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Configurational properties of athermal self-avoiding polymer chains at intermediate to high concentrations

Clive A Croxton

Department of Mathematics, University of Newcastle, Newcastle, NSW, 2308 Australia

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Abstract. A screened convolution approximation is introduced for the specification of internal and end-to-end probability distributions at various packing fractions. The competing effects of inter- and intra-chain exclusion are investigated, and the conformations of the chains determined as a function of packing fractions. The equation of state for relatively short chains at intermediate to high concentrations is determined.

1. Introduction

In the two preceding papers (Croxton 1979a, b, hereafter referred to as I and II respectively) a diagrammatic technique was developed of comparable status to the machine exact enumeration methods for relatively short polymer chains. In the studies reported in I and II the diagrammatic method was developed and cast into a simple convolution form which had the advantage of retaining the essential qualitative features of the system for short to intermediate isolated chains of self-avoiding segments, but degenerated into a random flight assembly of unit rods as the number of segments became large. Nevertheless, the essential features of the end-to-end probability distribution and the internal distributions, their dependence upon total chain length, and the location of the subset within the chain were determined, together with the radius of gyration of the chain.

In this paper we attempt to determine the effect on these characteristics for a polymeric system in which both intra- and inter-molecular interactions develop; in other words, to consider the effects on, for example, molecular span as a function of chain concentration for a monodisperse assembly of polymers having a specified number of segments N .

2. Inter- and intra-molecular interference

Numerous methods have been developed in various attempts to describe the conformations of an isolated self-avoiding macromolecule; the properties of such a system are determined as appropriate averages over all accessible conformations of the chain. The preservation of sequential order of the segments and cohesion of the chain severely restricts the number of accessible conformations which the system may adopt, and although no exact solution to the problem has been proposed so far, exact enumeration techniques on lattices of various geometries and dimensions have led to a relatively clear picture of the behaviour of relatively short isolated chains enabling extrapolations

to long contour lengths to be made (I). Such systems correspond to infinitely dilute polymeric solutions since interactions are purely intra-molecular; the enormously more difficult problem concerning the effect of *inter*-molecular interactions arising in solutions of moderate to high concentration has received relatively little attention. However, it is generally believed that inter-molecular interaction causes an overall reduction in chain dimensions. This is, of course, readily understood physically in terms of inter-molecular interference, in addition to intra-molecular or excluded volume effects. Monte Carlo studies by Bellemans and De Vos (1973) for polymer chains of length 10, 20 and 30 segments on simple cubic lattices up to 95% of bulk concentration appear to confirm the supposition. Indeed, the exponent γ in the expression for the mean square end-to-end separation

$$\langle R_n^2 \rangle \sim n^\gamma, \quad (1)$$

where $n = N - 1$ is the number of links, was determined to be 1.07 ± 0.01 at bulk concentration and for long chain lengths. This value is to be compared with $\gamma \sim 1.20$ which appears to characterise isolated polymers, and $\gamma \sim 1.00$ for an unrestricted random walk. Of immediate interest, however, is Flory's contention that at high concentrations the expansive *intra*-molecular effects become indistinguishable from the confining *inter*-molecular intersections, and so there is no net effect, the end-to-end probability distributions assuming a Gaussian form with $\gamma = 1$. An analysis by Fixman and Peterson (1964) at 100% concentration, and more recently by Edwards (1975), appears to support this conjecture. Unfortunately experimental evidence cannot yet unequivocally resolve the precise behaviour, and the question remains.

A recent simulation by Wall and Seitz (1977) for chains of length $n = 8$ as functions of concentration up to 95% of bulk on various two- and three-dimensional lattices shows that average chain dimensions decrease markedly with increasing concentration, and they suggest that the limiting bulk values of the shape parameters correspond to the values for eight-step random walks without step reversals (second-order walks).

Consider N_c chains of N freely jointed hard sphere segments of diameter σ confined within a volume V . We shall designate the packing fraction as

$$\eta = NN_c \pi \sigma^3 / 6V, \quad (2)$$

and the athermal partition function Z_{1N} for the first chain with its end segments held at a separation r_{1N} to be

$$Z(r_{1N}) = \int \dots \int \exp(-U_{N_c})(d\mathbf{r}^{NN_c})', \quad (3)$$

where $(d\mathbf{r}^{NN_c})' = d\mathbf{r}_2 \dots d\mathbf{r}_{NN_c}$ excluding $d\mathbf{r}_1, d\mathbf{r}_N$. The total interaction energy U_{N_c} is

$$U_{N_c} = \frac{1}{2} \sum_{\lambda=1}^{N_c} \sum_{\kappa=1}^{N_c} \sum_{i=1}^{NN_c-1} \phi_{i,i+1}^{\lambda\kappa} + \sum_{i>j}^{1, NN_c} \Phi(r_{ij}). \quad (4)$$

The second term represents the interaction between non-sequential segments whether they be on the same or different chains. The first term preserves monodisperse sequential order amongst N_c distinct chains $\alpha, \dots, \kappa, \lambda, \dots, N_c$ by means of an interaction

$$\phi_{i,i+1}^{\lambda\kappa} = \begin{cases} \infty, & r_{i,i+1} \neq 1, \quad \lambda = \kappa, \\ 0, & r_{i,i+1} = 1, \quad \lambda = \kappa, \\ 0, & r_{i,i+1} \geq 0, \quad \lambda \neq \kappa. \end{cases} \quad (5)$$

Further progress may be made as in I by writing

$$\exp(-\Phi(r_{ij})) = h(r_{ij}) - 1, \quad \exp(-\phi^{\kappa\lambda}(r_{i,i+1})) = \delta_{(r_{i,i+1})}^{\kappa\lambda}, \quad (6)$$

whereupon (3) becomes

$$Z(r_{1N}) = \int \dots \int \left(\prod_{\lambda=1}^{N_c} \prod_{\kappa=1}^{N_c} \prod_{i=1}^{NN_c-1} \delta^{\lambda\kappa}(r_{i,i+1}) \right) \left(\prod_{i>j}^1 \prod_{j=1}^{NN_c} (h(r_{ij}) - 1) \right) (dr^{NN_c}). \quad (7)$$

Expansion of the second product in the integrand, regrouping and weighting of topologically degenerate products is recognised as no more than the partition function for a hard sphere fluid of NN_c segments: resolution into discrete chains of N segments is effected by the first product in the above integrand. This term effectively restricts the accessible conformations which the 'fluid' diagrams may adopt. Of course, this is no more than a reformulation of the initial problem. It does, however, suggest how some qualitative progress may be made. If we continue to confine our attention to the first N segments constituting the first polymer chain we may regard each such segment as interacting with an effective density-dependent interaction $\Psi(r_{ij}|\eta)$ appropriate to a fluid at the packing density η under consideration. This neglects sequential ordering amongst segments $N+1 \rightarrow NN_c$, and amounts to a consideration of an isolated polymer in a solvent of its own segments. This is likely to be a good approximation at high densities where discussion is generally restricted to cell theory descriptions.

The effective density-dependent interaction referred to above is, of course, the potential of mean force related to the fluid radial distribution $g_{(2)}(r)$ through the Boltzmann factor: $g_{(2)}(r|\eta) = \exp(-\Psi(r|\eta)/kT)$. In the present analysis we adopt the Percus-Yevick (PY) representation of the radial distribution and endow each segment in the chain under consideration with the effective interaction $\Psi_{PY}(r|\eta)$. In the limit of low densities $\Psi(r|\eta)$ reverts to the hard sphere interaction, while at high densities interference and screening effects introduce oscillations in the effective interaction.

The equation of state of the multiple-chain system follows directly from the standard relation

$$P = kT \partial \ln Z(1N) / \partial V, \quad (8)$$

which leads to (Curro 1976)

$$\frac{PV}{N_c kT} = 1 - \frac{2\pi N NN_c}{3kT V} \int_0^\infty \Gamma_{(2)}(r) \nabla_1 \Phi(r) r^3 dr, \quad (9)$$

where $\Gamma_{(2)}(r)$ is an 'inter-chain radial distribution' defined by

$$\Gamma_{(2)}(r) = \frac{1}{4\pi} \left(\frac{V}{NN_c} \right)^2 \sum_{ij\kappa \neq \lambda} Z^{\kappa\lambda}(r_{ij}), \quad (10)$$

with $Z^{\kappa\lambda}(r_{ij})$ the normalised probability that segment i on chain κ is distance r_{ij} from segment j on chain λ . Attention is drawn to the fact that $\Gamma_{(2)}$ contains contributions to the pressure arising from *distinct* chains only: a simple consequence of Newton's third law applied *within* any given chain. In the case of simple (disconnected) fluids the total radial distribution appears in (9). Since intra-chain correlations do not contribute to the pressure virial, it is apparent from the outset that the external pressure will be less than that of a corresponding system of disconnected segments. Since we intend using the

total (internal + external) function $g_{(2)}^{\text{PY}}(r|\eta)$ for the effective inter-segment distribution, the *distinct* distribution in (9) follows as

$$\Gamma_{(2)}(\sigma|\eta) = g_{(2)}^{\text{PY}}(\sigma|\eta) - \frac{\pi}{144\eta^2} \sum_{ij} Z(ij|N)_{\eta,\sigma}. \quad (11)$$

The result has been given in terms of the contact values ($r = \sigma$) appropriate to the hard sphere interactions. $\sum_{ij} Z(ij|N)_{\eta,\sigma}$ refers to the superposition of all internal distributions within the N -mer at contact at the appropriate packing fraction. This term vanishes of course for fluid systems of disconnected segments, and contributes most strongly at low packing densities for short chains having large contact values $Z(ij|N)_{\eta,\sigma}$.

The equation of state for a system of N_c chains of length N is, finally,

$$\frac{PV}{N_c kT} = 1 + 4\eta N \left(g_{(2)}^{\text{PY}}(\sigma|\eta) - \frac{\pi}{144\eta^2} \sum_{ij} Z(ij|N)_{\eta,\sigma} \right). \quad (12)$$

The external pressure P may be identified with the osmotic pressure Π of an athermal polymer solution (no heat of mixing) where polymer-solvent interactions may be neglected. It should be noted that equation (12) correctly reduces to the equation of state of a hard sphere fluid in the PY approximation when $N \rightarrow 1$, $N_c \rightarrow N$ and $Z(ij|N) \rightarrow 0$. Application of approximation (11) is restricted to intermediate to high packing fractions, when the effective inter-segment interaction is reasonably described by the potential of mean force $\Psi(r|\eta)$. At low densities there is some difficulty, however, since local fluctuations in density attending the simultaneous interaction between two or more chains make the specification of a system density ambiguous.

The Flory-Huggins (FH) equation of state was also developed for intermediate packing fractions. In their analysis the osmotic pressure Π is determined as the free energy of mixing, and the solvent-polymer interaction is set equal to zero, whereupon

$$\Pi V / N_c kT = 1 - N[\eta^{-1} \ln(1 - \eta) + 1]. \quad (13)$$

Comparison with this equation of state will be made in § 4. At high packing fractions a cell model is generally adopted (Nanda and Simha 1964, Curro 1974, 1976):

$$PV / N_c kT = (1 + N/3)(1 - 0.805\eta^{1/3})^{-1}. \quad (14)$$

Such an equation of state is based essentially upon a solid state model and cannot be expected to reflect accurately the free rotational degrees of freedom implicit in the chain's specification.

As in I and II, the end-to-end $Z(1N)$ and interval $Z(1i|N)$, $Z(ij|N)$ distributions are determined as functions of the packing fractions through the relations

$$Z(1N) = H(1N) \int Z(1, N-1) \delta(N-1, N) d(N-1), \quad (15)$$

$$Z(1i|N) = Z(1i|N-1) \int Z(1N) Z(iN|N-1) dN, \quad (16)$$

$$Z(ij|N) = Z(ij|N-1) \int Z(1i|N) Z(1N) d1, \quad (17)$$

where

$$H(1N) = \exp(-\Psi(1N)).$$

3. Chain conformations

In figure 1 we show the development of the normalised end-to-end probability distribution Z_{1N} for $N = 4$ and 8 as a function of packing density. From a smooth curve at $\eta = 0$ corresponding to the isolated chain result, the distribution develops pronounced oscillations with increasing density. Apart from the first peak, subsequent oscillations in the distribution need not be, and in general are not, located at integral multiples of the segment diameter—a reflection of the chain flexibility. Indeed, the long-range form of Z_{1N} is determined more by the constraint of contour length than by geometrical packing. There is clearly a subtle interplay between the amplitude and location of a peak in determining its effect upon, for example, the second moment

$$\langle R_N^2 \rangle = \int Z(1N)r^2 dr. \quad (18)$$

The rapid growth of the $1N$ contact probability $Z(r_{1N} = 1)$ with density most certainly has the effect of depressing the value of the exponent γ . There is, however, no *a priori* reason to anticipate a limiting behaviour $\gamma \rightarrow 1$ as density and chain length increase. Certainly such distributions are not consistent with random walk behaviour, nor even the second-order random walk of the kind advocated by Wall and Seitz (1977), in which immediate step reversals to form loops of length two are forbidden, although longer loops and the double occupancies attending their formation are allowed. This is not to say, however, that the exponent cannot still be unity; indeed, such a situation characterises the theta point for realistic interactions, according to some definitions. For such realistic systems the theta point corresponds to the Boyle temperature of fluid systems when the net effects of attraction and repulsion cancel: in the case of a polymer the system is characterised by the exponent $\gamma = 1$. At lower temperatures the molecular conformations are dominated by the attractive interaction between non-adjacent segments, and γ decreases further. In the case of an athermal chain of hard spheres it is the effects of density rather than temperature which prevail, and it may well be that the theta point for dense assemblies occurs in the limit of maximum packing density.

As we observed in I and II, the present convolution approximation consistently underestimates the chain dimensions for isolated chains, although the essential qualitative features are believed to be retained, at least for chains of short to intermediate length. In figure 2 we show the mean square molecular span $\langle R_{1N}^2 \rangle$ as a function of packing fraction. The chains are seen to collapse rapidly with increasing concentration, and approach—though not necessarily tend to—the unrestricted random walk result $\langle R_{1N}^2 \rangle_0 = N - 1$. The apparent molecular expansion which develops at high concentrations for short chains is believed to be an artefact of the PY approximation, which is known to overestimate the amplitude of the oscillations in $\Psi^{\text{PY}}(r|\eta)$ at high densities. The effect is to weight expanded configurations unduly; this is particularly evident in figure 1 for $N = 4$ at high concentrations. For long chains this overestimate partially compensates the cumulative collapse attributable to the convolution approximation, and the curves are probably qualitatively acceptable, although the points of inflection are undoubtedly attributable to the competing effects of convolution collapse and PY expansion.

Bellemans and De Vos (1973), in a recent simulation, investigated the ratio $\langle R_{1N}^2 \rangle_\eta / \langle R_{1N}^2 \rangle_{\eta=0}$ for athermal chains on a simple cubic lattice as a function of packing fraction. Each site may be occupied either by one element of a chain molecule or by a solvent molecule. At low to intermediate concentrations the ratio decreases almost

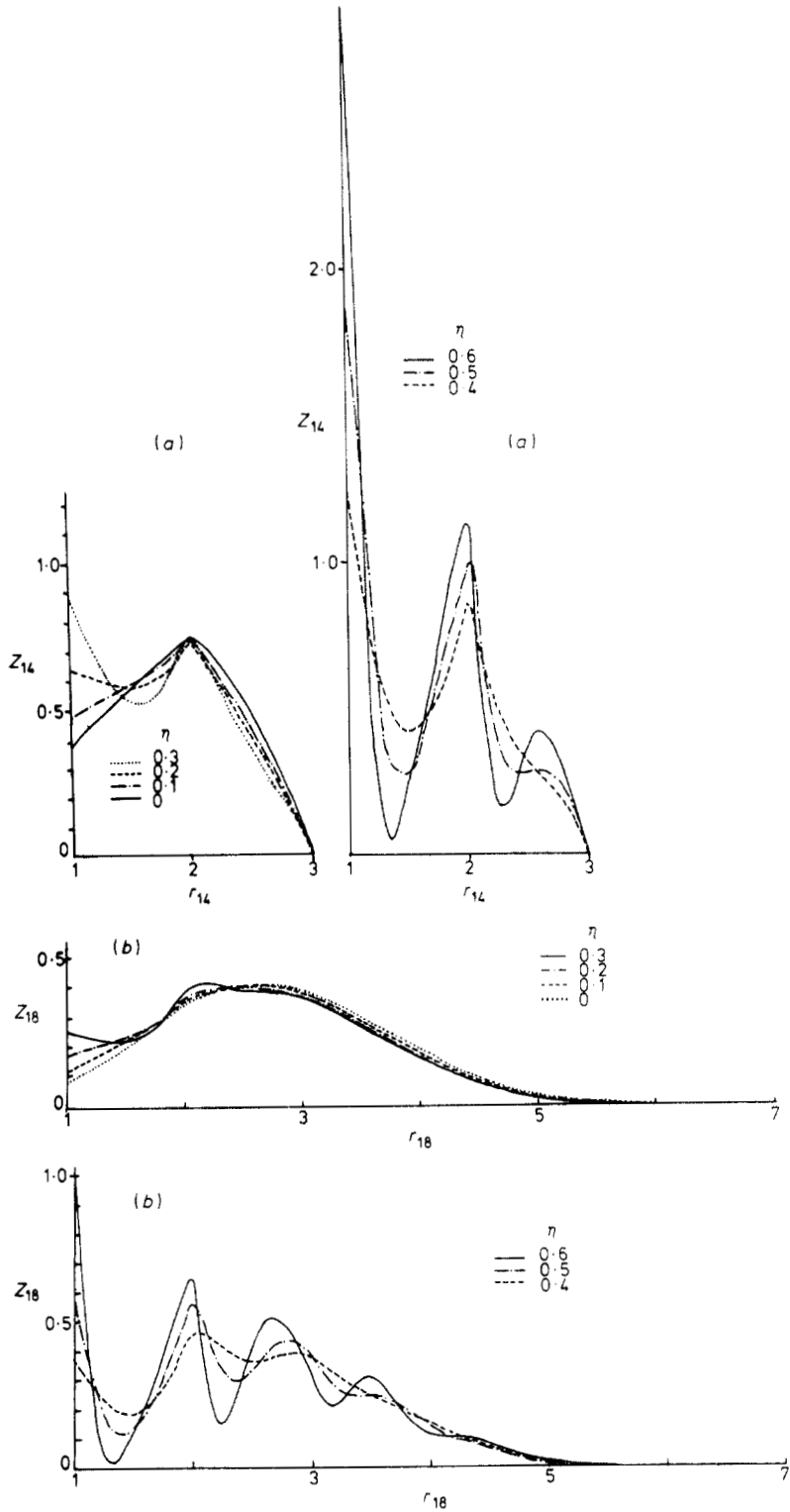


Figure 1. The development of the end-to-end probability distribution function $Z_{1,N}$ as a function of packing fraction η : (a) for $N = 4$; (b) for $N = 8$.

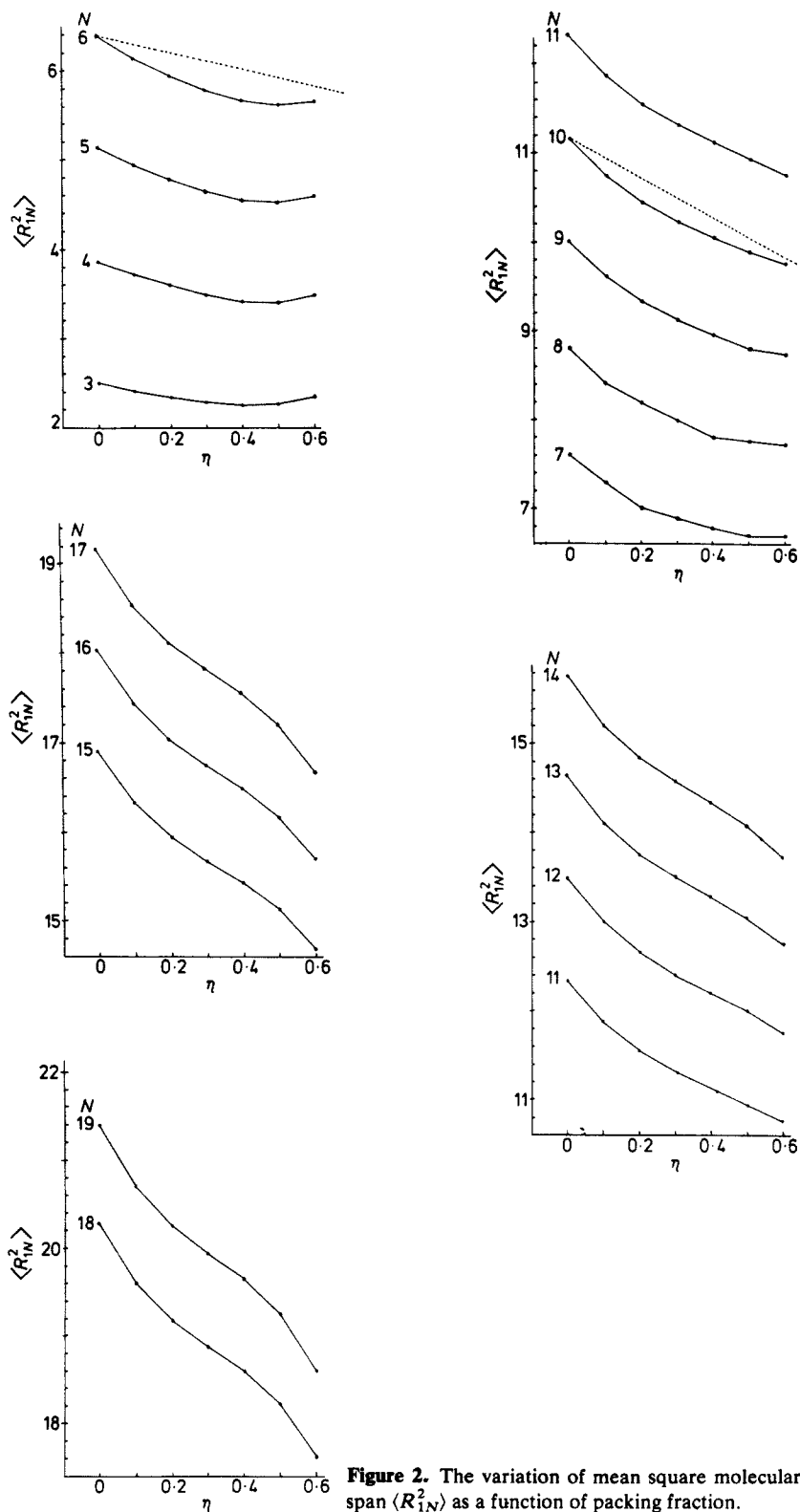


Figure 2. The variation of mean square molecular span $\langle R_{1N}^2 \rangle$ as a function of packing fraction.

linearly with η : a rough estimate suggests

$$\langle R_{1N}^2 \rangle_\eta / \langle R_{1N}^2 \rangle_{\eta=0} \sim 1 - 0.04(N-1)^{0.7} \eta + \dots,$$

and this is shown in figure 2 for $N=6, 10$. Both the machine simulations and the present results show a similar decrease with concentration, with a rather strong N dependence.

The internal distributions and molecular spans are considerably more complex. As in the case of isolated chains, the expansion of a given subset of segments depends both on the location of the subset within the chain and on the chain's contour length. Additionally, of course, these results are now functionally dependent on packing density. In figure 3 we show $\langle R_{1i|N}^2 \rangle_\eta - \langle R_{1i}^2 \rangle_\eta$ as a function of η . As in the case of an isolated chain, the effect of a 'tail' is to cause an expansion in the subset ($1i|N$) relative to a chain ($1i$), the expansion saturating with increasing N and ultimately showing a

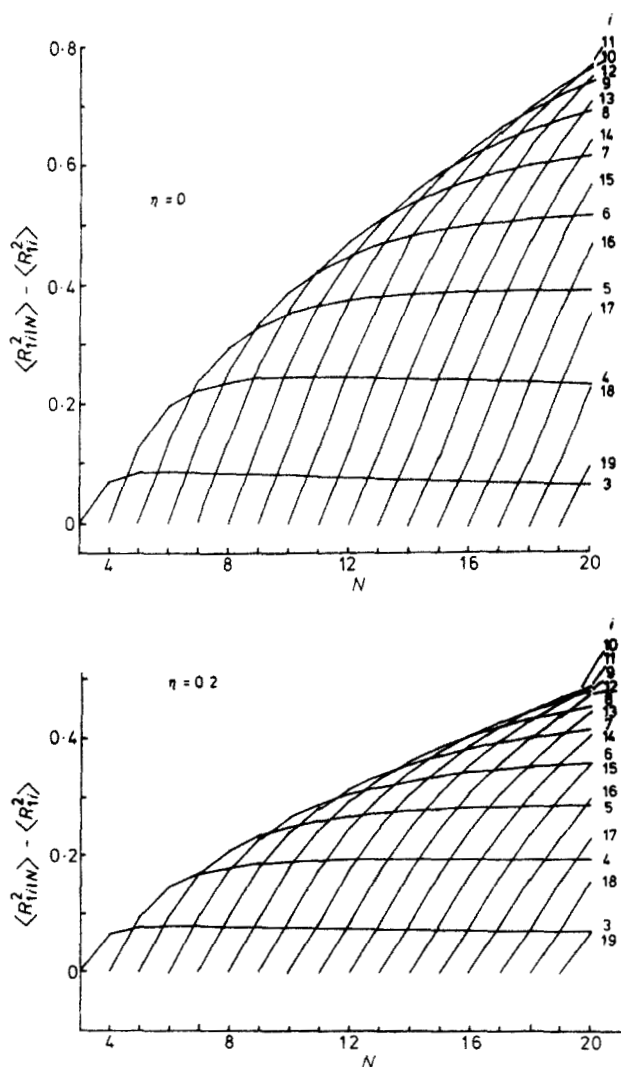


Figure 3. (continued on next page)

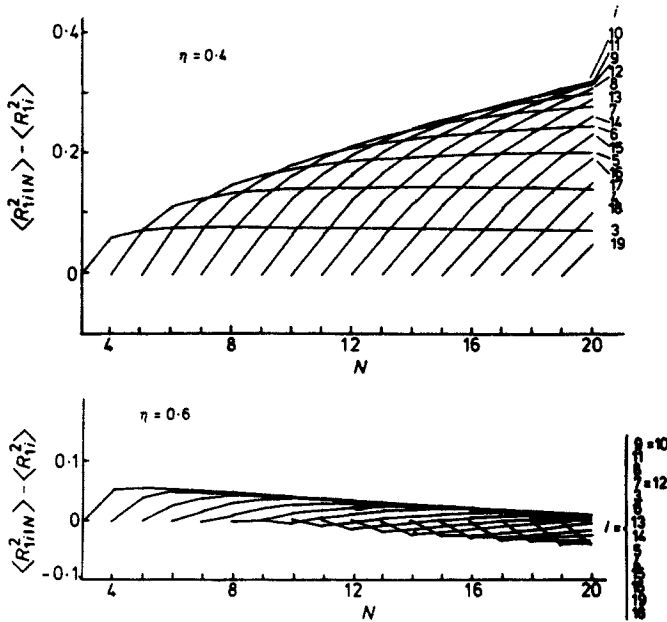


Figure 3. The relative expansion $\langle R_{1i|N}^2 \rangle_\eta - \langle R_{1i}^2 \rangle_\eta$ of a semi-internal subset with respect to its isolated counterpart at the same packing fraction.

weak collapse as the long tail ‘confines’ the subset. This is apparent only for relatively short subsets, though undoubtedly occurs ultimately for all subsets ($1 \leq i \leq N$) provided $N \gg i$. With increasing concentration the intra-molecular expansion is gradually offset by inter-molecular confinement, and at high concentrations for short subsets in long chains there is evidence that $\langle R_{1i|N}^2 \rangle_\eta - \langle R_{1i}^2 \rangle_\eta$ actually becomes negative.

Similar observations hold for the purely internal expansions $\langle R_{ij|N}^2 \rangle_\eta - \langle R_{ij}^2 \rangle_\eta$ (figure 4). As in the case of isolated chains an additional segment applied to the shorter of the two tails ($1 \rightarrow i-1$), ($j+1 \rightarrow N$) effects the greater expansion, although confinement suppresses the behaviour as η increases.

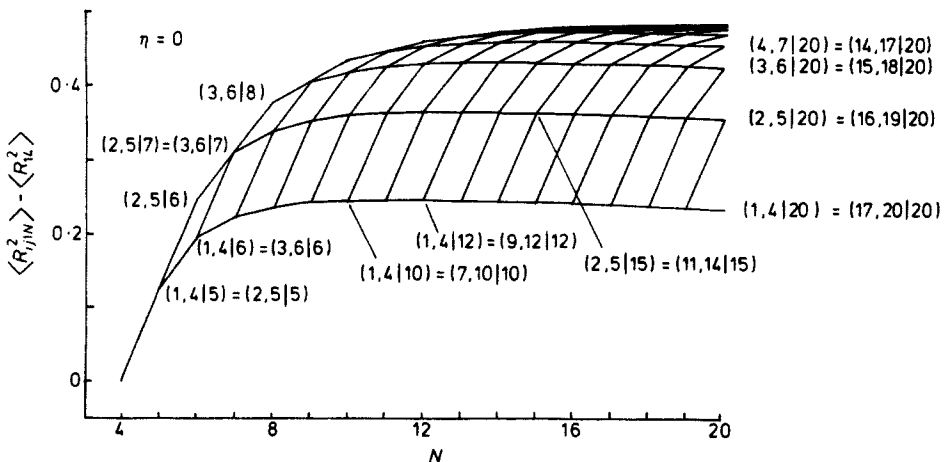


Figure 4. (continued overleaf).

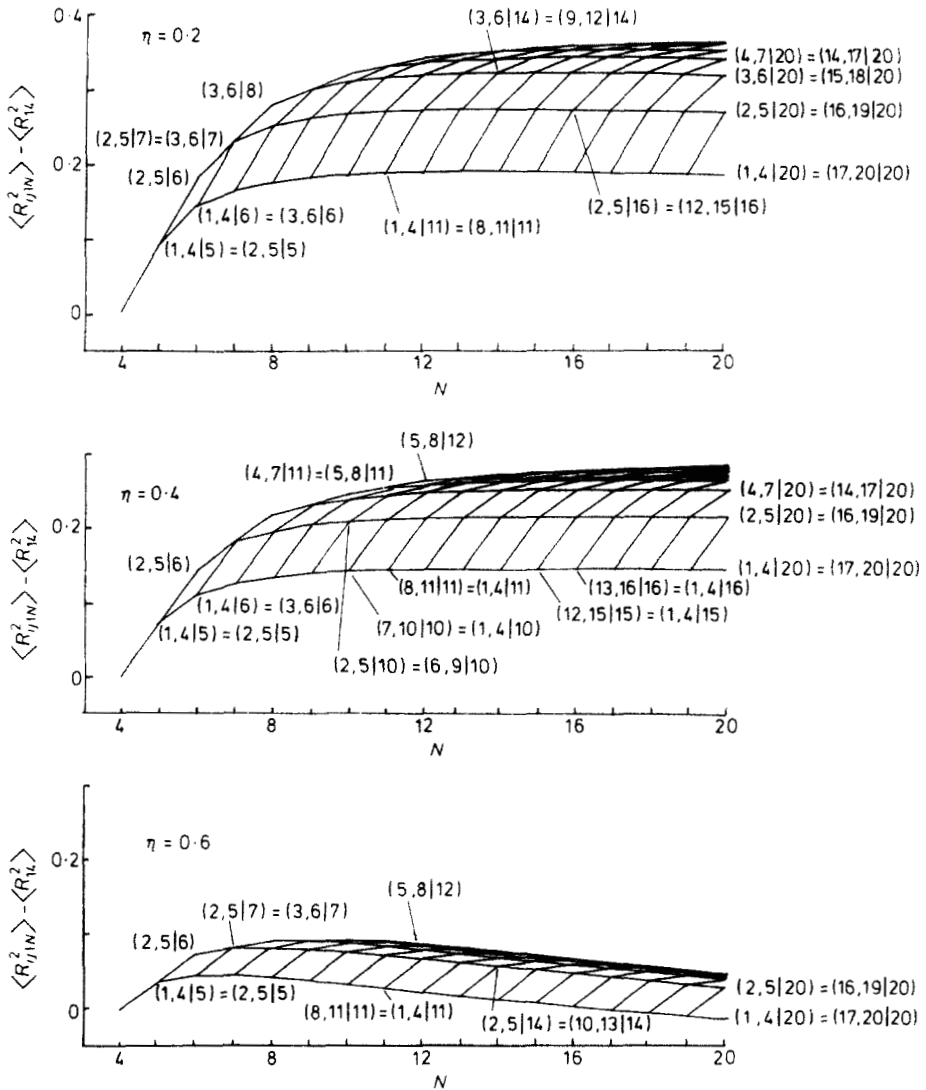


Figure 4. The relative expansion $\langle R_{ij|N}^2 \rangle - \langle R_{iL}^2 \rangle$ of a totally internal subset with respect to its isolated counterpart at the same packing fraction.

4. Equation of state at intermediate to high densities

The equation of state for an athermal monodisperse system of N_c chains of N segments has been determined in the screened convolution approximation (SCA) to be (equation (12))

$$\frac{PV}{N_c kT} = 1 + 4\eta N \left(g_{(2)}^{PY}(\sigma|\eta) - \frac{\pi}{144\eta^2} \sum_{ij} Z(ij|N)_{n,\sigma} \right).$$

The constraint that sequential ordering be preserved effectively reduces the number of those degrees of freedom which contribute to the pressure, and so the pressure will be

consistently less than that of a dissociated system of NN_c hard sphere segments by an amount which depends upon the intra-chain correlations $Z(ij|N)$. A comparison of the SCA, FH and PY hard sphere equations of state is shown for relatively short chains as a function of packing fraction in figure 5. Unfortunately there is no reliable machine simulation data available over this concentration range, although from an extrapolation of Curro's (1976) recent simulation it is clear that the hard sphere and FH isotherms bracket the true equation of state. It would therefore appear that the SCA provides the closest description so far. Further improvement may readily be achieved by the use of more accurate contact values of the radial distribution $g_{(2)}(\sigma|\eta)$: the PY value is known to be an overestimate. The internal contact amplitudes $Z(ij|N)_{\eta,\sigma}$ are also overestimated in the SCA, however, although this is likely to be subordinate to the error in $g_{(2)}(\sigma|\eta)$.

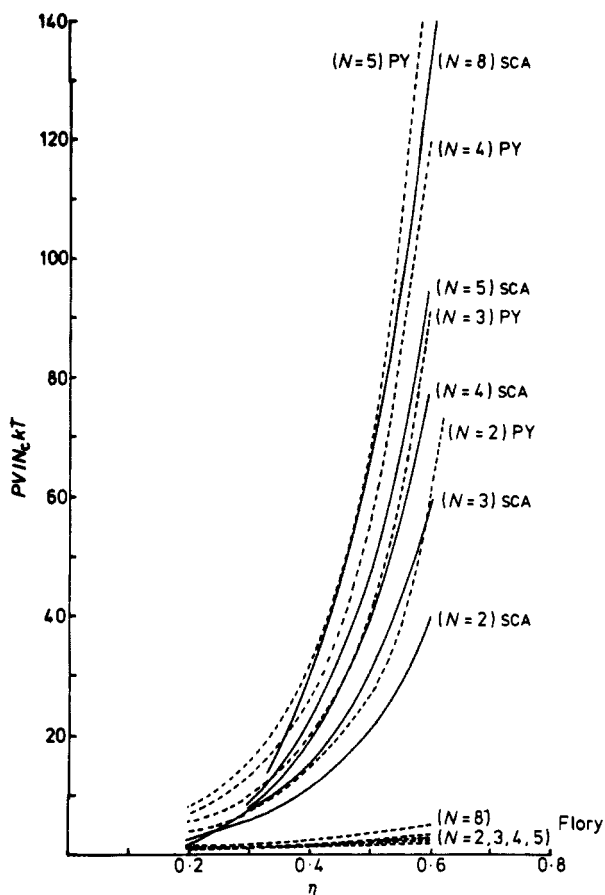


Figure 5. Comparison of the hard sphere fluid FH and screened convolution equations of state for relatively short polymer chains. The hard sphere fluid and FH isotherms are known to bracket the exact result.

5. Conclusions

The SCA accounts for the progressive collapse of chain dimensions with concentration as anticipated from *a priori* considerations. The end-to-end probability distribution

develops a pronounced oscillatory structure reflecting geometric exclusion effects within the chain at high packing fractions. The expansion of internal subsets of segments which arises in isolated chains on account of 'tail interference' is gradually suppressed with increasing density, and at high packing fractions may actually become negative with respect to an isolated system.

The equation of state shows a behaviour intermediate between that of a hard sphere fluid of the same number of segments and the FH isotherm, which are known to bracket the exact result. Unfortunately no machine isotherms are available at high packing fractions, although extrapolation of Curro's Monte Carlo data confirms the qualitative correctness of the screened convolution isotherm.

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