Friction Coefficient of Polymer Molecules in Dilute Solution near the Θ Point. 2. Concentration Dependence of the Friction Coefficient

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ABSTRACT: Pyun and Fixman's equivalent-sphere theory (1964) about the concentration dependence of the friction coefficient of random-coil polymers in dilute solution is reconsidered at three points. Correction of the calculation of the coefficient for the linear concentration dependence of the friction coefficient for hard spheres yields a value 7.01 rather than 7.16. Secondly, a simple procedure for obtaining an approximate value for the friction coefficient of the body representing two spheres in partial overlap (dumbbell) is described. Thus the ellipsoid of ill-defined size can be removed and an unambiguous theoretical value can be established for the concentration dependence of the friction coefficient of interpenetrable spheres. When the calculation is made along lines analogous to those which Pyun and Fixman followed for calculating the velocity of two separate spheres in hydrodynamic interaction, the new value for a system in the Θ state is about 20% larger than reliable experimental values found for polystyrene in cyclohexane. When, alternatively, the approximation is applied to more recent exact numerical data for the velocity of two interacting spheres, agreement is reached with the experimental value within the error margin. The rapid increase of the concentration dependence of the friction coefficient with temperature through the Θ point is a sensitive measure of the temperature dependence of the excluded volume of the polymer molecules. This was reason to reconsider also the thermodynamic aspect of the P-F theory and to replace the uniform segment distribution of the friction equivalent sphere by the modified Flory-Krigbaum potential for calculating the distribution function for a second sphere in the vicinity of a first one. The temperature dependence of the osmotic second virial coefficient and the Flory parameter ψ, evaluated from sedimentation experiments, thus become 11% higher and agree within the error margin with the values calculated by applying a theory by Yamakawa, which uses the same potential function but a quite different model for the hydrodynamic interaction. Equations are applied to data for polystyrene in cyclohexane. A dependence on the molecular weight is found for $(dA_2/dT)_\Theta$ and ψ.

1. Introduction

In another paper[1] we reported about a reliable differential method for determining the concentration and temperature dependence of sedimentation coefficients of macromolecules in dilute solution. We now interpret the results obtained for the Θ system polystyrene (PS)-cyclohexane (CH) in terms of the hydrodynamic and thermodynamic interaction between the molecules, making use of an appropriate theory.

Although it is based on the simple model of interpenetrable spheres of uniform segment density to represent chain molecules, up till now the theory by Pyun and Fixman[2] (P-F) has been the most satisfactory. It was developed in response to a theory by Yamakawa,[3] which considered Gaussian segment distributions but was not wholly successful in that it predicted a vanishing concentration dependence of the friction coefficient in a Θ solution. This prediction has not come true.

Although the P-F theory is right in predicting a nonvanishing concentration effect at the Θ point, some dissatisfaction is felt with regard to the fact that the numerical value can vary due to the introduction of ellipsoids of various sizes for approximating the friction coefficient of a pair of overlapping spheres (dumbbell).

In the present paper this aspect will be reconsidered. An approximate calculation of the friction coefficient of a dumbbell will enable us to avoid the ellipsoid and to arrive at an unambiguous value for the concentration dependence of the friction coefficient of soft interpenetrable spheres. The calculation will be made once in a manner which conforms with the P-F theory and once again by using exact numerical data for the velocity of two equal spheres in hydrodynamic interaction obtained by Goldman, Cox, and Brenner.[6]

Another point is that Pyun and Fixman employed a sphere of uniform segment density with a radius equal to that of the friction-equivalent sphere for calculating the thermodynamic interaction. Since in real chain molecules two-thirds of the number of segments are at a larger distance from the mass center than the radius of the friction-equivalent sphere, the interaction is restricted to too small a volume and, presumably, in that region is too strong. We will apply the Flory-Krigbaum (F-K) potential in order to derive a relation between $(dk_s/dT)_\Theta$ (k_s is the coefficient for the linear concentration dependence of the friction coefficient) and $(dA_2/dT)_\Theta$ (A_2 is the osmotic second virial coefficient). Use of the original F-K potential allows a comparison to be made of our experimental results for the PS-CH system with data which in the past have been obtained from many osmotic and light-scattering studies. A modified F-K potential fits the first-order perturbation theory for A_2 and was used by Yamakawa in his theory for k_s.

2. The Soft Equivalent Sphere Model

A small concentration dependence of the friction coefficient (f) of polymer molecules in dilute solution is expressed as follows:

$$f = f_0(1 + k_s c + ...) \tag{1}$$

f_0 is the friction coefficient at infinite dilution.

The solvent in the interior of the equivalent sphere is trapped and Stokes' law is applied to define the radius of the sphere so as to give it the friction coefficient of the chain molecule at infinite dilution.

The concentration is expressed in terms of the volume fraction Φ of equivalent spheres, so we have

$$k_s c \Leftrightarrow k_\phi \Phi \tag{2a}$$

$$\Phi = N V_e \tag{2b}$$

N is the number density of spheres and V_e the sphere's volume. The foregoing implies that

$$k_s = k_\phi N_A V_e / M \tag{3a}$$

$$V_e = (4\pi/3)a^3 \tag{3b}$$

$$a = [f]/6\pi \tag{3c}$$

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a is the radius of the sphere and $[f]$ the intrinsic friction coefficient of the chain molecule.

In the theory by Pyun and Fixman the thermodynamic interaction is assumed not to extend beyond the surface of the equivalent sphere. k_ϕ is then given by

$$k_\phi = 7.01 - \kappa(B) \tag{4}$$

. (The value 7.16 calculated by Pyun and Fixman is incorrect. See Appendix.)

For hard spheres $\kappa = 0$ and $k_\phi = 7.01$. The function $\kappa(B)$ represents the reduction in the concentration effect due to the occurrence of pairs of overlapping spheres. It is

$$\kappa(B) = 24 \int_0^1 \left\{ \frac{v_d(x)}{v_s(1)} - 1 \right\} g(x, B) x^2 \, dx \tag{5}$$

$x = r/2a$, where r is the distance between the centers of the double sphere, $v_d(x)$ is the velocity of an isolated double sphere (dumbbell) with a reduced center-to-center distance x and is averaged with respect to all directions of the center-to-center vector, and $v_s(1)$ is the velocity of an isolated sphere in the same force field.

$g(x, B)$ is the radial distribution function for two spheres at thermodynamic equilibrium. When calculated for the uniform-density sphere with a radius as defined by (3c), it is

$$g(x, B) = \exp\left\{ -\frac{\Delta G(x, B)}{kT} \right\} = \exp\{-B(1 - x)^2(2 + x)\} \tag{6}$$
$$(0 \le x \le 1)$$

where ΔG is the potential of the average force between the two spheres. B is given by

$$B = \frac{3\beta n^2}{8\pi a^3} = \frac{\beta n^2}{2V_e} \tag{7}$$

in which n is the number of segments of a molecule and β is the excluded volume for segment–segment interaction.

Following up Pyun and Fixman we express B in the excluded-volume variable z

$$z = \left(\frac{3}{2\pi \langle l_0^2 \rangle} \right)^{3/2} \beta n^2 \tag{8}$$

by making use of Stokes' law (3c) and Kirkwood and Riseman's equation

$$[f] = \frac{1}{2} \left(\frac{3\pi}{2} \right)^{3/2} \langle l_0^2 \rangle^{1/2} \alpha_f \tag{9}$$

where α_f is the expansion factor for the friction radius. We obtain

$$B = \frac{2^9}{9\pi} z \alpha_f^{-3} = 18.12 z \alpha_f^{-3} \tag{10}$$

Kotera et al.[4] and Noda et al.[5] thought to have expanded the range of the thermodynamic interaction by replacing the radius of the equivalent sphere in eq 7 (not in the definition of x) by the radius of gyration of the chain molecule. They thus obtained

$$B' = 3\pi^{1/2} z \alpha_g^{-3} = 5.31 z \alpha_g^{-3} \tag{11}$$

Another suggestion by Noda, of the same tenor, is to give that value to the numerical coefficient in eq 6 which causes the series expansion of A_2 for the uniform-density sphere to fit the first-order perturbation theory. This choice leads to

$$B'' = 8.85 z \alpha_g^{-3} \tag{12}$$

However, since V_e in eq 2b and the hard-sphere value for k (7.01) are unchanged, these alterations cannot remove the fact that the thermodynamic interaction is restricted to overlapping friction-equivalent spheres. For given values of β and n these alterations effect a decrease in the intensity of the interaction which is much larger than follows from a correct introduction of a more reliable potential function for the average force between two macromolecules, as we will show.

For comparing experimental results with data in the literature we need the Flory notation which is useful in the vicinity of the Θ point. It follows from a comparison of corresponding quantities that

$$\beta n^2 = \psi \left(1 - \frac{\Theta}{T} \right) \frac{(M\bar{v}_p)^2}{N_A M_1 \bar{v}_1} \tag{13}$$

Accordingly, B as given by (7) becomes

$$B = \psi \left(1 - \frac{\Theta}{T} \right) \frac{(M\bar{v}_p)^2}{M_1 \bar{v}_1 N_A V_e} \tag{14}$$

ψ is the parameter for the entropy of mixing polymer segments with solvent and $M_1\bar{v}_1$, $M\bar{v}_p$, and $N_A V_e$ are the molar volumes of the solvent, the dissolved polymer, and—by extension—the equivalent spheres.

For a given value of B, the function $\kappa(B)$ depends through v_d on the hydrodynamic model chosen to approximate the friction coefficient of a double sphere. Pyun and Fixman avoided the problem of calculating the friction coefficient of a dumbbell and offered a choice of three ellipsoids, each with an axial ratio equaling that of the dumbbell $(1 + x)$, but with the length of the dumbbell, its volume, or a volume equal to that of the double sphere without constriction, i.e., a cylinder of height r and diameter $2a$ covered by two half-spheres. For these three models the numerial values for $\kappa(0)$ have been recalculated with an electronic computer. They are listed in Table I together with that for two other approximations to be discussed in sections 3 and 5.

Only the vicinity of the Θ state will be considered. This restriction is allowable on the gound of the prominence of the Θ condition in the theory of dilute polymer solutions and on the fact that at $T = \Theta$ the origin of any definite difference between theoretical and experimental values for k_s must be found in the treatment of the hydrodynamic interaction because the effect of the thermodynamic interaction on the distribution of polymer molecules will be at a minimum.

For showing the large differences in $(k_\phi)_\Theta$ that go with small differences in the friction coefficient of overlapping molecules, the average length of the major axis has been calculated for each ellipsoid. To this end the center of the second constituent sphere was placed at all distances $0 \le x \le 1$ from the center of the first one and statistical weight was assigned in proportion to the volumes of the spherical shells. The ratios of these averages to the corresponding average of the dumbbell are listed in the first row of Table I. Axes have been chosen as characteristic quantities because for a given axial ratio the friction coefficient is defined by a linear dimension. It is seen that a change in the axis by 7% results in a change in $(k_\phi)_\Theta$ by 32%.

3. Outline of the Dumbbell Approximation

The uncertainty in the value for $(k_\phi)_\Theta$ resulting from the introduction of ellipsoids of different sizes can be avoided by using a different model which we will call the dumbbell approximation. The model is a logical extension of the P–F theory for the hydrodynamic interaction between two equal

Table I
Variations on the Equivalent-Sphere Model: Numerical Values for a Few Quantities Related to k_ϕ and Five Functions $\kappa(B)$ at $B = 0$ ($T = \Theta$), Each Resulting from a Different Approximation for the Friction Coefficient of a Dumbbell

	ellipsoids of equal axial ratio and different sizes (P-F)			dumbbell approx		
	1	2	3	eq 32	eq 38	exptl value[a]
R_{ml}[b]	1	1.031	1.069	1	1	
$\kappa(0)$ (eq 5)	4.95	4.64	4.16	4.24	4.25	
$(k_\phi)_\Theta = 7.01 - \kappa(0)$ (P-F)	2.06	2.37	2.85	2.77	[c]	2.35 ± 0.15
$(k_\phi)_\Theta = 6.55 - \kappa(0)$[d]	1.60	1.91	2.39	[c]	2.30	
$(dk_\phi/dB)_\Theta = -(d\kappa/dB)_\Theta$ (eq 4)[e]	1.44	1.34	1.28	1.27	1.27	
$(dk_\phi/dB)_\Theta$[f]	(1.10)	0.995	(0.95)	0.944	not calcd	*h*
$(dk_\phi/dB)_\Theta$[g]	(1.31)	1.209	(1.16)	1.147	not calcd	*h*

[a] Calculated by eq 21 and 22 of paper 1.[1] [b] Ratio of the mean length of the major axis to that of the dumbbell. [c] Dissimilar approximation. [d] 6.55 exact value for hard spheres (section 5). [e] Thermodynamic interaction calculated by using the equivalent sphere of uniform segment density. [f] Thermodynamic interaction calculated by using the original Flory-Krigbaum potential (eq 48, $\mu = 1$). [g] Thermodynamic interaction calculated by using the modified Flory-Krigbaum potential, fitting the first-order perturbation theory for A_2 (eq 48, $\mu = 2.135$). [h] No experimental value. Preferred value (1.147) used for the evaluation of $(dA_2/dT)_\Theta$ and ψ from experiments (section 9).

spheres and the reliability of the velocity calculated for the dumbbell will be roughly the same. Thus, the discussion about which ellipsoid fits the experimental data best can be replaced by a more relevant discussion about the reliability of the soft-sphere model for calculating the hydrodynamic interaction between chain molecules in translation.

The model involves the calculation of four numerical data about the angular average friction coefficient or velocity of a dumbbell as a function of x in the range $0 \leq x \leq 1$. Fitting a smooth curve through these values will provide the average velocity of a dumbbell for each value of x.

The data are the following.

The friction coefficient of coincident spheres is simply that for a simple sphere.

The rate of change of the angular average friction coefficient for $x = 0$, i.e., $(df/dx)_{x=0}$, can be found out through an analysis of the expression for the friction coefficient of a prolate ellipsoid and by observing the similar symmetry of ellipsoids of revolution and dumbbells.

The velocity and its first derivative with respect to x can also be calculated for $x = 1$. To this end we first consider the symmetry of the hydrodynamic interaction between two identical spheres traveling through an otherwise empty, unbounded viscous medium.

In Stokes' approximation of the equation of motion for the fluid (Navier–Stokes equation) the terms representing the inertial effects are neglected. The resulting differential equation is linear in the velocity components which for two interacting identical spheres implies that the velocities of translation are equal in magnitude and direction. Rotations about axes at right angles to the directions of the external force and the line of centers are of equal magnitude and have opposite signs (theorem of Faxén[8]).

It follows from the foregoing that the center-to-center vector is unaffected by the hydrodynamic interaction, as is also the case for touching spheres. Hence, it is only the rotations that have to be suppressed to arrive at a "touching" dumbbell. The suppression of rotation conforms to reality because rotations will be severely hampered when the domains of real chain molecules interpenetrate. Besides, a motion of overlapping spheres relative to each other is inconsistent with the concept of immobilized solvent within an equivalent sphere.[2]

The application of imaginary restraining torques will leave the symmetry unchanged, so that the center-to-center vector will also be unaffected under interaction without rotation. As a consequence, when the component spheres of a dumbbell are separated, its velocity components will be continuous with the velocity components for a pair of nonrotating interacting spheres. For a given orientation of the center-to-center vector this provides two numerical values for the dumbbell state, namely, the velocity and its first derivative with respect to x, both for $x = 1$. The values should be averaged for all orientations.

For obtaining consistency with the P–F approximation for the interaction between rotating spheres, the interaction between nonrotating spheres should be calculated in a similar manner. The four numerical values will be accommodated in a third-degree polynomial in x. A value for $\kappa(0)$ is obtained by using eq 5.

The reliability of the approximation will match that obtained by Pyun and Fixman for two separate spheres in hydrodynamic interaction. Although no data will be obtained for intermediate distances $0 < x < 1$, the velocity and its first derivative for $x = 0$ are exact, whereas for $x = 1$ the calculated values will be as good or bad as those derived in the P–F theory for two touching spheres in passive rotation.

Exact values for the velocity and its first derivative for nonrotating touching spheres can be taken from numerical data tabulated by Goldman et al.[6] We will make use of them in combination with the exact value for the concentration dependence of the friction coefficient of hard spheres obtained by Batchelor.[9]

4. Calculation

The calculation of the velocity components for a pair of interacting nonrotating spheres is shown in the Appendix. The result is as follows:

$$\frac{v_i'(1,2)}{v_s(1)} = \left\{1 + \frac{1}{4}(3y + y^3 - 3y^4 - 3y^8)\right\}\delta_{i1} + \frac{3}{4}\left\{y - y^3 - 4y^4 + 8y^6 - 2y^8 + \frac{y^7(1-y^2)(5-3y^2)(5-6y^2)}{1 + 5y^3 - 6y^5}\right\}\cos\theta_i \cos\theta_1 + \frac{3}{8}y^7\frac{1 + 8y^2 - 10y^3 - 5y^4 + 4y^5 + 8y^6 - 10y^7 + 4y^9}{1 - 2y^3 + 4y^5 - 5y^6 + 2y^8} \times (\delta_{i1} - \cos\theta_i \cos\theta_1) \quad (0 < y \leq \tfrac{1}{2}) \quad (15)$$

Here $v_i'(1,2)$ is the velocity component i of a nonrotating sphere at the position $\bar{R}_1$ when a second nonrotating sphere is at $\bar{R}_2$, $y \equiv a/r$, where r is the center-to-center distance,

$\cos\theta_i$ ($i = 1, 2, 3$) are the direction cosines of this line with respect to the direction of the external force, which is parallel to axis 1, and δ_{ij} is the Kronecker delta.

For a comparison the velocity is also given for a rotating sphere in interaction with a second rotating sphere

$$\frac{v_i(1,2)}{v_s(1)} = \left\{1 + \frac{1}{4}(3y + y^3 - 3y^8)\right\}\delta_{i1} + \frac{3}{4}\left\{y - y^3 - 5y^4 + 8y^6 - 2y^8 + \frac{y^7(1-y^2)(5-3y^2)(5-6y^2)}{1 + 5y^3 - 6y^5}\right\}\cos\theta_i\cos\theta_1 - \frac{{}^{15}/_{8}y^{11} - 3y^{13}}{1 - {}^{5}/_{2}y^3 + 4y^5}(\delta_{i1} - \cos\theta_i\cos\theta_1) \qquad (0 < y \leq {}^{1}/_{2}) \quad (16)$$

This expression resulted from a revision of the calculation by Pyun and Fixman (see Appendix).

If the line of centers is in the direction of the external force, then no torque is acting on the spheres and the velocities according to eq 15 and 16 are equal.

Since in both interaction models the velocity components are an even function of the direction cosines and since upon transferring the origin of the coordinate system from the center of one sphere to that of the other all three cosines change their sign, the velocity components of sphere 2 equal those of sphere 1 and the center-to-center vector is unaffected.

It follows from eq 15 and 16 that for all orientations of the line of centers the velocity of a pair of spheres in the direction of the external force exceeds that of a single sphere. (Table I in Pyun and Fixman's paper is misleading on this point, giving the reciprocal of the quantity stated in the caption.)

The velocity of a pair of touching spheres without rotation follows from eq 15 by substituting $y = {}^{1}/_{2}$ and is

$$\{v_i'(1,2)/v_s(1)\}_{y=1/2} = 1.3623\delta_{i1} + 0.2212\cos\theta_i\cos\theta_1 \quad (17)$$

whereas according to eq 16 for a pair of spheres with passive rotation it is

$$\{v_i(1,2)/v_s(1)\}_{y=1/2} = 1.4026\delta_{i1} + 0.1809\cos\theta_i\cos\theta_1 \quad (18)$$

For the line of centers in the direction of axis 1 the velocity according to eq 17 and 18 is equal to 1.5836, which is 2.2% higher than the exact result derived for this special relative position.[10]

The angular average of $\cos\theta_i\cos\theta_1$ is $\delta_{i1}/3$, so that

$$\langle\{v_i'(1,2)/v_s(1)\}_{y=1/2}\rangle_\theta = 1.4361\delta_{i1} \quad (19)$$

and

$$\langle\{v_i(1,2)/v_s(1)\}_{y=1/2}\rangle_\theta = 1.4630\delta_{i1} \quad (20)$$

The suppression of rotation thus increases the average flow resistance for touching spheres by 1.8%. Consequently, in the equivalent-sphere model a small abrupt increase in the velocity occurs when two polymer globules lose contact and start to rotate.

Next we take the first derivative of $\vec{v}'(1,2)$ with respect to y for $y = {}^{1}/_{2}$. One obtains

$$\frac{1}{v_s(1)}\left(\frac{\partial v_i'(1,2)}{\partial y}\right)_{y=1/2} = 0.6051\delta_{i1} + 0.0359\cos\theta_i\cos\theta_1 \quad (21)$$

After averaging it follows that

$$\frac{1}{v_s(1)}\left\langle\left(\frac{\partial v_i'(1,2)}{\partial y}\right)_{y=1/2}\right\rangle_\theta = 0.6161\delta_{i1} \quad (22)$$

Switching to the variable x ($=r/2a$) gives for the angular average velocity of a dumbbell of touching spheres in the direction of the external force

$$v_d/v_s(1) = 1.4361 \qquad (x = 1) \quad (23a)$$

and for its first derivative with respect to x for the same center-to-center distance

$$\frac{1}{v_s(1)}\left[\frac{dv_d}{dx}\right]_{x=1} = -0.3080 \qquad (x = 1) \quad (23b)$$

Corresponding data can be determined for the other end of the x interval.

For $x = 0$, i.e., for coincident spheres, the friction coefficient is that of the single sphere

$$f_d = f_s \qquad (x = 0) \quad (24)$$

We next examine how the friction coefficient increases when the spheres are slightly separated.

The angular average friction coefficient of a prolate ellipsoid was quoted by Pyun and Fixman as

$$f_{ell} = 6\pi\eta R(x) \times (2x + x^2)^{1/2}/[(1 + x)^{1/3}\ln\{1 + x + (2x + x^2)^{1/2}\}] \quad (25)$$

where R is the radius of a sphere with a volume equal to that of the ellipsoid and $1 + x$ is again the axial ratio. Since the radius a of the equivalent sphere is fixed and the volume of the ellipsoid is not, R will be a function of x.

According to (25) f_{ell} is the product of a part conforming to Stokes' equation and a form factor. Expansion of the latter gives for (25)

$$f_{ell} = 6\pi\eta R(x)\left(1 + \frac{4}{45}x^2 - \frac{244}{2835}x^3 + \ldots\right) \quad (26)$$

In the form factor a term linear in x is absent.

The symmetries of the cylinder covered with half-spheres and of the ellipsoid are similar. The dimensions of both are defined by means of R and x, and for $x \to 0$ they both revert to spherical shape. The presumption then is that the linear term will be also absent in the expansion for the capped cylinder.

More support is found by examining the sphericity, which is defined as the ratio of the surface area of the volume-equivalent sphere to the area of the object under consideration.

The volume of the cylinder with half-spheres is $(4\pi/3)a^3(1 + {}^{3}/_{2}x)$, so the radius of the volume-equivalent sphere will be $a(1 + {}^{3}/_{2}x)^{1/3}$. The area of the latter then equals $4\pi a^2(1 + {}^{3}/_{2}x)^{2/3}$, whereas the capped cylinder has an area $4\pi a^2(1 + x)$. We thus have for the sphericity $(1 + {}^{3}/_{2}x)^{2/3}/(1 + x) = 1 - {}^{1}/_{4}x^2 + \ldots$. Once more the initial variation is of the order x^2.

These facts are consistent with the hydrodynamic properties of spherelike objects as studied by Brenner.[11] One of his conclusions is that the angular average friction coefficient of a slightly deformed sphere equals that of a sphere of the same volume.

Finally comparing the dumbbell with the capped cylinder, we observe that the crucial feature is the depth of the constriction which starts off proportional to x^2 and therefore does not produce a linear term either.

Consequently, for the friction coefficient of a dumbbell it may be postulated that

$$f_d = 6\pi\eta R(x)\{1 + \mathcal{O}(x^2)\} \quad (27)$$

The volume of the dumbbell is $(4\pi/3)a^3(1 + {}^{3}/_{2}x - {}^{1}/_{2}x^3)$. Expressing R in terms of a and x and substituting $f_s = 6\pi\eta a$, eq 27 becomes

$$f_d = f_s(1 + {}^{3}/_{2}x - {}^{1}/_{2}x^3)^{1/3}\{1 + \mathcal{O}(x^2)\} \quad (28)$$

From this it follows that a fourth numerical datum for f_d is given by

$$df_d/dx = \tfrac{1}{2}f_s \qquad (x = 0) \tag{29}$$

Since the external force on two overlapping molecules is twice that acting on a single molecule, the velocity is related to the friction coefficient as follows:

$$v_d/v_s(1) = 2f_s/f_d \qquad (0 \le x \le 1) \tag{30}$$

Expressing eq 24 and 29 in terms of the variable v_d we obtain

$$v_d/v_s(1) = 2 \qquad (x = 0) \tag{31a}$$

$$\frac{1}{v_s(1)}\frac{dv_d}{dx} = -1 \qquad (x = 0) \tag{31b}$$

With x increasing from zero to unity the velocity of the dumbbell should decrease monotonically without passing a point of inflection. This requirement is fulfilled by the numbers obtained because the slope of a straight line connecting the coordinate $v_d(x)$ for $x = 0$ and $x = 1$ lies between the first derivatives for these positions ($-1 < -0.5639 < -0.3080$).

The assumption seems justified that a third-degree polynomial in x, which includes the values (23a,b) and (31a,b) will approximate the exact value of $v_d(x)/v_s(1)$ for a dumbbell as closely as was attained by Pyun and Fixman for two touching spheres in free rotation.

The polynomial is found to be

$$v_d/v_s(1) = 2 - x + 0.616x^2 - 0.180x^3 \qquad (0 \le x \le 1) \tag{32}$$

Substitution in eq 5 followed by integration for $B = 0$ yields $\kappa(0) = 4.24$ (Table I). This value is close to that for the third ellipsoid which has the same volume and axial ratio as the cylinder with two half-spheres. This comes as no surprise because removing the constriction from the dumbbell to obtain the capped cylinder will somewhat raise the friction resistance after which a deformation of the cylinder to an ellipsoid of the same volume and axial ratio will slightly lower it.

Since the dumbbell approximation matches the P–F calculation for the interaction between separate spheres better than the ellipsoids, we may regard $(k_\phi)_\Theta = 2.77$, among the four values listed in the third row of Table I, as the proper result for the P–F theory.

5. A Theoretical Value for $(k_\phi)_\Theta$ Derived from More Recent Numerical Data

In 1972 Batchelor[9] presented the exact value for k_ϕ for hard spheres. He arrived at 6.55 instead of Pyun and Fixman's 7.01 (after correction). Batchelor based his computation on exact expressions for the velocity of two spheres in a line parallel to the direction of the external force, calculated by Stimson and Jeffery,[12] and for the velocity (with rotation) of two spheres in a line at right angles to that direction, calculated by Goldman et al.[6]

In their paper Goldman and co-workers also tabulated exact numerical data for the velocity of a pair of nonrotating spheres. A few of them are in Table II.

It follows from the numbers in the first row that the velocity of the touching double sphere as a function of the direction of the center-to-center line with respect to the direction of the external force is

$$\{v_i'(1, 2)/v_s(1)\}_{y=1/2} = 1.37990\delta_{i1} + 0.17015 \cos\theta_i \cos\theta_1 \tag{33}$$

The angular average velocity then is

$$\langle\{v_i'(1, 2)/v_s(1)\}_{y=1/2}\rangle_\theta = 1.43662\delta_{i1} \tag{34}$$

Table II
Exact Reduced Velocities for Two Touching or Nearly Touching Spheres without Rotation Arranged Parallel or at Right Angles to the Direction of the External Force[a]

$y = a/r$	$v_\parallel(1, 2)/v_s(1)$	$v_\perp(1, 2)/v_s(1)$
$^1/_2$	1.55005	1.37990
0.49878	1.54937	1.37914
0.49751	1.54866	1.37832
0.47833	1.53759	1.36547
0.44342	1.51599	1.34111
0.37386	1.46616	1.28942
⋮	⋮	⋮
0	1	1

[a] From Stimson and Jeffrey[12] and Goldman et al.[6]

A plot of difference quotients against $^1/_2 - y$ and extrapolation to $^1/_2 - y = 0$ yields

$$\{\partial v_i'(1, 2)/\partial y\}_{y=1/2}/v_s(1) = (0.62 \pm 0.01)\delta_{i1} - (0.06 \pm 0.01) \cos\theta_i \cos\theta_1 \tag{35}$$

from which it follows that

$$\langle\{\partial v_i'(1, 2)/\partial y\}_{y=1/2}\rangle_\theta/v_s(1) = (0.60 \pm 0.01)\delta_{i1} \tag{36}$$

We thus have the following data for the dumbbell of touching spheres

$$v_d/v_s(1) = 1.4366 \qquad (x = 1) \tag{37a}$$

and

$$(dv_d/dx)/v_s(1) = -0.300 \pm 0.005 \qquad (x = 1) \tag{37b}$$

Note the small difference with the values (23a,b).

The third-degree polynomial which includes (31a,b) and (37a,b) is

$$v_d/v_s(1) = 2 - x + 0.61x^2 - 0.17x^3 \qquad (0 \le x \le 1) \tag{38}$$

Substitution of (38) in (5) and integration for $B = 0$ gives $\kappa(0) = 4.25$. Thus a more correct theoretical value for the coefficient of concentration dependence of the friction coefficient for the equivalent-sphere model becomes $(k_\phi)_\Theta = 6.55 - 4.25 = 2.30$. This result is close to the experimental value for the PS–CH system (Table I).

6. Equivalent Spheres and the Concentration Effect at the Θ Point

It should not be concluded from this unexpected agreement that in the Θ state the hydrodynamic interaction between two equivalent spheres in an unbounded medium cannot be much different from the interaction between two chain molecules with the same center-to-center vector. Rather it is the drift velocity (i.e., the velocity of one particle relative to the perturbed solvent flow due to the other) that will be the same for spheres and chains. It follows that the translational velocities can only be equal if not only $(k_\phi)_\Theta$ for the uniform distribution of particles in a closed volume but also the volume flow by a single particle and the propelled solvent in an unbounded medium is equal for spheres and chains. A discussion of this point may provide a better view of the properties of the equivalent-sphere model.

We consider the flow of solvent in the direction of motion of a single sphere migrating through an unbounded medium. Although a summation in the solution of Stokes' approximation of the flow equations is not possible, the solvent flow can be shown to be proportional to the velocity and volume of the sphere. It is substantially larger for the equivalent sphere than for a chain molecule. This conclusion is reached by comparing the flow caused by the equivalent sphere with the total flow caused by n separate

spheres, each with a friction coefficient equal to $(1/n)$th of that of the equivalent sphere. Because f is proportional to the linear dimension of a sphere and the flow varies with the third power of the linear dimension, the total flow decreases inversely with n^2. This sharp reduction prompts the conclusion that the partially drained bead–string model, which has the same friction resistance as the equivalent sphere but is an intermediate between the single sphere and the set of separate spheres, produces much less solvent flow.

We say "partially drained" on purpose because for an undrained molecule the flow cannot possibly be smaller than for the equivalent sphere. As a matter of fact, the nondrained condition of a chain molecule is nonexistent. This conclusion is reached in the following argument.

For a number of segments above several hundreds the ratio of the radius of gyration of a chain molecule to the radius of the nondrained friction equivalent sphere is about one and a half. Suppose all segments were inside the sphere. When one segment is put outside the sphere, it will be exposed to the solvent flow. For keeping the total friction force unaltered, a small flow must be allowed to pass through the sphere. Since roughly two-thirds of the number of segments of a chain are at a greater distance from the mass center than the radius of the equivalent sphere, many segments must be transferred for attaining the extension of a chain molecule and a considerable flow must pass through the inner parts of the domain of the chain. This conclusion is contrary to the prevailing view on this point but is supported by a study by Ooms et al.[13] of the permeability distribution of a nonuniform segment cloud of spherical symmetry and the contribution to the friction coefficient by the successive spherical shells.

The solvent flow considered above refers to the flow in an unbounded medium. For a homogeneous distribution of particles in a closed volume the net flow of volume by solvent and particles must vanish. Since a larger flow of volume must be restrained for spheres than for chains, the condition will interfere more strongly with the migration of equivalent spheres than with that of chains. Since nonetheless we have found $(k_\phi)_\Theta$, and with that the drift velocity, to be nearly equal, we may conclude that the velocity of a pair of equivalent spheres in hydrodynamic interaction in an unbounded medium is larger than the velocity of a pair of chain molecules with the same center-to-center vector.

7. Temperature Dependence of k_s at the Θ Point

We also consider $(dk_s/dT)_\Theta$. It follows from eq 3a that

$$\frac{dk_s}{dT} = \frac{N_A V_e}{M}\left(\frac{dk_\phi}{dT} + k_\phi \frac{d \ln V_e}{dT}\right) \tag{39}$$

It was argued in section 1 that the unmodified P–F theory will provide no correct relation between the temperature derivatives of k_s and A_2. Yet we first apply the P–F expression for k_ϕ in order to know the differences in the values for $(dA_2/dT)_\Theta$ and ψ that will arise when the modified Flory–Krigbaum potential is used for calculating the thermodynamic interaction.

In terms of the parameters for the statistically equivalent chain, A_2 is given by

$$A_2 = \frac{N_A \beta n^2}{2M^2}\{1 + \mathcal{O}(z)\} \tag{40}$$

This first term is independent of the assumed segment distribution.[14] Since $\beta = 0$ and $z = 0$ at $T = \Theta$, it follows from eq 4, 7, and 40 that

$$\left(\frac{dk_\phi}{dT}\right)_\Theta = \left(\frac{dk_\phi}{dB}\right)_\Theta \left(\frac{dA_2}{dT}\right)_\Theta \frac{M^2}{N_A V_e} \tag{41}$$

At choice one may substitute

$$\left(\frac{dA_2}{dT}\right)_\Theta = \frac{\psi \bar{v}_p^2}{\Theta M_1 \bar{v}_1} \tag{42}$$

which follows by elimination of βn^2 from eq 13 and 40.

From eq 5 we have

$$\left(\frac{dk_\phi}{dB}\right)_\Theta = 24 \int_0^1 \left\{\frac{v_d(x)}{v_s(1)} - 1\right\}(1 - x)^2(2 + x)x^2 \, dx \tag{43}$$

Numerical values of this derivative for the three ellipsoids and the dumbbell approximations are in the fifth row of Table I. It is seen that the variation in $(dk_\phi/dB)_\Theta$ with a change in the hydrodynamic model for overlapping spheres is markedly smaller than for $(k_\phi)_\Theta$.

With respect to the temperature dependence of V_e we derive from eq 3b,c and 9

$$\left(\frac{d \ln V_e}{dT}\right)_\Theta = \frac{3}{2}\frac{d}{dT} \ln \langle l_0^2 \rangle + 3\left(\frac{d\alpha_f}{dT}\right)_\Theta \tag{44}$$

It was shown previously[1] that

$$(d\alpha_f/dT)_\Theta = C_f M^{1/2} \tag{45}$$

in which C_f is independent of M.

We introduce eq 41, 44, and 45 into (39) and return partially from the symbols k_ϕ and V_e to k_s, using eq 3a. For showing explicitly the dependence on M, we finally substitute

$$(k_s)_\Theta = \boldsymbol{k}_\Theta M^{1/2} \tag{46}$$

All this transforms (39) into

$$\left(\frac{dk_s}{dT}\right)_\Theta = \left\{3\boldsymbol{k}_\Theta C_f + \left(\frac{dk_\phi}{dB}\right)_\Theta \left(\frac{dA_2}{dT}\right)_\Theta\right\} M + \frac{3}{2}\left(\frac{d}{dT} \ln \langle l_0^2 \rangle\right)\boldsymbol{k}_\Theta M^{1/2} \tag{47}$$

The relative variation of k_s due to the third term is of the small magnitude 1×10^{-3} deg^{-1}, so unless the enthalpy of mixing polymer segments with solvent is very small, $(dk_s/dT)_\Theta$ is proportional to M. Given reliable values for $\boldsymbol{k}_\Theta$ and C_f, $(dA_2/dT)_\Theta$ and ψ can be calculated from the temperature dependence of k_s. For the evaluation of experiments that value for $(dk_\phi/dB)_\Theta$ seems preferable which goes with the theoretical value for $(k_\phi)_\Theta$ for which the difference with the experimental value is smallest.

It will be shown in the next section that eq 47 also applies when the F–K potential is employed for calculating the thermodynamic interaction. Although the function $k_\phi(B)$ will be different from eq 4, the thermodynamic dependence of k_ϕ is still defined by the parameter B.

8. Introducing the Modified Flory–Krigbaum Potential

We recalculate $(dk_\phi/dB)_\Theta$ by introducing the normalized Gaussian potential

$$\Delta G(r, \langle r_g^2 \rangle)/kT = \beta n^2 \left(\frac{3\mu}{4\pi \langle r_g^2 \rangle}\right)^{3/2} \exp\left(-\frac{3\mu r^2}{4\langle r_g^2 \rangle}\right) \tag{48}$$

$\langle r_g^2 \rangle^{1/2}$ is the radius of gyration of the coiled polymer. The

parameter μ is unity in the original F–K potential and should be given the value 2.135 to make the potential compatible with the first-order perturbation theory for A_2.[14]

Since in the ranges $0 < r < 2a$ and $r > 2a$ different functions will be used for the hydrodynamic interaction, we retain the dimension of the equivalent sphere as the reference length and express $\langle r_g^2 \rangle$ in terms of its radius a and volume V_e. This is done making use of the relationship $\langle r_g^2 \rangle = \langle l^2 \rangle / 6$ and eq 3c and 9. Neglecting the small difference in the expansion factors, we obtain $\langle r_g^2 \rangle = (64/9\pi)a^2$. Equation 48 thus changes into

$$\Delta G(x, B)/kT = \mu^{3/2} \frac{27\pi 3^{1/2}}{2^9} B \exp\left(-\mu \frac{27\pi}{2^6} x\right) \quad (49)$$

B is given by (14).

In the P–F theory the thermodynamic interaction is confined to overlapping spheres and the average radial distribution for separate soft spheres is independent of the temperature and equals that for hard spheres. This is not true for the Gaussian potential. As a consequence, for calculating $(dk_\phi/dT)_\Theta$, using (49), we cannot start from eq 4 and 5 but should take up the P–F theory at an earlier point.

The external force acting on a sphere is invariant for a change in the concentration effect, so the product of the friction coefficient and the average velocity at a given low concentration equals that at infinite dilution. We thus may write

$$f(c)/f(0) = v_s(1)/v_s = 1 + k_s c = 1 + k_\phi \Phi \quad (50)$$

This equation ignores a small difference in the buoyancy. In the calculation of the concentration effect wall effects are eliminated by considering the average drift velocity $\vec{v}$. This quantity is defined

$$\vec{v} = \vec{v}_s - \vec{v}_f \quad (51)$$

$\vec{v}_f$ is the average solvent velocity.

The net volume is zero, so

$$\Phi \vec{v}_s + (1 - \Phi)\vec{v}_f = 0 \quad (52)$$

The relation between $\vec{v}$ and k_ϕ is then found to be

$$v/v_s(1) = 1/[(1 + k_\phi \Phi)(1 - \Phi)] \quad (53)$$

We split Pyun and Fixman's expression for the average sphere velocity $\vec{v}_s$ under binary interaction as follows:

$$\vec{v}_s = \vec{v}_s(1) + N\left\{\int_{r \le 2a} [\vec{v}_d(\vec{r}) - \vec{v}_s(1)] g(r)\, d\vec{r} + \int_{r > 2a} [\vec{v}_s(1, 2) - \vec{v}_s(1)] g(r)\, d\vec{r}\right\} + \mathcal{O}(N^2) \quad (54)$$

$\vec{v}_s(1)$ is the velocity of sphere 1 with its center at $\vec{R}_1$ in the absence of sphere 2, $\vec{v}_s(1, 2)$ is the velocity of sphere 1 when a second sphere is at $\vec{R}_2$, $\vec{r}$ equals $\vec{R}_2 - \vec{R}_1$, $\vec{v}_d(\vec{r})$ is the velocity of the dumbbell with center-to-center vector $\vec{r}$, and $g(r)$ is the equilibrium distribution function for two spheres and is related to the potential of the average force according to

$$g(r) = \exp[-\Delta G(r)/kT] \quad (55)$$

where $\Delta G(r)$ refers to (48).

The average solvent velocity $\vec{v}_f$ is given by

$$\vec{v}_f = N \int_{r > a} \vec{v}_f(1, 2) h(r)\, d\vec{r} + \mathcal{O}(N^2) \quad (56)$$

where $\vec{v}_f(1, 2)$ is the solvent velocity at $\vec{R}_1$ when a sphere is at $\vec{R}_2$ and $h(r)$ is the solvent–sphere distribution function. Since no change in the potential is involved in displacing an isolated sphere with respect to the solvent, $h(r) = 1$.

Subtracting eq 56 from eq 54 and dividing the result by $v_s(1)$ gives for the reduced drift velocity after some rearrangement of terms

$$\frac{v}{v_s(1)} = 1 + N\left\{\int_{r<2a}\left[\frac{v_d(\vec{r})}{v_s(1)} - 1\right] g(r)\, d\vec{r} - \int_{a<r<2a} \frac{v_f(1, 2)}{v_s(1)}\, d\vec{r} + \int_{r>2a}\left[\frac{v_s(1, 2)}{v_s(1)} - 1 - \frac{v_f(1, 2)}{v_s(1)}\right] g(r)\, d\vec{r} - \int_{r>2a} \frac{v_f(1, 2)}{v_s(1)}[1 - g(r)]\, d\vec{r}\right\} + \mathcal{O}(N_2) \quad (57)$$

In the P–F theory $g(r) = 1$ for $r > 2a$, so g as a function of r only appears in the first integral term, which takes the form of eq 5. Although the integration extends to infinity, the chosen arrangement causes the third integral to be finite because the integrand contains terms of the order r^{-4} and lower only.

As previously with respect to eq 19 and 20 the integrations require the averaging of $\cos\theta_i \cos\theta_1$. The volume of the spherical shell is expressed in x $(=r/2a)$ for the range of integration $0 < r < 2a$ and in y $(=a/r)$ for the range $r > 2a$

$$4\pi r^2\, dr = 24 V_e x^2\, dx = -3V_e \frac{dy}{y^4} \quad (58)$$

Equation 57 then becomes

$$\frac{v}{v_s(1)} = 1 + \Phi\left\{24\int_0^1\left[\frac{\bar{v}_d^\theta}{v_s(1)} - 1\right] e^{-\Delta G/kT} x^2\, dx - 3\int_{1/2}^1 \frac{\bar{v}_f^\theta}{v_s(1)} \frac{dy}{y^4} + 3\int_0^{1/2}\left[\frac{\bar{v}_s^\theta(1, 2)}{v_s(1)} - 1 - \frac{\bar{v}_f^\theta(1, 2)}{v_s(1)}\right] e^{-\Delta G/kT} \frac{dy}{y^4} - 3\int_0^{1/2} \frac{\bar{v}_f^\theta(1, 2)}{v_s(1)}(1 - e^{-\Delta G/kT}) \frac{dy}{y^4}\right\} + \mathcal{O}(\Phi^2) \quad (59)$$

where the bar and superscript θ denote an angular average.

For a Θ system ΔG vanishes and the numerical value for (59) follows from the work by Pyun and Fixman when rectified according to the note added to Appendix eq 24′.

Differentiating eq 53 with respect to the temperature and neglecting terms of the second and higher order in Φ produces

$$\frac{dk_s c}{dT} = \frac{dk_\varphi \Phi}{dT} = -\frac{d}{dT}\frac{v}{v_s(1)} + \frac{d\Phi}{dT} \quad (60)$$

After substitution for ΔG from eq 49 in (59) and differentiation of (59) with respect to T, we choose $T = \Theta$ and rearrange to obtain

$$\left(\frac{d}{dT}\frac{v}{v_s(1)}\right)_\Theta = \{\kappa(0) - 6.01\}\left(\frac{d\Phi}{dT}\right)_\Theta - \frac{81\pi 3^{1/2}}{2^9}\mu^{3/2}\left(\frac{dB}{dT}\right)_\Theta \Phi \times \left\{8\int_0^1\left[\frac{\bar{v}_d^\theta}{v_s(1)} - 1\right] e^{-\mu(27\pi/2^6)x^2} x^2\, dx + \int_0^{1/2}\left[\frac{\bar{v}_s^\theta(1, 2)}{v_s(1)} - 1\right] e^{-\mu(27\pi/2^6 y^2)} \frac{dy}{y^4}\right\} + \mathcal{O}(\Phi^2) \quad (61)$$

Table III
Variation of $(dA_2/dT)_\Theta$ and the Entropy of Mixing Parameter ψ with the Molecular Weight[a]

$10^{-3}\bar{M}_w$	$10^5(dk_s/dT)_\Theta M^{-1}$, (mL·mol)/(g²·deg)	P-F + dumbbell approx				Yamakawa[b]	
		$10^5(dA_2/dT)_\Theta$,[b] (mL·mol)/(g²·deg)	ψ [b]	ψ [c]	ψ [d]	$10^5(dA_2/dT)_\Theta$, (mL·mol)/(g²·deg)	ψ
98	1.13 ± 0.05	0.84 ± 0.05	0.325 ± 0.02	0.39	0.29	0.84 ± 0.04	0.325 ± 0.02
160	1.06 ± 0.03	0.78 ± 0.04	0.30 ± 0.01	0.36	0.27	0.79 ± 0.03	0.305 ± 0.01
190	0.98 ± 0.05	0.71 ± 0.05	0.27 ± 0.02	0.33	0.25	0.73 ± 0.04	0.28 ± 0.02
411	0.97 ± 0.03	0.70 ± 0.04	0.27 ± 0.01	0.33	0.24	0.72 ± 0.03	0.28 ± 0.01
860	0.92 ± 0.02	0.66 ± 0.03	0.26 ± 0.01	0.31	0.23	0.68 ± 0.02	0.265 ± 0.01
1800	0.86 ± 0.02	0.61 ± 0.03	0.24 ± 0.01	0.29	0.21	0.64 ± 0.02	0.25 ± 0.01

[a] From the temperature dependence of k_s for PS-CH ($T = \Theta$). [b] Modified Flory-Krigbaum potential, fitting the first-order perturbation theory for A_2. [c] Original Flory-Krigbaum potential. [d] Thermodynamic interaction calculated by using equivalent spheres of uniform segment density.

For $\kappa(0)$ and $\bar{v}_d{}^\theta$ we take ellipsoid 2 and the dumbbell approximation, eq 32. For the integrand in the second integral we use eq 16. After evaluation of the integrals, which was done graphically, eq 61 is substituted in (60). In addition a substitution is made for $(dB/dT)_\Theta$ from eq 14 and 42. We thus may write

$$\left(\frac{dk_s c}{dT}\right)_\Theta = \{7.01 - \kappa(0)\}\left(\frac{d\Phi}{dT}\right)_\Theta + Q_d(\mu)\left(\frac{dA_2}{dT}\right)_\Theta \frac{M^2}{N_A V_e}\Phi \quad (62)$$

$Q_d(\mu)$ is the numerical factor, the value of which varies with μ and the hydrodynamical model to represent overlapping spheres.

At the Θ point the difference between k_ϕ, as given by (4), and its value calculated with the F-K potential vanishes. We further substitute $\Phi/V_e = N = cN_A/M$, subtract the thermal expansion of the solution, and divide by c to obtain

$$\left(\frac{dk_s}{dT}\right)_\Theta = (k_\varphi)_\Theta \frac{N_A}{M}\left(\frac{dV_e}{dT}\right)_\Theta + Q_d(\mu)\left(\frac{dA_2}{dT}\right)_\Theta M \quad (63)$$

We compare this expression with (47). The first term to the right in (63) corresponds to the first and third terms of (47). $Q_d(\mu)$ may be equated to $(dk_\phi/dB)_\Theta$ on the ground of eq 4 and the fact that ΔG given by (6) as well as by (49) is governed by the same single parameter B. For the combination of spheres with ellipsoid 2 Q_d becomes 0.995 ($\mu = 1$) or 1.209 ($\mu = 2.135$); for spheres with the dumbbell approximation it is 0.944 ($\mu = 1$) or 1.147 ($\mu = 2.135$) (Table I, bottom rows). The differences for each of the two combinations with 1.34 and 1.27, respectively, are nearly equal, so similar differences will arise for ellipsoids 1 and 3.

9. Discussion

It follows from a comparison of the numbers in the last and third last rows of Table I and from eq 47 and 42 that substitution of the modified F-K potential for the potential derived from the uniform-density sphere will increase the values for $(dA_2/dT)_\Theta$ and ψ by only 11%. We compare this increase with the difference resulting when the suggestion by Kotera et al. and Noda et al. is followed, as discussed in section 2. The volume V_e in eq 39 then still refers to the friction-equivalent sphere, whereas V_e in (41) becomes the volume of the sphere described by the radius of gyration. Since the latter is 1.5 times the friction radius, the resulting increase in the calculated values for $(dA_2/dT)_\Theta$ and ψ is by a factor $1.5^3 \approx 3.4$. This implies a 240% change, whereas our correction is 11%!

We apply eq 47 to the experimental data for the PS-CH system, obtained in the experimental paper.[1] The empirical relation for $(dk_s/dT)_\Theta$ has been determined as

$$\left(\frac{dk_s}{dT}\right)_\Theta = (0.3 \pm 0.1) + (0.87 \mp 0.05) \times 10^{-5} M \text{ mL g}^{-1} \text{ deg}^{-1} \quad (64)$$

This expression does not fulfill the requirement that dk_s/dT vanishes for $M \to 0$. The author holds the view that the linear but not proportional relation is an apparent one and covers a dependence of $(dA_2/dT)_\Theta$ and ψ on M. So we discard this expression and apply eq 47 to the individual values for $(dk_s/dT)_\Theta$ stated in Table III. Since with $k_\phi = 6.55$ for hard spheres the dumbbell approximation gives agreement with the experimental results, we choose $(dk_\phi/dB)_\Theta = 0.944$.

Using $\boldsymbol{k}_\Theta = (0.062 \pm 0.004)$ mL g$^{-3/2}$ mol$^{-1/2}$ and $C_f = (0.87 \pm 0.04) \times 10^{-5}$ (g mol)$^{-1/2}$ deg^{-1},[1] we have $3\boldsymbol{k}_\Theta C_f = (0.16 \pm 0.01) \times 10^{-5}$ g^{-2} mL mol deg^{-1}. With d ln $\langle l_0^2\rangle/dT = (0.4 \pm 0.2) \times 10^{-3}$ deg^{-1} the last term of (47) is found to be insignificant in the range of M used.

The results for $(dA_2/dT)_\Theta$ and ψ are in the table. Values for ψ were calculated with eq 42 ($\bar{v}_p = 0.934$ mL/g).

A marked decrease of these quantities with increasing M shows up, which is not covered by the theory. Furthermore, a comparison of $3\boldsymbol{k}_\Theta C_f$ with the second column of the table shows that the expansion of individual chains takes a share smaller than 20% in the increase of k_s. The main contribution is by the increased mutual repulsion of the molecules.

For comparison we also apply Yamakawa's equation[3] for k_s, although it predicts $(k_s)_\Theta = 0$. For vinyl polymers Yamakawa recommends a limiting expression valid under the same conditions as required for eq 9, i.e., in theory a vanishing dependence of k_s and $[f]$ on the friction coefficient of individual segments

$$k_s = \lambda(X) A_2 M \quad (65)$$

X is proportional to z (eq 8) and therefore is zero at the Θ point.

The value of $\lambda(X)$ includes the expansion of individual chains as well as their mutual repulsion. Since $\lambda(0) = 1.345$ we have

$$\left(\frac{dk_s}{dT}\right)_\Theta = 1.345\left(\frac{dA_2}{dT}\right)_\Theta M \quad (66)$$

The values for $(dA_2/dT)_\Theta$ and ψ calculated with (66) and (42) agree within the error margin with those following from the modified P-F theory (Table III). This is unexpected. Although the thermodynamic model is the same, the hydrodynamic model is widely different.

When, finally, we take a glance at Imai's expression[7] for k_s

$$k_s = \frac{N_A}{8\pi^{3/2}} \frac{nb^2}{M}[f] \qquad (nb^2 = \langle l_0^2 \rangle) \tag{67}$$

we conclude that it is utterly deficient with respect to the excluded-volume effects. The intermolecular repulsion is not included at all, while the expansion of individual chains is only accounted for in its linear dimension.

We will compare our results with those obtained in osmotic and light-scattering studies of the PS–CH system. These deal with solutions which are in thermodynamic equilibrium and at mechanical rest. Nonetheless an incomplete survey reveals values for ψ that vary by a factor 2, ranging from 0.19 to 0.38.[16-20]

An osmotic study of PS–CH for a variation of $(dA_2/dT)_\Theta$ and ψ with M was made by Krigbaum.[17] For four PS samples with number-average molecular weights 50 000, 125 000, 359 000, and 566 000 he found ψ to be 0.36, 0.33, 0.29, and 0.29, respectively.

Krigbaum used the original F–K potential, so these values should be compared with ours in column 5 of Table III. They are seen to be in the same range. Since a dependence of ψ on M is not covered by the theory, Krigbaum presumed moisture to be the origin of the variation with the molecular weight. He stored the solutions in a water bath at 40 °C for a couple of days prior to measurement. Convincing evidence was not produced, however. In prolonged experiments, taking appropriate precautions, he investigated only one different sample ($\bar{M}_n$ = 203 000). For this he found ψ = 0.35.

In our experiments the nominal water content was 0.01% or less. Since water baths were used for short times in preparing the solutions, the actual content may have been higher. A variable amount of water contamination, however, is denied by the experimental data: the random errors in $(d \ln s/dT)_\Theta$ vs. $c/(1 + k_s c)$ (Figure 4, ref 1) are small and ψ varies smoothly with M.

Although an effect by water cannot be excluded, other possible origins should also be considered.

Morawetz[21] has pointed out that the vanishing of the excluded volume for a chain as a whole may be effected by a balancing of repulsive and attractive contributions from regions at different distances from the center of the molecule. These contributions can be derived from separate potential functions, the sum of which is the potential of the average force between two macromolecules.

Now, a ψ which decreases with increasing M can only be explained from a repulsive and an attractive potential function which draw further apart as M increases. This requirement is not fulfilled by Olaj's interpretation of Morawetz separation of potentials.[22] Olaj associated the repulsive potential with the smoothed distribution of the segments and the attractive potential with the smoothed distribution of all sites that are neighboring upon the segments. The distance between the potentials thus defined diminishes with increasing M.

We also call attention to the work by Mijnlieff and Jaspers,[23] who studied the sedimentation velocity of high molecular weight poly(α-methylstyrene) in the poor solvent cyclohexane and the good solvent toluene at concentrations for which the hydrodynamical individuality of the particles is removed. In this condition the solvent is pressed through a quasi-network (plug-flow). When the differences in solvent viscosity and buoyancy were allowed for, the permeability in cyclohexane at $T = \Theta$ was found to be more than 3 times larger than in toluene. Upon a rise in temperature, the permeability in cyclohexane diminishes rapidly, whereas in toluene it slowly increases. These facts are a strong indication for the occurrence of local association of chain sections in cyclohexane. Associated chain sections may take part of the same chain or of different chains. When they are fairly long-lived, a complete mutual penetration of molecules will be impeded. Close clusters will be less numerous than is predicted by the Flory–Krigbaum potential. Upon a temperature rise the average expansion of clusters can only be smaller in that case and so will $(dA_2/dT)_\Theta$ and ψ. For providing a satisfactory explanation for the variation with M, this effect should become more pronounced as the molecular weight increases.

An effect of this kind should also manifest itself in an upward curvature in the plot of $(k_s)_\Theta$ vs. $M^{1/2}$. In our experiments up to $\bar{M}_w$ = 860 000 a curvature was not significant (Figure 3, ref 1). However, when higher molecular weights are included, an upward curvature shows up.[24]

Although the observed decrease of ψ with increasing M is not satisfactorily explained, we believe it to be real and not due to moisture in view of the systematic character of its variation found by us from sedimentation and by Krigbaum from osmotic experiments.

The agreement in results obtained by applying the modified Pyun–Fixman theory or the theory by Yamakawa suggests that sedimentation velocity experiments may yield reliable values for $(dA_2/dT)_\Theta$ and ψ.

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Appendix (Section 4). Velocity Components of Two Spheres in Hydrodynamic Interaction without Rotation

1. Formal Course of the Pyun–Fixman Theory for the Velocity Components of a Sphere in the Presence of Another One under Interaction with Passive Rotation. Suppression of terms which represent inertial effects gives Stokes' approximation of the Navier–Stokes equation

$$\eta \text{ div grad } \vec{v} - \text{grad } p = 0 \tag{1'}$$

η is the solvent viscosity and p the pressure. Incompressibility is assumed, so we have

$$\text{div } \vec{v} = 0 \tag{2'}$$

These equations are basic to the theory. Pyun and Fixman developed the calculation of the velocity of a sphere 1 in the presence of a sphere 2 of equal size and weight as follows:

$$\vec{v}_s(1, 2) = \vec{v}_s(1) + {}^2\vec{S}(\vec{r}_{12})\cdot\vec{v}_s(2) + {}^3\vec{E}(\vec{r}_{12}):[\vec{\nabla}_2{}^2\vec{S}(r_{21})]^{sym}\cdot \vec{v}_s(1) + {}^3\vec{E}(\vec{r}_{12}):[\vec{\nabla}_2{}^3\vec{E}(\vec{r}_{21})]^{sym}:[\vec{\nabla}_1{}^2\vec{S}(\vec{r}_{12})]^{sym}\cdot\vec{v}_s(2) + \ldots \tag{3'}$$

$\vec{v}_s(1)$ is the velocity of sphere 1 in the absence of sphere 2. ${}^2\vec{S}(\vec{r}_{12})\cdot\vec{v}_s(2)$ is the primary perturbation of the solvent velocity due to sphere 2 at the position of the center of sphere 1 at a vector distance $\vec{r}_{12}$ from sphere 2 in the absence of sphere 1. ${}^2\vec{S}(\vec{r}_{12})$ is a dyadic tensor, the components of which in a rectangular coordinate system are

$$S_{ij} = \frac{3}{4}\left[\left(\frac{a}{r} - \frac{a^3}{r^3}\right)n_i n_j + \left(\frac{a}{r} + \frac{1}{3}\frac{a^3}{r^3}\right)\delta_{ij}\right] \tag{4'}$$

Here a is the radius of the sphere and $\vec{n} \equiv \vec{r}/r$ is a unit vector from the sphere center.

A reflection $1 \rightarrow 2 \rightarrow 1$ arises from the interaction of sphere 2 with a spatially constant gradient of the magnitude of the gradient of the primary perturbation that sphere 1 would induce at the position of the center of sphere 2 in the latter's absence. The nabla operator ∇_i has

the center of sphere i as the point of reference. The interaction with the remaining part of the gradient is disregarded. ${}^3\vec{E}(\vec{r}_{21})$ is a triadic tensor

$$E_{ikl} = -\frac{5}{2}\left(\frac{a^3}{r^2} - \frac{a^5}{r^4}\right)n_i n_k n_l - \frac{1}{2}\frac{a^5}{r^4}(\delta_{ik}n_l + \delta_{il}n_k) \quad (5')$$

and is symmetric in k and l, so only the symmetric part of the velocity gradient is effective. The antisymmetric part represents a uniform rotation. In this field sphere 2 revolves passively without perturbing the flow.

The next contribution to the velocity of sphere 1 is obtained in a mathematically similar manner from the interaction with the twice-reflected perturbation $2 \rightarrow 1 \rightarrow 2 \rightarrow 1$ starting from sphere 2 and is represented by the fourth term of eq 3'. This scheme continues.

Since $\vec{v}_s(2) = \vec{v}_s(1)$, ${}^2\vec{S}(\vec{r}_{21}) = {}^2\vec{S}(\vec{r}_{12})$, $\vec{\nabla}_2 = -\vec{\nabla}_1$, and ${}^3\vec{E}(\vec{r}_{21}) = -{}^3\vec{E}(\vec{r}_{12})$, the fourth and higher terms of eq 3' may be condensed to

$${}^3\vec{E}(\vec{r}_{12}):{}^4\vec{Q}:[\vec{\nabla}_2{}^2\vec{S}(r_{21})]^{\text{sym}}\cdot\vec{v}_s(1) \quad (6')$$

where ${}^4\vec{Q}$ is a quartic tensor defined by

$${}^4\vec{Q}: \equiv \sum_{n=1}^{\infty}\{[\vec{\nabla}_2{}^3\vec{E}(\vec{r}_{12})]^{\text{sym}};\}^n \quad (7')$$

Q_{pqkl} and $R_{pqkl} \equiv [\vec{\nabla}_2{}^3\vec{E}(\vec{r}_{12})]_{pqkl}{}^{\text{sym}}$ are related by

$$Q_{pqkl} = R_{pqkl} + R_{pqij}Q_{ijkl} \quad (8')$$

where the notation implies the summation convention.

2. Hydrodynamic Interaction without Rotation. (a) Modifying the Perturbation Tensor. In section 3 it was argued that with increasing center-to-center distance the velocity components for the dumbbell state are continuous with the velocity components for a pair of interacting nonrotating spheres. We have to modify therefore the P–F treatment outlined above to remove the rotation.

Suppressing the rotation gives rise to an extra perturbation. An extension of the tensor (5') must be found such that double contraction with a spatially constant asymmetric velocity gradient will yield the velocity perturbation due to a nonrotating sphere. This extension, of necessity, is antisymmetric in k and l because contraction with a constant symmetric gradient should produce zero.

We can start from the solution of a textbook problem by Landau and Lifshitz[25] for the velocity of a fluid contained between two concentric spheres of radii R_1 and R_2 revolving with angular speeds ω_1 and ω_2 around different axes

$$\vec{v} = \frac{R_1{}^3R_2{}^3}{R_2{}^3 - R_1{}^3}\left\{\left(\frac{1}{r^3} - \frac{1}{R_2{}^3}\right)\vec{\omega}_1 \times \vec{r} + \left(\frac{1}{R_1{}^3} - \frac{1}{r^3}\right)\vec{\omega}_2 \times \vec{r}\right\} \quad (R_1 < r < R_2) \quad (9')$$

For $\omega_1 = 0$ and for $R_2 \rightarrow \infty$ we have a sphere at rest in an unbounded fluid, for which the velocity pattern is given by

$$\vec{v} = \left(1 - \frac{R_1{}^3}{r^3}\right)\vec{\omega}_2 \times \vec{r} \quad (10')$$

Since the uniform rotation is $\vec{w}_2 \times \vec{r}$, the perturbation due to a nonrotating sphere of radius a is

$$\vec{v}_p = -\frac{a^3}{r^3}\vec{\omega}_2 \times \vec{r} \quad (11')$$

It follows that the excess perturbation arising from suppression of the rotation of a sphere in a uniform asymmetric velocity gradient ${}^2\vec{\alpha}$ is given by

$$\vec{v}_p{}' = -\frac{a^3}{r^3}{}^2\vec{\alpha}^{\text{anti}}\cdot\vec{r} \quad (12')$$

where ${}^2\vec{\alpha}^{\text{anti}}$ is the antisymmetric part of ${}^2\vec{\alpha}$.

The correspondence between eq 11' and 12' implies that

$$\begin{aligned} -\tfrac{1}{2}(\alpha_{23} - \alpha_{32}) &= \omega_{2,x} \\ -\tfrac{1}{2}(\alpha_{31} - \alpha_{13}) &= \omega_{2,y} \\ -\tfrac{1}{2}(\alpha_{12} - \alpha_{21}) &= \omega_{2,z} \end{aligned} \quad (13')$$

The triadic tensor, which through a double contraction with α_{kl} yields this same perturbation, is

$$E'_{ikl} = -\frac{1}{2}\frac{a^3}{r^2}(\delta_{ik}n_l - \delta_{il}n_k) \quad (14')$$

With this result the extension of tensor 5' has been obtained.

(b) Velocity Components of a Sphere in the Presence of a Second One under Interaction without Rotation. We now consider the sequence of reflected perturbations to which sphere 1 is subjected.

When axis 1 is in the direction of the external force

$$[\vec{v}_s(1)]_i = \delta_{i1}u \quad (15')$$

Since the unperturbed motion does not involve rotation, the primary perturbation due to sphere 2 remains unchanged

$$[{}^2\vec{S}(\vec{r}_{12})\cdot\vec{v}_s(2)]_i = \tfrac{3}{4}[(y + \tfrac{1}{3}y^3)\delta_{i1} + (y - y^3)n_i n_1]u \quad (16')$$

where $y \equiv a/r$ and $0 < y \leq {}^1/_2$.

The first additional perturbation is caused by suppressing the rotation of sphere 2 in the reflection $1 \rightarrow 2 \rightarrow 1$. Unlike spheres in passive rotation, the perturbations are not obtained by merely multiplying the symmetric parts of the tensors concerned. Therefore, when the derivatives of velocities are taken, the proper order of the indices must be observed. In accordance with the relationship between velocity and gradient in a uniform gradient field, namely

$$\begin{aligned} v_k &= \alpha_{kl}x_l \\ \alpha_{kl} &= \partial v_k/\partial x_l \end{aligned} \quad (17')$$

the antisymmetric part of the gradient of ${}^2\vec{S}$ should become

$$[\vec{\nabla}_2{}^2\vec{S}(\vec{r}_{21})]_{klm}{}^{\text{anti}} = \frac{1}{2}\left(\frac{\partial S_{km}}{\partial x_l} - \frac{\partial S_{lm}}{\partial x_k}\right) = -\frac{3}{4a}y^2(\delta_{km}n_l - \delta_{lm}n_k) \quad (18')$$

Since it is a received reflection and $\vec{E}'$ is odd, a minus sign must be assigned and the first extra perturbation acting on sphere 1 becomes

$$-{}^3\vec{E}'_{ikl}[\vec{\nabla}_2{}^2\vec{S}(\vec{r}_{21})]_{klm}{}^{\text{anti}}[\vec{v}_s(1)]_m = -\tfrac{3}{4}y^4(\delta_{i1} - n_i n_1)u \quad (19')$$

This is added to the "natural" perturbation $1 \rightarrow 2 \rightarrow 1$ (eq 35, P–F) to give

$$-(E_{ikl} + E'_{ikl})[\vec{\nabla}_2{}^2\vec{S}(\vec{r}_{21})]_{klm}[\vec{v}_s(1)]_m = -[\tfrac{3}{4}(y^4 + y^8)\delta_{i1} + 3(y^4 - 2y^6 + \tfrac{1}{2}y^8)n_i n_1]u \quad (20')$$

The gradient tensors of both the natural and the additional first reflection are asymmetric and both of them give rise, therefore, to variations in the linear as well as the rotational velocity of the receiving sphere; the latter have to be suppressed. This pattern repeats itself in the higher reflections, so a direct summation of all additional

perturbations does not seem feasible. Instead of this we follow Pyun and Fixman and use eq 6′, 7′, and 8′ to calculate mutatis mutandis the total perturbation resulting from the sum of the higher reflections.

For

$$^4\vec{R}^1 \equiv \vec{\nabla}_2[^3\vec{E}(\vec{r}_{12}) + {}^3\vec{E}'(\vec{r}_{12})]$$

we derive

$$R'_{pqkl} = B(y)n_pn_qn_kn_l + C(y)\delta_{pk}n_qn_l + L(y)\delta_{pl}n_qn_k + F(y)(\delta_{qk}n_pn_l + \delta_{ql}n_pn_k + \delta_{pq}n_kn_l) + Y(y)\delta_{pk}\delta_{ql} + X(y)\delta_{pl}\delta_{qk} \quad (21')$$

where

$$B = -\tfrac{5}{2}(5y^3 - 7y^5) \qquad L = \tfrac{1}{2}(3y^3 - 5y^5)$$
$$Y = \tfrac{1}{2}(y^3 + y^5) \qquad C = -\tfrac{1}{2}(3y^3 + 5y^5)$$
$$F = \tfrac{5}{2}(y^3 - y^5) \qquad X = -\tfrac{1}{2}(y^3 - y^5)$$

From this $^4\vec{Q}'$ follows by virtue of a relationship identical with (8′)

$$Q'_{pqkl} = \beta(y)n_pn_qn_kn_l + \gamma(y)\delta_{pk}n_qn_l + \lambda(y)\delta_{pl}n_qn_k + \chi(y)\delta_{qk}n_pn_l + \psi(y)\delta_{qk}n_pn_k + \phi(y)\delta_{pq}n_kn_l + \upsilon(y)\delta_{pk}\delta_{ql} + \xi(y)\delta_{pl}\delta_{qk} \quad (22')$$

The notation of $\beta(y)$ etc. is shortened when they are collected in pairs according to need in eq 25′ below.

$$\varphi = \tfrac{5}{2}(y^3 - y^5)/(1 - y^5)(1 + 5y^3 - 6y^5)$$

$$\gamma + \lambda = -5y^5(1 - y)/\{(1 - 2y^3 + 4y^5 - 5y^6 + 2y^8)(1 - y^5)\}$$

$$\gamma - \lambda = -3y^3(1 - 3y^3 + 2y^5)/\{(1 - 2y^3 + 4y^5 - 5y^6 + 2y^8)(1 - y^3)\}$$

$$\chi + \psi = 5y^3(1 - y^2)(1 + y^3)/\{(1 - 2y^3 + 4y^5 - 5y^6 + 2y^8)(1 - y^5)\}$$

$$\chi - \psi = -6y^6(1 - y^2)/\{(1 - 2y^3 + 4y^5 - 5y^6 + 2y^8)(1 - y^3)\}$$

$$\upsilon + \xi = y^5/(1 - y^5)$$

$$\upsilon - \xi = y^3/(1 - y^3)$$

On account of the postulated incompressibility $R'_{ppkl} = 0$ and $Q'_{ppkl} = 0$, whence

$$B + C + L + 5F = 0 \quad (23')$$

$$\beta + \gamma + \lambda + \chi + \psi + 3\phi = 0 \quad (24')$$

(The corresponding relationship to (24′) in the treatise by Pyun and Fixman should read $\beta + 4\gamma + 3\phi = 0$, rather than $\beta + 4\gamma + \phi = 0$. As a consequence, a few subsequent equations in their text are erroneous and the fraction terms in eq 16 of our main text differ from the corresponding terms derived by Pyun and Fixman in their eq 41 and 43. Finally, for hard spheres k_ϕ is calculated to be 7.01 rather than 7.16 (cf. eq 4).)

By a multiple contraction the sum of the higher reflections is then evaluated to be

$$-(E_{ipq} + E'_{ipq})Q'_{pqkl}[\vec{\nabla}_2{}^2\vec{S}(\vec{r}_{21})]_{klm}[\vec{v}_s(1)]_m = \frac{3}{8}y^4[(5 - 8y^2 + 3y^4)\{4\phi - 2(\upsilon + \xi)\}n_in_1 - \{(1 + y^2)(\gamma - \lambda) - (1 - y^2)(\chi - \psi) + (y^2 + y^4)(\gamma + \lambda) - (y^2 - y^4)(\chi + \psi) + 2(\upsilon - \xi) + 2y^2(\upsilon + \xi)\}(\delta_{i1} - n_in_1)]u \quad (25')$$

Upon substitution of eq 22′ this expression can be reduced by a suitable combination of terms. The result is

$$\frac{3}{4}y^7\left[\frac{(1 - y^2)(5 - 3y^2)(5 - 6y^2)}{1 + 5y^3 - 6y^5}n_in_1 + \frac{1 + 8y^2 - 10y^3 - 5y^4 + 4y^5 + 8y^6 - 10y^7 + 4y^9}{2(1 - 2y^3 + 4y^5 - 5y^6 + 2y^8)} \times (\delta_{i1} - n_in_1)\right]u \quad (26')$$

Collecting the various terms of eq 15′, 16′, 20′, and 26′, we obtain for the velocity components of a nonrotating sphere in interaction with a similar second one, expression 15 given in the main text.

References and Notes

(1) J. J. H. Mulderije, *Macromolecules*, **13**, 1207 (1980).
(2) C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **41**, 937 (1964).
(3) H. Yamakawa, *J. Chem. Phys.*, **36**, 2995 (1962).
(4) A. Kotera, F. Saito, and T. Hamada, *Polym. J.*, **3**, 421 (1972).
(5) I. Noda, K. Mizutani, and F. Kato, *Macromolecules*, **10**, 618 (1977).
(6) A. J. Goldman, R. G. Cox, and H. Brenner, *Chem. Eng. Sci.*, **21**, 1151 (1966).
(7) S. Imai, *J. Chem. Phys.*, **52**, 4212 (1970).
(8) See C. W. Oseen, "Hydrodynamik", Akademische Verlagsgesellschaft, Leipzig, 1927, p 157.
(9) G. K. Batchelor, *J. Fluid Mech.*, **52**, 245 (1972).
(10) Reference 8, p 162.
(11) J. Happel and H. Brenner, "Low Reynolds Number Hydrodynamics", Prentice-Hall, New York, 1967, Chapter 5.
(12) M. Stimson and G. B. Jeffrey, *Proc. R. Soc. London, Ser. A*, **111**, 110 (1926).
(13) G. Ooms, P. F. Mijnlieff, and H. L. Beckers, *J. Chem. Phys.*, **53**, 4123 (1970).
(14) See H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1971, Chapter 4.
(15) See P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapter 12.
(16) W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).
(17) W. R. Krigbaum, *J. Am. Chem. Soc.*, **76**, 3758 (1954).
(18) W. R. Krigbaum and D. O. Geymer, *J. Am. Chem. Soc.*, **81**, 1859 (1959).
(19) H. Fujita, A. M. Linklater, and J. W. Williams, *J. Am. Chem. Soc.*, **82**, 379 (1960).
(20) F. A. Orofino and J. W. Mickey, *J. Chem. Phys.*, **38**, 3512 (1963).
(21) H. Morawetz, J. R. Cho, and P. J. Gans, *Macromolecules*, **6**, 624 (1973).
(22) O. F. Olaj, *Makromol. Chem.*, **177**, 3427 (1976).
(23) P. F. Mijnlieff and W. J. M. Jaspers, *Trans. Faraday Soc.*, **67**, 1837 (1971).
(24) F. A. H. Peeters, Thesis, Rijksuniversiteit te Leiden, 1979.
(25) L. D. Landau and E. M. Lifshitz, "Fluid Mechanics", Addison-Wesley, Reading, Mass., 1959, p 69.