

A new equation of state for athermal chains

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A new equation of state for fluids containing athermal chain molecules is developed and compared to simulation results and existing theories in three, two, and one dimensions. The new expression, which builds upon the generalized Flory theory, contains no adjustable parameters and relates the compressibility factor of an n -mer fluid to the compressibility factors of monomer and dimer fluids at the same volume fraction. Comparisons with Monte Carlo results for three- and two-dimensional freely jointed chains show very good agreement, and the overall accuracy of the new expression appears comparable to Wertheim's thermodynamic perturbation theory of polymerization. In one dimension the new expression reduces to the exact result. Application of the equation to chain models with internal constraints and overlapping hard sites is discussed and illustrated through comparisons with Monte Carlo results for rigid trimers. An extension of our approach to arbitrary reference fluids shows that the generalized Flory and new equations are the first two members of a family of increasingly accurate equations of state for chains.

I. INTRODUCTION

In recent years, there has been continuing interest in the development of theoretically based equations of state for chain-molecule fluids.¹⁻⁴ Interest in chain fluids stems, in part, from their richly varied static and dynamic properties,⁵⁻⁸ and, in part, from their central importance to the natural gas and petroleum industries. A rigorous, molecular description of these fluids is complicated, though, by their asymmetric structure, their large number of internal degrees of freedom, and the coupling that exists between intra- and intermolecular interactions which induces long-range correlations in the system.⁹⁻¹³ In view of our relatively primitive understanding of chain fluids, it seems advantageous to develop ways of relating their behavior to the behavior of simpler, more easily understood fluids. In this article we explore such an approach through the use of mean-field approximations.

The hard-sphere-chain model (or "pearl-necklace" model) provides an intuitively appealing starting point for the study of chain fluids. Each molecule is modeled as a series of freely-jointed, tangent, hard spheres which interact through site-site potentials. As a result, temperature does not influence the configurational space distribution of the chains and the fluid is athermal. Use of the pearl-necklace model simplifies the nature of the site-site interactions while retaining the essential geometric features of the chain, and allows one to explore the effects of molecular geometry and internal flexibility on the local structure of the fluid. At the same time, the hard chain system can serve as a reference fluid about which attractive interactions may be introduced as perturbations. In this sense, the pearl-necklace model can play a role in the study of more realistic chain fluids analo-

gous to that played by the hard-sphere monomer in the study of more complex monatomic fluids.

One of the most successful approaches to studying the pressure of monatomic systems has been to combine a microscopic theory for the local structure of the fluid with a statistical-mechanical expression relating the local structure to the compressibility factor. The general procedure can be broken into two steps: In the first step, one constructs a model (or performs a simulation) for the radial distribution function, which summarizes pair correlations between neighboring sites; in the second step, the radial distribution function is inserted into either the compressibility¹⁴ or pressure¹⁵ (virial) equation to obtain a prediction for the compressibility factor. In such a fashion, a considerable amount has been learned about the thermodynamics of simple fluids.¹⁶

Unfortunately, both the description of local correlations and the implementation of the compressibility and virial equations become considerably more complicated for molecular fluids. The presence of bonded neighbors to either side of a site makes the local fluid structure asymmetric, complicating the description of intermolecular site-site correlations. In addition, coupling between intra- and intermolecular interactions leads to long-range self-screening, or "correlation-hole," effects not present in simple fluids.⁹⁻¹³ Since the compressibility equation requires integrations over both distance and density,^{4,14} this route to the pressure requires a model for the local structure that is accurate at all distances and intermediate concentrations. The virial equation, on the other hand, requires structural information at only one density; however, for molecular fluids interacting through site-site potentials, it can no longer be written simply in terms of pair correlations, but requires a knowledge of three-site correlations between two neighboring chains.^{17,18}

In light of the number of approximations required in

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following the more traditional paths to the pressure, it seems worthwhile to consider what progress can be made through the development of simpler, albeit more approximate, mean-field theories. Two of the most widespread and commonly used mean-field models for chains are the Flory²⁰ and Flory–Huggins²¹ theories. Though originally developed for chains on a lattice, they have been successful in modeling many properties of real polymer systems.^{22–24} However, in comparison with recent Monte Carlo studies of off-lattice chains, the Flory and Flory–Huggins equations of state have been found to severely underestimate the pressure.^{2,25–27} By following the same probabilistic assumptions underlying the Flory and Flory–Huggins theories, but taking explicit account of the continuous-space nature of real chain fluids, Dickman and Hall² were able to derive generalizations of these theories which gave much better agreement with simulation results.^{2,25,26}

In this article, we build upon the generalized Flory theory of Dickman and Hall to derive a new equation of state for athermal chain fluids. Whereas the generalized Flory theory was based on an approximate relationship between the properties of a chain fluid and those of a monomer reference fluid, the new equation employs information from both monomer and dimer reference fluids. The resulting expression, which is simple in form and contains no adjustable parameters, relates the compressibility factor of a chain fluid to the compressibility factors of monomer and dimer fluids at the same volume fraction. The equation can be applied to three-, two-, and one-dimensional fluids, and is readily extended to chain models with bond-length-to-hard-sphere-diameter ratios (l/σ) other than one, or to models with additional internal constraints such as fixed bond angles or restricted torsional rotations. In implementing the equation in three dimensions we have employed the Carnahan–Starling equation of state for monomers²⁸ and the Tildesley–Streett equation of state for dimers.²⁹ In two dimensions we have used the Henderson–Kratky equation for monomers^{30,31} and an expression recently derived by Boublík for dimers.³²

Comparisons with the Monte Carlo results of Dickman and Hall²⁵ for three-dimensional, pearl-necklace 4-mers, 8-mers, and 16-mers show very good agreement, particularly for the shorter chains. Very good agreement is also obtained in comparison with simulation results for rigid trimers^{33,34} with $l/\sigma < 1$. In two dimensions, the new equation also compares favorably to Monte Carlo results² for freely jointed 5-mers, though its values are systematically high. In one dimension, the equation becomes exact.

Wertheim has recently introduced two, more sophisticated equations of state for flexible chains, based on his thermodynamic perturbation theory of polymerization (TPT).³ A detailed comparison of his results to ours suggests that, relative to the Monte Carlo results, his first order approximation (TPT1) is somewhat less accurate than our equation, while his second order approximation (TPT2) is slightly more accurate. As measured by the average of the absolute value of the percentage deviation from the Monte Carlo results, TPT2 is approximately 0.4% more accurate than our equation for 4-mer fluids, 2.2% more accurate for 8-mer fluids, and 2.9% more accurate for 16-mer fluids. The lar-

gest errors, however, occur at low densities, so that at volume fraction greater than 0.2 the differences between the two equations are less than 1% for each of the three chain lengths examined.

By extending our basic approach, it is possible to relate the compressibility factor of a n -mer fluid to the compressibility factors of any two shorter chain fluids. The more similar the two reference fluids are to the n -mer fluid, the more accurate the resulting expression will be. In this context, the generalized Flory equation and the new equation described in this paper become the first two members of a family of increasingly accurate equations of state.

We begin, in Sec. II, by reviewing the Flory and generalized Flory theories, focusing particularly on their estimates for the chain insertion probability, which is the key link between the microscopic and macroscopic descriptions of the fluid. The new equation of state is derived in Sec. III by improving upon the generalized Flory estimate for the insertion probability. In Sec. IV we compare the equation's predictions to Monte Carlo results and to exact results in three, two, and one dimensions, focusing particularly, though not exclusively, on the pearl-necklace model. We also compare the predictions of the new equation to Monte Carlo results for rigid trimers with $l/\sigma < 1$ and discuss the extension of the equation to three-dimensional, freely rotating chain models, and two-dimensional chains with bond angles restricted to $\pm 90^\circ$ and 180° . In addition, a tabular comparison of the new equation's predictions to TPT1 and TPT2 is made. Finally, in Sec. V we further discuss the approach outlined in Sec. III to show how, in principle, increasingly accurate equations of state may be obtained.

II. REVIEW OF FLORY AND GENERALIZED FLORY THEORIES

In the Flory²⁰ (F) and Flory–Huggins²¹ (FH) theories, the configurational-space description of the chains is simplified by restricting the molecules to lie at discrete points on a lattice. The system is then characterized by specifying the number of sites (monomers) per chain n and the occupation fraction ϕ which is the fraction of lattice positions occupied by chains. For convenience, we let $P^*(\phi, n) = P(\phi, n, T)/kT$, where $P(\phi, n, T)$ is the pressure of a n -mer fluid at occupation fraction ϕ and kT is the product of Boltzmann's constant and the temperature.

The starting point for the derivation of the F and FH equations is the "osmotic equation of state,"²

$$P^*(\phi, n) = \frac{\phi}{n} [1 - \ln p_n(\phi)] + \frac{1}{n} \int_0^\phi \ln p_n(\phi') d\phi' \quad (1)$$

which relates the pressure to the insertion probability $p_n(\phi)$, defined to be the probability of inserting a randomly chosen n -mer into a random configuration of n -mers at occupation fraction ϕ without creating an overlap. Equation (1) is exact in the macroscopic limit, so the problem of obtaining accurate equations of state is reduced to developing reasonable estimates for the chain insertion probability. [Equation (1) is also valid for systems with attractive or many-body inter-

actions, though p_n becomes a function of both T and ϕ and can no longer be interpreted simply as the probability of inserting a chain without creating an overlap.^{2]}

The term osmotic in reference to Eq. (1) derives from the fact that the lattice fluid may be viewed in two different ways. If one considers all of the lattice sites to be occupied—a fraction ϕ by chains and a fraction $(1 - \phi)$ by monomers—then Eq. (1) gives the osmotic pressure of the solution. Alternatively, if only the chains are present and the monomer sites are vacant, Eq. (1) yields the thermodynamic pressure of the pure chain fluid. For off-lattice fluids, the continuous-space analog of Eq. (1) gives only the thermodynamic pressure, though, following Ref. 2, we will continue to refer to it as the osmotic equation of state.

In general, the probability of inserting a chain into a chain fluid without creating an overlap is a difficult quantity to estimate. Conceptually, however, the process is simplified by imagining that the chain is inserted one site at a time. On the lattice, the probability of inserting the first site is given exactly by $(1 - \phi)$, since that is the chance of picking an empty site at random. The probability of inserting the second and successive sites will be different, though, due to the influence of neighboring chains and intramolecular correlations on the local structure of the fluid. In the Flory theory, these effects are ignored, and $(1 - \phi)$ is taken as the estimate for the insertion probability of each of the n sites. The Flory estimate for the chain insertion probability is then

$$p_n^F(\phi) = (1 - \phi)^n. \quad (2)$$

The net effect of the Flory approximation is to treat the n sites as if they were inserted at random throughout the fluid, rather than being grouped together in a connected chain. Thus, the Flory theory ignores the detailed structure of the fluid and treats the system in an average, or *mean-field*, sense.

In reality, the probability of successfully inserting the i th site of a chain is somewhat greater than that for the first site, since the fact that $i - 1$ sites have previously been inserted means that a neighboring molecule is less likely to be found nearby. Thus, the Flory theory tends to underestimate the chain insertion probability. The Flory–Huggins theory tries to account for this effect by adding in a correction term to Eq. (2) which, in an approximate way, incorporates the effects of chain connectivity.^{2,35}

Substitution of Eq. (2) into Eq. (1) leads to the Flory equation of state

$$Z^F(\phi, n) = 1 - \frac{n}{\phi} [\ln(1 - \phi) + \phi], \quad (3)$$

where $Z(\phi, n)$ is the compressibility factor, $Z(\phi, n) = P^*(\phi, n)/\rho_n$, and ρ_n is the number density of chains, $\rho_n = \phi/n$. A similar, though somewhat more complicated, expression can be obtained from the Flory–Huggins theory.² Unlike the F equation, the FH expression depends explicitly on the lattice coordination number.

Comparisons with Monte Carlo results for athermal lattice chains show that the F and FH equations give reasonably accurate predictions for the compressibility factor, particularly at intermediate and high densities where chain interpenetration increases the accuracy of the mean-field ap-

proximations.^{27,36–38} The Flory equation tends to overestimate the pressure over the entire density range, while the Flory–Huggins equation goes from overestimating the pressure at low densities to underestimating it at higher densities. As might be expected from the neglect of intra- and intermolecular correlations, the agreement generally worsens with increasing chain length.

Though originally derived for lattice fluids, the F and FH theories have often been applied to continuous-space systems.^{22–24} Generally, this is accomplished by replacing the occupation fraction ϕ appearing in Eq. (3) by the volume fraction η , and, for the FH model, associating the lattice coordination number with the average number of nearest neighbors at close packing.² The volume fraction is defined as the volume of space occupied by the chains, divided by the total volume of the system,

$$\eta = \frac{n\pi\sigma^3}{6} \rho_n \quad (4)$$

where ρ_n is the number density of n -mers, $\rho_n = N/V$. Comparisons with simulation results for off-lattice chains, however, show that the traditional F and FH theories severely underestimate the pressure of continuous-space fluids.^{2,25–27}

Dickman and Hall² discuss origins of this discrepancy, which they trace not so much to the nature of the probabilistic assumptions underlying the F and FH models, but, rather, to the intrinsic differences between lattice and continuous-space fluids. This difference is most easily seen by considering a simple monatomic fluid, where there are no intramolecular correlations to complicate the analysis. On the lattice [Fig. 1(a)], the probability of inserting a monomer into a monomer fluid is given exactly by the Flory estimate, $(1 - \phi)$, so that for $n = 1$ the F equation of state is exact. For continuous-space fluids, however, the analogous estimate of $(1 - \eta)$ is much too large, since much of the empty space in the fluid lies in excluded regions surrounding each site and in interstitial regions between sites that are too small to accommodate a monomer [Fig. 1(b)]. Indeed, Dickman and Hall found that the continuous-space monomer insertion probability decayed exponentially with volume fraction rather than linearly.

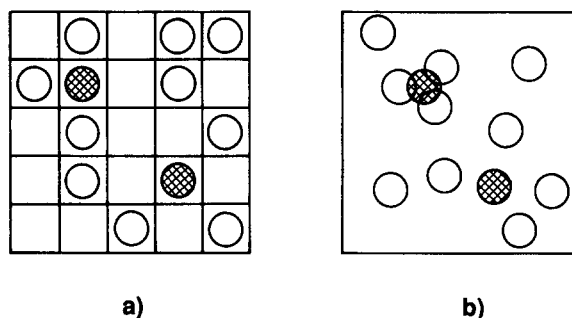


FIG. 1. Illustration of the difference between lattice and continuous-space insertion probabilities for a simple monomer fluid. Monomers being inserted are represented by shaded circles. (a) On the lattice each empty site is, by definition, large enough to accommodate a new monomer, so $p_1(\phi) = 1 - \phi$. (b) In the continuous-space fluid some of the empty space will lie in excluded regions surrounding each site and in interstitial regions too small to accommodate a new monomer, so $p_1(\eta) < 1 - \eta$.

The starting point for the derivation of the generalized Flory (GF) equation is the continuous-space version of the osmotic equation of state,²

$$P^*(\eta, n) = \frac{\eta}{v_n} [1 - \ln p_n(\eta)] + \frac{1}{v_n} \int_0^\eta \ln p_n(\eta') d\eta'. \quad (5)$$

Here v_n is the volume occupied by a n -mer, ($v_n = n\pi\sigma^3/6$), and $p_n(\eta)$ is the continuous-space chain insertion probability. Reviewing for a moment, the Flory estimate for the insertion probability [Eq. (2)] consisted of two parts: a base factor of $(1 - \phi)$, which was the probability of inserting a monomer; and an exponent n which was the number of monomers being inserted. In extending this expression to off-lattice fluids, Dickman and Hall replaced each of these quantities by their continuous-space analogs. The continuous-space analog of the base is the probability of inserting a monomer into a continuous-space chain fluid. Since this is, in general, a complicated and unknown quantity, they approximated the probability of inserting a monomer into a chain fluid by $p_1(\eta)$, the probability of inserting a monomer into a monomer fluid at the same volume fraction [see Fig. 2(a)]. The physical motivation behind this approximation is that at intermediate and high densities, where there is significant chain-chain interpenetration, an individual chain segment finds itself surrounded on all sides by other chain segments. Thus, as the density is increased, it becomes increasingly difficult for a monomer to distinguish between neighbors that are members of the same chain and neighbors that are not, so, to a first approximation, the structure of a chain fluid can be modeled by the structure of a simple hard-sphere fluid. These, of course, are the same physical arguments underlying the Flory and Flory-Huggins lattice theories,^{2,20-21} as well as Croxton's screened convolution

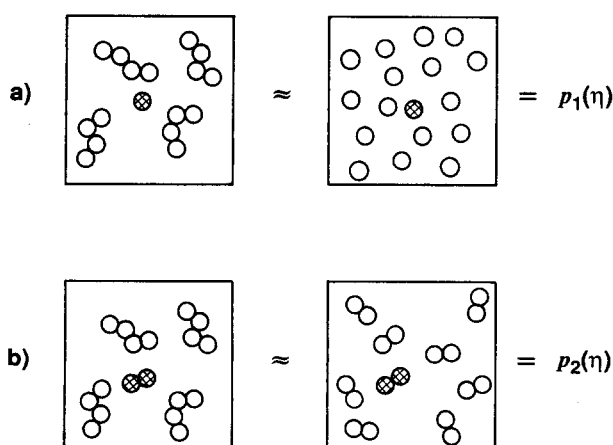


FIG. 2. Approximations involved in the GF and GF-D theories: (a) In the GF theory, the probability of inserting a monomer (denoted by the shaded circle) into a chain fluid is approximated by the probability of inserting a monomer into a monomer fluid at the same volume fraction, $p_1(\eta)$; (b) in addition, in the GF-D theory the probability of inserting a dimer into a chain fluid is approximated by the probability of inserting a dimer into a dimer fluid, $p_2(\eta)$. Physical arguments suggest that the second approximation will be more accurate than the first.

approximation.¹ At low densities, though, the approximation will begin to break down, since in regions where a chain is located the local density will be much higher than average, and in regions between chains the local density will be much lower.³⁸ Under these circumstances, the "patchy" local density of the chain fluid does not resemble the uniform density of a monomer fluid at the same volume fraction. Consequently, at low densities this approximation leads to underestimates for the chain insertion probability and, hence, overestimates for the pressure. Accordingly, the GF, and GFH theories tend to overestimate the second virial coefficient just as the F and FH theories overestimate the lattice-based second virial coefficient.³⁶

The second step in the transcription from lattice to continuous-space deals with the exponent n appearing in Eq. (2). Upon first consideration, it seems as though the factor n should be retained as the exponent in the generalized theory since, after all, n monomer sites are being inserted. However, a closer inspection suggests that the continuous-space exponent should be somewhat smaller. To see this, it is useful to consider the factor n in Eq. (2) not as the number of sites per chain, but, rather, as the ratio of the amount of space occupied by the chain to the amount of space occupied by a monomer. In developing this idea for continuous-space fluids, Dickman and Hall² made use of the concept of an "exclusion volume," which characterizes the size of the hole needed in the fluid to successfully insert the n -mer. The exclusion volume of an n -mer, $v_e(n)$, is defined as the amount of space excluded by the chain to the centers of sites on other molecules. It is not difficult to show that $v_e(n)$ is just the crossed second virial coefficient of a chain-monomer mixture, i.e., the coefficient of the $\rho_1\rho_n$ term in the virial expansion for the pressure.

Dickman and Hall used the monomer and n -mer exclusion volumes to develop a continuous-space analog of the exponent n . These ideas are illustrated for a dimer fluid in Fig. 3. The two solid circles represent the hard-sphere sites of diameter σ ; the dashed curves denote the associated exclusion volumes of radius σ . The GF estimate for the probability of inserting the first site is $p_1(\eta)$. Insertion of the first site requires a hole in the fluid, which is free of the centers of neighboring sites, of volume $4\pi\sigma^3/3$. Thus, the exclusion volume of the first site is $v_e(1) = 4\pi\sigma^3/3$. In that this is the amount of space required by one monomer, $v_e(1)$ becomes

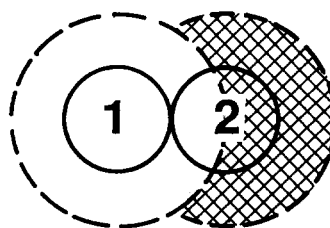


FIG. 3. Use of exclusion volumes to estimate the insertion probability of a dimer. The two hard sites of diameter σ are denoted by the solid circles and the associated exclusion volumes, which must be free of the centers of other sites in order to avoid an overlap, are denoted by the dashed curves. Insertion of the first site requires a hole in the fluid (an exclusion volume) of volume $4\pi\sigma^3/3$. The second site requires a smaller hole in the fluid (represented by the shaded region) and, hence, will be easier to insert.

the continuous-space analog of one lattice site. The second site, however, will require a smaller hole in the fluid (denoted by the shaded region in Fig. 3), by virtue of being next to site 1, and, hence, will be easier to insert. The relative ease of inserting the second site compared to the first can be gauged by comparing the size of the cavity required to insert the second site to the size of the cavity required to insert the first site. Letting $v_e(2)$ denote the exclusion volume of the dimer (that is, the cavity required by both sites), the ratio of the volume required by the second site to that required by the first is given by $[v_e(2) - v_e(1)]/v_e(1)$, which is less than one.

Combining these ideas, the GF estimate for the conditional probability of adding on the second site, given that the first has been successfully inserted, becomes

$$p_1(\eta)^{[v_e(2) - v_e(1)]/v_e(1)} \quad (6)$$

In this fashion one can build up a chain of n sites by continuing to insert additional monomers, each time comparing the size cavity required for the new site to the size of the cavity required for the first site. The GF estimate for the insertion probability of the entire chain is then the product of the individual insertion probabilities for each of the n sites,

$$p_n^{\text{GF}}(\eta) = p_1(\eta)^{v_e(n)/v_e(1)} \quad (7)$$

Notice that in the lattice fluid each chain site occupies the same amount of space—namely, one lattice site. Thus, on the lattice $v_e(n) = nv_e(1)$, and the GF exponent reduces to the F exponent n .

Substitution of Eq. (7) into Eq. (5) leads to the GF equation of state,²

$$Z_n^{\text{GF}}(\eta) = \frac{\lambda_n v_n}{v_1} Z_1(\eta) + 1 - \frac{\lambda_n v_n}{v_1} \quad (8)$$

which relates the compressibility factor of a n -mer fluid to the compressibility factor of a monomer fluid at the same volume fraction. Here, v_n denotes the volume of a n -mer and λ_n is a parameter which depends on the monomer and chain exclusion volumes through the relation $\lambda_n = v_1 v_e(n)/[v_n v_e(1)]$. The generalized Flory–Huggins (GFH) equation of state can be derived by following a similar procedure using the more sophisticated GFH estimate for the chain insertion probability.² In evaluating Eq. (8), Dickman and Hall used the Carnahan–Starling equation of state for monomers.²⁸

The values employed for the exclusion volumes will depend upon the particular molecular model being studied. For the freely jointed hard chain, $v_e(n)$ is obtained by averaging over all possible configurations of an isolated n -mer. For short chains, the exclusion volumes can be evaluated from geometrical considerations using the formulas derived by Lustig³⁹ for the volumes of overlapping hard spheres. The exclusion volumes for $n = 1, 2,$ and 3 are⁴⁰

$$\begin{aligned} v_e(1) &= \frac{4}{3} \pi \sigma^3, \\ v_e(2) &= \frac{9}{4} \pi \sigma^3, \\ v_e(3) &\approx 9.826 05 \sigma^3. \end{aligned} \quad (9)$$

For $n > 4$ the exact evaluation of $v_e(n)$ becomes an increasingly difficult task; however, it can be estimated from²

$$v_e(n) \approx v_e(3) + (n - 3)[v_e(3) - v_e(2)]. \quad (10)$$

Comparisons of the GF and GFH equations to Monte Carlo results for the compressibility factor of two- and three-dimensional chains have shown relatively good agreement.^{2,25,26} The GF equation tends to overestimate the pressure, while the more accurate GFH equation goes from overestimating the pressure at low densities to underestimating it at higher densities.

III. DEVELOPMENT OF NEW EQUATION

The relatively good agreement obtained from the GF and GFH equations in comparison with Monte Carlo results suggests that the mean-field approach can be a fairly accurate, yet comparatively simple, means of studying complex molecular fluids. In going from the lattice to the continuous-space picture, the key step was replacement of the lattice-based estimate for the monomer insertion probability by its more appropriate, continuous-space counterpart. Both the F and GF theories, however, derive their estimates for p_n from the probability of randomly inserting n monomers into the fluid. By relying on the random insertion of monomers, neither of these theories is able to explicitly account for chain connectivity—i.e., that successive sites must be inserted next to one and other rather than being scattered throughout the fluid at random {though the GF equation accounts for connectivity partially through the use of exclusion volumes [see expression (6)]}.

We have found, though, that the role of intramolecular nearest-neighbor correlations can be incorporated into the GF model, in an approximate fashion, through the use of dimer equations of state. Implicitly, through Eq. (5), dimer equations of state contain information, not only about the probability of inserting a single site into the fluid, but, in addition, information about the probability of adding a second site next to the first one. By building this type of information into our estimate for the insertion probability, we can begin to incorporate the effects of chain connectivity into our model. Implementation of this idea leads to a new equation of state for athermal chains, which we refer to as the generalized Flory-dimer (GF-D) equation.

Our object, then, is to construct a more accurate estimate for the conditional probability of inserting a new site next to one already present in the fluid. To this end, we begin by making two approximations relating the chain fluid to monomer and dimer reference fluids. As was the case in the GF theory, the probability of inserting a monomer into a chain fluid is approximated by the probability of inserting a monomer into a monomer fluid, $p_1(\eta)$ [Fig. 2(a)]. In addition, in the GF-D theory the probability of inserting a dimer into a chain fluid is approximated by the probability of inserting a dimer into a dimer fluid at the same volume fraction, $p_2(\eta)$ [Fig. 2(b)]. Indeed, this second approximation should be more accurate than the first, since the structure of the dimer fluid more closely resembles the structure of a chain fluid than does the structure of the monomer fluid.

Within the context of these two approximations, since $p_1(\eta)$ is the probability of inserting a monomer and $p_2(\eta)$ is the probability of inserting a dimer, the ratio $p_2(\eta)/p_1(\eta)$ is the conditional probability of adding a second site next to one already present in the fluid. This ratio then provides a way of building up longer chains by tacking on additional sites, one at a time. The general procedure is illustrated in Fig. 4. Again, the circles denote the hard-sphere sites while the larger dashed curves represent the associated exclusion volumes. The quantities on the right-hand side are the new estimates for the conditional probability of adding in the last site, given that the previous sites have been successfully inserted. The probability of inserting the first site is the same as in the GF theory, $p_1(\eta)$. The new estimate for the probability of inserting the second site is $p_2(\eta)/p_1(\eta)$, which can be compared with the GF estimate of $p_1(\eta)^{[v_e(2) - v_e(1)]/v_e(1)}$. The situation becomes more complicated when we turn to the third site, since its insertion probability is unknown. It seems reasonable to expect, though, that the probability of adding the third site to the second is approximately equal to the probability of adding the second site to the first, and we can try to correct for the difference between the two by comparing the size of the hole (exclusion volume) required to insert the third site (denoted by the horizontally shaded region in Fig. 4) to that required to insert the second site (denoted by the crossed-hatched region in Fig. 4). If the third

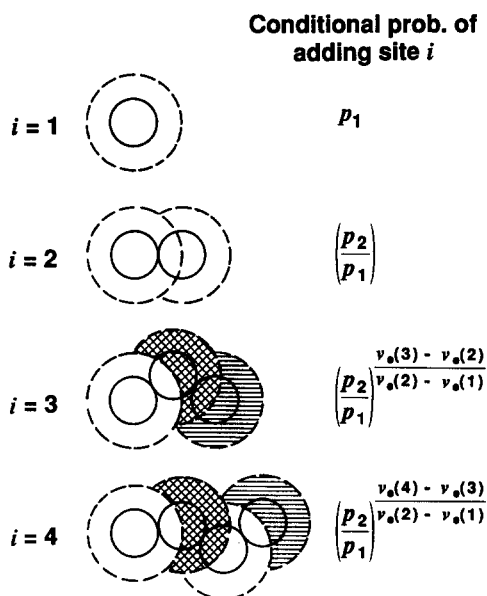


FIG. 4. Development of the GF-D estimate for the chain insertion probability. A chain is inserted one site at a time. The solid circles represent the hard sites and the dashed curves are the associated exclusion volumes. The value of i denotes the site being inserted. Numerical quantities on the right are the GF-D estimates for the conditional probability of adding site i , given that the previous $i - 1$ sites have been successfully inserted. For $i > 3$ the probability of inserting site i is related to the probability of inserting site 2 by comparing the size of the hole (exclusion volume) required by site i (denoted by the horizontally shaded region) to the size of the hole required by site 2 (denoted by the cross-hatched region). The ratio of these two exclusion volumes appears as the exponent in the GF-D estimate for the conditional probability of inserting site i . The insertion probability of the entire chain is the product of the conditional probabilities for each site.

site requires a larger hole than the second site, then one expects that it will be proportionally harder to insert, and conversely, if the third site requires a smaller hole than its predecessor, it should be proportionally easier to insert. Since the ratio of these two exclusion volumes is given by

$$\frac{v_e(3) - v_e(2)}{v_e(2) - v_e(1)}, \quad (11)$$

the GF-D estimate for the conditional probability of adding in the third site becomes

$$\left(\frac{p_2(\eta)}{p_1(\eta)}\right)^{[v_e(3) - v_e(2)]/[v_e(2) - v_e(1)]}. \quad (12)$$

Similarly, the probability of inserting the fourth site can be estimated by comparing the size of the hole it will require (again represented by the horizontally shaded region in Fig. 4) to the size of the hole required by site 2 (represented by the cross-hatched region in Fig. 4). Proceeding in this fashion, each of the n sites may be inserted.

The probability of inserting the entire chain is then given by the product of the individual site insertion probabilities,

$$\begin{aligned} p_n(\eta) &= p_1(\eta) \left[\frac{p_2(\eta)}{p_1(\eta)}\right] \left[\frac{p_2(\eta)}{p_1(\eta)}\right]^{[v_e(3) - v_e(2)]/[v_e(2) - v_e(1)]} \\ &\quad \times \dots \left[\frac{p_2(\eta)}{p_1(\eta)}\right]^{[v_e(n) - v_e(n-1)]/[v_e(2) - v_e(1)]} \\ &= p_1(\eta) \left[\frac{p_2(\eta)}{p_1(\eta)}\right]^{[v_e(n) - v_e(1)]/[v_e(2) - v_e(1)]}. \end{aligned} \quad (13)$$

One can gain insight into how this improves upon the GF estimate by comparing Eq. (13) to Eq. (7). In the GF theory, the basic building block of a chain is the monomer. Accordingly, the probability of inserting the chain is estimated from the probability of inserting a monomer, raised to a power which describes the effective number of monomers which are to be inserted. In the new equation, the basic building block becomes the conditional probability of tacking an additional site on to one already present in the fluid. As a result, the improved estimate for $p_n(\eta)$ is equal to the product of the probability of inserting the first site and the conditional probability of adding on a new site raised to a power which describes the effective number of new sites which must be added.

For convenience, let

$$Y_n = \frac{v_e(n) - v_e(2)}{v_e(2) - v_e(1)}. \quad (14)$$

Equation (13) can then be written more compactly as

$$p_n(\eta) = p_1(\eta)^{-Y_n} p_2(\eta)^{Y_n + 1}. \quad (15)$$

Substitution of Eq. (15) into Eq. (5) then gives

$$\begin{aligned} P^*(\eta, n) &= \frac{\eta}{v_n} [1 + Y_n \ln p_1(\eta)] - \frac{Y_n}{v_n} \int_0^\eta \ln p_1(\eta') d\eta' \\ &\quad - \frac{\eta}{v_n} (Y_n + 1) \ln p_2(\eta) \\ &\quad + \frac{(Y_n + 1)}{v_n} \int_0^\eta \ln p_2(\eta') d\eta'. \end{aligned} \quad (16)$$

By comparing Eq. (16) to Eq. (5) evaluated for $n = 1$ and $n = 2$, the monomer and dimer insertion probabilities may be eliminated in favor of the monomer and dimer pressures. One then obtains

$$P^*(\eta, n) = \frac{v_2}{v_n} (Y_n + 1)P^*(\eta, 2) - \frac{v_1}{v_n} Y_n P^*(\eta, 1) \quad (17)$$

in which the chain, monomer, and dimer pressures are all evaluated at the same volume fraction. This result may be expressed more compactly in terms of the chain, monomer, and dimer compressibility factors, obtained by dividing both sides of Eq. (17) by ρ_n . Since, at a given volume fraction η ,

$$\rho_n = \frac{v_1}{v_n} \rho_1 = \frac{v_2}{v_n} \rho_2 \quad (18)$$

we obtain

$$Z^{\text{GF-D}}(\eta, n) = (Y_n + 1)Z(\eta, 2) - Y_n Z(\eta, 1). \quad (19)$$

Equation (19) is the new equation of state referred to in the title, in which the compressibility factor of the chain is related to the compressibility factors of monomer and dimer fluids at the same volume fraction and to the ratio of exclusion volumes Y_n , given by Eq. (14).

In implementing the GF-D equation, we have used the Carnahan–Starling equation of state for monomers²⁸

$$Z(\eta, 1) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (20)$$

and the Tildesley–Streett equation of state for dimers²⁹

$$Z(\eta, 2) = \frac{1 + 2.456\,96\eta + 4.103\,86\eta^2 - 3.755\,03\eta^3}{(1 - \eta)^3}. \quad (21)$$

The coefficients in Eq. (21) were determined by fitting the general functional form of the expression to Monte Carlo results for dimers. While a number of more theoretically based equations of state for hard dimers have been developed in the literature,^{41–43} Eq. (21) appears to be the most accurate, and thus, should allow the most accurate assessment of the approximations underlying our model. In addition, Tildesley and Streett have parametrized their equation as a function of the bond-length-to-hard-sphere-diameter ratio l/σ (only the values for $l/\sigma = 1$ are listed above), so their equation can also be used to study chain models with other l/σ values.

IV. COMPARISON WITH SIMULATION

A. Three-dimensional fluids

In Figs. 5–7, we compare the predictions of the GF-D equation to the Monte Carlo results of Dickman and Hall²⁵ for freely jointed 4-mers, 8-mers, and 16-mers. Also shown are the predictions of the Flory (F), Flory–Huggins (FH), generalized Flory (GF), and generalized Flory–Huggins (GFH) equations, which are discussed in more detail in Ref. 2.

The Monte Carlo results were obtained using a new simulation technique which incorporated hard walls in the sim-

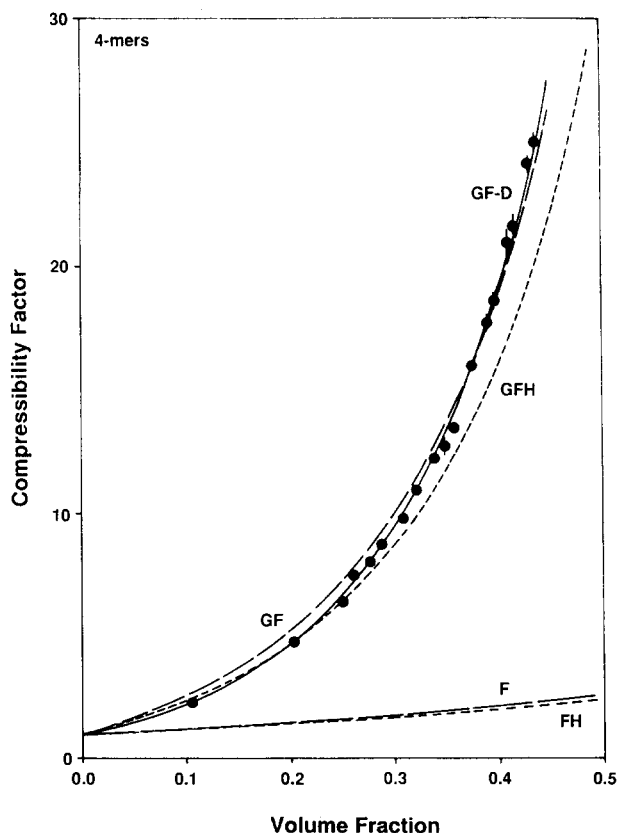


FIG. 5. Compressibility factor vs volume fraction for three-dimensional, freely jointed 4-mers. Points are the simulation results of Dickman and Hall (Ref. 25). Curves are the predictions of theoretical equations of state described in the text.

ulation cell. This allowed the pressure to be calculated from the density of sites in contact with the hard walls. Figure 6 also includes two new state points which we obtained using the same method. These points were part of a study examining the effect of the distance between the hard walls on the pressure. In Dickman and Hall's study, the distance between the two hard walls in the simulation cell varied from 10σ to 16σ . For the two state points examined here, the distance was increased to 27.8σ at $\eta = 0.0659$ and to 19.6σ at $\eta = 0.1303$. The values obtained for the bulk-fluid volume fractions and compressibility factors are ($\eta = 0.0659 \pm 0.0001$, $Z = 1.94 \pm 0.04$) and ($\eta = 0.1303 \pm 0.0004$, $Z = 3.86 \pm 0.04$). No significant size effects are observed at these densities.

As illustrated by Figs. 5 and 6, very good agreement is obtained between the GF-D equation and the Monte Carlo results for 4-mer and 8-mers, though in both cases the GF-D equation tends to overestimate the pressure. As has been noted in previous studies,^{2,25,26} the GF and GFH equations give qualitatively accurate predictions while the F and FH equations give predictions that are much too low.

For 16-mers, though, the quantitative agreement between the GF-D equation and the simulation results is less satisfactory, possibly reflecting the increasing influence of long-range intramolecular correlations on the structure of the chain fluid. Long-range intramolecular correlations affect the accuracy of the GF-D equation in two ways. First,

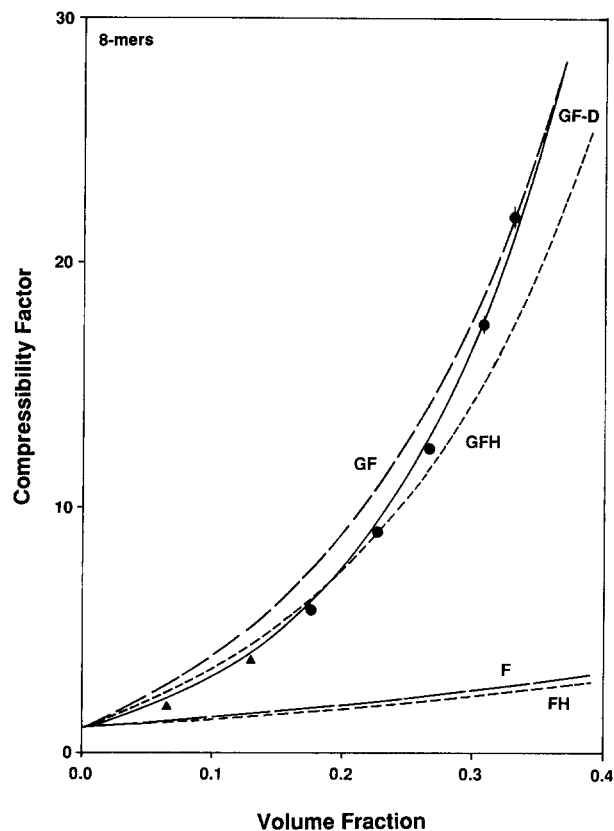


FIG. 6. Compressibility factor vs volume fraction for three-dimensional, freely jointed 8-mers. Points are simulation results: ●, Dickman and Hall (Ref. 25); ▲, present work. Curves are the predictions of theoretical equations of state described in the text.

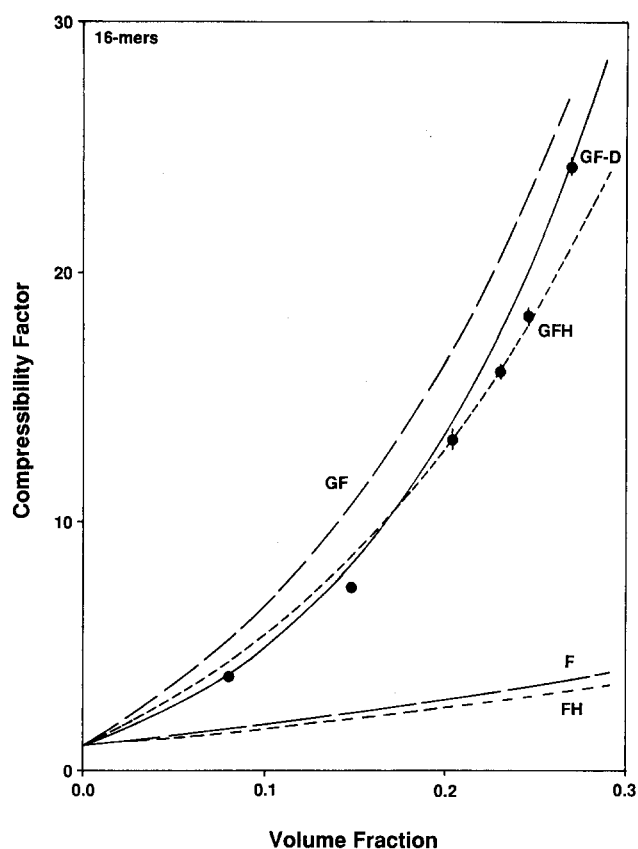


FIG. 7. Compressibility factor vs volume fraction for three-dimensional, freely jointed 16-mers. Points are the simulation results of Dickman and Hall (Ref. 25). Curves are the predictions of theoretical equations of state described in the text.

they decrease the accuracy of the approximate expression used to evaluate the exclusion volumes, Eq. (10). A rigorous calculation of the exclusion volumes of long chains is a difficult geometrical problem. In Eq. (10), the exclusion volume of the chain is approximated from $v_e(2)$ and $v_e(3)$ by superimposing successive sequences of trimer segments. However, for longer chains, which can fold back on themselves, there can be overlaps between exclusion regions associated with sites separated by several bonds. These types of overlap are not properly accounted for by Eq. (10), which will tend to overestimate the true chain exclusion volume. By overestimating the size of the hole required to insert the chain, the use of Eq. (10) will lead to artificially high predictions for the pressure. In principle, this defect could be remedied by performing more accurate calculations for $v_e(n)$.

A second defect inherent in our mean-field approach arises from the use of monomer and dimer reference fluids to model the structure of the chain fluid. In effect, this approximation neglects the influence of coupling between long-range intra- and intermolecular interactions on the fluid's structure. For long chains, such coupling can lead to self-screening and correlation-hole effects^{4,9-13} which are absent in simple fluids and much less pronounced in dimer fluids. Thus, as the chain length increases, the local structure of the chain fluid becomes less and less similar to the local structure of the dimer and monomer reference fluids. This is particularly true at lower densities, where there is little chain-

chain interpenetration and the local density becomes "patchy," with regions of relatively high site density separated by regions of relatively low site density.³⁸ As a result, the use of $p_1(\eta)$ and $p_2(\eta)$ as described in Fig. 2 will probably tend to underestimate the true monomer and dimer insertion probabilities, particularly for longer chains and at lower densities. Fortunately, in the GF-D theory these two quantities appear primarily as a ratio, $p_2(\eta)/p_1(\eta)$, [see Eq. (13)] allowing for a partial cancellation of errors. Not surprisingly though, the largest relative errors between the GF-D equation and the simulation results occur at low densities. At higher densities, where the chain segments are forced to pack closer together, the underlying approximations should become more accurate.

Wertheim has recently introduced two new equations of state for athermal chains based on his thermodynamic perturbation theory of polymerization (TPT).³ TPT employs a reference fluid of hard monomers which can chemically bond together to form a polydisperse mixture of chains. The two equations of state result from a first- and second-order implementation of the theory (TPT1 and TPT2). While these equations describe a polydisperse mixture, when evaluated at an average degree of polymerization $n = 4, 8, \text{ or } 16$, they show remarkably good agreement with the simulation results of Dickman and Hall.

In Tables I-III we present a tabular comparison of the

TABLE I. Comparison of GF-D and TPT predictions for the compressibility factor of three-dimensional, freely jointed 4-mers with Monte Carlo (MC) results of Dickman and Hall (Ref. 25). GF-D predictions obtained using Eq. (10) are listed under the heading GF-D/TS; predictions obtained using Eq. (22) are listed under GF-D/BN.

$Z(\eta,4)$					
η	MC	GF-D/TS	GF-D/BN	TPT1	TPT2
0.1072	2.25 ± 0.06	2.34	2.33	2.37	2.30
0.2050	4.73 ± 0.05	4.82	4.73	4.88	4.74
0.2520	6.40 ± 0.17	6.73	6.59	6.82	6.64
0.2620	7.46 ± 0.16	7.22	7.07	7.32	7.13
0.2780	8.02 ± 0.11	8.08	7.91	8.19	7.99
0.2890	8.70 ± 0.07	8.73	8.55	8.85	8.64
0.3100	9.80 ± 0.14	10.12	9.90	10.27	10.03
0.3230	10.93 ± 0.13	11.08	10.85	11.25	11.00
0.340	12.2 ± 0.1	12.49	12.24	12.68	12.42
0.3490	12.7 ± 0.3	13.31	13.04	13.52	13.24
0.3590	13.5 ± 0.1	14.28	14.00	14.51	14.23
0.376	16.10 ± 0.17	16.11	15.81	16.38	16.08
0.3940	17.8 ± 0.3	18.31	18.00	18.63	18.32
0.399	18.7 ± 0.3	18.98	18.67	19.31	18.99
0.4100	21.0 ± 0.5	20.54	20.22	20.91	20.58
0.417	21.7 ± 0.4	21.60	21.29	22.00	21.67
0.4302	24.2 ± 0.2	23.77	23.46	24.23	23.88
0.437	25.1 ± 0.3	24.98	24.68	25.47	25.12

Monte Carlo (MC) results with the predictions of TPT1, TPT2, and GF-D. The predictions of Eq. (19) obtained using the Tildesley and Streett equation of state for dimers [Eq. (21)] are listed under the heading GF-D/TS. Each of the theoretical equations tends to overestimate the pressure. Relative to the MC results, the GF-D equation appears to be more accurate than TPT1, but slightly less accurate than TPT2.

While use of the TS dimer equation represents perhaps the most honest assessment of the accuracy of Eq. (19), we noticed, in the course of our studies, that slightly better predictions for the compressibility factor could be obtained using a less accurate dimer equation of state in place of Eq. (21). Tables I–III list, under the heading GF-D/BN, the compressibility factors obtained from the GF-D equation when evaluated using the dimer equation of state suggested by Boublík and Nezbeda,⁴¹

TABLE II. Comparison of GF-D and TPT predictions for the compressibility factor of three-dimensional, freely jointed 8-mers with Monte Carlo (MC) results of Dickman and Hall (Ref. 25). GF-D predictions obtained using Eq. (10) are listed under the heading GF-D/TS; predictions obtained using Eq. (22) are listed under GF-D/BN. The two MC values obtained in this study are denoted by *.

$Z(\eta,8)$					
η	MC	GF-D/TS	GF-D/BN	TPT1	TPT2
0.0659	1.90 ± 0.06	2.21	2.21	2.26	2.15
0.0659	1.94 ± 0.04*
0.1303	3.86 ± 0.04*	4.17	4.11	4.27	4.04
0.1306	3.79 ± 0.08	4.18	4.12	4.28	4.05
0.1765	5.84 ± 0.07	6.24	6.11	6.40	6.07
0.2270	9.05 ± 0.23	9.44	9.19	9.67	9.24
0.2670	12.43 ± 0.17	12.90	12.55	13.23	12.70
0.308	17.5 ± 0.3	17.63	17.15	18.09	17.47
0.3320	21.9 ± 0.4	21.12	20.56	21.68	21.00

TABLE III. Comparison of GF-D and TPT predictions for the compressibility factor of three-dimensional, freely jointed 16-mers with Monte Carlo (MC) results of Dickman and Hall (Ref. 25). GF-D predictions obtained using Eq. (10) are listed under the heading GF-D/TS; predictions obtained using Eq. (22) are listed under GF-D/BN.

$Z(\eta,16)$					
η	MC	GF-D/TS	GF-D/BN	TPT1	TPT2
0.0802	3.76 ± 0.21	3.90	3.88	4.03	3.73
0.1480	7.32 ± 0.23	8.28	8.11	8.56	7.96
0.2045	13.2 ± 0.4	14.02	13.62	14.48	13.60
0.231	15.9 ± 0.3	17.63	17.09	18.20	17.19
0.247	18.2 ± 0.3	20.16	19.52	20.80	19.71
0.2717	24.1 ± 0.3	24.68	23.89	25.47	24.25

$$Z_2(\eta) = \frac{1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha^2\eta^3}{(1 - \eta)^3} \quad (22)$$

Here, α is a “shape factor,” which depends on the volume, surface area, and mean curvature of the molecule and characterizes its asymmetry. Equation (22) was originally derived by Boublík⁴⁴ for convex molecules; Boublík and Nezbeda⁴¹ extended it to dimers by making suitable approximations for α . Following these authors, we set $\alpha = 1.5$ for the tangent-hard-sphere dimer. [Incidentally, Eq. (22) also provided the functional form for the fitted TS equation of state, Eq. (21).] As Tables I–III show, use of Eq. (22) in place of Eq. (21) leads to better predictions for the chain compressibility factors at low and moderate densities. The improved agreement with the MC results may be due to a cancellation of errors between the slightly low predictions of Eq. (22) when applied to tangent hard dimers and the (apparently) high predictions of the GF-D theory. While not advocating this type of empiricism, we simply note that Eq. (22) could prove useful in obtaining reference properties of hard-chain fluids to be used in conjunction with perturbation expansions.

Quite recently, another statistical mechanical theory for the pressure of hard-chain fluids has been developed by Schweizer and Curro,⁴ based on their extension of the RISM

(reference interaction site model) integral theory for local structure to polymer fluids.^{11,19} They combined their results for the site-site pair correlation function with a superposition approximation for three-body correlations in order to evaluate the virial equation of state. Comparisons with simulation results for dimers and 4-mers showed good agreement. However, predictions obtained for 16-mers were approximately 40% smaller than the MC results listed in Table III. This raises an important issue concerning the expected accuracy of the mean-field equations of state discussed here, as well as TPT, when applied to longer chains. Presumably, RISM, with its explicit consideration of intramolecular and intermolecular correlations, will more accurately reflect the structure of the chain fluid and the associated self-screening and correlation-hole effects than will our simpler mean-field arguments. At the same time, though, the relatively good agreement obtained between TPT, GF-D, and the MC results makes it difficult to dismiss the trends seen in Figs. 5–8. Further simulation work, particularly for longer chains and at higher densities, would go a long way towards clarifying this matter.

Up to this point we have concentrated primarily on freely jointed chain models. However, the GF-D equation, as well as the GF and GFH equations, can also be applied to other molecular models by evaluating the appropriate exclusion volumes. As an example, we consider the freely rotating

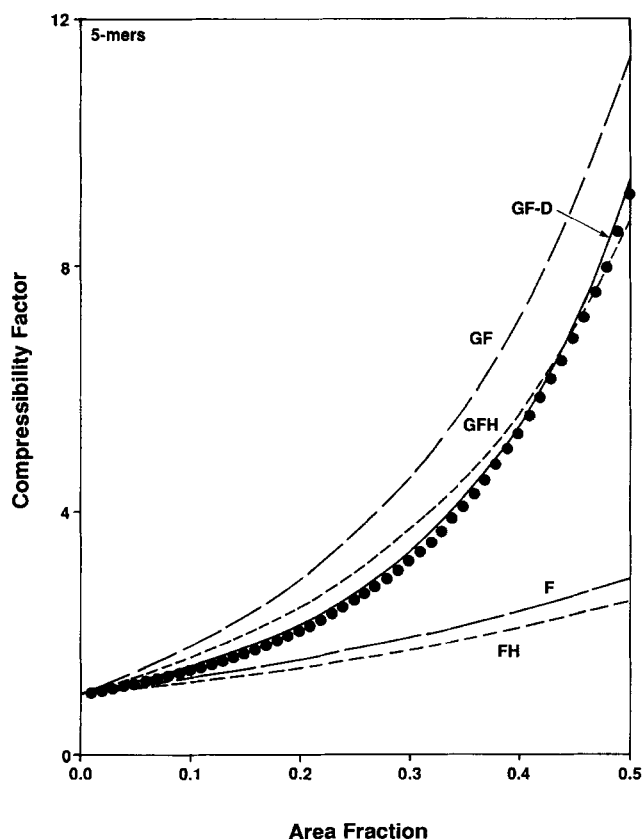


FIG. 8. Compressibility factor vs area fraction for two-dimensional, freely jointed 5-mers. Points are the simulation results of Dickman and Hall (Ref. 2). Curves are the predictions of theoretical equations of state described in the text.

chain⁴⁵ consisting of a series of tangent hard spheres with fixed bond angles of $109^{\circ}28'$ (which correspond to the tetrahedral bond angles along an alkane chain backbone). Naturally, $v_e(1)$ and $v_e(2)$ are the same as for the freely jointed model (see Eq. 9); $v_e(3)$ is found to be $9.939\ 66\sigma^3$. As before, Eq. (10) can be used to estimate the exclusion volumes of longer chains. The larger value of $v_e(3)$ implies that the freely rotating chain will be more difficult to insert than its freely jointed counterpart. As a result, the pressure of the freely rotating chain fluid should be larger than pressure of the freely jointed chain fluid at the same volume fraction. For 4-mers, the GF-D equation predicts an increase in pressure of 1.5% at $\eta = 0.25$, growing to 1.8% at $\eta = 0.45$. Naturally, the trend is more pronounced for 16-mers; at $\eta = 0.25$ the increase is 3.2%, while at $\eta = 0.45$ it is 3.5%.

The mean-field theories discussed here can also be applied to molecular models with l/σ values other than 1. These types of models are often used in studies of small polyatomic molecules and have direct application to alkane chains, where the effective hard-sphere diameter of a methyl group is roughly 2.5 times greater than the length of a carbon-carbon bond.⁴⁶ Use of a more realistic value of l/σ in conjunction with the freely rotating chain model could pave the way to studying increasingly more complex and realistic n -alkane models.

In Table IV we compare the predictions of the GF, GFH, and GF-D equations with the simulation results of Streett and Tildesley³³ and of Boublík³⁴ for rigid trimers with fixed bond angles and $l/\sigma < 1$. Streett and Tildesley studied a linear trimer fluid at $\eta = 0.4697$ and $l/\sigma = 0.4485$. Boublík simulated a linear-trimer fluid at $\eta = 0.4533$ and $l/\sigma = 0.5$, as well as a trimer fluid with fixed, 90° bond angles at $\eta = 0.3988$ and $l/\sigma = 0.5$. The exclusion volumes for these three models are found to be $v_e(3) = 6.959\ 56\sigma^3$, $7.264\ 93\sigma^3$, and $7.036\ 02\sigma^3$, respectively. The GF-D predictions in Table IV were obtained using the TS dimer equation²⁹ evaluated at the appropriate l/σ values. Also shown in Table IV, under the headings BN and R, are the theoretical predictions reported by Boublík for the compressibility factors. These values were obtained by applying Eq. (22) to the trimer fluids. In the column labeled BN, the shape factor α was evaluated following the procedure outlined by Boublík and Nezbeda.⁴¹ In the column labeled R, the shape factor was evaluated from the second virial coefficient, following the procedure developed by Rigby.⁴²

The GF-D predictions for these trimer models are in very good agreement with the simulation results and are comparable in accuracy to the BN and R values. The GF and GFH equations considerably overestimate the compressibility factors. Part of this error can be traced to their use of a pure monomer reference fluid. For these trimer models, though the first site to be inserted is indeed a simple hard sphere, the two remaining sites are shaped like hard crescents. Both the GF and GFH theories must approximate these crescents by hard spheres with the same exclusion volumes. The GF-D equation, on the other hand, by using a dimer reference fluid which is also a function of l/σ , is able to explicitly account for the irregular shapes of the second and third sites. The TS equation is particularly convenient in this

TABLE IV. Comparison of theoretical predictions for the compressibility factors of rigid trimers with Monte Carlo results of Streett and Tildesley (Ref. 33) (*) and of Boublík (Ref. 34) (†).

Model	l/σ	η	$Z(\eta,3)$					
			MC	GF-D	BN	R	GF	GFH
Linear	0.4485	0.4697	$12.84 \pm 0.64^*$	12.76	13.54	13.34	17.01	15.54
Linear	0.5	0.4533	$12.88 \pm 0.32^\dagger$	12.17	12.69	...	15.88	14.45
Rt. angle	0.5	0.3988	$8.34 \pm 0.21^\dagger$	8.49	8.19	...	10.87	10.01

respect since it is parametrized as a function of l/σ .

The main difficulty in applying these equations to longer chains with $l/\sigma < 1$ is obtaining accurate estimates for the exclusion volumes. For these models, the occurrence of four-fold overlaps of exclusion volumes associated with four adjacent sites along the chain backbone will become increasingly important. These fourfold overlaps are not properly accounted for by Eq. (10). When $l/\sigma = 1$ these overlaps have little effect on $v_e(n)$, but as l/σ is decreased, they will play an increasingly important role. Consequently, Eq. (10) will tend to overestimate the true exclusion volume. Conceivably, by numerically evaluating $v_e(4)$ using the formulas derived by Lustig,³⁹ more accurate estimates for $v_e(n)$ could be obtained from

$$v_e(n) \approx v_e(4) + (n-4)[v_e(4) - v_e(3)]. \quad (23)$$

B. Two-dimensional fluids

Though our primary interest lies in three-dimensional chain fluids, we have also considered the behavior of the various mean-field equations of state in one and two dimensions. The motivation behind these comparisons is that, in general, the higher the dimensionality of configuration space, the more accurate mean-field approaches, which ignore the fine details of the fluid's local structure, tend to be. Since the GF-D equation appears to be fairly accurate for three-dimensional fluids, it is of interest to test its performance in the more constrained geometries of one and two dimensions, where excluded volume effects become more pronounced. This is of interest not only from a mathematical point of view, but also because of possible applications to modeling chains in small pores and on surfaces.

In implementing the generalized equations in two dimensions, we have used the monomer equation of state developed by Henderson³⁰ with the empirical modification suggested by Kratky,³¹

$$Z(\eta,1) = \frac{1 + 0.112\eta^2}{(1-\eta)^2}. \quad (24)$$

For the dimer compressibility factor, we have used the equation of state recently proposed by Boublík,³²

$$Z(\eta,2) = \frac{1 + (\gamma-1)\eta + \gamma^2\eta^2/8}{(1-\eta)^2}, \quad (25)$$

which might be considered the two-dimensional analog of Eq. (22). Here, γ is the two-dimensional shape factor, which depends on the area and perimeter of the molecule. Boublík considered several approximations for both γ and η in applying Eq. (25) to dimer fluids and obtained particularly good

results, in comparison with Monte Carlo values,^{26,47} by using an "enlarged dumbbell" representation of the dimer to evaluate these two quantities. The shape of the enlarged dumbbell is chosen to encompass all the area excluded to any part of a neighboring molecule by the hard dimer. The appropriate shape factor is

$$\gamma = \frac{(5\pi/3)^2}{\pi(\pi + 2\sqrt{3})} \approx 1.321. \quad (26)$$

In addition, in evaluating Eq. (25) the area fraction η is replaced by a new area fraction $\hat{\eta}$ chosen so that the number density of enlarged dumbbells at area fraction $\hat{\eta}$ is the same as the number density of dimers at an area fraction of η , i.e.,

$$\hat{\eta} = \frac{\pi + 2\sqrt{3}}{2\pi} \eta \approx 1.0513\eta. \quad (27)$$

(These choices for γ and η are denoted by "cIII" in Ref. 32.)

The two-dimensional "exclusion areas" for the monomer, dimer, and trimer are⁴⁰

$$\begin{aligned} v_e(1) &= \pi\sigma^2, \\ v_e(2) &= \frac{4\pi\sigma^2}{3} + \frac{\sqrt{3}\sigma^2}{2}, \\ v_e(3) &\approx 6.88159\sigma^2, \end{aligned} \quad (28)$$

where the last value was obtained by averaging over all allowable trimer configurations. The exclusion areas for longer chains can be estimated from Eq. (10).

In Fig. 8 the predictions of the F, FH, GF, GFH, and GF-D equations are compared with the Monte Carlo results of Dickman and Hall² for two-dimensional, freely jointed 5-mers. The Monte Carlo results were obtained using the "test-chain insertion method," in which the insertion probability is numerically estimated from repeated trial insertions of a test chain into a simulated fluid. The qualitative trends displayed in Fig. 8 are the same as for the three-dimensional fluids, with the GF-D equation giving the most accurate predictions. The quantitative agreement, however, is not quite as good. (Compare, e.g., Figs. 5 and 8.) This is not too surprising though, since in two-dimensions, where it is impossible for a chain to form a loop without self-interacting, long-range intramolecular correlations play a more important role.

In analogy with the freely rotating chain model discussed in Sec. III A we have also considered a two-dimensional chain with bond angles restricted to $\pm 90^\circ$ or 180° . Naturally, $v_e(1)$ and $v_e(2)$ are the same as for the freely jointed model. The trimer exclusion area for this model, obtained by averaging over the three possible conformations, is

$v_e(3) = 6.88282\sigma^2$. This value is nearly identical to the freely jointed $v_e(3)$ [see Eq. (28)]. Thus, the GF-D equation (as well as the GF and GFH equations) predicts that the two models should exhibit nearly the same thermodynamic behavior. This may account, in part, for the good agreement observed by Dickman and Hall² between their MC results for flexible 5-mers and Okamoto's MC results for the restricted-angle 5-mers.²⁷

C. One-dimensional fluids

In the one-dimensional fluid, all of the molecules are constrained to lie along a single line. The only difference between a chain and a monomer is the length of the hard line segment representing the molecule. Thus, by rescaling the characteristic length, the pure monomer and pure chain fluids become identical. All the thermodynamic properties of the hard-segment fluids can (in the macroscopic limit) be written as functions of η and T , and, as a result, the compressibility factor of the n -mer fluid at η is equal to the compressibility factor of the monomer fluid at η , i.e.,

$$Z(\eta, n) = Z(\eta, 1). \quad (29)$$

Likewise, we have

$$p_n(\eta) = p_1(\eta). \quad (30)$$

For the one-dimensional hard-segment fluid, the equation of state is given *exactly* by

$$Z(\eta, 1) = \frac{1}{1 - \eta}. \quad (31)$$

Equation (31) is often attributed to Tonks⁴⁸ though, as Robledo and Rowlinson⁴⁹ have noted, its general validity was recognized by Rayleigh as early as 1891.⁵⁰

We now turn to the predictions of the approximate, mean-field equations of state relative to this exact result. The "exclusion length" of a one-dimensional n -mer is given exactly by $v_e(n) = (n + 1)\sigma$. Thus, the factor Y_n needed in the GF-D equation is equal to $(n - 2)$ [see Eq. (14)]. As a result, the GF-D equation of state reduces to the exact expression given above. This agreement is somewhat fortuitous though, and arises from the fact that the quantity $p_2(\eta)/p_1(\eta)$ appearing in the GF-D estimate for the insertion probability, Eq. (13), is equal to 1 in one dimension. The use of this ratio in Eq. (13) was, however, an approximation in itself.

In Fig. 9 the predictions of the other mean-field equations are compared with the exact result for a one-dimensional, 5-mer fluid. A systematic study of the behavior of these equations as a function of chain length reveals the following trends. The GF equation is the least accurate of the four; it consistently overestimates the pressure with the errors increasing steadily with chain length. This behavior can be traced to the use of a monomer reference fluid to represent the structure of the chain fluid. Partitioning N chains of length $n\sigma$ into Nn monomers of length σ results in less efficient packing of the line segments. Much of the empty space in the monomer fluid will lie in gaps between segments that are too small to accommodate an additional monomer. When the monomers are grouped together in chains, the total number of intermolecular gaps decreases by $N(n - 1)$.

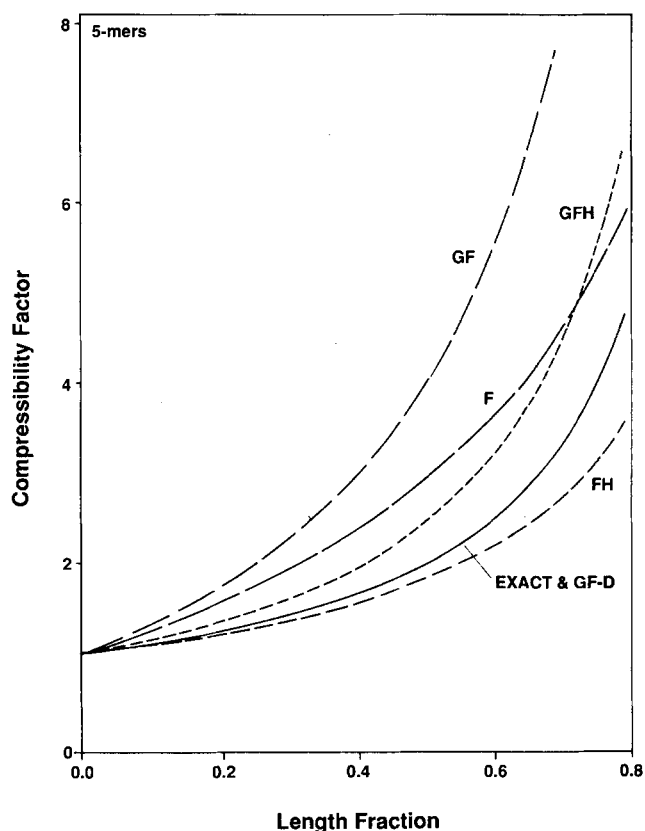


FIG. 9. Compressibility factor vs length fraction for one-dimensional 5-mers. In one dimension the GF-D equation becomes exact (solid curve). Other curves are the predictions of theoretical equations of state described in the text.

Since, for a given η , the amount of void space in the system is fixed, the fewer the number of gaps in which the void space can be distributed, the larger the average void gap will be. Consequently, the true chain insertion probability (pressure) will be considerably larger (smaller) than the GF estimate. All of the continuous-space, mean-field equations considered here suffer from this defect to the extent that they use a monomer fluid (or a dimer fluid, in the case of GF-D) to represent the chain fluid. Naturally, these arguments also apply in two and three dimensions though apparently the effects are much less pronounced. In one dimension the GF theory underestimates the insertion probability by a factor $p_1(\eta)^{(n-1)/2}$ [see Eqs. (7) and (30)], so that the error grows without bound as n increases.

Better results are obtained from the GFH equation, though it too overestimates the pressure at all densities. Again the agreement worsens with increasing chain length, but, unlike the GF theory, the errors approach a finite limit. The F theory goes from underestimating the pressure for $n = 2$, to overestimating it for $n \geq 3$ —a trend not observed in the higher dimensional fluids, at least at the chain lengths and densities examined here. This behavior can be traced to two competing effects: the use of a lattice-based estimate for the insertion probability, which tends to overestimate $p_n(\eta)$; and the use of a monomer fluid to represent the structure of a chain fluid, which tends to underestimate $p_n(\eta)$.

Apparently, in two and three dimensions the former effect dominates, while in one dimension the latter becomes more important. Like the GF theory, as n increases the errors in the F equation grow without bound. The FH equation, on the other hand, underestimates the pressure at all densities. However, in the limit as $n \rightarrow \infty$ the FH equation becomes exact, with the error vanishing as n^{-1} .

In view of this surprising trend displayed by the FH equation in one dimension, one wonders whether the lattice-based equations might also become more accurate in two or three dimensions in the large n limit. In this context, it is interesting to note that in studies of long three-dimensional chains ($n = 500, 2000, \text{ and } 4000$), Schweizer and Curro observed improved agreement between their RISM-based predictions for the compressibility factor and the F equation of state.⁴

V. GENERALIZATION OF APPROACH

A number of approximations were introduced in Sec. III which allowed the n -mer fluid to be related to monomer and dimer fluids. By following a similar procedure, the compressibility factor of a n -mer fluid can be related to the compressibility factors of any two shorter chain fluids, and the more similar the two reference fluids are to the n -mer fluid, the more accurate the resulting expression will be. In this section we generalize the approach of Sec. III to show how, in principle, increasingly accurate equations of state may be obtained.

As a starting point, we make two approximations, similar in spirit to those employed in Sec. III, aimed at relating the properties of the n -mer fluid to the properties of a $(n-1)$ -mer fluid and a $(n-2)$ -mer fluid at the same volume fraction. In the first approximation, approximation I, we assume that the probability of inserting a $(n-1)$ -mer into a n -mer fluid is approximately equal to the probability of inserting a $(n-1)$ -mer into a $(n-1)$ -mer fluid at the same volume fraction, $p_{n-1}(\eta)$. Likewise, we assume that the probability of inserting a $(n-2)$ -mer into a n -mer fluid is approximately equal to $p_{n-2}(\eta)$. Physically, one expects that the longer the chains, the more accurate this type of approximation will be, since the $(n-1)$ -mer and $(n-2)$ -mer fluids will also exhibit excluded-volume and correlation-hole effects. That is, the probability of inserting a 15-mer into a 16-mer fluid is probably more similar to the probability of inserting a 15-mer into a 15-mer fluid, than, say, the probability of inserting a monomer into a dimer fluid is to the probability of inserting a monomer into a monomer fluid.

The second approximation, approximation II, centers on estimating the conditional probability of adding the n th site to a $(n-1)$ -mer which has already been successfully inserted into a n -mer fluid. Within the context of approximation I, the ratio $p_{n-1}(\eta)/p_{n-2}(\eta)$ is the conditional probability of attaching the $(n-1)$ th site to the $(n-2)$ -mer. In analogy with expression (11) and Eq. (12), we relate the probability of adding the n th site onto the $(n-1)$ -mer to the probability of adding the $(n-1)$ th site onto the $(n-2)$ -mer by comparing the exclusion volume required for the n th site to the exclusion volume required for the

$(n-1)$ th site, i.e., the conditional probability of adding the n th site onto the $(n-1)$ -mer is approximated by

$$\left[\frac{p_{n-1}(\eta)}{p_{n-2}(\eta)} \right]^{[v_e(n) - v_e(n-1)]/[v_e(n-1) - v_e(n-2)]}$$

Again, physical arguments suggest that the longer the chain, the more accurate this approximation will be. Intuitively, one expects that as the chain length increases, the exclusion volume required to insert the last site will approach the exclusion volume required to insert the next-to-the-last site, so that the ratio of exclusion volumes appearing in the exponent of the above expression will be nearly 1. Note that Eq. (10) predicts this behavior for $n \gg 4$, while the more accurate Eq. (23) predicts it for $n \gg 5$.

Using approximations (I) and (II), our estimate for the chain insertion probability becomes

$$p_n(\eta) = p_{n-1}(\eta) \times \left[\frac{p_{n-1}(\eta)}{p_{n-2}(\eta)} \right]^{[v_e(n) - v_e(n-1)]/[v_e(n-1) - v_e(n-2)]} \quad (32)$$

where the first term on the right-hand side represents the probability of inserting the first $n-1$ sites and the second term is the conditional probability of tacking on the n th site. This expression may be written more compactly by defining a factor $Y_{n,i}$

$$Y_{n,i} = \frac{v_e(n) - v_e(i)}{v_e(i) - v_e(i-1)}, \quad (33)$$

analogous to the factor Y_n defined by Eq. (14). [In terms of this new definition, the quantity Y_n in Eqs. (14)–(19) becomes $Y_{n,2}$.] The insertion probability can then be written in a form similar to Eq. (15),

$$p_n(\eta) = p_{n-2}(\eta)^{-Y_{n,n-1}} p_{n-1}(\eta)^{Y_{n,n-1}+1}. \quad (34)$$

This result can be substituted into the osmotic equation of state [Eq. (5)] to obtain an expression for the compressibility factor. An analysis similar to that of Eqs. (16)–(19) leads to the recursion relation

$$Z(\eta, n) = (1 + Y_{n,n-1})Z(\eta, n-1) - Y_{n,n-1}Z(\eta, n-2) \quad (35)$$

in which the compressibility factor of the n -mer fluid is related to the compressibility factors of the $(n-1)$ -mer and $(n-2)$ -mer fluids. In general, though, the properties of these reference fluids will also be unknown. However, by reapplying Eq. (35) recursively, one can work backwards until reaching reference fluids for which accurate equations of state are available. Each time the recursion relation is reapplied, though, approximations I and II are invoked, so the resulting expression becomes less and less accurate.

This procedure of working backwards to shorter reference fluids is equivalent, of course, to solving the recursion relation, Eq. (35), which takes the form of a linear, second-order difference equation. Its general solution is easily found by the following procedure. Letting

$$a_k \equiv \ln[Z(\eta, k) - Z(\eta, k-1)]. \quad (36)$$

Equation (35) may be written

$$a_k - a_{k-1} = \ln Y_{k,k-1}. \quad (37)$$

Summing both sides of this expression from $k = i + 1$ to $k = j$ gives

$$a_j - a_i = \ln \left(\prod_{k=i+1}^j Y_{k,k-1} \right), \quad (38)$$

or, in terms of compressibility factors,

$$\begin{aligned} Z(\eta, j) - Z(\eta, j-1) \\ = [Z(\eta, i) - Z(\eta, i-1)] \prod_{k=i+1}^j Y_{k,k-1}. \end{aligned} \quad (39)$$

This expression, in turn, may be summed from $j = i + 1$ to $j = n$, leading to

$$\begin{aligned} Z(\eta, n) = Z(\eta, i) + [Z(\eta, i) - Z(\eta, i-1)] \\ \times \sum_{j=i+1}^n \prod_{k=i+1}^j Y_{k,k-1}. \end{aligned} \quad (40)$$

However, from Eq. (33) we have

$$\sum_{j=i+1}^n \prod_{k=i+1}^j Y_{k,k-1} = Y_{n,i} \quad (41)$$

so that Eq. (40) simplifies to

$$Z(\eta, n) = (1 + Y_{n,i})Z(\eta, i) - Y_{n,i}Z(\eta, i-1). \quad (42)$$

Equation (42), which relates the compressibility factor of the n -mer to the compressibility factors of any two shorter chains, then represents the generalization of Eq. (19) to arbitrary reference fluids. By setting $i = 2$, one obtains the GF-D equation. Conceptually, one can also set $i = 1$ by defining a "0-mer" fluid as a collection of point particles with momentum but no volume—i.e., an ideal gas. By setting $i = 1$ and $Z(\eta, 0) = 1$ in Eq. (42), one obtains the GF equation [Eq. (8)]. In this context, the GF and GF-D equations can be viewed as the first two members of a family of increasingly accurate equations of state for chains. While more accurate reference equations are not generally available for $i > 3$, by fitting curves to simulation results for chains of intermediate length, Eq. (42) might yield accurate predictions for considerably longer chains.

VI. SUMMARY

The development of a rigorous, analytical theory for chain-molecule fluids, which explicitly includes long-range inter- and intra-molecular interactions and the attendant excluded-volume and correlation-hole effects, poses a formidable theoretical problem. In light of our relatively elementary understanding of such fluids, it seems advantageous to develop ways of relating their behavior to the behavior of simpler, more easily understood fluids. In this article, we have explored such an approach through the application of mean-field approximations.

By building upon the generalized Flory estimate for the chain insertion probability, we have derived a new equation of state for athermal chains which relates the compressibility factor of a n -mer fluid to the compressibility factors of a monomer and dimer fluid at the same volume fraction. This result represents an improvement over the GF theory in

that, by using both dimer and monomer reference fluids, it incorporates, in an approximate way, the effects of chain connectivity. Like its predecessor, however, the new equation is unable to explicitly account for longer-range intramolecular correlations—a defect inherent in the mean-field approach. Nevertheless, the result appears to be reasonably accurate and applicable to a wide variety of chain models. Comparisons with Monte Carlo results for three-dimensional, freely jointed chains showed excellent agreement, particularly for the 4-mer and 8-mer fluids, and the overall accuracy appears comparable to Wertheim's thermodynamic theory of polymerization (TPT). Comparisons were also made with exact and simulation results in one and two dimensions, which served to highlight the nature of the underlying mean-field approximations. Very good, though slightly high, predictions were obtained for two-dimensional, freely jointed 5-mers, while in one dimension the new equation was exact.

For three-dimensional 16-mers, the predictions of both the GF-D equation and TPT appear to be somewhat high, presumably reflecting the increasing role of long-range intramolecular correlations. In light of this trend, and the opposite effect predicted by the more sophisticated RISM approach, one should be wary of applying the GF-D equation to considerably longer chains until simulation results are available to clarify this discrepancy.

Aside from its underlying simplicity, an appealing quality of the mean-field approach discussed here is the way in which long chains can be "built up" one site at a time, allowing the properties of relatively complex fluids to be inferred from a knowledge of simpler fluids. If a monomer is used as the basic building block, then one obtains the GF equation, while if one supplements this with dimer insertion probabilities, then the GF-D equation is obtained. As the generalizations of Sec. V showed, the GF and GF-D equations can be viewed as the first two members of a family of increasingly accurate equations of state.

Another potential advantage of the mean-field approach is its versatility. While we have focused primarily on pearl-necklace models here, other models incorporating more details of molecular architecture can be examined by evaluating the appropriate exclusion volumes. Two such examples briefly considered here were chains with fixed bond angles and rigid trimers with overlaps between bonded neighbors, for which good agreement with simulation results was observed.

In addition, it appears that these arguments are also applicable to fluids with intermolecular attractions, to mixtures of chains and monomers, and to mixtures of chains of different lengths. Furthermore, the GF-D equation [as well as its extension, Eq. (42)] can be applied to lattice fluids by replacing the continuous-space monomer and dimer equations of state by their lattice-based counterparts. Since the exclusion volume of a lattice chain is exactly equal to the chain length, comparisons with simulation results would allow a direct assessment of the accuracy of the mean-field approximations depicted in Fig. 2. Theoretical and computational studies bearing on these questions are currently in progress.

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