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# Neutron scattering from a series of compatible polymer blends: Significance of the Flory $\chi_F$ parameter

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In polymer blends the Flory  $\chi_F$  parameter, describing the short range interactions between chain segments, is frequently represented by a structureless point-like interaction. However, in the mean field approximation, the influence of this parameter is directly enhanced by the degree of polymerization of the chains. This large enhancement is also effective with regard to the short range spatial structure of  $\chi_F(r)$  and makes it possible to detect these structural details from a small angle neutron scattering experiment. We present a new way of representing the neutron data so as to explicitly determine these details and we demonstrate the method for the system polytetramethyl carbonate/deuterated polystyrene. The temperature dependence displayed by this system appears to be anomalous within the mean field approximation. However, we show that it can be successfully interpreted in terms of a structural model for  $\chi_F(r)$  which consists of spatially separated positive and negative contributions within a 1–10 Å range. This form is supported by examining the relation of  $\chi_F$  to the pseudopotential interactions between the segments. In the experimental part of this work we also compare our model with SANS data from two other systems (a) polyvinylmethyl ether/deuterated polystyrene, and (b) polyparamethyl styrene/deuterated polystyrene. The last two show a "normal" behavior and are consistent with a relatively structureless  $\chi_F$  parameter.

## I. INTRODUCTION

The interactions of polymer molecules with each other in a melt or concentrated state is well described by the mean field theory pioneered by de Gennes.<sup>1</sup> This approach considers the polymer chains as experiencing an average potential field due to the presence of all the other chains. Its validity, like all mean field theories, rests on the fluctuations about the mean field being small. For long polymer chains this approximation becomes better as the chain length or degree of polymerization increases.<sup>2–4</sup> For a binary polymer system (A,B) a mean field is defined for each component. The basic quantities of interest are the volume fraction correlation functions defined by, for example

$$S_{AB}(\mathbf{q}) = \langle \phi_A(\mathbf{q}) \phi_B(-\mathbf{q}) \rangle, \quad (1.1)$$

where  $\phi_A(q)$  and  $\phi_B(q)$  are the Fourier components of the microscopic concentration fluctuations

$$\phi_A(\mathbf{r}) = V_A \sum_{\alpha} \sum_i \delta(\mathbf{r} - \mathbf{r}_i^{\alpha}). \quad (1.2)$$

$V_A$  is the partial volume of an A segment and  $\mathbf{r}_i^{\alpha}$  is its position vector on a chain  $\alpha$  with degree of polymerization  $N_A$ . A similar definition holds for  $\phi_B(r)$ . The scattering of neutrons by this system is determined by these concentration correlation functions. A useful simplification occurs if the system can be considered to be incompressible, since then

$\phi_A(\mathbf{q}) = -\phi_B(\mathbf{q})$  and the neutron scattering intensity is entirely determined by  $S(\mathbf{q}) = S_{AA}(\mathbf{q}) = S_{BB}(\mathbf{q}) = -S_{AB}(\mathbf{q})$ . The mean field approximation of de Gennes gives  $S(q)$  as

$$\frac{1}{S(\mathbf{q})} = \frac{1}{S_A^0(\mathbf{q})} + \frac{1}{S_B^0(\mathbf{q})} - 2\chi_F, \quad (1.3)$$

where  $\chi_F$  is the usual Flory–Huggins interaction parameter and the  $S_A^0(q)$ ,  $S_B^0(q)$  are related to the structure factor of the unperturbed single chains by

$$S_A^0(\mathbf{q}) = \frac{\phi_A}{N_A} \sum_{i,j=1}^{N_A} \langle \exp i\mathbf{q} \cdot (\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\alpha}) \rangle, \quad (1.4)$$

where  $\phi_A$  is the average volume fraction of the A polymer. The size of the polymer chains governs the  $q$  dependence of  $S_A^0(q)$  and  $S_B^0(q)$  as can be seen by expanding the exponential in Eq. (1.4) to give

$$S_A^0(q) = \phi_A N_A [1 - (1/3)q^2 R_{gA}^2 + \dots], \quad (1.5)$$

where  $R_{gA}$  is the radius of gyration

$$R_{gA}^2 = \frac{1}{N_A} \sum_{i,j=1}^{N_A} \langle (\mathbf{r}_i^A - \mathbf{r}_j^A)^2 \rangle. \quad (1.6)$$

Again for small  $q$ , Eq. (1.3) is normally written in the form

$$\frac{1}{S(q)} = 2(\chi_S - \chi_F) + q^2 l^2, \quad (1.7)$$

where

$$2\chi_S = \frac{1}{\phi_A N_A} + \frac{1}{\phi_B N_B}, \quad (1.8)$$

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and

$$I^2 = \frac{1}{3} \left[ \frac{R_{gA}^2}{\phi_A N_A} + \frac{R_{gB}^2}{\phi_B N_B} \right]. \quad (1.9)$$

$l$  is of the order of about a fourth of the Kuhn segment length since  $R_{gA}^2 = N_A l_A^2 / 6$ , that means in the order of few angstrom units. The concentration and  $q$  dependence of the small angle neutron scattering (SANS) intensity are now given explicitly by the Eqs. (1.7) and (1.8). Only the temperature dependence remains implicit in these equations and this is normally assumed to occur in the interaction parameter  $\chi_F = \chi_F(T)$ . In this work we will present SANS data on concentration fluctuations present in three different polymer blends:

- (A) polyvinyl-methyl-ether/deuterated polystyrene (PVME/PS<sub>D</sub>),
- (B) polymethyl-styrene/deuterated polystyrene (PMS/PS<sub>D</sub>),
- (C) polytetramethyl carbonate/deuterated polystyrene (PTMC/PS<sub>D</sub>).

Our intention is to discuss the dependence of the scattered neutron intensity on the scattering vector in the context of the mean field result Eq. (1.7).

## II. EXPERIMENTAL

For the small angle neutron scattering experiments the three systems mentioned above were prepared from polymers characterized in Table I. System A (PVME/PS<sub>D</sub>) is a well known compatible system with a lower critical solution temperature.<sup>5</sup> It was prepared by dissolving both compo-

nents in toluene then cast into films. After drying in vacuum at 50 °C for 3 days and at 150 °C for 10 h, samples were formed by melting at about 100 °C into disks of 1 mm thickness and 13 mm diam.

System B (PMS/PS<sub>D</sub>) exhibits an upper critical solution temperature.<sup>6</sup> The two components of system B were dissolved in benzene. After evaporation the solvent by freeze drying for a period of two days, samples were formed into disks of the same size as for system A.

Finally, system C (PTMC/PS<sub>D</sub>) showing a LCST-like system A<sup>7</sup> was mixed by solving in methylene chloride and then cast into films, which were dried in vacuum beginning with 50 up to 180 °C with an increasing temperature program for a period of 1 week. After this procedure samples were prepared by melting the polymer mixture and forming into disks.

The small angle neutron scattering experiments (SANS) were executed with the SANS facility at the Riso National Laboratory, Roskilde, DK. This instrument was installed at the cold source of the 10 MW research reactor DR3. Thermal neutrons are available in a range  $2.5 < \lambda < 30$  Å, which could be monochromated within an accuracy of typically 10% to 20% by a mechanical velocity selector. For the experiments neutron wavelengths of  $\lambda = 10$  Å and  $\lambda = 15$  Å were used. The scattered neutrons were collected by a two-dimensional H<sup>3</sup> detector with a sensitive area of 40 × 40 cm. The whole area was divided into 64–64 channels. The distance between sample and detector was 3 m. The data evaluation was executed by a PDP11 (RT11 system) computer. The inhomogeneous sensitivity of the area detector was corrected by the incoherent scattering of water. All the data were calibrated by the incoherent scattering of polyethylene standard sample.

TABLE I. Sample characterization. The volume fraction of polystyrene was in all cases  $\phi = 0.5$ .

System	Component 1	$M_w$ [g/mol]	$M_w/M_n$	Component 2	$M_w$ [g/mol]	$M_w/M_n$
A	PVME <sup>a)</sup> $\left[ \text{CH}_2 - \underset{\text{OCH}_3}{\text{CH}} \right]_n$	99.000	2.13	b) PS <sub>D</sub>	39.000	1.05
B	PMS <sup>b)</sup> $\left[ \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right]_{0.4} \left[ \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right]_{0.6}$	61.400	1.06	b) PS <sub>D</sub>	38.100	1.05
C	PTMC <sup>c)</sup> $\left[ \text{CH}_3 - \underset{\text{CH}_3}{\text{C}} - \text{O} - \underset{\text{CH}_3}{\text{C}} - \text{O} - \text{C}(=\text{O}) - \text{O} \right]_n$	130.000	$\geq 2$	b) PS <sub>D</sub>	105.000	1.06

<sup>a</sup> Supplied by Aldrich, Europe.

<sup>b</sup> Prepared by Dr. Antonietti, University of Mainz.

<sup>c</sup> Prepared by Dr. Serini, Bayer AG, Leverkusen.

### III. RESULTS

In Figs. 1–3 we present the inverse of the neutron scattering intensity taken at different temperatures plotted as a function of  $q^2$ , for the three different blends A–C, respectively. The PVME/PS<sub>D</sub> (Fig. 1) and PMS/PS<sub>D</sub> (Fig. 2) mixtures show a behavior directly in accord with the mean field prediction given by Eq. (1.7). As the temperature is varied a series of parallel lines are obtained, indicating that only the intercept  $2[\chi_S - \chi_F(T)]$  is changing with temperature and not the slope given by  $l^2$ . In contrast to this expected behavior the PTMC/PS<sub>D</sub> blend, shown in Fig. 3, is significantly different and not in immediate accord with Eq. (1.7). For this blend not only the intercept but also the slope depend on the temperature, with the slope decreasing as  $\chi_F(T)$  approaches  $\chi_S$ . The slope changes by almost an order of magnitude as the temperature is increased from 220 to 246 °C. In the mean field result the slope is determined by  $l^2$  given by Eq. (1.9) and the magnitude of this effect is too large to consider the  $R_g$ 's as being temperature dependent due to inter- or intra-interaction effects. In the next section we show that this result can still be interpreted within the mean field formalism by assigning a spatial structure to the  $\chi_F$  parameter.

### IV. DISCUSSION

The Flory  $\chi_F$  parameter is normally regarded as arising from a structureless, short range, monomer–monomer contact interactions. In the small angle neutron scattering range its spatial dependence can be described by a delta function so that

$$\chi_F(\mathbf{r}) = \chi_F^0 \delta(\mathbf{r}). \quad (4.1)$$

For concentration fluctuations the spatial scale is determined, in Eq. (1.3), by the single chain structure factors  $S^0$  and is of the order of the radius of gyration of the polymer chains. Eq. (4.1) would therefore seem to be an entirely adequate approximation for  $\chi_F(r)$ , since any spatial variation

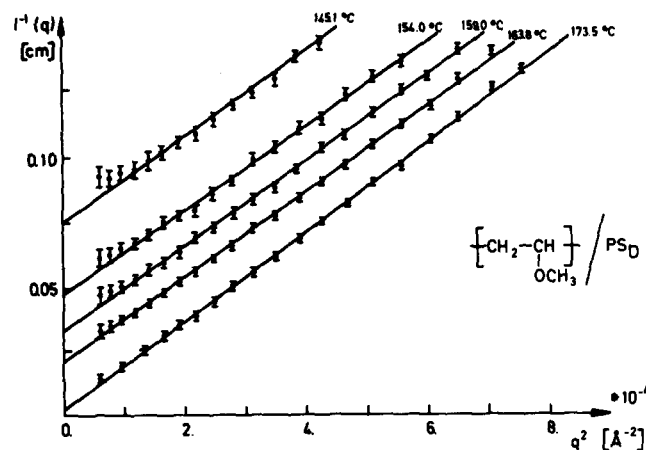


FIG. 1. Inverse neutron scattering intensity  $I^{-1}(q)$  vs the square of the scattering vector  $q$  for the blend PVME/PS.

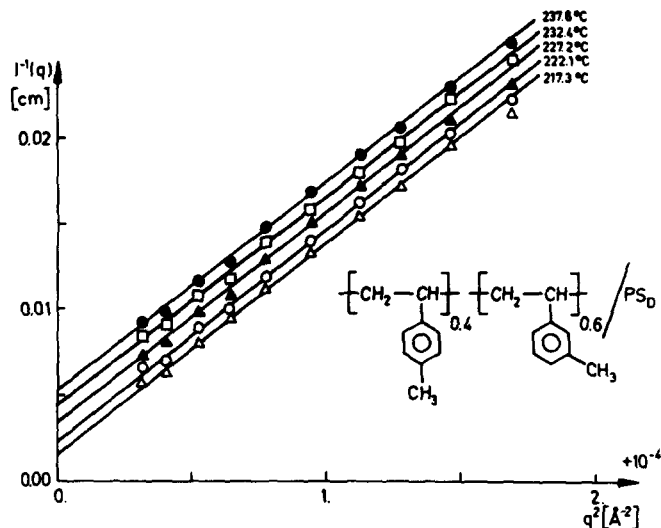


FIG. 2.  $I^{-1}(q)$  vs  $q^2$  for the blend PMS/PS.

can only be of the order of a Kuhn segment length. However, it is our intention, in this paper, to show that the experimental results on the (PTMC/PS<sub>D</sub>) system do require some spatial structure to be assigned to  $\chi_F(r)$ . Later in this section we will propose a particular functional form for  $\chi_F(r)$ , but for the moment we will assume an arbitrary form for  $\chi_F(r)$  or equivalently  $\chi_F(q)$ . The application of the mean field

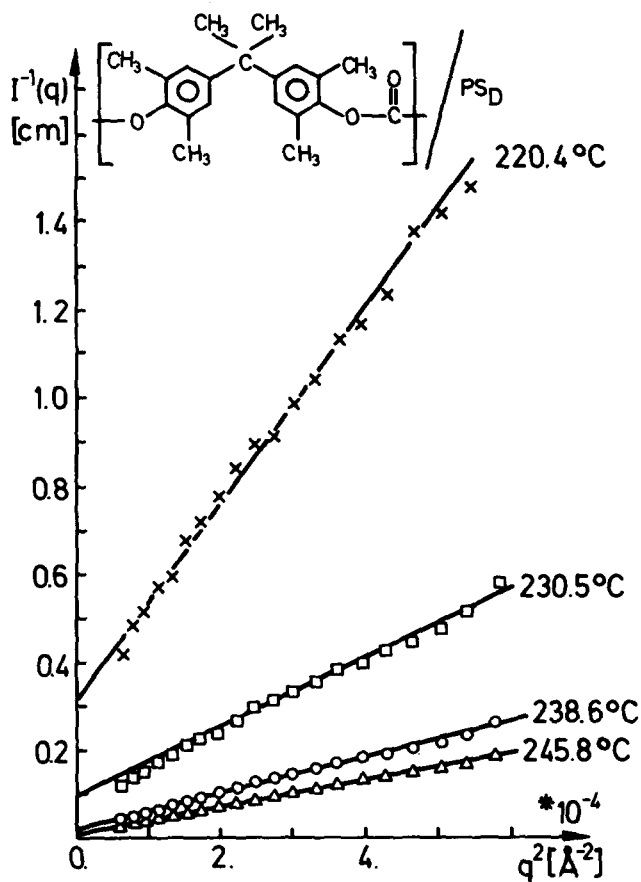


FIG. 3.  $I^{-1}(q)$  vs  $q^2$  for the blend PTMC/PS showing the anomalous behavior.

approximation is unaffected by this generalization and we obtain the result (1.3) but with  $\chi_F$  replaced by  $\chi_F(q)$ .

We rewrite the small  $q$  approximation to the mean field result (1.7) in a form which retains the natural scale length of  $R_g$ . For clarity of exposition we will consider the case  $N_A = N_B = N$  and  $R_{gA}^2 = R_{gB}^2 = R^2$ . Then Eq. (1.7) can be written as

$$\frac{N}{S(q)} = \left\{ \frac{1}{\phi_A \phi_B} - 2N\chi_F(q) \right\} + \frac{1}{3} q^2 R^2 / \phi_A \phi_B. \quad (4.2)$$

By choosing  $qR$  as the correctly scaled variable appropriate to the experimental situation the resulting form of Eq. (4.2) emphasizes that the  $\chi_F(q)$  is amplified by the large factor  $N$  corresponding to the degree of polymerization. Correspondingly the spatial structure of  $\chi_F(q)$  is also enhanced by this factor. To see this in detail we write for a spherically symmetric  $\chi_F(q)$ ,

$$\chi_F(q) = \chi_F^0(1 - Kq^2 + \dots), \quad (4.3)$$

where  $K$  defines the structural details of  $\chi_F(r)$  and is given by

$$K = \frac{1}{3} \frac{\int_0^\infty \chi_F(r) r^4 dr}{\int_0^\infty \chi_F(r) r^2 dr}. \quad (4.4)$$

If  $\chi_F(r)$  were a monotonically decreasing function of  $r$ , then  $K$  would approximately measure the  $(\text{range})^2$  of the potential. For example if  $\chi_F(r) \sim e^{-r/b}$ , then  $K \sim b^2$  and is positive. However, we do not choose to write  $K$  in this form, because as we will shortly show, the experimental results suggest that in some cases  $\chi_F(r)$  is *not* monotonically decreasing and in these circumstances  $K$  may be positive or negative. We also comment here that  $K$  appears in the mean field result (4.2) as  $NK$ . That is, the structural features of  $\chi_F(r)$  are also amplified by the polymerization factor  $N$ . If we use the  $q$  dependence (4.3) of  $\chi_F(q)$  in the original expression (1.7) for  $S(q)$  then we get

$$S^{-1}(q) = 2(\chi_S - \chi_F^0) + q^2(l^2 + 2\chi_F^0 K). \quad (4.5)$$

A form similar to this was also obtained by Binder, see Eq. (3.20) of Ref. 3. To complete our analysis we will also assume that the major temperature dependence is still to be found in the parameter  $\chi_F^0(T)$ , so that we will regard  $K$  as being temperature independent.

The "anomalous" results shown in Fig. 3 for the polytetramethyl carbonate/deuterated polystyrene blend can be understood in terms of a negative value for  $K$ . To see this directly we replot the experimental results of Fig. 3 in the following manner: we rewrite the scattering intensity from (4.5) in the Ornstein-Zernicke form

$$S^{-1}(q) = S_0^{-1}(1 + q^2 \xi^2), \quad (4.6)$$

where

$$S_0^{-1} = S^{-1}(q=0) = 2(\chi_S - \chi_F^0), \quad (4.7)$$

and

$$\xi^2 = \frac{l^2 + 2\chi_F^0 K}{2(\chi_S - \chi_F^0)}.$$

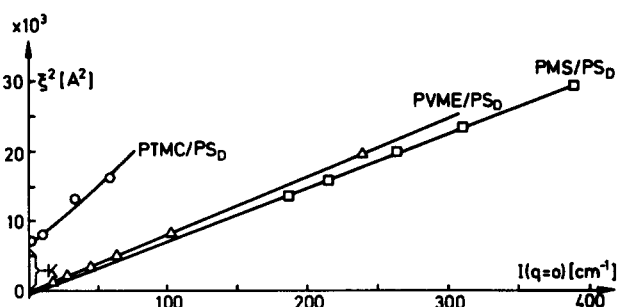


FIG. 4. The square of the correlation length  $\xi$  from Eq. (4.6) plotted as a function of the intensity  $I$  at  $q=0$  according to Eq. (4.8).

The Flory  $\chi_F$  parameter can then be eliminated in favor of the scattering intensity at  $q=0$ , i.e.,  $S_0$ , to give

$$\xi^2 = S_0(l^2 + 2K\chi_S) - K. \quad (4.8)$$

If  $K$  is independent of temperature, this equation suggests that at all temperatures a plot of the  $\xi^2(T)$  vs  $S_0(T)$  will give a straight line, with the intercept at  $S_0(T) = 0$  determining the value of  $K$  directly. The experimental results of Figs. 1–3 have been replotted in this manner and are shown in Fig. 4. They confirm the relation (4.8) and give for the PTMD/PS<sub>0</sub> system a large negative value for  $K$  of the order of 6000 Å<sup>2</sup>. A very rough estimation of the slope of the straight line in Fig. 4, which is given by  $(l^2 + 2\chi_S)$  yields with  $l = 15$  Å and  $K = -6000$  Å<sup>2</sup> a value of  $\chi_S = 0.003$  in good agreement with the value calculated from Eq. (1.8).

Such a large and negative value for  $K$  would appear to be at variance with the assumption that  $K$  defines the structural details of the short range interaction  $\chi_F(r)$ . As we have already commented, if  $\chi_F(r)$  were a monotonically decreasing function of  $r$ , then it follows from the definition (4.4) that  $K$

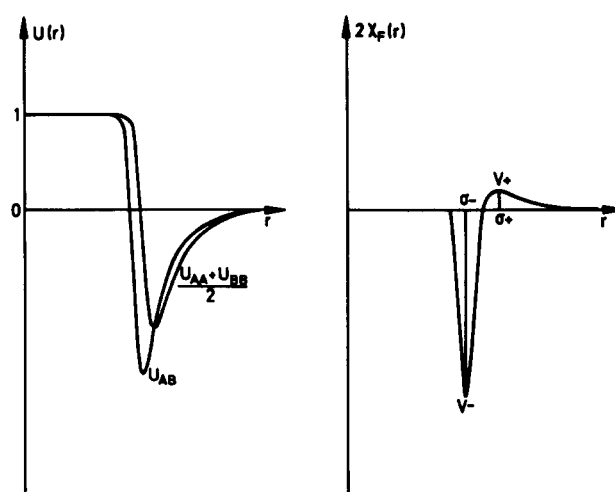


FIG. 5. (a) Schematic spatial dependence of the pseudopotentials  $(U_{AA} + U_{BB})/2$  and  $U_{AB}$ . (Curves calculated from 12/6 Lennard-Jones potentials.) These curves serve only the purpose of demonstration, the actual L-J parameter play no role for the discussion of this oversimplified model. (b) Schematic spatial dependence of  $\chi_F(r)$  based on the pseudopotentials of (a).

will be positive and that  $K$  should be of the order of the range of the square of the interaction distance, i.e.,  $5\text{--}10 \text{ \AA}^2$ . The anomaly can be resolved if we assume that  $\chi_F(r)$  changes sign as a function of  $r$  as sketched in Fig. 5(b). Then, under suitable conditions, the two integrals in (4.4) could be of opposite sign. This behavior is not so unexpected, since we know from the theory of dense liquids that interactions between particles are best described by pseudopotentials<sup>9</sup>  $U_{AA}$ ,  $U_{BB}$ , and  $U_{AB}$ , where for example

$$U_{AA}(r) = 1 - \exp[-V_{AA}(r)/RT], \quad (4.9)$$

and  $V_{AA}$  is the direct interaction between two A segments. The spatial dependence of the  $U$ 's is sketched in Fig. 5(a) for  $(U_{AA} + U_{BB})/2$  and a different  $U_{AB}$ . A "first principles" derivation of the mean field equations<sup>9</sup> shows that the relevant interaction parameters are  $\chi_{FA}(q)$  and  $\chi_{FB}(q)$ , where

$$\chi_{FA}(q) = \frac{U_{AA}(q)U_{BB}(q) - U_{AB}^2(q)}{2U_{AA}(q)}, \quad (4.10)$$

and similarly for  $\chi_{FB}(q)$ . A similar relation has been obtained by Benoit *et al.*<sup>8</sup> In the limit that  $U_{AA}(q)$ ,  $U_{BB}(q)$ , and  $U_{AB}(q)$  are not very different from each other, we can write them as

$$U_{AA}(q) = U_0(q) + \epsilon_{AA}(q),$$

and similarly for  $\epsilon_{BB}(q)$  and  $\epsilon_{AB}(q)$ . If the  $\epsilon$ 's are very much less than  $U_0(q)$ , then the Flory  $\chi_F(q)$  is given by

$$\begin{aligned} \chi_F(q) &\approx \chi_{FA}(q) \approx \chi_{FB}(q) \\ &\approx \left[ \frac{\epsilon_{AA}(q) + \epsilon_{BB}(q)}{2} - \epsilon_{AB}(q) \right]. \end{aligned} \quad (4.11)$$

This relation in  $q$  space transforms directly back into  $r$  space, so that

$$\chi_F(r) = \frac{1}{2} \{ \epsilon_{AA}(r) + \epsilon_{BB}(r) \} - \epsilon_{AB}(r).$$

The resulting form for  $\chi_F(r)$ , corresponding to the pseudopotentials shown in Fig. 5(a), is sketched in Fig. 5(b). Note that these figures are drawn only for the purpose of demonstration. The real interaction potential  $\chi_F(r)$  between chain segments will be highly anisotropic, of course. To complete and illustrate our analysis we will use the simple form

$$\chi_F(r) = V_+ \delta(r - \sigma_+) - V_- \delta(r - \sigma_-) \quad (4.12)$$

to describe the schematic form of Fig. 5(b), where we use delta functions of strengths  $V_+$  and  $V_-$  located at  $\sigma_+$  and  $\sigma_-$  to represent the repulsive and attractive parts of  $\chi_F(r)$ . The parameter  $K$  is given directly from Eq. (4.4),

$$K = \frac{1}{3} \left\{ \frac{V_+ \sigma_+^4 - V_- \sigma_-^4}{V_+ \sigma_+^2 - V_- \sigma_-^2} \right\} \quad (4.13)$$

or

$$\frac{3K}{\sigma_-^2} = \frac{\lambda p^2 - 1}{\lambda p - 1}, \quad (4.14)$$

with  $p = (\sigma_+/\sigma_-)^2$  and  $\lambda = V_+/V_-$ .

A sketch of  $K$  in dependence on  $\lambda$  for a given value of  $p$  is plotted in Fig. 6(a). In addition the change of

$$\chi_F^0(T) = V_-(T) \sigma_-^2 (\lambda p - 1) \quad (4.15)$$

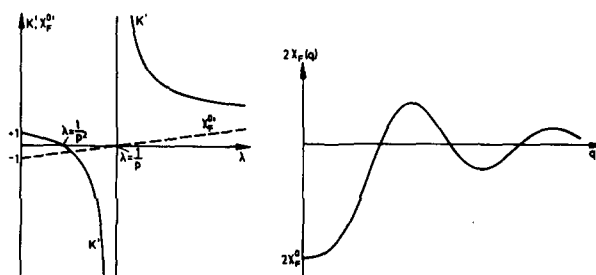


FIG. 6. (a) The structure parameter  $K' = 3K/\sigma_-^2$  [ $K$  is defined by Eq. (4.4)] in dependence on  $\lambda = V_+/V_-$ . Further  $\chi_F^0 = \chi_F^0/V_- \sigma_-^2$  is plotted according to Eq. (4.15). (b) Fourier transform  $2\chi_F(q)$  from the interaction potential of Fig. 5(b).

is shown. One can see that in the range  $1/p^2 < \lambda < 1/p$   $K$  will be negative and can range from zero to infinity. On the other hand, in the same range  $\chi_F^0$  is negative, so that  $2\chi_F^0 K$  appearing in Eq. (4.5) is positive. It may be noticed that the system PTMC/PS has a "lower critical solution temperature,"<sup>7</sup> that means at low temperatures  $\chi_F^0$  is negative and decreases in amount during heating in accordance with Fig. 3 and Eq. (1.7). The expected  $q$  dependence of  $\chi(q)$  is sketched in Fig. 6(b). It was obtained by Fourier transform of Fig. 5(b).

This simple model describes qualitatively the experimentally observed behavior of the system PTMC/PS if one assumes that the "geometry" of the interaction described by the parameters  $p$  and  $\lambda$  depends only little on temperature and that the main temperature dependence of  $\chi_F^0$  is due to the depth of potential  $V_-(T)$  according to Eq. (4.15). The observed value of  $K$  (see Fig. 4) is so large that even with a Flory parameter of let us say  $\chi_F^0 = -10^{-3}$  the product  $2\chi_F^0 K$  is in the same order of magnitude as  $l^2$ . In contrast, if one assumes that  $K = 0$  and that the "expansion" of the coils at lower temperatures is due to changes of  $l$  with temperature than an unreasonable value of  $-20.8 \text{ \AA}/K$  for the temperature coefficient results from the data of Fig. 3.

## V. CONCLUSIONS

We have shown that in the mean field approximation the influence of not only the Flory parameter  $\chi_F$  but also the short range structural details are amplified by the degree of polymerization. The data of polytetramethyl carbonate/deuterated polystyrene, which is anomalous from the standpoint of a point-like interaction, can be successfully interpreted using a short range spatial model for  $\chi_F(r)$ . A new method of data analysis is proposed, based on the Ornstein-Zernicke form for concentration fluctuations, which exhibits the structural details of  $\chi_F(q)$  directly. We find that  $\chi_F(r)$  must contain both repulsive and attractive spatial parts to account for the experimental data. The plausibility of this form is supported by examining the relationship of  $\chi_F$  to the pseudopotentials acting between the segments.

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