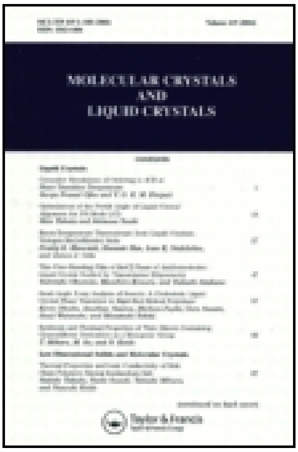

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Integral Equation Theory of Homopolymer Melts†

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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 coworkers 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 long linear chain this set approximately reduces to a single integral equation which we have solved numerically for the case of Gaussian and freely-jointed chain 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 approximately (RPA) approach of deGennes, 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 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,

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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. Other related versions of this work have been reported elsewhere.[3-7,26]

Recent theoretical progress for the structure of one-component polymer liquids has been limited primarily to the work of deGennes who has successfully applied the random phase approximation (RPA) to describe the scattering from partially labelled melts.[1,8] In this case, the structure factor is determined by concentration fluctuations which are long range in the labelled system. In the unlabelled 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.[9-11] In these theories rather artificial lattice or cell models, which are really more appropriate to solids, are generally resorted to. In addition, 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 coworkers.[12-13] 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[14] 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.[12,15] In addition, the RISM theory has been successfully applied to interpret the structure factors measured experimentally by scattering techniques.[16] In the present investigation, the RISM theory is formulated in a fashion which renders the polymer 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.

II) 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

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

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.[14] Integral equation theories for $g(r)$ are based on the well known Ornstein-Zernike equation[14] which defines the direct correlation function $C(r)$.

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

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 Equation (2).

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

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 Equation (2) suggests that $C(r)$ can be viewed as an effective pair potential which remains finite even for singular interactions. It can be shown[14] that for a system with weak pair interactions $v(r)$, or for large interparticle separations, that $C(r) = -v(r)/k_BT$, 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

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

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.[14]

Chandler and Andersen[13] 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[13]:

$$\underset{\sim}{h}(r) = \int d\vec{r}' \int d\vec{r}''\underset{\sim}{\omega}(|\vec{r} - \vec{r}'|)\underset{\sim}{C}(|\vec{r}' - \vec{r}''|)\,[\underset{\sim}{\omega}(r'') + \rho\underset{\sim}{h}(r'')] \tag{5}$$

where ρ is the number density of molecules and $\underset{\sim}{h}(r)$, $\underset{\sim}{C}(r)$, and $\underset{\sim}{\omega}(r)$ 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,

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

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

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, Equation (6a) is exact for a hard core potential, and Equation (6b) is the fundamental approximation. Equations (5) and (6) constitute the RISM equations for molecular fluids.[13] 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 Equation (5) only in an average (not instantaneous) sense via the equilibrium distributions $\omega_{\alpha\gamma}(r)$. Therefore, the effect 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 has been recently formulated,[17a] but the complexity of the resultant theory is enormously enhanced.

In addition, a new reformulation of the RISM equations which is fully consistent diagramatically has been recently constructed.[17b] 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, Equations (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 4-point correlation function was necessary.[18] 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,[1,19] demonstrated from computer simulations[2] and deduced from neutron scattering experiments.[20,21] 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 theta 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 Equation (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 deGennes RPA theory mentioned earlier to describe labelled polymer melts. We have recently developed a scheme for specifically removing chain segment overlaps on a length scale less than the hard sphere diameter while treating the remainder of the intramolecular distribution as ideal.[6,7]

For a linear polymer composed of N identical sites or monomers, Equations (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 long linear chains where end effects can be neglected.[5] With this approximation, all the intermolecular correlation functions in Equations (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 Equation (5) reduce to a single integral equation given by

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

where $\omega(r) = \sum_{\alpha} \omega_{\alpha\gamma}(r)$ and $\rho_m = N\rho$ denotes the monomeric density. The closure relations in Equation (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, Equation (8) can be written in Fourier transform space as,

$$\hat{h}(k) = \hat{\omega}^2(k)\hat{C}(k) + \rho_m\, \hat{\omega}(k)\hat{C}(k)\hat{h}(k) \tag{10}$$

where the caret symbol denotes Fourier transformation.

As an initial application of this integral equation approach for the polymer chain, consider a model comprised of freely-jointed hard spheres of diameter σ. In this limit of complete flexibility, the intramolecular structure in the melt obeys Gaussian statistics given by[22]

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

$$\hat{\omega} = (1 - f^2 - 2f/N + 2f^{N+1}/N)(1 - f)^{-2} \tag{11b}$$

where $f = \exp(-k^2\sigma^2/6)$.

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 chains.[23]

III) COMPUTATIONAL PROCEDURE

Lowden and Chandler[16,25] have shown that the solution of the RISM equation is equivalent to the following variational principle:

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

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 to the Percus-Yevick theory for hard spheres.[14] Note that the representation for $C(r)$ in Equation (13) automatically satisfies the second of the closure conditions in Equation (9b) and its Fourier transform can be evaluated analytically. With this representation for $C(r)$, the variational principle in Equation (11) reduces to a set of m coupled nonlinear algebraic equations.

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

In accord with previous work on small molecules[16,25] and the quantum electron problem,[24] we take $m = 4$ which is adequate for an accurate numerical solution of the RISM equations.

The nonlinear equations in Equation (14) were solved numerically 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 Equation (13). The structure factor, which is the spatial Fourier transform of the total density fluctuation correlation function, is given by

$$\begin{aligned}\hat{S}(k) &= N^{-1} \sum_{\alpha,\gamma=1}^{N} [\hat{\omega}_{\alpha\gamma}(k) + \rho \hat{h}_{\alpha\gamma}(k)] \\ &= \frac{\hat{\omega}(k)}{1 - \rho_m \hat{\omega}(k)\hat{C}(k)}\end{aligned} \tag{15}$$

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

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

IV) RESULTS AND DISCUSSION

A. Radial distribution function

Results are shown in Figure (1) for the radial distribution of a 16000 unit, linear chain at various densities ranging from $\rho_m\sigma^3 = 0.60$ to 1.0. Note that the abcissa is scaled by the radius of gyration ($R_G^2 = N\sigma^3/6$) for a linear chain. The existence of the "correlation hole," also found for the Gaussian ring,[3,4] is clearly seen in Figure (1) and is a result of the partial exclusion of monomers on different chains from inside a given polymer chain due to intermolecular excluded volume interactions and intramolecular constraints. In the intermediate length scale regime, $\sigma << r < R_g$, $g(r)$ approaches its limiting value of unity in an approximately Coulomb r^{-1} fashion, thereby indicating long range correlations in the melt due to chain connectivity.

It can also be observed in Figure (1) that $g(r)$ jumps discontinuously from zero to a finite contact value $g(\sigma^+)$ at $r = \sigma^+$ as expected for a hard core system. The contact value of the radial distribution function is an increasing function of density and decreasing function of N and can be used to compute the equation-of-state for the hard core chain system as will be discussed in detail elsewhere.

Figure (2) shows the radial distribution functions for the more realistic model of a (nonoverlapping) freely jointed chain at fixed density for chain lengths of $N = 20$, 200, and 2000. The details of this calculation are reported elsewhere.[6,7] Note that the nonoverlapping freely jointed chain exhibits structure for short chains, similar to small molecular fluids, but this structure becomes less pronounced and the correlation hole becomes deeper as the chain length increases at fixed density.

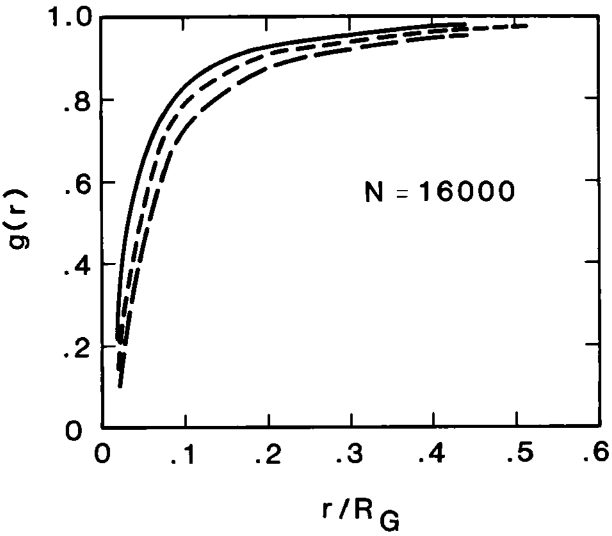

FIGURE 1 The intermolecular radial distribution function for a linear Gaussian polymer chain of 16000 repeat units calculated from Equations (9) as a function of the scaled separation where $R_G^2 = N\sigma^2/6$. Results are shown for $\rho_m\sigma^3$ = 0.60 (long dash), 0.80 (short dash) and 1.00 (solid curve).

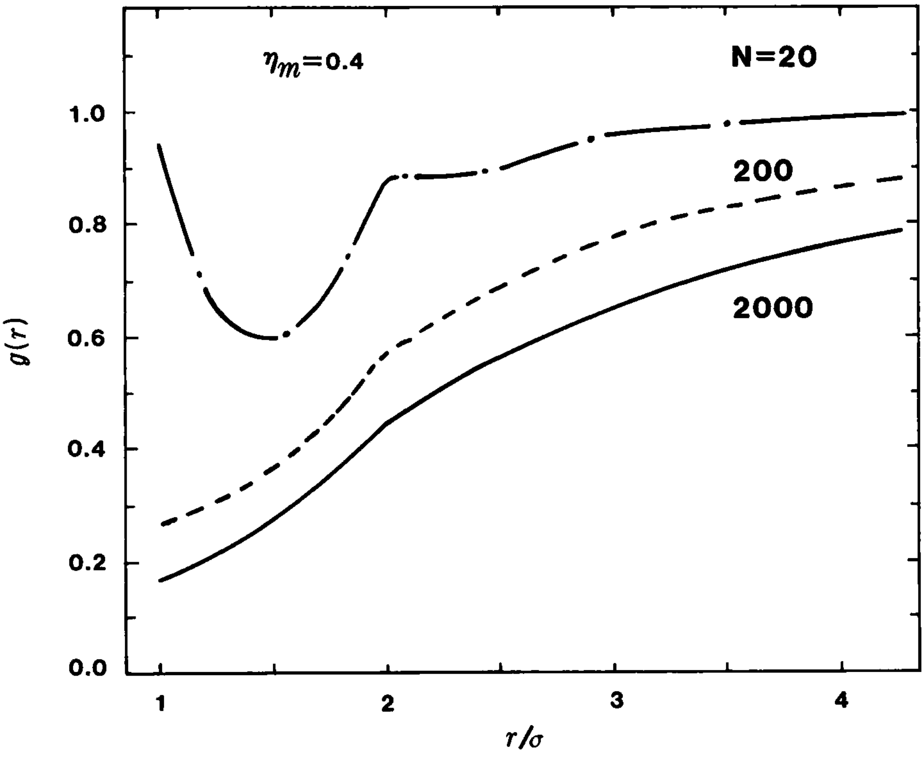

FIGURE 2 Intermolecular radial distribution functions of nonoverlapping freely jointed chains for three values of N at fixed packing fraction $\eta_m = \pi\rho_m\sigma^3/6$.

B. Structure factor

The structure factor can be computed from Equation (15). Illustrative results are shown in Figure (3) for a linear Gaussian chain of 16000 units at various monomer densities. Note that the breadth or linewidth of the structure factor increases at higher densities. This linewidth is an inverse measure of the spatial length scale over which total density fluctuations decay and can be seen to be of the order of a few monomer diameters. As was found for the case of rings,[3,4] this correlation or screening length decreases with density. In the intermediate wavevector regime, $R_g^{-1} < k < \sigma^{-1}$, the functional form of the structure factor is a simple Lorenztian. This follows from Equation (15) since $\hat{\omega}_0(k) \sim 12/(k\sigma)^2$ for a Gaussian chain and the direct correlation function can be accurately represented as a quadratic function of wavevector: $\hat{C}(k) = \hat{C}(0) + k^2\hat{C}''(0)/2$ in the intermediate regime. Substituting these forms in Equation (15) yields

$$\hat{S}(k) \sim \xi^{-1}/(k^2 + \xi^{-2}), \qquad (17)$$

corresponding to a Yukawa decay: $S(r) \sim r^{-1} \exp(-r/\xi)$ where the screening length ξ is given by

$$\xi^{-2} = -12\sigma^2\rho_m\hat{C}(o)/[1 - 6\rho_m\sigma^{-2}\hat{C}''(o)]. \qquad (18)$$

An analysis of the shape of the curves in Figure (3) indicates non-Lorentzian

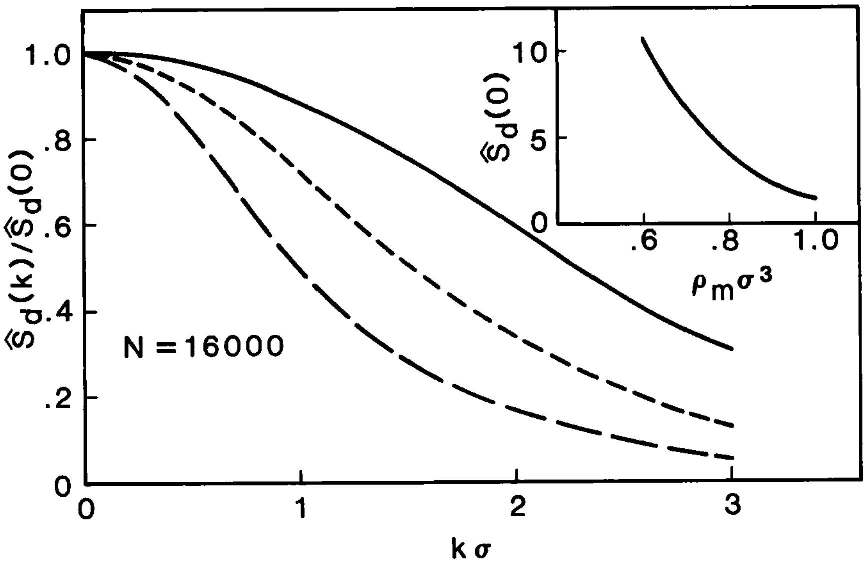

FIGURE 3 The normalized static structure factor ($\hat{S}_d(k) = \hat{S}(k) - 1$) as a function of dimensionless wavevector for linear Gaussian chains of 16000 repeat units. Results are shown for densities $\rho_m\sigma^3$ = 0.60 (long dash), 0.80 (short dash) and 1.00 (solid curve). The inset is a plot of the zero wavevector structure factor versus dimensionless density for a linear chain of N = 16000 units.

behavior at large wavevectors, $k\sigma > 1$, such that $\hat{S}^{-1}(k)$ increases faster than k^2. This behavior arises from the fact that both the direct correlation function and $\hat{\omega}(k)$ exhibit[3-7] nonquadratic dependence for wavevectors $k\sigma > 1$.

The isothermal compressibility κ_T is related to the structure factor at zero wavevector according to

$$\hat{S}(0) = \rho_m k_B T \kappa_T \tag{19}$$

where k_B is Boltzmann's constant and T is the absolute temperature. $\hat{S}_d(0) = \hat{S}(0) - 1$ is plotted in the inset of Figure (3) for a linear Gaussian chain of 16000 units. As expected, the $\hat{S}_d(0)$ decreases as the density increases reflecting the fact that the system becomes more incompressible at high densities.

At larger wavevectors ($k\sigma > 1$), one expects the intermolecular radial distribution function and structure factor of a real polymer chain to exhibit specific features due to the short range chemical structure of the polymer (e.g., constant bond angles, rotational potentials etc.). The Gaussian model employed here, of course, does not exhibit any of these structural details. These effects could be introduced by using more realistic models for the ideal polymer chain such as the "worm-like chain" or the "rotational isomeric state chain." Such models will be studied in future investigations.[26]

The structure factor for the nonoverlapping freely jointed chain[6,7] is shown in Figure (4) as a function of chain length at fixed density. Note the crossover from Lorentzian type behavior at small wave vectors for $N = 2000$ to a monotonically increasing function, characteristic of small molecular fluids, for $N = 20$. It can also be observed in this figure that a peak is observed at high wave vectors for the nonoverlapping freely jointed chain model, which is due to a combination of the constant bond constraint and intermolecular packing effects.[6,7]

V) 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 and freely jointed polymer chains interacting with hard core repulsions. In the present investigation, we adopted the relatively crude single polymer distribution functions: the Gaussian and nonoverlapping freely jointed chains. The model can be made considerably more realistic on short length scales by including chain stiffness effects through a worm-like 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, and the application of the integral equation theory to polymer blends[27] and copolymers.

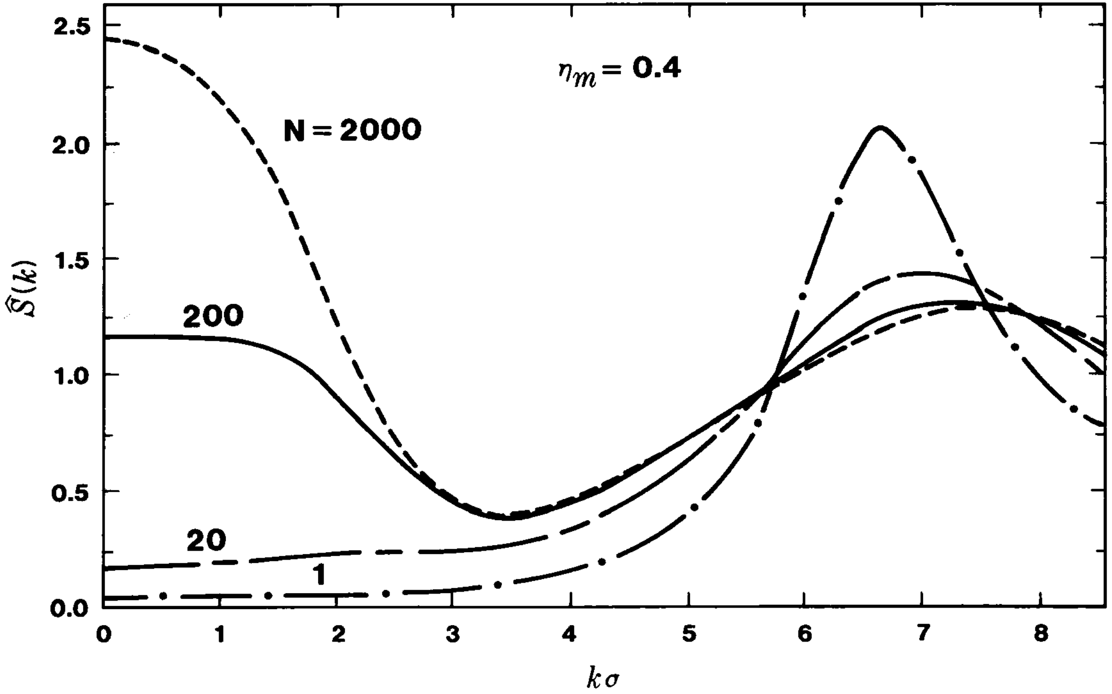

FIGURE 4 Structure factor of nonoverlapping freely jointed melt at fixed packing fraction ($\eta_m = \pi\rho_m\sigma^3/6$) for three values of N. The atomic hard sphere Percus-Yevick result is also shown.

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23. Chandler and coworkers have recently developed a theory for the quantum solvated electron in a hard sphere fluid.[17,24] By utilizing the isomorphism between the Feynmann path integral formulation of quantum mechanics and the equilibrium statistical mechanics of polyatomic fluids, the electron can be treated formally as a classical Gaussian ring polymer of infinite degree of polymerization with spring constants proportional to the number of monomers. Their theory employs the RISM equation to describe, in a self-consistent fashion, the intramolecular and intermolecular correlation functions. The resulting integral equation theory is quite similar in mathematical structure to our Equations (9)–(11), but the quantum nature of the electron results in significantly different physical behavior.
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