimada theory for the wormlike and helical wormlike chains. Therefore the theory also predicts that the increase in Ψ with increasing solvent power depends in general on M. The second may be explained by considering possible effects of chain ends. Both effects are then analyzed by a comparison with experiment. Thus it is emphasized that the two-parameter theory should be considered a limiting law for extremely large M.

I. Introduction

In the past 10-odd years, there have been presented many experimental results that indicate clearly the breakdown of the two-parameter theory of dilute polymer solutions.[1] Among them, the most remarkable ones are two observations for the second virial coefficient A_2. One is the rather well-known result[2,3] that for flexible polymers in good solvents the interpenetration function Ψ appearing in A_2 first decreases with increasing molecular weight M and then reaches the constant limiting value. Here, by "flexible" we mean chains such that the ratio of the mean-square radius of gyration $\langle S^2 \rangle$ to M is independent of M in the unperturbed state (i.e., at the Θ temperature at which A_2 vanishes for large M) and over the ordinary range of M in which $\langle S^2 \rangle$ can be determined from light scattering measurements. The other is the recent finding[4–6] that A_2 does not vanish but increases with decreasing M for flexible chains at Θ in the range of small M in which $\langle S^2 \rangle_0/M$ depends on M, where the subscript 0 denotes the unperturbed value. The object of the present paper is to reconsider the theory of A_2 in order to explain these observations.

The first problem is believed to be closely related to chain stiffness, as pointed out by Huber and Stockmayer[4] (although for the region of low M). The reason for this is that the Yamakawa–Stockmayer–Shimada theory[7–9] for the Kratky–Porod (KP) wormlike chain[10] and the helical wormlike (HW) chain[11,12] predicts that the chain stiffness has significant effects on the excluded-volume expansion factor α_S for $\langle S^2 \rangle$ and also on Ψ even for such large M that $\langle S^2 \rangle_0/M$ is independent of M. Thus we reexamine the behavior of Ψ for *flexible* chains on the basis of this theory. As for the second problem, we consider possible effects of chain ends since there must be an additional term that does not vanish at Θ for any M but becomes negligibly small for large M. In this connection, we must note that none of the existent theories with consideration of the ternary-cluster integral can give a consistent explanation of such behavior of $A_{2,\Theta}$ and the M independence of Θ in its ordinary range.[13]

II. Effects of Chain Stiffness

For convenience, we begin by summarizing a generalization of the Yamakawa–Stockmayer theory[7] of the expansion factor α_S for the KP chain to the HW chain.[8,9] The latter chain[11,12] may be described essentially in terms of the three model parameters: the constant differential-geometrical curvature κ_0 and torsion τ_0 of its characteristic helix taken at the minimum of the potential energy and the static stiffness parameter λ^{-1} as defined as the bending force constant divided by $k_B T/2$ with k_B the Boltzmann constant and T the absolute temperature. When we apply it to a given real chain, we need an additional parameter, i.e., the shift factor M_L as defined as the molecular weight per unit contour length. In this section, all lengths are measured in units of λ^{-1}, for simplicity.

For the HW chain of total contour length L, the unperturbed mean-square radius of gyration $\langle S^2 \rangle_0$ is given by

$$\langle S^2 \rangle_0 = \frac{\tau_0^{\,2}}{\nu^2}\langle S^2 \rangle_{0,\mathrm{KP}} + \frac{\kappa_0^{\,2}}{\nu^2}\left[\frac{L}{3r}\cos\phi - \frac{1}{r^2}\cos(2\phi) + \frac{2}{r^3L}\cos(3\phi) - \frac{2}{r^4L^2}\cos(4\phi) + \frac{2}{r^4L^2}e^{-2L}\cos(\nu L + 4\phi)\right] \quad (1)$$

where

$$\nu = (\kappa_0^{\,2} + \tau_0^{\,2})^{1/2}$$

$$r = (4 + \nu^2)^{1/2}$$

$$\phi = \cos^{-1}(2/r) \quad (2)$$

and $\langle S^2 \rangle_{0,\mathrm{KP}}$ is the $\langle S^2 \rangle_0$ for the KP chain having the same λ^{-1} as that of the HW chain and is given by

$$\langle S^2 \rangle_{0,\mathrm{KP}} = \frac{L}{6} - \frac{1}{4} + \frac{1}{4L} - \frac{1}{8L^2}(1 - e^{-2L}) \quad (3)$$

Note that the KP chain is a special case of the HW chain with $\kappa_0 = 0$.

Consider then the HW chain on which $n + 1$ beads are arrayed with spacing a between them along the contour, and suppose that there exist excluded-volume interactions between them expressed in terms of the usual binary-cluster integral β. For this perturbed chain, the expansion

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factor α_S, as defined as

$$\langle S^2 \rangle = \langle S^2 \rangle_0 \alpha_S{}^2 \tag{4}$$

is assumed to be a function only of the parameter $\tilde{z}$ defined by

$$\tilde{z} = (3/4)K(L)z \tag{5}$$

In eq 5, z is the excluded-volume parameter defined by

$$z = (3/2\pi)^{3/2}BL^{1/2} \tag{6}$$

where

$$B = \beta/a^2c_\infty{}^{3/2} \tag{7}$$

with

$$\begin{aligned} c_\infty &= \lim_{L\to\infty} (6\langle S^2 \rangle_0/L) \\ &= (4 + \tau_0{}^2)/(4 + \kappa_0{}^2 + \tau_0{}^2) \end{aligned} \tag{8}$$

and $K(L)$ is given as a function only of L (independent of κ_0 and τ_0) in a very good approximation as follows:[9]

$$\begin{aligned} K(L) &= \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} \qquad \text{for } L > 6 \\ &= L^{-1/2}\exp(-6.611L^{-1} + 0.9198 + 0.03516L) \\ &\qquad\qquad \text{for } L \le 6 \end{aligned} \tag{9}$$

We note that, in the coil limit of $L \to \infty$, eq 6 is identical with the definition of the usual excluded-volume parameter z. However, it is important to see from eqs 1 and 9 that, as L is increased, the coefficient $K(L)$ approaches more slowly the coil limiting value than does the ratio $\langle S^2 \rangle_0/L$, so that $\tilde{z}$ also slowly becomes z. In other words, the effect of chain stiffness on α_S remains rather large even for such large L that $\langle S^2 \rangle_0/L$ reaches almost its coil limiting value $c_\infty/6$. As for α_S itself as a function of $\tilde{z}$, it is convenient to adopt the Domb–Barrett equation[14]

$$\begin{aligned} \alpha_S{}^2 = {} & [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + \\ & 8\pi^{3/2}\tilde{z}^3]^{2/15}[0.933 + 0.067\exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \end{aligned} \tag{10}$$

Now we consider the second virial coefficient A_2. The generalization of the Yamakawa–Stockmayer theory[7] of A_2 (for $n \gg 1$) may be written in the form

$$A_2 = (N_A c_\infty{}^{3/2}L^2B/2M^2)h \tag{11}$$

with

$$h = 1 - Q(L,d)z + ... \tag{12}$$

where N_A is Avogadro's number and d is the cutoff parameter. This parameter should be chosen to equal the diameter of the chain since it is reasonable to have the touched-bead model in the stiff-chain or rod limit.[7] The coefficient Q as a function of L and d is assumed to be independent of the HW model parameters κ_0 and τ_0 since this is the case with $K(L)$. Then Q is given by eq 96 with eq 119 of ref 7, and it approaches its coil limiting value 2.865 for large L irrespective of the value of d.

Equation 11 may be rewritten in the form

$$A_2 = 4\pi^{3/2}N_A(\langle S^2 \rangle^{3/2}/M^2)\Psi \tag{13}$$

where Ψ is the interpenetration function defined by

$$\Psi = (6\langle S^2 \rangle_0/c_\infty L)^{-3/2}\bar{z}h \tag{14}$$

with

$$\bar{z} = z/\alpha_S{}^3 \tag{15}$$

We assume that h is a function only of the parameter $\hat{z}$ defined by

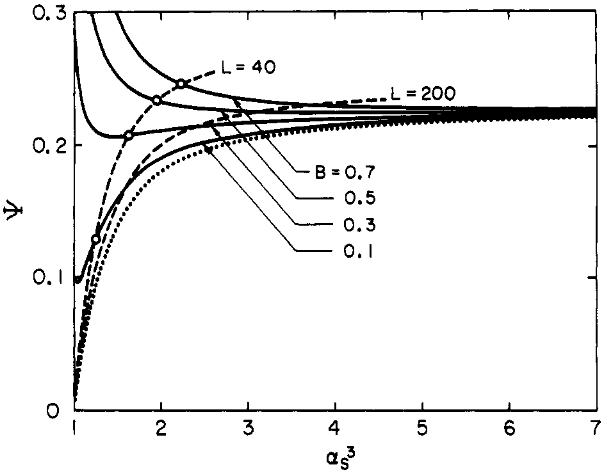

Figure 1. Ψ plotted against $\alpha_S{}^3$. The dotted curve represents the ($L \to \infty$) two-parameter theory values (see the text).

$$\hat{z} = (Q/2.865)\bar{z} \tag{16}$$

so that in the coil limit $\hat{z}$ becomes $\bar{z}$. Note that in this limit the assumption $h = h(\bar{z})$ is equivalent to making the uniform-expansion approximation to the expansion of each of the chains in contact.[1]

The problem is then a determination of the functional form of $h(\hat{z})$ that may be combined with eq 10. This can be done in such a way that in the coil limit the values of $h(\bar{z})$ as a function of z with α_S given by eq 10 (with $\tilde{z} = z$) are as close as possible to those of the Barrett function[15] $h(z)$ at any z, i.e.

$$h(\bar{z}) \simeq (1 + 14.3z + 57.3z^2)^{-0.2} \tag{17}$$

The result thus obtained reads

$$h(\hat{z}) = (1 + 7.74\hat{z} + 52.3\hat{z}^{27/10})^{-10/27} \tag{18}$$

We note that in the coil limit the difference between the values of Ψ calculated from eq 14 with eq 18 and with the Barrett equation for h does not exceed 3%.

For numerical calculations of Ψ, we must assign a proper value to d. For flexible chains, we may take d = 0.2–0.5. In this range of d, the dependence of Q on L does not very much change with d and the average dependence is produced for d = 0.3. Therefore, we choose d = 0.3 for all flexible chains, for simplicity. Then $Q(L)$ (for $L \gtrsim 1$) is given in a very good approximation by

$$\begin{aligned} Q(L) = {} & -\frac{128\sqrt{2}}{15} - 2.531L^{-1/2} - 2.586L^{-1} + 1.985L^{-3/2} - \\ & 1.984L^{-2} - 0.9292L^{-5/2} + 0.1223L^{-3} + \frac{8}{5}x^{5/2} + \\ & \frac{2}{3}\left(8 + \frac{1}{6}L^{-1}\right)x^{3/2} + (8 - 13.53L^{-1} + 0.2804L^{-2})x^{1/2} + \\ & (-0.3333L^{-1} + 5.724L^{-2} - 0.7974L^{-3})x^{-1/2} + \\ & (-0.3398L^{-2} + 0.7146L^{-3})x^{-3/2} \end{aligned} \tag{19}$$

with

$$x = 1 + 0.961L^{-1} \tag{20}$$

It is seen that $Q(L)$ also approaches slowly its coil limiting value, the first-order deviation from the latter being of order $L^{-1/2}$ as in the case of $K(L)$.

For illustration, in this paper we take as an example the case of atactic polystyrene (a-PS), for which κ_0 = 3.0 and τ_0 = 6.0.[5] In Figure 1 are shown values of Ψ thus calculated as a function of $\alpha_S{}^3$ from eq 14 with eqs 1–3, 5, 6, 9, 10,

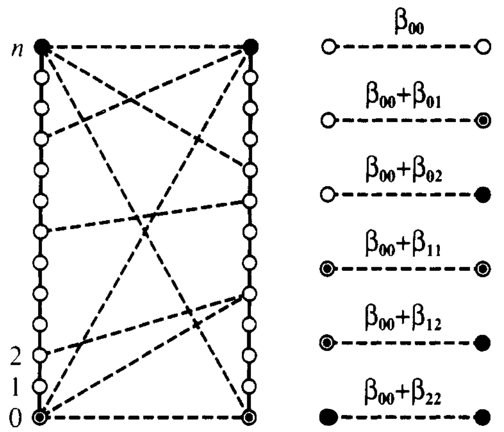

Figure 2. Six kinds of intermolecular contacts and binary-cluster integrals.

15, 16, and 18–20. The dotted curve represents the two-parameter theory values (very close to the Domb–Barrett values) in the coil limit. The solid curves represent the values for the case in which L (or M) is changed at constant B, while the dashed curves represent the values for the case in which B is changed at constant L (or M). It is seen that the two-parameter theory prediction is obtained as the asymptotic limit of $L \rightarrow \infty$ or $B \rightarrow 0$. For a-PS, the ratio $\langle S^2\rangle_0/M$ is actually independent of M for $L \geq 40$ ($6\langle S^2\rangle_0/c_\infty L = 0.96$ at $L = 40$). This bound is indicated by the unfilled circle for each value of B. The sharp increase in Ψ with decreasing L for L much smaller than this bound is of course due to the factor $(6\langle S^2\rangle_0/c_\infty L)^{-3/2}$ on the right-hand side of eq 14. A comparison with experiment is made in section IV.

We note that Nickel[16] has derived a similar behavior of Ψ, considering the finiteness of the number of bonds in the Gaussian chain.

III. Effects of Chain Ends

For convenience, we consider a chain composed of $n + 1$ beads numbered 0, 1, 2, ..., j, ..., n from one end to the other but attach the label "0" to the $n - 1$ intermediate beads with $j = 1 - (n - 1)$, the label "1" to the end bead with $j = 0$, and the label "2" to the other end bead with $j = n$. Then there are six kinds of intermolecular binary-cluster integrals, which we designate by β_{00}, $\beta_{00} + \beta_{01}$, $\beta_{00} + \beta_{02}$, $\beta_{00} + \beta_{11}$, $\beta_{00} + \beta_{12}$, and $\beta_{00} + \beta_{22}$, as illustrated in Figure 2. Thus the single-contact term $A_2^{(1)}$ of A_2 is readily obtained as

$$A_2^{(1)} = (N_A/2M^2)[(n+1)^2\beta + 4(n+1)\beta_1 + 4(\beta_2 - 2\beta_1)] \quad (21)$$

where β, β_1, and β_2 are defined by

$$\beta = \beta_{00}$$

$$2\beta_1 = \beta_{01} + \beta_{02}$$

$$4\beta_2 = \beta_{11} + 2\beta_{12} + \beta_{22} \quad (22)$$

and thus β is the usual binary-cluster integral, and β_1 and β_2 are the *excess* effective ones associated with the chain ends.

For oligomers with small n, A_2 may be approximated by $A_2^{(1)}$. (Then, if we take the repeat unit as a single bead, we have $n = x - 1$ with x the degree of polymerization.) However, the higher-order contact terms also become important as n is increased. Those terms containing β may be taken into account by introducing the function h. If we ignore those containing β_1 and β_2 in a first approximation, then A_2 may be written approximately in the form

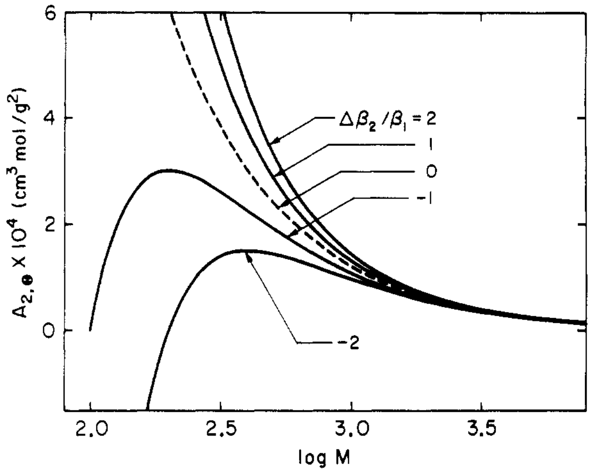

Figure 3. $A_{2,\Theta}$ plotted against the logarithm of M for the indicated values of $\Delta\beta_2/\beta_1$ with $\beta_1 = 10$ Å^3 and $M_0 = 100$.

$$A_2 = A_2^{(HW)} + a_1M^{-1} + a_2M^{-2} \quad (23)$$

where $A_2^{(HW)}$ is the A_2 given in section II, and

$$a_1 = 2N_A\beta_1/M_0$$

$$a_2 = 2N_A\Delta\beta_2 \quad (24)$$

with M_0 the molecular weight of the bead and with

$$\Delta\beta_2 = \beta_2 - 2\beta_1 \quad (25)$$

Note that the term $A_2^{(HW)}$ is valid for $L \gtrsim 1$ ($n \gg 1$), and we may put $h = 1$ for $L \lesssim 1$. For large M (in its ordinary range), the second and third terms on the right-hand side of eq 23 may be suppressed, so that $A_2^{(HW)}$ must vanish at the Θ temperature. Therefore, we have for the A_2 at Θ

$$A_{2,\Theta} = a_1M^{-1} + a_2M^{-2} \quad (26)$$

For illustration, in Figure 3 are plotted values of $A_{2,\Theta}$ calculated from eq 26 with $\beta_1 = 10$ Å^3 and $M_0 = 100$ against the logarithm of M for the indicated values of $\Delta\beta_2/\beta_1$. It is interesting to see that in some cases $A_{2,\Theta}$ exhibits a maximum in the oligomer region. In this connection, we must note that such behavior of A_2 was already observed a long time ago for a-PS[17] and atactic poly(methyl methacrylate) (a-PMMA),[18] though in good solvents, and it was given an explanation by Sotobayashi and Springer,[19] who considered the effect of chain ends on the enthalpy term of A_2. Thus it is clear that both effects of chain stiffness and chain ends on A_2 in general become significant in the oligomer region, in which an analysis of experimental data for A_2 should be based on eq 23.

IV. Comparison with Experiment

Interpenetration Function. Figure 4 shows plots of Ψ against $\alpha_S{}^3$ for fractions of a-PS in benzene at 25.0 and 30.0 °C. The data are those obtained from light scattering measurements at 25.0 °C by Miyaki et al. (filled circles),[2,20] at 30.0 °C by Yamamoto et al. (unfilled circles),[21] and at 30.0 °C by Fukuda et al. (semifilled circles).[22] The dotted curve represents the two-parameter theory values, and the solid curve represents the best-fit theoretical values calculated with (reduced) $B = 0.9$. This value of B is about

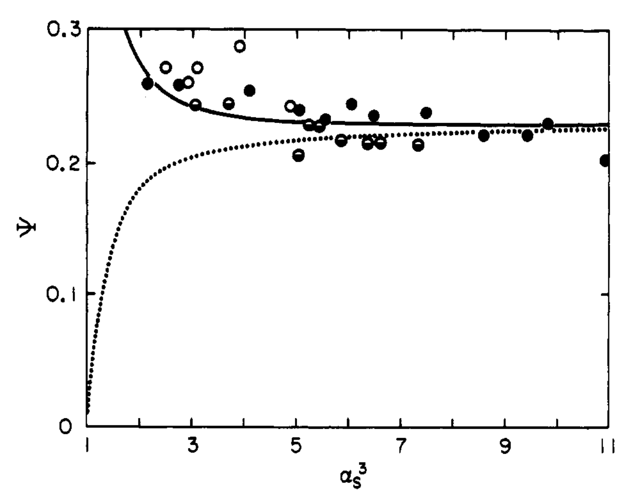

Figure 4. Plots of Ψ against $\alpha_S{}^3$ for a-PS in benzene: (●) data at 25.0 °C by Miyaki et al.;[2,20] (○) data at 30.0 °C by Yamamoto et al.;[21] (⊖) data at 30.0 °C by Fukuda et al.[22] The solid curve represents the best-fit theoretical values with $B = 0.9$, and the dotted curve represents the two-parameter theory values.

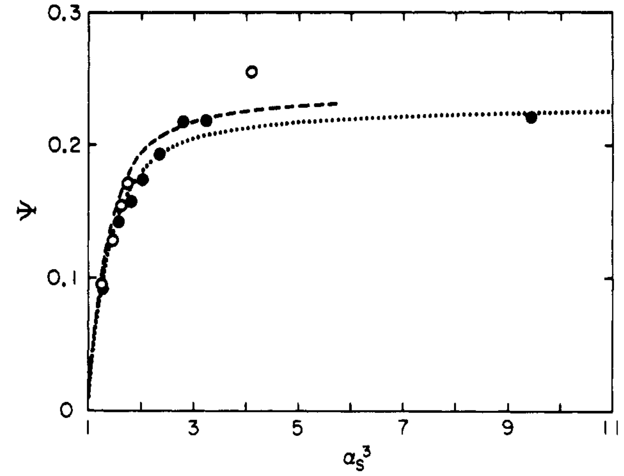

Figure 5. Plots of Ψ against $\alpha_S{}^3$ for a-PS in cyclohexane at various temperatures and in benzene at 25.0 °C: (○) data for $M_w = 1.34 \times 10^6$; (●) data for $M_w = 3.19 \times 10^7$, all due to Miyaki et al.[2,20] (see the text). The dashed and dotted curves represent the $L = 400$ and ∞ theoretical values, respectively.

3 times as large as the value (~0.3) determined from $\langle S^2 \rangle$ for a-PS in good solvents[23] by the use of eq 10. However, the theory may well explain the decrease in Ψ with increasing α_S or M.

Figure 5 also shows plots of Ψ against $\alpha_S{}^3$ for two fractions of a-PS with the weight-average molecular weights $M_w = 1.34 \times 10^6$ (unfilled circles) and 3.19×10^7 (filled circles) in cyclohexane at various temperatures and in benzene at 25.0 °C, where each data point with the largest α_S is the one in benzene, all the data being due to Miyaki et al.[2,20] The data for the fraction with the larger M_w may well be explained by the ($L \rightarrow \infty$) two-parameter theory (dotted curve), while the dashed curve represents the best-fit theoretical values calculated with (reduced) $L = 400$ for the lower fraction. The value 1.34×10^6 of M_w corresponds to $L = 1620$ since $\lambda^{-1} = 22.5$ Å and $M_L = 36.7$ Å^{-1} for a-PS.[5] Therefore, the former value of L is only about one-fourth of the latter. However, the theoretical prediction is consistent with the observed behavior of Ψ in that its increase with increasing B (solvent power) depends in general on M, it forming no single-composite curve.

As seen above, the agreement between theory and experiment is not complete since the values of B and L estimated are not very reasonable. This is probably due to the uniform-expansion approximation made in the evaluation of the function h and also the scaling approximations, i.e., the replacement of the intramolecular z by $\tilde{z}$ and of the intermolecular z by $(Q/2.865)z$, the latter probably being less serious.

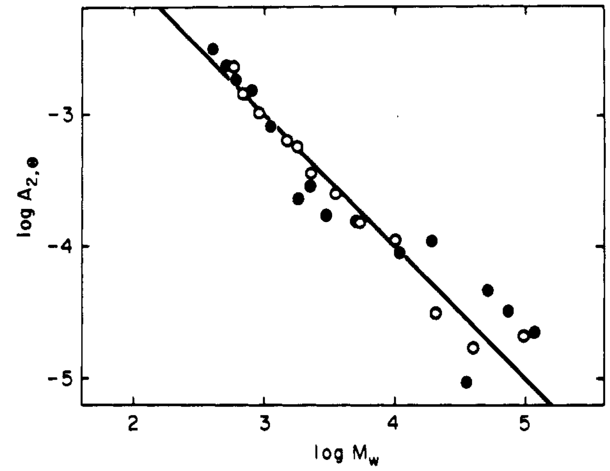

Figure 6. Double-logarithmic plots of $A_{2,\Theta}$ against M_w: (○) data by Konishi et al.[5] for a-PS in cyclohexane at 34.5 °C; (●) data by Tamai et al.[6] for a-PMMA in acetonitrile at 44.0 °C. The best-fit straight line has a slope of −1.

A_2 at the Θ Temperature. Figure 6 shows double-logarithmic plots of $A_{2,\Theta}$ against M_w with the data obtained in our laboratory from small-angle X-ray scattering measurements for a-PS in cyclohexane at 34.5 °C (unfilled circles)[5] and for a-PMMA in acetonitrile at 44.0 °C (filled circles).[6] Although these data are not very accurate, we can draw tentatively a common best-fit straight line of slope −1, as shown in the figure. From this straight line, we obtain $\beta_1 = 85$ Å^3 (per repeat unit) along with $\Delta\beta_2 = 0$ for both systems. (Of course, β_1 and $\Delta\beta_2$ must in general depend on a polymer–solvent system.) This value of β_1 is not a magnitude of unreasonable order as the binary-cluster integral for polymer beads and simple molecules.[24] Therefore, the dependence of $A_{2,\Theta}$ on M in the range of small M may be regarded as arising from the effects of chain ends.

V. Conclusion

It has been shown that if effects of chain stiffness are taken into consideration, the theory may explain the decrease in the interpenetration function Ψ with increasing molecular weight M observed for flexible polymers in good solvents even in the ordinary range of M in which the unperturbed mean-square radius of gyration $\langle S^2 \rangle_0$ is proportional to M. The theory also predicts that the increase in Ψ with increasing solvent power depends in general on M, it forming no single-composite curve as a function of the expansion factor α_S. The effect of chain stiffness on α_S remains rather large even in the range of M above, although vanishingly small for very large M, and this has a significant effect on the behavior of Ψ above. (The *quasi*-two-parameter theory with the scaled excluded-volume parameter $\tilde{z}$ may be regarded as valid for α_S.) On the other hand, the nonvanishing of the second virial coefficient A_2 for small M at the Θ temperature may be explained by considering possible effects of chain ends. Of course, both effects on A_2 become significant in the oligomer region. In sum, the Gaussian chain model is only asymptotically valid for the description of the excluded-volume effects in dilute polymer solution and the original ($L \rightarrow \infty$) two-parameter theory should be considered a limiting law for extremely long chains.

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