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COMMUNICATIONS

Local structure of polyethylene melts

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In 1987, Curro and Schweizer introduced the first tractable off-lattice statistical-mechanical theory for dense polymer melts: polymer-RISM theory (reference interaction site model).^{1,2} The theory, which is based on an integral-equation approach for the pair correlation functions, affords a first-principles look at the structure and thermodynamic behavior of polymeric systems without resorting to the mean-field and lattice-based approximations inherent in earlier theories. Subsequent developments examined the radial distribution function, static structure factor, and equation of state of model homopolymer melts,^{3,4} as well as the intermolecular structure, phase stability, and apparent χ parameter of model binary blends.⁵ However, because the focus of previous work has been on idealized Gaussian, free-jointed, and wormlike chain models, the quantitative accuracy of the theory when applied to actual chemical systems has yet to be demonstrated. In this Communication we report preliminary results on the first such application of polymer-RISM theory to a chemically-realistic chain model—namely, a rotational-isomeric-state model of polyethylene—and compare our predictions for the static structure factor to x-ray scattering results obtained at 1 atm and 430 K. A more detailed discussion of the method and results is forthcoming.⁶

Our approach is based on an interaction site model of polymer structure. Extensive experimental and simulation work on a variety of liquids has demonstrated that the structure of dense, nonassociating fluids is dominated by the harsh repulsive intermolecular forces, which can be accurately modeled by effective hard sites, thus reducing the determination of local structure to an entropically-driven, geometrical packing problem.⁷⁻⁹ Accordingly, in this study each chain is modeled by a series of N linked hard sites of diameter d , with each site representing a CH_2 (or terminal CH_3) group. Carbon-carbon bond lengths are fixed at $l = 1.54 \text{ \AA}$ and bond angles at 112° , in line with the generally accepted experimental values. Torsional rotations are represented using Flory's three-state rotational-isomeric-state model¹⁰ with the *gauche* conformations located at $\pm 120^\circ$ relative to the *trans*. The *gauche* conformers are assigned an energy of 500 cal/mol relative to *trans*, and successive *gauche*⁺/*gauche*⁻ combinations are given an additional energy of 2000 cal/mol to account for the "pentane effect," arising from steric interaction between sites separated by four bonds.¹⁰

Intermolecular site-site correlations are described using the RISM integral-equation formalism, originally developed by Chandler and Andersen¹¹ for small rigid-molecule fluids and extended to flexible polymers by Schweizer and Curro.^{1,2} The principal result of the theory is a prediction for the intermolecular radial distribution function, $g(r)$, which describes the relative probability of finding two sites on *different* chains separated by a distance r , averaged over all possible pairs of sites along the chain backbones.

The starting point for the theoretical development is a generalized Ornstein-Zernike-like equation, which decomposes the total correlation function, $h(r) \equiv g(r) - 1$, into two contributions: a "direct" component, propagated directly between the two molecules of interest; and an "indirect" component, mediated through other molecules in the fluid. In Fourier space the equation takes the simple form^{2,11}

$$\hat{h}(k) = \hat{w}(k)\hat{c}(k)[\hat{w}(k) + \rho_m\hat{h}(k)]. \quad (1)$$

Here, $c(r)$ denotes the direct correlation function, and $\hat{w}(k)$ is the single-chain structure factor

$$\hat{w}(k) = \frac{1}{N} \sum_{\alpha,\gamma} \hat{w}_{\alpha\gamma}(k), \quad (2)$$

where $w_{\alpha\gamma}(r)$ is the probability density of finding sites α and γ on the *same* chain separated by a distance r .

To uniquely determine $h(r)$ and $c(r)$, the Percus-Yevick closure relations are introduced:^{11,12} $h(r) = -1$ for $r < d$ and $c(r) = 0$ for $r > d$, where d is the hard-site diameter. The first relation is exact and reflects the impenetrability of the hard sites, while the second is approximate and stems from a literal interpretation of the direct nature of $c(r)$. We solve Eq. (1) numerically using the variational approach suggested by Lowden and Chandler⁸ and described elsewhere.²⁻⁴

In essence then, given a knowledge of the structure of a single chain, Eq. (1) describes the packing of chains in the melt and the consequent thermodynamic behavior. Unfortunately, in flexible polymeric systems the intramolecular structure is coupled nonlinearly to the intermolecular structure and, in principle, must be determined self-consistently.^{3,11} This difficulty may be circumvented, however, by invoking the fact that in dense melts chains are "ideal," so that, to a first approximation, intramolecular structure can be ob-

tained from a single-chain calculation in which long-range excluded volume and medium-induced interactions are assumed to cancel.¹⁰ To account for nonphysical overlaps arising from the neglect of intramolecular excluded volume, a small ($\sim 3\%$) density correction is applied as discussed previously.^{3,4}

Even with this simplification, a determination of the structure factor for an ideal rotational-isomeric-state chain remains a complicated problem. Flory's matrix techniques¹⁰ provide a formally exact solution but become intractable for high polymers; Monte Carlo simulation also provides an unambiguous route. However, to retain the computational convenience of polymer-RISM theory, we have devised the following approximate scheme. Intrachain separations of five or less bonds are handled exactly using a rigorous rotational-isomeric-state enumeration which explicitly accounts for chain-end effects and angle interdependencies (i.e., the pentane effect). Longer range correlations are approximated using the Koyama distribution,¹³

$$\hat{\omega}_{\alpha\gamma}(k) \approx \frac{\sin B_n k}{B_n k} e^{-A_n^2 k^2}; \quad n \equiv |\alpha - \gamma| \geq 6, \quad (3)$$

which was originally developed for the wormlike chain and more recently shown to be quite accurate for semiflexible and pearl-necklace chains with excluded volume.⁴ The parameters A_n and B_n are chosen so that $\omega_{\alpha\gamma}(r)$ produces the correct second and fourth moments of the true rotational-isomeric-state distribution.

To determine A_n and B_n we calculated $\langle r_n^2 \rangle$ for $n \leq 99$ and $\langle r_n^4 \rangle$ for $n \leq 29$ (imbedded in an infinitely long chain) and fit the results to the scaling form $\langle r_n^{2q} \rangle = C_n^{(2q)} l^{2q} n^q$; $q = 1, 2$. When combined with the known infinite-chain limits,^{10,14} plots of $1/C_n^{(2q)}$ vs $1/n$ can be accurately represented by quadratic polynomials, providing an interpolation formula for moments beyond the calculated range. Evaluation of Eq. (3), along with the exact short-range contributions, and substitution into Eq. (2) then yields the single-chain structure factor. Preliminary comparisons with the Monte Carlo results of Honeycutt have shown this to be an accurate and computationally-efficient method.⁶

The remaining piece of information to be supplied is the effective hard-sphere diameter of a methylene group. In this study we have examined melt structure for two values of d . The first is motivated by several molecular dynamics simulations performed on sophisticated interaction-site-models of n alkanes which employed a Lennard-Jones (LJ) intersite potential with well depth $\epsilon = 72$ K and LJ diameter $\sigma = 3.923$ Å.¹⁵ To make contact with these calculations, we employ the Andersen-Weeks-Chandler (AWC) perturbation theory, which determines an effective hard-site diameter by matching the Helmholtz free energy of the hard- and repulsive soft-core chains.^{3,4,9} For the conditions of interest this procedure yields $d = 3.70$ Å. On the other hand, the packing calculations of Slonimskii *et al.*¹⁶ suggest a value $d \sim 3.86$ Å, while our recent density-functional work on polyethylene freezing suggests an upper limit $d \leq 3.93$ Å.¹⁷ Accordingly, for purposes of comparison, we also perform RISM calculations using $d = 3.9$ Å.

To assess the accuracy of the theory, two of us (A.H.

and A.H.N.) performed x-ray diffraction on a spectrophotometric-grade polyethylene obtained from Aldrich Chemical Co. with a reported molecular weight of 90 000 (wt. avg.). The experiment was conducted at 1 atm and 430 K, from which we deduce a melt density of 0.7796 g/cc.¹⁸ Accordingly, the RISM calculations were performed on a homopolymer melt with $N = 6429$ and $\rho_m = 0.03354$ Å⁻³. Diffraction data were collected for values of the momentum transfer 0.3 Å⁻¹ $< k < 16$ Å⁻¹ and analyzed treating CH₂ groups as single scattering sites. A detailed discussion of the experimental technique and data reduction is given in Ref. 19. Particular care was taken to obtain accurate results in the vicinity of the first diffraction peak, as the scattering in this range is very sensitive to irregular surface features of the viscous melt. We believe the present data to be more reliable than that previously obtained at 413 K.¹⁹ (A comparison of this earlier data with RISM predictions obtained using a related, but less sophisticated, model to evaluate Eq. 3 has appeared elsewhere.¹⁷)

Experimental results for the static structure factor, $\hat{S}(k) \equiv \hat{\omega}(k) + \rho_m \hat{h}(k)$, along with the RISM predictions using $d = 3.70$ and 3.90 Å are shown in Fig. 1. Also shown is the experimental $\hat{S}(0)$, determined from Zoller's compressibility data.¹⁸ The inset presents an expanded view of the amorphous-halo region. While the $d = 3.70$ Å curve is seen to be in qualitatively good agreement with the data, particularly at higher wave vectors, the $d = 3.90$ Å curve is in near quantitative agreement over the entire experimental range. This suggests that the effective LJ σ of a CH₂ site may be somewhat larger than 3.923 Å. (Indeed, fixing d at 3.90 Å and ϵ at 72 K, application of the AWC theory predicts

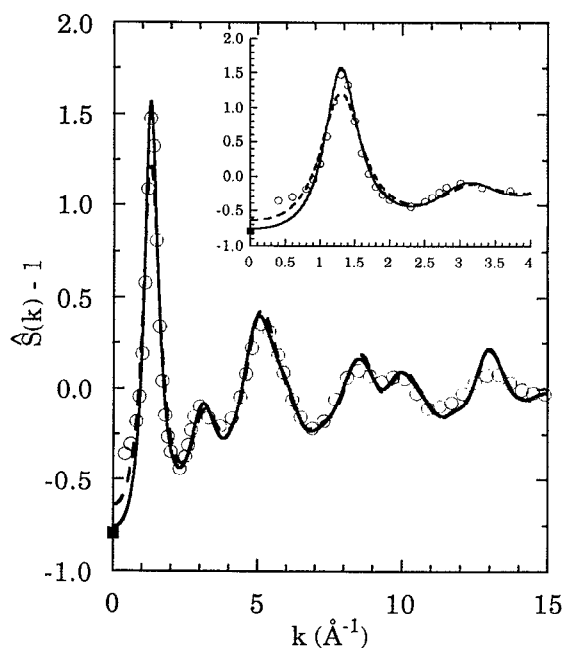


FIG. 1. Static structure factor (minus the trivial self-scattering term) vs wave vector. Circles are x-ray diffraction results for polyethylene at 1 atm and 430 K. Curves are predictions of polymer-RISM theory for a rotational-isomeric-state model with hard-site diameters of 3.70 Å (dashed) and 3.90 Å (solid). The filled square is the experimental $\hat{S}(0) - 1$ deduced from Zoller's thermodynamic measurements (Ref. 18). An expanded view of the first peak is shown in the inset.

$\sigma \sim 4.14 \text{ \AA}$.) Slight discrepancies between theory and experiment at high wave vector (for example, in the peak at 13 \AA^{-1}) can be entirely attributed to bond and angle vibrations, which are absent in our model. When a proper accounting for these oscillations is made, the agreement again becomes quantitative.⁶ The relatively good agreement between the $d = 3.90 \text{ \AA}$ curve and the experimentally-determined compressibility at $k = 0$, however, must be regarded as somewhat fortuitous, given the absence of attractive interactions and soft-core repulsions in our model.

An appealing feature of RISM theory is that it allows an unambiguous separation of the inter- and intramolecular contributions to the total scattering [$\rho_m \hat{h}(k)$ and $\hat{\omega}(k)$]. These are shown for the more accurate $d = 3.90 \text{ \AA}$ calculation in Fig. 2. (Curves for the $d = 3.70 \text{ \AA}$ model are qualitatively similar.) As expected, the large- k regime is dominated by intramolecular scattering. The small bumps in $\rho_m \hat{h}(k)$ for $k > 6 \text{ \AA}^{-1}$ arise almost exclusively from the use of hard-core repulsions and disappear if the AWC correction is used to map the structure onto a repulsive LJ system.⁶ This soft-core correction also slightly damps the intermolecular peaks at $k \approx 3.15$ and 4.85 \AA^{-1} ; however, significant intermolecular structure persists out to $k \approx 6 \text{ \AA}^{-1}$, suggesting that the common empirical technique of deducing intramolecular structural parameters (bond lengths, bond angles, etc.) by fitting expressions for the single-chain structure factor to the high k portion of the total scattering curve should be restricted to $k \gtrsim 6 \text{ \AA}^{-1}$. A comparison of Figs. 1 and 2 reveals that although the first peak in $\hat{S}(k)$ is due primarily to intermolecular scattering, intramolecular contributions broaden the peak and modify both its height and, to a lesser extent, its location from $\rho_m \hat{h}(1.33) \approx 1.06$ to $\hat{S}(1.30) - 1 \approx 1.57$. A similar effect is observed in the subsidiary peak at 3.1 \AA^{-1} .

A second advantage of RISM theory is that the scattering predictions are easily inverted to yield pair correlation functions, without the experimental difficulties associated with truncation errors and unphysical termination ripples. In Fig. 3, intermolecular site-site radial distribution func-

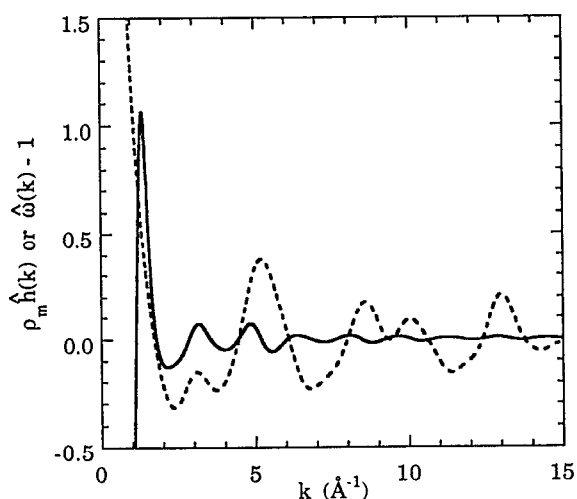


FIG. 2. Intermolecular [$\rho_m \hat{h}(k)$] and intramolecular [$\hat{\omega}(k)$] contributions to the total scattering as a function of wave vector [$\hat{S}(k) = \hat{\omega}(k) + \rho_m \hat{h}(k)$]; $\rho_m \hat{h}(k)$, solid line; $\hat{\omega}(k) - 1$, dashed line. In the zero-wave-vector limit, $\hat{\omega}(0) \equiv N = 6429$ and $\rho_m \hat{h}(0) = -6428.760$.

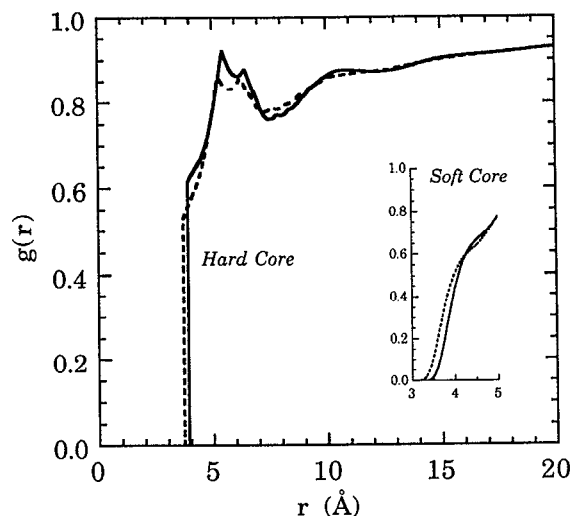


FIG. 3. Polymer-RISM predictions for the site-site intermolecular radial distribution function: $d = 3.70 \text{ \AA}$, dashed line; $d = 3.90 \text{ \AA}$, solid line. The inset shows the associated soft-core (LJ) distribution functions for $\epsilon = 72 \text{ K}$ and $\sigma = 3.923 \text{ \AA}$ (dashed line), $\sigma = 4.14 \text{ \AA}$ (solid line).

tions $g(r)$, are shown for the two hard-core systems; the inset shows the associated soft-core functions in the vicinity of $r = d$ obtained by applying the AWC perturbative correction for purely repulsive LJ sites with $\epsilon = 72 \text{ K}$; $\sigma = 3.923$ and 4.14 \AA .^{9,11} The hard-site curves exhibit a richer and more complex structure than seen in tangent hard-sphere chains,⁴ due to the presence of multiple length scales (i.e., $d \neq l \neq \text{persistence length} [\sim 6 \text{ \AA}]$). Although both curves in Fig. 3 exhibit a pronounced peak and evidence of layering, $g(r)$ is consistently less than one, indicating a relative absence of intermolecular neighbors on all local length scales. Also, the first peak, which occurs at contact for tangent hard-sphere chains, shifts out to the vicinity of $d + l$. The enhanced local structure in the $d = 3.90 \text{ \AA}$ curve stems from the larger diameter, which, for a given site density, increases the effective packing fraction of the fluid. Cusps in the profiles can be identified, and their physical and mathematical origin have been discussed elsewhere.^{8,11} Beyond about 20 \AA , $g(r)$ approaches its uncorrelated value of unity in a roughly Yukawa fashion, with a screening length on the order of the chain's radius of gyration ($\sim 130 \text{ \AA}$). This behavior is characteristic of the universal "correlation-hole" regime.³

Previous work has established polymer-RISM theory's utility as a tractable means of elucidating the properties of idealized polymer models. The present Communication demonstrates that it can also be applied with quantitative accuracy to experimental systems without empiricism or loss of computational convenience. In the process we have devised an accurate means of estimating the single-chain structure factor based on the Koyama distribution and have found that significant intermolecular scattering persists to wave vectors $\sim 6 \text{ \AA}^{-1}$. Efforts directed at a more thorough understanding of the temperature, density, and chain-length dependence of local structure are in progress.

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