Theory of Polymer Melts: An Integral Equation Approach[†]

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ABSTRACT: A general theory is developed for the equilibrium structure of dense polymer melts. This theory is based on an integral equation approach developed by Chandler and co-workers for molecular liquids. We are able to construct a tractable formalism for the polymer problem by employing the fact that a polymer molecule in a melt is ideal. This leads to a set of integral equations for the intermolecular radial distribution functions. In the case of a polymer ring, this set reduces to a single integral equation, which we have solved numerically for the case of Gaussian intramolecular statistics with repeat units interacting via hard-core repulsions. From this solution we obtained the radial distribution function, structure factor, and compressibility as functions of liquid density and degree of polymerization. Unlike the random phase approximation (RPA) approach of de Gennes, the present theory allows for density fluctuations. These density fluctuations, which decay on a length scale comparable to a few monomer units, are crucial for the calculation of the structure factor and thermodynamic properties such as the equation of state of the polymer fluid. Generalizations of the present theory to include linear chains, chain stiffness effects, and attractive interactions are possible.

Introduction

In recent years there have been significant advances in the understanding of polymer solutions.[1] Through the use of scaling, renormalization group, and self-consistent field techniques, universal predictions can be made relevant to length scales on the order of the radius of gyration of the polymer. A recurrent theme in the literature is the neglect of short-range chemical effects and an emphasis on the relatively long wavelength properties of chain molecules. In dense polymer liquids, on the other hand, many of the interesting questions concern short-range structure and correlations for which the appropriate length scale is of the order of the polymer segment size. Furthermore, in polymer liquids the intermolecular interactions are very strong and cannot be treated perturbatively. As a result, a detailed, molecular theory of polymer melts has remained a virtually intractable problem. In addition, computer simulations involving Monte Carlo and molecular dynamics calculations have been generally limited to small systems and short chains.[2] In the present work, we develop a microscopic, off-lattice, equilibrium theory for polymer melts using statistical mechanical techniques developed for small molecules. This theory provides not only a detailed structural picture of the melt through the intermolecular radial distribution functions but also enables the calculation of thermodynamic properties, including the equation of state. A brief version of this work has been reported elsewhere.[3]

Recent theoretical progress for the structure of one-component polymer liquids has been limited primarily to the work of de Gennes who has successfully applied the random phase approximation (RPA) to describe the scattering from partially labeled melts.[1,4] In this case, the structure factor is determined by concentration fluctuations which are long range in the labeled system. In the unlabeled melt, on the other hand, the RPA theory predicts zero scattering since there are no concentration fluctuations and density fluctuations are neglected because of the assumption of liquid incompressibility. In addition, the simple RPA theory is independent of the explicit thermodynamic state and the details of the intermolecular interactions. The physical basis of these simplifications is the expectation that in dense fluids screening effects cause the density fluctuations to decay rapidly on a length scale of a few monomers. Density fluctuations and short-range order, however, are in general important for physical properties and phenomena which are sensitive to local correlations. For example, the thermodynamics and equation of state of a polymer melt are not amenable to the simple RPA treatment. Also, a microscopic understanding of first-order phase transformations such as the freezing of polymer liquids and the isotropic–nematic liquid-crystalline transition requires a detailed description of short-range structural correlations.

Earlier theories, unrelated to the RPA approach, have been developed which describe the thermodynamics and equation of state of polymer liquids.[5-7] In these theories rather artificial lattice or cell models, which are really more appropriate to solids, are generally resorted to. In addition, crude random mixing or mean-field approximations are invoked. In order to introduce sufficient disorder into the model to describe a liquid, the concept of free volume is often employed. Although such treatments yield good agreement with experimental data on polymer liquids, physically ambiguous adjustable parameters often enter and the artificiality of such models is of concern. In the present approach, we avoid these problems by constructing a realistic model of a polymer liquid in three-dimensional, continuous space which is analyzed in a statistical mechanical framework which has been successfully employed for small molecule fluids.

The modern theory of small molecule liquids has been pioneered by Chandler and co-workers.[8,9] This theory is frequently referred to as the "reference interaction site model" or RISM theory (not to be confused with the rotational isomeric state model). This approach is a generalization to molecules of the Percus–Yevick[10] theory of atomic fluids. In the RISM theory, a molecule is viewed as consisting of a collection of spherically symmetric interaction sites or chemical subunits connected by covalent bonds. The total potential energy between two molecules is taken to be a sum over all pairs of interaction sites. Since the structure of dense nonassociated fluids is dominated by strong repulsive forces, the interaction between chemical subunits can be mimicked to a high degree of approximation by hard-core potentials. At liquid densities, good qualitative, and sometimes quantitative, agreement is found between the radial distribution functions of small molecules calculated by the RISM theory and corresponding computer simulation results.[8,11] In addition, the RISM theory has been successfully applied to interpret the structure factors measured experimently by scattering techniques.[12] In the present investigation, the RISM theory is formulated in a fashion which renders the poly-

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mer melt problem tractable. This generalization is accomplished by making use of the well-established result that the conformation of a polymer chain in the melt is unperturbed down to nearly monomer length scales.

Theory

We begin our theoretical discussion by reviewing the RISM theory. The content of this approach is most clearly seen by analogy with the theory of simple atomic fluids. The quantity of central interest is the radial distribution function $g(r)$ which is defined by

$$\rho^2 g(r) = \left\langle \sum_{i\neq j}^{N} \delta(\vec{r}_i)\delta(\vec{r} - \vec{r}_j) \right\rangle \qquad (1)$$

where $\vec{r}_i$ is the position of the ith atom in the fluid, N is the total number of particles, ρ is the number density, and the brackets denote an equilibrium ensemble average. Physically $\rho g(r)$ is the density of particles at a distance r from a given particle. The radial distribution function describes the average two-body or pair structure of the liquid and can be related to the thermodynamic properties of a system interacting via pair potentials.[10] Integral equation theories for $g(r)$ are based on the well-known Ornstein–Zernike equation[10] which defines the direct correlation function $C(r)$.

$$h(r) = C(r) + \rho \int \mathrm{d}\vec{r}'\, C(|\vec{r} - \vec{r}'|)h(r') \qquad (2)$$

In the above equation, $h(r)$ is called the total correlation function and is simply related to $g(r)$ according to $h(r) = g(r) - 1$. The physical significance of the direct correlation function can be seen by iterating eq 2.

$$h(|\vec{r} - \vec{r}'|) = C(|\vec{r} - \vec{r}'|) + \rho \int \mathrm{d}\vec{r}''\, C(|\vec{r} - \vec{r}''|)C(|\vec{r}'' - \vec{r}'|) + \rho^2 \int \mathrm{d}\vec{r}'' \int \mathrm{d}\vec{r}'''\, C(|\vec{r} - \vec{r}''|)C(|\vec{r}'' - \vec{r}'''|)C(|\vec{r}''' - \vec{r}'|) + \ldots \qquad (3)$$

The total correlation $h(|\vec{r} - \vec{r}'|)$ between particles at $\vec{r}$ and $\vec{r}'$ consists of simply connected chains of "direct correlations" between these reference particles and intermediate particles. For example, the second term on the right-hand side of the above equation represents the contribution to the correlation of particles at $\vec{r}$ and $\vec{r}'$ due to an intermediate particle at $\vec{r}''$. An attractive feature of the integral equation approach is its explicit dependence on the microscopic intermolecular interactions via the direct correlation function. The structure of eq 2 suggests the $C(r)$ can be viewed as an effective pair potential which remains finite even for singular interactions. It can be shown[10] that for a system with weak pair interactions $v(r)$, or for large interparticle separations, that $C(r) = -v(r)/k_{\mathrm{B}}T$, where k_{B} is Boltzmann's constant and T is absolute temperature. These and other considerations suggest that $C(r)$ for a dense system will have a spatial range comparable to $v(r)$. This idea is the basis of the successful Percus–Yevick approximation for hard spheres which can be stated as

$$C(r) = 0, \qquad r > \sigma \qquad (4)$$

where σ is the hard-sphere diameter. Such an approximation is equivalent to neglecting a certain class of diagrams in the rigorous Mayer cluster expansion.[10]

Chandler and Andersen[9] have generalized the Ornstein–Zernike equation to the case of a molecular fluid by employing an interaction site model of molecular structure described by intramolecular probability distribution functions, $\omega_{\alpha\gamma}(r)$, between sites or chemical subunits α and γ on the same molecule. The set of functions $[\omega_{\alpha\gamma}(r)]$ represents the normalized probability that two sites in a molecule are separated by a distance r. If the intermolecular pair correlations in a liquid are propagated in a sequential manner by "direct" intermolecular and intramolecular pair correlations, then the generalized site–site Ornstein–Zernike matrix integral equations follow:[9]

$$\mathbf{h}(r) = \int \mathrm{d}\vec{r}' \int \mathrm{d}\vec{r}''\, \omega(|\vec{r} - \vec{r}'|)\mathbf{C}(|\vec{r}' - \vec{r}''|)[\omega(r'') + \rho\mathbf{h}(r'')] \qquad (5)$$

where ρ is the number density of molecules and $\mathbf{h}(r)$, $\mathbf{C}(r)$, and $\omega(r)$ are $N \times N$ matrices with matrix elements $h_{\alpha\gamma}(r)$, $C_{\alpha\gamma}(r)$, and $\omega_{\alpha\gamma}(r)$ for molecules consisting of N sites. Thus, $h_{\alpha\gamma}(r) = g_{\alpha\gamma}(r) - 1$ where $g_{\alpha\gamma}(r)$ is the intermolecular radial distribution function between sites α and γ, and $C_{\alpha\gamma}(r)$ is the corresponding direct correlation function. If the direct correlation functions are short range, then the appropriate closure relations for the RISM theory can be written by analogy with the Percus–Yevick theory,

$$h_{\alpha\gamma}(r) = -1, \qquad r < \sigma_{\alpha\gamma} \qquad (6a)$$

$$C_{\alpha\gamma}(r) = 0, \qquad r > \sigma_{\alpha\gamma} \qquad (6b)$$

where $\sigma_{\alpha\gamma}$ is the distance of closest approach between sites α and γ on different molecules. As in the case of the Percus–Yevick theory, eq 6a is exact for a hard-core potential, and eq 6b is the fundamental approximation. Equation 5 and 6 constitute the RISM equations for molecular fluids.[9] The RISM theory is a nonperturbative approach that incorporates the constraints of intramolecular structure in determining the packing of molecules in the liquid state. Its primary utility lies in providing a quantitative description of the short-range order and local fluctuations in the disordered fluid. For flexible molecules it is important to realize that information concerning the intramolecular conformations enters eq 5 only in an average (not instantaneous) sense via the equilibrium distributions $\omega_{\alpha\gamma}(r)$. Therefore, the effects of polymer conformational fluctuations on the intermolecular pair correlations are not explicitly taken into account, and in this sense the RISM approach is a mean field theory. However, it must be emphasized that this feature does *not* imply that intermolecular density fluctuations and local correlations are neglected. A generalized version of the RISM approach that explicitly includes conformational fluctuations in a self-consistent fashion has been recently formulated,[13a] but the complexity of the resultant theory is significantly enhanced.

In addition, a new reformulation of the RISM equations which is fully consistent diagramatically has been recently constructed.[13b] However, the new version is again far more complex than the original RISM theory and has not been numerically implemented even for small molecules. Indeed, considering the crude models of polymer structure generally employed, a more sophisticated theoretical approach does not seem warranted at present.

In principle, eq 5 and 6 could be directly applied to the flexible polymer problem. A difficulty arises, however, because of an apparent coupling between the intramolecular distributions $\omega_{\alpha\gamma}(r)$ and the intermolecular distributions $h_{\alpha\gamma}(r)$. Strictly speaking, these two sets of functions should be determined in a self-consistent manner since in general the intramolecular structure is a functional of the intermolecular correlations and vice versa. Such a program has been fully carried out for liquid n-butane for which knowledge of a complex four-point correlation function was necessary.[14] For long polymers, multipoint distribution functions of very high order are required in principle. Such quantities are very difficult to compute reliably, consequently the polymer melt problem would seem to be virtually intractable. In this paper we circumvent this difficulty by invoking the fact that polymer chains are "ideal" in the melt. This ideality has been predicted from theoretical arguments,[1,15] demonstrated from computer simulations[2] and deduced from neutron scattering experiments.[16,17] Ideality in the melt implies that the intramolecular excluded volume, of prime importance in a dilute solution with a good solvent, is nearly balanced in the melt by intermolecular excluded volume forces. Thus the configuration of a chain in the melt can be properly calculated by theories for a single chain without excluded volume interactions. In other words, a polymer chain in a melt has a configuration which is characteristic of that chain in a Θ solvent. The rotational isomeric state model, for example, has been shown to give good results for such chains. Introduction of this ideality condition, then, allows the $\omega_{\alpha\gamma}(r)$ functions in eq 5 to be computed independently thereby considerably simplifying the problem.

It should be mentioned that this ideality assumption is not completely exact since the possibility of intramolecular chain overlap can occur. This unphysical behavior, however, would be minimized by using a model for the intramolecular structure which includes short-range constraints, such as constant bond angle, rotational barriers, etc., which preclude overlap on short length scales. Nevertheless, some long-range, intrachain overlap would be expected to persist. One can argue, however, that since the ideal chain $\omega_{\alpha\gamma}$ function is known to be a good approximation, in an average sense, the resulting *inter*molecular correlation functions would likewise be accurate. It should be pointed out that the ideality approximation (with intrachain overlap) leads to good results in related theories, including the rotational isomeric state model to describe polymers in theta solvents and the de Gennes RPA theory mentioned earlier to describe labeled polymer melts. Finally, we have recently developed a scheme for explicitly removing all intramolecular overlaps which is discussed in detail elsewhere.[22]

For a linear polymer composed of N identical sites or monomers, eq 5 correspond to $N(N+1)/4$ independent, coupled, nonlinear integral equations since the intermolecular distribution functions $g_{\alpha\gamma}(r)$ depend on the specific positions α along one chain and γ on a neighboring chain. In this paper we will consider, for simplicity, the polymer ring. Mathematically, this corresponds to the absence of end effects. On physical grounds, such a simplification is expected to be accurate for long linear chains at short length scales. On the other hand, both synthetic and biological ring polymers are of considerable interest in their own right. As a consequence of the symmetry of the ring, all the intermolecular correlation functions in eq 5 and 6 are equivalent. Thus

$$h(r) = g(r) - 1 = h_{\alpha\gamma}(r) \tag{7a}$$

$$C(r) = C_{\alpha\gamma}(r) \tag{7b}$$

which results in an enormous simplification since the matrix equations in eq 5 reduce to a single integral equation given by

$$h(r) = \int d\vec{r}\,' \int d\vec{r}\,'' \, \omega(|\vec{r} - \vec{r}\,'|)C(|\vec{r}\,' - \vec{r}\,''|)[\omega(r'') + \rho_{\mathrm{m}}h(r'')] \tag{8}$$

where $\omega(r) = \sum_\alpha \omega_{\alpha\gamma}(r)$ and $\rho_{\mathrm{m}} = N\rho$ denotes the monomeric density. The closure relations in eq 6 now become

$$h(r) = -1, \qquad r < \sigma \tag{9a}$$

$$C(r) = 0, \qquad r > \sigma \tag{9b}$$

Making use of the convolution theorem, eq 8 can be written in Fourier transform space as

$$\hat{h}(k) = \hat{\omega}^2(k)\hat{C}(k) + \rho_{\mathrm{m}}\hat{\omega}(k)\hat{C}(k)\hat{h}(k) \tag{10}$$

where the caret symbol denotes Fourier transformation.

As an initial application of this integral equation approach for the polymer ring, consider a model comprised of freely jointed hard spheres of diameter σ. In the limit of complete flexibility, the intramolecular structure in the melt obeys Gaussian statistics given by[18]

$$\hat{\omega}(k) = \sum_{\alpha=1}^{N} \hat{\omega}_{\alpha\gamma}(k) \tag{11a}$$

$$\hat{\omega}_{\alpha\gamma}(k) = \exp[-\sigma^2 k^2 |\alpha - \gamma|(N - |\alpha - \gamma|)/6N] \tag{11b}$$

Note that the statistical correlation length and the hard-core diameter are identical so the present model is completely characterized by a single length scale. Equations 9–11 can now be used to calculate the intermolecular radial distribution function for a melt of hard core, Gaussian polymer rings.[19]

Computational Procedure

Lowden and Chandler[12,21] have shown that the solution of the RISM equation is equivalent to the following variational principle:

$$\frac{\delta I_{\mathrm{RISM}}}{\delta C(r)} = 0, \qquad r < \sigma \tag{12a}$$

where, for a molecule composed of identical sites, the functional I_{RISM} is given by

$$I_{\mathrm{RISM}} = \rho_m^2 \int C(r)\, d\vec{r} - \frac{1}{8\pi^3}\int d\vec{k}\,[\rho_m\hat{\omega}(k)\hat{C}(k) + \ln[1 - \rho_m\hat{\omega}(k)\hat{C}(k)]] \tag{12b}$$

In order to make use of this variational approach, Lowden and Chandler took the direct correlation function $C(r)$ to have the form

$$C(r) = H(r - \sigma)\sum_{i=1}^{m} a_i\left(\frac{r - \sigma}{\sigma}\right)^{i-1} \tag{13}$$

where $H(x)$ is the step function which is unity for $x < 0$ and vanishes for $x > 0$. Equation 13 with $m = 4$ is identical in form to the exact solution of the Percus–Yevick theory for hard spheres.[10] Note that the representation for $C(r)$ in eq 13 automatically satisfies the second of the closure conditions in eq 9b and its Fourier transform can be evaluated analytically. With this representation for $C(r)$, the variational principle in eq 11 reduces to a set of m coupled nonlinear algebraic equations.

$$\frac{\partial I_{\mathrm{RISM}}}{\partial a_i} = 0, \qquad i = 1, ..., m \tag{14}$$

In accord with previous work on small molecules[12,21] and the quantum electron problem,[20] we take $m = 4$ which is adequate for an accurate numerical solution of the RISM equations.

The nonlinear equations in eq 14 were solved numerically by using standard techniques to give the four coefficients a_i. Once having these coefficients, the properties of interest can be easily computed. The direct correlation function follows immediately from eq 13. The structure factor, which is the spatial Fourier transform of the total density fluctuation correlation function, is given by

$$\hat{S}(k) = N^{-1}\sum_{\alpha,\gamma=1}^{N}[\hat{\omega}_{\alpha\gamma}(k) + \rho\hat{h}_{\alpha\gamma}(k)] = \frac{\hat{\omega}(k)}{1 - \rho_{\mathrm{m}}\hat{\omega}(k)\hat{C}(k)} \tag{15}$$

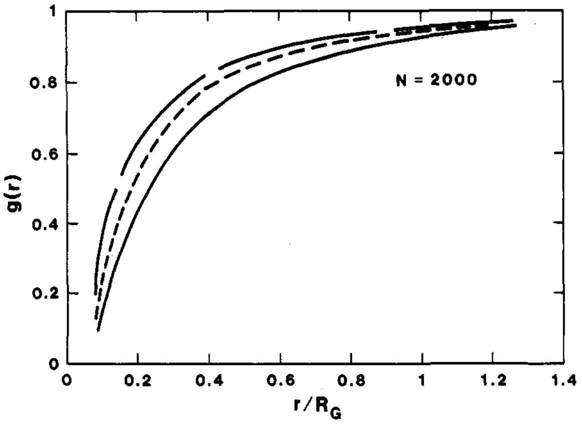

Figure 1. Radial distribution function vs. separation (scaled by the radius of gyration of a Gaussian ring) for N = 2000 with reduced monomer densities of $\rho_m\sigma^3$ = 0.6 (solid curve), 0.8 (short dash), and 1.0 (long dash). The corresponding contact values, $g(\sigma^+)$, are 0.095, 0.139, and 0.204, respectively.

The intermolecular radial distribution function can be found by Fourier inversion of $\hat{h}(k)$.

$$g(r) = 1 + \frac{1}{2\pi^2 r}\int_0^\infty k \sin (kr)\, \mathrm{d}k \left[\frac{\hat{\omega}^2(k)\hat{C}(k)}{1 - \rho_m\hat{\omega}(k)\hat{C}(k)} \right] \tag{16}$$

Results and Discussion

A. Radial Distribution Function. Results for the intermolecular pair correlation function of a 2000-unit ring are shown in Figure 1 for several liquid densities. Note that the abcissa is scaled by the radius of gyration ($R_G^2 = N\sigma^2/12$) of a Gaussian ring polymer. As required for hard-core systems, $g(r)$ jumps discontinuously from zero to a finite contact value, $g(\sigma^+)$, which is an increasing function of density. The equation of state can be determined from knowledge of the contact value via the virial theorem.[2,22] With increasing separation, $g(r)$ monotonically approaches its uncorrelated bulk value of unity. The lack of specific structural features in $g(r)$ is a result of the simple Gaussian model adopted for the intramolecular polymer statistics. The "correlation hole" effect,[1] however, is clearly present in our results and reflects the partial exclusion of monomers on different rings from inside a given polymer coil due to intermolecular excluded volume interactions and intramolecular constraints. As the liquid density increases, both the short-range order (as indicated by the magnitude and slope of $g(r)$ at contact) and the degree of interpenetration of polymer coils increase, and hence the width of the correlation hole is diminished.

The dependence of $g(r)$ on the degree of polymerization N is shown in Figure 2 for a fixed density. As N increases, the contact value decreases; however, the overall degree of interpenetration, i.e.,

$$\int_0^{R_G} g(r)\, \mathrm{d}\vec{r}$$

increases. The latter trend is a consequence of the fact that the compactness of a random coil decreases as the inverse of its radius. From Figure 2 it is clear that finite size coil effects are more important on longer length scales than at very small interparticle separations.

B. Structure Factor and Density Fluctuations. In Figure 3 we have plotted the results for the structure factor $\hat{S}_d(k)$, which is the structure factor defined in eq 15 minus the self term ($\hat{S}_d(k) = \hat{S}(k) - 1$), at two densities for the 2000 unit ring. In this figure, the solid line on the log–log plot is the prediction for a Lorentzian dependence on the wave vector $k\sigma$. The latter behavior is appropriate at intermediate wave vectors ($R_g^{-1} < k < \sigma^{-1}$) for semidilute solutions.[1] From the figure it is clear that the ring polymer exhibits Lorentzian behavior only over a limited range of $k\sigma$ (~0.4–1.0). This behavior is not unexpected and is due to a combination of two effects. The first relates to the wave vector dependence of the intramolecular structure factor $\hat{\omega}(k)$ for the polymer ring. It can be seen from Figure 4 that $\hat{\omega} \sim 12(k\sigma)^{-2}$ for $k\sigma > 0.4$ in the intermediate wave vector regime. Note that this asymptotic behavior is approached slower, and in a nonmonotonic fashion, for the ring than for the corresponding linear polymer. The second effect is reflected in a wave-vector dependence of the direct correlation function $\hat{C}(k)$. In Figure 5 we have plotted $\hat{C}(k)$ as a function of wave vector. Note that for $k\sigma < 1$, the direct correlation function varies by only 15% or so and can be accurately approximated by a quadratic expansion: $\hat{C}(k) \sim \hat{C}(0) + \hat{C}''(0)k^2/2$. Thus from eq 15 we get Lorentzian behavior over a very limited range

$$\hat{S}(k) \sim \frac{12}{B(\sigma k)^2 - 12\rho_m\hat{C}(0)} \tag{17}$$

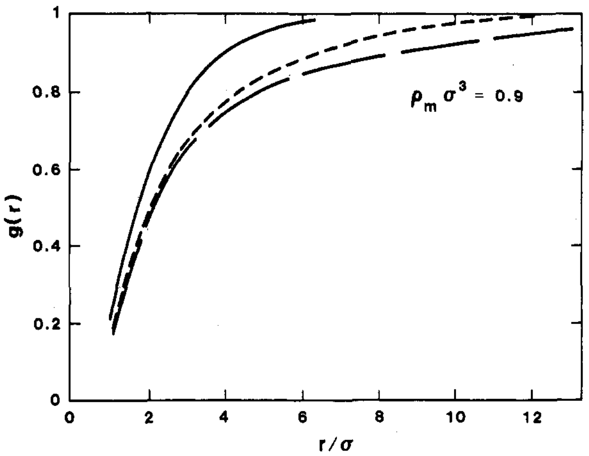

Figure 2. Radial distribution function vs. separation (in units of the hard-sphere diameter σ) for a reduced monomer density of 0.9 and three values of N = 100 (solid curve), 500 (short dash), and 2000 (long dash). The corresponding contact values are 0.206, 0.175, and 0.169, respectively.

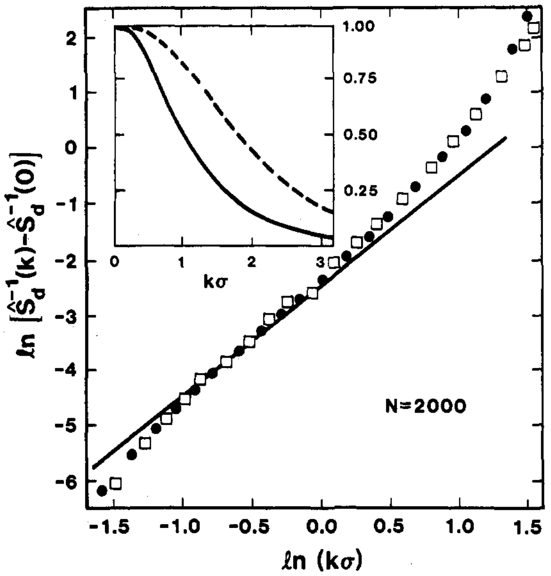

Figure 3. log–log plot of the inverse of the structure factor $\hat{S}_d(k)$ minus its k = 0 value as a function of the dimensionless wave vector. The solid circles (open squares) are for $\rho_m\sigma^3$ = 0.6 (0.9). The straight line has a slope of 2. The inset is a linear plot of $\hat{S}_d(k)/\hat{S}_d(0)$ for $\rho_m\sigma^3$ = 0.6 (solid curve) and 0.9 (dashed).

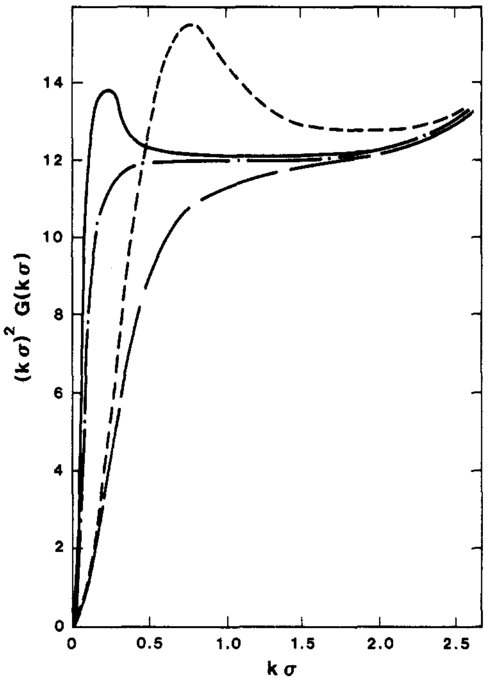

Figure 4. Intramolecular structure factor, $G = N^{-1}\sum_{\alpha,\gamma}\hat{\omega}_{\alpha\gamma}(k)$, times the wave vector squared as a function of dimensionless wave vector. The solid and short-dashed curves are for 2000- and 100-unit Gaussian rings, respectively. The dash–dot and long-dash curves are for 2000- and 100-unit Gaussian linear chains, respectively, and correspond to the standard Debye functions.

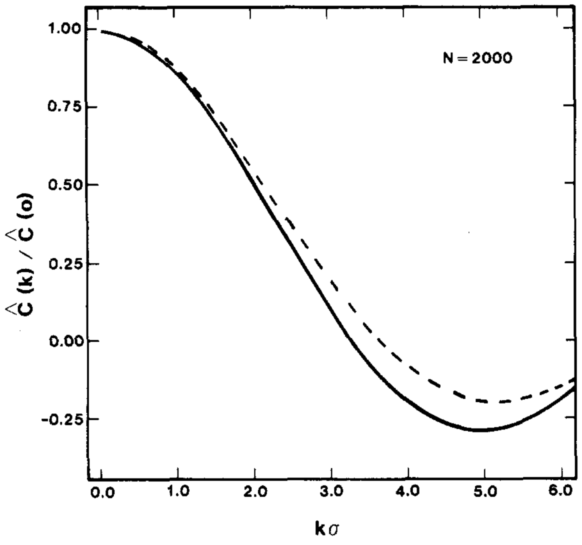

Figure 5. Fourier transform of the direct correlation function normalized by its zero wave vector value for a 2000-unit Gaussian ring polymer melt at densities of $\rho_m\sigma^3 = 0.6$ (solid curve) and 0.9 (dashed). The $k = 0$ value of $-\rho_m C(k)$ is 0.288 for $\rho_m\sigma^3 = 0.9$ and 0.077 for $\rho_m\sigma^3 = 0.6$.

where $B = 1 - 6\rho_m\sigma^{-2}\hat{C}''(0)$. For $k\sigma > 1$, $\hat{C}(k)$ decays rapidly due to the finite range of the intermolecular interactions and the presence of short-range order in the liquid. The behavior of the structure factor at large wave vectors reflects the complex contributions of both the intramolecular structure factor and the direct correlation function.

The spatial range of density correlations in a liquid are often qualitatively characterized in terms of a screening length ξ. For a Lorentzian structure factor this arises naturally since $S(r) \sim r^{-1}\exp(-r/\xi)$. For our more complex case an analogous length can be defined as the distance over which the structure factor decays to one-half its initial value, i.e., $\hat{S}(k\sigma=\sigma/\xi) = 0.5\hat{S}(0)$. This screening length is plotted in Figure 6 as a function of inverse degree of polymerization for different densities. Its magnitude is of the order of one monomer diameter and decreases with density as an approximate power law of the form $\xi \sim \rho^{-\eta}$, where the exponent η decreases from ~1.5 for $N = 2000$ to ~1.2 for $N = 100$. At fixed monomer density, the screening length increases monotonically (and hence density fluctuations decay slower) with the number of repeat units. This trend is consistent with the reduction in short-range order [i.e., $g(\sigma^+)$] as N increases (see Figure 2). It is also interesting to note that the minimum number of repeat units above which ξ scales in a simple $1/N$ fashion is a decreasing function of density.

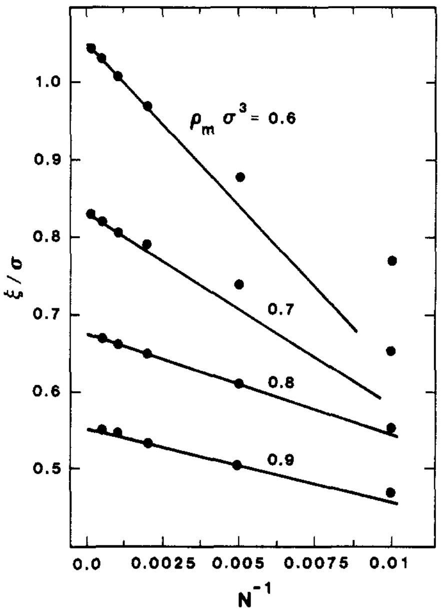

Figure 6. Screening length in units of the monomer diameter as a function of inverse degree of polymerization for several liquid densities. The solid circles are the theoretical results and the straight lines are linear fits to the three highest degree of polymerization points.

It should be noted that for the case of a freely jointed ring studied here, the structure factor for small length scales ($k\sigma > 1$) would not be expected to describe a real polymer, since the Gaussian approximation for the ideal polymer would not be accurate for large wave vectors because of stiffness effects. The theory presented here would be pertinent to real polymers for $k\sigma > 1$, however, if a more realistic model for the unperturbed structure were employed to calculate $\hat{\omega}(k)$.

A thermodynamic measure of the density fluctuations in the polymer melt is the isothermal compressibility κ_T, which can be found from the zero wave vector limit of the structure factor.

$$\hat{S}(0) = \rho_m k_B T \kappa_T \tag{18}$$

$\hat{S}(0)$ can be easily obtained from the a_i coefficients in eq 13. From eq 15 we can write

$$\hat{S}(0) = \frac{N}{1 - \rho_m N\hat{C}(0)} \tag{19a}$$

It can also be shown that in the zero wave vector limit, $\hat{C}(0)$ can be expressed as

$$\hat{C}(0) = 4\pi\sigma^3\sum_{i=1}^{m}(-1)^{i-1}a_i\left(\frac{1}{i} - \frac{2}{i+1} + \frac{1}{i+2}\right) \tag{19b}$$

Equations 18 and 19 thus provide a convenient way to calculate the compressibility. In Figure 7, $\hat{S}(0)$ is plotted over a range of densities as a function of inverse chain

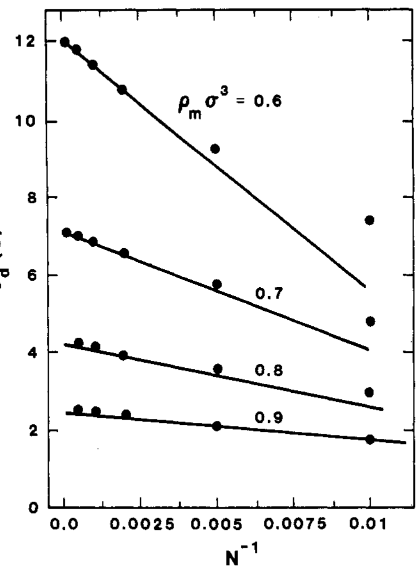

Figure 7. Same as Figure 6 except for the zero wave vector limit of the structure factor minus the self correlation: $\hat{S}_d(0) = \hat{S}(0) - 1$.

length. It can be shown that $\hat{S}(0)$ has an approximate power law dependence on density, $\hat{S}(0) \sim \rho_m^{-\lambda}$, where λ is about 4 and decreases weakly with N. At fixed monomer density, the dependence of the compressibility on the degree of polymerization is very similar to that found for the screening length and for the same qualitative physical reasons. Finally, the equation of state can, in principle, be determined from a knowledge of the compressibility via integration over density.[10,22]

C. Comparison to the RPA Theory. As mentioned previously, the RPA theory developed by de Gennes[1] would lead to zero scattering when applied to homogeneous polymer melts since density fluctuations are ignored. It is therefore devoid of content for describing the structure factor of unlabeled, one-component melts. However, the incompressibility condition, together with the ideality assumption for the intramolecular chain structure, can be used to get a crude estimate of the intermolecular radial distribution function $g(r)$. For zero scattering we can write in Fourier space for the incompressible melt,

$$\hat{S}(k) = \hat{\omega}(k) + \rho_m\hat{h}(k) = 0 \qquad (20)$$

Inversion of the Fourier transform leads to the following simple result for the incompressible polymer melt:

$$-\rho_m h(r) = \omega(r) \qquad (21)$$

corresponding to a prediction for the deviation from the bulk density around a reference monomer which is independent of liquid density and interparticle forces. Equation 21 is plotted in Figure 8 along with the results from the present theory for $N = 2000$ at densities $\rho_m\sigma^3 = 0.6$ and 1.0. It can be seen that the incompressibility assumption becomes very good on large length scales $r > 2\sigma$. This is consistent with the fact that the screening length shown in Figure 6 indicates that density fluctuations decay on a length scale of a couple of monomers. We can also observe in Figure 8 that the incompressibility approximation improves with increasing density. This is reasonable since the compressibility approaches zero at high densities. It should be emphasized that although the simple incompressibility result in eq 21 is accurate at large length scales, it is of no value in the calculation of thermodynamic properties which are local properties depending critically on the value of $g(r)$ near contact. Indeed, for more realistic models of polymer structure the radial distribution function displays specific short range structural features which have no analogue in the RPA result.[22]

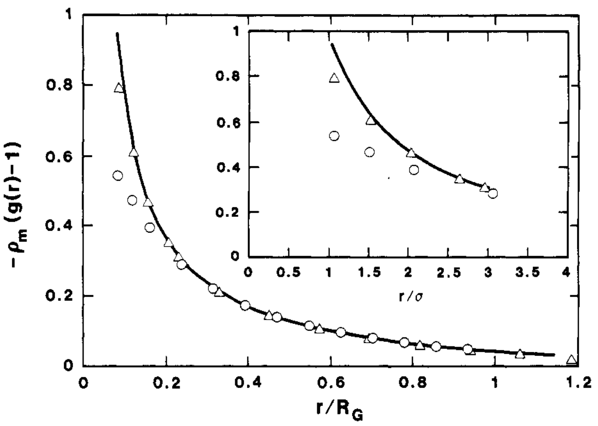

Figure 8. Negative of the correlated part of the local intermolecular density, $-\rho_m h(r)$, as a function of scaled distance for a 2000-unit Gaussian ring melt. The open circles (triangles) are the RISM theory results for $\rho_m\sigma^3 = 0.6$ (1.0). The solid curve is the density-independent RPA prediction discussed in the text. The inset is an expanded plot of the short distance behavior. Note that the abscissa is in units of σ rather than the radius of gyration.

Whereas the RPA theory predicts zero scattering for the homogeneous melt, it does produce scattering from labeled melts due to concentration fluctuations, which agrees well with neutron scattering experiments[1] at relatively small wave vectors. The RPA prediction for the structure factor of a system of polymer chains labeled at sites α and γ along the chain backbone is given in our notation as

$$\hat{S}_{\alpha\gamma}(k) = \hat{\omega}_{\alpha\gamma}(k) - \frac{\sum_{\beta=1}^{N}\hat{\omega}_{\alpha\beta}(k)\sum_{\tau=1}^{N}\hat{\omega}_{\tau\gamma}(k)}{\sum_{\alpha,\gamma=1}^{N}\hat{\omega}_{\alpha\gamma}(k)} \qquad (22a)$$

In the case of a ring polymer all sites are equivalent on the average, therefore

$$\sum_{\beta=1}^{N}\hat{\omega}_{\alpha\beta}(k) = \hat{\omega}(k)$$

and thus eq 22a reduces to

$$\hat{S}_{\alpha\gamma}(k) = \hat{\omega}_{\alpha\gamma}(k) - (\hat{\omega}(k)/N) \qquad (22b)$$

For simplicity, consider polymer rings in which one monomer is labeled on each ring. The RPA structure factor then takes the simple form

$$\hat{S}_{11}(k) = 1 - (\hat{\omega}(k)/N) \qquad (22c)$$

The integral equation theory presented in this paper can also be used to calculate the scattering from labeled systems. For the labeled ring, we obtain

$$\hat{S}_{\alpha\gamma}(k) = \hat{\omega}_{\alpha\gamma}(k) + \rho\hat{h}(k) \qquad (23a)$$

which reduces to the following for singly labeled system:

$$\hat{S}_{11}(k) = 1 + \rho\hat{h}(k) \qquad (23b)$$

Figure 9 shows a comparison between the RPA prediction and the present theory for the case of a melt of rings ($N = 500$) each labeled at monomer 1. It can be observed from this figure that the two theories agree closely. As expected, the RPA theory becomes closer to our predictions at higher densities (and larger N) since the incompressibility assumption is more accurate in this limit. It is interesting to note that the RPA prediction for the labeled polymer ring system in eq 22b is obtained simply by substitution of the incompressibility condition in eq 21 into eq 23a.

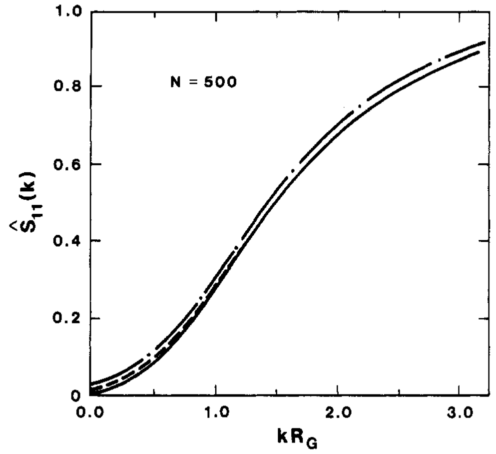

Figure 9. Structure factor for a labeled melt composed of 500-unit rings with a single labeled monomer on each ring. The solid curve is the RPA prediction, while the dash–dot (short-dash) curve is the RISM result for $\rho_m\sigma^3 = 0.6$ (0.9). For the higher density case the RISM and RPA curves are essentially indistinguishable on the scale of the graph for $kR_G \gtrsim 1.5$.

Thus the content of the RPA theory for polymer rings consists only of the simple assumption of incompressibility. This is not the case, however, for the linear polymer system described by eq 22a.

Conclusion

In this paper we have introduced an integral equation method for the intermolecular radial distribution function of a polymer melt for arbitrary polymer structure, molecular weight, and liquid density. We have applied this theory to a melt of Gaussian polymer rings interacting with hard-core repulsions. This theory can also be employed to treat long linear chain systems in a computationally tractable, but approximate, manner by neglecting chain end effects. One can argue that if end effects are unimportant, then the set of radial distribution functions $g_{\alpha\gamma}(r)$ in eq 5 are nearly equal, and the matrix RISM equations reduce to a single integral equation as was found for the ring system. With this approximation, the linear polymer case can be solved in an analogous manner to the ring, with the intramolecular distribution $\hat{\omega}(k)$ in eq 11 appropriately chosen for a linear chain.[23] In the present investigation, we adopted the simplest possible single polymer distribution function: the Gaussian ring. The model can be made considerably more realistic on short length scales by including chain stiffness effects through a wormlike model or the rotational isomeric state approximation for $\hat{\omega}(k)$. Such generalizations will allow a detailed interpretation of experimental wide-angle X-ray scattering on polymer melts. Finally, the effect of attractive interactions superimposed on the hard-core pair potential can be analyzed by employing perturbation theory or adopting a more general closure relation for the integral equations. Future work by us will focus on these questions along with equation-of-state predictions, polydispersity effects, self-consistent determination of the intramolecular structure, and the application of the integral equation theory to polymer blends and copolymers.

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