

# Monte Carlo Calculation of the Osmotic Second Virial Coefficient of Off-Lattice Athermal Polymers

Arun Yethiraj,\*† Kevin G. Honnell,‡ and Carol K. Hall†

Department of Chemical Engineering, The North Carolina State University, Raleigh, North Carolina 27695-7905, and Macromolecular Physics Group, 248 CPL, Phillips Petroleum Company, Bartlesville, Oklahoma 74004

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**ABSTRACT:** The osmotic second virial coefficient,  $B_2$ , of off-lattice athermal polymers is calculated using a Monte Carlo procedure. Chain lengths,  $n$ , ranging from 3 to 128 are studied. We find that  $B_2/n^2 \sim n^{-0.25 \pm 0.02}$  for  $n \rightarrow \infty$  consistent with scaling theories but different from earlier Monte Carlo estimates. The predictions of  $B_2$  from various analytical equations of state for hard chains are tested against the simulation results and found to be quite poor. The generalized Flory dimer equation is modified by forcing it to reproduce the Monte Carlo values for the second virial coefficient; this significantly improves the compressibility factor predictions of the theory at low densities.

## 1. Introduction

Over the last 10 years there has been considerable effort devoted to obtaining accurate molecular-based equations of state for fluids composed of chainlike molecules.<sup>1-8</sup> Accurate equations of state for chain fluids are of obvious practical importance in the design of processes in the petroleum and natural gas industry; molecular-based equations offer the advantage that they are expected to be accurate beyond the range of conditions where they have been tested or their parameters have been fit to data. Partly because of the practical importance and partly because of the challenge they offer to the theorist, chain molecule fluids have been extensively studied in recent years and several equations of state have been developed using mean field arguments,<sup>1,6</sup> integral equations,<sup>2,4,7</sup> and geometric arguments.<sup>8</sup>

Much effort has been focused on simple models of chain fluids. Study of simple models enables one to obtain a better understanding of the physics of complex chain fluids; more realistic interactions may then be incorporated once the simple models are well understood. The advances in computer simulation of molecular fluids in recent years, of course, allows one to directly test the approximations against "exact" simulation results. A popular model for polymers has been the freely-jointed hard chain, and several equations of state for this model are now available.<sup>1-8</sup> The freely-jointed hard chain model includes the most essential features of chain molecules, i.e., their flexibility and large-scale asymmetry; other interactions such as attractions may be added on as perturbations to this model. In that sense, the hard chain model is expected to play the same role in the study of chain fluids as the hard sphere model has played in the study of simple fluids.

A successful class of hard chain equations of state are those derived using mean field arguments.<sup>1,6</sup> These equations generally relate the properties of the chain molecule fluid to properties of fluids composed of smaller molecules such as monomers or dimers. Mean field theories are generally quite accurate, especially at high densities where the approximations become meaningful. At low densities, however, their performance tends to be somewhat less satisfactory than at high densities.

In this paper, we investigate the low-density PVT behavior of freely-jointed hard chain fluids by using Monte Carlo integration to evaluate the second virial coefficient. The second virial coefficient becomes equivalent to the osmotic second virial coefficient of a polymer solution if, in the context of the McMillan-Mayer theory,<sup>9</sup> one interprets the site interactions as the solvent-mediated potential of mean force. Chain lengths ranging from  $n = 3$  to  $n = 128$  are studied. Several investigations of the second virial coefficient of polymers have been reported in the literature, via both theory<sup>10-18</sup> and numerical calculations.<sup>19-26</sup> Since the numerical calculations have been restricted to lattice models of polymers, we investigate an off-lattice model of polymers. One objective of this work is to test the behavior of various hard chain equations of state in the limit of very low density. Another objective is to try and improve the low-density behavior of the mean-field equations of state by including information about the second virial coefficient. We also investigate the scaling behavior of the second virial coefficient as a function of chain length, which has been of considerable interest in recent years.<sup>24,27</sup>

We find that, for large chain lengths, the variation of the second virial coefficient,  $B_2$ , with  $n$  approaches a power law behavior, as expected from scaling theory. Fitting a straight line through the  $\ln(B_2/n^2)$  vs  $\ln(n-1)$  data for the chain lengths studied here suggests a power law exponent of  $-0.337 \pm 0.007$ , which is considerably lower than the scaling prediction<sup>10,15</sup> of  $\sim -0.2$  to  $-0.25$ . However, if we plot  $d[\ln(B_2/n^2)]/d[\ln(n-1)]$  vs  $1/n$  and extrapolate to  $1/n \rightarrow 0$ , we obtain a power law exponent of  $-0.25 \pm 0.02$  which, within errors, is consistent with scaling predictions.<sup>10,15</sup> This suggests that the prediction of scaling theory for the power law exponent is accurate, but only in the limit of very large  $n$ . In other words, as far as the virial coefficient is concerned, a chain length as high as 128 is certainly not in the scaling regime.

We test  $B_2$  predictions of the generalized Flory dimer (GF-D) equation of state of Honnell and Hall<sup>6</sup> and the first- (TPT1) and second- (TPT2) order thermodynamic perturbation theories of Wertheim.<sup>2</sup> All of the above equations of state predict that  $B_2$  scales as  $n^2$  for large  $n$  and therefore considerably overestimate  $B_2$  for  $n$  greater than  $\sim 10$ . A low-density correction is incorporated into the GF-D theory by forcing it to reproduce the second virial coefficient obtained via the Monte Carlo calculation; this significantly improves the GF-D predictions for the

\* Author to whom correspondence should be addressed. Present address: Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801.

† The North Carolina State University.

‡ Phillips Petroleum Co.

compressibility factor at low densities.

The rest of this paper is organized as follows: in section 2 we describe the Monte Carlo calculations; in section 3 we present results for  $B_2$ , discuss the scaling with chain length, and modify the GF-D theory; and in section 4 we summarize our results and present our conclusions.

## 2. Monte Carlo Method

The virial expansion for the compressibility factor takes the form<sup>28</sup>

$$\beta P/\rho = 1 + B_2\rho + B_3\rho^2 + \dots \quad (1)$$

where  $P$  is the pressure,  $\rho$  is the molecular number density of the fluid,  $B_2$  and  $B_3$  are the second and third virial coefficients, respectively,  $\beta = 1/k_B T$ ,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature.

The second virial coefficient,  $B_2$ , may be evaluated from<sup>29</sup>

$$B_2 = -\frac{1}{2} \int \exp[-\beta u_1(\Omega_1) - \beta u_2(\Omega_2)] f_{12}(\mathbf{r}, \Omega_1, \Omega_2) d\mathbf{r} d\Omega_1 d\Omega_2 \quad (2)$$

where  $u_1$  and  $u_2$  are the intramolecular potentials of polymer molecules 1 and 2

$$f_{12}(\mathbf{r}, \Omega_1, \Omega_2) = \exp(-\beta u(1,2)) - 1 \quad (3)$$

is the Mayer  $f$  function,  $u(1,2)$  is the intermolecular pair potential, and  $\int \dots d\Omega$  represents an integration over all orientations, normalized so that  $\int \dots d\Omega = 1$ .

For hard chains, configurations with intramolecular overlap make no contribution to the virial coefficient, and this results in

$$B_2 = -\frac{1}{2} \langle f_{12} \rangle \quad (4)$$

where the average is over all configurations of both molecules without intramolecular overlap and over all relative distances and relative orientations. For hard chains, the  $f$  function takes on a value of  $-1$  if the two molecules overlap and a value of  $0$  if the two molecules do not overlap, and the calculation of  $B_2$  thus effectively reduces to evaluating the volume of overlap of two chains averaged over all possible configurations. We use two different but statistically equivalent methods, methods A and B, to evaluate  $B_2$ . These are described separately below.

**Method A.** In this approach,  $N_p$  completely independent chain conformations are first generated. For a chain length of  $n < 64$  we generate these conformations via self-avoiding random walks, and for longer chains we use a dimerization procedure.<sup>30</sup> A pair of chains is then selected. One of the pair is placed with its center of mass in the center of a cubic box of side length,  $L$ ; the center of mass of the other is placed  $N_c$  times at random positions in the box, and at a random orientation relative to the first chain. The average value of the  $f$  function is calculated over these  $N_c$  attempts. The process is repeated for all pairs of chains from the initial ensemble of  $N_p$  chains, and the average value of the  $f$  function is calculated. The total number of independent chain configurations is therefore  $N_p(N_p - 1)N_c/2$ . In this work we use  $N_p = 100 - 500$ ,  $N_c = 1000$ , and  $L$  is chosen so that it is larger than twice the maximum span of the pair of chains begin considered. To obtain statistical errors, the process is repeated five times. Errors are reported as the standard deviation of the average value of  $B_2$  in each run about the average value of  $B_2$  over all runs.

**Method B.** In this approach, two chains grown by self-avoiding random walks are placed in a box. The chains

**Table I**  
Values of  $B_2^*$  Obtained via Monte Carlo Calculation

$n$	method A	method B
2	$5.70 \pm 0.001$	$5.70 \pm 0.06$
3	$10.32 \pm 0.40$	$10.34 \pm 0.19$
4	$15.82 \pm 0.01$	$15.75 \pm 0.28$
6	$29.46 \pm 0.21$	$29.63 \pm 0.44$
8	$45.96 \pm 0.08$	$45.95 \pm 0.46$
12	$87.58 \pm 0.15$	$87.46 \pm 1.35$
16	$139.43 \pm 0.40$	$139.39 \pm 0.28$
20	$200.57 \pm 0.24$	$200.13 \pm 3.94$
24	$271.62 \pm 3.47$	$269.11 \pm 3.06$
32	$436.66 \pm 1.44$	$438.16 \pm 4.14$
64	$1408.5 \pm 8.2$	$1435.1 \pm 112.6$
128	$4619.9 \pm 112.7$	$4575.1 \pm 292.7$

<sup>a</sup> In units of the cube of the hard site diameter.

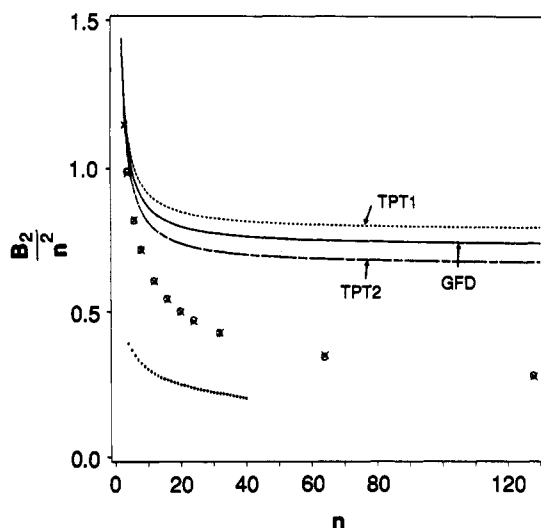
are moved around independently of each other using the Metropolis recipe<sup>31</sup> (applied only to intramolecular interactions); the "translation-jiggling" move of Dickman and Hall<sup>5</sup> is used to move the chains. Periodic boundary conditions are employed in all directions. After a certain number of attempted moves the system is checked for overlap between the two chains; the average value of the  $f$  function is thus obtained. Generally each chain is moved about 5 million times in each run, and overlap between the two chains is checked about once every 20 attempted moves. Five independent runs, each starting with new chain conformations, are performed and errors are reported as the standard deviation of the average value of  $B_2$  in each run about the average value of  $B_2$  over all runs.

Both the methods described above are equivalent and should give the same results for the virial coefficient. Method A has the advantage that all the configurations are completely independent. Method B has the advantage that more configurations are averaged over, although many of these configurations are correlated. Method A is more computationally intensive and the calculation for  $n = 128$  ( $N_p = 100$ ) took about 11 days on a DecStation 3100 workstation. Both method A and method B reproduce accurately the second virial coefficient for tangent diatomics, which is known exactly.<sup>32</sup>

## 3. Results and Discussion

**A. Numerical Results for the Second Virial Coefficient.** In Table I we report numerical values for the second virial coefficient,  $B_2$ , obtained via both methods described earlier, for chain lengths ranging from  $n = 2$  to  $n = 128$ . Here we are working in dimensionless units where the virial coefficient is scaled by the cube of the hard site diameter. The values of the second virial coefficient obtained via the two methods are in good agreement with each other and are within each other's error bars in all cases. The agreement between the two methods gives us confidence in our calculation. The calculations for  $n = 2$  are in excellent agreement with the exact result,  $B_2 = 5.70086$ .<sup>32</sup> Since the data using method A have much smaller error margins (when compared to the data from method B), in the analysis presented in the rest of this paper we will use only these data, i.e., column 2 of Table I.

In Figure 1 we compare the calculated second virial coefficients (we plot  $B_2/n^2$  vs  $n$  for convenience) to the predictions of the generalized Flory dimer theory of Honnell and Hall<sup>6</sup> and the first- and second-order thermodynamic perturbation theory of Wertheim.<sup>2</sup> Other equations of state recently proposed by Chapman et al.,<sup>3</sup> Chiew,<sup>7</sup> and Boublik et al.<sup>8</sup> yield predictions for  $B_2$  identical to TPT1. We see that all the theories are fairly accurate for



**Figure 1.** Comparison of  $B_2/n^2$  from lattice calculations (\*) of Bellemans and Janssens<sup>19</sup> and off-lattice calculations using method A (O) and method B (X) of this work to predictions of the GF-D theory (—),<sup>6</sup> and the first-order (---) and second-order (···) thermodynamic perturbation theories.<sup>2</sup>

small chain lengths but tend to considerably overestimate the value of the virial coefficient as the chain length is increased. This is consistent with the observation that the above equations of state tend to overestimate the pressure at low densities; the errors in the theories are particularly apparent when we look at the second virial coefficient. For large  $n$  all the theories predict that  $B_2 \sim n^2$ ; this scaling is also predicted by the lattice-based theories of Flory,<sup>33</sup> Huggins,<sup>34</sup> and Bawendi and Freed.<sup>35</sup> We will discuss the large  $n$  behavior in more detail shortly. Also shown in the figure are the Monte Carlo calculations for lattice chains reported by Bellemans and Janssens.<sup>19</sup> We see that the second virial coefficient of the lattice model of polymer is always lower than that of the off-lattice model. The lattice model also shows a faster approach to scaling; i.e., the  $B_2$  vs  $n$  curve seems to settle down faster than the off-lattice model. The qualitative trends are similar, however, in both the lattice and the off-lattice models.

**B. Scaling of the Second Virial Coefficient with Chain Length.** For large  $n$  one might expect the second virial coefficient to obey a power law in  $(n-1)$ .<sup>36</sup> This power law behavior is generally expressed as

$$B_2/n^2 \sim (n-1)^{-\gamma} \quad (5)$$

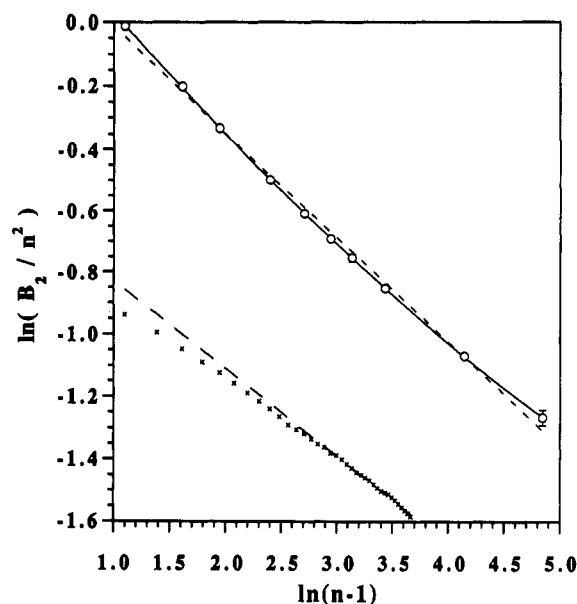
where  $\gamma$  is the scaling exponent and  $(n-1)$  is the number of segments in the polymer. A simple expression for the power law behavior may be derived using scaling theory. In the limit of large  $n$  and in good solvents, monomeric contacts between two chains will be strongly disfavored, and the chains will effectively behave as hard spheres toward each other.<sup>36</sup> If the diameter of these hard spheres is characterized by some global polymer dimension such as the root mean square end-to-end distance,  $R_F$ , then  $B_2 \sim R_F^3$ . Since  $R_F$  exhibits the power law behavior<sup>36</sup>

$$R_F \sim (n-1)^\nu \quad (6)$$

we have (for large  $n$ )

$$B_2/n^2 \sim (n-1)^{3\nu-2} \quad (7)$$

or  $\gamma = 2 - 3\nu$ . The value of  $\gamma$  may be obtained from various estimates for  $\nu$ : the Flory value<sup>29</sup> for  $\nu (=0.6)$  gives  $\gamma = 0.2$ ; the des Cloizeaux value<sup>10</sup> for  $\nu (=0.592)$  gives  $\gamma = 0.224$ ; the Oono-Freed value<sup>12</sup> for  $\nu (=0.5833)$  gives  $\gamma = 0.25$ ; the generally accepted simulation value<sup>24</sup> of  $\nu = 0.588$  gives  $\gamma = 0.236$ .



**Figure 2.** Variation of  $\ln(B_2/n^2)$  with  $\ln(n-1)$ . Symbols are from Monte Carlo calculations of off-lattice (O) chains (this work) and lattice (X) chains.<sup>19</sup> Lines are least squares fits to data: linear fit to all off-lattice data points (---), quadratic fit to all off-lattice data points (—), and linear fit to lattice data points for  $n \geq 20$  (---).

These values for  $\gamma$  are not, however, consistent with Monte Carlo estimates for  $\gamma$  obtained via lattice simulations that have been reported in the literature.<sup>19,21</sup> For example, Bellemans and Janssens<sup>19</sup> reported  $\gamma = 0.28 \pm 0.005$  and Olaj and Lantschbauer<sup>21</sup> reported  $\gamma \approx 0.33$ . These values are significantly higher than the scaling result, i.e.,  $0.2 \leq \gamma \leq 0.25$ . It has been suggested that these Monte Carlo estimates might be misleading due to logarithmic corrections to scaling.<sup>22</sup> Also, Bellemans and Janssens<sup>19</sup> studied fairly short chains,  $n \leq 40$ .

We calculate the scaling exponent from our Monte Carlo calculations. Equation 5 may be written as

$$\ln(B_2/n^2) = -\gamma \ln(n-1) + \text{constant} \quad (8)$$

and  $\gamma$  may be estimated from the slope of a  $\ln(B_2/n^2)$  vs  $\ln(n-1)$  curve if the data for  $B_2$  are in the scaling regime. If, however, the chain lengths we have considered ( $n \leq 128$ ) are not in the scaling regime, we would expect the  $\gamma$  in eq 8 to be a function of  $n$  and to approach the scaling value in the limit of infinite  $n$ . In this case it is more appropriate to differentiate eq 8 with respect to  $\ln(n-1)$  and write

$$-\gamma(n) = d \ln(B_2/n^2) / d \ln(n-1) \quad (9)$$

$$\gamma = \lim_{n \rightarrow \infty} \gamma(n) \quad (10)$$

where  $\gamma(n)$  is the local slope of the  $\ln(B_2/n^2)$  vs  $\ln(n-1)$  curve. We analyze the data using both the methods discussed above.

In Figure 2 we plot  $\ln(B_2/n^2)$  vs  $\ln(n-1)$  for both the off-lattice simulations of this work (from method A) and the lattice simulations of Bellemans and Janssens.<sup>19</sup> Also depicted are least squares linear and quadratic fits to the off-lattice simulation results, and a least squares linear fit to the lattice simulation results for  $n \geq 20$ . A straight line fits both the off-lattice and the lattice simulation data reasonably well. The quadratic fits the off-lattice simulation results extremely well. Clearly, any smooth line drawn through the off-lattice simulation results will not

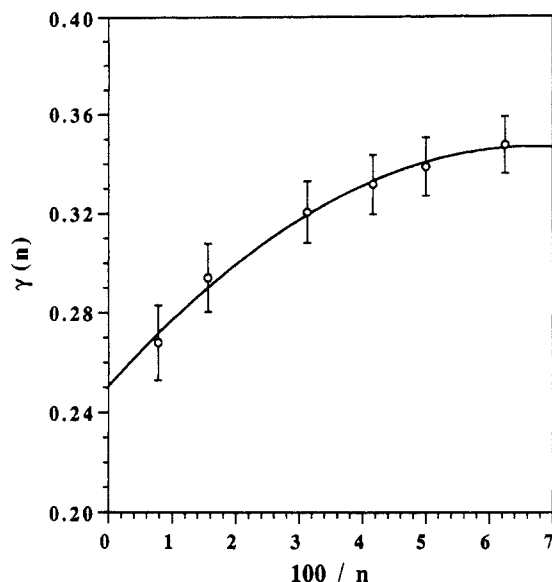


Figure 3. Variation of  $\gamma(n)$  with inverse chain length for off-lattice chains obtained from Monte Calculations (O). The line is a least squares quadratic fit to the data.

have constant slope even for the largest  $n$  values displayed; the lattice simulations, on the other hand, seem to have constant slope for  $n \geq 20$ . We can conclude that the lattice simulations approach the scaling limit faster than the off-lattice simulations.

A straight line fit to the off-lattice data gives a  $\gamma$  value of  $0.337 \pm 0.007$ , which is consistent with the lattice calculations of Olaj and Lantschbauer.<sup>21</sup> However, the curvature in the plot in Figure 2 suggests that the data are *not* in the scaling regime, but rather in a crossover regime. Therefore, one expects the scaling exponent for large  $n$  to be different from the above value of  $\gamma \approx 0.337$ .

To estimate the limiting value of  $\gamma$  as  $n \rightarrow \infty$ , we need to calculate the local slope of the curve in Figure 2 for all the data points shown. Differentiating discrete data (especially data separated by large intervals) is generally quite difficult, so instead we fit a polynomial to the simulation data in Figure 2 and differentiate this polynomial. In fitting a polynomial there is a trade-off: as we increase the order of the polynomial we get a better fit, but also a greater uncertainty in the coefficients and hence in the slope,  $\gamma(n)$ . The curve in Figure 2 is, however, quite smooth and suggests that a low-order polynomial might be sufficient. In fact, the off-lattice data are quite well represented by a quadratic polynomial. We therefore fit a quadratic to the off-lattice data for  $n \geq 16$  (since we are interested in the  $n \rightarrow \infty$  limit we ignore the data for smaller  $n$ ) and differentiate this polynomial to obtain  $\gamma(n)$  at the values of  $n$  where we have Monte Carlo results. In performing the fit to the  $\ln(B_2/n^2)$  vs  $\ln(n-1)$  curve, we find that including the statistical errors in the simulation data into the fitting procedure tends to weight the data for small  $n$  more than the data for large  $n$  (since errors are smaller for small  $n$ ). On the other hand, since we will eventually extrapolate the slope of this curve to infinite  $n$ , we would like to weight the large  $n$  data more since these data points are closer to the scaling regime. We therefore perform the fit without taking the statistical simulation errors into account (thus weighting all points equally) and obtain estimates for the errors in the fitted polynomial function from the covariance matrix of the fitted parameters and the goodness of the fit.

In Figure 3 we plot the calculated values of  $\gamma(n)$  vs  $100/n$ . Clearly,  $\gamma(n)$  is a decreasing function of  $n$ ; in fact it is

a rather slowly increasing function of  $1/n$ . This is consistent with the observation that there are logarithmic corrections to scaling for finite  $n$ .<sup>24,27</sup> Also shown in the figure is a quadratic polynomial fit to  $\gamma(n)$ . Extrapolating to  $100/n = 0$ , we find that

$$\gamma = \lim_{n \rightarrow \infty} \gamma(n) \approx 0.25 \pm 0.02 \quad (11)$$

where the uncertainty in the exponent is obtained from the uncertainty in the zeroth-order coefficient of the polynomial that is fit to the  $\gamma(n)$  vs  $1/n$  curve (here the errors in the  $\gamma(n)$  themselves are considered in fitting the polynomial). This value is consistent with the scaling predictions<sup>10,12</sup> and corresponds to a value of  $\nu = 0.583 \pm 0.007$ .

If we repeat the above procedure taking the statistical errors in the simulation data into account, we obtain an exponent of  $\gamma \approx 0.24 \pm 0.09$ , which is consistent with the exponent estimated above, although the uncertainty is much larger.

### C. Low-Density Correction for the GF-D Equation.

It has been found that the GF-D equation of state is very accurate for the pressure at high densities but tends to overestimate the pressure at low densities, especially for long chains.<sup>6</sup> This is probably because the predictions of the GF-D equation for the second virial coefficient are not very good (due to a breakdown in the mean field approximations), and get worse as the chain length is increased. An obvious way to modify the GF-D equation to improve its performance is to incorporate a low-density correction by including knowledge of the second virial coefficient. We include this correction by subtracting the second virial coefficient predicted by the GF-D equation from the GF-D equation, and adding on the "correct" second virial coefficient obtained via the Monte Carlo calculation. The new compressibility factor prediction is given by

$$Z = Z_{\text{GF-D}} + (B_{2,\text{MC}} - B_{2,\text{GF-D}})\rho \quad (12)$$

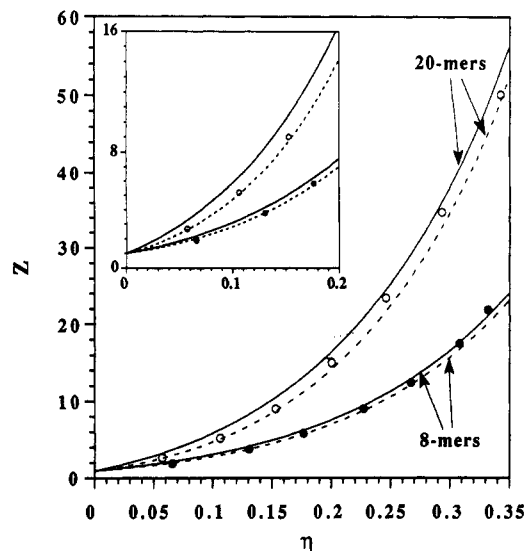
where  $Z$  is the compressibility factor, and the subscript MC refers to Monte Carlo; i.e.,  $B_{2,\text{MC}}$  is obtained from Table I. The second virial coefficient predicted by the GF-D equation<sup>6</sup> is

$$B_{2,\text{GF-D}} = n(2.85726 + 0.730458(n-2)) \quad (13)$$

which is valid for  $n \geq 3$ , and scales as  $n^2$  for large  $n$ .

We find that including the correction as above significantly improves the low-density performance of the GF-D equation. In Figure 4 we compare the low-density compressibility factor predictions of the GF-D equation with and without the second virial coefficient correction to simulation data of Dickman and Hall<sup>5</sup> for 8-mers and Yethiraj and Hall for 20-mers.<sup>37</sup> Here  $\eta$  represents the volume fraction of the chains,  $\eta = \rho n \pi \sigma^3 / 6$ . The improvement in the GF-D predictions is particularly significant for the 20-mers; this was to be expected because the GF-D predictions for  $B_2$  are quite poor for  $n \geq 10$  (see Figure 1). For 8-mers the correction results in poorer predictions for the compressibility factor at high densities, tending to underestimate the value of the compressibility factor for  $\eta$  greater than about 0.3. We have observed a similar trend in composition with 16-mer fluids. For 20-mers, however, the correction does not worsen the GF-D predictions at higher densities, at least up to  $\eta = 0.35$  (the highest density for which simulation results are available).

It is of practical interest to obtain a closed-form expression for  $B_2$  which may be used to modify hard chain equations of state. Therefore, we fit the Monte Carlo data to a functional form. It is difficult to fit the data for all



**Figure 4.** Comparison of GF-D theory predictions for the compressibility factor without the low-density correction (—) and with the low-density correction (---) to Monte Carlo simulation data for 8-mers<sup>8</sup> and 20-mers.<sup>37</sup> The inset shows the low-density behavior.

$n$  to the same functional form, so we concentrate on  $n \geq 12$ ; this is reasonable, since the virial coefficient predicted by the GF-D theory is fairly accurate for  $n < 12$ . We use a functional form similar to that derived by Kosmas and Kosmas,<sup>17</sup> and the final result is

$$B_2 = \frac{n^2}{(1.240\sqrt{n-1} - 1.408)^{1/2}} \quad (14)$$

Clearly eq 14 is not valid for small  $n$ . The  $B_2$  values given by eq 14 differ from the Monte Carlo values by about 4.6% for  $n = 6$ , by 1.8% for  $n = 8$ , and by less than 0.5% for  $12 \leq n \leq 128$ . Equation 14 has the correct scaling relationship (as observed in our Monte Carlo calculations) for large  $n$ .

#### 4. Summary and Conclusions

The second virial coefficient of off-lattice polymers is obtained via a Monte Carlo calculation. The polymer molecules are modeled as a pearl necklace of freely-jointed hard spheres; chain lengths ranging from 3 to 128 are studied.

We find that, for large  $n$ , the second virial coefficient,  $B_2$ , scales as  $B_2/n^2 \sim n^{-\gamma}$  where  $\gamma = 0.25 \pm 0.02$ . This result is consistent with the scaling theory prediction of  $\gamma \approx 0.23$ ,<sup>10</sup> but not consistent with lattice simulations which reported values of  $\gamma = 0.28$ <sup>19</sup> and  $0.33$ .<sup>21</sup> We believe that the higher values of  $\gamma$  reported in earlier simulations are probably because the slow approach to scaling of these model systems was not taken into account. We therefore verify that there are significant corrections to scaling for finite  $n$ .

The second virial coefficient predictions of various theories for hard chains are tested against the Monte Carlo data. It is found that all the analytical equations of state examined here yield the wrong scaling exponent for  $B_2$  and significantly overestimate the value of the second vir-

ial coefficient for chains with  $n \geq 10$ . A low-density correction is incorporated into the GF-D theory by forcing it to reproduce the second virial coefficient obtained via the Monte Carlo calculation; this results in a significant improvement in the GF-D predictions for the compressibility factor at low densities but decreases the accuracy of the GF-D theory at high densities.

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