Moderately concentrated solutions of polystyrene: 4. Elastic and quasi-elastic light scattering at the Flory theta temperature*

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Elastic and quasi-elastic light scattering data are given for moderately concentrated solutions of a polystyrene ($M_w = 8.6 \times 10^5$) in cyclohexane at the Flory theta temperature. The concentrations studied gave $[\eta]c$ from 0.6 to 8.3, with $[\eta] = 76 \, \mathrm{cm^3 \, g^{-1}}$. A maximum in the scattered intensity *versus* scattering angle is discussed in terms of a net repulsion among chain centres obtaining at the Flory theta temperature. A double-exponential decay observed in the quasi-elastic light scattering behaviour is discussed in terms of a model involving relaxation effects giving rise to a q-independent exponential component, and one that depends on q^2. As predicted by the model, these effects are more pronounced at the Flory theta temperature than in good solvents.

INTRODUCTION

In parts 1–3 (refs. 1–3, respectively), moderately concentrated solutions of polystyrene were studied near the upper or lower critical consolute temperatures, so that the second virial coefficient A_2 is about zero[4,5]. It was found in part 2 that the Rayleigh ratio $R(q, c)$ exhibited a maximum as a function of the modulus q of the scattering vector q for concentrations c such that $(6.8 N_A R_G^3/M)c \approx [\eta]c$ is in the range 1 to 6, where R_G is the root-mean-square radius of gyration at infinite dilution, M is the molecular weight and $[\eta]$ is the intrinsic viscosity. In this study we will report the photon-count correlation function $g^{(1)}(\tau; q, c)$ for similar solutions under conditions for which $A_2 = 0$. The correlation function will be represented as[6,7]:

$$g^{(2)}(\tau; q, c) - 1 = [g^{(2)}(0; q, c) - 1][g^{(1)}(\tau; q, c)]^2 \quad (1)$$

$$g^{(1)}(\tau; q, c) = \sum_{v=1}^{m} r_v \exp(-\gamma_v K_1 \tau) \quad (2)$$

where r_v and γ_v may each depend on q and c, $\sum r_v = 1$, and the first cumulant K_1 is given by:

$$K_1(q, c) = -\lim_{\tau=0} \frac{\partial g^{(1)}(\tau; q, c)}{\partial \tau} \quad (3)$$

With use of equation (2), $\sum r_v \gamma_v = 1$.

It is convenient to discuss $R(q, c)$ and $K_1(q, c)$ in terms of the repeat-unit pair correlation function $g(r)$[7,8]. Thus:

$$R(q, c) = KcMP(q, c)F(q, c) \quad (4)$$

$$MP(q, c)F(q, c)/m_0 = \int_V g(r) \exp(i\boldsymbol{q} \cdot \boldsymbol{r}) \, d\boldsymbol{r} \quad (5)$$

where $P(q, c)$ and $F(q, c)$ are the intramolecular and intermolecular structure factors, respectively, and M and m_0 are the molecular weights of the polymer chain and the repeat unit, respectively. An expression for $K_1(q, c)$ in terms of $g(r)$ is discussed below, as are specific functions to represent $P(q, c)$ and $F(q, c)$. We note, however, that for a monodisperse solute $F(0, c)$ is related to the equilibrium osmotic modulus K_{OS}:

$$K_{OS} = c \, \partial \Pi / \partial c = cRT/MF(0, c) \quad (6)$$

Furthermore, in the following, we will express $F(q, c)$ in terms of $P(q, c)$, a q-dependent interference factor $H(q, c)$ and a q-independent function $\Gamma(c)$[2,7]:

$$F^{-1}(q, c) = 1 + cP(q, c)H(q, c)\Gamma(c) \quad (7)$$

where both $P(q, c)$ and $H(q, c)$ are unity for zero q, so that:

$$\frac{KcM}{R(0, c)} = F^{-1}(0, c) = 1 + c\Gamma(c) \quad (8)$$

In most cases, $F(0, c) \leqslant 1$ (for a polymer solution, exceptions to the latter would usually correspond to incipient phase separation). In the limit for large q, $F(\infty, c) = 1$, and $P^{-1}(q, c)$ tends to proportionality with q^ε, where ε is model-specific, e.g. $\varepsilon = 2$ for a random-flight chain[7,8]. Since $P(q, c)$ decreases and $F(q, c)$ increases with increasing q (excepting extrema that occur with certain models, e.g. hard spheres[9]), a maximum in $R(q, c)$ *versus* q is possible for $q > 0$. Such a maximum will occur if $\partial \ln R(q, c)/\partial q^2 = 0$, where

$$\frac{\partial \ln R(q, c)}{\partial q^2} = \frac{\partial \ln P(q, c)}{\partial q^2}\left(1 + \frac{\partial \ln F(q, c)}{\partial \ln P(q, c)}\right) \quad (9)$$

Thus, if $P(q, c)$ exhibits no extrema for $q > 0$, then maxima in $R(q, c)$ require $\partial \ln F/\partial \ln P = -1$. As discussed below, with dilute solutions, $H(q, c)$ is often nearly unity, in

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which case $-\partial \ln F/\partial \ln P$ cannot be unity. The behaviour for moderately concentrated solutions is discussed in the following.

The first cumulant may be expressed in terms of an apparent diffusion constant $D_{app}(q, c)$ defined as[7,8]:

$$D_{app}(q, c) = K_1(q, c)/q^2 \qquad (10)$$

where (with neglect of a factor of the solvent volume fraction, which is nearly unity for c of interest here):

$$D_{app}(q, c) = \frac{M}{N_A \Xi(q, c)} \frac{M_{LS}(q, c)}{c} \qquad (11)$$

Here, $M_{LS}(q, c) = cRT/MP((q, c)F(q, c)$ and $\Xi(q, c)$ reduces to the translational friction coefficient Ξ^0 at infinite dilution. For $qR_G \ll 1$, $D_{app}(q, c)$ reduces to the mutual diffusion coefficient, given by:

$$D_M(c) = K_{OS}/\zeta_M \qquad (12)$$

where $\zeta_M = N_A \Xi(c)c/M$ is the friction factor per unit volume, with $\Xi(c)$ equal to $\Xi(0, c)$. This expression will be compared with experimental data on solutions at the Flory theta temperature in the following.

Of course, $\Xi(c)$ reduces to $\Xi^0 = kT/D_T^0$ at infinite dilution, with D_T^0 the translational diffusion constant, and in that same limit $K_{OS} = cRT/M$, making $D_M(c)$ equal to D_T^0 at infinite dilution. In the following, it is convenient to express Ξ^0 in terms of a hydrodynamic radius, as:

$$R_H = \Xi^0/6\pi\eta_S \qquad (13)$$

with η_S the solvent viscosity.

An approximate dynamic model has been presented leading to $g^{(1)}(\tau; q, c)$ in the form of equation (2) with $m = 2^{10,11}$. A slightly modified development of that model is given in the Appendix, where it is shown that the parameters in equation (2) are given by:

$$r_1 = 1 - r_2 = (1 - \gamma_2)/(\gamma_1 - \gamma_2) \qquad (14)$$

$$\gamma_n = \frac{1}{2\kappa}\{(1 + f\kappa) - (-1)^n[(1 + f\kappa)^2 - 4\kappa]^{1/2}\} \qquad (15)$$

where $\kappa = K_1\tau_R$ and $f = 1 + \Delta L/L$. Here, L is defined as $K_{OS} + \frac{4}{3}G_e$, with G_e the equilibrium modulus, and τ_R is a time constant for the (assumed) exponential relaxation of fluctuations ΔL. The behaviour predicted by equations (14) and (15) is shown in *Figure 1*. As discussed below, possible values of ΔL may include the relaxation of fluctuations ΔK in the osmotic modulus or ΔG in the shear modulus. With this model:

$$K_1(q, c) = q^2 D_M(c) = q^2 L/\zeta_M \qquad (16)$$

If $f \approx 1$, $g^{(1)}(\tau; q, c)$ collapses to a single exponential term at all q. However, if $f > 1$, two exponential terms contribute to $g^{(1)}(\tau; q, c)$. The limiting values of $\gamma_1 K_1/q^2$ and $\gamma_2 K_1$ predicted for $fD_M q^2\tau_R > 1$ are independent of q, and equal to $D_{gel} = fD_M$ and $(f\tau_R)^{-1}$, respectively, where:

$$D_{gel} = (L + \Delta L)/\zeta_M \qquad (17)$$

Thus, for $q^2 D_{gel}\tau_R > 1$, the scattering probes the response of a viscoelastic pseudo-gel, with a diffusion coefficient D_{gel} proportional to the unrelaxed modulus $L + \Delta L$, and a characteristic relaxation time $f\tau_R$. Because $\gamma_2 \leqslant \gamma_1$, the contributions with subscripts 2 and 1 are sometimes referred to as the slow and fast modes, respectively[10,11]. For larger q, the weighting factor of the exponential term with $\gamma_2 K_1 = (f\tau_R)^{-1}$ is given by $r_2 = (f-1)/f$. Thus, this contribution is negligible if $f - 1 = \Delta L/L \ll 1$.

For a swollen crosslinked polymer gel, $L = K_{OS} + \frac{4}{3}G_e$, and one can expect comparable relaxation times for the relaxation of fluctuations in the osmotic and shear moduli, so that $\Delta L = \Delta K + \frac{4}{3}\Delta G$. Further, since τ_R will be of the order of the longest Rouse relaxation time for the chain between crosslink loci, it is unlikely that $\tau_R D_M(c)q^2$ could become large enough to cause observable non-exponential behaviour in $g^{(1)}(\tau; q, c)$ on the light scattering timescale, even if $f > 1$. Equivalently, the effective values of $K_{OS}(0)$ and $G(0)$ on the light scattering timescale are normally so close to the equilibrium values K_{OS} and G_e, respectively, that $\Delta L \approx 0$ and $f = 1$, as assumed in the first use of the preceding treatment, made to explain the observed exponential $g^{(1)}(\tau; q, c)$ for polymer gels[12].

For a polymer solution, as studied here, $G_e = 0$, or $L = K_{OS}$, so that $\Delta K \ll \Delta G = G(0)$. In this case, D_{gel} refers to the pseudo-gel behaviour arising from entanglement constraints. Although the osmotic-modulus relaxation time may remain of the order of the longest Rouse relaxation time, the shear-modulus relaxation time may be considerably larger if c is large enough to produce entanglement effects[3,13,14]. In the latter case, τ_R becomes the shear-modulus relaxation time. In any case, since $\Delta K \ll \Delta G$, it will be assumed that $\frac{3}{4}\Delta L \approx \Delta G = G(0)$, and that on the light scattering timescale $G(0)$ may be approximated by the pseudo-network modulus G_N, given by[7,8]:

$$G_N = \frac{cRT}{M_e}\left(\frac{c}{\rho}\right)^{1+s'} \qquad (18)$$

where M_e is the molecular weight between entanglement loci (for undiluted polymer) and ρ is the polymer density. The exponent s' is zero for a solution with $A_2 = 0$, but may be larger for a solution with $A_2 \gg 0$; see below[7,8]. Since the relaxation of the shear modulus is dominant,
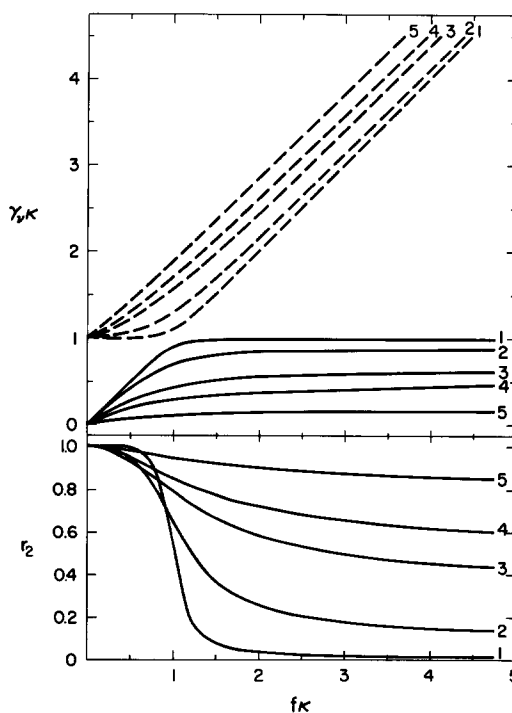

Figure 1 The parameters given by equations (14) and (15) as a function of $f\kappa = fK_1\tau_R$ for various values of f: bottom, r_2; top, $\gamma_1\kappa$ (----) and $\gamma_2\kappa$ (——). Values of f are 1.01, 1.1, 1.5, 2.0 and 5.0 for curves 1 through 5, respectively

$\Delta L = 4G_N/3$ and $f \approx 1 + 4G_N/3K_{OS}$. With equations (6) and (18):

$$\frac{G_N}{K_{OS}} = \frac{M}{M_e} F(0, c) \left(\frac{c}{\rho}\right)^{1+s'} \tag{19}$$

Thus, f will tend to be larger with poor solvent than with good solvent conditions owing to the factor $F(0, c)$; see below. As c is reduced to the level below which entanglement effects no longer sustain the pseudo-network needed to make $G(0) \approx G_N$, τ_R becomes of the order of the longest Rouse relaxation time, and $G(0)$ is no longer approximated by G_N. An approximate measure of this concentration may be the concentration c'' such that for $c > c''$ the steady-state recoverable compliance $R^{(S)}$ is proportional to G_N^{-1} with G_N given by equation (18). Typically, c''/c' is 2–4, where c' is the concentration for an abrupt change in $\partial \ln \eta / \partial \ln c$ (see part 1).

EXPERIMENTAL

The materials used here are described in parts 1 and 2, and the light scattering methods are described elsewhere[7,15]. Polystyrene PC 6a was used in this study. Conical shaped cells (6 ml) were used, as in part 2. Solutions were filtered into the clean cells through a membrane filter (0.45 μm pore size), and sealed under vacuum after degassing. The cells were then centrifuged in a swinging bucket rotor (5000g). The (unnormalized) photon-count correlation function $G^{(2)}(k; \Delta \tau)$ was computed from M sets of data, each set comprising $T = 2^{12}$ sampling intervals, with each interval of duration $\Delta \tau$[15]:

$$G^{(2)}(k; \Delta \tau) = \frac{1}{MT} \sum_{i=1}^{M} \left(\sum_{j=1}^{T} n_j n_{j+k} \right)_i \tag{20}$$

where n_j is the photon-count number in the jth interval, and k is an integer. In the instrument used, $\Delta \tau$ may be set equal to $(3.2/\mu s)2^N$, where N may be varied from 0 to 16, and k may be varied from 1 to 512. Data were collected over a range of $\Delta \tau$ and k sufficient to characterize curvature in $g^{(2)}(\tau; q, c)$ for $g^{(2)}(\tau; q, c) - 1 \gtrsim 10^{-3}$. Here, $g^{(2)}(\tau; q, c)$ was calculated as the ratio $G^{(2)}(k; \Delta \tau)/G^{(2)}(\infty; \Delta \tau)$ at q and c, with $\tau = k\Delta \tau$, and $G^{(2)}(\infty; \Delta \tau)$ calculated as the square of the mean count rate $\langle n \rangle$ per interval, averaged over the M independent experiments[15]; M was adjusted to make the total number of counts $MT\langle n \rangle$ of order 10^6. For example, $\Delta \tau$ could be made small and k large to span the entire range in τ needed in even increments, or the needed range could be spanned by a combination of experiments at different $\Delta \tau$ and k, so that larger increments are used for large than for small τ.

Static light scattering was measured with the same apparatus using a beam expander to form a scattering volume about 3 mm in height. As described elsewhere[15], the incident beam was chopped and the data acquisition system was used to determine the mean count rate free of contributions from dark current. A secondary standard was used to calibrate the response to an absolute Rayleigh ratio, as discussed elsewhere[15]. Reproducibility of $R(q, c)$ was within 0.5% over a period of months.

RESULTS

Elastic scattering

For dilute solutions, the experimental results give

$M_w = 8.66 \times 10^5$ and $R_G = 27.0$ nm, in good accord with results reported in the literature[16,17]. The intrinsic viscosity is equal to 76 ml g^{-1} in cyclohexane at the Flory theta temperature.

As shown in *Figure 2*, for $T = \Theta$ the scattering $R(q, c)$ exhibits a maximum for $q^{-1} = q_M^{-1} \approx 40$–50 nm for $[\eta]c$ in the range 2–10, similar to the behaviour reported in part 2. We remark, however, that although the q_M and the $R(q, c)$ for $q > q_M$ obtained here are similar to those reported in part 2, the value of $\partial R(q, c)/\partial q^2$ for $q < q_M$ obtained here is smaller than that found in the earlier work using cyclopentane. As with the previous study, the maximum in $R(q, c)$ is lost with increasing T.

The dependence of $R(0, c)/c$ on c shows that $\Gamma(c)$ depends on c, even when $A_2 = 0$. With the results obtained here, $\Gamma(c) > 0$, even though $A_2 = 0$; see below. Values of $\Gamma(c)$ are given in *Figure 3*. The results give somewhat larger $\Gamma(c)$ than computed from data on $\partial \pi / \partial c$ given in ref. 18 for the lower $c[\eta]$ range, but agree with data on $\Gamma(c)$ given in ref. 19 for larger $c[\eta]$. The reason for the discrepancy at the lower $c[\eta]$ is unknown to us. It is assumed that $P(q, c) = P(q, 0)$ at the Flory theta temperature, so that $H(q, c)$ may be computed from the observed $R(q, c)$, with the results shown in *Figure 4*. The decrease of $H(q, c)$ with increasing q for small q is a reflection of the maximum in $R(q, c)$. (It should be noted that the function $H(q, c)$ was denoted $Q(q, c)$ in part 2, but the notation is changed here to avoid confusion with a function introduced in the following, denoted $Q(q)$ by convention.)

As in part 2, $H(q, c)$ will be represented by the empirical expressions:

$$H(q, c) = \sum_{v=1}^{2} H_v(q, c) \tag{21a}$$

$$H_v(q, c) = h_v(c) \exp(-2\varepsilon_v a^2 q^2) \tag{21b}$$

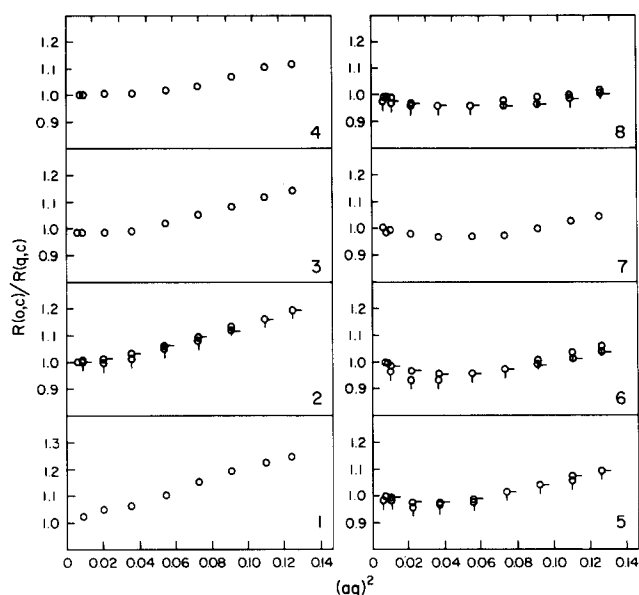$$2a^2 = \lim_{q=0} \frac{\partial P^{-1}(q, c)}{\partial q^2} \tag{22}$$

Figure 2 Plots of $R(0, c)/R(q, c)$ *versus* $(aq)^2$ for solutions of polystyrene in cyclohexane at 34.8°C: $[\eta]c$ equals 0.091, 0.60, 1.15, 1.73, 2.68, 4.64, 4.69, 6.54 for panels 1 through 8, respectively; $a = 11$ nm. Data for experiments on a given sample at different times are identified by the pips
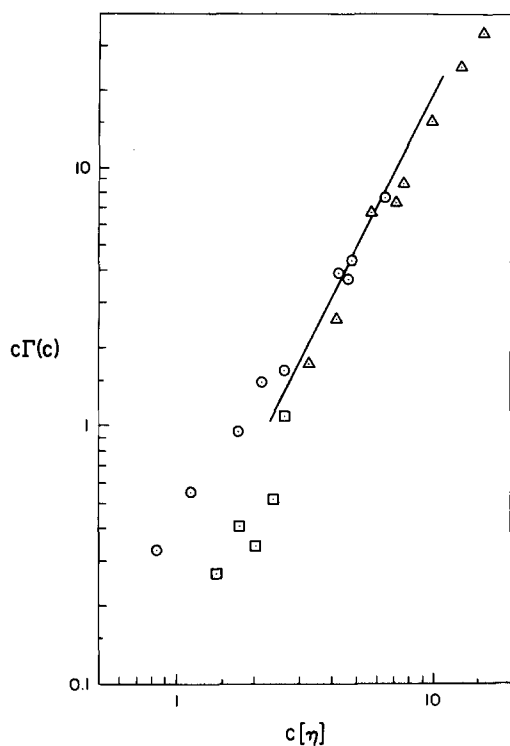
Figure 3 Bilogarithmic plot of $c\Gamma(c)$ *versus* $[\eta]c$ for solutions of polystyrene in cyclohexane at 34.8°C. The circles, squares and triangles are for data reported here and in refs 18 and 19, respectively. The full line represents equations (32) and (33) with $k_3 = 0.195$ (i.e. $c\Gamma(c) = 0.195(c[\eta])^2$)
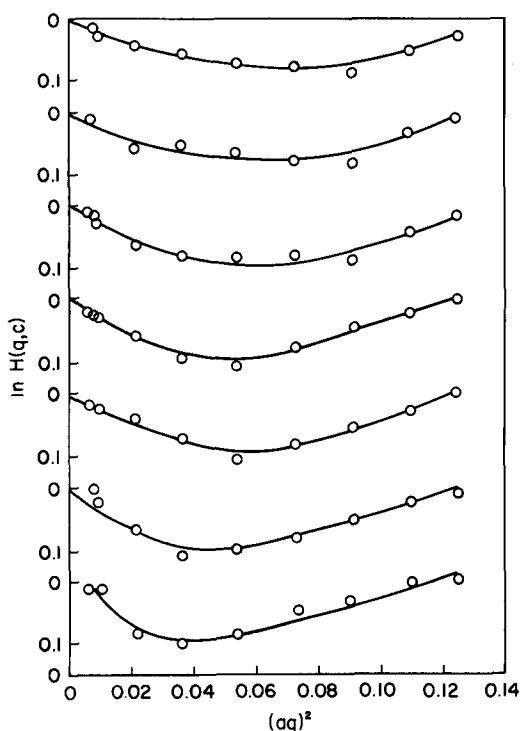

Figure 4 Plots of $\ln H(q, c)$ *versus* $(aq)^2$ for the solutions identified in the caption to *Figure 2*; $a = 11$ nm. The full curves are merely to guide the eye

A partial justification for the form of these expressions is discussed in the next section. In the limit of infinite dilution, $a^2 = R_G^2/6$. Thus, $6a^2$ represents the mean-square radius of gyration at concentration c. By analogy with the behaviour for low c, $P(q, c)$ is assumed to have the

form:

$$P(q, c) \approx [1 + (aq)^2]^{-2} \tag{23}$$

for flexible-chain polymers[7]—this relation provides a close approximation (within 10%) to the Debye expression[7] for $P(q, 0)$ for $qR_G < 2.4$. As mentioned above, a^2 is presumed to be equal to $R_G^2/6$ at the Flory theta temperature.

Extrapolation of $KcM/R(q, c)$ for $q > q_M$ to $q = 0$ gives an intercept $1 + ch_2(c)\Gamma(c)$. Estimates of $h_1(c)$ were obtained by analysis of the data with $q < q_M$ using a plot of $\ln\{[R(q, c)/KcM] - P(q, 0)[1 + cH_2(q, c)\Gamma(c)]\}$ *versus* q^2. This treatment gives $h_1(c)$ nearly independent of c $(h_1(c) \approx 0.83 \pm 0.05)$, and $h_1(c) \approx 0.2h_2(c)$, in comparison with $h_1(c) \approx h_2(c)$ observed in part 2. Further, $c\Gamma(c) \approx 0.195([\eta]c)^2$ here for $c[\eta] > 2$ (see *Figure 3*), in comparison with $c\Gamma(c) \approx 0.50([\eta]c)^2$ reported for polystyrene in cyclopentane.

A correlation length b defined as:

$$b^2 = \frac{\partial R(0, c)/R(q, c)}{\partial q^2} \tag{24}$$

is sometimes introduced in discussion of $R(q, c)^{11,19-21}$. Evidently, for the results obtained here, b so defined is a function of q, and is negative for small q. A useful comparison with prior treatments may be obtained by inspection of b calculated for $q > q_M$. Values of b obtained in this range of q are essentially independent of q; the results are given in *Figure 5* in the form b/b_0 *versus* $[\eta]c$, where $b_0^2 = R_G^2/3$. Results from part 1 are included for comparison.

Quasi-elastic scattering

Data on $g^{(2)}(\tau; q, c)$ were analysed in the form $Z(\tau; q, c) = \{\ln[g^{(2)}(\tau; q, c) - 1]^{1/2} + D_{APX}q^2\tau\}$ *versus* $q^2\tau$, where D_{APX} is chosen to be close to $D_M = K_1 q^{-2}$. This form is motivated by the cumulant expansion[6,7]:

$$\ln g^{(1)}(\tau; q, c) = -K_1\tau + \tfrac{1}{2}\mu_2(K_1\tau)^2 - \tfrac{1}{6}\mu_3(K_1\tau)^3 + \cdots \tag{25}$$

where μ_2 is a normalized second cumulant ($\mu_2 K_1^2$ being the second cumulant), etc. The cumulant expansion may be used in equation (1) to give the relation:

$$Z(\tau; q, c) = \tfrac{1}{2}\ln[g^{(2)}(0; q, c) - 1] - (D_{app} - D_{APX})q^2\tau + \cdots \tag{26}$$
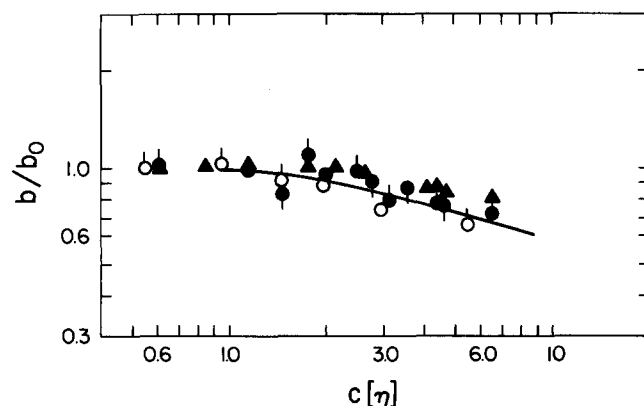

Figure 5 Bilogarithmic plot of b (see equation (24)) *versus* $c[\eta]$, for solutions of polystyrene at the Flory theta temperature. The triangles give the results obtained here for solutions in cyclohexane (34.8°C). The remaining data are taken from part 2 (see *Figure 8* of part 2 for notation)

where D_{APX} is an estimate of D_{app} (e.g. obtained by an initial analysis with $D_{APX} = 0$). The initial slope of $Z(\tau; q, c)$ versus $q^2\tau$ is expected to be independent of q, and equal to the difference between D_M and D_{APX}. Since the difference may be made small, an expanded scale may be used for $Z(\tau; q, c)$ to facilitate estimation of D_M. As expected, $\partial Z/\partial(q^2\tau)$ was found to be independent of q for small τ.

Values of $D_M(c)$ computed from $K_1(q, c)$ for small q and $[\eta]c < 0.2$ are fitted by:

$$D_M(c) = D_T^0(1 + k_D[\eta]c) \qquad (27)$$

where $D_T^0 = 1.48 \times 10^{-7} \text{cm}^2 \text{s}^{-1}$ and $k_D = -0.53$ (see below). These results are in good agreement with values reported in the literature[22-27]. The results obtained for $D_M(c)/D_T^0$ for the entire range studied here are given in *Figure 6*. The results are similar to data reported in two other studies at the Flory theta temperature[28,29], but differ from data on solutions of polystyrene in tetrahydrofuran[30,31] for which $A_2 \gg 0$, e.g. see ref. 7.

For larger q, the observed $g^{(2)}(\tau) - 1$ could not be fitted by a single-exponential function for solutions with $[\eta]c \gtrsim 1$, e.g. see *Figure 7*. The results could be approximated by use of equation (2) with $m = 2$. In this analysis, the four parameters $(r_1, r_2 = 1 - r_1, \gamma_1 \text{ and } \gamma_2)$ were determined by a non-linear least-squares fit of equation (2) $(m = 2)$ to the experimental data. Since the root-mean-square (r.m.s.) deviation of the experimental data from the computed $g^{(2)}(\tau; q, c)$ seemed to be systematic in τ, and to be slightly larger than the r.m.s. noise, an alternative inversion of equation (2) was also examined. In the latter, an inverse Laplace transform method[32-34] was used to invert equation (2). The method was implemented by procedures described elsewhere[34], using four or five points $(m = 4 \text{ or } 5)$ spaced at equal increments of $\ln \gamma$, from $\ln \gamma_{min}$ to $\ln \gamma_{max}$. Here, γ_{max}^{-1} is no smaller than the smallest $K_1 \Delta\tau$ used, and γ_{min}^{-1} is no larger than the value of $K_1\tau$ for which $g^{(2)}(\tau; q, c) - 1$ is above the

Figure 7 The photon-count correlation function for a solution of polystyrene PC 6a in cyclohexane at 34.8°C ($c[\eta] = 6.54$, $\theta = 120°$). The plot gives experimental data, along with the $g^{(2)}(\tau)$ calculated with equations (1) and (2), using four terms as discussed in the text. The residuals to the fit are shown in the insert

Figure 8 Plots of r_ν versus $K_1\gamma_\nu$ computed from $g^{(2)}(\tau)$ for a solution of polystyrene PC 6a in cyclohexane at 34.8°C ($c[\eta] = 6.54$, $\theta = 120°$). The data were computed with $m = 4$, as discussed in the text (see *Figure 7*). Although one such set of four contributions represent the data, the results for four computations using different γ_ν sets are interleaved to illustrate better the breadth of the distribution—the r_ν shown are normalized to sum to unity over the four sets

noise level. In practice the values of γ_1 and γ_2 determined in the fit of equation (2) with $m = 2$ were used to guide the choice of γ_{min}, γ_{max} and m. A typical result is given in *Figure 7*, along with the residual error in the fit to $\ln[g^{(2)}(\tau) - 1]$. This process was repeated for several γ_{min}, using the same increment in $\ln \gamma$ to reconstruct $r(\gamma)$, as shown in *Figure 8* for one example. A binodal distribution is apparent in *Figure 8*. Each peak may be characterized by an average $\bar{r}_i$ and $\bar{\gamma}_i$ by a cumulant analysis on the component of $g^{(1)}(\tau)$ computed for the γ range spanned by the peak. Under conditions for which the two modes could be clearly identified, the results on $\bar{r}_i$ and $\bar{\gamma}_i$ obtained in the latter treatment were found to agree within 4–6% with the parameters determined with $m = 2$. Situations where two modes could not be clearly identified are not treated here. The breadth of the individual modes could usually be characterized by $(\mu_2)_i \approx 0.1-0.2$, where $(\mu_2)_i$ is the normalized second cumulant for the ith mode. These are larger than expected if $g^{(1)}(\tau)$ is actually given by equation (2) with $m = 2$, with the addition of random noise. For example, for $g^{(1)}(\tau)$ computed over the usual
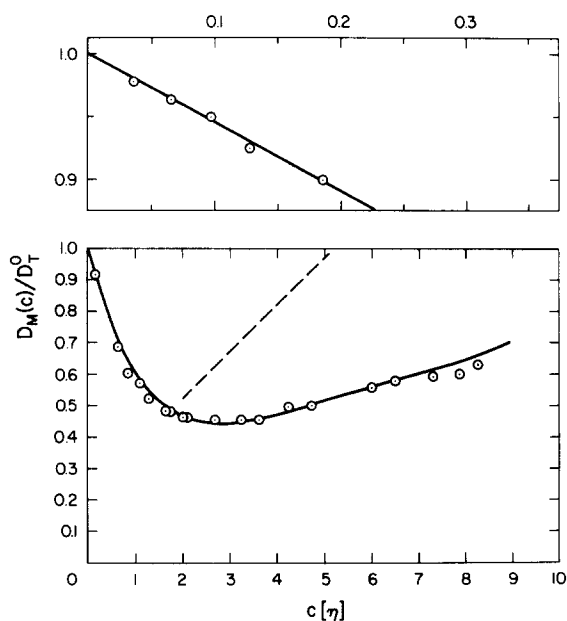

Figure 6 Plots of D_M/D_T^0 versus $c[\eta]$ of polystyrene in cyclohexane at 34.8°C for solutions at dilute (upper) and moderate (lower) concentrations ($D_T^0 = 1.48 \times 10^{-7} \text{cm}^2 \text{s}^{-1}$ and $[\eta] = 76 \text{cm}^3 \text{g}^{-1}$). The broken and full curves in the lower panel represent the use of equations (54) and (57), respectively
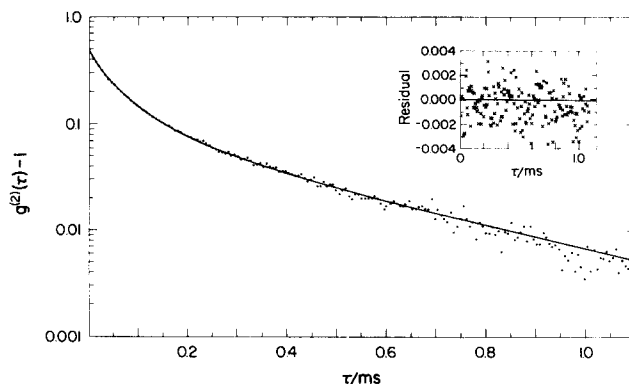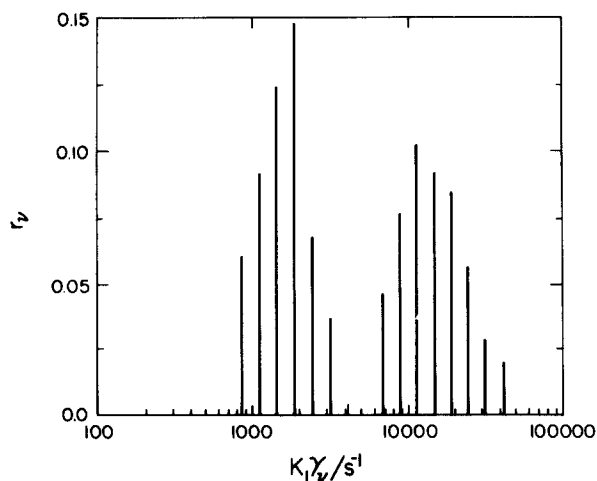
τ range using the $\bar{r}_i$ and $\bar{y}_i$ found as above, and including random noise, the inverse Laplace transform analysis leads to two modes, each characterized by $\mu_2 \approx 0.05$; this is close to the resolution limit of the method for the τ range used[34]. Even though the inverse Laplace transform analysis suggests that equation (2) with $m = 2$ is not strictly followed here, the dominant feature of two distinct modes is confirmed. In the discussion to follow, the breadth of the individual modes will be neglected, and equation (2) will be used with $m = 2$. Results are shown in *Figures 9* and *10* for several concentrations. The data are presented as the parameters $\bar{r}_2$ ($\bar{r}_1 = 1 - \bar{r}_2$), $K_1\bar{y}_1$ and $K_2\bar{y}_2$. The full curves in *Figures 9* and *10* are discussed below.

DISCUSSION

Elastic scattering

Behaviour at the Flory temperature. The principle feature in the static scattering is the dependence of $\Gamma(c)$ on c at the Flory theta temperature. According to the usual treatments utilized at low c, the function $g(r)$ appearing in equation (5) may be expressed in terms of the potential of mean force on N solute molecules[35]. Expansion of $g(r)$ in a series in c gives $\Gamma(c)$ and $H(q, c)\Gamma(c)$ as series in a reduced concentration $\hat{c}$, such that[35,36]:

$$c\Gamma(c) = 2\psi_2\hat{c} + 3\psi_3\hat{c}^2 + \cdots \tag{28a}$$

$$cH(q, c)\Gamma(c) = 2Q(q)\psi_2\hat{c}$$
$$+ \{3W(q)\psi_3 + 4[P(q, c)Q^2(q) - W(q)]\psi_2^2\}\hat{c}^2 + \cdots \tag{28b}$$

where $\hat{c}$ is given by:

$$\hat{c} = N_A R_G^3 c / M \tag{29}$$

and the dimensionless ψ_j are defined by:

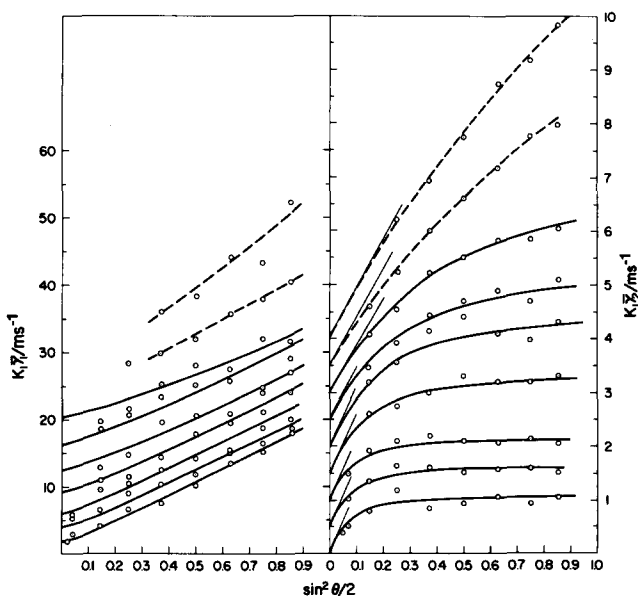$$\psi_j = A_j M (M / N_A R_G^3)^{j-1} \tag{30}$$

Figure 9 Plots of $K_1\bar{y}_1$ and $K_2\bar{y}_2$ versus $\sin^2(\theta/2)$ for solutions of polystyrene in cyclohexane at 34.8°C. The curves for $K_1\bar{y}_1/\text{ms}^{-1}$ and $K_1\bar{y}_2/\text{ms}^{-1}$ are offset by 2.0 ms^{-1} and 0.5 ms^{-1} between data sets, respectively, for clarity. Concentrations decrease from bottom to top, in the order given in *Table 1*, except for the uppermost two data sets, for which $c[\eta]$ is equal to 2.12 and 1.66, respectively. The full curves give $K_1\bar{y}_1$ or $K_1\bar{y}_2$ calculated with equation (15) using the parameters in *Table 1*. The broken curves are merely to guide the eye
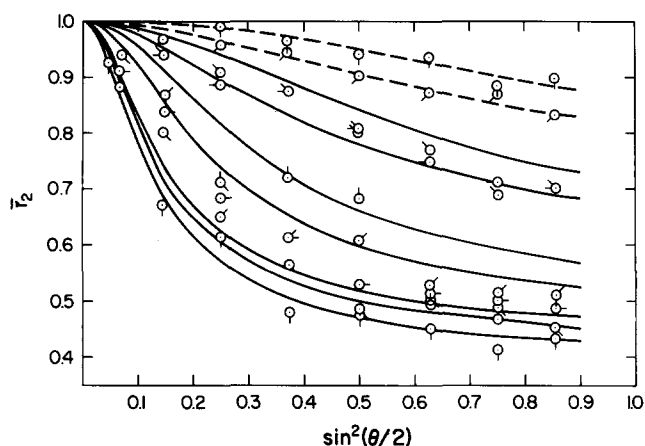

Figure 10 Plot of $\bar{r}_2$ versus $\sin^2(\theta/2)$ for solutions of polystyrene in cyclohexane at 34.8°C. Starting at the bottom of the figure, the pips rotate anticlockwise with decreasing $c[\eta]$ in the order given in *Table 1* except for the uppermost two data sets, for which $c[\eta]$ is equal to 2.12 and 1.66, respectively. The full curves represent $\bar{r}_2$ calculated with equations (14) and (15) using the parameters in *Table 1*. The broken curves are merely to guide the eye

with A_j the jth virial coefficient; $\hat{c}$ is of order unity when the average separation of chain centres is R_G. Since $[\eta] \approx 6.8 N_A R_G^3 / M$ for flexible-chain polymers with large M[7,35], $\hat{c} \approx [\eta]c/6.8$. The functions $Q(q)$ and $W(q)$ are discussed below. As seen in equation (28), $c\Gamma(c)$ is equal to $3\psi_3\hat{c}^2$ or $\Gamma(c) = 3A_3 M c$, for small c if $A_2 = 0$, permitting determination of A_3 under such circumstances. Under conditions with $A_2 = 0$, to first order, A_3 may be expressed in terms of an interaction parameter z_3[37,38]:

$$A_3 M^3 / N_A^2 R_G^6 = (4\pi)^3 z_3 / 3 \tag{31}$$

In fact, a theoretical treatment for moderately concentrated solutions gives (see the Appendix)[39]:

$$\Gamma(c) = 3(1 - k_0 z_3^{1/2}) A_3 M c \tag{32}$$

for $A_2 = 0$ and small z_3, where $k_0 = (5/24)(2\pi/3)^{1/2} \approx 0.30$. Thus, under these conditions $\Gamma(c) \approx 3A_3 M c$, even though the sample is not dilute—a similar approximation has been used previously to estimate z_3[38,40]. Making this identification, the results in *Figure 3* give $\psi_3 = 3.00$ and $z_3 = 0.0045$. If expressed in the form:

$$3A_3 M^3 / N_A^2 R_G^6 = k_3([\eta] M / N_A R_G^3)^2 \tag{33}$$

convenient for use in the following, then $k_3 = 0.195$ for the system studied.

The appearance of $A_3 > 0$ under conditions for which $A_2 = 0$ implies that the ternary cluster integral β_3 for segmental interactions does not vanish when $A_2 = 0$. The parameter z_3 is independent of M and proportional to β_3. In general, the binary cluster integral β_2 is expected to depend markedly on T, being zero at some temperature, whereas β_3 is positive and only weakly dependent on T[2,40–42]. For the system studied here and in part 2, z_3 computed from $\Gamma(c)$ is independent of M, as expected, with $z_3 \approx 0.0045$ for polystyrene in cyclohexane, or $z_3 \approx 0.012$ for polystyrene in cyclopentane. Similar values have been reported elsewhere[40,41].

Calculation of A_2 using a perturbation theory shows that for A_2 nearly zero:

$$\psi_2 = 4\pi^{3/2}(\hat{z} + \cdots) \tag{34a}$$

$$\hat{z} = z + 8z_3[(M/4n_0m_0)^{1/2} - 1] \tag{34b}$$

where n_0 is a constant of order unity[38], $z_3 \propto \beta_3$, and $z \propto \beta_2 M^2 R_{G,0}^{-3}$. (The original treatment[37] including ternary interactions differs negligibly from equation (34) for large M, through omission of the term -1 in the square brackets in the expression for $\hat{z}$.) Consequently, ψ_2 may be considered to depend on an interaction parameter $\hat{z}$ that is proportional to $M^{1/2}$, and vanishes when $A_2 = 0$. As $z_3 > 0$, this requires that $z < 0$ when $\hat{z} = 0$. Data on $A_2(T)$ for polystyrene in cyclopentane have been analysed[4] to give $\hat{z} = 0.0050(1 - \Theta/T)M^{1/2}$. If $z_3 \neq 0$, then the coefficient 0.0050 must comprise contributions from both z and z_3.

In terms of the parameters in equation (7), the correlation length b is given by:

$$b^2 = b_0^2[1 + c\Gamma'(c)(\partial H/\partial P^{-1})]/[1 + c\Gamma(c)] \quad (35)$$

where $b_0^2 = 2a^2 = R_G^2/3$. In the simplest case, $\partial H/\partial P^{-1}$ is zero, as frequently obtained in dilute solutions[7], but for the solutions studied here the situation is more complex; see *Figure 4*. For $q < q_M$, $\partial H/\partial P^{-1}$ is negative if $[\eta]c > 0.5$, and since $c\Gamma'(c)(\partial H/\partial P^{-1}) < -1$, b^2 is also negative. For $q > q_M$, $\partial H/\partial P^{-1}$ is positive and almost independent of q if $[\eta]c > 0.5$, so that b likewise is positive and independent of q. Of course, this relation fits the observed b/b_0 using equation (21) to represent $H_2(q, c)$, as should be expected. It has been assumed[8] that for moderately concentrated solutions, $g(r)$ can be represented by the Ornstein–Zernicke approximation, $g(r) \propto (\xi_0/r)\exp(-r/\xi_0)$, in which case $b = \xi_0$ for all q, and:

$$\xi_0(c) \propto R_G/\{\hat{c}[1 + c\Gamma(c)]\}^{1/3} \quad (36)$$

where the factor in the denominator is dimensionless. This expression may be expressed in the form:

$$R_G/\xi_0(c) = \{([\eta]c)^{(2+p)}S([\eta]c)/6.8\}^{1/3} \quad (37)$$

Here, $p = 1(1-\mu)/\mu$, where $\mu = 3v - 1 \approx \partial \ln[\eta]/\partial \ln M$, with $v = \partial \ln R_G/\partial \ln M$, and:

$$S([\eta]c) = \frac{1 + c\Gamma(c)}{([\eta]c)^{1+p}} \quad (38)$$

This relation gives $R_G/\xi_0(c) \propto [\eta]c$ for large c at the Flory theta temperature ($p = 1$) since S tends to a constant with increasing $[\eta]c$, e.g. S tends to about k_3 for $A_2 = 0$. Although the predicted inverse proportionality of b on c has been reported[19,21], the result obtained here is more complicated, and equation (37) overestimates the dependence of b on c. A possible model to estimate the function H in equation (7) is discussed in the next section.

Smooth-density models at the Flory temperature. In the preceding it was observed that for a moderately concentrated solution under conditions with $A_2 = 0$ and A_3 small, the simple behaviour given by equation (28a) truncated at the second term suffices to describe $c\Gamma(c)$. Under these conditions, the renormalization needed in the moderately concentrated solution leads to considerable simplification. It follows that this same simplification applies to equation (28b), so that calculation of $W(q)$ and $Q(q)$ will provide an estimate of $H(q, c)$. In the following, use is made of a smooth-density model to estimate the functions appearing in equation (28). In so-called smooth-density models, the actual chain is replaced by an object with spherical symmetry and a potential of mean force $V(S_{ij})$ on molecules with centre-of-mass separation S_{ij}[35]. Under certain approxi-

mations[35], these models lead to the results:

$$Q(q)P(q,c)\psi_2 = -2\pi R_G^{-3} \int_0^\infty S_{12}^2 G_{12} \frac{\sin(qS_{12})}{qS_{12}} dS_{12} \quad (39)$$

$$W(q)P(q,c)(3\psi_3 - 4\psi_2^2) =$$

$$-R_G^{-6} \iiint \frac{\sin(qS_{12})}{qS_{12}}\{[G_{12}G_{13}G_{23} + G_{13}G_{23}]$$

$$+ (1 + G_{12})(1 + G_{13})(1 + G_{23})Y_{123}\} dS_{12} \, dS_{13} \, dS_{23} \quad (40)$$

where the integration in equation (40) is over all separations of the centres of mass under the constraint that $S_{12} + S_{13} + S_{23} = 0$. In these expressions:

$$G_{ij} = \exp[-V(S_{ij})/kT] - 1 \quad (41)$$

$$Y_{123} = \exp[-\Delta V(S_{12}, S_{13}, S_{23})/kT] - 1 \quad (42)$$

where $\Delta V(S_{12}, S_{13}, S_{23})$ is to account for interactions among three chains that do not vanish with vanishing $V(S_{ij})$—ΔV is usually put equal to zero[35] (see below).

Of course, these relations also give A_2 and A_3 in the limit of zero q. Inspection of equations (39) and (40) in that limit shows that A_3 need not be zero when A_2 vanishes, even under conditions for which $\Delta V = 0$. Thus, G_{12} need not be zero to obtain $A_2 = 0$, rather an integral over G_{12} must be zero. Consequently, with G_{12} not zero, the multiple integral needed to compute A_3 may not vanish even though $A_2 = 0$. However, with the most commonly used expressions for a class of 'two-parameter theories', $\Delta V = 0$, and $V(S_{ij})$ is scaled by an interaction parameter z that vanishes when $A_2 = 0$. With such a model, G_{12} is identically zero when $z = 0$, and consequently A_3 vanishes along with A_2 when $z = 0$. The use of two such potentials to compute A_2 is discussed in the Appendix along with the calculation of A_3 for one case. With two-parameter models, ψ_3 may be expressed in the form:

$$\psi_3 = \psi_2^2 J(\psi_2) \quad (43)$$

where the function $J(\psi_2)$ depends on the model. For example, for a model discussed in the Appendix:

$$J(\psi_2) = \psi_2/3\pi^{3/2}(1 + k_\varepsilon\psi_2)^{3/2} \quad (44)$$

where k_ε is a constant appearing in an expression for $Q(q)$ (see equation (A.24) in the Appendix)—k_ε is expected to be close to zero.

As revealed by the c^2 dependence of $c\Gamma(c)$ observed when $A_2 = 0$, the approximations in the two-parameter theories must fail with increasing c as the polymer segment density increases. A revised treatment could be attempted with $V(S_{ij})$ not identically zero under conditions for zero A_2, containing contributions that scale with β_2 and β_3. Alternatively, we will more simply let $V(S_{ij})$ scale with $\hat{z}$, and approximate the particular effects of non-zero z_3 by use of a potential $\Delta V/kT$ that scales with z_3, being non-pairwise additive with the potential dependent on $\hat{z}$. In this case, ψ_3 becomes a function of both $\hat{z}$ and z_3 if $A_2 \neq 0$. Unfortunately, theoretical guidance on ΔV is lacking. To investigate the features of non-zero ΔV, we will approximate Y_{123} in the spirit of a Flory–Krigbaum smoothed-segment-density model (see the Appendix), with Y_{123} the product of three Gaussian functions:

$$Y_{123} = (-Y\sigma_3^3)^3 \exp[-\sigma_3^2(S_{12}^2 + S_{13}^2 + S_{23}^2)/R_G^2] \quad (45)$$

where both Y and σ_3 are expected to depend on z_3.

Further, since $\hat{z}=0$, the G_{ij} are all zero and ψ_3 becomes a function of z_3 alone. Equation (45) is motivated by the form of a potential discussed in the Appendix (equation (A.25)). Under these conditions, calculation with equation (40) gives (for conditions with $A_2=0$):

$$A_3 M^3/N_A^2 R_G^6 = (\pi^3/3^{5/2})(Y\sigma_3)^3 \qquad (46a)$$

$$W(q) = \exp[-\varepsilon'(qR_G)^2/3] \qquad (46b)$$

$$\varepsilon' = (1/2\sigma_3^2) - 1 \qquad (46c)$$

It may be noted that $\varepsilon'=0$ for $\sigma_3^{-2}=2$, with $\varepsilon'>0$ for larger σ_3^{-1} and $\varepsilon'<0$ for smaller σ_3^{-1}. Consideration of equation (9) shows that a maximum in $R(q)$ requires $\varepsilon'>0$, or $\sigma_3^{-2}>2$ with this model. The experimental data for $q<q_M$ give $\varepsilon'\approx 10$. Accordingly, $\sigma_3^{-1}\approx 4.7$ and $Y=3.4$. Thus, in this model the maximum in $R(q, c)$ *versus* q results from a net repulsion among chain centres under conditions with $A_2=0$.

Quasi-elastic scattering

The mutual diffusion coefficient. The experimental results obtained here give $R_H=20\,\text{nm}$ and $R_G/R_H=1.35$ at the Flory theta temperature. According to the theoretical treatment[38,40], under this condition:

$$R_G/R_H = (R_{G,0}/R_{H,0})(1 - 20.31 z_3 + \cdots) \qquad (47)$$

where $R_{G,0}/R_{H,0}=8/3\pi^{1/2}\approx 1.505$ for a flexible chain with large M[35]. With the estimate $z_3=0.0045$, R_G/R_H is predicted to be 1.37, in good accord with the measured value.

For dilute solutions, the use of equation (12) is facilitated by expansion of K_{OS} and ζ_M in virial expansions, to give equation (27) to first order, with[35]:

$$k_D = (2 - C_2)\frac{A_2 M}{[\eta]} - C_1 \qquad (48)$$

Thus, at the Flory theta temperature, $k_D = -C_1$. Theoretical expressions for C_1 may be expressed in the form:

$$C_1 = B(4\pi N_A/3)R_H^3/M[\eta] \qquad (49)$$

where theoretical estimates of the numerical coefficient B vary from unity to 2.23[43-46]. By comparison, the experimental value $C_1=0.53$ gives $B=1.7$.

For moderately concentrated solutions the use of equation (12) requires a hydrodynamic model to represent ζ_M. According to one treatment given in the scaling limit with $\hat{c}\gg 1$[7,8]:

$$\frac{\Xi^0}{\Xi(c)} = \frac{R_H}{M}\frac{\zeta(0)}{\zeta(c)}\left(m_0\int_V |r|^{-1}g(r)\,dr\right) \qquad (50a)$$

$$= \frac{R_H}{\xi_0(c)}\frac{\zeta(0)}{\zeta(c)}F(0, c)\frac{m_1}{m_2} \qquad (50b)$$

where $\zeta(c)$ is a repeat-unit friction factor at concentration c, and:

$$m_n = \int_0^\infty x^n g(x)\,dx \qquad (51)$$

with $x=r/\xi_0$. Combination of equations (6), (12) and (50) gives:

$$\frac{D_M(c)}{D_T^0} = \frac{R_H}{\xi_0(c)}\frac{\zeta(0)}{\zeta(c)}\frac{m_1}{m_2} \qquad (52)$$

If the pair correlation function is given by the

Ornstein–Zernicke relation $g(x)=x^{-1}\exp(-x)$, then $m_1=m_2$[47], and making use of equation (37) for ξ_0:

$$D_M(c)\zeta(c)/D_T^0\zeta(0) = (R_H/R_G)\{([\eta]c)^{2+p}S([\eta]c)/6.8\}^{1/3} \qquad (53)$$

where S is given by equation (38). Making use of the relation $c\Gamma(c)\approx k_3([\eta]c)^2$ obtained here for solutions of polystyrene in cyclohexane at the Flory theta temperature ($k_3=0.195$ for the former), equation (53) becomes:

$$\frac{D_M(c)\zeta(c)}{D_T^0\zeta(0)} = K_\xi[\eta]c\{1 + k_3^{-1}([\eta]c)^{-2}\}^{1/3} \qquad (54)$$

where $K_\xi=(R_H/R_G)(k_3/6.8)^{1/3}$, or $K_\xi=0.23$ with $R_G=1.35R_H$. This result, which shows the proportionality of $D_M(c)\zeta(c)$ with c predicted by this model for large $[\eta]c$, is compared with the experimental data in *Figure 6*; the agreement with equation (54) is poor. Here, use is made of the expression $\xi(c)/\zeta(0)=\exp(b_T\bar{w})$ determined in parts 1 and 3, where $\bar{w}$ is the weight fraction polymer and b_T is a constant (2.7 at the temperature studied here); the disparity would be larger if it is assumed that $\zeta(c)=\zeta(0)$.

The deviation from equation (54) is attributed to the expression for $\Xi(c)$ leading to equation (50). According to the relations given above, *for $\hat{c}\gg 1$*:

$$\frac{\Xi(c)}{\Xi^0} = [1 + c\Gamma(c)]\frac{\xi_0(c)}{R_H}\frac{\zeta(c)}{\zeta(0)} \qquad (55)$$

For $\hat{c}\ll 1$, a series expansion of $\Xi(c)$ gives[35]:

$$\Xi(c)/\Xi^0 = \{1 + k_1[\eta]c + k_2 c\Gamma(c) + \cdots\}[\zeta(c)/\zeta(0)] \qquad (56a)$$

$$\approx [1 + c\Gamma(c)]^{k_2}\exp(k_1[\eta]c)[\zeta(c)/\zeta(0)] \qquad (56b)$$

where k_1 and k_2 are constants; the factor $\zeta(c)/\zeta(0)$, which is close to unity for small c, is included for convenience. The expression:

$$\Xi(c)/\Xi^0 = [1 + c\Gamma(c)]$$
$$\times \{\exp(-k_1[\eta]c)[1 + c\Gamma(c)]^{1-k_2} + R_H/\xi_0(c)\}^{-1}[\zeta(c)/\zeta(0)] \qquad (57)$$

provides a reasonable representation of both equations (50) and (55) for the range of c studied here. As seen in *Figure 6*, use of this relation in equation (12) fits the experimental results with $K_\xi=0.173$, $k_1=0.95$ and $k_2=0.5$. These values of k_1 and k_2 are in the range expected for flexible-chain polymers[35]. This result indicates that the conditions required for the use of equation (50) alone for $\Xi(c)$ are not met for the range of $[\eta]c$ studied here. The value of 0.17 for K_ξ in place of the theoretical 0.23 may reflect the approximations made in the derivation of equation (50) or in the form used for $g(r)$.

The nature of $g^{(2)}(\tau; q, c)$. As discussed above, $[g^{(2)}(\tau; q, c) - 1]^{1/2}$ is an exponential function of τ for $[\eta]c<1$, but displays a non-exponential behaviour fitted by equation (2) (with $m=2$) for $[\eta]c>2$ and large q. The parameters $K_1\bar{y}_1$ and $K_1\bar{y}_2$ and weight factor $\bar{r}_2=1-\bar{r}_1$ given in *Figures 9* and *10*, respectively, show that $K_1\bar{y}_1/q^2$ and $K_1\bar{y}_2$ tend to constants, independent of q, with increasing q. The behaviour is similar to that given by the theoretical model discussed in the 'Introduction'. With this model, the limiting value of $K_1\bar{y}_1$ for $q=0$ is given by τ_R^{-1}, and the limiting values of $K_1\bar{y}_2$ and r_2 for large q are $(f\tau_R)^{-1}$ and $(f-1)/f$, respectively. Under appropriate circumstances, these relations may provide

Table 1 Parameters for non-exponential photon-count correlation[a]

$c[\eta]$	$cM_w/\rho M_C$	D_M/D_T^0	τ_R (ms)	f	$(f-1)c/\rho$
8.31	2.84	0.635	0.55	1.62	0.063
7.91	2.70	0.601	0.51	1.67	0.065
7.33	2.51	0.595	0.48	1.70	0.063
6.54	2.24	0.581	0.30	1.75	0.060
6.06	2.07	0.568	0.22	1.78	0.058
4.25	1.45	0.493	0.16	2.10	0.058
3.66	1.25	0.459	0.12	2.00	0.045

[a] $[\eta] = 76 \text{ cm}^3 \text{g}^{-1}$; $\rho M_C = 33\,200$; and $D_T^0 = 1.48 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$

estimates of f and τ_R. The initial tangent to $K_1\gamma_1$ is equal to K_1. As shown in *Figure 9*, that initial tangent is observed only for very small q for the solutions studied here. The experimental data on $\bar{r}_2$ ($=1-\bar{r}_1$), $\bar{\gamma}_1$ and $\bar{\gamma}_2$ as functions of q were fitted by a non-linear least-squares regression using equations (14) and (15) to obtain the two parameters τ_R and f to fit the observations best. The calculated curves are compared with experimental data in *Figures 9* to *10*, and values of τ_R and f are given in *Table 1*. The satisfactory agreement between experiment and the calculated curves provides support for the approximate dynamic model. The values of τ_R and $(f-1)(c/\rho)$ are compared with the theoretical predictions in the following; the latter product is seen to be essentially independent of c. Consequently, variation of f with c is small (but not entirely negligible) over the range of c studied. The variation of τ_R is more pronounced. Thus, with decreasing c, for the solutions studied here τ_R decreases to such an extent that $f\kappa$ does not exceed unity by much. In that case, $r_2 \gg r_1$ and $g^{(1)}(\tau; q, c)$ is dominated by the contribution with $v=2$, i.e. r_2 approaches unity and near-single-exponential behaviour is obtained, even though f exceeds unity.

As discussed in the 'Introduction', $f-1 = \Delta L/K_{OS}$ for a polymer solution. If $\Delta L = 4G_N/3$, use of equations (19) and (38) gives:

$$f - 1 = \frac{4G_N}{3K_{OS}} \approx \frac{4}{3} \frac{(\rho/c)^{1-3s-s'}}{([\eta]_e \rho)^{1/\mu}} S^{-1}([\eta]c) \qquad (58)$$

for $\hat{c} > 1$, where $[\eta]_e$ is the intrinsic viscosity for a polymer with $M = M_e$ (in the solvent used to determine f), with M_e the molecular weight between entanglements. The exponent s' is defined in equation (19) and $s = (1-p)/3$. As discussed in part 3, $s' = 0$ for $A_2 = 0$, and one approximate treatment[8] gives $s' = 1/4$ for large A_2 if $\mu = 4/5$; these results are reproduced with $s' = s = (2\mu - 1)/3\mu$, which gives $1 - 3s - s' = (4 - 5\mu)/3\mu$. The latter is unity for $\mu = 1/2$ and zero for $\mu = 4/5$. Under conditions for which $A_2 = 0$, then $\mu = 1/2$, $s = s' = 0$ and $S = 0.195 + ([\eta]c)^{-2}$ for polystyrene in cyclohexane at the Flory theta temperature. Using constants for polystyrene in cyclohexane at 34.8°C, $(f-1)(c/\rho) \approx 0.062$, in good agreement with experiment (see *Table 1*). In this calculation, $M_e = 16\,000$, in accord with measurements[48] on $R_N = G_N^{-1}$ and other data[13,49] on G_N.

For a solution under conditions with $A_2 \gg 0$, the exponent $1 - 3s - s'$ is equal to $(4 - 5\mu)/3\mu$ if $s = s' = (2\mu - 1)/3\mu$, as discussed above. (Note that $[\eta]_e > [\eta]_{e,\Theta}$.) Use of the appropriate parameters for polystyrene in toluene, including an estimate for S based on the data in part 2, gives $f - 1 \approx 0.012(\rho/c)^{0.1}$, so that $f \approx 1$. Consequently, non-exponential behaviour in $g^{(1)}(\tau; q, c)$ should be much suppressed in that system. This trend

was observed in this study with increasing temperatures $T > \Theta$ for solutions of polystyrene in cyclohexane. A more detailed discussion of behaviour in good solvents is given elsewhere[50,51].

According to the theoretical model given above, in the range $q^2 > f\kappa$ for which $\gamma_2 K_1$ is independent of q, $(\gamma_2 K_1)^{-1} = f\tau_R$. With the constitutive equation discussed in the Appendix:

$$\tau_R \approx (\eta - \eta_s)R_N \qquad (59)$$

where η is the solution viscosity and $R_N = G_N^{-1}$. More realistically, $g(t)$ should be expressed as a sum of weighted exponentials with:

$$g(t) = \sum g_i \exp(-t/\tau_i) \qquad (60)$$

where $\sum g_i = 1$ and $\tau_i > \tau_{i-1}$. In this case, it is reasonable to approximate τ_R by the average τ_c defined by:

$$\tau_c = (\eta - \eta_s)R^{(S)} \qquad (61)$$

where $R^{(S)}$ is the steady-state recoverable compliance, given by:

$$R^{(S)} = R_N \frac{\sum g_i \tau_i^2}{(\sum g_i \tau_i)^2} \qquad (62)$$

As discussed in part 3, $R^{(S)} \approx 3R^{(N)}$ for polystyrene solutions. Values of τ_C and $\tau_N \approx \tau_C/3$ calculated with η and $R^{(S)}$ based on data in parts 1 and 3 are given in *Figure 11*, along with τ_R as a function of $cM/\rho M_C$. Here $M_C = 31\,000$ is the critical molecular weight from viscometry (see part 1). The results give τ_R between τ_N and τ_C, tending towards τ_N for larger $cM_w/\rho M_C$, and towards τ_C for smaller $cM_w/\rho M_C$. This appears to be reasonable, in consequence of the loosening character of the pseudo-network with decreasing $cM_w/\rho M_C$.

Although f increases with decreasing c, the parameter $f\kappa q^{-2} = fD_M\tau_R q^2$ decreases with decreasing c owing to the marked dependence of $\tau_R \approx \tau_C$ on c. Consequently, even though f may exceed unity, the condition $f\kappa \gg 1$ required to observe $\gamma_2 K_1$ independent of q is not met in light scattering studies if c is too small. For the concentration range of interest, in a system for which
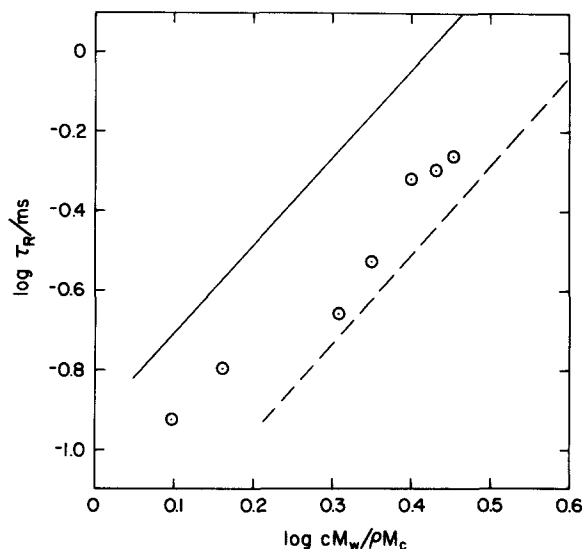

Figure 11 Bilogarithmic plot of τ_R *versus* $cM_w/\rho M_C$ for solutions of polystyrene in cyclohexane at 34.8°C ($\rho M_C = 33\,200$). The full and broken lines give τ_C and $\tau_C/3 \approx \tau_N$ based on data in parts 1 and 3

$A_2 = 0$, $R^{(S)} \approx 3/G_N$ (part 3) and:

$$\eta \approx N_A K_\eta (cM/\rho M_e)^{3\cdot4}\zeta(c) \qquad (63)$$

where K_η is a constant (part 1). Thus, using equations (18) and (59), $D_M \tau_C$ is proportional to $R_H^2 (cM/\rho M_e)^{2\cdot4}$, and $fD_M \tau_R$ decreases rapidly with decreasing c if $\tau_R \approx \tau_C$.

CONCLUSIONS

The maximum in $R(q, c)$ observed as a function of q for moderately concentrated solutions of polystyrene at (or near) the Flory theta temperature is ascribed to an effective repulsion among chain centres, as in a liquid. The repulsion is not predicted by the classical two-parameter theories of polymer solutions, but can be understood in terms of three-body interactions that do not vanish at the theta temperature. Interchain interactions are also implicated in non-exponential behaviour observed in the quasi-elastic light scattering. The effect, which gives a (nearly) double-exponential decay in the electric-field correlation function, can result in one component with a q-independent time constant. A viscoelastic model, found to represent the data obtained here, predicts that the non-exponential behaviour should be much stronger at the Flory theta temperature than under 'good solvent' conditions.

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APPENDIX

A dynamic model for $g^{(1)}(\tau; q, c)$

Following the treatment in refs. 10–12, the displacement $u(r, t)$ of a material point on a polymer chain (e.g. a repeat unit) at position r at time t is assumed to obey the relation:

$$\text{div } \sigma(t) - \zeta_M \frac{\partial u(r, t)}{\partial t} + A(r, t) = 0 \qquad (A.1)$$

where $\sigma(t)$ is the stress tensor for a volume element containing the material point, $\zeta_M = N_A \Xi(c)c/M$ and $A(r, t)$ is a randomly fluctuating force acting at r (i.e. the effects of Brownian motion among the solvent molecules on the polymer chain). Further it is assumed that the components of $\sigma(t)$ may be expressed by the constitutive equation for a linear viscoelastic material such that (in

Cartesian coordinates)[13]:

$$\sigma_{ij}(t) = 2 \int_{-\infty}^{t} G(t-s) \frac{\partial \varepsilon_{ij}(s)}{\partial s} ds$$

$$+ \delta_{ij} \int_{-\infty}^{t} [K_{OS}(t-s) - \tfrac{2}{3} G(t-s)] \frac{\partial \varepsilon_{kk}(s)}{\partial s} ds \quad (A.2)$$

where δ_{ij} is the Kronecker delta,

$$\varepsilon_{ij}(t) = \frac{1}{2} \left(\frac{\partial u_i(t)}{\partial x_j} + \frac{\partial u_j(t)}{\partial x_i} \right) \quad (A.3)$$

and the summation convention is assumed for double indices. In equation (A.2), $G(t)$ is the shear modulus, which may be expressed as:

$$G(t) = G_e + \Delta G_0 g(t/\tau_R) \quad (A.4)$$

where $\Delta G = G(0) - G_e$ and τ_R is an average relaxation time. The equilibrium compliance G_e is zero for a fluid. Although $g(t/\tau_R)$ would typically represent a sum of weighted exponential functions of t (see text)[3,13], it is convenient for purposes here to let $g(t/\tau_R) \approx \exp(-t/\tau_R)$. The osmotic modulus $K_{OS}(t)$ for the pseudo-network formed by the copiously intertwining polymer chains in a moderately concentrated solution is equal to $M_{LS}(0, c) = c \, \partial\Pi/\partial c$ for large t (i.e. at equilibrium), so that:

$$K_{OS}(t) = K_{OS} + \Delta K k(t/\tau'_R) \quad (A.5)$$

where $\Delta K = K_{OS}(0) - K_{OS}$, $k(t/\tau'_R)$ is a function that decreases from unity for $t = 0$ to zero for $t = \infty$, and τ'_R is an average relaxation time that may or may not be equal to τ_R; see below. In the theoretical treatment, equation (A.1) is used to obtain a solution for the Fourier transform $u(q, \omega)$ of the displacement vector $u(r, t)$. Owing to the isotropic nature of the effects of interest, one may put $q = (0, 0, q)$ without loss of generality, with $\hat{u} = (\hat{u}_1, \hat{u}_2, \hat{u}_3)$. Solution for $\hat{u}_3(q, \omega)$ for no external forces then gives[10,11]:

$$\Omega^*(q, \omega)\hat{u}_3(q, \omega) = 0 \quad (A.6)$$

where

$$\Omega^* = \Omega' + i\Omega'' \quad (A.7a)$$

$$\Omega'(q, \omega) = \frac{q^2}{1 + (\omega\tau_R)^2} \{ L[1 + (\omega\tau_R)^2] + (\omega\tau_R)^2 \, \Delta L \} \quad (A.7b)$$

$$\Omega''(q, \omega) = \frac{q^2 \omega\tau_R}{1 + (\omega\tau_R)^2} \left(\frac{\zeta_M}{q^2 \tau_R} [1 + (\omega\tau_R)^2] + \Delta L \right) \quad (A.7c)$$

Here, $L = K_{OS} + \tfrac{4}{3} G_e$, and ΔL is equal to $\tfrac{4}{3}\Delta G(0)$ if $k(t/\tau'_R) \approx 0$, or to $\Delta K + 4\Delta G_0/3$ if $k(t/\tau'_R) = g(t/\tau_R) = \exp(-t/\tau_R)$. With this result, $g^{(1)}(\tau; q, c)$ is given by[10,11]:

$$g^{(1)}(\tau; q, c) = S(\tau; q, c)/S(0; q, c) \quad (A.8a)$$

$$S(\tau; q, c) = \int_{-\infty}^{\infty} \{ \Omega''(\omega, q)/[\Omega^*(\omega, q)]^2 \} \exp(i\omega\tau) \, d \ln \omega \quad (A.8b)$$

With the preceding expressions, $g^{(1)}(\tau; q, c)$ is given by equation (2) with r_1, r_2, γ_1 and γ_2 given by equations (14) and (15) of the text. Accordingly, the first cumulant K_1 is equal to $q^2 L/\zeta_M$, and the normalized second cumulant given by $(\sum r_\nu \gamma_\nu^2) - 1$ is equal to $\Delta L/L$.

A renormalized treatment of the osmotic pressure

Equation (32) is not given in ref. 39, but may be

obtained from an expression given there for the free energy of mixing per unit volume ΔG as a function of the volume fraction ϕ of the solute. In general, Π is related to ΔG by:

$$\Pi = \phi^2 \frac{\partial \Delta G/\phi}{\partial \phi} \quad (A.9)$$

In ref. 39 ΔG is expressed as:

$$\Delta G = \Delta G_{FH} + \Delta G_{XS} \quad (A.10)$$

for moderately concentrated solutions, where ΔG_{FH} is the Flory–Huggins free energy of mixing, and ΔG_{XS} accounts for contributions to ΔG from concentration fluctuations important at moderate concentration:

$$\frac{V_1 \Delta G_{FH}}{RT} = \frac{\phi}{n} \ln \phi + (1-\phi) \ln(1-\phi) + \chi\phi(1-\phi) + (w - \tfrac{1}{6})\phi^3 \quad (A.11)$$

$$\frac{V_1 \Delta G_{XS}}{RT} = \frac{1}{24\pi\xi^3} - \frac{9}{16\pi} \frac{B\phi}{\alpha^2 \xi} \quad (A.12)$$

Here, V_1 is the molar volume of the solvent, B is equal to $(\tfrac{1}{2} - \chi) + w\phi$, $n = v_2 M/V_1$ with v_2 the polymer specific volume, α is the ratio of the mean-square radius of gyration to the value at infinite dilution at the Flory theta temperature, and $\xi(N_A/V_1)^{1/3}$ is a concentration-dependent correlation length; the correlation length would be proportional to R_G at infinite dilution. The theory provides an expression for α as an implicit function of B/ϕ (for large n):

$$B/\phi = \alpha^3 [A(\alpha)]^2 / \{ [9A(\alpha)/16\pi] + (\alpha^3/6) \} \quad (A.13)$$

where $A(\alpha) = (\alpha^5 - \alpha^3)/4.216$. In addition $\alpha^2 \phi\xi$ is given as an implicit function of B/ϕ:

$$\alpha^2 \phi\xi = \alpha^3 A(\alpha)/(B/\phi) \quad (A.14)$$

With these relations, ΔG_{XS} may be expressed in the form:

$$\frac{V_1 \Delta G_{XS}}{RT} = \phi^3 [F(B/\phi) - (B/\phi)] \quad (A.15)$$

where

$$F(B/\phi) = \frac{1}{24\pi} \left(\frac{16\pi}{9} \right)^3 [\alpha^2 f(B/\phi)]^3 + (B/\phi)[1 - f(B/\phi)] \quad (A.16)$$

where $f(B/\phi) = 9/16\pi\alpha^2\phi\xi$. (The term $-B\phi^2$ exactly cancels a like term in $V_1 \Delta G_{FH}/RT$.) Calculation of Π gives:

$$\frac{\Pi V_1}{RT} = \frac{\phi}{n} - (\tfrac{1}{2} - \chi)\phi^2 \frac{\partial F(B/\phi)}{\partial(B/\phi)} + 2\phi^3 F(B/\phi) - \Delta(\phi) \quad (A.17)$$

where $\Delta(\phi) = \ln(1-\phi) + \phi + (\phi^2/2) + (\phi^3/3)$ is small for ϕ of interest here.

In the limit of small B/ϕ, $F(B/\phi)$ is given by:

$$\lim_{(B/\phi) \to 0} F(B/\phi) = (B/\phi)[1 - (5/16\pi)(6B/\phi)^{1/2}] \quad (A.18)$$

Consequently, for conditions with $\chi = 1/2$ (i.e. at the Flory theta temperature):

$$\lim_{\substack{\chi = 1/2 \\ w \to 0}} \frac{\Pi V_1}{RT} = \frac{\phi}{n} + 2[1 - (5/16\pi)(6w)^{1/2}]w\phi^3 - \Delta(\phi) \quad (A.19)$$

With the correspondence $A_3 Mc^2 = 2wn\phi^2$ (valid for small

w and for $A_2 = 0$), this result leads to equation (32) of the text, with neglect of $\Delta(\phi)$. In the consideration of the limit with $\chi = 1/2$ in ref. 39, it was assumed that w remained large, leading to a result for Π given below. (In addition, certain coefficients were inadvertently omitted in some of the expressions presented in ref. 39.)

We remark that in the limit of large B/ϕ, $F(B/\phi)$ is given by:

$$\lim_{B/\phi \to \infty} F(B/\phi) = [1 + 27/12] \frac{2}{27} \left(\frac{16\pi}{9}\right)^2 \left(\frac{9 \times 4.216}{16\pi}\right)^{3/4}$$

$$\times (B/\phi)^{3/4} \approx 6.08(B/\phi)^{3/4} \qquad (A.20)$$

(The term 27/12 in the square brackets was omitted in ref. 39.) With this result:

$$\lim_{B/\phi \to \infty} \frac{\Pi V_1}{RT} = \frac{\phi}{n} + 12.16 \left[1 - \frac{3}{16} \frac{1 - 2\chi}{B} \right] B^{1/4} \phi^{9/4} + \Delta(\phi)$$

$$(A.21)$$

For example, if $w = 0$, the factor in the square brackets reduces to 5/8, or if $\chi = 1/2$, that factor becomes unity, making the second term proportional to $w^{3/4}\phi^3$ for large w, by comparison with the result in equation (A.19) for small w. Finally, we note that $F(B/\phi)$ may be approximated as $(B/\phi)/[1 + (B/\phi)^{1/4}/6.08]$ within 4%, allowing an analytic estimate of Π for intermediate B/ϕ as a function of χ, w and ϕ.

Two-parameter smoothed-density models

In general, for the two-parameter models, ψ_2 and ψ_3 are each expected to approach limiting values for large z, and to reduce to zero for $z = 0$. Various expressions[35] for $V(S_{ij})/kT$ have been used to compute A_2. For example, the well known Flory–Krigbaum potential[35] given by:

$$V(S_{ij})/kT = 3^{3/2} z \alpha^{-3} \exp(-3S_{ij}^2/4R_G^2) \qquad (A.22)$$

with $\alpha = R_G/R_{G,0}$ has been used to compute $Q(q)$ as well as A_2. The latter result gives[35]:

$$A_2 M^2/N_A R_G^3 \approx (4\pi^{3/2}/2.30) \ln(1 + 2.30z\alpha^{-3}) \quad (A.23)$$

Numerical results[36] for $Q(q)$ calculated with equation (39) may be represented by:

$$Q(q) \approx \exp\{-\varepsilon[P^{-1}(q, 0) - 1]\} \approx \exp[-\varepsilon(qR_G)^2/3]$$

$$(A.24a)$$

for $qR_G < 3$, with

$$\varepsilon = k_\varepsilon A_2 M^2/N_A R_G^3 \qquad (A.24b)$$

where $k_\varepsilon \approx 0.005$ (oscillations in $Q(q)$ vitiate this expression for larger q). A similar relation for hard spheres ($V = \infty$ for $S_{ij} < 2R$ and zero otherwise) gives $Q(q)$ approximately represented by equation (A.24), with $k_\varepsilon = 0.028$ for $qR_G < 1.3$.

The potential:

$$V(S_{ij})/kT = -\ln[1 - G\sigma^3 \exp(-\sigma^2 S_{ij}^2/R_G^2)]$$

$$= \sum_{n=1}^{\infty} [(G\sigma^3)^n/n] \exp(-n\sigma^2 S_{ij}^2/R_G^2) \quad (A.25a)$$

such that

$$G_{ij} = -G\sigma^3 \exp(-\sigma^2 S_{ij}^2/R_G^2) \qquad (A.25b)$$

with G and σ functions of the interaction parameter z, has been used to compute both A_2 and A_3 (with $\Delta V = 0$), to give[52]:

$$A_2 M^2/N_A R_G^3 = (\pi^{3/2}/2)G \qquad (A.26)$$

$$A_3 M^3/N_A^2 R_G^6 = (\pi^3/3^{5/2})\sigma^3 G^3 = (8/\pi^{3/2} 3^{5/2})\sigma^3 \psi_2^3 \quad (A.27)$$

Evaluation of $Q(q)$ using equation (A.27) gives $Q(q)$ in the form of equation (24) with:

$$\varepsilon = (3/4\sigma^2) - 1 \qquad (A.28)$$

Elimination of σ in terms of the parameter k_ε gives equation (44) of the text, where k_ε is expected to be small (e.g. $k_\varepsilon \approx 0.005$ according to a treatment discussed above). Thus, for large z, such that $\psi_2 \approx 6.8$, $A_3 M/(A_2 M)^2$ tends to the limit 0.41 if $k_\varepsilon = 0$, in comparison with 5/8 for hard spheres[9,35]. The limit 0.41 is close to the value 0.45 deduced in part 2 for solutions of polystyrene in toluene or benzene.