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Compressibility-Based Hard-Site Models of Linear Polyethylene and the Normal Alkanes

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ABSTRACT: In the development of an interaction potential for polyethylene, the effects of attractions and excluded volume are often difficult to separate. Here we consider an experimental quantity which is dominated by the excluded volume (the compressibility) and require that a hard-site model of polyethylene predict the experimental compressibility. The site diameter in the model is varied until this requirement is met. We use a rotational isomeric state model of polyethylene, and the compressibility of the model is calculated with polymer reference interaction site model (PRISM) theory. The experimental compressibility is found from the Olabisi–Simha equation of state. The effects of state variables and chain length on the site diameter are investigated.

I. Introduction

Accurate knowledge of the interchain potential interaction is essential for the realistic modeling of polymeric systems. For the case of polyethylene, a qualitative understanding of these interactions has existed for some time. When the methylene group is treated as a single, spherical unit, its diameter is about 4 Å, and the well depth of a methylene–methylene interaction is about 60 K. Unfortunately, greater accuracy in the potential appears to be hindered by a dependency on both state variables and chain length.

In previous work by Curro et al.,[1] the site diameter was determined to be 3.90 Å from wide-angle X-ray scattering, and the well depth was calculated at a temperature 430 K by comparison with equation of state information. Although similar in spirit, the current investigation probes variations in the hard-site diameter in the absence of extensive X-ray scattering information.

We model the interchain methylene–methylene potential as hard sites. The single parameter in the model potential—the site diameter—is adjusted so that calculations of the compressibility agree with experimental measurements, and we explore the dependence of the hard-site diameter upon temperature, pressure, density, and chain length.

Because different macroscopic system properties depend strongly on different regions of the intermolecular potential, the hard-site model of polyethylene will be accurate for certain properties and inaccurate for others. For instance, the short-ranged, repulsive interactions dictate the liquid state structure as probed by scattering experiments, and, consequently, the resulting scattering function, or structure factor, can be understood in terms of repulsions alone.[2] Since the repulsions can be thought of as excluded volume forces, it is not surprising that kinetic phenomena, such as diffusion, which rely upon free volume, are highly sensitive to the correct description of the short-ranged interactions.[3] On the other hand, long-ranged van der Waals attractions are essential for the correct treatment of thermodynamic properties and, in particular, for the accurate portrayal of the equation of state.[1] Finally, the crystal structure is most influenced by the location of the well in the site–site potential.

The accuracy of the potential interactions depends upon both the overall mathematical form selected and the type of experiments which the potentials are expected to describe. Often either the equation of state or the crystal structure is used to determine the intermolecular potentials. Since both of these quantities are sensitive balances between the repulsive and attractive aspects of the potential, properties such as diffusion and scattering functions which strongly depend upon only the repulsive or "excluded volume" forces may well be poorly described. Indeed, Lopez-Rodriguez et al.[4] found that the equation of state of polyethylene can be described equally well by potentials with entirely different excluded volumes. In addition to the issues discussed above, the intermolecular potentials conceivably may depend upon the model, intramolecular potentials. The local, liquid state structure in the vicinity of a monomer will depend to a degree upon whether the backbone that the site is attached to is a highly ordered, rotational isomeric state (RIS)[5] chain or a more detailed one which includes torsional vibrations.

Liquid structure—both in small molecules and in polymers—is largely determined by the repulsive aspect of the intermolecular potentials. Consequently, there has been a large amount of work dedicated to the mapping of full potentials onto excluded volume or "hard site" models. Hard-site models have a single parameter—the site diameter—which must be "tuned" to model a particular system. For site–site separations less than one diameter, the hard-site potential energy is infinite, and, otherwise, it is zero.

One would naively expect that all, or at least most, of the available intermolecular potentials between spherical, CH_2, monomer sites would, when mapped to a hard site, result in similar diameters. Such is not the case.[3] For chains with continuous rotational potentials, the monomer diameters range from a low of 3.40 Å to a high of 3.85 Å, and, for long-chain polyethylene modeled with an RIS backbone, a hard-sphere diameter of 3.90 Å is required to describe the amorphous halo region of wide-angle X-ray scattering.[2]

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In spite of such large ambiguities, the modeling of polyethylene as an RIS chain of spherical, hard, methylene sites has several appealing attributes. First, the structure factor can be interpreted in a straightforward manner.[2] Second, the potential interaction contains a single parameter: the hard-sphere diameter. And, third, the full, continuous, Lennard-Jones (LJ) style, methylene–methylene potential should collapse to the hard-site model through the appropriate mapping, and, therefore, the hard-site model of polyethylene can be used to assess the accuracy of continuous potential models.

We are interested in the variation of the hard-site model of polyethylene with temperature, pressure, density, and chain length. The most direct approach is to compare the structure factor arising from different diameters to the experimental scattering intensities. This has been done for polyethylene at 430 K, 1 atm, and a chain length of 6429 sites, and, as mentioned above, a diameter of 3.90 ± 0.05 Å is required to give good agreement with the height of the amorphous halo peak in the structure factor.

Unfortunately, accurate scattering studies on well-characterized polyethylene melts are scarce. On the other hand, the zero wave vector ($k = 0$) component of the structure factor can be found directly from the equation of state. By requiring that the structure factor of our hard-site model have the experimental value at zero k, we will, in this work, be able to explore variations in the diameter.

Care must be taken in such an approach. The zero k region of the structure factor is less accurately described by the hard-site model than higher k regions. However, except for fluids near the critical point, the hard-site model is seen to work well at $k = 0$ for atoms, small molecules, and, most recently, polyethylene.[2] Consequently, although exact agreement with hard-site diameters based upon the amorphous halo should not be expected, we do expect trends predicted from a hard-site modeling of the zero k intercept of the structure factor to be reasonably accurate.

The remainder of the paper is organized as follows. In section II, equations of state for linear polyethylene and alkanes are discussed. These equations of state supply the experimental, isothermal compressibility. Section III discusses PRISM liquid state theory. This theory permits the calculation of the isothermal compressibility from the atomistic modeling of the systems. By modeling the polymeric systems as rotational isomeric state, hard-site chains, the hard-site diameter can be adjusted so that the isothermal compressibility calculated from PRISM assumes its experimental value. The results of this matching procedure are reported in section IV. Finally, in section V, our results are discussed.

II. Semiempirical Equations of State and the Isothermal Compressibility

There are a number of empirical and semiempirical equations of state for linear polyethylene in current usage. Many of these date from the 1960s[6–9] and are limited by the range and quality of the experimental information available at the time. More recently, Olabisi and Simha[10] have fit the Simha equation of state[8] for polyethylene over a wider range of temperature and pressure than the previous studies. In addition, Olabisi and Simha have included alkanes in their study, which permits the investigation of polyethylene and the alkanes within the same formalism. Consequently, we have, except for a few comparative studies of polyethylene, used the Simha equation of state with the Olabisi and Simha parameters in this work.

Table 1. Olabisi–Simha Scaling Parameters for Linear Polyethylene and the Normal Alkanes[10]

material	T^*, K	V^*, cm^3/g	P^*, bar
C_7	5888	1.2365	7648
C_9	6500	1.2235	7600
C_{11}	6910	1.2131	7580
C_{13}	7277	1.2059	7552
C_{17}	7797	1.1955	7520
C_{20}	7979	1.1900	7490
C_{30}	8700	1.1800	7460
C_{40}	9068	1.1738	7433
LPE	10046	1.1548	7160

For computational ease, we use the Simha equation of state in the approximate Tait form.[10] In reduced coordinates, this semiempirical equation of state of polymer melts proposed by Olabisi and Simha[10] is

$$\tilde{V}(\tilde{P},\tilde{T}) = 0.9018 \exp(23.8345\tilde{T}) \times [1.0 - 0.0894 \ln\{1.0 + 1.0427\tilde{P} \exp(49.22\tilde{T})\}] \quad (2.1)$$

where the tildes identify the reduced pressure, $\tilde{P} = P/P^*$; the reduced specific volume , $\tilde{V} = V/V^*$; and the reduced temperature $\tilde{T} = T/T^*$. The starred quantities are the scaling parameters characteristic of the particular system of interest. The chain length dependence is implicit in these parameters, and, for the reader's convenience, a list of the scaling parameters[10] for the alkanes and linear polyethylene (LPE) is placed in Table 1.

The isothermal compressibility, κ, which is the primary quantity of interest in this work, is found by direct differentiation of the equation of state. In particular, the isothermal compressibility is given by the relation

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad (2.2)$$

In the following sections we make use of the Fourier transform of the direct correlation function at zero wave vector, $\hat{c}(0)$, instead of the isothermal compressibility κ. This quantity is inversely proportional to the isothermal compressibility and occurs naturally in PRISM integral equation theory. In particular, the relationship between $\hat{c}(0)$ and κ is given by

$$\hat{c}(0) = -(\varrho_L{}^2 k_B T \kappa)^{-1} \quad (2.3)$$

where ϱ_L is the liquid density and k_B is the Boltzmann constant.

In Table 1, we find the scaling parameters both for the short chain length (N) alkanes and for polyethylene in the limit $N \rightarrow \infty$. The need to predict the PVT behavior for intermediate members of the series suggests that we examine the chain length dependence of the scaling parameters. Based on these tabulated results for linear polyethylene and alkanes, we note the relations

$$\ln T_N{}^* = 9.221 - 2.86377 N^{-0.85024} \quad (2.4)$$

and

$$V_N{}^* = 1.154314 + 0.39708 N^{-0.80148} \quad (2.5)$$

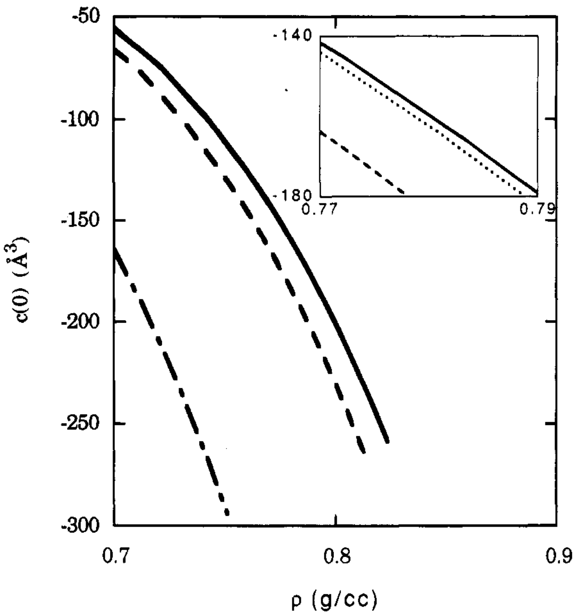

Figure 1. The direct correlation function in the Fourier transform space at zero wave vector of the *n*-alkanes and polyethylene at $T = 298$ K. Corresponding chain lengths are $N = 6429$ sites (the solid line), $N = 1000$ sites (the dotted line), $N = 100$ sites (the dashed line), and $N = 10$ sites (the dashed–dotted line). The inset displays an expanded view at $N = 1000$ and 6429.

In addition, we obtain the third scaling parameter from the empirical correlation[11]

$$\ln\left(\frac{P_N{}^*V_N{}^*}{T_N{}^*}\right) = 1.3191 - \left(\frac{3.0}{2.01}\right)(T_N{}^* \times 10^{-4}) \qquad (2.6)$$

Figure 1 shows the isothermal compressibility, in terms of the Fourier transform of the direct correlation function at zero wave vector $\hat{c}(0)$, of different chain length alkanes at 298 K and 1 atm. We observe a sharp convergence of $\hat{c}(0)$ with an increase in N toward the infinite chain length limit. This implies that, in terms of the isothermal compressibility, alkanes become "polymeric" at a chain length of about 1000.

As mentioned above, there are a number of frequently used equations of state for polyethylene. The chain length dependence for most of those has not been explored. In section IV(A), we will discuss the predictions for the excluded volume for polyethylene, and it will be seen that the Olabisi–Simha equation of state (Eq 2.1), which does depend upon chain length, is in good agreement with the majority of the other equations of state in the long-chain limit.

III. PRISM Liquid State Theory

The polymer reference interaction site model (PRISM) theory[12] is an extension to flexible polymers of the RISM theory of Chandler and Andersen.[13] In PRISM theory, each polymer is taken to consist of a chain of spherically symmetric sites, and where, for long-chain molecules, end effects are included only in an average sense. The correlation between any pair of intermolecular sites is taken as the average over the pair correlation between sites at any position along the chain. The intersite direct correlation function $c(r)$ is related to the intersite radial distribution function $g(r)$ via the RISM equation,

$$\begin{aligned}\hat{h}(\mathbf{k}) &= \hat{\omega}(\mathbf{k})\hat{c}(\mathbf{k})\hat{\omega}(\mathbf{k}) + \varrho_m\hat{\omega}(\mathbf{k})\hat{c}(\mathbf{k})\hat{h}(\mathbf{k}) \\ &= \hat{\omega}(\mathbf{k})\hat{c}(\mathbf{k})\hat{S}(\mathbf{k})\end{aligned} \qquad (3.1)$$

where the carets denote the Fourier transform with respect to wave vector $\mathbf{k}$; $h(r)$ is the total correlation function defined as $h(r) = g(r) - 1$; ϱ_m is the monomer density; and $\hat{S}(\mathbf{k})$ is the static structure factor. All the information about the intramolecular structure of the polymer molecules enters the theory through the function $\omega(r)$,

$$\omega(r) = \frac{1}{N}\sum_{ij}\omega_{ij}(r) \qquad (3.2)$$

where $\omega_{ij}(r)$ is the probability density that sites i and j on the same chain are a distance r apart. For sites less than six sites apart, $\omega_{ij}(r)$ is found by explicitly averaging over all permissible conformations in the RIS[5] model. For sites separated by a greater number of sites, the approximate Koyama distribution[12,14] is used. This is a convolution of a rigid rod and a Gaussian chain, which in Fourier transform space is,

$$\omega_{ij}(k) = \frac{\sin(B_N k)}{B_N k}e^{-A_N{}^2k^2} \qquad (3.3)$$

where $N = |i - j|$. The two parameters A_N and B_N are adjusted so that the first two moments of the Koyama distribution match the corresponding moments of the RIS model at each N.

The PRISM equation is finally closed by the Percus–Yevick (PY) relations for hard sites: $g(r) = 0$ for $r < d$, and $c(r) = 0$ for $r > d$. For a detailed discussion of the PRISM theory, the reader is referred to refs 2 and 12.

The static structure factor is related to the Fourier transform of the correlation functions,

$$\hat{S}(k) = \frac{\hat{\omega}(k)}{1 - \hat{\omega}(k)\hat{c}(k)} \qquad (3.4)$$

At zero wave vector, $k = 0$, the Fourier transform of the self-correlation function $\omega(k{=}0) = N$. Using this relation, eq 3.4 reduces to

$$\hat{S}(0) = \frac{N}{1 - N\hat{c}(0)} \qquad (3.5)$$

Combining eqs 2.3 and 3.5 relates the experimental value of the isothermal compressibility to the structure factor at zero wave vector.

By adjusting the hard-site diameter, the zero wave vector behavior of the model systems (as predicted by PRISM) can be brought into agreement with experimental observations. The experimental value of the isothermal bulk compressibility of a melt of a specific chain length N and at specific pressure and temperature can be found from eq 2.2. From eqs 2.3 and 3.5, the isothermal compressibility can be transformed into the static structure factor at zero wave vector $\hat{S}(0)$. The structure factor is calculated for various site diameters until $\hat{S}(0)$ assumes its experimental value.

IV. Results

In this section we present the results of applications of the methodology discussed in section III. In part A we concentrate upon linear polyethylene, which we model as an RIS chain of 6429 sites. The variation in hard-site diameter with changes in temperature and density is explored and comparisons of predictions from several equations of state are made. In part B, we extend our analysis to shorter chains and study the effect chain length has upon site diameter.

A. Polyethylene. The structure factor of linear polyethylene has been accurately described with PRISM theory using a hard-site model with a diameter of 3.90 Å. Since scattering information for polyethylene melts is currently only available at a temperature of 430 K and a pressure of 1 atm, we are not able to use direct comparison between molecular models and scattering to probe variations in the hard-site diameter.

On the other hand, as discussed above, direct comparison between molecular models and the isothermal compressibility permits the variation in site diameters to be explored over a wide range of state conditions. Because, in this approach, we are neglecting the effect of attractions on the compressibility, we expect the predicted diameters to be somewhat smaller than those found from matching the amorphous halo region of the structure factor (where attractions have little or no effect) to experimental X-ray results. We find the difference in the diameters predicted through the two routes to be about 5%. We do not expect the magnitudes of the diameters found in this manner to be as accurate as those found from scattering data; however, we do expect the trends in the diameter with changes in temperature, pressure, and density to be similar for the two routes.

The simplest mapping of soft- to hard-site potentials is due to Barker and Henderson (BH)[15] and views d as a function of temperature alone,

$$d = \int_0^\infty (1 - e^{-\beta u(r)})\, dr \tag{4.1}$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, and $u(r)$ is the repulsive part of the site–site potential. Consequently, the rate of change of d with β is given in the BH formalism by

$$\frac{d(d)}{d\beta} = \int_0^\infty u(r) e^{-\beta u(r)}\, dr \tag{4.2}$$

and, because $u(r)$ is greater than zero, the rate of change of d with β is positive as well. In other words, d can be expected to decrease with increasing temperature. This expectation is confirmed by our results. Over a temperature range from 400 to 600 K at a constant pressure of 1 atm, we find approximately linear behavior with d decreasing from 3.80 to 3.48 Å.

The hard-site diameter predicted by eq 4.1 will be a function of temperature alone and, in particular, for constant temperature, will be a constant. On the other hand, the methodology of Weeks, Chandler, and Andersen (WCA)[16] introduces a, usually small, density dependence to the diameter. At constant pressure, we observe in Figure 2 an increase in d with increasing density. For a 0.01 g/cm^3 increase in density, the diameter increases by 0.025 Å. Since, at constant pressure, temperature decreases as the density increases, the diameter would be expected to increase from either the BH or WCA expressions.

In Figure 3, two isotherms are shown. The site diameter appears to be highly sensitive to density, and not at all as would be envisioned from BH theory. Strictly speaking, the semiempirical equation of state which we have based our predictions upon is fit over the temperature range 415–470 K, the pressure range 1–2000 bar, and the density range 0.77–0.8 g/cm^3. We plot a considerably larger density range in Figure 2 to illustrate the crossover predicted at low density. This crossover occurs as the pressures start to become negative and, accordingly, the system becomes unstable.

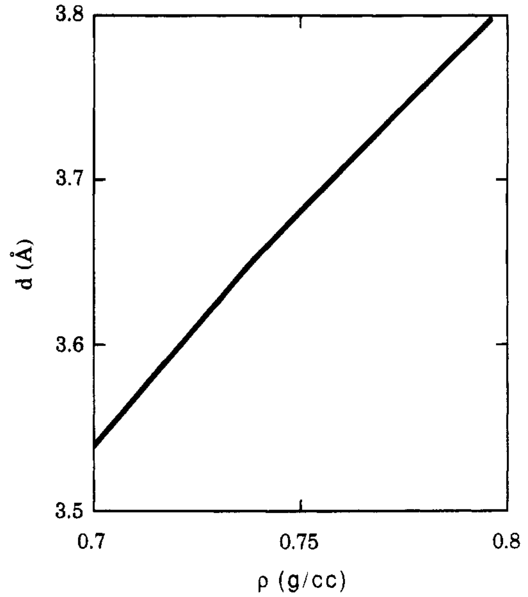

Figure 2. Hard-sphere diameter of polyethylene at $P = 1$ atm and $N = 6429$.

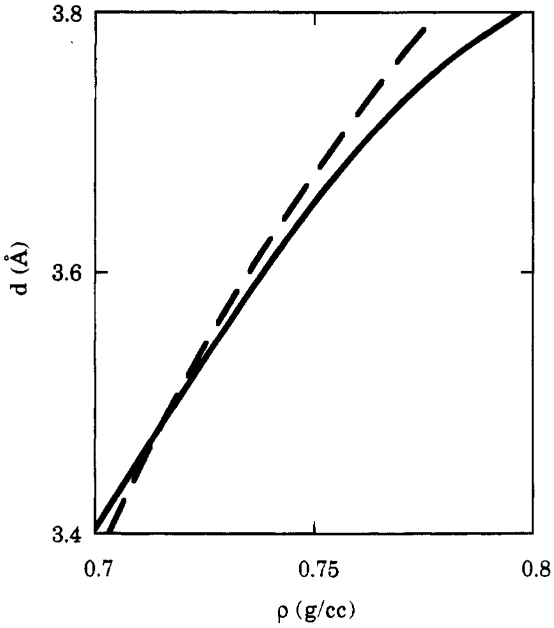

Figure 3. Hard-sphere diameter of polyethylene at $T = 430$ K (the solid line) and $T = 298$ K (the dashed line). Both curves are for 6429 site chains.

The Tait form of the Olabisi–Simha equation of state is one of a number available for polyethylene. It has the advantage of having been applied to short-chain alkanes, which will permit us to explore chain length effects on the hard-sphere diameter. However, before this behavior is addressed, it is of interest to compute the hard-sphere diameters of polyethylene which result from different equations of state. The hard-sphere diameter predicted from the Olabisi–Simha semiempirical equation of state at 1 atm and 415 K is 3.775 Å. Use of the Sanchez–Lacombe[17] equation of state pre-

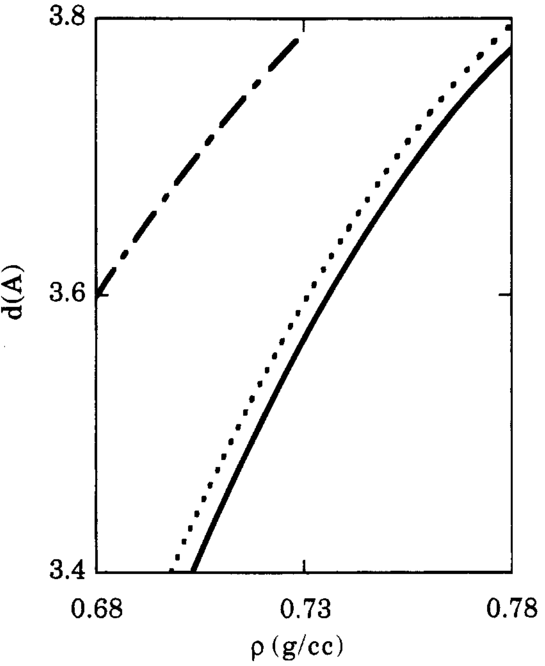

Figure 4. Hard-sphere diameter of *n*-alkanes at $T = 298$ K. The three curves correspond to $N = 1000$ sites (the solid line), $N = 100$ sites (the dotted line), and $N = 10$ sites (the dashed–dotted line).

dicts a d of 3.77 Å at that pressure and temperature. A d value of 3.76 Å is obtained from the full, Simha "hole theory" equation of state.[8,11] These predictions for d are in surprisingly good agreement and give us confidence in the Tait form of the Olabisi–Simha semiempirical equation of state. On the other hand, we obtain a very low value of d (3.5 Å) from the Flory-Orwoll-Vrij equation of state [9] modified for polyethylene by Zoller [18]. The isothermal compressibility calculated from their theory seems high to us and we attribute the low value of d to a high degree of branching in the experimental samples.

B. Chain Length Dependence. The qualitative trends for the hard-site diameter of short chains are the same as for polyethylene: the diameter increases with increasing density at fixed temperature and chain length (Figure 4); increases with increasing density at fixed pressure and chain length (Figure 5); and decreases with increasing temperature at fixed pressure and chain length (Figure 6).

For short chains, an increase in temperature results in a decrease in d at low temperature and an increase in d at high temperature (Figure 7) just as for polyethylene (Figure 3). In the case of 100 site chains, however, the crossover occurs at considerably higher density than it does for polyethylene.

It is difficult to compare potentials for long and short chains. The liquid regime varies with chain length, and, in order to explore, for instance, the dependence of the site diameter upon chain length at constant temperature, the equation of state of the short chains must be extrapolated beyond the range where it was fitted to experimental measurements.

Given the above caveat, the variation of site diameter with change in chain length at constant temperature and pressure is of great interest and was one of our primary reasons for undertaking this research. As seen in Figure 8, a rapid increase in diameter is observed with increasing chain length at low chain lengths. By a chain length of 20–30 sites, the diameter has saturated at what is more or less the infinite chain value. Although it is tempting to try to relate the transition from rapid rise to plateau to the onset of polymeric behavior and the entanglement length, it should be remembered that we begin to interpolate the equation of state data at this point.

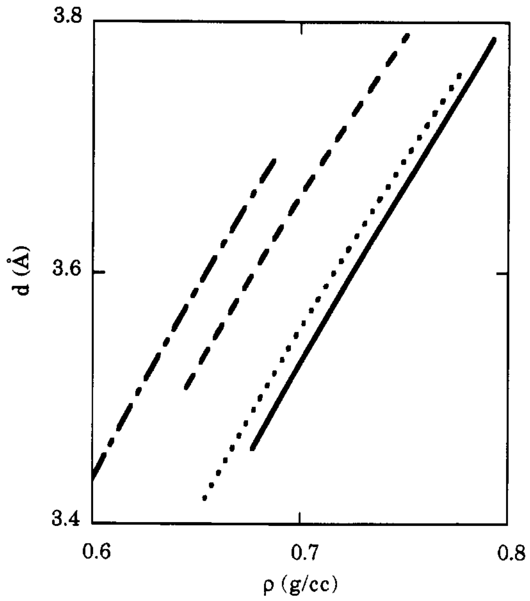

Figure 5. Variation of hard-sphere diameter with density of *n*-alkanes at $P = 1$ atm. Corresponding chain lengths are $N = 1000$ sites (the solid line), $N = 100$ sites (the dotted line), $N = 20$ sites (the dashed line), and $N = 10$ sites (the dashed–dotted line).

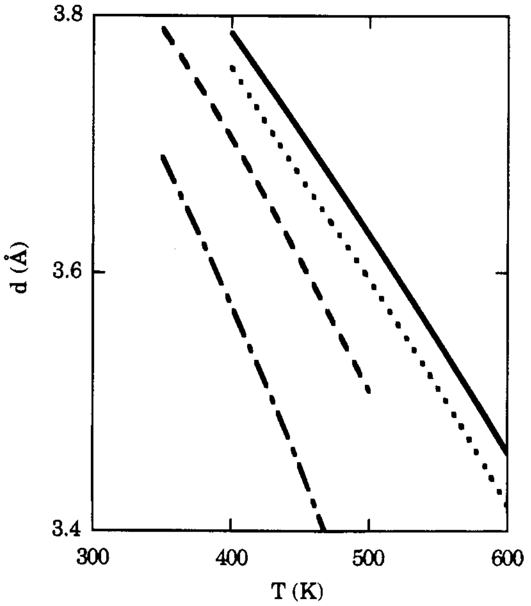

Figure 6. Variation of hard-sphere diameter with temperature of the *n*-alkanes at $P = 1$ atm. Corresponding chain lengths are $N = 1000$ sites (the solid line), $N = 100$ sites (the dotted line), $N = 20$ sites (the dashed line), and $N = 10$ sites (the dashed–dotted line).

V. Discussion

The hard-sphere diameters of CH_2 groups in linear polyethylene and in *n*-alkanes are obtained via comparison of the experimental isothermal compressibility of the liquids to that predicted from PRISM calculations. Our main goal was to observe the variation in a CH_2 hard-sphere size with a change in temperature, pres-

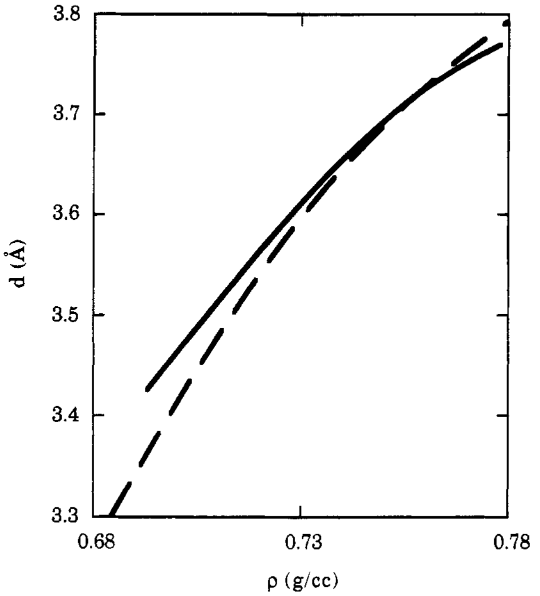

Figure 7. Hard-sphere diameter of polyethylene at $T = 430$ K (the solid line) and $T = 298$ K (the dashed line). Both curves are for 100 site chains.

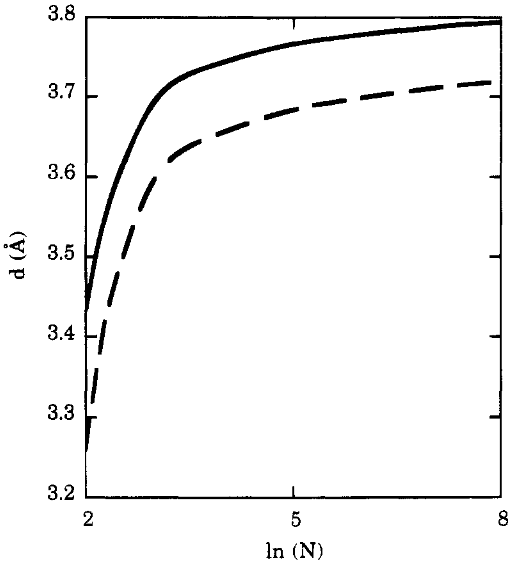

Figure 8. Comparison of hard-sphere diameter of *n*-alkanes and polyethylene with the variation in chain length. The solid curve corresponds to a temperature of $T = 400$ K, and the dashed curve corresponds to $T = 450$ K. Both curves are for a pressure of $P = 1$ atm.

sure, and density as well as chain length. In previous work,[2] a select few alkane and polyethylene systems have been mapped onto hard-site chains by requiring that the region near the amorphous halo peak in the structure factor be reproduced by PRISM integral equation theory. The nonzero wave vector behavior of the structure factor is dominated by repulsive, excluded volume forces and is well represented by hard-site models. On the other hand, zero wave vector behavior is influenced by the attractive tail of the site–site potential. Consequently, the most direct mapping to the hard-site model of the chains is through nonzero wave vector scattering information; however, zero wave vector information is broadly available in the guise of the isothermal compressibility.

In other words, the site diameter depends upon the wave–vector where the PRISM structure factor is matched to the experimental one. This can be illustrated in the low-density limit by expanding the structure factor $\hat{S}(\mathbf{k})$ of the fully interacting system about the hard-site system in the "blip" function,

$$\hat{S}(\mathbf{k}) = \hat{S}_0(\mathbf{k}) + \int \mathrm{d}\mathbf{r}\, \varrho^2 \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \Delta e(r) \qquad (5.1)$$

where $\hat{S}_0(\mathbf{k})$ is the structure factor of the repulsive hard-sphere system; $\Delta e(r) = \mathrm{e}^{-\beta U_0(r)} - \mathrm{e}^{-\beta U_0(r)}$; and $U(r)$ is the intermolecular potential. If $\hat{S}(\mathbf{k})$ is required to equal $\hat{S}_0(\mathbf{k})$ at a particular k, we find

$$\int_d^\infty \mathrm{d}\mathbf{r}\, \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}[e(r) - 1] = -\int_0^d \mathrm{d}\mathbf{r}\, \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \qquad (5.2)$$

This expression can be solved for d, which is, clearly, a function of k. For the special case of $k = 0$, eq 5.2 reduces to

$$-\int_d^\infty \mathrm{d}\mathbf{r}\, [e(r) - 1] = \frac{4}{3}\pi d^3 \qquad (5.3)$$

which is an expression similar to the Barker–Henderson equation except that both attractive and repulsive aspects of the potential are retained in $e(r)$. By writing $U(r) = u_0(r) + v(r)$, where $u_0(r)$ is the repulsive component of $U(r)$, and $v(r)$ is the attractive component, the difference between d^3 and the diameter (cubed) for the strictly repulsive case, $d_r^{\,3}$, can be written as

$$d^3 - d_r^{\,3} = \frac{3}{4\pi}\beta \int v(r) \mathrm{e}^{-\beta u_0(r)}\, \mathrm{d}\mathbf{r} \qquad (5.4)$$

Since $v(r) < 0$, the diameter calculated from the isothermal compressibility is expected to be less than d_r. Indeed, we find a d for polyethylene of about 3.77 Å through the isothermal compressibility, and a d from fitting scattering in the amorphous halo region (i.e., d_r) of 3.90 Å.

Up to this point, the hard-sphere diameter we have predicted is based on the consideration that the two-body potential is strictly hard in nature. A single-parameter, interaction potential (i.e., hard sites) is the best one can do by using only a single experimental input (i.e., the compressibility). A two-parameter, interaction potential (i.e., Lennard-Jones) is physically more intuitive, and, in future work, we will explore methods which use PRISM in prediction schemes for Lennard-Jones potentials.

The amount by which the effective hard-site diameter is changed by using a full Lennard-Jones potential instead of a hard-site potential is of immediate interest. Literature values of Lennard-Jones methylene–methylene interactions can be incorporated into the scheme used in this paper as follows. The direct correlation function of the full, interacting system can be thought of as

$$\hat{C}(0) = \hat{C}_{\mathrm{HS}}(0) + \hat{C}_{\mathrm{pert}}(0) \qquad (5.5)$$

where $\hat{C}_{\mathrm{HS}}(0)$ is the direct correlation function of the hard-site chains and $\hat{C}_{\mathrm{pert}}(0)$ is the correction given by perturbation theory. Consequently, given a Lennard-Jones potential, the contribution to the direct correlation function from attractions can be stripped off using eq 5.5, and the remaining hard-site contribution combined with PRISM theory can be used to predict the hard-site diameter. We consider here the modeling with LJ interactions of polyethylene ($N = 6429$) at a temperature of 430 K and a density of 0.78 g/cm^3. From the potential parameters obtained by Ryckaret and Bellemans[19] (σ_{LJ}

= 3.923 Å and ϵ/k_B = 72 K), we observe an increase in the hard-sphere diameter over the results of section IV by about 0.3 Å. A different set of LJ parameters (σ_{LJ} = 4.36 Å and ϵ/k_B = 38.7 K) proposed by Curro et al.[1] increases the hard-sphere sizes by about 0.15 Å.

It is surprising that the contribution to the compressibility by the attractive tail of the potential has so little effect on the excluded volume. This is best understood by remembering that the compressibility is related to the rate of change of the pressure with an increase of density. At liquid densities, the excluded volume dominates this slope, a phenomena which is often used to explain the behavior of the compressibility factor ($Z = PV/NRT$).

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