Structure of polymer solutions: scaling and modelling on an electronic computer

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The computer simulation method has been used to examine the equilibrium characteristics of flexible-chain concentrations in model lattices in θ solvents and good solvents. The mean square radius of inertia, and the radial distribution functions of density of the units around an isolated (average) unit and around the centre of gravity of an arbitrary isolated chain have been calculated. The results of a 'computer experiment' have been compared with those predicted by scaling theory. In general 'experimental' results are in good agreement with the formulae of scaling theory and with the picture of the 'blob' concept.

Keywords Polymer solutions; structure; scaling; modelling; electronic computer

INTRODUCTION

Recent years have been marked by considerable progress in the study of concentrated polymer solutions.

New experimental techniques, first and foremost the study of the fine structure of a polymer solution, including the structure of individual 'marked' chains, by the method of neutron scattering in a solution of partially deuterated polymer, have stimulated the setting-up of theoretical investigations.

This work is developing in two directions. In the area of analytical theories, a new approach has been worked out which is based on the analogy discovered between the description of a polymer system, on the one hand, and magnetic material close to the point of phase transition, on the other. This has enabled the theory of polymer systems to take advantage of developments in the theory of phase transitions, and in particular it has enabled the principle of scale transformation (scaling) to be carried over to polymer systems.

The other direction is in connection with the direct modelling of polymer systems on an electronic computer by the Monte Carlo method, i.e. with the setting-up of computer experiments.

In the present work we will discuss and compare some results of the theory of scaling and computer experiments which provide information on the equilibrium structure of solutions of flexible-chain polymers.

SCALING AND THE CONCEPT OF 'BLOBS' IN POLYMER CHAINS

In this section we present the results of research on the constitution diagram of polymer solutions, striving to underline the principles and physical content of the overall approach.

In the mid-1970s, De Gennes[1,2] and Des Cloizeaux[3] discovered that the statistical laws governing lattice models of polymer systems (an isolated polymer chain and a polymer solution of given concentration) can be described by the same relations as statistical laws governing the lattice system of spins undergoing a second-order transition.

Here different characteristics prove to be equivalent in the 'polymer' and 'magnetic material' systems, for example $1/N \sim \Delta T/T$, $c \sim -\Delta S$, etc. (where N is the degree of polymerization, the length of the polymer chain; c, the concentration of the polymer solution; $\Delta T = T - T_c$; T_c the critical temperature in the magnetic material; ΔS, the entropy of the magnetic material in an external field).

The origin of the similarity between the polymer and the magnetic material can be explained on the basis of simple considerations. It is well known that, in a coiled-up Gaussian or swollen polymer chain, large-scale fluctuations of dimensions, of the order of the actual dimensions, occur.

Thus, for the radius of gyration of a Gaussian coil[4]:

$$(R^2-\overline{R^2})^2=\tfrac{4}{15}(\overline{R^2})^2$$

Correspondingly, macroscopic fluctuations of density are observed in the coil, i.e. the interaction radius of these fluctuations turns out to be of the order of the dimensions of the coil and increases to an unlimited degree with growth in N. The unlimited increase in the interaction radius is also characteristic for the spin system, but in this case it is only observed close to the critical point. This explains the equivalence of the values $1/N$ and $\Delta T/T$.

The analogy found between the polymer and the magnetic material enabled the ideas and the methods of the physics of critical phenomena[5] to be carried over to polymer systems, and the limits of approximation of the mean field, on which the classic work of Flory[6] has been based, to be exceeded. Of importance here is the principle of scaling (scale transformation), according to which a change in the external conditions has the effect of a change of scale on the physical characteristics of the system.

In other words, an exponential dependence of the physical characteristics of the system on the external parameters (for polymers—on the degree of polymerization, the concentration of the solutions, the parameter of the excluded volume of units, the parameter of chain rigidity, etc.) is postulated. To determine the corresponding exponents (critical indices of the theory of phase transitions), regions of physical conditions are distin-

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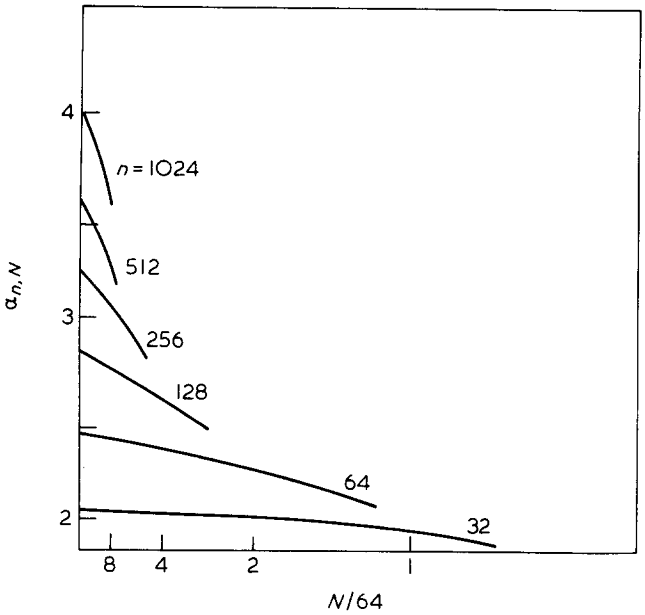

Figure 1 Dependence of the coefficient of swelling $\alpha_{n,N}$ of a segment of a chain of n units on the full length of the chain N. The graph is constructed in accordance with the data of ref.8. At the extreme right-hand point of each curve, $n = N$

guished in which the values of any index can be established from general considerations: the results link up at the boundary of the regions.

For polymer solutions, one of the inherent boundaries of the regions is the critical concentration for entanglement of the macromolecules, $c/$, introduced by Simha[7,23] as long ago as 1951 and determining the concentration at which the macromolecules in the solution occupy the entire volume.

The concentration c^* depends on the mean concentration of units within an isolated macromolecule:

$$c^* \sim N/R^3 \tag{1}$$

where

$$R \sim N^{\nu} \tag{2}$$

is the mean radius of inertia of the isolated macromolecule; $\nu = \nu_F = 0.6$ and $\nu = \nu_e = 0.5$ for cases of a good ($T > \theta$) solvent and a θ solvent; where all the coefficients have been omitted.

When $c < c^*$ the solution is termed dilute, and with $c > c^*$ it is termed semi-dilute since $c^* \ll 1$ when $N \gg 1$.

The principle of scaling can be used in connection with any characteristic of a macromolecule. Examining, for example, the correlation radius of the density ξ, we have[2]:

$$\xi \sim \begin{cases} R, c < c^* \\ N^0 \sim R\left(\dfrac{c}{c^*}\right)^x, c > c^* \end{cases} \tag{3}$$

where the relations $\xi \sim R$ and $\xi \neq \xi(N)$ are based on *a priori* physical considerations, and the second part of the second line indicates crosslinking. Equations (1)–(3) enable x to be found and correspondingly the concentration dependence of ξ:[2]

$$\xi \sim c^{-\nu/(3\nu-1)} \sim \begin{cases} c^{-3/4} & T > \theta \\ c^{-1} & \theta \end{cases} \tag{4}$$

In determining the interaction radius of the density, ξ characterizes the dimensions of the regions of non-uniformity in polymer solutions. It is revealed directly in experiments on the scattering of neutrons in polymer solutions. In addition, this value occupies a fundamentally important place in the physics of polymer systems, having served as a basis for the concept of 'blobs'. The starting point is the interpretation of ξ^3 as such an element of the volume that the segment of polymer chain—'blob'—located in it (and also in any smaller volume) retains all the characteristics inherent in this same segment not subjected to the influence of external conditions. Thus, in a solution of prescribed concentration c the chain segments in the volume, $\xi^3(c)$ retains the characteristics corresponding to an isolated segment not subjected to the influence of other chains (and also of the remaining part of the given chain).

It is worth noting that a necessary part of this interpretation is the supposition that, in the isolated chains, the properties of any segment of the chain are independent of the dimensions and properties of the chain as a whole, and depend only on the interactions within this segment. Here we consider it helpful to give data from direct modelling on an electronic computer which bear out this supposition.

As can be seen from *Figure 1*, the dimensions of the segment of the polymer chain depend mainly on the properties of this segment and only slightly on the full length of the chain and the nature of the interaction in its remaining part.

'Blobs' appear as the main thermodynamic and structural unit of the solution with all the values of c such that $c > c^*$; much as the macromolecule as a whole is the unit when $c < c^*$. The dimensions of the 'blobs' determine the osmotic pressure of the solution[2]:

$$\pi/T \sim 1/\xi^3 \tag{5}$$

and the dimensions of individual macromolecules are represented by Gaussian chains of N/n_b 'blobs'[2]:

$$R^2 \sim \left(\frac{N}{n_b}\right)\xi^2 \sim N\xi^{(2\nu-1)/\nu} \sim \begin{cases} Nc^{-1/4} & T > \theta \\ N & \theta \end{cases} \tag{6}$$

Here n_b is the number of units in a 'blob', connected with ξ by a condition equivalent to (3):

$$\xi \sim n_b^{\nu} \tag{7}$$

The structure of individual 'blobs' depends on the magnitude of the excluded volume effects in them, as a measure of which use can be made of the parameter:

$$z_b \sim \frac{v\tau n_b^2}{V_\theta(n_b)} \sim \tau n_b^{1/2} p^{-3/2} \tag{8}$$

changing to the normal parameter z for the entire chain[6,9,10] when $n_b = N$, i.e. in the region of dilute solutions. In equation (8), v is the intrinsic volume of the unit, $V_\theta(n_b)$ is the θ volume of the chain of n_b units, $\tau = (T - \theta)/T$, and p is the parameter of chain rigidity, equal to the ratio of the length of the rigid segment to its diameter[11]. The influence of the volume effects is assessed from the 'yes–no' principle which is characteristic of scaling. When $|z_b| < 1$ the blobs are considered un-

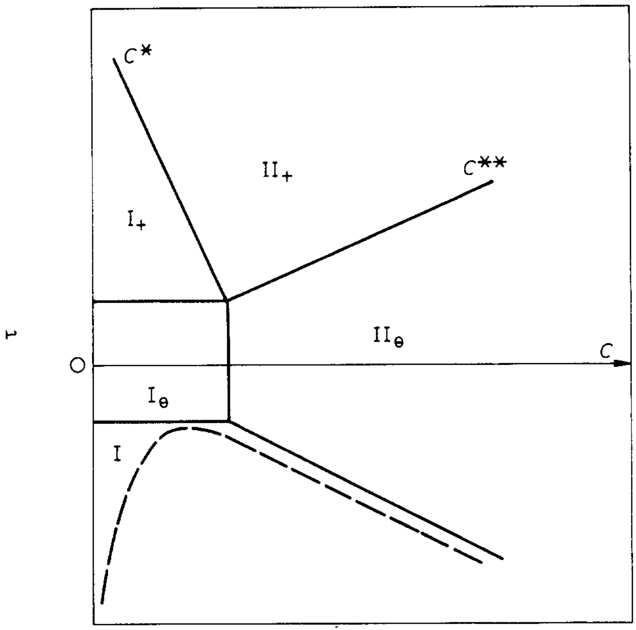

Figure 2 Constitution diagram of a polymer solution. I, regions of weak solution; II, regions of undiluted solution; I_θ and II_θ, θ regions; I_+ and II_+, regions of favourable excluded volume effects $\tau > 0$; I, region of adverse excluded volume changes effects., The broken curve is the phase interface

swollen and Gaussian, while when $z_b > 1$ the coefficient of swelling of the blobs $\alpha_b = R/R_\theta$ bears an asymptotic relation to z_b, so that:

$$\alpha_b \sim \begin{cases} z_b^{1/5} & z_b > 1 \\ 1 & |z_b| < 1 \end{cases} \tag{9}$$

The region $\tau < 0$ and $|z_b| > 1$ corresponds to globularization of the 'blobs'. Subsequently we shall limit ourselves to the region $\tau \geqslant 0$.

The boundary between the two sets of conditions of behaviour of the 'blobs'—swollen and Gaussian 'blobs'—is the condition:

$$z_b^* \sim 1 \tag{10}$$

which with $z_b = z$ produces also the condition of division of the region of dilute solution into two sets of conditions of behaviour of the chains as a whole.

The complete constitution diagram of a polymer solution is constructed in refs. 12 and 13 and takes the form presented in *Figure 2*. In the diagram, regions I and II correspond to weak and undiluted solutions, with the boundary determined by (1), taking into account the dependence of the dimensions of the isolated chain on its rigidity and the excluded volume effects.

The indices indicate the nature of the volume effects in the structural units of each of the regions. In region I_+ the macromolecules swell as a whole, while in the II_+ region the volume interactions take place only within the 'blobs'. In regions I_θ and II_θ the volume interactions are small, so that both the macromolecules as a whole and the individual 'blobs' are Gaussian in these conditions. Here the II_θ region of θ behaviour of the 'blobs' increases with concentration on account of reduction in the dimensions of the 'blobs' in accordance with (4). The boundaries of the θ regions correspond to condition (10) for the entire chain in the case of I_θ and for the 'blobs' in the case of II_θ.

Expressions for the boundaries of the regions and for the characteristics of the chains and 'blobs' in the different regions are summarized in *Table 1*. (This table refers only to flexible chains. For rigid chains with $p \gg 1$ see ref. 14.) It is evident that all the relationships are linked at the boundaries. The $\mathrm{II}_+ \rightarrow \mathrm{II}_\theta$ boundary can be intersected by altering c with a fixed τ value, and therefore it is presented in *Table 1* in the equivalent forms $\tau^* = \tau(c)$ and $c^{**} = c(\tau)$.

We shall turn our attention to the following relationships in *Table 1*. While the volume effects (growth in τ) and rigidity (growth in p) increase the dimensions of the chains as a whole, the dimensions of the individual 'blobs' and the number of units in them with a given concentration turn out to be the smaller, the greater the values of p and τ. (In the I_+ and II_+ regions, these values are always present in the form of the product $p\tau$.) In this case the mean density of the units in a 'blob':

$$c_b \sim n_b/\xi^3 \sim c \tag{11}$$

is independent of the rigidity and excluded volume and depends only on the concentration of the solution.

In order to understand the dependence of n_b and ξ on p and τ, we shall examine the mean density of the intrinsic units of the segment of an isolated chain of n units. For example, let the value of z_n in the given segment exceed unity. Then

$$c_n \sim \frac{n}{s^3(n)} \sim (n^4 p^3 \tau^3)^{-1/3} \sim (s^4 p\tau)^{-1/3} \tag{12}$$

where s^3 is the volume of the segment.

With a given n (or s) value, the more rigid the chain and the greater the distance between τ and the θ point, the smaller is the density of the units of the segment in its volume. Reduction in n (or s) causes an increase in the mean density of c_n.

A similar result corresponds also to Gaussian segments with $z_n < 1$.

Thus, isolating volumes of different size close to the outline of the chain, we obtain a greater density in them the smaller the volume isolated. Equation (11) shows that such a chain segment, the mean density of which is equal to the mean density of the units in the solution, is an inherent element of a concentrated solution, i.e. is a 'blob' retaining intrinsic characteristics. The solution is a system of contacting 'blobs' the dimensions of which decrease as the concentration increases and with a given concentration depend on p and τ in accordance with (12).

In volumes smaller than ξ^3, the chain segments also do not change.

Table 1 Constitution diagram of polymer solution for flexible chains

Region	$\bar{R}^2$	ξ^2	n_b	Boundaries
I_Θ	Np		N	
				$\tau^* \sim (Np^{-3})^{-1/2}$
I_+	$(N^3\tau p)^{2/5}$		N	
				$c^* \sim (N^4\tau^3p^3)^{-1/5}$
II_+	$N(\tau pc^{-1})^{1/4}$	$(\tau pc^3)^{-1/2}$	$(\tau^3p^3c^5)^{-1/4}$	
				$\tau^* \sim p^3c$
				$c^{**} \sim \tau p^{-3}$
II_Θ	Np	$(pc)^{-2}$	$p^{-3}c^{-2}$	
				$c^* \sim (Np^3)^{-1/2}$
I_Θ				

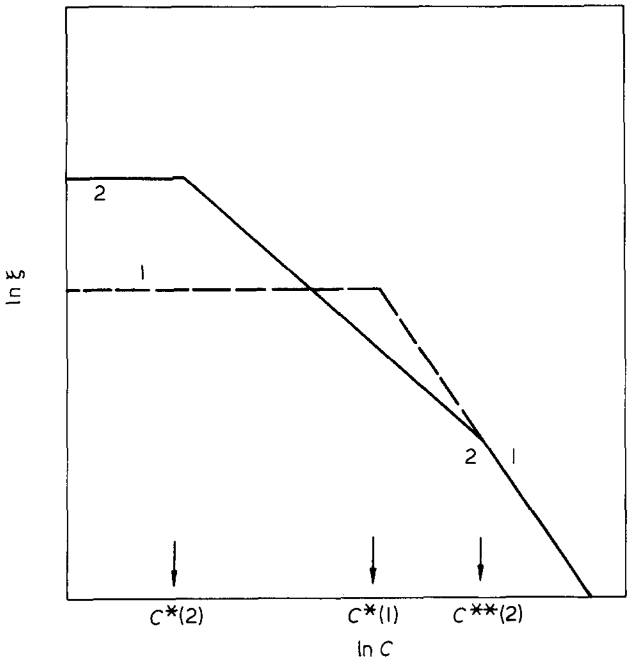

Figure 3 Diagram of the concentration dependence of the correlation radius of density ξ. Broken line (1), value corresponds to $I_\theta \rightarrow II_\theta$ transition; full line (2), value of ξ corresponds to $I_+ \rightarrow II_+ \rightarrow II_\theta$ transitions

The concentration dependence of the dimensions of the 'blobs' with different values of N, p and τ, following the data of *Table 1*, are shown diagrammatically in *Figure 3*.

MODELLING OF POLYMER SOLUTIONS ON AN ELECTRONIC COMPUTER: NON-UNIFORMITY OF DISTRIBUTION OF UNITS IN SOLUTIONS

In this section we shall discuss the results of the modelling of polymer solutions, carried out by us on an electronic computer using the Monte Carlo method, drawing comparison with the data of the previous section.

We examined a flexible chain model in a simple cubic lattice where the probabilities of *trans* and *cis* isomers present were the same. The Kuhn segment $A = 1.5$, and having determined the asymmetry of the segment accordingly by the ratio of the length of the Kuhn segment to its thickness, we have $p = 1.5$. Each of the N chain units contained an impenetrable nucleus which is one lattice cube unit in volume; it reacted with any other units of its own, or from a foreign chain present in any of four adjacent lattice units, at energy ε. A positive ε characterized a favourable contact of polymer with polymer, as opposed to polymer with solvent (the solvent was modelled by empty lattice units), a negative ε indicated forces of repellance existing between randomly approaching chain units. The value of ε represents the free energy of the polymer–polymer contact (as opposed to the polymer–solvent contact) and is analogous with parameter χ occurring in the solution theory of Flory.

The quality parameter of the solvent used in this paper is $\tau = (\varepsilon_\theta - \varepsilon)/\varepsilon_\theta$, where $\varepsilon_\theta \simeq -0.3$[15,16]. We shall give data for cases of θ solvent with $\tau = 0$, and a good athermal solvent with $\varepsilon = 0$ and $\tau = 1$.

The effects of concentration were considered using periodic limiting conditions, namely by dividing all the space into cubes of edge l, which were equally filled with the polymer chains. One from amongst the possible states which was considered by the method is illustrated in *Figure 4*, which shows that chain part I protrudes from one cube into an adjacent until it reaches the given length N, while another chain II enters from the opposite end at the same time, and is regarded as a 'foreign chain'. Having constructed one chain of N units in one cube, we proceeded to do so in all the others, and then followed it by making another chain, etc., until all the space was filled with them to some degree, c. The conformation of each chain, the selection of its start and orientation were produced by means of a random counter; the overall number of ways in which the filling with chains was produced was $(1\text{–}1.5) \times 10^3$.

The construction method of each separate chain was identical with that described elsewhere (see for example ref. 16) (Rosenbluth method). A chain unit was accordingly added in one of five unoccupied lattices bordering onto the 'growing end', i.e. the number of forbidden configurations in this series, which was considered by way of a special standardization, so that all the plotted conformations finally had the same probability. In the event of even a single chain unit extension probability, such an addition was made and the chain termination occurred only at the dead end. The 'sample', i.e. particular filling method, was then considered unsuccessful, and the 'sample' was rejected from examination; the plotting of chains (construction) was started afresh.

The systems filled in various manners represented an assembly from which the average of all the values interesting us was obtained. The calculated numbers of intramolecular contacts, etc., were naturally got for all the chains regardless of whether they finished inside their own

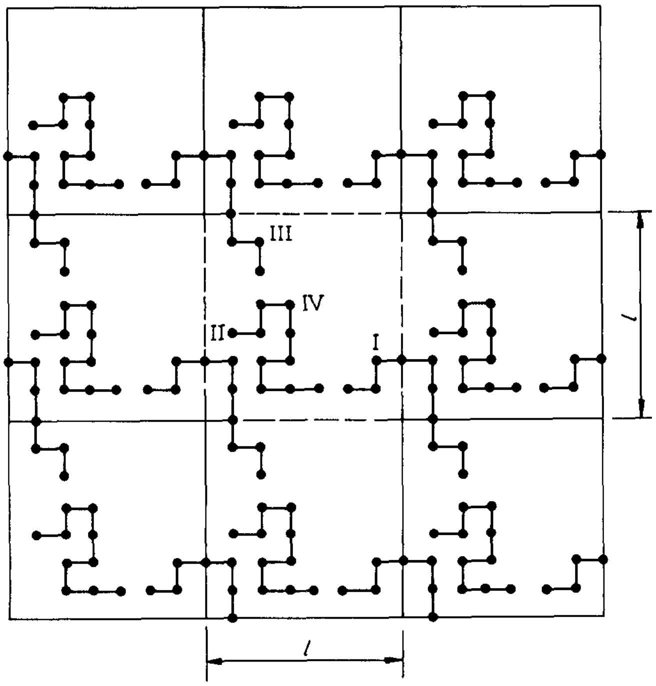

Figure 4 The positions of chains consisting of 10 chain units in a cube of $l = 7$ under periodic limiting conditions. I, II and III, chains intersecting the edge of the cube; IV, a chain completely inside a cube

cube or in any adjacent one. The intramolecular contacts were calculated for all the chains inside one cube.

The edge l of each cube was varied from 11 to 21 and the number of chain units N were 60 to 120, so that it was possible to study the system at concentrations $c=nN/l^3$ from zero to $c\simeq 0.7$ (n = number of chains starting in a particular cube). The findings were independent in practice of the selected l and were almost exclusively determined by chain length N, the solvent quality ε and concentration c.

It must be emphasized that all the results refer to systems which are at equilibrium. The kinetic factors capable of freezing any non-equilibrated states were not considered in the calculation.

The discussion of other characteristics of this system are to be found in refs. 17–19.

Certain characteristics of similar model systems have also been investigated in refs. 20–22. On the whole the results of all the authors are in agreement.

Unfortunately, the length of the chains examined in the computer experiment is limited to values of $N\leqslant 120$. For them the conditions $N\gg n_b\gg 1$ and $(\overline{R^2})^{1/2}\gg\xi\gg l$ (l is the length of the unit), conjectured when deriving the relations of the previous section, turn out to be poorly fulfulled. Therefore, in a number of cases it is necessary to limit oneself to qualitative comparisons only.

We shall examine the values c^* and c^{**} for our system (*Figure 2*). There is a degree of uncertainty in determining each of these. We shall assume that c^* corresponds to the condition[23] $c^*=1/[\eta]$, where $[\eta]$ is the intrinsic viscosity of the solution. Then

$$c^*=\frac{N}{6(\overline{R^2})^{3/2}} \tag{13}$$

where $\overline{R^2}$ is the mean square of the radius of inertia of the isolated chain. For a chain of 60 units, $c^*=0.15$ and 0.07 for a θ solvent and an athermal solvent respectively; for a chain of 120 units, $c^*=0.12$ and 0.043. The value of c^{**} depends greatly on p and τ. Examining the expressions of *Table 1* without the additional coefficients, we obtain $c^{**}=1$ and 0.3 when $p=1$ and 1.5 respectively and $\tau=1$.

We shall begin with an analysis of the correlations in the distribution of the units. In *Figure 5* the radical functions of the distribution of density of the units around an isolated (average) unit of the chain in solutions of different concentration are presented. Averaging is carried out for the different chains. On the abscissa, the $(\overline{R^2})^{1/2}_{c\to 0}$ values are shown for the examined chains with $N=60$.

As can be seen from the figure, where the total density $\rho(s)=\rho_i(s)+\rho_e(s)$ of the units of the region's own (i) and other (e) chains is set apart, non-uniformity of density distribution takes place in both regions I and II of the constitution diagram. The scale of non-uniformity diminishes with growth in concentration both in the θ solvent and in the good solvent. In the θ solvent, only the interchain contribution $\rho_e^{(\theta)}(s)$ depends on concentration, while in the case of the good solvent a growth in concentration affects both $\rho_i(s)$, approaching $\rho_i^{(\theta)}(s)$, and $\rho_e(s)$.

With a given concentration, the size of the region of non-uniformity, i.e. the value of the correlation radius of ξ, in θ conditions is appreciably greater than in the athermal solvent (*Figure 5*). This effect correlates with the dependence presented in *Table 1* of the correlation radius of density ξ on τ in the II_+ region, according to which $\xi\sim\tau^{-1/4}$. For the conditions under examination with $c^*<c<c^{**}$, we have, in accordance with *Table 1*, $\xi_\theta/\xi_{\tau=1}\sim c^{-1/4}$.

The intermolecular distribution function $\rho_e(s)$ with large s values approaches c, while in the region of small s values it diminishes both in the θ solvent and in the good solvent, the screening effect being considerably greater in the good solvent. For the θ solvent, the data are described approximately by the formula:

$$\rho_e^{(\theta)}(s)\simeq c[1-\rho_i^{(\theta)}(s)] \tag{14}$$

corresponding to the average (within the range of c) occupation of all the sites free from units (full curves in *Figure 5*).

It is worth noting, however, that the value of the total density of the units $\rho^{(\theta)}(s)\simeq c+(1-c)\rho_i^{(\theta)}(s)$ which is obtained in this approximation turns out to be different from the limiting value of c in the entire region of $\rho_i^{(\theta)}(s)\neq 0$, i.e. in the entire volume of the coil. On the other hand, according to the discussion of the previous section, the value of the correlation radius of density ξ with $c>c^*$ should not depend on the full dimensions of the coil.

As is shown in ref. 24, in θ conditions the value of ξ_θ depends on the third virial coefficient of interaction of the units. The approximate equation (14) does not take into account triple correlations of the units, and the accuracy of the computer experiment (limited in this case to small c values) proves to be inadequate for revealing their existence (cf. *Figure 8* below).

In the good solvent, reduction in $\rho_e(s)$ in the region of small s values, which is greater than the reduction in the θ solvent, occurs against a background of smaller (or at least, no greater) intrinsic density of the units with small s values, so that the effect does not amount even approximately to simple elimination of the occupied sites.

For analysis of the concentration dependence of ξ, ξ can be determined approximately (within the accuracy of the coefficient) from the relation:

$$\rho_i(\xi)=c \tag{15}$$

For Gaussian chains in a θ solvent, calculation gives

$$\rho_i^{(\theta)}(s)\sim\frac{1}{s}-\mathrm{O}(N^{-1/2})$$

The results of the computer experiment are described well by this expression, and here the correction term for chains with $N\sim 100$ is not negligible. Hence, in accordance with (15), we obtain

$$\xi^{(\theta)}\sim[c+\mathrm{O}(N^{-1/2})]^{-1}$$

in accordance with the data in *Table 1* for long chains, $\xi^{(\theta)}\sim c^{-1}$. For chains in the good solvent the value of ξ was determined by means of equation (15) from graphs of the function $\rho_i(s)$ with different c values. As is evident from *Figure 6*, the values obtained correspond to the relationship $\xi\sim c^{-0.71}$ in good agreement with $\xi\sim c^{-3/4}$ for region II_+ as per *Table 1*.

The variation of the density of the units in polymer solutions, i.e. the presence of regions where $\rho(s)>c$, means

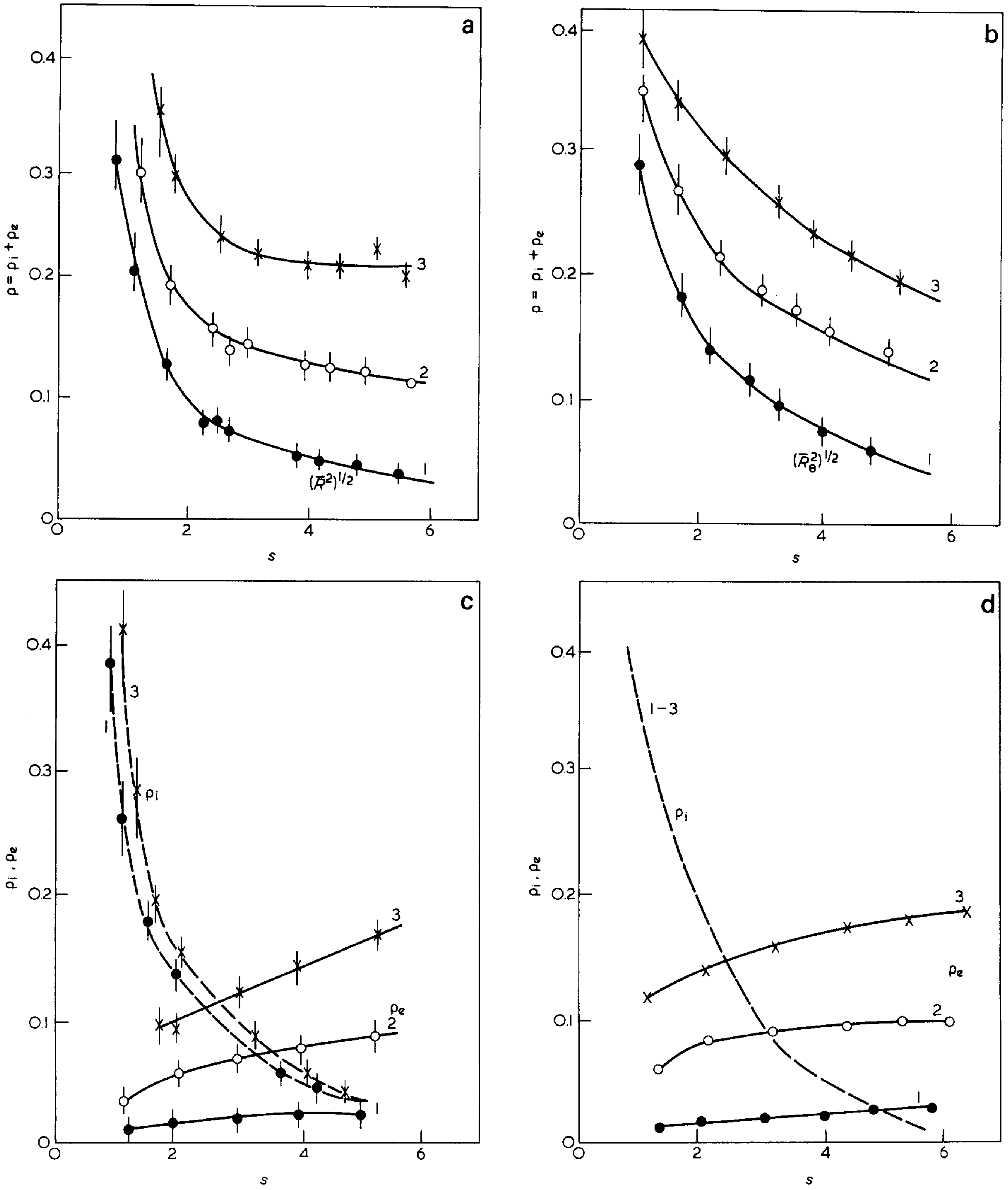

Figure 5 Radial functions of the distribution of density of units around an isolated (average) chain unit. The total density of units $\rho = \rho_i + \rho_e$ with $\varepsilon=0$ (a) and $\varepsilon=\varepsilon_\theta$ (b); ρ_i and ρ_e functions with $\varepsilon=0$ (c) and $\varepsilon=\varepsilon_\theta$ (d); the full curves in (d) are in accordance with (14). The concentration of the solution $c=0.0037$ (1), 0.11 (2) and 0.19 (3). $N=60$ for all concentrations

that there are also concentrations of sites unoccupied by polymer chains, i.e. holes occupied by solvent. In *Figure 7* paired hole–hole radial distribution functions $g_{00}(s)$ are presented for solutions of different concentrations. Comparison of data for good solvents and θ solvents shows that a stronger interaction of units in θ solvents also leads to stronger interaction of the holes.

We shall examine the distribution of the density of units $\tilde{\rho}(s)$ (those of the chain and other units) around the centre of gravity of an arbitrary isolated chain (*Figure 8*) as yet another characteristic of the non-uniformity of a solution. This value has been calculated by us in a wider range of concentrations, including $c > c^{**}$. Successive smoothing of the non-uniformity of the solution can be seen with

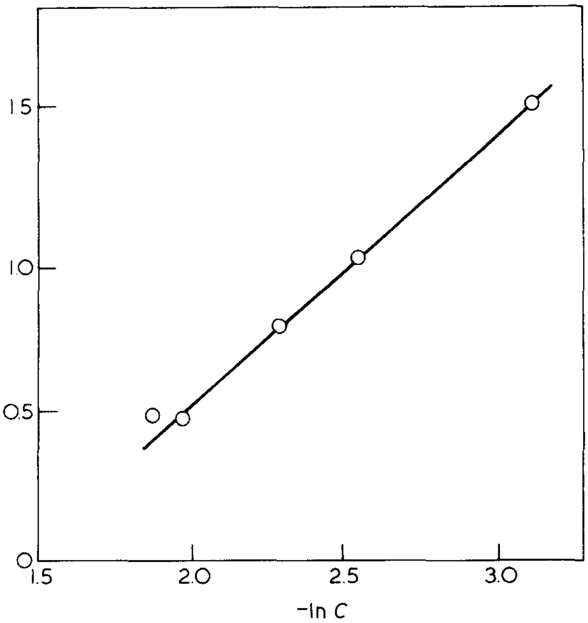

Figure 6 The concentration dependence of ξ with $\varepsilon = 0$ and $N = 60$

increase in concentration.

For θ conditions with $\tau = 0$, the distribution of density of the chain's own units $\tilde{\rho}_i^{(\theta)}(s)$ is independent of concentration, while the function $\tilde{\rho}_e^{(\theta)}(s)$ with small c values is described approximately by (14) with replacement of $\rho_e^{(\theta)}$ and $\rho_i^{(\theta)}$ by $\tilde{\rho}_e^{(\theta)}$ and $\tilde{\rho}_i^{(\theta)}$. With increase in concentration, the deviations of $\tilde{\rho}_e^{(\theta)}(s)$ from the approximate equation (14), connected it seems with triple correlations of density, as discussed above, becomes appreciable in *Figure 8*.

In a good solvent with concentrations $c^* < c < c^{**}$, reduction in $\rho_e(s)$ in the region of small s values is considerably greater than in the θ solvent. With $c > c^{**}$ the differences between cases of good solvent and θ solvent are eliminated to a considerable degree, $\tilde{\rho}_e(s) \simeq \tilde{\rho}_e^{(\theta)}(s)$ and $\tilde{\rho}_i(s) \simeq \rho_i^{(\theta)}(s)$. This is in full agreement with the diagram of *Figure 2*, since with $\tau = 1$ and $c > c^{**}$ the state of the system corresponds to the same region II_θ as does the state of the system with $\tau = 0$. It is worth noting that the comparatively large values of $\tilde{\rho}_i(s)$ in the system examined are not connected with a low N value.

In conclusion of this section, we shall examine the concentration dependence of the dimensions of the chain as a whole. According to the data of *Table 1* in θ conditions with $\tau = 0$, the dimensions of the chain should not depend on concentration, which is also observed in the computer experiment (*Figure 9b*). We have already noted above that in θ conditions the more detailed characteristics of chains—functions of the distribution of density of their units around a unit of a chain $\rho_i^{(\theta)}(s)$ and around the centre of gravity of a chain $\tilde{\rho}_i^{(\theta)}(s)$—are also independent of concentration.

For a good solvent, *Table 1* forecasts a reduction in the dimensions of chains to θ values with increase in concentration on account of the elimination of swelling of chains. In *Figure 9a* the concentration dependence of $\bar{R}^2$ is presented, following from *Table 1* with its literal interpretation. In the $c^* < c < c^{**}$ region, $\bar{R}^2/N$ values should lie on a single curve for various molecular masses. With $p > 1$ and $\tau = 1$, there is the limit of $c^{**} < 1$, where $\overline{R^2}(c^{**}) = \overline{R_\theta^2}$, and with further growth in concentration there is no dependence of $\overline{R^2}$ on c.

In the region of small c values right down to $c/$ in region I_+, a concentration dependence of $\overline{R^2}$ also should not be observed.

The results of a computer experiment presented in *Figure 9b* for chains with $N = 60$ and 120 show that in both cases $\overline{R^2}$ diminishes with increase in c to θ values. In this case, instead of diagrammatic step curves, more or less smooth relationships are observed. For $N = 120$, the data of the computer experiment are in good agreement with the relationship $\overline{R^2}(c)$ constructed in accordance with *Table 1* with $p = 1.5$ and $\tau = 1$ and with little smoothing. For all N values, no initial plateau of $\overline{R^2} \neq \overline{R^2}(c)$ appears in the region of small concentrations. It seems that the rare random collisions of the molecular coils in weak solutions lead in good solvents to partial reduction in the swelling of the coils. In this region of concentrations, reduction in $\overline{R^2}$ with concentration is approximately linear (cf. ref. 25). It is clear that a plateau in the region of small c values appears when presenting the course of $\overline{R^2}(c)$ on a logarithmic scale, since with $c < c^*$ the dependence of $\overline{R^2}$ on c is not of an exponential nature.

INTER-UNIT CONTACTS IN POLYMER SOLUTIONS

An important characteristic of a polymer solution is the numbers of contacts between the units of the same or various chains, and the dependence of these values on the quality of the solvent, the concentration of the solution, etc. The number of contacts n_i and n_e calculated per monomer, standardized for the number of sites in the first coordination sphere around a unit, determines the local density of units ρ_i and ρ_e about the frame of the chain. Although the ρ_i and ρ_e values were contained in the functions $\rho_i(s)$ and $\rho_e(s)$ examined in the previous section, we consider it helpful to investigate them in greater detail.

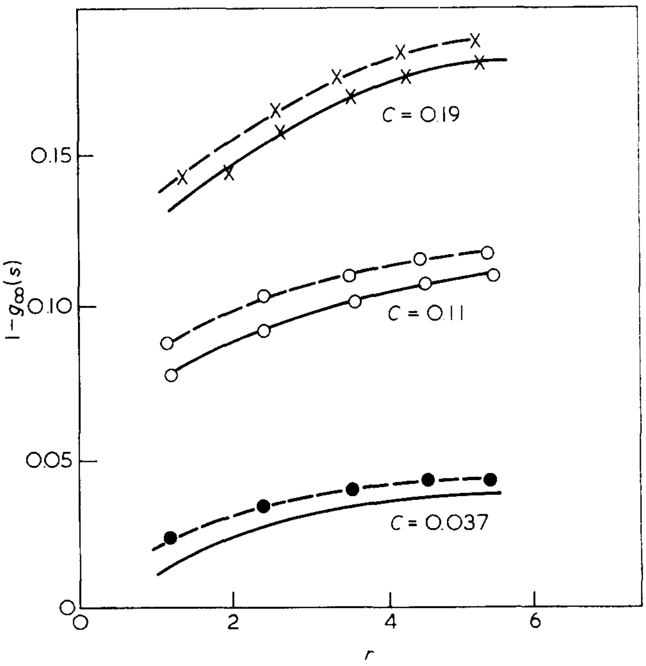

Figure 7 Hole–hole radial distribution functions with $\varepsilon = 0$ (broken curves) and ε_θ (full curves), $N = 60$

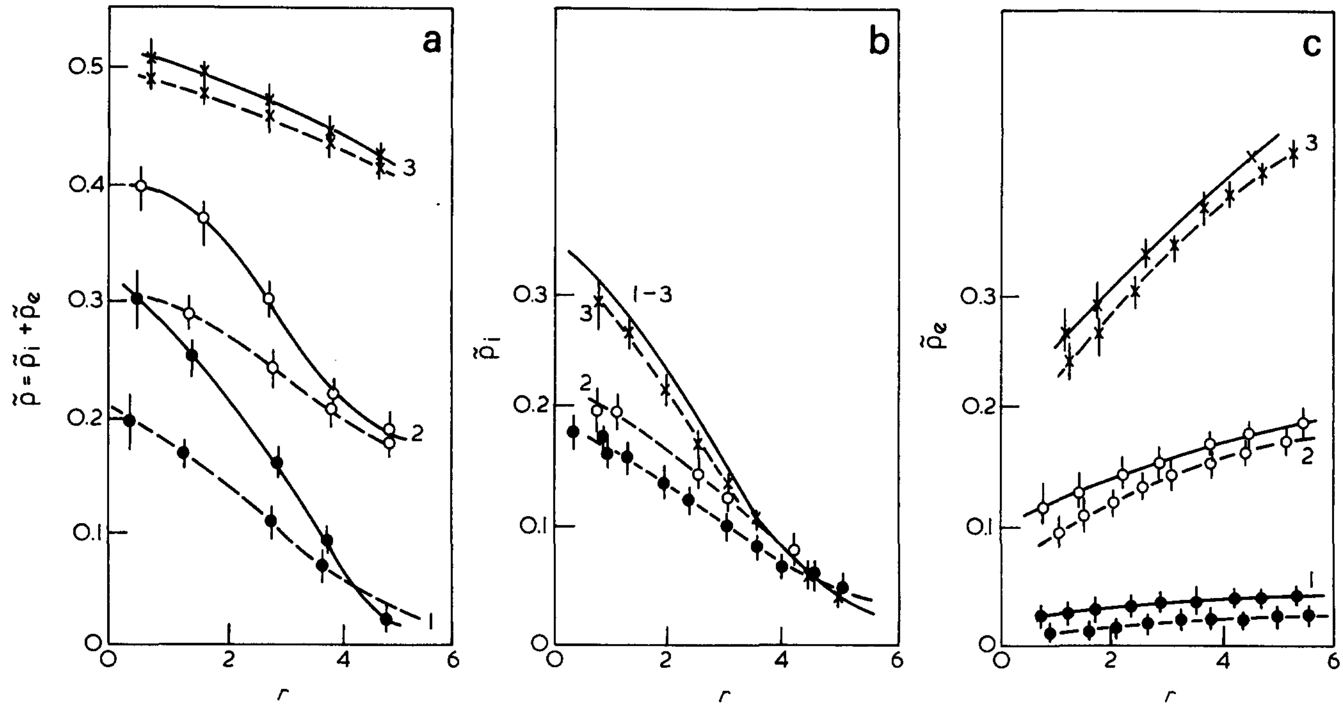

Figure 8 The distribution of the density of units around the centre of gravity of an isolated chain. The total density of units $\tilde\rho=\tilde\rho_i+\tilde\rho_e$ (a), $\tilde\rho_i$ (b) and $\tilde\rho_e$ (c) with $\varepsilon=0$ (broken curves) and ε_θ (full curves). The concentration of the solution $c=0.037$ (1), 0.19 (2) and 0.46 (3)

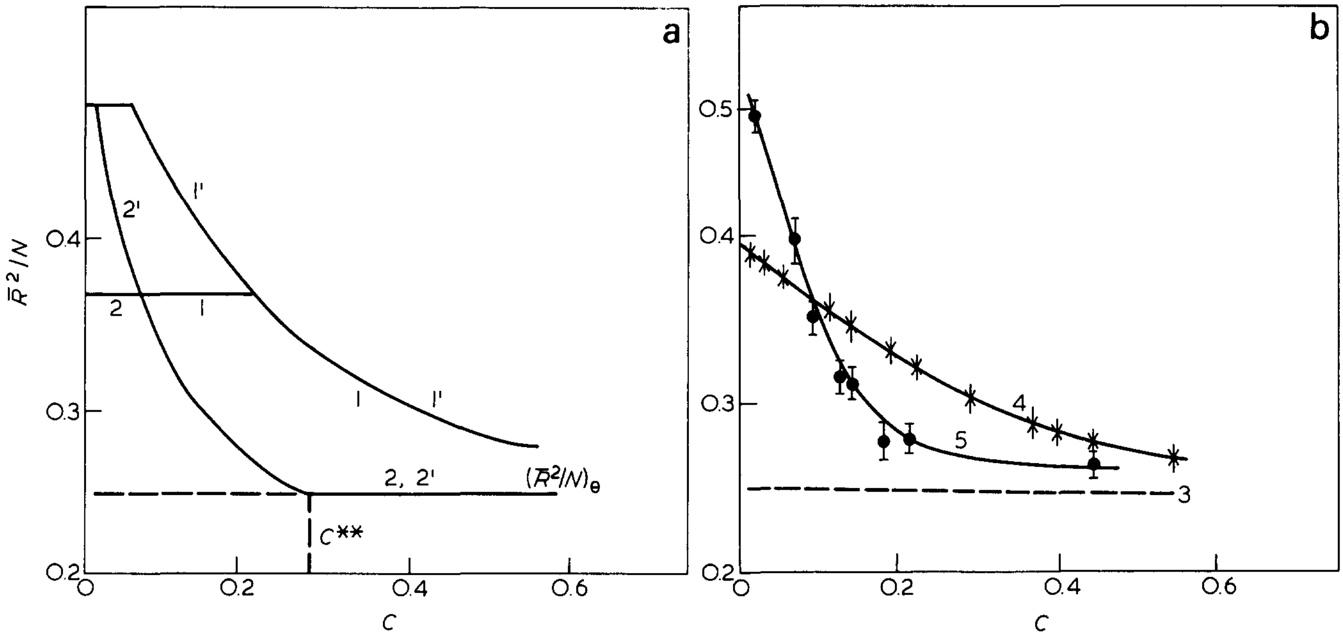

Figure 9 The concentration dependence of the dimensions of chains: (a) in accordance with *Table 1* with $\tau=1$ and $\rho=1$ (1) and 1.5 (2); (b) in accordance with the data of computer experiment with ε_θ (3), $\varepsilon=0$ and $N=60$ (4), and $\varepsilon=0$ and $N=120$ (5)

As was shown in ref. 2, in a good solution ($\tau=1$) in the II_+ region (diagram in *Figure 2*), the number of intermolecular contacts calculated per monomer is represented by the expression:

$$n_e\sim\frac{\pi}{kT}\frac{1}{c} \tag{16}$$

Generalization of this expression for the case of $\tau<1$ gives for region II_+:

$$n_e\sim\frac{\pi}{kT}\frac{1}{c\tau} \tag{17}$$

(We shall note that, in ref. 13, expression (16) was used incorrectly for assessing n_e with $\tau\neq1$.).

Inserting the value π/kT from (16) into (17) along with the dependence of n_e on the parameters of the system as per *Table 1*, we obtain the dependence of n_e on the parameters in the II_+ region presented in *Table 2*. The condition of continuity of n_e at the II_+–II_θ boundary and the relation between the parameters at this boundary (*Table 1*) gives for the II_θ region:

$$n_e \sim c \tag{18}$$

It follows from the requirement of continuity of n_e in transition between regions of concentrated and dilute solution and the evident condition $n_e \to 0$ with $c \to 0$ that, in the I_+ and I_θ regions, n_e is also represented by increasing power functions of c. Analysis shows that it is natural to identify these functions with the corresponding functions in the II_+ and II_θ regions (the boundary of applicability of the expression of n_e for θ regions passes in this case through $c^{**} \sim \tau p^{-3}$ for the entire concentration range).

As can be seen from *Table 2*, in θ regions the interchain contacts of the units are present in proportion to their mean concentration. The relation:

$$\frac{n_e^{(+)}(c)}{n_e^{(\theta)}(c)} \sim \left(\frac{c}{\tau}p^3\right)^{1/4} \tag{19}$$

where according to the condition for the boundary between the regions (*Tables 1* and *2*) the right-hand part is always less than unity, shows that, with improvement in the quality of the solvent in solutions of a prescribed concentration, the number of interchain contacts is reduced. In other words, reduction in the energy advantage of the polymer–polymer contact, in comparison with the polymer–solvent contact (parameter ε of the lattice model), leads to a reduction in the number of interchain contacts. With growth in the rigidity of the chain, this effect is levelled out and the value of $n_e^{(+)}$ grows, approaching $n_e^{(\theta)}$.

Table 2

Region	n_e	n_{be}
I_Θ^*	c	Nc
I_+^*	$(c^5\tau^{-1}p^3)^{1/4}$	$N(c^5\tau^{-1}p^3)^{1/4}$
II_+	$(c^5\tau^{-1}p^3)^{1/4}$	τ^{-1}
II_Θ	c	$c^{-1}p^{-3}$

* The boundary of applicability of these expressions passes through $c^{**} \sim \tau p^{-3}$

A characteristic feature of $n_e^{(+)}$ is the deviation from proportional increase with concentration; we have $n_e \sim c^{5/4}$, which directly indicates the inapplicability in this case of the concept of the mean field. The course of $n_e = n_e(c)$ is presented diagrammatically in *Figure 10*.

Knowing n_e and the number of units n_b in a 'blob' (*Table 1*), it is possible to assess the number of contacts required for a 'blob' n_{be}, and in this way to obtain yet another characteristic of the pattern of the 'blobs' in a solution. The dependences of n_{be} on the parameters of the system are presented in *Table 2* and in *Figure 10*. In regions I, n_{be} grows with concentration (linearly in the θ region, as $c^{5/4}$ in the region of good solvent). This is connected with growth in n_e with constancy of the dimensions of the 'blob' macromolecule as a whole.

With a critical concentration c^* of overlapping of macromolecules in conditions of a good solvent, the number of contacts calculated per 'blob' (macromolecule with c^*) amounts to $n_{be} \sim \tau^{-1}$, and this quantity maintains a constant value in the entire II_+ region with a prescribed τ value. With $\tau = 1$, $n_{be} \sim 1$, and consequently a chain segment that is of the order of the mean distance between the two interchain contacts is the independent unit—'blob'. This segment retains the properties characteristic of an isolated chain, and its dimensions ξ determine the correlation radius of density. Thus, with $\tau = 1$, each interchain contact leads to screening of the density correlations in the solution. As the quality of the solvent deteriorates (τ diminishes), the effectiveness of the screening action of the contacts decreases. The correlation radius of ξ depends on the size of the chain segment taking part in the τ^{-1} intermolecular contact.

With a fixed quality of solvent, growth in concentration in the II_+ region leads to increase in n_e, and correspondingly n_b decreases so that the condition $n_{be} = n_b n_e = \text{constant}$ (c) is fulfilled.

A different behaviour of n_{be} is observed in the θ regions. At the c^* transition point from the I_θ to the II_θ region, n_{be}

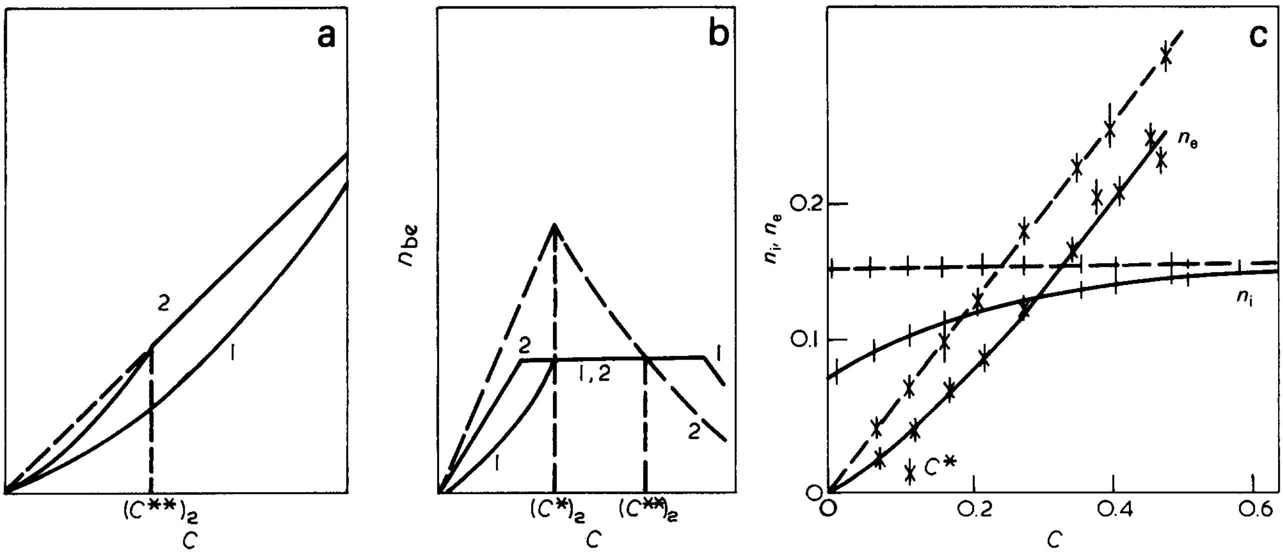

Figure 10 The concentration dependence of local density. (a) and (b) Diagrammatic relationships of (a) $n_e(c)$ and (b) $n_{be}(c)$ in accordance with *Table 1*. Broken lines, $\text{I}_\theta \to \text{II}_\theta$ transition; full curves, $\text{I}_+ \to \text{II}_+ \to \text{II}_\theta$ transitions; $(p^3/\tau)_2 > (p^3/\tau)_1$. (c) Data of computer experiment for n_i and n_e with $\varepsilon = 0$ (full curves) and ε_θ (broken curves)

$\sim N^{1/2}p^{-3/2}$, i.e. with occupation of the volume by Gaussian spheres, there are $\sim N^{1/2}$ contacts of each chain with others. This corresponds to the mean number of contacts arising with location of a chain of N units in a medium with a unit density $c/=N^{-1/2}p^{-3/2}$, and indicates the free penetration of Gaussian spheres into each other. It is worth bearing in mind that in a good solvent the number of intermolecular contacts of the chain with c^* is independent of N, i.e. the chains are only in slight contact with each other.

With growth in c and transition into the II_θ region, the number of contacts in a 'blob' begins to decrease on account of the fact that the length of the segment in the 'blob' $n_b \sim c^{-2}$ decreases with c more intensely than the density of the contacts $n_e \sim c$ grows. The inconstancy of the number of paired contacts in a 'blob' in the II_θ region shows directly that, as has already been discussed above, it is not these paired contacts which govern the dimensions of the region of non-uniformity in θ conditions.

We believe that the non-equivalence of the values n_b and $1/n_e$ in θ conditions should become apparent in an upsetting of the equilibrium (determined by n_b) and dynamic (determined by the number of contacts n_e) interaction radii.

The entire examination so far has completely ignored the existence of intrinsic intrachain local density ρ_i. Data from the computer experiment are presented in *Figure 10*. It is evident that in θ conditions $\rho_i^{(\theta)} \simeq$ constant (c), and with $\tau=1$, ρ_i increases with growth in concentration, approaching $\rho_i^{(\theta)}$. It is worth noting that, within the limits of the computer experiment, we do not find the constancy of ρ_i, i.e. a local structure of the chain, in the region of low c values which is forecast by scaling.

As demonstrated by *Figure 10*, the relationship $\rho_e(c)$ observed in the computer experiment as a whole is similar to the diagrammatic relationship examined above. In θ conditions, $\rho_e^{(\theta)}$ increases in proportion to c. With $\tau=1$, $\rho_e(c)$ is always less than in θ conditions, and the relationship $\rho_e(c)$ is curved, i.e. it corresponds to a power function with a power index exceeding unity in accordance with *Table 2*.

At the same time there are also differences associated, it seems, with the value $\rho_i \neq 0$ and its concentration dependence. In a θ solvent, the observed relationship $\rho_e^{(\theta)}$ is described approximately by the straight line $\rho_e^{(\theta)} \simeq Kc$, where $K=0.65$. Evidently, with random occupation of all the empty sites, it should be expected that $K=(1-\rho_i^{(\theta)})$ $=0.85$ (cf. ref. 6).

Analysis of the relationships $\rho_i(c)$ and $\rho_e(c)$ with $\tau=1$ showed that with $c<c^{**}$ they are presented approximately in the form

$$\rho(c)=\rho_i(c)+\rho_e(c)=\rho_i(c=0)+Ac^{1.25} \qquad (20)$$

and with $c>c^{**}$ the relationship $\rho(c)$ approaches a linear one. This result correlates with the data of *Table 2*.

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