Integral-Equation Theory of the Structure of Polymer Melts

Kenneth S. Schweizer and John G. Curro

Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 14 October 1986)

A general, analytically tractable, nonperturbative theory of the equilibrium structure of dense polymer melts is proposed on the basis of modern integral-equation theories of molecular liquids. Calculations are presented for polymer rings obeying Gaussian statistics and interacting via hard-core repulsions. The correlation hole, compressibility, and static structure factor are found to be sensitive functions of liquid density and degree of polymerization.

Theoretical understanding of the structure of polymer solutions has increased dramatically in the past two decades because of the development of scaling, renormalization-group, and self-consistent-field techniques.[1-4] On the other hand, the dense polymeric liquid is characterized by very strong intermolecular interactions and has remained virtually intractable analytically. Moreover, Monte Carlo and molecular-dynamics simulations of both lattice and continuum models of polymer melts are extremely computationally intensive and have generally been limited to small systems composed of relatively short chains.[5] The purpose of this Letter is to present the first systematic, continuum analytic approach to the equilibrium structure of polymer melts based on nonperturbative statistical mechanical theories of molecular fluids. The central result of our work is the calculation of the intermolecular radial distribution function for the polymer liquid. This quantity is of significance not only for structural reasons, but also because it provides a direct route to the calculation of all the thermodynamic properties, including an equation of state beyond the artificial lattice or cell models.

The modern theory of one-component atomic and small-molecule liquids has advanced to a mature stage.[6,7] In the absence of strong attractive forces, short-range order is controlled by the harsh repulsive forces which define molecular shape. Quantitative off-lattice theories for molecular liquids based on this concept have been pioneered by Chandler and co-workers[6] utilizing a representation of a molecule as a collection of overlapping spherical interaction sites or chemical subunits connected by covalent bonds. Within such a model the intermolecular pair potential is a sum over spherically symmetric site-site potentials, $v_{\alpha\gamma}(r)$, where r is the distance between sites α and γ on different molecules. The structural information in this approach is contained in the generalized Ornstein-Zernike matric integral equations[6]

$$h(r) = \int d^3r' \int d^3r'' \, \omega(|\mathbf{r}-\mathbf{r}'|) C(|\mathbf{r}'-\mathbf{r}''|)[\omega(r'') + \rho h(r'')], \tag{1}$$

where ρ is the molecular number density, h, C, and ω are square matrices of rank N (for molecules containing N interaction sites) with elements $h_{\alpha\gamma}(r)$, $C_{\alpha\gamma}(r)$, and $\omega_{\alpha\gamma}(r)$, respectively. More specifically, $h_{\alpha\gamma}(r) \equiv g_{\alpha\gamma}(r) - 1$, where $g_{\alpha\gamma}(r)$ is the intermolecular site-site radial distribution function, $C_{\alpha\gamma}(r)$ is the corresponding direct correlation function, and $\omega_{\alpha\gamma}(r)$ is the *intra*molecular probability distribution function for sites α and γ on the same molecule and describes chemical connectivity and flexibility. The direct correlation function defined in Eq. (1) can be interpreted[6] physically as an effective pair potential in the liquid and is thermodynamic state and intramolecular structure dependent. The integral equation approach is particularly appealing since the microscopic intermolecular interactions enter explicitly via the direct correlation function.[7] For flexible molecules the intramolecular and intermolecular correlations must be determined self-consistently. Since rapidly varying repulsive forces dominate the dense liquid structure, the problem is generally simplified by adopting a hard-core interaction for $v_{\alpha\gamma}(r)$ resulting in the so-called "reference interaction site model" (RISM).[6] To uniquely determine $h(r)$ and $C(r)$ the following closure relations for Eq. (1) are introduced:

$$h_{\alpha\gamma}(r) = -1, \quad r < \sigma_{\alpha\gamma}, \tag{2a}$$

$$C_{\alpha\gamma}(r) = 0, \quad r > \sigma_{\alpha\gamma}, \tag{2b}$$

where $\sigma_{\alpha\gamma}$ is the distance of closest approach between sites α and γ. Equation (2a) is an exact relation, while Eq. (2b) is a central approximation of the RISM theory and is analogous to the closure employed in the successful Percus-Yevick theory for atomic hard-core fluids.[7] The above theory is a nonperturbative, many-body approach which explicitly incorporates the constraints of intramolecular structure in determining the intermolecular packing arrangements. The accuracy and reliability of the RISM theory at liquid densities has been extensively documented by comparison with both experiments

246   © 1987 The American Physical Society

and computer simulation.[6]

Because of the apparent coupling between the intramolecular distributions $\omega_{a\gamma}(r)$ and the intermolecular pair correlation functions $h_{a\gamma}(r)$ for flexible molecules, the application of the RISM approach to high polymers would seem to be virtually intractable. In this work we circumvent this difficulty by invoking theoretical[5,8] and recent neutron scattering studies[9] which have unequivocally established that the single-chain configurational statistics are unperturbed, down to nearly monomer length scales, in the melt. That is, the intramolecular distribution function of each chain is essentially indistinguishable from that of an isolated polymer in a theta-solvent. This fact permits the insertion of the unperturbed, system-specific distributions for the functions $\omega_{a\gamma}$ in Eq. (1), thereby bypassing the need for a simultaneous, self-consistent determination of both the intramolecular and intermolecular correlations.

As an initial application we consider the freely jointed chain model in which the polymer consists of N hard spheres or beads of diameter σ connected by universal joints. Each bead represents a statistical segment which may, in general, consist of several chemical subunits. This model corresponds to a completely flexible chain described[1] by a Gaussian intramolecular distribution function of the form $\hat{\omega}_{a\gamma}(k) = \exp(-k^2\sigma^2|a-\gamma|/6)$, where we have taken the bond length between nearest-neighbor beads to be equal to the hard-sphere diameter and the caret symbol to denote Fourier transformation. Substitution of this relation into the RISM equations (1) yields a set of $N(N+1)/4$ independent, coupled nonlinear integral equations for the intermolecular pair correlation functions. In practice, numerical solution for large N is very difficult, although possible in principle. Since our primary interest is in long chains, we consider for simplicity the analogous Gaussian "ring" polymer. The intramolecular site-site distribution function for the ring molecule is[10]

$$\hat{\omega}_{a\gamma}(k)$$
$$= \exp[-\sigma^2 k^2 |a-\gamma|(N-|a-\gamma|)/6N]. \quad (3)$$

For relatively short length scales and large N we expect, on physical grounds, that end effects will be insignificant implying the ring and chain polymer intermolecular correlations will be nearly equivalent.[11] In addition, there is considerable interest in synthetic and biological ring polymers of variable degrees of polymerization.[12] As an obvious consequence of the ring symmetry the intermolecular correlation functions are independent of site labels: $h_{a\gamma}(r) = h(r)$ and $C_{a\gamma}(r) = C(r)$. This results in enormous technical simplification since the matrix RISM equations reduce[13] to a single integral equation which in Fourier-transform space is given by

$$\hat{h}(k) = \hat{\omega}(k)\hat{C}(k)\hat{\omega}(k) + \rho_m\hat{\omega}(k)\hat{C}(k)\hat{h}(k), \quad (4)$$

with the closure relations $h(r) = -1$, $r < \sigma$ and $C(r) = 0$, $r > \sigma$. Here, $\rho_m \equiv \rho N$ is the statistical segment or bead density, and $\hat{\omega}(k) \equiv \sum_{a=1}^{N}\hat{\omega}_{a\gamma}(k)$ is the intramolecular ring polymer structure factor. To numerically solve Eq. (4) we have followed established procedures[6,14] based on a functional variational principle which can be reduced to a small number (four in our case) of coupled, nonlinear algebraic equations.[15] This analysis yields an accurate numerical solution for $\hat{C}(k)$ and the intermolecular pair correlation function, $g(r) = h(r) + 1$, is obtained from Fourier inversion of Eq. (4). The corresponding structure factor relevant to scattering experiments is given by

$$\hat{S}(k) = \hat{\omega}(k) + \rho_m\hat{h}(k)$$
$$= \hat{\omega}(k)[1 - \rho_m\hat{\omega}(k)\hat{C}(k)]^{-1}. \quad (5)$$

An extensive numerical study of the ring polymer was carried out[15] as a function of reduced density $\rho_m\sigma^3$ and degree of polymeriztion N. Representative results for the radial distribution function at a low and high liquid density and two values of N are presented in Fig. 1. As required for hard-core systems, $g(r)$ jumps discontinuously from zero to a finite contact value which is an increasing function of density and decreasing function of N. Knowledge of the contact value, $g(\sigma^+)$, determines the equation of state via the virial theorem.[5] Of particular interest is the "correlation hole" structure of $g(r)$ reflecting the partial expulsion of monomers on different rings from inside a tagged polymer coil due to the intermolecular excluded volume interactions and intramolecular constraints. From Fig. 1, it is clear that interpretation is enhanced with increasing density and/or degree of polymerization. The latter trend is a consequence of en-
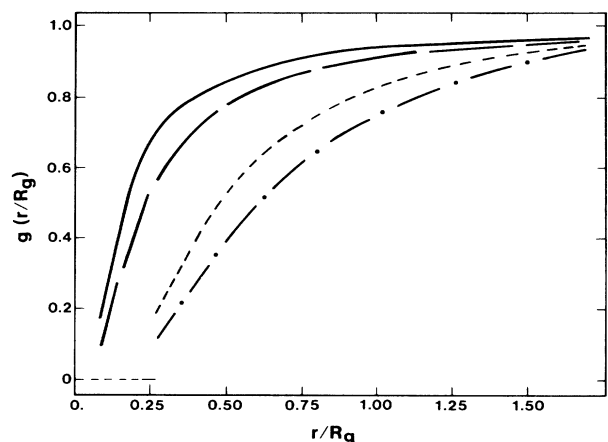

FIG. 1. Intermolecular radial distribution function as a function of the scaled separation where $R_g^2 = N\sigma^2/12$ is the ring polymer radius of gyration. Results are shown for $\rho_m\sigma^3 = 0.9$ and $N = 2000$ (solid line), $N = 200$ (long-dashed line); $\rho_m^3 = 0.6$ and $N = 2000$ (short-dashed line), $N = 200$ (dash-dotted line).

tropic mixing effects and the fact that the density of a random coil of entropic mixing effects and the fact that the density of a random coil (walk) decreases as the inverse of its radius. The intermolecular correlations can be experimentally probed in detail by x-ray scattering[16] in conjunction with complementary neutron scattering measurements on deuterated samples[9] in order to separate out the intramolecular contributions. Alternatively, intermolecular excitation transfer can be employed as an indirect measure of the correlation hole.[17]

The structure factors for the high–molecular-weight systems are plotted in Fig. 2 and are not describable in terms of any simple analytic function. The nonuniversal form of $\hat{S}(k)$ in the ring polymer melt is due to a combination of two physical effects. The first relates to the differences between the ring and linear polymer intramolecular structure factors at small $(kR_g \lesssim 1$, where R_g is the radius of gyration) and intermediate $(R_g^{-1} < k^{-1} < \sigma^{-1})$ wave vectors. It is well known[10] that $\hat{\omega}(k)$ for the ring decays slower at small k than the corresponding linear chain. In addition, although the ring $\omega(k)$ eventually scales in the k^{-2} Debye-function fashion, it approaches this limiting behavior slower than the chain and in a nonmonotonic manner.[10] The second consideration is that at high densities the details of interparticle interactions are important and are reflected in a wave-vector dependence of the direct correlation function. At large wave vectors $\hat{S}(k)$ reflects the complex behavior of both the direct correlation function and the intramolecular structure factor. In this regime, the

random-flight model is an obviously oversimplified description, but, the presence of significant scattering intensity at large wave vectors is a general feature of the dense liquid.

A related thermodynamic property of considerable interest is the isothermal compressibility which is proportional to the static density fluctuations and hence $\hat{S}(0)$. Detailed calculations for the dense melt reveal that $\hat{S}(0)$ increases by roughly 50% on going from an $N = 100$ to an $N \rightarrow \infty$ polymer at fixed monomer density, which is consistent with the increased degree of interpenetration for larger rings. At fixed N, $\hat{S}(0)$ is a strong function of density varying approximately as $\rho_m^{-\lambda}$, where $\lambda = 4.15$ for $N \gtrsim 2000$ and decreases to $\lambda = 3.98$ for $N = 100$. The density dependence of the compressibility permits a determination of the equation of state via integration of a standard thermodynamic relation.[7]

Another structural quantity of interest is the mean distance, or "screening length," over which density fluctuations decay in the liquid. As a reasonable measure of such a length scale we have adopted the distance over which the structure factor decays to one half its initial zero-wave-vector maximum, i.e., $\hat{S}(k\sigma \equiv 2\pi\sigma/\xi) = 0.5$. With this definition ξ is of the order of $5 \pm 2\sigma$ and decreases with density as an approximate power law of the form $\xi \sim \rho_m^{-\eta}$, where η decreases monotonically from 1.55 for $N = 2000$ to 1.21 for $N = 100$.

Finally, the present theory can also be applied to calculate the scattering patterns from partially labeled (e.g., deuterated) polymers.[15] Such a problem has been considered by de Gennes, who constructed a simple and successful theory based on the random-phase approximation and the assumption of liquid incompressibility.[1,4] For the limiting case of one labeled monomer per ring our results are in very close agreement with the predictions of de Gennes in the high-density and large-N regime. However, it should be emphasized that the incompressibility assumption employed to derive the random-phase-approximation expressions yields a theory which is independent of the explicit intermolecular interactions and liquid density, and corresponds to an $\hat{S}(k)$ that is identically zero in the unlabeled melt. It is therefore largely devoid of content for the problems which we have considered.

In conclusion, we have performed the first microscopic calculations of the intermolecular structure of dense polymer melts based on an analytically tractable, nonperturbative continuum theory. Our approach is distinguished by its ability to compute the thermodynamic and pair correlation functions for arbitrary density, degree of polymerization, and intramolecular structure. The specific hard-core model considered can be viewed as a reference system about which perturbation theory can be performed to incorporate the effects of continuous repulsions and weak attractive interactions on both the structure and equation of state. The theory can be for-
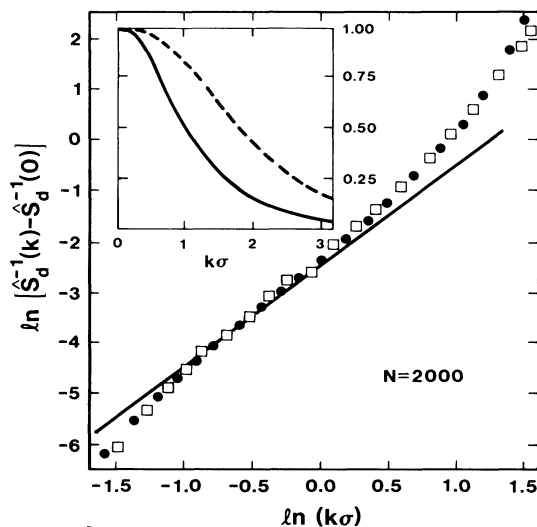

FIG. 2. Log-log plot of the inverse of the structure factor [with the trivial self-correlation subtracted $\hat{S}_d(k) = \hat{S}(k) - 1$] minus its $k = 0$ value as a function of dimensionless wave vector. The circles (squares) are for $\rho_m\sigma^3 = 0.6$ (0.9). The straight line corresponds to Lorenztian behavior. The inset is a linear plot of $\hat{S}_d(k)/\hat{S}_d(0)$ for $\rho_m\sigma^3 = 0.6$ (solid line) and 0.9 (dashed line).

mulated in a computationally tractable fashion for long linear polymers.[15] In addition, chain stiffness and rotational isomerism can be included thereby permitting a realistic treatment of local chemical structure.[15] The feasibility of such extensions within the context of a functionally practical formalism is encouraging for a variety of future system-specific applications such as intermolecular energy transport and polymer phase transitions.

[1]P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979).

[2]Y. Oono, Adv. Chem. Phys. **61**, 301 (1985).

[3]S. F. Edwards, Proc. Phys. Soc. (London) **88**, 265 (1966); see also G Jannink and P. G. de Gennes, J. Chem. Phys. **48**, 2260 (1968).

[4]P. G. de Gennes, J. Phys. (Paris) **31**, 235 (1970).

[5]See, for example, J. G. Curro, J. Chem. Phys. **64**, 2496 (1976), and Macromolecules **12**, 463 (1979); M. Vacatello, G. Avitabile, P. Corradini, and A. Tuzi, J. Chem. Phys. **73**, 543 (1980).

[6]D. Chandler, in *Studies in Statistical Mechanics VIII*, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1982), p. 275, and references cited therein.

[7]J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).

[8]P. J. Flory, Proc. Roy. Soc. London, Ser. A **234**, 60 (1956), and Pure Appl. Chem. **56**, 305 (1984); D. N. Theodorou and V. W. Suter, Macromolecules **18**, 1467 (1985).

[9]D. G. H. Ballard, G. D. Wignall, and J. Schelton, Eur. Polym. J. **9**, 965 (1973); H. Hayashi, P. J. Flory, and G. D. Wignall, Macromolecules **16**, 1328 (1983).

[10]E. F. Casassa, J. Polym. Sci., Part A **3**, 605 (1965).

[11]The possibility of unbreakable topological knots created during the ring polymerization process is not allowed for in our theory.

[12]See, for example, D. Geiser and H. Hocker, Macromolecules **13**, 653 (1980); A. Baumgartner, J. Chem. Phys. **76**, 4275 (1982).

[13]P. Cummings and G. Stell, Mol. Phys. **46**, 383 (1982).

[14]L. J. Lowden and D. Chandler, J. Chem. Phys. **59**, 6587 (1973), and **61**, 5228 (1975).

[15]J. G. Curro and K. S. Schweizer, to be published.

[16]G. R. Mitchell, R. Lovell, and A. H. Windle, Polymer **23**, 1273 (1982); G. W. Longman, G. D. Wignall, and R. P. Sheldon, Polymer **17**, 485 (1976).

[17]G. H. Fredrickson, Macromolecules **19**, 441 (1986).