

# A Born–Green–Yvon equation for flexible chain-molecule fluids.

## II. Applications to hard-sphere polymers

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Using the method of Born, Green, and Yvon we have recently derived a coupled set of integral equations for the intermolecular site–site distribution functions which describe the microscopic equilibrium structure of a fluid of flexible chain molecules. Here, we carry out an average over this set of equations to arrive at a single equation for the average intermolecular distribution function. Intramolecular distribution functions appearing in this equation are approximated by results for isolated chain molecules. Numerical calculations have been performed over a range of fluid densities for chains composed of 8, 16, 20, and 50 tangent hard spheres. The resulting intermolecular distribution functions are in good to fair agreement with simulation data. This structural information is used to compute second virial coefficients and pressure equations of state via the virial route to thermodynamics. Although the theory consistently underestimates the pressure, it gives very accurate results for the second virial coefficient for all chain lengths studied. © 1995 American Institute of Physics.

### I. INTRODUCTION

Polymeric materials are ubiquitous in today's world and demand for new materials possessing prespecified properties presents a real challenge for polymer scientists. The *ab initio* design and synthesis of new polymers is a formidable task. Thus the apparently simple idea of creating new materials by mixing or blending existing polymers is extremely attractive. However, prediction of the properties of such polymeric mixtures, or even of the pure polymeric components, is by no means simple, and we are still a long way from a thorough theoretical understanding of such materials.<sup>1</sup> A microscopic, statistical mechanical approach will certainly be required to address such fundamental, yet subtle, questions as the thermodynamic stability of a polymeric mixture.

The starting point for such an approach is a theory for the microscopic structure of a polymeric fluid. This structural information, generally expressed in terms of site–site intermolecular correlation functions, can be used to compute the macroscopic thermodynamic properties of the bulk fluid. The microscopic structure of a polymeric fluid is inherently complex due to long-range intramolecular correlations arising from the “self-connectedness” of the polymer molecules.<sup>2</sup> Even at low density, such fluids display nontrivial structure characterized by a so-called correlation hole in the site–site intermolecular distribution function. At high densities the structure of such a fluid does begin to resemble that of a simple atomic or molecular liquid although, for long chain molecules, remnants of the correlation hole persist.<sup>3–5</sup> In the case of simple fluids, integral equation theories have proven to be the most successful approach to computing such fluid structure.<sup>6,7</sup> Extension of these theories to polymeric fluids is currently a topic of much interest.<sup>8–12</sup>

In a recent publication<sup>12</sup> (hereafter referred to as Paper I) we utilized the theory developed by Born and Green and Yvon (BGY)<sup>13,14</sup> for simple fluids to derive an integral equation for the site–site intermolecular distribution functions for

a fluid of flexible chain molecules. In that work we presented numerical results on the structure and thermodynamics of short hard-sphere chain fluids which compared well with simulation data. Here, we apply the same approach to polymeric fluids composed of tangent hard-sphere chains with lengths ranging from 8 to 50. For these longer chains calculation of the complete set of site–site intermolecular distribution functions is unwieldy and a single average distribution function provides a concise and adequate description of the system. By carrying out the appropriate averages over the coupled set of BGY equations given in Paper I we arrive at a single equation for this average distribution function. A set of intramolecular distribution functions is still required to solve this BGY equation and here, as in our earlier work, we make use of the distribution functions for an isolated chain molecule.

Average site–site intermolecular distribution functions have been computed via this BGY approach over a range of fluid densities for chains composed of 8, 16, 20, and 50 tangent hard spheres. Qualitatively, these results compare quite well with computer simulation results. Quantitatively, although the overall agreement between theory and simulation tends to worsen with increasing chain length, for intermediate and high volume fractions the value of these distribution functions at contact is given with reasonable accuracy for all chain lengths. This structural information provided by the BGY theory has been used to compute thermodynamic properties of the hard-sphere polymer fluid. In particular, we use the virial path to thermodynamics to compute second virial coefficients and pressure equations of state. The second virial coefficients are given very accurately by the theory for all chain lengths studied. The computed pressure equations of state are well behaved, however, at intermediate and high densities the pressure is consistently underestimated, with the disparity between theory and simulation increasing with increasing chain length.

An outline of this paper follows: In Sec. II we present a

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BGY equation for the average site–site intermolecular distribution function for a hard-sphere polymer fluid. The intramolecular distribution functions, required to solve this BGY equation, are given in Sec. III while results for the intermolecular distribution functions are presented in Sec. IV. Thermodynamic properties are given in Sec. V and, finally, in Sec. VI we discuss the approximations made in the present theory and discuss our results in relation to other relevant theories.

## II. THE BGY EQUATION

As in Paper I, we consider a fluid of  $N$  identical flexible chain molecules in a volume  $V$  at temperature  $T$ . Each molecule, or  $n$ -mer, is a linear chain of  $n$  tangent hard spheres of diameter  $\sigma$  connected by “universal joints.” The microscopic structure of this fluid can be described in terms of a set of intermolecular distribution functions  $g^{(i,j)}(r)$  and intramolecular distribution functions  $w^{(il)}(r)$ . The intermolecular  $g^{(i,j)}(r)$  functions are proportional to the probability density that two sites  $i$  and  $j$  on two different chain molecules will be a distance  $r$  apart. Similarly, the intramolecular  $w^{(il)}(r)$  functions are proportional to the probability density that two sites  $i$  and  $l$  on the same chain molecule will be separated by a distance  $r$ . For the longer chain molecules considered in this work ( $n \geq 8$ ), knowledge of the complete set of intermolecular functions provides an unnecessarily detailed description of the system. The much simpler average site–site distribution function defined as

$$\bar{g}(r) = \frac{1}{n^2} \sum_{i,j}^n g^{(i,j)}(r) \quad (1)$$

provides ample structural information, and is sufficient to compute the thermodynamics of a fluid of flexible chain molecules; in the present work we restrict our attention to this average function. With regard to the intramolecular functions, we will continue to consider a set of specific  $w^{(il)}(r)$  functions (as opposed to an average intramolecular distribution) although we will make the simplifying approximation that these functions depend only on the difference  $m = |i - l|$ , being independent of the specific sites  $i$  and  $l$ . Thus for an  $n$ -mer, we need consider a set of only  $n - 1$   $w_m(r) \equiv w^{(il)}(r)$  functions.

In Paper I we gave a general BGY equation for flexible chain molecules which relates the specific intermolecular site–site distribution function  $g^{(i,j)}(r)$  to a set of multisite distribution functions. To solve this equation we made use of a set of superposition approximations which reduced the multisite functions in terms of the average intermolecular site–site function  $\bar{g}(r)$ . We also made the additional simplifying approximation of neglecting a set of terms in the general BGY equation which were due to interactions between sites distant from the two generic reference sites ( $i$  and  $j$ ). Working within this scheme of approximations one can write down a single, relatively simple BGY equation for the average intermolecular site–site distribution function for tangent hard-sphere  $n$ -mers as follows:

$$\begin{aligned} \ln \bar{g}(x) = & - \sum_{m=1}^{n-1} c1_m \frac{\bar{g}(1)}{n1_m(1)} \int_x^{m+1} dr \frac{I1_m(r)}{n1_m(r)} \\ & - \sum_{m=1}^{n-1} c2_m \frac{\bar{g}(1)}{n2_m(1)} \int_x^{m+2} dr \frac{I2_m(r)}{n2_m(r)} \\ & - n\pi\rho\sigma^3 \bar{g}(1) \int_{x-1}^{x+1} dt \frac{1-(t-x)^2}{x} t[\bar{g}(t)-1] \\ & - 2(n-1)\pi\rho\sigma^3 \frac{\bar{g}(1)}{n1_1(1)} \int_x^\infty dr \frac{K(r)}{n1_1(r)}, \quad x \geq 1, \end{aligned} \quad (2)$$

and  $\bar{g}(x < 1) = 0$ , where  $\rho = N/V$  is the number density of chains and distances are scaled by the hard sphere diameter  $\sigma$ . The combinatoric factors in the first two terms of the above equation are given by

$$c1_m = 4 \frac{(n-m)}{n}, \quad (3)$$

$$c2_m = 8 \frac{(n-m)(n-1)}{n^2(1+\delta_{m,1})}, \quad (4)$$

where  $\delta_{a,b}$  is the Kronecker delta function while the corresponding two chain integral kernels are

$$I1_m(r) = \frac{\pi}{r^2} \int_{r-1}^{r+1} ds w_m(s) s(r^2 + 1 - s^2), \quad (5)$$

$$\begin{aligned} I2_m(r_{ab}) = & \hat{r}_{ab} \cdot \int d\mathbf{r}_c w_m(r_{ac}) \int d\mathbf{r}_d w_1(r_{bd}) \\ & \times \sigma \delta(r_{cd} - \sigma) \hat{r}_{cd} \frac{\bar{g}(r_{bc})}{n2_m(r_{bc})} \frac{\bar{g}(r_{ad})}{n2_m(r_{ad})} \end{aligned} \quad (6)$$

( $\hat{r}$  denoting a unit vector) and the site–site superposition approximation normalization functions are given by

$$n1_m(r_{ab}) = \frac{\int d\mathbf{r}_c w_m(r_{ac}) \bar{g}(r_{bc})}{\int d\mathbf{r}_c w_m(r_{ac})}, \quad (7)$$

$$n2_m(r_{ab}) = \frac{\int d\mathbf{r}_c w_m(r_{ac}) \int d\mathbf{r}_d w_1(r_{bd}) \bar{g}(r_{cd}) \Theta_{ad} \Theta_{bc}}{\int d\mathbf{r}_c w_m(r_{ac}) \int d\mathbf{r}_d w_1(r_{bd}) \Theta_{ad} \Theta_{bc}}, \quad (8)$$

where  $\Theta(r)$  is the Heaviside step function which vanishes for  $r < \sigma$  and is unity otherwise. Finally, the three chain integral kernel  $K(r)$  is given by Eqs. (18) and (B9) of Ref. 15. In the case of  $n = 1$ , Eq. (2) reduces to the well known BGY equation for a hard-sphere fluid<sup>13,14,16</sup> while for  $n = 2$  this equation reduces to our previously derived BGY equation for hard-sphere dimers [Eq. (17) of Ref. 15]. For  $n \geq 3$  the full set of specific site–site  $g^{(i,j)}(r)$  functions can still be computed within the present theory by inserting the average  $\bar{g}(r)$  function, computed from Eq. (2), into the right-hand side of the superposition approximation equations given in Paper I. These superposition approximations are in turn inserted into the BGY equation of Paper I which can then be solved for any desired  $i, j$  pair.

TABLE I. Mean squared end-to-end distance for isolated tangent hard-sphere  $(m+1)$ -mers used in the beta-distribution approximation for the intramolecular functions  $w_m(r)$ . Values for  $m \leq 7$  are from the simulation study of Denlinger and Hall (Ref. 20) while the accurate scaling relationship for  $m \geq 8$  is constructed from the simulation results of Kranbuehl *et al.* (Ref. 21).

$m$	$\langle r^2 \rangle / \sigma^2$
4	6.29
5	8.55
6	10.8
7	13.3
$\geq 8$	$1.166m^{1.258}$

### III. INTRAMOLECULAR DISTRIBUTION FUNCTIONS

Solution of the above BGY equation [Eq. (2)] requires knowledge of the set of  $n-1$  intramolecular  $w_m(r)$  functions. In principle, these functions can be computed self-consistently within the BGY formalism. However, here, as in Paper I, we will approximate these functions with distribution functions for isolated chain molecules. Specifically, we approximate each  $w_m(r)$  function by the end-to-end distribution function of an isolated tangent hard sphere  $(m+1)$ -mer. For  $m=1,2,3$  these  $w_m(r)$  functions can be computed exactly (see Paper I). For  $m \geq 4$  exact calculation of the single chain distribution functions becomes difficult and we make the further approximation of representing these functions with the following two parameter truncated beta distribution:

$$w_m(r) = \frac{1}{4\pi\sigma r^2} \frac{1}{N_m} \left( \frac{r}{m\sigma} \right)^{a-1} \left( 1 - \frac{r}{m\sigma} \right)^{b-1} \quad (9)$$

$$1 \leq r/\sigma \leq m; \quad m \geq 4,$$

where the normalization constant is given by

$$N_m = mB(a,b)[1 - I_{1/m}(a,b)] \quad (10)$$

and  $B(a,b)$  and  $I_x(a,b)$  are the beta and incomplete beta functions, respectively.<sup>17</sup> This truncated beta distribution is identically zero for  $r < \sigma$  and  $r > m\sigma$  and satisfies the normalization condition

$$\int dr 4\pi r^2 w_m(r) = 1. \quad (11)$$

The  $\nu$ th moment of this distribution is given approximately by<sup>18</sup>

$$\langle r^\nu \rangle = \frac{\Gamma(a+\nu)\Gamma(a+b)}{\Gamma(a)\Gamma(a+b+\nu)} (m\sigma)^\nu, \quad (12)$$

and thus the two parameters  $a$  and  $b$  could be set by inputting the correct second and fourth moments of the end-to-end distribution function for an isolated tangent hard-sphere  $(m+1)$ -mer. This is analogous to what is done in the semiflexible chain (SFC) model of Honnell *et al.*<sup>19</sup> Here, we take a slightly simpler approach, fixing the “ $a$ ” parameter through Eq. (12) by inputting the correct second moment (values of which are given in Table I) while simply setting  $b=2(m+1)^{1/2}$ . This choice of parameters produces a distribution function quite similar to the Koyama distribution used in the

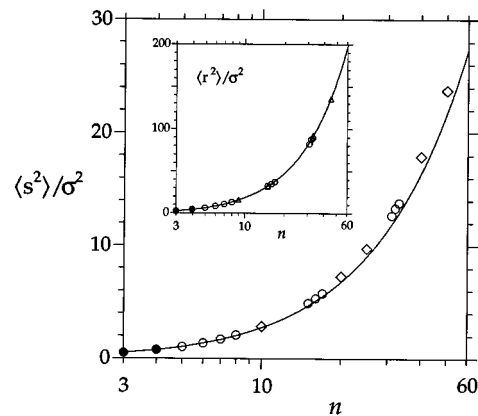


FIG. 1. Mean squared radius of gyration  $\langle s^2 \rangle$  and mean squared end-to-end distance  $\langle r^2 \rangle$  (inset) for isolated tangent hard-sphere  $n$ -mers. Solid lines are computed from the approximate intramolecular distribution functions used in this work (Sec. III). Symbols are exact results (●) (Ref. 12) and simulation results of Denlinger and Hall (○) (Ref. 20), Kranbuehl *et al.* (△) (Ref. 21), and Dautenhahn and Hall (◇) (Ref. 22).

SFC model although, unlike the SFC model, this truncated beta distribution is identically zero for all unphysical values of  $r$ .

In Fig. 1 we show the mean squared end-to-end distance  $\langle r^2 \rangle$  and the mean squared radius of gyration  $\langle s^2 \rangle$  for isolated tangent hard-sphere  $n$ -mers as computed from the above truncated beta distribution compared with values obtained from simulation. Of course,  $\langle r^2 \rangle$  is forced to be correct by our construction of the distribution function. However, the fact that  $\langle s^2 \rangle$  is also given accurately provides evidence of the validity of the approximation  $w_m(r) = w^{(il)}(r)$ , where  $m = |i-l|$ , independent of the specific sites  $i$  and  $l$ .

In Fig. 2 we plot the full intramolecular distribution

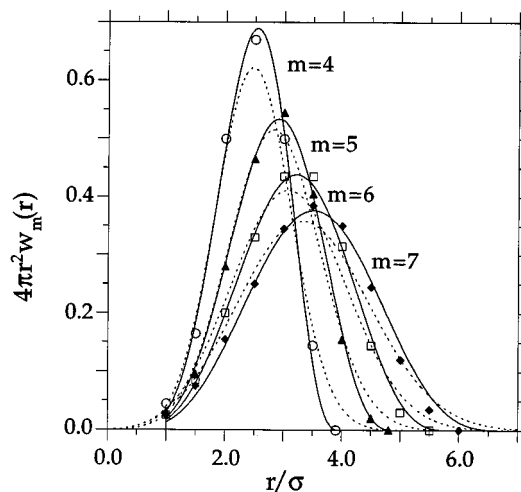


FIG. 2. Intramolecular distribution functions  $w_m(r)$  ( $4 \leq m \leq 7$  as indicated) for tangent hard-sphere  $8$ -mers. Solid lines are results from the truncated beta-distribution approximation given by Eq. (9). Symbols are simulation results of Yethiraj *et al.* (Ref. 4) for  $w^{(il)}(r)$  ( $i=1, l=m+1$ ) for  $8$ -mers at 10% volume fraction and dashed lines are the corresponding results from the SFC model of Honnell *et al.* (Ref. 19).

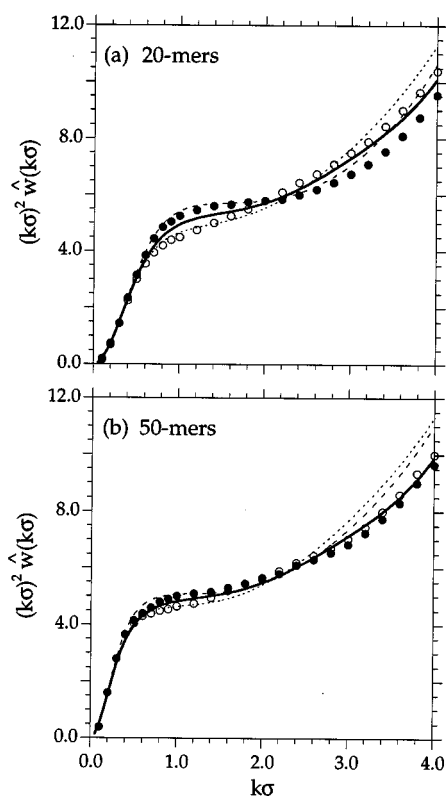


FIG. 3. Kratky plots of the average intramolecular distribution function  $\hat{w}(k)$  for tangent hard-sphere 20-mers (a) and 50-mers (b). The solid lines were computed from the approximate intramolecular distribution functions used in this work (Sec. III). Symbols are simulation results of Yethiraj and Hall (Refs. 5, 24) and dashed lines are the corresponding results from the SFC model of Honnell *et al.* (Ref. 19) for volume fractions (a)  $\eta=0.1$  ( $\circ, \dots$ ),  $\eta=0.3$  ( $\bullet, \dots$ ) and (b)  $\eta=0.2$  ( $\circ, \dots$ ),  $\eta=0.3$  ( $\bullet, \dots$ ).

functions  $w_m(r)$  as given by the truncated beta distribution for  $4 \leq m \leq 7$ . These are compared with simulation results for  $w^{(il)}(r)$  ( $i=1, l=m+1$ ) for tangent hard sphere 8-mers at 10% volume fraction<sup>4</sup> and the SFC model distribution functions for the same system (computed using  $\langle r^2 \rangle$  from Ref. 4). The corresponding exact distribution functions for  $m=2$  and 3 are shown in Fig. 1 of Paper I. As noted in Paper I, these intramolecular distribution functions are density dependent and thus, while the isolated chain results agree very well with the 10% volume fraction simulation results, this agreement will certainly not be maintained at higher volume fractions.<sup>4,5,23</sup> We will address this density dependence of the  $w_m(r)$  functions in future work where we will solve for these functions self-consistently within the BGY formalism.

For chains longer than  $n=8$  simulation results for the specific  $w^{(il)}(r)$  functions are not available, however, results for an average of the intramolecular distribution functions are available in the following  $k$ -space representation:

$$\hat{w}(k) = 1 + 2 \frac{n-1}{n} \frac{\sin(k\sigma)}{k\sigma} + \frac{8\pi}{nk} \int_0^\infty dr r \times \sin(kr) \sum_{m=2}^{n-1} (n-m) w_m(r). \quad (13)$$

In Fig. 3 we plot this average  $\hat{w}(k)$  function in standard Kratky form for tangent hard-sphere 20-mers and 50-mers as computed from the above truncated beta distribution. Also shown in these figures are simulation results of Yethiraj and Hall<sup>5,24</sup> and corresponding SFC model results (computed using  $\langle r^2 \rangle$  values from Ref. 5). In these Kratky plots the  $k\sigma < 1$  region is determined primarily by the global chain dimensions (e.g., as given by  $\langle r^2 \rangle$  and  $\langle s^2 \rangle$ ) while the  $k\sigma > 3$  region is sensitive to the local structure of the chains as determined by  $w_2(r)$  and  $w_3(r)$ . The SFC model does poorly in the  $k\sigma > 3$  region since it provides a rather poor representation of the  $m=2,3$   $w_m(r)$  functions. The truncated beta distribution does a fair job over the full  $k\sigma$  range although it does not give a completely accurate representation of an isolated chain, being slightly too large in the  $1 < k\sigma < 2$  region and slightly too small in the  $2 < k\sigma < 4$  region. However, these deviations suggest that this model may be reasonably realistic for a wider range of volume fractions.

#### IV. INTERMOLECULAR DISTRIBUTION FUNCTIONS

Combining the above approximations for intramolecular distribution functions with the BGY equation for the average intermolecular distribution function [Eq. (2)] provides a tractable integral equation theory for the microscopic structure of a fluid of tangent hard-sphere flexible chain molecules of arbitrary length. We have solved Eq. (2) for chains varying in length from  $n=8$  to  $n=50$  over a range of fluid densities. Details of the numerical solution are the same as described in Paper I except that for the longer chains considered here the integral equation must be solved across a larger grid. It turns out that a grid smaller than the chain length is sufficient for longer chains since the oscillations in  $\bar{g}(r)$  are rapidly damped out (e.g., we use a grid with  $r_{\max}=20\sigma$  for chains of length 50).

In Figs. 4–7 we compare the  $\bar{g}(r)$  results of the BGY theory with computer simulation results for a range of chain lengths  $n$  and volume fractions  $\eta = n(\pi/6)\rho\sigma^3$ . At low den-

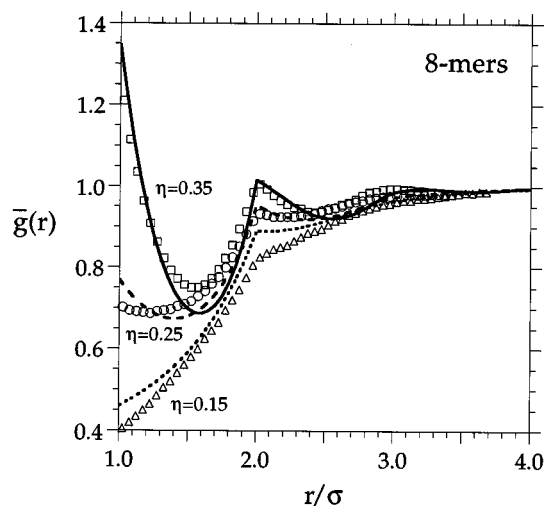


FIG. 4. Average intermolecular site-site distribution functions  $\bar{g}(r)$  for tangent hard-sphere 8-mers at the indicated volume fractions  $\eta$  as computed from the BGY theory (lines) compared with Monte Carlo results (symbols) (Ref. 4).

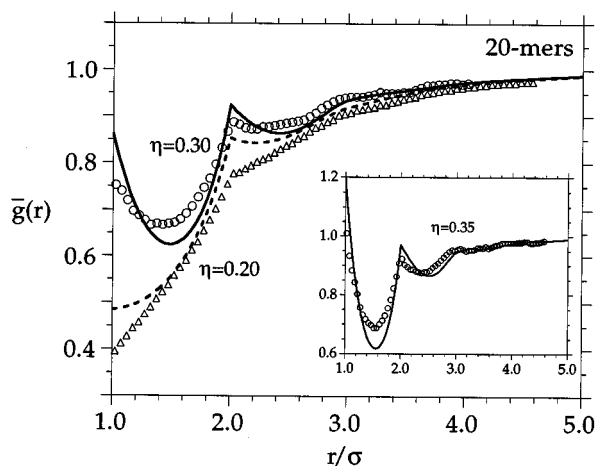


FIG. 5. Average intermolecular site-site distribution functions  $\bar{g}(r)$  for tangent hard-sphere 20-mers at the indicated volume fractions  $\eta$  as computed from the BGY theory (lines) compared with Monte Carlo results (symbols) (Refs. 5, 24).

sities these distribution functions are characterized by a pronounced correlation hole in the region from  $r = \sigma$  (contact) out to roughly  $r = 2\langle s^2 \rangle^{1/2}$  (i.e., the size of the chain). This correlation hole arises from the self-shielding of sites on the same chain. At a given density, the correlation hole deepens with increasing chain length as seen in Fig. 7. The distribution functions also display a cusp (or discontinuous slope change at low density) at  $r = 2\sigma$  (i.e., at a distance equal to the hard sphere diameter plus the bond length) which is a well-known feature of hard-sphere molecular fluids.<sup>26</sup> In comparison with the simulation data the BGY theory generally overestimates the distribution function at low densities while, at higher densities, the BGY results tend to slightly

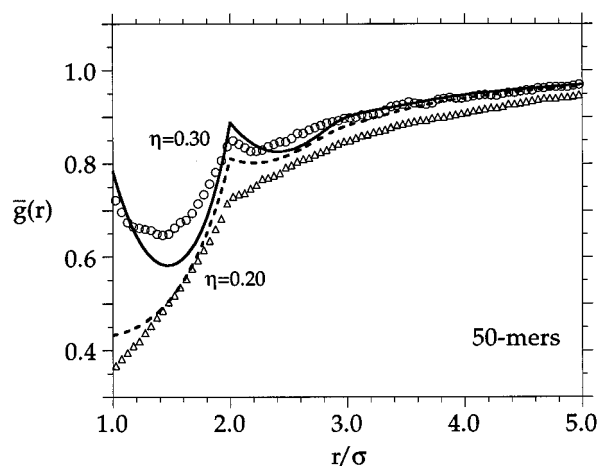


FIG. 6. Average intermolecular site-site distribution functions  $\bar{g}(r)$  for tangent hard-sphere 50-mers at the indicated volume fractions  $\eta$  as computed from the BGY theory (lines) compared with Monte Carlo results (symbols) (Ref. 5).

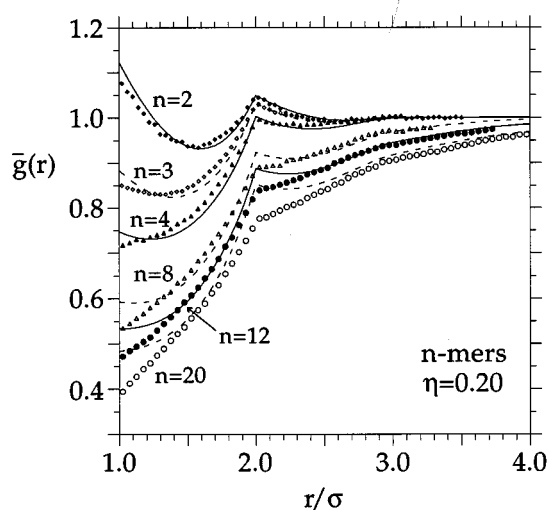


FIG. 7. Average intermolecular site-site distribution functions  $\bar{g}(r)$  for tangent hard-sphere  $n$ -mers ( $2 \leq n \leq 20$  as indicated) at  $\eta = 0.20$  as computed from the BGY theory (lines) compared with Monte Carlo results (symbols) for  $n = 2$  (Ref. 25),  $n = 3$  (Ref. 23),  $n = 4, 8, 12$  (Ref. 4), and  $n = 20$  (Refs. 5, 24).

overestimate the value at contact and at the cusp while exaggerating the depth of the first minimum. Overall, the accuracy of the BGY  $\bar{g}(r)$  results appear to diminish with increasing chain length for all densities, although the accuracy at contact seems to be maintained at higher densities.

## V. THERMODYNAMICS

The average intermolecular site-site distribution function  $\bar{g}(r)$  can be used to compute a variety of thermodynamic properties of the flexible hard-sphere chain fluid. As discussed in Paper I, there are a number of "routes" which can be followed leading from fluid structure to equilibrium thermodynamics. Here, we limit ourselves to computing the second virial coefficient,  $B_2$ , and the pressure equation of state (i.e., compressibility factor),  $\beta P/\rho$ , via the virial route. The relevant expressions for  $B_2$  and  $\beta P/\rho$  are given by Eqs. (23) and (19) of Paper I, respectively.

In Fig. 8 we plot the second virial coefficient (in units of  $\sigma^3$ , divided by  $n^2$ ) for tangent hard sphere  $n$ -mers with  $2 \leq n \leq 50$  as computed from the BGY  $\bar{g}(r; \rho \rightarrow 0)$  results. Also shown are the simulation results of Hall and co-workers<sup>22,27</sup> and results from the generalized Flory dimer (GFD) theory of Honnell and Hall.<sup>28</sup> The BGY theory is seen to do remarkably well over the entire range of chain lengths while the GFD theory, which is known to perform better at high rather than low densities, greatly overestimates  $B_2$  for chains of length  $n \geq 4$ .

In Fig. 9 we plot the full pressure equation of state for tangent hard-sphere 8-mers and 16-mers as computed from the BGY  $\bar{g}(r)$  results. Also shown in this figure are simulation data<sup>28-30</sup> and results from the GFD theory. Although the pressure results from the BGY theory are qualitatively well behaved, they consistently underestimate the simulation values. This disparity increases going from 4-mers (see Fig. 4 of Paper I) to 8-mers to 16-mers. Clearly the virial path to the

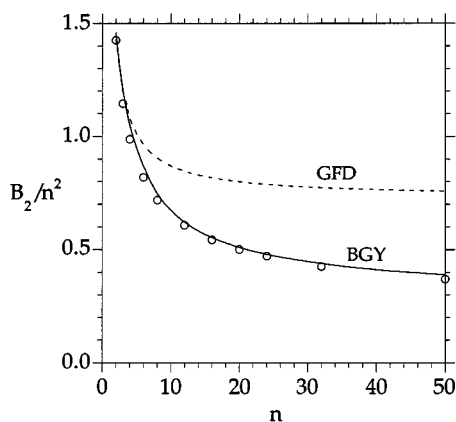


FIG. 8. Second virial coefficient  $B_2$  (in units of  $\sigma^3$ , scaled by  $n^2$ ) for tangent hard-sphere  $n$ -mers, as computed from the BGY theory via the virial path (—), compared with simulation results (O) (Refs. 22, 27) and the generalized Flory-dimer theory (---) (Ref. 28).

pressure is becoming increasingly inaccurate with increasing chain length. The virial pressure is comprised of two terms, one involving the contact value of the site-site distribution function  $\bar{g}(\sigma)$  and one involving a three-site distribution function.<sup>31,32</sup> Since the BGY results are reasonably accurate at contact it must be the three-site term which is the source of the error. However, whether this error is to be attributed primarily to the normalized superposition approximation, which is used to reduce the three-site term, or to subtle inaccuracies in the computed  $\bar{g}(r)$  is not immediately clear. In any case, these results suggest that an alternate path to the thermodynamics should be considered for long chains. In particular, the energy path<sup>33</sup> appears attractive since it only requires values of the distribution function at contact (where the BGY theory tends to perform well). This path requires computation of the distribution function, at each density, for a series of hard-sphere chain fluids in which the hard sphere diameter

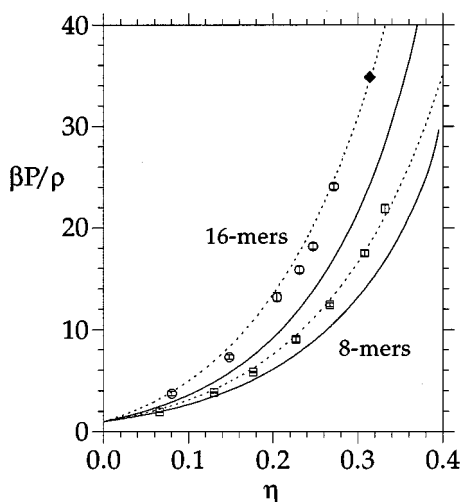


FIG. 9. Compressibility factor  $\beta P/\rho$  as a function of volume fraction  $\eta$  for tangent hard-sphere 8-mers (lower curves and squares) and 16-mers (upper curves and circles), as computed from the BGY theory via the virial path (—), compared with simulation results ( $\square, \circ, \blacklozenge$ ) (Refs. 28–30) and the generalized Flory-dimer theory (---) (Ref. 28).

varies from zero to  $\sigma$ . Of course, exploration of this and other routes to the thermodynamics will provide an important test of the thermodynamic consistency of our theory, however, we have yet to carry out this set of calculations.

## VI. DISCUSSION

In this work we have presented a BGY equation for the average intermolecular site-site distribution function for a fluid of flexible tangent hard-sphere chain molecules. This equation was constructed by averaging over the coupled set of equations for the specific intermolecular site-site functions derived in Paper I. The following approximations were introduced in Paper I in order to achieve a tractable theory: (1) Those terms in the exact BGY equations which arise from interactions between pairs of sites distant from the two reference sites are neglected; (2) A set of normalized site-site superposition approximations is used to reduce multisite distribution functions in terms of the average intermolecular distribution function; (3) Intramolecular distribution functions are approximated by the corresponding functions for an isolated chain molecule. These three approximations are discussed in detail in Paper I.

In regard to the third approximation, in our earlier work we used exact results for the isolated chain intramolecular functions. Here, however, we have made use of an approximate representation of these functions since exact results are difficult to obtain for the longer chain molecules considered in this work. Use of the isolated chain intramolecular functions is certainly valid at low densities. However, at higher densities certain consequences of this approximation should be noted. For example, this approximation ignores the density dependence of the chain dimensions. In particular  $\langle r^2 \rangle$  and  $\langle s^2 \rangle$  are known to decrease with increasing volume fraction (i.e., the peaks in Fig. 2 shift left and the initial plateau regions in Fig. 3 move up with increasing  $\eta$ ). Thus in our model the chains are overly “expanded” at higher densities and this may account for the overestimate of both the magnitude of the contact value and the depth of the first minimum of our computed  $\bar{g}(r)$  functions at higher densities. Clearly at melt densities ( $\eta > 0.4$ ) the intramolecular structure of the chains is much more realistically given by the structure of an ideal chain (as suggested by Flory<sup>34</sup> and confirmed by neutron scattering experiments<sup>35</sup>). As noted in Paper I, in future work we plan on eliminating this isolated chain approximation altogether by computing these intramolecular functions self-consistently within the BGY approach.

The results obtained from the present theory for the average intermolecular distribution functions for tangent hard-sphere  $n$ -mers with  $8 \leq n \leq 50$  are in good to satisfactory agreement with existing simulation data. The performance of the theory appears to improve with increasing density while the overall agreement between theory and simulation diminishes somewhat with increasing chain length. Using the virial route to thermodynamics, the theory consistently underestimates the pressure of the hard-sphere polymer fluid while the second virial coefficient is given very accurately for all chain lengths studied ( $2 \leq n \leq 50$ ).

Integral equation theories for polymer fluids are currently the topic of much active research interest. At present there are no less than four other theories, in addition to our own, for computing the site–site intermolecular distribution functions for hard-sphere chain-molecule fluids. These are the PRISM theory of Curro and Schweizer,<sup>8</sup> the Percus–Yevick theory of Chiew,<sup>9</sup> the density functional theory of Kierlik and Rosinberg (KR)<sup>10</sup> and, most recently, Attard's own version of the BGY approach.<sup>11</sup> Both the Chiew and KR theories give fairly good results for tangent hard-sphere 4-mers, however, they do not perform nearly as well for 8-mers and the present BGY theory appears to be somewhat more accurate than either of these theories for longer chain molecules (i.e.,  $n \geq 8$ ). Attard's recent theory, which provides a self-consistent means of computing both the intra- and intermolecular distribution functions for flexible chain molecules, yields results for 4-, 8-, and 12-mers at 20% volume fraction which are as good as or slightly better than the results obtained from the present BGY theory. However, Attard's approach requires the simultaneous calculation of the complete set of specific site–site distribution functions, and thus direct extension of this approach to longer chain molecules will be rather computationally demanding. By far the most widely tested of the integral equation theories for hard-sphere polymers is the PRISM theory of Curro and Schweizer. Yethiraj *et al.* have made extensive comparisons between their own computer simulation results and the results from PRISM theory, using the best-case scenario in which simulation results for the intramolecular distribution functions are used in the PRISM calculations.<sup>4,5</sup> In general, PRISM theory overestimates the value of the average site–site intermolecular distribution function in the vicinity of contact and tends to become more accurate with increasing density. For the chain lengths studied in this work the BGY theory gives more accurate results near contact for all densities. For the shortest chains considered here ( $n=8$ ) the results from the BGY theory are as good as or slightly better than those obtained from PRISM at all densities. For the longer chains, although the BGY results are somewhat better in the vicinity of contact, the PRISM results are more accurate beyond contact where the BGY theory tends to exaggerate the first minimum and overestimate the cusp of the distribution functions.

The results reported here demonstrate that the BGY approach provides a viable theoretical framework for the study of polymeric fluids. We are currently working on several extensions of the present theory. Of primary interest is a self-consistent solution for both the intra- and intermolecular distribution functions within the BGY formalism. Other topics of interest are the recasting of the theory in terms of an average intramolecular distribution function, rather than the specific functions themselves, in order to facilitate calculations for even longer chain molecules, and the exploration of alternate routes to thermodynamics such as the energy route. Finally, the investigation of chain molecule fluids interacting via site–site potentials other than the hard-sphere potential is

of great interest. The square-well potential is particularly relevant to this approach since this is the potential used in most lattice model calculations of polymeric fluids. Lipson and co-workers have employed the BGY theory to describe such lattice polymers<sup>36,37</sup> and it will be interesting to compare the lattice and continuum results derived from the same theory.

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