Temperature and concentration dependence of diffusion coefficient in dilute solutions*

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Temperature and molecular weight dependence of k_D in $D(C) = D(0)[1 + Ck_D]$, where $D(C)$ is the diffusion coefficient for the density fluctuations in a dilute polymer solution, is investigated by first expressing $D(C)$ as a function of the static structure factor $S(q,C)$ within the framework of the Kirkwood–Riseman theory. The continuous transition of k_D from negative values under theta conditions to positive values in good solvents is calculated using various models for the intermolecular interaction potential and the results are presented graphically as function of a reduced variable $\bar{S}/R_H$ that combines both molecular weight and temperature effects. It is shown that the negative value of k_D at the theta temperature can be explained at least partially, in terms of an increase in the chain dimensions of two overlapping molecules. The concentration dependence of the self-diffusion coefficient is also discussed.

INTRODUCTION

The concentration dependence of the diffusion coefficient $D(C)$ in dilute solutions is represented by

$$D(C) = D(1 + Ck_D)$$

where D is the diffusion coefficient in the zero-concentration limit, C is the concentration of polymer molecules, and the constant k_D is independent of concentration. The earlier calculations of k_D were based on $k_D = 2MA_2 - k_S$, which follows from the Gibbs–Duhem formulation[1]. In this expression M denotes the polymer molecular weight, A_2 is the osmotic second virial coefficient, and the constant k_S is the coefficient of the linear term in C in the expansion of the frictional coefficient $f(C)$ $= f_p(1 + k_s C + ...)$.At the theta temperature $A_2 = 0$ and $k_D = -k_s$. Extending the Kirkwood–Riseman theory for f, Yamakawa[2] calculated k_s in 1962 as $k_S = 1.2\,MA_2$ which implies that k_s vanishes at the theta temperature. In 1964 Pyun and Fixman[3] computed k_S as a function of the .ond virial coefficient for polymer segments by approximating the polymer molecules as interpenetrable spheres of uniform segment density with a constant radius a. They found that k_S decreases from 7.16 in the good solvent limit (i.e., hard sphere limit) to $k_S = 2.23$ at the theta temperature, when the concentration is measured as a volume fraction taking the volume of each molecule as $4\pi a^3/3$. Contrary to Yamakawa's[2] original conclusion, their result predicted that $D(C)$ decreases with concentration at the theta temperature. In his book Yamakawa[1] modified his earlier result as $k_S = 1.2\,MA_2 + N_A V_m/M$ where N_A is the Avogadro's number and V_m is the hydrodynamic volume of the solute molecule. According to this result, $k_S = 1$ at the theta temperature when concentration is in volume fraction. The experimen-

tal evidence is that $D(C)$ decreases with concentration at the theta temperature and increases in good solvents[4-7].

In this paper we re-examine the theory of the diffusion coefficient, and investigate the variation of k_D as a function of temperature and molecular weight. In an accompanying paper[5] we compare various theoretical predictions with the results of the recent light scattering experiments. The present theoretical approach differs from the earlier studies in several respects. First, we obtained the expression of the diffusion coefficient from the generalized Langevin equation satisfied by the intermediate scattering function, rather than using Gibbs–Duhem formulation. This approach distinguishes between the short-time (D_0), and the long-time (D) diffusion coefficients. D_0 yields the Kirkwood's approximation[1] to the diffusion coefficient, and does not include the coupling between internal and centre of mass motion of the polymer. The difference $D_1 = D - D_0$ is due to this coupling as pointed out by Horta and Fixman[8] in 1968, and more recently by Fixman[9]. Fixman[9] estimated the correction D_1/D to be 1.679 for flexible chains in the zero-concentration limit, well within experimental accuracy. Here we neglect D_1 for simplicity, and investigate the concentration dependence of the dominant contribution D_0. We show that in this approximation, k_D can be expressed quite generally in terms of the pair correlation function of molecules, and the equilibrium segment distribution about the centre of mass. The previous results follow as special model calculations. Secondly, the present approach indicates the possibility of explaining the observed decrease in $D(C)$ with concentration at the theta temperature, at least in part, in terms of an increase in the chain dimensions of two overlapping molecules. Finally, the present calculations show the inadequacy of describing the chain dimension by a single radius; one needs the hydrodynamic radius R_H, radius of gyration R_G and the effective range $\bar{S}$ of the intermolecular interaction to characterize polymer dimensions in finite concentrations. These dimensions are temperature dependent, and their ratios influence the variation of k_D with temperature.

THEORY

In light scattering experiments, the diffusion coefficient is determined by representing the measured normalized intermediate scattering function $S(q,t)$ by $\exp(-Dq^2t)$. In order to observe the translational diffusion only, the momentum transfer wave number q is adjusted so that $qR_G \ll 1$. The time interval of the experiment is adjusted in such a way that $S(q,t)$ decays appreciably but yet remains above the noise level, i.e., $Dq^2t \sim 1$. Hence, we must investigate $S(q,t)$ in the limit of $q\to 0$, $t\to\infty$ but $q^2t=$fixed, which is known as the Markov limit. $S(q,t)$ satisfies the generalized Langevin equation as shown by Akcasu and Gurol[10]:

$$\dot{S}(\underline{q},t) = -\Omega(q)S(\underline{q},t) + \int_0^t du\varphi(\underline{q},u)S(\underline{q},t-u) \qquad (1)$$

where $\Omega(q)$ is the negative of the initial slope of $S(q,t)$. $\Omega(q)$ is also referred to as the 'first cumulant', 'characteristic frequency' and the 'relaxation frequency' in the literature. $\varphi(q,t)$ is the memory function. In the Markov limit (1) yields $\dot{S} = -Dq^2S$ with

$$D = D_0 - D_1 \qquad (2)$$

$$D_0 \equiv \lim_{q\to 0}\frac{1}{q^2}\Omega(q) \qquad (3)$$

and

$$D_1 = \lim_{q\to 0}\frac{1}{q^2}\int_0^\infty du\,\varphi(q,u) \qquad (4)$$

We show elsewhere[11] that D_1 is the same as the Fixman[9] correction, and arises from the deformation in the intramolecular segment distribution as a result the translational motion of the molecule. If the intramolecular distribution is approximated by its equilibrium form, $D_1 = 0$ and $D = D_0$ which indeed corresponds to the diffusion coefficient in the Krikwood[1] approximation as shown in reference 10. Since D_0 is obtained from the initial slope $\Omega(q)$ as indicated in equation (3), it describes the initial diffusion for short times. The current estimates of the correction term D_0/D is well within the experimental accuracy[9]. Here we ignore D_1 and focus our attention on D_0, and drop the subscript '0' henceforth.

The first cumulant $\Omega(q)$ is obtained as[10]

$$\Omega(q) = \frac{\langle \rho^*\mathscr{L}\rho\rangle}{\langle \rho^*\rho\rangle} \qquad (5)$$

where

$$\rho(\underline{q}) \equiv \sum_{d=1}^N \exp(i\underline{q}\cdot\underline{R}_j)$$

and denotes the Fourier transform of the monomer density. We do no distinguish between the density fluctuations $\delta\rho(\underline{q})=\rho(\underline{q})-N\delta_{\underline{q},0}$, and the density ρ because we always assume that $q\neq 0$ even when $q\to 0$. $\underline{R}_j$ denotes the positions of the monomers that are assumed to be identical. The cornered bracket implies thermal

average over the equilibrium configuration-space distribution function $\psi_0(\underline{R}_1,...,\underline{R}_n)$. N is the total number of monomers in the system of volume V. $\mathscr{L}$ is a linear time-independent operator operating on the monomer coordinates, and governs the time-evolution of ρ through $\dot{\rho} = -\mathscr{L}\rho$. When $\mathscr{L}$ is modelled as the adjoint of the Kirkwood–Riseman diffusion operator we obtain from equations (3) and (5)

$$D = \lim_{q\to 0}\left[\frac{1}{NS(\underline{q})}\sum_{j,k=1}^N \langle D^{jk}\exp(i\underline{q}\cdot\underline{R}_{jk})\rangle\right] \qquad (6)$$

where the z-axis is parallel to $\underline{q}$. D^{jk} denotes $\underline{q}\cdot\underline{D}^{jk}\cdot\underline{q}/q^2$, where $\underline{D}^{jk}$ is the conventional diffusion tensor in the Kirkwood–Riseman theory[1], and is defined as

$$D^{jk} = k_BT[\xi^{-1} + (1-\delta_{jk})T^{jk}] \qquad (7)$$

Here also $T^{jk} = \underline{q}\cdot\underline{T}(\underline{R}_{jk})\cdot\underline{q}/q^2$, where $\underline{T}(\underline{R})$ is the usual Oseen tensor[3], and is given by

$$T(\underline{R}) = (1+\cos^2\theta)/8\pi\eta R \qquad (8)$$

where θ is the angle between $\underline{q}$ and $\underline{R}$. In equations (7) and (8) k_BT is the temperature of the solution, ξ is the friction coefficient per monomer, and η is the viscosity of the solvent. In equation (6), we have also introduced the static structure factor $S(\underline{q})$:

$$S(\underline{q}) = N^{-1}\langle \rho^*\rho\rangle \qquad (9)$$

In the zero concentration limit, we may set $q\to 0$ in equation (6) and obtain with $S(q\to 0)=N$

$$D(0) = N^{-2}\sum_{j,k=1}^N \langle D^{jk}\rangle \qquad (10)$$

which is the diffusion coefficient in the Kirkwood approximation at the theta temperature. The temperature dependence of $D(0)$ has been investigated through equation (10) by modelling the equilibrium distribution $\psi_0(\underline{R}_{jk})$ to include the excluded volume effects[12]. At finite concentrations the limit $q\to 0$ will be taken at a later stage to avoid divergencies when the thermodynamic limits are taken[13]. Equation (6) can be cast into

$$D(C) = \lim_{q\to 0}\left\{[D_m/S(\underline{q}.C)]\left[1+\frac{\xi}{(2\pi)^3}\int d\underline{k}\,T(\underline{q}-\underline{k})[S(\underline{k},C)-1]\right]\right\} \qquad (11)$$

where $D_m = k_BT/\xi$ and denotes the diffusion coefficient of an isolated monomer (or bead). $T(\underline{k})$ is the Fourier transform of $T(\underline{R})$:

$$T(\underline{k}) = (1-\cos^2\alpha)/\eta k^2 \qquad (12)$$

where α is the angle between $\underline{k}$ and $\underline{q}$. The form of equation (11) is interesting because it expresses the diffusion coefficient as a function of the static structure factor. The temperature and concentration dependence of $D(C)$ is implicit in $S(q,C)$.

The small-q limit of $S(q,C)$ is well known:

$$S(q\to 0,C) = n[1+n_p\int d^3R\,g(R)] \qquad (13)$$

where n_p and n are the number of polymers per unit volume and monomers per molecule, respectively. $g(R)$ is the pair correlation function at finite concentration. The concentration, as well as the temperature dependence of $g(R)$ has been investigated numerically by Koyoma[14] using the B–G–Y integral equation and the Flory–Kriegbaum potential for the intermolecular pair potential $V(R)$. In this work we need $g(R)$ only in the zero concentration limit where it is given by

$$g(R) = \exp[-V(R)/k_B T] - 1 \qquad (14)$$

In the lowest order in concentration $S(q \to 0, C)$ is expressed in terms of the second virial coefficient A_2 for the osmotic pressure:

$$S(q \to 0, C) = n[1 - (n_p/N_A)2M^2 A_2] \qquad (15)$$

It is convenient to introduce two characteristic lengths at this stage of the analysis. The first is the effective radius of interaction $\bar{S}$ defined by

$$A_2 \equiv (16\pi N_A/3M^2)\bar{S}^3 \qquad (16)$$

This is simply a measure of A_2 in length units, and represents the hard sphere radius that yields the correct virial coefficient when $V(R)$ in equation (14) is represented by a hard sphere potential with a range of $2\bar{S}$. It increases with temperature and vanishes at the theta temperature.

The second characteristic length is the hydrodynamic radius R_H defined by

$$R_H \equiv k_B T / 6\pi\eta D(0) \qquad (17)$$

where $D(0)$ is the diffusion coefficient in the zero concentration limit. Both R_H and $D(0)$ are functions of temperature. Their temperature dependence was discussed in detail elsewhere[12].

With these definitions equation (15) can be written as

$$S(q \to 0, C) = n(1 - 8X^3 C) \qquad (18a)$$

where $\qquad X \equiv \bar{S}/R_H \qquad (18b)$

and $\qquad C \equiv 4\pi R_H^3 n_p/3 \qquad (18c)$

The definition of the volume fractions C in equation (18c), to replace the polymer concentration n_p, in terms of the hydrodynamic volume $V_H = 4\pi R_H^3/3$ is only for convenience. The radius of gyration R_G could also be used to introduce volume fraction. Since $R_G(T)/R_H(T)$ is available for an isolated molecule as function of temperature[15,16] the final results can be expressed easily in one of these two choices at any temperature.

In equation (11) we need the concentration dependence of $S(q, C)$ for all values of q. In the lowest order in concentration we obtain (see Appendix A)

$$S(q, C) = S_s(q) + (N_p - 1)[S_p(q) - S_s(q)] \qquad (19)$$

where $S_s(q)$ is the static structure factor of a single isolated chain, N_p is the number of polymer molecules, and $S_p(q)$ is the static structure factor of a pair of identical molecules in the infinite dilution limit, i.e.,

$$S_p(q) \equiv \frac{1}{2n} \sum_{A,B=1}^{2} \sum_{\alpha,\beta=1}^{n} \langle \exp[i q \cdot (\underline{R}_{AB} + \underline{S}_{A\alpha} - \underline{S}_{B\beta})] \rangle \qquad (20)$$

where $\underline{R}_1$ and $\underline{R}_2$ denote the centre of masses of the two molecules of the pair, $\underline{R}_{AB} = \underline{R}_A - \underline{R}_B$, and $\underline{S}_{A\alpha}$ are the position vectors of the monomers about the centre of mass. The ensemble average in equation (20) involves the jount distribution $\psi(S_1, S_2; R_1, R_2)$ at infinite dilution. Here S_A ($A = 1, 2$) denotes $\underline{S}_{A1}, \ldots \underline{S}_{An}$ collectively and describes an intramolecular state of the Ath polymer. In equations (19) and (20), and henceforth, the quantities with arguments not displaying C explicitly, are to be interpreted at infinite dilution.

The joint distribution function ψ can be factorized as $\psi = \psi_{12}(\underline{R})\psi_c(\underline{S}_1, \underline{S}_2|\underline{R})$ with $\underline{R} = \underline{R}_{12}$, where ψ_{12} denotes the distribution function of the centre of masses, and is related to the pair correlation function $g(R)$ by $\psi_{12}(R) = [1 + g(R)] V^{-2}$. The conditional distribution $\psi_c(\underline{S}_1 \underline{S}_2|\underline{R})$ includes the deformation in the intramolecular distributions during a binary encounter of two molecules when the separation distance of their centre of masses is $\underline{R}$. Clearly $\psi_c(\underline{S}_1, \underline{S}_2|\underline{R}) \to \psi_0(\underline{S}_1)\psi_0(\underline{S}_2)$ as $|\underline{R}| \to \infty$, where $\psi_0(\underline{S})$ represents the intramolecular monomer distribution of an isolated molecule. It will be shown that the observed concentration dependence of the diffusion coefficient at the theta temperature may be attributed to the correlation $[\psi_c(\underline{S}_1, \underline{S}_2|\underline{R}) - \psi_0(\underline{S}_1)\psi_0(\underline{S}_2)]$ of the intramolecular distributions.

We observe from equation (20) that

$$S_p(q \to 0) = n[1 + \delta_{q,0} + V^{-1}\int d\underline{R}\, g(R)] \qquad (21)$$

which yields $S_p(q \to 0) = n[1 + \delta_{q,0}]$ in the limit of $V \to \infty$. In particular $S_p(q \to 0) = n$ when $q \neq 0$ but is extremely small.

Substituting equation (20) into equation (11) we find

$$D(C) = D\{1 + N_p[D_p/D - 1]\}[1 - 8X^3 C]^{-1} \qquad (22)$$

where D denotes the short time translational diffusion coefficient of an isolated chain, which is obtained from equation (11), replacing $S(\underline{k}, C)$ by $S_s(\underline{k})$ and using $S_s(0) = n$, as

$$D = (D_m/n)\left[1 + (\zeta/8\pi^3)\int d\underline{q}\, T(-\underline{q})[S_s(\underline{q}) - 1]\right] \qquad (23a)$$

or, replacing $T(\underline{k})$ by its directional average $\langle T(\underline{k}) \rangle = 2/3\eta k^2$, as

$$D = (D_m/n)\left[1 + (\zeta/3\eta\pi^2)\int_0^{\infty} dq[S_s(q) - 1]\right] \qquad (23b)$$

Equation (23b) leads to Kirkwood's approximation for the diffusion coefficient when $S_s(q)$ is calculated for a Gaussian unperturbed chain.

D_p in equation (22) denotes the translational diffusion coefficient of the centre of mass of a pair of molecules at infinite dilution limit, and defined by

$$D_p = \lim_{q \to 0}(D_m/n)\{1 + (\zeta/8\pi^3)\int d\underline{k}\, T(\underline{q} - \underline{k})[S_p(\underline{k}) - 1]\} \qquad (24)$$

where $S_p(\underline{k})$ is defined in equation (20). The calculation of the concentration dependence of the diffusion coefficient

has now been reduced to the calculation of $S_p(q)$, the static structure factor of an isolated pair of molecules.

We mention parenthetically that the concentration dependence of the first cumulant $\Omega(q,C)$ at any q can be obtained in a similar way as

$$\Omega(q,C) = \Omega(q))\{1 + N_p[\Omega_p(q)S_p(\underline{q})/\Omega(q)S_s(\underline{q}) - 1]\}\cdot$$

(25a)

$$\{1 + N_p[S_p(\underline{q})/S_s(\underline{q}) - 1]\}^{-1}$$

where $\Omega_p(q)$ and $\Omega(q)$ are the first cumulants of a pair of molecules and a single molecule, respectively, and are defined by

$$\Omega_p(q) \equiv q^2 S_p^{-1}(\underline{q})D_m\left\{1 + (\xi/8\pi^3)\int d\underline{k}\, T(\underline{q}-\underline{k})[S_p(\underline{k}) - 1]\right\}$$

(25b)

and a similar expression for $\Omega(q)$ in which $S_p(\underline{q})$ is replaced by $S_s(\underline{q})$. Equation (25) provides a convenient starting point for the investigation of concentration effects on the first cumulant especially in the intermediate q-region. Although such an investigation is desirable in view of the recent emphasis on light and neutron scattering experiments in this q-region, in which the first cumulant is measured[18], we focus our attention here, to the translational diffusion coefficient only.

The pair structure function $S_p(\underline{q})$ in equation (20) can be written as

$$S_p(\underline{q}) = V^{-1}\int d\underline{R}[1 + g(R)]S_p(q|R)$$

(26a)

where $S_p(q|R)$ denotes the static structure factor of a pair of molecules separated by a distance R. Its definition follows from equation (20) as the directional average, with respect to the directions of R, of

$$S_p(q|\underline{R}) = n^{-1}\langle|\rho(\underline{q})|^2\rangle_c + n^{-1}Re[\langle\rho_A(\underline{q})\rho_B(-\underline{q})\rangle_c\exp(i\underline{q}\cdot\underline{R})]$$

(26b)

where $\underline{R} = \underline{R}_{AB}$, and denotes the vector distance between the centre of masses of the pair of molecules, and $\rho_A(\underline{q})$ and $\rho_B(\underline{q})$ are densities about the centre of mass, i.e.,

$$\rho_A(\underline{q}) = \sum_{j=1}^{n}\exp(i\underline{q}\cdot\underline{S}_{Aj})$$

(26c)

The overall averages in the first and second terms of equation (26b) are the conditional averages with $\psi_c(\underline{S}|\underline{R})$ and $\psi_c(\underline{S}_A,\underline{S}_B|\underline{R})$, respectively. In order to separate the contribution of the correlation between the intramolecular distributions we first introduce S_p^0 $(q|R)$ which is calculated by ignoring the aforementioned correlations. Its definition follows from equation (26b) by replacing the conditional distributions $\psi_c(\underline{S}|\underline{R})$ and $\psi_c(\underline{S}_A,\underline{S}_B|\underline{R})$ by $\psi_0(\underline{S})$ and $\psi_0(\underline{S}_A)\psi_0(\underline{S}_B)$ respectively. One obtains from equation (26b)

$$S_p^0(q|R) = S_s(q) + n^{-1}j_0(qR)|\langle\rho(\underline{q})\rangle|^2$$

(27)

where $j_0(x)$ is the spherical Bessel function of order zero. We then express $S_p(\underline{q})$ in equation (26a) as

$$S_p(\underline{q}) = (4\pi/V)\int_0^\infty dR\, R^2[1 + g(R)][S_p(q|R) - S_p^0(q|R)]$$

$$+ (4\pi/V)\int_0^\infty dR\, R^2[1 + g(R)]S_p^0(q|R) \quad (28)$$

The first term in equation (28) now represents the effect of the deformation in the intramolecular distributions of a pair of molecules. The integrand vanishes where $R > 2R_c$ where R_c is the range of the correlations between the intramolecular distributions (see Appendix A).

We now introduce, using equations (26b) and (27) in equation (24), $D_p(R)$ and $D_p^0(R)$ as

$$D_p(R) = (D_m/2n)\left\{1 + (\xi/3\eta\pi^2)\int_0^\infty dk[S_p(k|R) - 1]\right\}$$

(29a)

and

$$D_p^0(R) = (D/2)\left[1 + (2R_H/\pi n^2)\int_0^\infty dk\, j_0(kR)|\langle\rho(k)\rangle|^2\right] \quad (29b)$$

where we have also used $\langle T(\underline{k})\rangle = (2/3\eta k^2)$, $S_p(q\to0|R) = 2n$ and $T(\underline{q}) = 0$ (cf. equation (12) with $\alpha = 0$). The latter removes infinities as $V\to\infty$[13]. $D_p(R)$ and D_p^0 (R) denote, respectively, the translational diffusion coefficients of a randomly oriented pair of molecules separated by a distance R with and without correlations between intramolecular distributions.

We may digress to present the explicit forms of $S_p^0(q|R)$ and $D_p^0(R)$ when the mean monomer density $\langle\rho(\underline{q})\rangle$ in equation (29b) is approximated by a Gaussian distribution[1], i.e., $\langle\rho\rangle = n\exp[-q^2R_G^2/6]$. In this case equation (27) becomes

$$S_p^0(q|R) = S_s(q) + nj_0(qR)\exp(-q^2R_G^2/3) \quad (30a)$$

which is the static structure factor of a pair of molecules separated by a distance R in the absence of correlations. Similarly, equation (29b) yields after some algebra involving equation (33a):

$$D_p^0(R) = (D/2)[1 + (R_H/R)\mathrm{erf}(\sqrt{3}R/2R_G)] \quad (30b)$$

which is the translational diffusion coefficient of a pair of molecules, in the absence of correlations, as a function of the separation distance. The second terms in equation (30b) account for the hydrodynamic interaction. When $R\to\infty$, D_p^0 $(R)\to D/2$ as expected, D_p^0 $((0) = (D/2)[1 + (R_H/R_G) (3/\pi)^{1/2}]$ which is the diffusion coefficient of the pair when the molecules completely overlap. At the theta temperature $R_H/R_G = 0.664$[12,13] and the enhancement due to the hydrodynamic interaction is about 1.65.

Combining equations (22), (24) and (28), we express $D(C)$ as

$$D(C) = D(1 - k_SC)/(1 - 8X^3C) \quad (31)$$

where $k_S = k_{SO} + k_{SC}$ and

$$k_{SO} = -(3/2\pi^2 R_H^2) \int_0^x dq\, g(q) |\langle \rho(q)\rangle|^2 / n^2 \qquad (32a)$$

$$k_{SC} = (6/R_H^3 D) \int_0^{2R_c} dR\, R^2 \exp[-V(R)/k_B T][D_p^0(R) - D_p(R)] \qquad (32b)$$

The definition of $D_p(R)$ and $D_p^0(R)$ are given in equation (29). Equation (31) determines the concentration dependence of the diffusion coefficient in the lowest order in concentration in terms of the diffusion coefficients of a pair of molecules and a single molecule at the infinite dilution limit. At the theta temperature $V(R) = 0$, $X = 0$ and $g(k) = 0$ so that $D(C) = D[1 - k_{SC}C]$. The coefficient k_{SC} vanishes when the correlation between the intramolecular monomer distributions is neglected because then $D_p^0(R) = D_p(R)$ as discussed above. Equation (31) yields the short-time diffusion coefficient exactly. However, it corresponds to Kirkwood's approximation to the long-time diffusion coefficient, as discussed in the Introduction. The rest of this paper is devoted to the calculation of k_S in equation (31) using various models for $V(R)$ and $D_p(R)$ as functions of temperature and molecular weight. The validity of the final practical results is determined mainly by the accuracy of these models. Undoubtedly, better models can, and will be found in the future. The significant contribution of this paper is considered to be the general formalism presented above rather than the numerical calculations in the subsequent sections.

Calculation of k_{SO}

We start with equation (32a) and substitute $\langle \rho(q) \rangle = n \exp[-q^2 R_G^2/6]$ for the mean density. We obtain, after some algebra involving

$$\int_0^\infty dt\, \exp(-t^2/\gamma)\sin(Rt)/t = (\pi/2)\mathrm{erf}(\gamma R/2) \qquad (33a)$$

the following expression:

$$k_{SO} = -(3/R_H^2) \int_0^x dR\, R\, g(R)\mathrm{erf}(\sqrt{3}R/2R_G) \qquad (33b)$$

In order to calculate k_{SO} explicitly we need $g(R)$, which we approximate using three well-known models for the mean intermolecular potential $V(R)$ in equation (14).

Hard sphere model. Using $V(R) = 0$ for $R > 2\bar{S}$ and $V(R) = \infty$ for $R < 2\bar{S}$, where $\bar{S}$ is the radius of interaction introduced in equation (16), one obtains from equations (14) and (33a)

$$k_{SO} = 6X^2 Z(\sqrt{3}X R_H/R_G) \qquad (34)$$

where

$$Z(u) \equiv (1/2u^2)[(2u^2 - 1)\mathrm{erf}(u) + (2/\sqrt{\pi})u\exp(-u^2)] \qquad (35)$$

One can verify for future reference that $Z(\infty) = 1$, and $Z(x) \to (4x/3\sqrt{\pi})$ as $x \to 0$. It is noted that the result k_{SO}

$= 6(\bar{S}/R_H)$, obtained by Akcasu and Benmouna[13] in good solvents by approximating the distance between two monomers belonging to two different chains by the separation distance between the centre of the masses, follows from equation (34) with $R_G \to 0$. The result by Altenberger and Deutch[11] for hard spheres is obtained by further assuming that $\bar{S} = R_H$. The variation of k_{SO} with $\bar{S}/R_H$ will be discussed later.

Uniform-density sphere model[19]. This model assumes

$$V(R)/k_B T = K\bar{z}(1-x)^2(2+x) \quad , \quad x \leqslant 1$$
$$V(R)/k_B T = 0 \quad , \quad x \geqslant 1 \qquad (36a)$$

where $x \equiv R/2R_0$, and R_0 is the radius of the sphere with uniform segment density. The constant K is given by

$$K \equiv 3\sqrt{\pi}(R_G/R_0)^3 \qquad (36b)$$

and $\bar{z}$ is the conventional modified excluded volume parameter

$$\bar{z} = (1/4\pi)^{3/2} v N^2 / R_G^3 \qquad (36c)$$

where v is the binary cluster integral for a pair of segments. Using this potential in equations (14) and (33b) we obtain

$$k_{SO} = 4(R_H/R_0) X^3 Y_1(\bar{z})/Y_2(\bar{z}) \qquad (37)$$

where

$$Y_1(\bar{z}) \equiv \int_0^1 dx\, x\{1 - \exp[K\bar{z}(1-x)^2(2+x)]\} \cdot \mathrm{erf}[\sqrt{3}x(R_0/R_G)] \qquad (38a)$$

and

$$Y_2(\bar{z}) \equiv \int_0^1 dx\, x^2\{1 - \exp[-K\bar{z}(1-x)^2(2+x)]\} \qquad (38b)$$

In obtaining equation (37) we multiplied and divided the right hand side of equation (33b) by $\bar{S}^3$ and used in the denominator

$$\bar{S}^3 = (3/8) \int_0^\infty dR\, R^2[1 - \exp(-V(R)/K_B T)] \qquad (39a)$$

which yields the relation between $\bar{S}$ and $\bar{z}$ in the present model as

$$(\bar{S}/R_0) = [3 Y_2(\bar{z})]^{1/3} \qquad (39b)$$

Since A_2 and hence $\bar{S}$ are measurable quantities, only the ratio $Y_1(\bar{z})/Y_2(\bar{z})$ in equation (37) is calculated approximately with the model potential. The ratio (R_G/R_0) enters equation (38a) as an adjustable parameter. We adopt $(R_G/R_0) \approx 1.185$ that corresponds to $K = 8.85$ used by Yamakawa[1] in the calculations of A_2 using equation (39). Note that $\bar{S} \to R_0$ in the good solvent limit of $\bar{z} \to \infty$. Since $R_H/R_G = 0.537$ in this limit[15], we find $\bar{S}/R_H = 1.57$ as the

maximum value of $\bar{S}/R_H$. One also observes in equation (38a) that $Y_1(\infty) = Z(\sqrt{3}R_0/R_G)/2$ where $Z(x)$ is defined in equation (35). Hence in the good solvent limit we find $k_{SO} = 6(\bar{S}/R_H)^2 Z(\sqrt{3}\bar{S}/R_G)$ which is identical to the value of k_{SO} in the hard sphere case. Using, $(\bar{S}/R_H) = 1.57$, $R_G/\bar{S} = 1.185$, and $Z(1.5) = 0.79$, one obtains the maximum value of k_{SO} as $k_{SO} = 11.68$.

Flory-Krigbaum potential[20]. Using:

$$V(R)/k_B T \equiv U \exp(-3R^2/4 R_G^2) \qquad (40)$$

where $U \equiv 3\sqrt{3}\,\bar{z}$, in equations (14) and (33b) we obtain

$$k_{SO} = 4(6/\pi)^{1/2}(R_H/R_G)X^3 F_1(U)/F_2(U) \qquad (41)$$

with

$$F_1(U) \equiv \sqrt{2} \int_0^\infty dx \cdot x[1 - \exp(-Ue^{-x^2})] \int_0^x dt \exp(-t^2) \qquad (42a)$$

and

$$F_2(U) \equiv \int_0^\infty dx \cdot x^2[1 - \exp(-Ue^{-x^2})] \qquad (42b)$$

$\bar{S}$ is related to $\bar{z}$ in this model by

$$\bar{S}/R_G = [F_2(U)/\sqrt{3}]^{1/3} \qquad (42c)$$

One can express $F_1(U)$ and $F_2(U)$ as infinite series in powers of U as was done in the calculation of A_2 by Flory and Krigbaum. We note that $F_1(0)/F_2(0) = 1$ and $F_1(U)/F_2(U) \rightarrow (3/4)(2\pi)^{1/2}/(\text{Ln}U)^{1/2}$ as $U \rightarrow \infty$. From equations (42b) and (42c) we also find $\bar{S}/R_G \rightarrow (\text{Ln}U/\sqrt{3})^{1/2}$. The implication is that $\bar{S}/R_G$ and k_{SO} diverge at the limit of $\bar{z} \rightarrow \infty$ in the present model.

Calculation of k_{SC}

We start with equation (32b). We need explicit forms of $V(R)$, $D_p(R)$ and $D_p^0(R)$ to be able to calculate k_{SC}. $D_p^0(R)$ has already been calculated in equation (30b) for a Gaussian chain, and in equation (B-5) (see Appendix B) in the case of uniform density sphere model. The main difficulty in calculating k_{SC} lies in formulating the translational diffusion coefficient of a pair of molecules, i.e., $D_p(R)$, in the presence of correlations between intramolecular distributions. We consider two models.

Prolate ellipsoid model. In this model $D_p(R)$ is taken as the translational diffusion coefficient of a randomly oriented prolate ellipsoid[21] with a major axis $(R_0 + R/2)$ and a minor axis R_0, so that

$$D_p(R)/D = (2x + x^2)^{-1/2} \text{Ln}[1 + x + (2x + x^2)^{1/2}], 0 \leqslant x \leqslant 1$$

where $x = R/2R_0$. Pyun and Fixman[3] used this model in their work on the friction coefficient. They chose the cut-off R_c in equation (32b) and R_0 as the hydrodynamic radius R_H, and modelled $V(R)$ as the potential calculated for uniform density spheres of radius R_0. In order to make

contact with their work, we add and subtract $1/2$ in the integrand in equation (32b), and split k_{SC} into two parts: $k_{SC} = k'_{SC} + k''_{SC}$. The first part involves $D_p(R)/D$, i.e.,

$$k'_{SC} = -(6/R_H^3) \int_0^{2R_c} dR\, R^2 \left[\frac{D_p(R)}{D} - \frac{1}{2}\right] \exp[-V(R)k_B T] \qquad (43a)$$

which, in the prolate ellipsoid model, leads to

$$k'_{SC} = -24(R_0/R_H)^3 \int_0^1 dx \cdot x^2 \exp[-A(1-x)^2(2+x)]$$

$$\cdot \{2(2x + x^2)^{-1/2} \text{Ln}[1 + x + (2x + x^2)^{1/2}] - 1\} \qquad (43b)$$

with $x = R/2R_0$.

Equation (43b) reduces to $-K(A)$ introduced by Pyun and Fixman[3] (equation 51 in their work) with $A = K\bar{z}$ defined by equations (36b) and (36c), and $R_0 = R_H$. The second part involves $D_p^0(R)/D$, i.e.,

$$k''_{SC} = (6/R_H^3) \int_0^{2R_c} dR\, R^2 \left[\frac{D_p^0(R)}{D} - \frac{1}{2}\right] \exp[-V(R)/k_B T] \qquad (44)$$

It is interesting to note that the analysis by Pyun and Fixman[3] corresponds to a different separation of k_S as $k_S = -K(A) + (k_{SO} + k''_{SC})$. Starting from equations (22) and (24) one can show that k_{SO} and k_{SC} can be combined as

$$k_{SO} + k''_{SC} = -(9\eta/4\pi^2 R_H^2)\lim_{q \to 0} \int dk \left\{ T(q-k)|\langle \rho(k)\rangle|^2 n^{-2} \right.$$

$$\left. \int_{2R_c}^\infty dR\, R^2 j_0(kR)[1 + g(R)] \right\} \qquad (45)$$

Treating the polymers as spheres of radius R_H, and modifying the description of the hydrodynamic interactions between the spheres[3,22], Pyun and Fixman calculated equation (45) directly, with a different set of approximations, as $k_{SO} + k_{SC} = 7.16$. In the present analysis we separated k_{SO} and k''_{SC} by expressing the integration over R in equation (45) as the difference of integrations $(0, \infty)$ and $(0, 2R_c)$. The first part yields k_{SO} as given in equation (32a). The second part leads to

$$k''_{SC} = (6/\pi R_H^2) \int_0^{2R_c} dR\, R^2\, e^{-V(R)/k_B T} \int_0^\infty dk j_0(kR)|\langle \rho(\underline{k})\rangle|^2/n^2 \qquad (46)$$

which is identical to equation (44) with $D_p^0(R)/D$ from equation (29b). This procedure enables one to take the limit of $q \to 0$ using $T(\underline{q}) = 0$ (cf. equation (12)) and

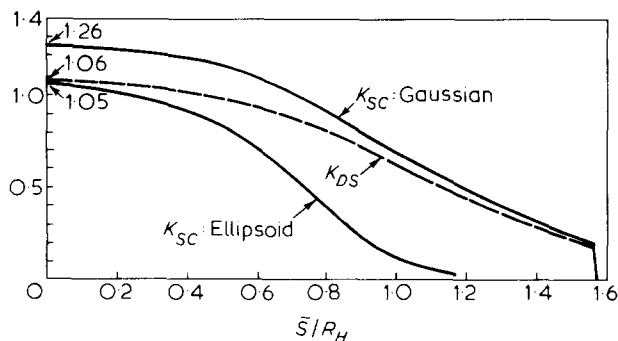$$\delta(\underline{k}) = (2\pi^2) \int_0^\infty dR\, R^2 j_0(kR)$$

Figure 1 The variation of k_S-Ellipsoid (equation 47), k_{SC}-Gaussian (equations (51) and (52)) and k_{DS} for self-diffusion (equation 64)

in obtaining the expression of k_{SO} in equation (32a). Note that $k_{SO} = 0$ at the theta temperature because it depends only on $g(R)$.

Pyun and Fixman evaluated k'_{SC} numerically using equation (43b) with $R_0 = R_H$. At the theta temperature they found $k'_{SC} = -4.948$ which resulted in $k_S = 7.16 - 4.948 = 2.21$. If we treat the polymers as point-particle scatterers without any internal structure, to be consistent with the ellipsoid model used in k'_{SC}, so that $\langle \rho(k) \rangle / n = 1$, we obtain $k''_{SC} = 6(R_0/R_H)^2$ at the theta temperature, which leads to $k_S = 6 - 4.948 = 1.052$ when $R_0 = R_H$. This value is close to $k_S = 1$ given by Yamakawa in his book[1].

In conclusion, the prolate ellipsoid model yields k_{SC} as a function of temperature as

$$k_{SC} = 12(R_0/R_H)^2 \int_0^1 dx\, x\, e^{-V(x)/k_BT} \left\{ 1 - 2x(R_0/R_H) \right.$$

$$\left. \cdot [2(2x + x^2)^{-1/2} \mathrm{Ln}\{1 + x + (2x + x^2)^{1/2}\} - 1] \right\} \quad (47)$$

which is obtained from equations (43b) and (46) with $\langle \rho(k) \rangle / n = 1$ and $x = R/2R_0$. The latter approximation in calculating k''_{SC} may be relaxed by taking into account the distribution of monomers within a chain. For example, one finds (see Appendix B)

$$k''_{SC} = 5.4(R_0/R_H)^2 \quad (48a)$$

in the case of a uniform density sphere of radius R_0, and

$$k''_{SC} = 6(R_c/R_H)^2 Z(\sqrt{3}\, R_c/R_G) \quad (48b)$$

in the case of a Gaussian chain. In equation (48b) the cut-off R_c is not specified. These results, however, are not consistent with the ellipsoid model for k'_{SC}, and hence we do not discuss them any further. We end this section by pointing out the sensitivity of k_{SC} to the choice of (R_0/R_H) in equation (47). For example at $T = \theta$, equation (47) reduces to $k_{SC} = (R_0/R_H)^2[6 - 4.948(R_0/R_H)]$ which yields 1.31 when $R_0/R_H = 0.808$ (maximum value), and vanishes when $R_0/R_H \cong 1.216$. The latter value is close to $R_0/R_H = (R_0/R_G)(R_G/R_H) = (1.185 \times 0.664)^{-1} = 1.271$, which corresponds to the value used in the calculation of A_2 (cf. equation (38)). In *Figure 1*, we plot k_{SC} as function of $\bar{S}/R_H$ as calculated from equation (47) with $R_0 = R_H$ and $\beta V(x) = A(1 - x)^2(2 + x)$, for comparison with the following model.

Gaussian chain model. In order to include the effect of intramolecular distribution on k_{SC}, we calculate $D_p^0(R)$ and $D_p(R)$ in the case of two Gaussian chains. The expression of $D_p^0(R)$ in this case was obtained in equation (30b) which we reproduce here in a slightly different form

$$D_p^0(R) = \tfrac{1}{2}D(R_G) + (k_BT/12\pi\eta R)\mathrm{erf}(\sqrt{3}R/2R_G) \quad (49)$$

In order to be able to calculate $D_p(R)$ in the presence of correlations between intramolecular distributions, we assume that they remain Gaussian during the binary encounter but only the radius of gyration varies with the intermolecular distance R. We let $R_G(R) = R_G + \Delta R_G(R)$ where R_G refers to $R_G(\infty)$ which is the radius of gyration of an isolated chain. This assumption enables one to obtain $D_p(R)$ from equation (29a) as

$$D_p(R) = \tfrac{1}{2}D[R_G(R)] + (k_BT/12\pi\eta R)\mathrm{erf}[\sqrt{3}R/2R_G(R)] \quad (50a)$$

which has the same form as in equation (49), for $D_p^0(R)$ is also obtained assuming a Gaussian chain with R_G. We note that $D[R_G(R)]$ in equation (50a) is the diffusion coefficient for a single Gaussian chain with $R_G(R)$. Treating $\Delta R_G(R)$ as a small quantity we expand $D_p(R)$ into a Taylor series to obtain

$$[D_p(R) - D_p^0(R)]/D = (-1/2)[1 + (R_H/R_G)(3/\pi)^{1/2}$$

$$\cdot \exp(-3R^2/4R_G^2)][\Delta R_G(R)/R_G] \quad (50b)$$

Both R_H and R_G in this expression are temperature dependent. Substitution of equation (50b) into equation (32b) yields

$$k_{SC} = 24 \int_0^\infty dx\, x^2 \frac{\Delta R_G(x)}{R_G} [1 + \alpha(3/\pi)^{1/2}\exp(-3\alpha^2 x^2)]$$

$$\exp[-V(x)/k_BT] \quad (51)$$

where $\alpha \equiv R_H/R_G$ and $x \equiv R/2R_H$. Here $\Delta R_G(x)$ contains the cut-off distance R_c implicitly. Unfortunately there is no theoretical model for $\Delta R_G(x)/R_G$ at present. The recent Monte Carlo calculations by Olaj, *et al.*[23] suggest a form (*Figure 1a*, op. cit., we ignore the negative portion of $R_G(x)$ for large x in this figure)

$$R_G^2(R)/R_G^2 = 1 + B\exp[-R^2/\sigma^2 R_G^2]$$

with $B \cong 0.2$ and $\sigma^2 \cong$ for 4-way cubic lattice under θ-condition, and a chain length $R_G^2 = 11.41$ lattice unit. Hence

$$\Delta R_G(x)/R_G \cong (B/2)\exp[-(4\alpha^2/\sigma^2)x^2] \quad (52)$$

Substituting equation (52) in equation (51b) we obtain at the theta temperature with $V(x) = 0$

$$k_{SC} = (3\sqrt{\pi}/8)B(\sigma/\alpha)^3 \{1 + \alpha(3/\pi)^{1/2}[1 + (3/4)\sigma^2]^{-3/2}\} \quad (53)$$

The value of $\alpha = R_H/R_G$ is 0.664 under theta conditions. If we use $B = 0.2$ and $\sigma^2 = 3/4$, we find $k_{SC} = 0.393$. The numerical value of k_{SC} is sensitive to the choice of σ which
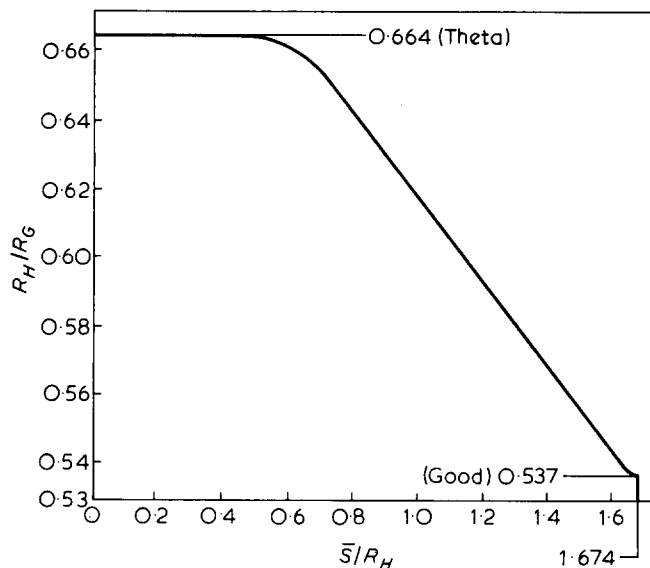
Figure 2 The variation of R_H/R_G with $\bar{S}/R_H$ that combines both molecular weight and temperature dependence of R_H/R_G

ference 19. *Figure 2* shows the variation of R_H/R_G with the reduced variable $X = \bar{S}/R_H$, in which the values of R_H/R_G are taken from reference 24. We converted N/N_τ to X as follows: In the improved blob theory of the swelling factor α_S numerically coincides[24] with the Flory formula $\alpha_S^5 - \alpha_S^3 = 1.67z$. Using $\bar{z} = z/\alpha_S^3$ we find $N/N_\tau = 6.22\bar{z}^2 (1 + 1.67\bar{z})^3$. Alternatively, $\bar{S}/R_H$ can be expressed as $\bar{S}/R_H = (R_G/R_H) [3\sqrt{\pi}/4\psi(\bar{z})]^{1/3}$ as discussed and referenced by Yamakawa[1] (equations 20.83). The values of R_H/R_G as a function of N/N_τ are given in reference 24. Elimination of $\bar{z}$ yields $\bar{S}/R_H$ as a function of N/N_τ. *Figure 3* shows $\bar{S}/R_H$ as a function of $\bar{z}$. Other choices of $\psi(\bar{z})$ than the one used in this procedure are possible as discussed by Yamakawa[1]. In this particular model the maximum value of $\bar{S}/R_H$ as $\bar{z} \to \infty$ (good solvent limit) turns out to be 1.674 if one uses $\psi(\infty) = (1/1.828)^1$. One also finds $\bar{S}/R_G = 0.988$ in this limit. It is observed in *Figure 2* that $\bar{S}/R_H \cong 0.75$ marks the transition from the theta $(\bar{S}/R_H = 0)$ to a good solvent behaviour.

Curve 3 in *Figure 4* shows the variation of k_D with X in the case of the hard sphere model. It is calculated using equation (54) in which k_{SO} and k_{SC} are determined through
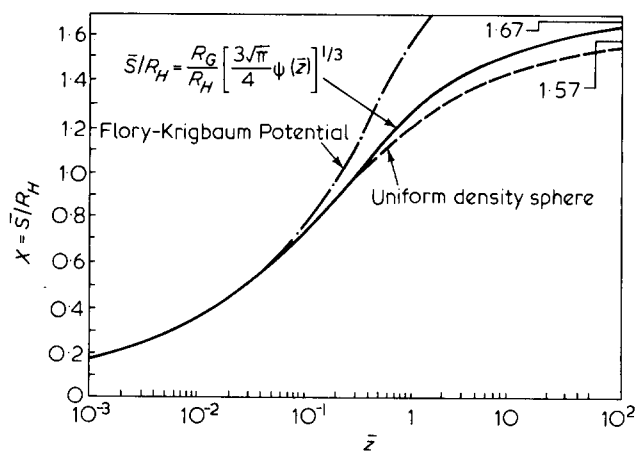
characterizes the range of the intermolecular correlations in equation (52) through σR_G. For example if we choose this range as $2R_H$, i.e., $\sigma = 2\alpha$, as was done in the ellipsoid model, then we find $k_{SC} \cong 1.26$. In the absence of a more reliable estimate of $\Delta R_G(R)$ it is impossible to narrow down the predictions of the theory. We use $\sigma = 2\alpha$ and $B = 0.2$ in the following numerical evaluation of k_{SC} through equations (51) and (52) with the uniform density sphere potential $\beta V(x) = 8.85\bar{z}(1 - y)^2(2 + y)$ for $y \leqslant 1$ and $\beta V(x) = 0$ for $y \geqslant 1$ where $y = R/2R_0 = x(R_H/R_0) = 1.185\alpha x$. The variation of k_{SC} with $\bar{S}/R_H$ is shown in *Figure 1*.

Numerical calculations

In the lowest order in concentration, equation (31) reduces to $D(C) = D[1 + k_D C]$ where

$$k_D = 8X^3 - k_{SO} - k_{SC} \tag{54}$$

The definition of k_{SO} and k_{SC} are given by equation (32a) and (32b) respectively. In this section we present the numerical evaluation of k_{SO}, k_{SC} and k_D, and discuss the variation of k_D with temperature and molecular weight for various models on a comparative basis. We use $X = \bar{S}/R_H$ as the independent variable which combines both molecular and temperature dependences. Moreover both $\bar{S}$, through the second virial coefficient, and R_H, through D, can be measured in the zero concentration limit.

Contrary to some of the earlier calculations of $k_D^{3,17}$ in which a polymer is characterized by a constant radius, three different dimensions, i.e., R_G, R_H and $\bar{S}$ are needed in the present analysis to describe the temperature dependence of k_D. They enter the calculations as ratios. The variation of R_H/R_G with temperature was calculated by Akcasu and Han[19] using the blob hypothesis. Recently, Akcasu, *et al*[24], refined these calculations by improving the blob hypothesis, and presented the variation of $\alpha_S = R_G(T)/R_G(\theta)$ $\alpha_H(T)/R_H(\theta)$, and $R_H(T))/R_G(T)$ as function of N/N_τ. The latter can be related to the excluded volume parameter z by $N/N_\tau = 6.22z^2$ as shown in re-

Figure 3 The variation of $\bar{S}/R_H$ as function of $\bar{z}$ in various theoretical models
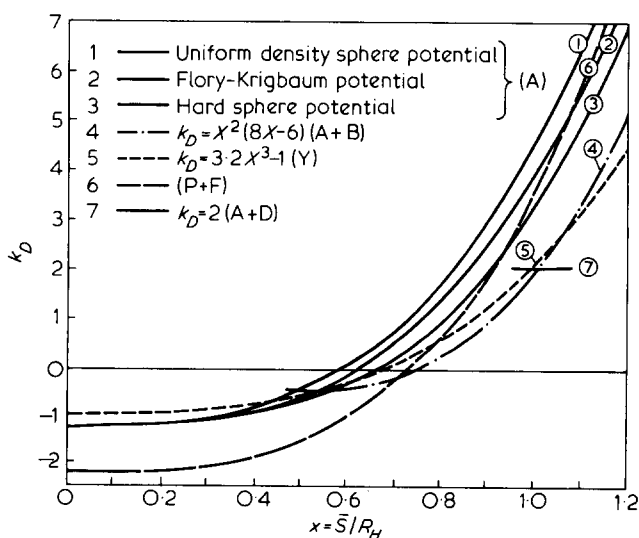

Figure 4 The variation of k_D in $D(C) = D(0) (1 + Ck_D)$ as function of $\bar{S}/R_H$ which combines both molecular weight and temperature dependence of k_D for various theoretical models

equations (34) and (51), respectively. $Z(\sqrt{3}\,XR_H/R_G)$ in equation (34) is calculated from equation (35). The values of R_H/R_G are taken from *Figure 2*. The values of k_{SC} are given in *Figure 1*. The way k_{SC} is calculated will be discussed shortly.

The variation of k_D in the case of the uniform density sphere model is shown in *Figure 4* by curve 1. k_{SO} in this case is obtained from equations (37) and (38). To be consistent, we related the parameter $\bar{z}$ to $\bar{S}$ through equation (39) using $\beta V(R) = 8.85\bar{z}(1 - x)^2(2 + x)$. The values of R_H/R_G as function of $\bar{z}$ are again taken from reference 24, i.e., those obtained with the modified blob hypothesis. As indicated in *Figure 3*, the maximum value of $\bar{S}/R_H$ as $\bar{z} \to \infty$ is 1.57 instead of 1.674 obtained previously using $S/R_G = [(3\pi^{1/2}/4)\psi(\bar{z})]^{1/3}$. The values of k_{SC}, that are used in *Figure 4*, are obtained from equation (51) with the uniform density sphere potential for $\beta V(R)$, and the consistent relationship between $\bar{z}$ and $\bar{S}/R_H$. The same values of k_{SC} have been used in all the three model calculations for simplicity because, first k_{SC}(theta) is the same in all three cases, and secondly k_{SC} contributes insignificantly to k_S when $\bar{S}/R_H \geqslant 1$ where the above subtleties make no difference.

Finally, we determined k_S in the case of Flory–Krigbaum potential from equations (41) and (42), and related $\bar{S}$ to $\bar{z}$ again through equation (39) consistently. The variation of k_D in this case is shown by curve 2 in *Figure 4*.

Curve 4 is plotted using

$$k_D = X^2(8X - 6) \tag{55}$$

which was obtained by Akcasu and Benmouna[13] approximating the vector distance between a pair of monomers belonging to two different polymers by the distance between the centre of masses. This approximation, which is the only one to get equation (55), is justified in good solvents where the interpenetration of molecules is not significant. Indeed it agrees well, when $X = \bar{S}/R_H \geqslant 0.7$, with the fresult corresponding to Flory–Krigbaum potential, as well as with

$$k_D = 3.2X^3 - 1 \tag{56}$$

given by Yamakawa[1].

Curve 6 in *Figure 4* represents

$$k_D = 8X^3 - 7.16 + K(A) \tag{57}$$

which was given by Pyun and Fixman[3]. We calculated $K(A)$ as a function of $\bar{z}$ from equation (43b) with the uniform-density sphere potential and $R_0 = R_H$, and relating $\bar{z}$ to $\bar{S}/R_H$ consistently.

The maximum value of the reduced variable $\bar{S}/R_H$ in the good solvent limit is calculated from

$$(S/R_H) = (R_G/R_H)[(3\pi^{1/2}/4)\psi(\bar{z})]^{1/3}$$

with $R_H/R_G \to 0.537$ and $\psi(\infty)$. The values of the interpenetration function in the limit of $\bar{z} \to \infty$ depends on the theoretical model used. With the notations of Yamakawa[1] we have $\psi(\infty) = 0.198$ (K, equations 20.77), 0.174 (FCM, equations 20.55) and 0.547 (KY, equations 20.83). The corresponding limiting values of $\bar{S}/R_H$ are, respectively, 1.19, 1.14 and 1.67. Using the published A_2-

data for polystyrene in benzene at 25°C and 30°C, Cotton[25] recently determined $\psi(\infty)$ as 0.245. The latter yields $\bar{S}/R_H \to 1.28$. As pointed out earlier, $\bar{S}/R_H$ diverges logarithmically as $\to \infty$ in the Flory–Krigbaum theory. In *Figure 4* we intentionally did not mark the maximum value of $\bar{S}/R_H$.

Self-diffusion

The self-diffusion coefficent, D_S, of a labelled chain in the presence of other unlabelled molecules has a different concentration dependence than that of $D(C)$ for the diffusion of density fluctuations. The definition of D_S follows from equation (6) as

$$D_S(C) = (D_m/n)\left[1 + (\xi/n)\sum_{j,k=1}^{n} '\langle T^{jk}\rangle\right] \tag{58}$$

where the summation over j and k involves only the monomers of the labelled chain. Following the same procedure leading to equation (11), we express D_S as

$$D_S(C) = (D_m/n)\left\{1 + (\xi/8\pi^3)\int d\underline{k}\, T(-\underline{k})[S_s(\underline{k}) - 1]\right\} \tag{59}$$

where $S_s(\underline{k})$ is the static structure factor of the labelled chain. The concentration dependence of D_S is implicit in $S_s(\underline{k})$. The latter would be independent of concentration in dilute solutions according to the blob hypothesis because the size of a concentration blob is larger than the dimensions of the labelled chain in the dilute regime. In this section we calculate the concentration dependence of D_S in the lowest order in C using the same perturbation analysis discussed in the text. We present only the main steps in the derivations. Expressing $D_S(C)$ as $D_S(C) = D[1 - Ck_{DS}]$ where D is the diffusion coefficient of a single chain in infinite dilution we find:

$$k_{DS} = -4\pi n_p \int_0^{2R_c} dR\, R^2 [D_{ps}^0(R)/D - 1]\exp[-\beta V(R)] \tag{60}$$

where $D_{ps}^0(R)$ is defined by:

$$D_{ps}^0(R) = (D_m/n)\left\{1 + (\xi/8\pi^3)\int d\underline{k}\, T(-\underline{k})[S_{ps}^0(k|R) - 1]\right\} \tag{61}$$

and denotes the diffusion coefficient of the labelled chain in a pair formed with an unlabelled partner at a distance R. $S_{ps}^0(k|R)$ is the static structure factor of the labelled chain in the pair. We model $D_{ps}^0(R)$, as before, as the diffusion coefficient of a Gaussian chain with an R-dependent radius of gyration, i.e., as $D_{ps}^0(R)/D = R_G/R_G(R)$. The R-dependence of $R_G(R)$ represents the effect of the unlabelled partner in the pair. Using equation (52) to model $R_G(R)$ as a Gaussian of R, we obtain:

$$k_{DS} = 12B \int_0^x dx.x^2\exp[-x^2(4\alpha^2/\sigma^2)]\exp[-\beta V(x)] \tag{62}$$

where $x \equiv R/2R_H$. We use again $B = 0.2$ and $\sigma = 2\alpha$ in

equation (62) and obtain:

$$k_{DS} = 2.4 \int_0^{\infty} dx.x^2 \exp[-x^2 - \beta V(x)] \qquad (63)$$

At the theta temperature where $V(x) = 0$, $k_{DS} = 1.063$. Its variation with temperature can be determined by specifying the intermolecular interaction potential $V(x)$. We present the results only in the case of uniform-density sphere model:

$$k_{DS} = 2.4\gamma^3 \left\{ \int_0^1 dx.x^2 \exp[-\gamma^2 x^2 - 8.85\bar{z}(1-x)^2(2+x)] \right.$$

$$\left. + \int_1^{\infty} dx.x^2 \exp(-\gamma^2 x^2) \right\} \qquad (64)$$

where $\gamma^{-1} = 1.185(R_H/R_G)$. The expression of k_{DS} in the case of Flory–Krigbaum potential can be obtained, if desired, in the form of an infinite summation. *Figure 1* shows the variation of k_{DS} with $\bar{S}/R_H$ as calculated from equation (64). The self-diffusion coefficient $D_S(C)$ and $D(C)$ coincide only in the zero-concentration limit. $D_S(C)$ always decreases with concentration, even in the good solvent limit where it drops to 0.187 from its value of 1.063 at the theta condition (see *Figure 1*), whereas $D(C)$ increases with concentration in dilute good solvents.

DISCUSSIONS

One of the points made in this paper is to show that the first cumulant $\Omega(q)$ at any q, and the short-time diffusion coefficient $D(C) = \lim \Omega(q)/q^2$ as $q \to 0$, can be expressed in terms of the static structure factor $S(q)$, within the framework of the Kirkwood–Riseman theory of solution dynamics. The functional relationship between $\Omega(q)$ and $S(q)$ is valid at any temperature and concentration. The concentration dependence of $\Omega(q)$ and $D(C)$ is implicit in $S(q)$. The chain statistics and excluded volume effects enter the analysis through $S(q)$. The present formalism thus reduces the calculation of $\Omega(q)$, which is a dynamic quantity to that of $S(q)$ which is an equilibrium property. This point is particularly interesting for relating dynamic scaling to static scaling laws.

Another point is that k_S in $D(C) = D(0)[1 - Ck_S][1 - 8CX^3]^{-1}$ is expressed in terms of the translational diffusion coefficient and the static structure factor of a pair of isolated molecules separated by a distance R. The situation is reminiscent of the kinetic theory of gases in which the concentration effects are included in the lowest order through binary interaction. An added complication in solution dynamics arises from the deformation of the intramolecular monomer distribution of the molecules of the pair during a binary encounter. The observed decrease in the diffusion coefficient with concentration at the theta temperature is attributed, here, to this deformation. The recent Monte Carlo calculations by Olaj et al.[23] provide the first quantitative demonstration of the deformation of the shapes of two molecules during a binary encounter, even under theta conditions, and yield the variation of the radius of gyration of molecules with the separation

distance R. The formalism developed in this paper shows how such detailed quantitative information about the equilibrium properties of a pair of molecules can be incorporated in the calculation of the concentration dependence of the diffusion coefficient. In fact, the decrease of $D(C)$ with concentration under theta conditions is explained, at least partly, by an increase of about 10% in the sizes of two overlapping polymers resulting from correlations in their intramolecular monomer distribution. No attempt has been made here to calculate the deformation of the molecule theoretically as a function of the separation distance.

The predictions of the various models for the concentration coefficient k_D are presented in *Figure 4*. They are compared to the experimental results in the accompanying paper. We observe in *Figure 4* that all the models predict similar trends with regard to the temperature dependence of k_D except for the hard sphere model with a constant radius (curve 7). In all cases k_D vanishes at a temperature corresponding to $\bar{S}/R_H \cong 0.72$. This value of $\bar{S}/R_H$ marks the transitions from theta to good solvent behaviour. In the good solvent region $k_D > 0$ and the diffusion coefficient increases with concentration. In this region, Yamakawa's result[1] (marked as 5) and Akcasu and Benmouna's[13] (marked as 4) are in good agreement. The latter was obtained by replacing the distance between two monomers, belonging to different molecules, by their separation distance. This assumption is justified, as pointed out by the authors, in the good solvent region where the molecular interpenetration is not significant. No other assumptions were needed to obtain $k_D = X^2(8X - 6)$. When extended to the theta region, the latter correctly predicts the sign of k_D, and the transition value $\bar{S}/R_H = 0.75$, but leads to $k_D = 0$ at the theta temperature, which is a result of neglecting interpenetration and deformation.

Altenberger and Deutch's calculations for hard spheres[17] yield $k_D = 2$ which coincides, in the vicinity of $\bar{S}/R_H = 1$, with equations (4) and (5).

The results by Pyun and Fixman[3] (marked as 6) and those obtained in this paper with various models (marked as 1, 2, and 3) predict a more rapid increase with $\bar{S}/R_H$ than the previous models, in the good solvent region. The theoretical predictions in the theta region are very sensitive to the models used to describe the translational diffusion of a pair of molecules. The values of k_D at the theta temperature ranges from -1 to -2.2. More refined models are needed in this temperature range.

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REFERENCES

1 Yamakawa, H., 'Modern Theory of Polymer Solutions', Harper and Row, New York (1971)
2 Yamakawa, H. *J. Chem. Phys.* 1962, **36**, 2995
3 Pyun, C. W. and Fixman, M. *J. Chem. Phys.* 1964, **41**, 937

4   Adam, M. and Delsanti, M. *Macromolecules* 1977, **10**, 1229
5   Han, C. C. and Akcasu, A. Z. *Polymer* 1981, **22**, 1019
6   Wandema, W. and Zeldenrust, H. *Polymer* 1977, **18**, 835
7   Selzer, J. C., to be published
8   Horta, A. and Fixman, M. *J. Am. Chem. Soc.* 1968, **90**, 3048
9   Fixman, M., to be published
10 Akcasu, A. Z. and Gurol, H. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1
11 To be submitted for publication
12 Benmouna, M. and Akcasu, A. Z. *Macromolecules* 1978, **11**, 1187
13 Akcasu, A. Z. and Benmouna, M. *Macromolecules* 1978, **11**, 1193
14 Koyama, R. *J. Phys. Soc. Jpn.*
15 Akcasu, A. Z. and Han, C. C. *Macromolecules* 1979, **12**, 276
16 Nose, T. and Chu, B. *Macromolecules* 1979, **12**, 1122
17 Altenberger, A. R. and Deutch, J. M. *J. Chem. Phys.* 1973, **59**, 894
18 Akcasu, A. Z., Benmouna, M. and Han, C. C. *Polymer* 1980, **21**, 866
19 Flory, P. J. *J. Chem. Phys.* 1945, **13**, 453; also in Reference 1
20 Flory, P. J. and Krigbaum, W. R. *J. Chem. Phys.* 1950, **18**, 1086; also in Reference 1
21 Lamb, H., 'Hydrodynamics', Dover, Sixth Ed. (1945)
22 Adelman, S. A. *J. Chem. Phys.* 1978, **68**, 49
23 Olej, F., Lantschbauer, W. and Pelinke, K. H. *Macromolecules* 1980, **13**, 299
24 Akcasu, Z. A., Benmouna, M. and Alkhafaji, S. *Macromolecules* 1981, **14**, 147
25 Cotton, J. P. *J. Phys. Lett.* 1980, **41**, 231

APPENDIX A

Concentration dependence of the structure factor

We start with

$$S(\underline{q},C) = S_s(\underline{q},C) + (N_p - 1)S_{INT}(\underline{q},C) \qquad (A-1)$$

where

$$S_s(\underline{q},C) \equiv \frac{1}{n} \sum_{\alpha,\alpha'=1}^{n} \langle \exp[i\underline{q}\cdot[\underline{S}_\alpha - \underline{S}_{\alpha'}]\rangle \qquad (A-2)$$

$$S_{INT}(\underline{q},C) \equiv \frac{1}{2n} \sum_{\substack{A,B=1}}^{2'} \sum_{\alpha,\beta=1}^{n} \langle \exp[i\underline{q}\cdot(\underline{R}_{AB}+\underline{S}_\alpha - \underline{S}_\beta)]\rangle \qquad (A-3)$$

S_s denotes the single-chain structure factor in the presence of others, and thus depends on concentration. S_{INT} represents the interference term for a pair of molecules, which, too, is a function of concentration. However, we need to evaluate it only in the zero-concentration limit, i.e., for an isolated pair of molecules, because the second term in equation (A-1) is already proportional to concentration.

The ensemble average in $S_s(\underline{q},C)$ involves the intramolecular monomer distribution $\bar{\psi}(\underline{S})$ of a single chain. We show below that its concentration dependence in the lowest order can be displayed as:

$$\psi(\underline{S}) = \psi_0(\underline{S}) + (N_p - 1)[\psi_p(\underline{S}) - \psi_0(\underline{S})] \qquad (A-4)$$

where $\psi_0(\underline{S})$ denotes the monomer distribution about its centre of mass of an isolated molecule, and $\psi_p(\underline{S})$ is the intramolecular distribution of one of the molecules in a pair. Using equation (A-4) in equation (A-2) we obtain

$$S_s(\underline{q},C) = S_s(\underline{q}) + [N_p - 1][S_{sp}(\underline{q}) - S_s(\underline{q})] \qquad (A-5)$$

where $S_s(\underline{q})$ is the structure factor of a single isolated chain, and $S_{sp}(\underline{S})$ is the structure factor of one of the molecules in a pair in the presence of the other. Substitution of equation (A-5) into (A-1) leads to equation (19) in the text with

$$S_p(\underline{q}) = S_{sp}(\underline{q}) + S_{INT}(\underline{q}) \qquad (A-6)$$

Derivation of equation A-4

The monomer distribution of a randomly selected molecule about its centre of mass can be written as:

$$\psi(\underline{S}) = \int d\underline{R}_2,..., d\underline{R}_N \psi_N(\underline{S};\underline{R}_2,..., \underline{R}_N)$$

where $\underline{S}$ denotes the positions of the monomers in the selected polymer, $\underline{R}_2;..., \underline{R}_N$ are the locations of the centre of masses of the remaining molecules, as measured from the centre of mass of the first molecule. ψ_N denotes the joint distribution in these variables. We introduce the conditional distribution $\psi_c(\underline{S}|\underline{R}_2,...,\underline{R}_N)$ as:

$$\psi_N(\underline{S};\underline{R}_2,...,\underline{R}_N) = \psi_c(\underline{S}|\underline{R}_2,...,\underline{R}_N)\psi_N(\underline{R}_2,...,\underline{R}_N) \qquad (A-7)$$

and consider a small volume Δ of radius $2R_c$ around the centre of mass of the selected molecule. The basic assumption is that the intramolecular distribution of the selected molecule is altered only when there are other molecules within Δ. This assumption is valid in the dilute regime in which the average distance between the centre of masses are larger than the molecular dimensions. Then,

$$\psi_c(\underline{S}|\underline{R}_2,...,\underline{R}_N) = \psi_0(\underline{S}) \qquad \text{, if all} \quad |\underline{R}_j| > 2R_c$$
$$= \psi_c(\underline{S}|\underline{R}_j) \qquad \text{, if only} \, |\underline{R}_j| < 2R_c$$
$$= \psi_c(\underline{S}|\underline{R}_j,\underline{R}_k), \text{ only if } |\underline{R}_j|,|\underline{R}_k| < 2R_c$$

and so on. Here, $\psi_c(\underline{S}|\underline{R})$ is the intramolecular distribution in one of the molecules of an isolated pair when their separation distance is R.

We divide the range of integration over $\underline{R}_j$ $(j = 2,...,N)$ in (A-7) as

$$\int_1 d R_j = \int_{V-\Delta} d R_j + \int_\Delta d R_j$$

Then

$$\psi(S) = \psi_0(S)\left({}^N\prod^{j=2} \int_{V-\Delta} d R_j \right)\psi_N(R_2...R_N)$$

$$+ \sum_{k=2}^{N} \int_\Delta d R_k \psi_c(S|R_k)\left(\prod_{\substack{j=2 \\ j \neq k}}^{N} \int_{V-\Delta} d R_j \right)\psi_N(R_2,...R_N) \qquad (A-8)$$

$$+ ....$$

We expand the integration on $\underline{R}_j$ in the first term of equation (A-8) once more:

$$\prod_{j=2}^{N} \int_{V-\Delta} d R_j = \prod_{j=2}^{N}\left(\int_V d R_j - \int_{V-\Delta} d R_j \right)$$

and use the normalization

$$\prod_{j=2}^{N} \int_1 d\underline{R}_j \psi_N(\underline{R}_2,...,\underline{R}_N) = 1$$

Then we find

$$\psi(\underline{S}) = \psi_0(\underline{S})\left[1 - \sum_{k=2}^{N} \int_{\Delta} d\underline{R}_k \psi_{12}(\underline{R}_k) + \ldots\right]$$

$$+ \sum_{k=2}^{N} \int_{\Delta} d\underline{R}_k \psi_c(\underline{S}|\underline{R}_k)\psi_{12}(\underline{R}_k) + \ldots \quad \text{(A-9)}$$

In the second term of equation (A-8) the range of integration $V - \Delta$ is replaced by V because the procedure applied to the first term leads to higher order terms in concentration. $\psi_{12}(\underline{R})$ is the pair distribution function. Rearranging equation (A-9) we obtain

$$\psi(\underline{S}) \cong \psi_0(\underline{S}) + (N_p - 1)\int_{R < 2R_c} d\underline{R}\,\psi_{12}(R)[\psi_c(\underline{S}|\underline{R}) - \psi_0(\underline{S})]$$

$$\text{(A-10)}$$

or

$$\psi(\underline{S}) \cong \psi_0(\underline{S}) + n_p \int_{R < 2R_c} d\underline{R}[1 + g(R)][\psi_c(\underline{S}|\underline{R}) - \psi_0(\underline{S})]$$

Since the integrand vanishes for $R > 2R_c$, we may extend the range of integration in equation (A-10) to the entire volume, and obtain equation (A-4).

APPENDIX B

Uniform density model

In this model one assumes that the monomers are uniformly and independently distributed within a sphere of radius R_0 and volume V_0. Hence $\psi_1(\underline{S})$ for an isolated chain is approximated by

$$\psi_1(\underline{S}) = V_0^{-n}\prod_{j=1}^{n} U(R_0 - |\underline{S}_j|) \quad \text{(B-1)}$$

where $U(x)$ is the step function. The static structure factor is found as

$$S_s(\underline{q}) = 1 + (n-1)[3j_1(qR_0)/qR_0]^2 \quad \text{(B-2)}$$

where $j_1(x)$ is the spherical Bessel function of order unity. The diffusion coefficient of a single molecule is calculated

substituting equation (B-2) into equation (23b) as

$$D = k_B T[(1/n\xi) + (1/5\pi\eta R_0)] \quad \text{(B-2)}$$

where we replaced $(n-1)/n$ by unity and used

$$\int_0^{\infty} dx\,j_1^2(x)/x^2 \cong \pi/15 \quad \text{(B-3)}$$

It is interesting to note that the friction coefficient for such a molecule is $5\pi\eta R_0$ instead of $6\pi\eta R_0$.

$S_p^0(q|R)$ follows from equation (27) with equation (B-2) as

$$S_p^0(q|R) = S_s(q) + n^{-1}j_0(qR)[3nj_1(qR_0)/qR_0]^2 \quad \text{(B-4)}$$

The translational diffusion coefficient for a pair of molecules in the absence distortion of the intramolecular distributions follows from equation (29b) with equation (B-4) as

$$D_p^0(R) = (D/2)\left[1 + (18|\pi)(R_H/R_0)\int_0^{\infty} dx.x^{-2}j_1^2(x)j^0(xR/R^0)\right]$$

$$\text{(B-5)}$$

In particular we find

$$D_p^0(0) = D - k_B T/2n\xi \quad \text{(B-6)}$$

In prolate ellipsoid model we need

$$(6/R_H^2)\int_0^{2R_0} dR\,R^2[D_p^0(R)/D - 1]$$

Substituting $D_p^0(R)/D$ from equation (B-5) we evaluate this quantity as $5.4(R_0/R_H)^2$ using

$$\int_0^{\infty} dx[j_1(x)/x]^2[j_0(2x/2x] \cong \pi/80 \quad \text{(B-7)}$$

We have demonstrated equations (B-7) and (B-3) only numerically.