

# Equation of state and critical behavior of polymer models: A quantitative comparison between Wertheim's thermodynamic perturbation theory and computer simulations

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We present an application of Wertheim's thermodynamic perturbation theory (TPT1) to a simple coarse grained model made of flexibly bonded Lennard-Jones monomers. We use both the reference hypernetted chain (RHNC) and mean spherical approximation (MSA) integral equation theories to describe the properties of the reference fluid. The equation of state, the density dependence of the excess chemical potential, and the critical points of the liquid-vapor transition are compared with simulation results and good agreement is found. The RHNC version is somewhat more accurate, while the MSA version has the advantage of being almost analytic. We analyze the scaling behavior of the critical point of chain fluids according to TPT1 and find it to reproduce the mean field exponents: The critical monomer density is predicted to vanish as  $n^{-1/2}$  upon increasing the chain length  $n$  while the critical temperature is predicted to reach an asymptotic finite temperature that is attained as  $n^{-1/2}$ . The predicted asymptotic finite critical temperature obtained from the RHNC and MSA versions of TPT1 is found to be in good agreement with the  $\Theta$  point of our polymer model as obtained from the temperature dependence of the single chain conformations. © 2000 American Institute of Physics. [S0021-9606(00)50725-9]

## I. INTRODUCTION

For a long time, the prediction of the equation of state of polymers from first principles was such a difficult task that it could not be solved without very idealized models with more or less meaningful empirical parameters. Perhaps the most successful of the early attempts was that of Prigogine,<sup>1</sup> who considered a lattice and introduced an ad-hoc empirical parameter known as the "number of degrees of freedom per monomer." Later on, Flory, Orwoll, and Vrij (FOVE)<sup>2-4</sup> extended this theory to the continuum at the cost of introducing some additional parameters, leading to what is now known as the FOVE theory. Another approach to the problem is based on the polymer+solvent and polymer+vacuum analogy. In this way, the well known Flory-Huggins<sup>5,6</sup> (FH) and Sanchez-Lacombe<sup>7</sup> equations of state have also been employed to describe the behavior of pure fluids.

On the other hand, the approach from liquid state theory has taken much longer to yield useful results, but has now reached a point where a rather satisfactory description of the equation of state of idealized polymer models in the continuum is affordable without the need for any empirical pa-

rameters whatsoever. The most popular approaches are the polymer reference interaction site model (PRISM) of Curro and Schweizer,<sup>8</sup> the generalized dimer Flory theory (GDF) of Honnell and Hall,<sup>9</sup> and the thermodynamic perturbation theory of Wertheim (TPT1).<sup>10</sup> The latter has been widely used not only because it yields results that are of similar or superior quality than other alternatives, but because it is the simplest and most tractable of all them and demands a minimum of information.

Originally, this theory was developed to consider fluids of associating hard spheres.<sup>11-14</sup> Later on, it was realized that in the limit of infinite associating strength, a polydisperse mixture of polymers was recovered.<sup>10</sup> Chapman, Jackson, and Gubbins extended the theory to monodisperse polymer fluids and rewrote the equations in a very convenient notation.<sup>15</sup> Later, by adding a mean field perturbative contribution, Jackson and Sears showed that the theory was able to describe the behavior of very different sorts of real fluids.<sup>16</sup> Meanwhile, it was realized that the theory could be used just as well to consider polymers made of attractive monomers.<sup>17,18</sup> In this way, it is possible to describe real fluids with improved accuracy with no need for a mean-field-like perturbation. Since then, the theory has achieved enormous popularity and has been applied to describe polymers

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of tangent Lennard-Jones beads<sup>19–22</sup> and square wells,<sup>23,24</sup> as well as to describe real fluids in chemical engineering applications.<sup>25–27</sup> Furthermore, modifications of the original theory have been proposed that allow one to describe realistic polymer models without the need for empirical parameters.<sup>28,29</sup>

A very interesting issue both from the practical and theoretical point of view is the behavior of the critical point of polymer fluids as the number of monomers increases. By invoking the polymer+solvent and polymer+vacuum analogy, one would expect from the FH theory that the pure polymer fluid should reach an asymptotic critical temperature, whereas the critical mass density should become vanishingly small. However, in a recent paper, Chatterjee and Schweizer<sup>30</sup> have pointed out that this analogy cannot be taken for granted because polymer+solvent criticality involves concentration fluctuations, while polymer+vacuum criticality involves total density fluctuations.<sup>31</sup>

On the other hand, based on a rather limited amount of data, several empirical correlations have been employed to predict the critical properties of substances such as polymethylene.<sup>32–35</sup> These correlations have predicted widely different behavior, ranging from infinite critical temperature<sup>35</sup> to finite asymptotic critical mass density.<sup>32,34,35</sup> More soundly based equations such as the FOVE have recently been employed to support the idea that the critical mass density could reach an asymptotic constant value.<sup>33</sup> However, such an approach relies on extending the applicability of the FOVE theory to densities below which it was not meant to be used.<sup>2</sup>

Renormalization group calculations, however, show that the FH mean field theory yields the correct asymptotic dependence in the long chain length limit,<sup>36,37</sup> albeit this asymptotic behavior is only reached for extremely long chains and the corrections to scaling are enormous even for typical chain length considered experimentally.<sup>38</sup>

More recently, new experimental techniques have allowed one to measure the critical points of longer *n*-alkanes whose critical temperature lies above the point where thermal decomposition starts.<sup>39–41</sup> These experiments show that the critical mass density reaches a maximum and then starts to decrease.<sup>39</sup> Simulation results of both realistic alkanes<sup>42</sup> and idealized polymer models<sup>43,44</sup> give support to this finding.

Surprisingly, very little attention has been devoted to the study of this problem from the point of view of the modern theories such as PRISM, GDF, or TPT1. In a recent paper, the PRISM was employed in an attempt to solve the question in the framework of an analytical tractable theory, leading to different predictions depending on the closure employed to solve the PRISM equation.<sup>30</sup> Other previous studies using TPT1 plus a mean field attractive contribution suggested that the critical mass density should vanish in the infinite chain length limit.<sup>45</sup> However, such a conclusion relied on the assumption that the mean field contribution increases linearly with the chain length, a point which at present cannot be taken for granted. Nikitin and co-workers<sup>41,46</sup> have recently presented a theory that may be considered as the simplest

possible approximation to Wertheim's theory and arrive at the same conclusion as in Ref. 45.

In this paper we will try to reach further understanding of this issue. In Sec. II, we will review the fundamentals of Wertheim's theory by using somewhat different but more physically appealing arguments suggested by Zhou and Stell.<sup>47</sup> We will then show by means of general arguments how the scaling laws for the critical properties are closely related to the virial coefficients (Sec. III). We will then apply TPT1 to a polymer model and briefly describe how to implement the theory in Sec. IV and in the Appendixes. Section V describes the details of the simulations performed to test the theory. We then devote Sec. VI to presenting our results and close with a brief conclusion.

## II. EQUATION OF STATE OF POLYMERS

### A. Preliminary definitions

We consider a monodisperse fluid of polymers made up of *n* monomers each. Nonbonded monomers of the same polymer and monomers belonging to different molecules interact through some pair potential,  $u_0$ , while adjacent monomers of the same molecule have an additional bonding potential,  $\Phi$ , responsible for the connectivity of the polymer. This potential is such that its action vanishes beyond some well defined interatomic distance. If eventually, two adjacent monomers were found outside this range, they would no longer be bonded and the *n*-mer would be considered to have broken. In practice, this can be avoided by making the well depth of the associating potential infinitely large.

Alternatively, we may consider an associating multicomponent mixture of *n* different monomeric species, *A*, *B*, *C*, etc. Each of these species interacts with members of its own species and with members of the remaining species by means of  $u_0$ . Furthermore, the bonding potential  $\Phi$  is responsible for associating reactions between monomers of type *A* with monomers of type *B*, monomers of type *B* with monomers of type *C*, and so on. More concisely, the association reaction taking place is of the form:



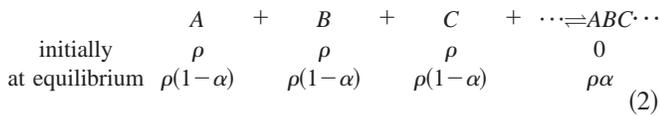
As the bonding potential is pairwise, the only requirement that is needed to define the “ $ABC \dots$ ” complex as an *n*-mer is that each of the adjacent pairs be found within the range of the bonding potential. Clearly, for an equimolar composition of such a mixture in the limit of complete association, we are lead to a system identical to that described in the preceding paragraph. From a physical point of view, this limit is reached for infinite well depths. However, in what follows it will prove useful to consider that the well depth has some arbitrary finite value. The system is then made of a mixture of free monomers and *n*-mers whose composition depends on the nature of the bonding potential.

Considering the similarity between the two systems described, we may get an approximation for the equation of state for the chain molecule by studying the behavior of the associating system. In order to do so, we will obtain an expression for the free energy in terms of the degree of association of the mixture. We will then relate the degree of

association to the structure of the system and introduce some simplifying assumptions for the  $n$ -body correlations. Finally, we will take the limit of complete association and get an equation of state for the chain fluid.

### B. The association reaction

Let us consider an associating system as that described before, which is initially prepared by mixing in equal proportions the pure monomers, so that there are  $N$  monomers of each species inside a volume  $V$  and the resulting number density of each of the species is  $\rho$ . The system will eventually reach a state of equilibrium, whereby a fraction of the monomers of each species has associated to form  $n$ -mers. Let this fraction be  $\alpha$ . Then, the remaining concentration of nonbonded monomers of each species is given by  $\rho(1-\alpha)$ , while, according to the stoichiometry of the reaction, the concentration of  $n$ -mers will be  $\rho\alpha$  (note that in the limit of complete association  $\rho$  will actually designate the polymer number density). Schematically, the process can be described as follows:



Obviously, the number of  $n$ -mers formed is  $V\rho\alpha = N\alpha$ , while the number of remaining free monomers of each species is  $N(1-\alpha)$ . The total Helmholtz free energy of the system,  $A = G - pV$ , is therefore given by

$$A(\alpha) = \sum_{i=1}^n N(1-\alpha)\mu_i(\alpha) + N\alpha\mu_{n\text{-mer}}(\alpha) - p(\alpha)V. \quad (3)$$

In what follows, we associate a number from 1 to  $n$  to each of the  $n$  species. Therefore,  $\mu_i$  stands for the chemical potential of species  $i$  in the mixture of composition given by  $\alpha$ .

It is important to realize that the composition of the mixture as given by the association degree is appropriate to a given model potential. In the above-mentioned expression for the free energy, we have considered a system of monomers that interact through some reference potential,  $u_0$ , while a bonding potential is responsible for the connectivity of the  $n$ -mer. Let us now consider a reference fluid made of monomers that interact through the reference potential but that have no association potential whatsoever. In this case, the free energy is best expressed in terms of the chemical potential of the monomers alone. For the sake of simplicity, we will denote this free energy as  $A(\alpha=0)$ , albeit from a strictly geometrical point of view,  $n$ -mers could form eventually even in the absence of a bonding potential:

$$A(\alpha=0) = \sum_{i=1}^n N\mu_i(\alpha=0) - p(\alpha=0)V. \quad (4)$$

The free energy of the associating system measured relative to that of the reference fluid is then given by

$$\begin{aligned} \frac{\Delta A}{N} &= \sum_{i=1}^n [\mu_i(\alpha) - \mu_i(\alpha=0)] \\ &+ \alpha \left[ \mu_{n\text{-mer}}(\alpha) - \sum_{i=1}^n \mu_i(\alpha) \right] \\ &- [p(\alpha) - p(\alpha=0)] \frac{V}{N}. \end{aligned} \quad (5)$$

This equation can be further simplified by invoking the condition of chemical equilibrium of the associating mixture, which reads

$$\sum_{i=1}^n \mu_i(\alpha) - \mu_{n\text{-mer}}(\alpha) = 0. \quad (6)$$

Substitution of Eq. (6) into Eq. 5 yields

$$\frac{\Delta A}{N} = \sum_{i=1}^n [\mu_i(\alpha) - \mu_i(\alpha=0)] - [p(\alpha) - p(\alpha=0)] \frac{V}{N}. \quad (7)$$

Let us now express the chemical potentials of each of the components in terms of an ideal and an excess contribution:

$$\mu_i(\alpha) = \mu_i^{\text{id}}(\alpha) + \mu_i^{\text{ex}}(\alpha) = \mu_i^0 + kT \ln \rho_i(\alpha) + \mu_i^{\text{ex}}(\alpha). \quad (8)$$

Introducing the above expression for the chemical potential into Eq. (7), we get

$$\begin{aligned} \frac{\Delta A}{N} &= kT \ln \prod_{i=1}^n \frac{\rho_i(\alpha)}{\rho_i(\alpha=0)} + \sum_{i=1}^n [\mu_i^{\text{ex}}(\alpha) - \mu_i^{\text{ex}}(\alpha=0)] \\ &- [p(\alpha) - p(\alpha=0)] \frac{V}{N}. \end{aligned} \quad (9)$$

If we now recall that  $\rho_i(\alpha) = \rho(1-\alpha)$  and  $\rho_i(\alpha=0) = \rho$ , we finally obtain

$$\begin{aligned} \frac{\Delta A}{N} &= nkT \ln(1-\alpha) + \sum_{i=1}^n [\mu_i^{\text{ex}}(\alpha) - \mu_i^{\text{ex}}(\alpha=0)] \\ &- [p(\alpha) - p(\alpha=0)] \frac{V}{N}. \end{aligned} \quad (10)$$

This is an exact equation for the difference in free energy between the associating system (with  $\alpha N$   $n$ -mers) and the reference nonassociating fluid of free monomers. As it stands, it may seem rather useless, because it is a function of the unknown quantities:  $\alpha$ ,  $\mu_i^{\text{ex}}(\alpha)$  and  $p(\alpha)$ . However, we shall see that in the low density limit, Eq. (10) becomes a function of the degree of association only and that this, in turn, may be obtained from knowledge of  $n$ -body correlations in the fluid. In a further approximation, the  $n$ -body correlations of the fluid will be expressed in terms of  $n$ -body correlations of a reference fluid of nonbonded monomers. Finally, by invoking a superposition approximation, we will express the  $n$ -body correlations in terms of two-body correlations and obtain an expression for the pressure that depends solely on known quantities of a reference fluid of spherical particles.

### C. The association reaction in the limit of low density

In the limit of low density, the equation of state of the associating system will depend only on the total number of particles in the fluid,  $N(\alpha)$ :

$$\frac{pV}{kT} = N(\alpha). \quad (11)$$

$N(\alpha)$  is simply obtained by summing the number of particles of each species:

$$N(\alpha) = \sum_{i=1}^n N(1-\alpha) + N\alpha = nN(1-\alpha) + N\alpha. \quad (12)$$

On the other hand, the number of particles of the completely unassociated system is simply  $N(\alpha=0) = nN$ . Therefore, the difference in pressure between the nonbonded system and the system with degree of association  $\alpha$  is

$$\Delta p(\alpha) \frac{V}{N} = -kT\alpha(n-1). \quad (13)$$

By using this expression and considering that, by definition, the excess chemical potentials vanish in the limit of low density, Eq. (10) becomes

$$\frac{\Delta A}{kTN} = n \ln(1-\alpha) + \alpha(n-1). \quad (14)$$

This is an exact equation for the difference in free energy in the limit of low density. Applying the standard thermodynamic relationship connecting the pressure with the free energy yields the exact expression for the difference in pressure in the limit of low density:

$$\frac{\Delta p}{kT\rho} = \rho \frac{\alpha(1-n)-1}{1-\alpha} \frac{\partial \alpha}{\partial \rho}. \quad (15)$$

In what follows, we will consider this expression to be valid in all the density range. The search of an equation of state for the associating system will thus be accomplished if we find an expression for the association degree in terms of known properties. Once this relation has been found, we will obtain an equation of state for the system of  $n$ -mers by taking the limit of complete association, i.e.,  $\alpha = 1$ .

### D. Relation between the degree of association and the structure of the fluid

#### 1. Expression for the degree of association in terms of the excess chemical potential of the components

First, consider the equilibrium constant of the reaction, defined as the ratio of the concentration of the products to that of the reactants:

$$K = \frac{\alpha\rho}{(1-\alpha)^n \rho^n}. \quad (16)$$

The connection of the equilibrium constant to the thermodynamics of the process may be obtained by expressing the chemical potential of each of the components as in Eq. 8 and substituting into the condition of chemical equilibrium,

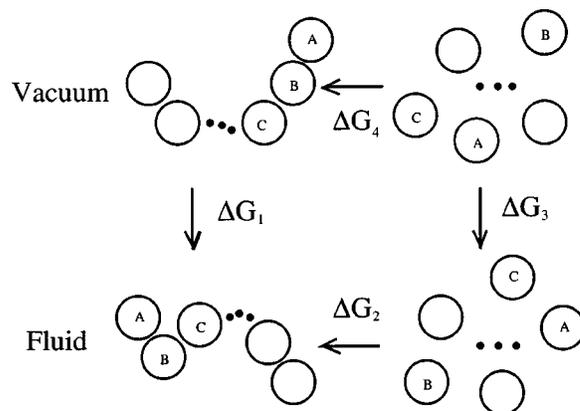


FIG. 1. Relating the structure of the fluid to the excess chemical potential of the components by means of a thermodynamic cycle.

Eq. (6). After some simple algebraic manipulations, we are lead to the following expression for the equilibrium constant:

$$kT \ln K + \mu_{n\text{-mer}}^0 - \sum_{i=1}^n \mu_i^0 + \mu_{n\text{-mer}}^{\text{ex}}(\alpha) - \sum_{i=1}^n \mu_i^{\text{ex}}(\alpha) = 0. \quad (17)$$

This expression may be further simplified by considering that, in the limit of low densities, the excess chemical potentials vanish. As a consequence of this, the low density equilibrium constant,  $K_0$ , is given as follows:

$$kT \ln K_0 = \sum_{i=1}^n \mu_i^0 - \mu_{n\text{-mer}}^0. \quad (18)$$

Substitution of this expression into Eq. (17), leads finally to a simple equation for the equilibrium constant in terms of the excess chemical potential of the components of the mixture:

$$kT \ln \frac{K}{K_0} = \sum_{i=1}^n \mu_i^{\text{ex}}(\alpha) - \mu_{n\text{-mer}}^{\text{ex}}(\alpha). \quad (19)$$

#### 2. Expression for the structure of the fluid in terms of the excess chemical potential of the components

In order to relate the structure of the fluid to the excess chemical potential of the components of the mixture, (i.e., A, B, C, etc., monomers and  $n$ -mers), let us consider the thermodynamic cycle of Fig. 1.

In the first step of the cycle, an isolated  $n$ -mer is dissolved into a fluid mixture with association degree  $\alpha$ . Initially, the total Gibbs free energy of the system is the sum of the free energy of the isolated  $n$ -mer,  $G_{n\text{-mer}}$  and the free energy of the mixture,  $G_{\text{mix}}(\alpha)$ . After dissolving the  $n$ -mer, the resulting free energy is that of the original mixture with an extra  $n$ -mer,  $G_{\text{mix}+n\text{-mer}}$ . The change in  $G$  is therefore:

$$\Delta G_1 = G_{\text{mix}+n\text{-mer}} - G_{\text{mix}} - G_{n\text{-mer}}. \quad (20)$$

In the thermodynamic limit, the difference  $G_{\text{mix}+n\text{-mer}} - G_{\text{mix}}$  becomes equal to the chemical potential of the  $n$ -mer in the mixture, while  $G_{n\text{-mer}}$  may be considered to be the chemical potential of the isolated  $n$ -mer (i.e., the free energy difference between a system with a single  $n$ -mer and an empty system). It is thus seen that

$$\Delta G_1 = \mu_{n\text{-mer}}^{\text{ex}}(\alpha). \quad (21)$$

In a second step,  $n$  uncorrelated monomers of type  $A$ ,  $B$ ,  $C$ , etc., dissolved in the mixture are brought together in such a way that the resulting  $ABC\cdots$  complex forms one of the many possible conformers of the  $n$ -mer, say, one such that the vector joining  $B$  to  $A$  is  $\mathbf{r}_{12}$ , that joining  $C$  to  $B$  is  $\mathbf{r}_{23}$ , etc. This event will occur according to a probability density given by the  $n$ -body correlation function of the mixture,  $\rho^n g(\mathbf{r}_{12}, \mathbf{r}_{23}, \dots, \mathbf{r}_{n-1,n})$ . The  $n$ -mer density is given as an integral of this function over all the conformations compatible with the monomer:

$$\rho_{n\text{-mer}} = \rho^n \int_v \cdots \int_v g(\mathbf{r}_{12}, \mathbf{r}_{23}, \dots, \mathbf{r}_{n-1,n}) \times d^3\mathbf{r}_{12} d^3\mathbf{r}_{23} \cdots d^3\mathbf{r}_{n-1,n}, \quad (22)$$

where  $v$  is the volume within the range of the bonding potential, i.e., any two adjacent monomers whose distance vector is not within this volume are not considered to be bonded.

The process of forming the  $n$ -mer from a set of  $n$  uncorrelated monomers may be considered as a chemical reaction of the form

$n$  uncorrelated monomers  $\rightleftharpoons n$  correlated monomers.

Friedman<sup>48</sup> has shown that such an equation is characterized by an equilibrium constant of the form  $K_{\text{eq}} = \rho_{n\text{-mer}}/\rho^n$ . Substitution of Eq. (22) into the expression for the equilibrium constant yields  $K_{\text{eq}} = \rho^n \Delta/\rho^n$ , where

$$\Delta = \int_v \cdots \int_v g(\mathbf{r}_{12}, \mathbf{r}_{23}, \dots, \mathbf{r}_{n-1,n}) d^3\mathbf{r}_{12} d^3\mathbf{r}_{23} \times \cdots d^3\mathbf{r}_{n-1,n}. \quad (23)$$

Now, the free energy of the whole process may be written down as

$$\Delta G = \Delta G_2 + kT \ln K_{\text{eq}}. \quad (24)$$

However, when the system reaches equilibrium,  $\Delta G = 0$ , so that we finally obtain

$$\Delta G_2 = -kT \ln \Delta. \quad (25)$$

Similar arguments to those put through for the first and second steps of the cycle lead to the conclusion that

$$\Delta G_3 = \sum_{i=1}^n \mu_i^{\text{ex}}(\alpha), \quad (26)$$

$$\Delta G_4 = -kT \ln \Delta_0, \quad (27)$$

where  $\Delta_0$  is the integral of Eq. (23) evaluated at zero density.

Substitution of Eqs. (21) and (25)–(27) into the net energy balance of the cycle,  $\Delta G_1 + \Delta G_4 = \Delta G_3 + \Delta G_2$ , leads to the desired equation relating the structure of the fluid with the excess chemical potential of the components of the mixture:

$$kT \ln \frac{\Delta}{\Delta_0} = \sum_{i=1}^n \mu_i^{\text{ex}}(\alpha) - \mu_{n\text{-mer}}^{\text{ex}}(\alpha). \quad (28)$$

A similar equation has been derived in a rather more formal way recently<sup>49</sup> for the particular case of infinitely short ranged association potentials. The derivation we have employed is based on the thermodynamic cycle presented by Zhou and Stell,<sup>47</sup> which allows one to extend their previous result to finite range potentials.

### 3. Expression for the degree of association in terms of the structure of the fluid

Substitution of Eq. (19) into Eq. (28) shows that the equilibrium constant is related to the  $n$ -body correlation function of the associating mixture through

$$\frac{K}{K_0} = \frac{\Delta}{\Delta_0}. \quad (29)$$

Finally, using the expression for  $K$  in terms of the degree of association, Eq. (16), we obtain the desired equation relating the degree of association with the structure of the system:

$$\frac{\alpha}{(1-\alpha)^n \rho^{n-1}} = \frac{K_0}{\Delta_0} \Delta. \quad (30)$$

### E. The equation of state

Previously, we obtained an approximate equation for the pressure in terms of the association degree of the mixture, Eq. (15). The density derivative of the association degree, required in such an expression is obtained from Eq. (30):

$$\frac{\partial \alpha}{\partial \rho} = \frac{1-\alpha}{\rho} \cdot \frac{(n-1)\alpha + \rho \alpha \frac{\partial \ln \Delta}{\partial \rho}}{1 + \alpha(n-1)}. \quad (31)$$

Substitution of this result into Eq. (15) yields an expression for the change in pressure due to the formation of the  $n$ -mers from a fluid of nonassociated monomers. This expression depends solely on the degree of association and the  $n$ -body correlation function of the associating system:

$$\frac{\Delta p}{kT\rho} = -\alpha \left( n-1 + \rho \frac{\partial \ln \Delta}{\partial \rho} \right). \quad (32)$$

By taking the limit of infinite association, which physically corresponds to infinitely increasing the well depth of the bonding potential, we would arrive at an equation for the pressure of the  $n$ -mer fluid relative to that of the monomer reference fluid. In order to do so, however, we would require the  $n$ -body correlation function of the associating system, which enters through  $\Delta$ . Unfortunately, quantitative understanding of such high order correlation functions is far beyond our present knowledge. We will therefore need to make some further approximations in order to get a tractable expression for the pressure.

### 1. Decoupling of the $n$ -body correlations

In order to simplify the problem of the  $n$ -body correlations, we invoke a so-called ‘‘linear’’ decoupling approximation, which attempts to describe the  $n$ -body correlation function in terms of  $n-1$  two-body correlation functions:

$$g^{(n)}(\mathbf{r}_{12}, \mathbf{r}_{23}, \dots, \mathbf{r}_{n-1,n}) = g^{(2)}(\mathbf{r}_{12})g^{(2)}(\mathbf{r}_{23}) \cdots g^{(2)}(\mathbf{r}_{n-1,n}). \quad (33)$$

Here it should be understood that  $g^{(2)}(\mathbf{r}_{12})$  stands for the pair correlation function of monomers of type *A* with monomers of type *B* in the multicomponent mixture of associating monomers,  $g^{(2)}(\mathbf{r}_{23})$  stands for the pair correlation function of monomers of type *B* with monomers of type *C*, and so on. Still, these two-body correlation functions may be quite difficult to obtain. In order to simplify the problem, consider one of these correlation functions, say,  $g^{(2)}(\mathbf{r}_{12})$ , in the limit of zero density:

$$g^{(2)}(\mathbf{r}_{12}; \rho=0) = \exp(-[u_0(\mathbf{r}_{12}) + \Phi(\mathbf{r}_{12})]/kT). \quad (34)$$

It can be seen that, in this limit, the pair correlation function may be exactly expressed in terms of the pair correlation function of a reference system with no bonding potential,  $g_0^{(2)}(\mathbf{r}_{12})$ , times the Boltzmann factor of the bonding potential:

$$g^{(2)}(\mathbf{r}_{12}; \rho=0) = g_0^{(2)}(\mathbf{r}_{12}; \rho=0) \exp(-\Phi(\mathbf{r}_{12})/kT). \quad (35)$$

Using the linear approximation to the *n*-body correlations and considering Eq. (35) to hold true at any density, the  $\Delta$  integral is simplified considerably, giving

$$\Delta = \delta^{n-1}, \quad (36)$$

where  $\delta$  is defined as

$$\delta = \int_v g_0^{(2)}(\mathbf{r}_{12}) \exp(-\Phi(\mathbf{r}_{12})/kT) d^3\mathbf{r}_{12}. \quad (37)$$

## 2. An equation of state for the *n*-mer in terms of the thermodynamics and structure of the monomers

As a consequence of the two approximations given for the *n*-body correlations, we are now able to write down an expression for the pressure of the *n*-mer in terms of the properties of the reference fluid. Indeed, after setting  $\alpha=1$ , substitution of Eq. (36) into Eq. (32) leads finally to the following result:

$$\frac{\Delta p}{kT\rho} = -[n-1] \left[ 1 + \rho \frac{\partial \ln \delta}{\partial \rho} \right]. \quad (38)$$

Note that as we are considering the limit of complete association,  $\rho$  is equal to the polymer number density.

Adding the contribution of the reference system to Eq. (38), we are now able to write down an equation for the compressibility factor,  $Z = p/kT\rho$  of the fluid of *n*-mers:

$$Z_{n\text{-mer}} = nZ_0 - (n-1) \left[ 1 + \rho \frac{\partial \ln \delta}{\partial \rho} \right], \quad (39)$$

where  $Z_0$  is the compressibility factor of the reference fluid, measured at the same monomer density as the *n*-mer fluid. This is a rather remarkable equation, as it gives the equation of state of a chain fluid from the properties of a fluid of monomers alone. Different versions of this equation will arise from the different theories available to describe the structure and thermodynamics of the fluid of monomers. In

Sec. IV we will consider two such theories in order to describe our model polymer. Let us recall at this point, however, that a simple, qualitative version of Eq. (39) may be obtained by simply considering that  $\delta$  does not depend on the density. In this way, the resulting equation no longer depends on the structure of the reference fluid. Nikitin, Pavlov, and Skripov<sup>46</sup> have explored this equation using the van der Waals equation of state for  $Z_0$  and find the same qualitative behavior as found in this work.

## F. Comparison with Wertheim's theory of association

The arguments we have put through in order to arrive at Eq. (39) are rather physical and intuitive. On the other hand, Wertheim has developed a very general theory of association based on a re-summed cluster expansion, where the significance of each of the approximations is mathematically well understood. It is interesting to compare the results of this rather formal theory with the physically appealing description that we have used, largely based on the work of Zhou and Stell.<sup>47</sup>

In the extension of Wertheim's theory of association, the compressibility factor of the chain molecule is given as

$$Z_{n\text{-mer}} = nZ_0 - (n-1) \left[ 1 + \rho \frac{\partial \ln \kappa}{\partial \rho} \right], \quad (40)$$

where  $\kappa$  is defined as

$$\kappa = \int_v g_0^{(2)}(\mathbf{r}_{12}) [\exp(-\Phi(\mathbf{r}_{12})/kT) - 1] d^3\mathbf{r}_{12}. \quad (41)$$

The limit of complete association requires that  $\Phi$  have an infinite well depth, so, within most of the range of the bonding potential, the Boltzmann factor is exceedingly bigger than 1. Therefore,  $\kappa$  and  $\delta$  become identical and Eq. (40) is essentially equal to Eq. (39).

Before proceeding to Sec. III, let us first summarize the approximations invoked to obtain Eq. (39):

- (1) Assume that the free energy difference between the reference system and the completely associated system takes the form of the low density limit in all the density range.
- (2) Decouple the *n*-body correlation function of the associating system into *n*-1 two-body correlation functions through a linear approximation.
- (3) Assume that the two-body correlation function of the associating system is given in terms of the two-body correlation function of a reference system with no bonding potential, as suggested by the exact low density limit.

## III. PREDICTIONS FOR THE SCALING LAWS OF THE CRITICAL PROPERTIES

We start by assuming that the critical density becomes small for large chain lengths, so that one can describe the equation of state in terms of a truncated virial expansion,

$$\frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3, \quad (42)$$

where  $\rho$  is the polymer number density. By applying the conditions for the critical point of pure fluids, i.e.,

$$\begin{aligned} \left(\frac{\partial p}{\partial V}\right)_{T_c} &= 0, \\ \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} &= 0, \end{aligned} \quad (43)$$

we obtain a set of equations for the critical temperature and density:<sup>45</sup>

$$B_2(T_c) + \sqrt{3B_3(T_c)} = 0, \quad (44)$$

$$\sqrt{3B_3(T_c)}\rho_c = 1. \quad (45)$$

By making a Taylor expansion on powers of the density, the first and second virial coefficients predicted by Wertheim's equation are found to be

$$\begin{aligned} B_2 &= n^2 \left( b_2 - \frac{n-1}{n} a_2 \right), \\ B_3 &= n^3 \left( b_3 - \frac{n-1}{n} a_3 \right), \end{aligned} \quad (46)$$

where  $b_2$  and  $b_3$  are the second and third virial coefficients of the reference fluid of nonbonded monomers, while  $a_2$  and  $a_3$  are the zeroth and first order coefficients in a monomer density expansion of  $\partial \ln \delta / \partial \rho$ . Of course, all these quantities are chain length independent.

Now, in order to solve Eq. (44) for the critical temperature we will need to linearize the virial coefficients with respect to the temperature. To do so, let us assume for the time being that there is a finite asymptotic critical temperature in the limit of infinite chain length, which we call  $\Theta$ , in analogy with the polymer + solvent case. We now make a series expansion of  $B_2$  and  $B_3$  in powers of  $\Delta T = \Theta - T$  up to first order, and consider the limit of this expression for large  $n$ , leading to

$$\begin{aligned} B_2(T) &= n^2(C_2 - C_2'\Delta T), \\ B_3(T) &= n^3(C_3 - C_3'\Delta T), \end{aligned} \quad (47)$$

where  $C_2 = b_2(\Theta) - a_2(\Theta)$  and  $C_3 = b_3(\Theta) - a_3(\Theta)$  while  $C_2'$  and  $C_3'$  are the corresponding derivatives with respect to temperature. Substitution of the linearized virial coefficients into the condition for the critical temperature leads to a quadratic equation for  $\Delta T$ . Solving for this equation yields  $\Delta T_c(n)$ , defined as  $\Theta - T_c(n)$ :

$$\begin{aligned} \Delta T_c(n) - \frac{C_2}{C_2'} &= \pm \frac{1}{2C_2'^2} \left( 12C_2'^2 C_3 - 12C_2 C_2' C_3' \right. \\ &\quad \left. + 9C_3'^2 \frac{1}{n} \right)^{1/2} \frac{1}{n^{1/2}} - \frac{3C_3'}{2C_2'^2} \frac{1}{n}. \end{aligned} \quad (48)$$

Equation (48) shows that  $\Delta T_c(n)$  must reach an asymptotic finite value, since the term on the right-hand side should ultimately vanish for large  $n$ . The requirement for  $T_c(n)$  to attain a finite asymptotic critical temperature equal to  $\Theta$  is then obeyed provided that  $C_2$  vanishes. If we now notice that

$$\lim_{n \rightarrow \infty} B_2(\Theta) = n^2 C_2, \quad (49)$$

we arrive at the conclusion that  $C_2$  must indeed vanish at the Boyle temperature of the infinitely long polymer,  $T_B^\infty$ , thus identifying the  $\Theta$  temperature with the Boyle temperature of the infinitely long polymer. From the definition of  $C_2$  we see that this temperature is attained when the following condition is obeyed:

$$b_2(T_B^\infty) - a_2(T_B^\infty) = 0. \quad (50)$$

Note also that the leading terms of the expansion [Eq. (48)] are of order  $n^{-1/2}$  and  $n^{-1}$ , just as predicted by the FH theory.

The case of the critical polymer density is much simpler. Substitution of the expression for  $B_3$  in the condition for the critical density shows that

$$\rho_c(n) \propto n^{-3/2}, \quad (51)$$

so that the critical mass density decreases with a power law proportional to  $n^{-1/2}$ , as predicted by the FH theory.

It is important to note that the above-mentioned arguments apply regardless of the specific form in which the reference fluid (thermodynamics and structure) is described. In particular, the simplest implementation of TPT1, proposed by Nikitin, Pavlov, and Skripov<sup>46</sup> considers  $\delta$  to be a constant. In such a case,  $a_2$  is zero at all temperatures. However, Eq. (50) shows that this simple version still predicts an asymptotic critical temperature which must obey the condition  $b_2(T_B^\infty) = 0$ . Obviously, this condition is obeyed for the Boyle temperature of the reference fluid.

Another interesting issue is the apparent universality of the compressibility factor as predicted by the truncated virial expansion of Eq. (42). Indeed, substitution of this equation into the condition for the critical point shows that, apart from Eq. (45), it must also hold that  $\rho_c = -B_2/(3B_3)$ . Using this expression for the critical density in the linear term of Eq. (42) and Eq. (45) in the quadratic term, it is seen that both terms cancel each other exactly. Dividing the resulting expression for the pressure by the critical density [Eq. (45)] then shows that

$$Z_c(n) = \frac{p_c}{\rho_c k T_c} = \frac{1}{3} + \frac{B_4}{(3B_3)^{3/2}} + \dots \quad (52)$$

Obviously, this result is independent on whatever assumption is made concerning the actual  $n$  dependence of the virial coefficients and shows that TPT1 predicts a finite asymptotic critical compressibility factor of about 1/3, irrespective of the nature of the polymer. In the context of TPT1, a constant compressibility factor implies that the critical pressure must decrease as  $n^{-3/2}$ .

#### IV. APPLICATION TO A POLYMER MODEL

Let us consider a polymer model such as that described in Sec. III A, with the reference fluid considered to be a truncated and shifted potential of the form:

$$u_0(r) = \begin{cases} V_{\text{LJ}}(r) - V_{\text{LJ}}(r_c) & r \leq r_c \\ 0 & r > r_c, \end{cases} \quad (53)$$

where  $r_c = 2 \times 2^{1/6}$  and  $V_{LJ}$  is the usual Lennard-Jones potential,

$$V_{LJ}(r) = 4\epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\}. \quad (54)$$

As to the bonding potential responsible for the connectivity between adjacent monomers, we will consider the (finite extendable nonlinear elastic) (FENE) potential, defined in terms of  $R_0$ , the maximum displacement between monomers and  $k_0$ , a sort of elastic constant:

$$\Phi(r) = \begin{cases} -k_0 R_0^2 \ln \left( 1 - \frac{r^2}{R_0^2} \right) - E_b & 0 < r < R_0 \\ 0 & r \geq R_0. \end{cases} \quad (55)$$

In order to ensure permanent connectivity of the  $n$ -mer, a constant,  $E_b$ , which is (conceptually) made infinitely large, is added to the actual FENE potential.

In what follows, we will set  $k_0 = 15\epsilon/\sigma^2$  and  $R_0 = 1.5\sigma$  and use the Lennard-Jones energy and range parameters as energy and length units, respectively. At liquidlike densities the most probable distance between nonbonded monomers is about  $1.12\sigma$ , which is bigger than the most probable distance  $0.96\sigma$  between bonded monomers. Note at this point that most of the previous applications of Wertheim's theory have been restricted to bonding potentials of infinitely short range, allowing for a single possible bond length. To our knowledge, only once has the effect of a soft bonding potential been considered previously.<sup>50</sup>

In Sec. II we related the equation of state of such a polymer fluid to the properties of the reference system of LJ monomers. What is now required is a theory for both the thermodynamics and the structure of the monomer fluid. We have obtained the required input from integral equation theory and thermodynamic perturbation theory. Let us consider each of them in turn.

### A. The reference hypernetted chain integral equation theory

In this approach, one attempts to calculate the exact pair correlation function, which is then used to evaluate the mechanical properties of the fluid. The Ornstein-Zernike (OZ) equation relates the total pair correlation function,  $h(r) = g(r) - 1$ , to a short range direct correlation function  $c(r)$ :

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{13})c(r_{23})d^3\mathbf{r}_3. \quad (56)$$

Additionally, this integral equation must be provided with a closure that relates  $c(r)$  to  $h(r)$ . We use the reference Hypernetted chain (RHNC) equation of Lado and Ashcroft.<sup>51,52</sup> Although this set of equations can only be solved numerically and convergence is not a trivial matter, an efficient algorithm due to Labik and Malijevisky<sup>53</sup> makes the calculations affordable with a modest amount of CPU time. Once  $g(r)$  is known, the pressure of the fluid may be calculated using the standard relation<sup>54</sup>

$$\frac{p}{k_B T} = \rho - \frac{\rho^2}{6k_B T} \int r \frac{du_0}{dr} g(r) 4\pi r^2 dr. \quad (57)$$

Similarly,  $\delta$  may be calculated using Eq. (37). Actually, solving the integral equation for each of the desired thermodynamic states may be rather cumbersome. In practice we solve the OZ+RHNC equation for several hundreds of state points and fit the pressure and  $\delta$ . Details of the procedure may be found in Appendix A.

### B. The perturbation theory of Tang and Lu

Perturbation theory was the first approach to give quantitative results for the thermodynamics of simple fluids at high density.<sup>55,56</sup> Compared to integral equation theory, it gives similar results at high densities at a smaller computational cost, with the advantage that the free energy is obtained directly, without the need for thermodynamic integration. On the other hand, the traditional perturbation theories of Barker and Henderson<sup>55</sup> and Weeks-Chandler-Andersen<sup>56</sup> are known to be rather poor at low densities because the underlying assumptions of these theories no longer hold true.<sup>57</sup> Fortunately, Tang and Lu have presented rather recently a second order perturbation theory for Lennard-Jones fluids which is very accurate both at low and high densities.<sup>58,59</sup> The success of this theory relies on a rather good description of the structure of the fluid, which is obtained from the OZ equation, supplemented by a simple closure known as the mean spherical approximation (MSA). The use of this closure is very convenient because it has allowed us to obtain a very good approximation to the actual free energy with a purely analytical equation. Furthermore, Tang and Lu have also been able to obtain analytic expressions for the pair correlation function using the MSA closure.<sup>57,60</sup> With minor modifications we were able to extend this theory to our truncated and shifted Lennard-Jones potential and obtain a lengthy but analytic expression for the thermodynamics and structure of our reference fluid. Details of the implementation are explained in Appendix B.

In what follows, we shall present the results of Wertheim's theory for our polymer model using both the RHNC and the MSA thermodynamic theories for the reference fluid. We will call each of the versions TPT1-RHNC and TPT1-MSA, following the original name for Eq. (39) due to Wertheim.<sup>10</sup>

### V. SIMULATION DETAILS

In order to test the TPT1 theory, we have performed extensive computer simulations. Chain length  $n = 10$  was chosen for a detailed comparison to the theory. We have calculated the pressure and chemical potential for five temperatures  $T = 1.68, 2.5, 3.0, 4.0,$  and  $5$ . The lowest value corresponds to a subcritical isotherm, while the highest value is above the  $\Theta$  temperature. The pressure isotherms were evaluated from the virial in  $NVT$  Monte Carlo simulations. The length  $L$  of the (cubic) simulation box was fixed to  $18\sigma$  units. The density dependence of the chemical potential was calculated using grand canonical Monte Carlo simulations. Chain conformations were sampled using local monomer displacements and slithering-snake-like motions. Particle insertions and deletions were performed following configurational bias grand canonical (CBGC) acceptance rules.<sup>44,61,62</sup>

In order to obtain the equation of state we employ cycles of 25 local moves, 25 reptations, and 10 CBGC moves. About 40 000 such cycles were performed so that at least a few thousand particle insertion–deletion attempts were accepted. The volume of the simulation box was chosen so that an average number of about 50 chain molecules was obtained.

In order to compare the theory to the simulations, we must make sure that the chemical potentials are expressed with respect to the same reference state. In order to do so, we define the excess chemical potential to be the difference between  $\mu$  and the chemical potential of an ideal gas of chains  $\mu_{id}$  with the full intramolecular interactions but no intermolecular interactions,

$$\mu^{ex} \equiv \mu - \mu_{id} \quad \text{with} \quad \mu_{id} = \ln \rho - (n-1) \ln C - \ln \langle W_0 \rangle. \quad (58)$$

The first term denotes the translational entropy. Contributions due to the integration over the momenta are ignored, because they contribute equally to the reference system and the interacting polymer liquid. To determine the ideal gas contribution we construct chains according to the Rosenbluth procedure. The distance  $l$  between bonded neighbors is chosen according to its Boltzmann weight  $p(|l|) = 4\pi l^2 \exp(-(u_0 + \Phi)/kT)/C$  where  $C$  is the normalization constant.  $W_0$  denotes the Rosenbluth weight of the chains due to nonbonded interactions, measured at zero density. Once the excess chemical potential has been obtained, it is compared to the excess chemical potential as predicted by the theory, which is evaluated using the standard thermodynamic relation:

$$\frac{\mu^{ex}}{k_B T} = \frac{A^{ex}}{N k_B T} + Z - 1. \quad (59)$$

The grand canonical ensemble allows also for an accurate measurement of the phase diagram, because the order parameter (i.e., the density) is not conserved and density fluctuations are efficiently equilibrated. We monitor the probability distribution  $P(\rho)$  of the density. Close to two phase coexistence, the probability distribution is bimodal: one peak corresponds to the vapor, the other corresponds to the liquid. The coexistence chemical potential  $\mu_{coex}$  is fixed by the condition of equal weight in both peaks:<sup>63</sup>

$$\int_0^{\rho^*} d\rho P(\rho) = \int_{\rho^*}^{\infty} d\rho P(\rho) \quad \text{with} \quad \rho^* = \int_0^{\infty} d\rho \rho P(\rho). \quad (60)$$

Far below the critical points the probability between the two peaks is very low, and we use a reweighting scheme to encourage the system to “tunnel” between the two phases. To this end we add a term  $k_B T \ln W(\rho)$  to the original Hamiltonian. Choosing  $W(\rho) \approx P(\rho)$  the system visits all densities with roughly equal probability. The probability distribution of the grand canonical ensemble is obtained via reweighting the distribution in the simulations,  $P_{MC}$ , according to  $P(\rho) = P_{MC}(\rho)W(\rho)$ . At very low temperatures the density of the liquid in coexistence with its vapor becomes very high and the configurational bias scheme becomes quite inefficient.

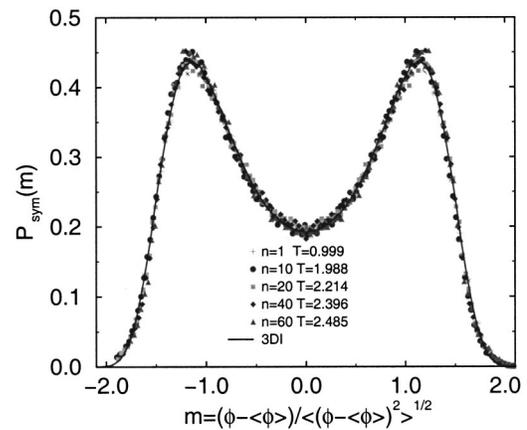


FIG. 2. Mapping of the probability distribution of the density onto the universal distribution of the 3D Ising universality class (line). The chain length  $n$  and the estimate for the critical temperature are indicated in the key.

Since the density of the vapor is very low, however, its pressure is vanishingly small. Hence, we employed  $NpT$  simulations at zero pressure to obtain the liquid density at coexistence.

At the critical point the correlation length of density fluctuations diverges and universal behavior is expected. For finite chain length the unmixing transition exhibits three-dimensional (3D) Ising universal behavior. We have located the critical point for chain length  $n = 1, 10, 20, 40,$  and  $60$  by mapping the symmetrized order parameter distribution  $P_{sym}(\rho) = [P(\rho) + P(\rho_c - \rho)]/2$  onto the universal scaling function of the (3D) Ising model. This symmetrization reduces field mixing corrections which are antisymmetric in  $\rho - \rho_c$  to leading order. Normalizing  $P_{sym}$  to unit variance and norm we eliminate all nonuniversal factors. The results of this mapping are presented in Fig. 2, where we have used system sizes  $L = 11.3, 13.8, 18, 22.5,$  and  $27$  for chain length  $n = 1, 10, 20, 40,$  and  $60$ , respectively. This method gives an accurate location of the critical temperature and density (finite size corrections to the critical density of the order  $L^{-(1-\alpha)/\nu}$  are neglected<sup>63</sup>). The locations of the critical points are collected in Table I.

## VI. RESULTS AND DISCUSSION

Let us first examine the thermodynamic data for the chains of ten monomers. Figure 3 shows the predictions of TPT1 for several pressure isotherms ( $kT/\epsilon = 5, 4, 3, 2.5,$  and  $1.68$ ) compared with simulation results. Both the RHNC and MSA versions of the theory are seen to give rather good estimates; at the highest temperatures, far above the estimated  $\Theta$  point of our model (see the following) as well as at the lowest, a subcritical isotherm. Overall, the RHNC version seems to describe the isotherms slightly better.

Results for the excess chemical potential of the chains are shown in Fig. 4. The agreement is also quite satisfactory, though the results are slightly worse than for the pressure isotherms, especially at the lowest temperatures and densities. Indeed, the main assumption of the theory, that the local environment of a monomer in the polymer fluid is similar to

TABLE I. Critical temperature,  $T_c$  and critical monomer density,  $n\rho_c$  as obtained from simulation (MC) and from TPT1 with either the RHNC version or the MSA version for the structure and thermodynamics of the reference fluid.

$n$	$T_c$ (MC)	$T_c$ (RHNC)	$T_c$ (MSA)
1	1.00	1.02	1.11
10	1.98	2.27	2.36
20	2.214	2.56	2.62
40	2.396	2.79	2.81
60	2.485	2.90	2.88
$\infty$	$\sim 3.3$	3.44	3.14

$n$	$n\rho_c$ (MC)	$n\rho_c$ (RHNC)	$n\rho_c$ (MSA)
1	0.321	0.376	0.323
10	0.245	0.207	0.217
20	0.206	0.145	0.184
40	0.172	0.108	0.150
60	0.1523	0.091	0.140

that of the monomer fluid, breaks down in the low density limit. The fluid is then made of isolated clusters of  $n$  monomers, rather than of single monomers uniformly distributed in space. Likewise, the theory is unable to describe the density dependence of the single chain internal energy and entropy.

The liquid–vapor coexistence curve of the 10-mer as obtained from simulation and theory is shown in Fig. 5. Both the RHNC and MSA versions overestimate the critical temperature as obtained from simulation by about 15%. Of course, this is expected for any classical theory. On the other hand, far away from the critical point, results from both versions of the theory are seen to yield fair agreement with simulation. The MSA version is somewhat more convenient, however, because it allows one to calculate the coexistence at low temperatures with no additional cost, while it becomes rather problematic to calculate the coexistence for the RHNC version below the reference fluid critical temperature. The reason for this is that the RHNC integral equation presents a region of no solutions below this point, so that the resulting

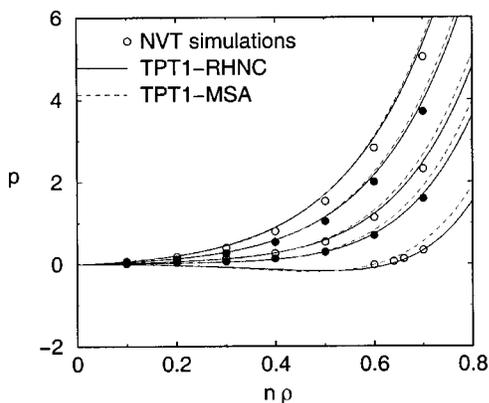


FIG. 3. Pressure against monomer density for chains of ten monomers. All quantities are given in Lennard-Jones reduced units. Symbols are  $NVT$  simulation data while lines are predictions from TPT1; full line, RHNC version; dashed line, MSA version. From top to bottom, pressure isotherms at  $T = 5, 4, 3, 2.5,$  and  $1.68$  reduced LJ units.

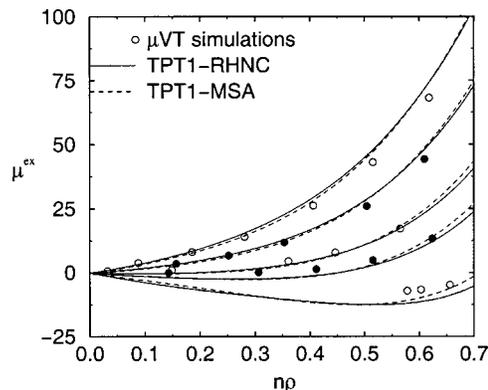


FIG. 4. Excess chemical potential against monomer density for chains of ten monomers. All quantities are given in Lennard-Jones reduced units. Symbols are grand canonical simulation data, while lines are predictions from TPT1; full line, RHNC version; dashed line, MSA version. From top to bottom, chemical potential isotherms at  $T = 5, 4, 3, 2.5,$  and  $1.68$  LJ reduced units.

equation of state is no longer defined inside the liquid–vapor envelope.

We have also investigated the critical points of chains of 20, 40 and 60  $n$ -mers, in an attempt to study the behavior of TPT1 for longer chains. Table I gives a summary of the simulation results, obtained by finite size scaling, together with predictions from TPT1-RHNC and TPT1-MSA. Both versions overestimate the critical temperatures by about 15% for all chain lengths studied. However, the MSA and RHNC predictions seem to converge as the chain length increases. On the other hand, the critical monomer densities are always underestimated, though the MSA version seems to give much better agreement than the RHNC version. In the latter theory the density decreases much too fast compared to the MC results. The overall behavior of the critical parameters is illustrated in Fig. 6, where both  $T_c$  and  $\rho_c$  are plotted against  $n^{-1/2}$ , the predicted asymptotic scaling law for both of these properties. It is seen that for chain lengths up to 60 mono-

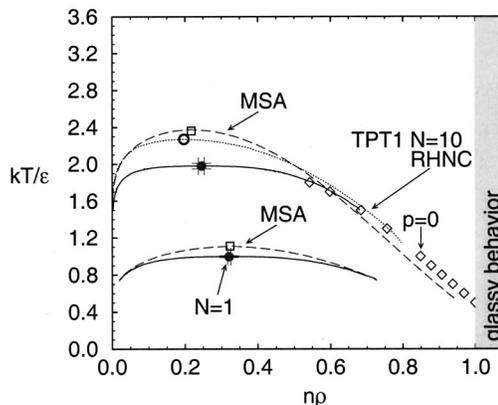


FIG. 5. Liquid–vapor coexistence curves of a 10-mer as obtained from grand canonical simulations (solid lines) and  $NpT$  simulations at  $p=0$  (diamonds), compared with TPT1-RHNC (dotted line) and TPT1-MSA (dashed line). The closed circle presents the critical point as extracted from finite size scaling of the MC data. The open circle and the open square denote the critical point of the TPT1-RHNC and the TPT1-MSA, respectively. The simulation results and TPT1-MSA calculations for monomers ( $n=1$ ) are also included.

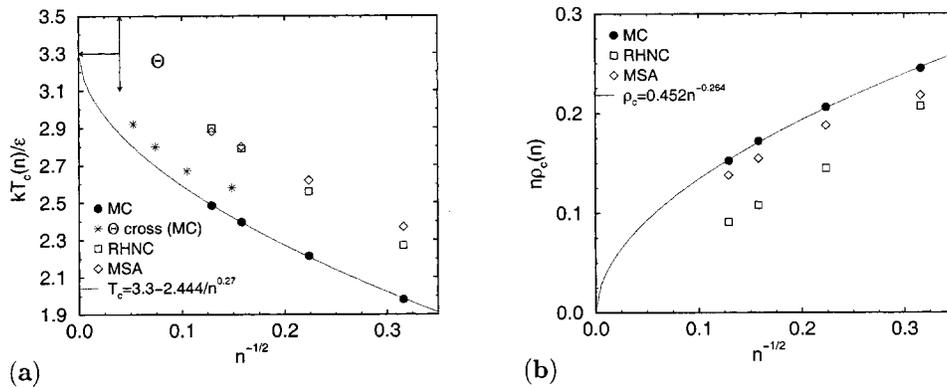


FIG. 6. Critical temperatures (a) and critical monomer densities (b) in the MC simulations and the perturbation theory. In panel (a) the temperatures of the intersections of  $R_c^2(T)/(n-1)$  for neighboring chain lengths are also included. For  $n \rightarrow \infty$  the values tend to the  $\Theta$  temperature.

mers, the critical properties are far from reaching their asymptotic behavior, so that the simulations do not allow us to unambiguously assess the predicted scaling laws.

Although the calculation of the critical point of fluids larger than about 100 monomers by computer simulation becomes prohibitively expensive, we can estimate the  $\Theta$  point of our polymer model by an analysis of the temperature dependence of the polymer extension. Figure 7 shows a plot of the mean squared end to end distance divided by  $n-1$  as a function of temperature for various chain lengths. In the infinite chain length limit, the intercept of two such plots occurs at the  $\Theta$  point of the polymer model. Extrapolation of the results gives as an estimate  $\Theta \approx 3.3$ . As to the theory, fitting the critical temperature predicted by TPT1-RHNC to a power law of the form  $T_c = T_c^\infty + bn^{-1/2} + cn^{-1}$  in the range  $10^2 - 10^7$  gives  $T_c^\infty = 3.44$ . On the other hand, by searching for the root in Eq. (50), we find that TPT1-MSA predicts  $T_c^\infty = 3.14$ . Assuming that the  $\Theta$  point is indeed the critical point of the infinitely long chain, as suggested by the considerations of Sec. III, it would seem that TPT1 is capable of giving an excellent prediction for the  $\Theta$  point of the polymer, even though the actual prediction may vary somewhat depending on the theory used to describe the reference fluid. Remarkably, considering that  $\delta$  is density independent and using the simple van der Waals equation of state, Nikitin, Pavlova, and Popov<sup>41</sup> have shown that TPT1 predicts an asymptotic critical temperature  $T_c^\infty = \frac{27}{8}T_c^0$ . As  $T_c^0$ , the critical temperature of the reference fluid, is approximately 1.0 LJ reduced units, we find that the simplest TPT1 approach already gives an excellent prediction for the  $\Theta$  point of  $T_c^\infty = 3.375$ . This is, however, somewhat fortuitous as it was shown in Sec. III that this TPT1-van der Waals approach of Nikitin actually predicts that  $\Theta$  is equal to the Boyle temperature of the monomer fluid,  $T_B^0$ , which is about  $T_B^0 = 2.58$ . Thus, the relatively good estimate of  $T_c^\infty$  turns out to be a consequence of the overprediction of  $T_B^0$  implicit in the van der Waals equation of state.

Recently, Chatterjee and Schweizer<sup>30</sup> have analyzed the behavior of the critical point of infinite chain lengths using the PRISM theory. For two of the closures employed, the same behavior as that predicted by TPT1 is observed, at least concerning (i) vanishing critical density and (ii) finite critical temperature. The power laws are, however, different. The critical monomer density is predicted to vanish with a weaker dependence, which may be either  $-1/3$  or  $-1/4$  de-

pending on whether the RMPY/HTA or the MSA closures are used. The critical temperature is predicted to reach a finite critical value with the same exponents as the critical density. However, there was no *a priori* reason for choosing one closure over the others and several different trends could be obtained depending on the closure that was used. It is pleasing to see that TPT1 is able to give a unique conclusion, independent of the molecular theory used to describe the monomer fluid.

## VII. CONCLUSION

In this paper we have used the formalism of Zhou and Stell<sup>47</sup> to extend the TPT1 theory to polymers with variable bond length. By using rigorous molecular theories for the reference fluid of nonbonded monomers we have been able to explore two versions of the theory that allow one to give a good description of the fluid without the need for any empirical data for the polymer. Comparison with numerical simulations show that both the RHNC version and the MSA version give good agreement with the simulation data. At low temperatures, the RHNC version seems to be more reliable, while at high temperatures there is apparently little difference. The MSA version is seen to give fair predictions for the critical points of the longer chains, with the advantage

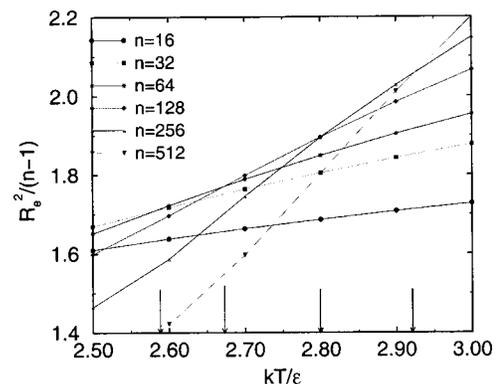


FIG. 7. Temperature dependence of end-to-end distance of a single chain in the vicinity of the  $\Theta$  temperature. The crossings of the ratios  $R_e^2(T)/(n-1)$  for neighboring chain lengths are indicated by arrows. The crossing points converge to the  $\Theta$  temperature in the limit of infinite chain length  $n \rightarrow \infty$ .

that it is almost analytic. The  $\Theta$  point of the model is predicted in very good agreement by the RHNC version, as well as by the MSA version.

Concerning the critical behavior of long chains, it has been shown that TPT1 predicts an approach of the critical temperature to the  $\Theta$  point with a power law of  $n^{-1/2}$ . This is the correct behavior for the infinitely long polymer chain, as mean field behavior must be recovered in the infinitely long chain limit. The  $\Theta$  point has been shown to be the Boyle temperature of the infinitely long polymer while the critical mass density is predicted to vanish with a power law of  $n^{-1/2}$ . All of these predictions concerning the scaling behavior of the critical points of the pure monomer fluid are seen to agree exactly with the mean field (Flory–Huggins) predictions for the critical behavior of polymer+solvent mixtures. This gives further support to the idea that pure polymer equations of state may be used as effective equations of state for the polymer+continuum-solvent system and vice versa, polymer+solvent equations of state may be used for the polymer+vacuum case; a formal proof of this intuitively appealing idea is, however, difficult.

In a subsequent paper<sup>64</sup> we use the implementation of TPT1 proposed here to describe the equation of state, together with a self-consistent field theory to study the surface and interfacial properties of a polymer+solvent system.

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## APPENDIX A: FITTING THE RHNC DATA FOR THE MONOMER FLUID

Rather than solving the integral equation of each of the state points desired, which would be rather expensive, we followed a similar approach to that used by Johnson, Zollweg, and Gubbins<sup>65</sup> to describe the Lennard-Jones fluid. We solved the RHNC integral equation for a set of 756 states in the range  $1.1 \leq T \leq 6.0$  and  $0 < \rho < 0.85$ , we calculated the resulting compressibility factor [see Eq. (57)] and then fit the data to a modified Benedict–Webb–Rubin (BWR) equation of state, given by

$$\rho kT(Z-1) = \sum_{i=1}^8 a_i \rho^{i+1} + F \sum_{i=1}^6 b_i \rho^{2i+1}, \quad (\text{A1})$$

where  $F = \exp(-\gamma\rho^2)$ , while the exact form of the  $a_i$  and  $b_i$  coefficients is given in Table II. Once the fit to  $Z$  is performed, the free energy may be determined from

$$A/N = \sum_{i=1}^8 \frac{a_i \rho^i}{i} + \sum_{i=1}^6 b_i G_i. \quad (\text{A2})$$

The  $G_i$  coefficients obey the following recursive relation:

TABLE II. The  $a_i$  and  $b_i$  temperature dependent coefficients of the BWR equation of state (A1). The  $x_j$  are adjustable parameters whose actual values are given in Table III.

$i$	$a_i$	$b_i$
1	$x_1 T + x_2 \sqrt{T} + x_3 + x_4/T + x_5/T^2$	$x_{20}/T^2 + x_{21}/T^3$
2	$x_6 T + x_7 + x_8/T + x_9/T^2$	$x_{22}/T^2 + x_{23}/T^4$
3	$x_{10} T + x_{11} + x_{12}/T$	$x_{24}/T^2 + x_{25}/T^3$
4	$x_{13}$	$x_{26}/T^2 + x_{27}/T^4$
5	$x_{14}/T + x_{15}/T^2$	$x_{28}/T^2 + x_{29}/T^3$
6	$x_{16}/T$	$x_{30}/T^2 + x_{31}/T^3 + x_{32}/T^4$
7	$x_{17}/T + x_{18}/T^2$	...
8	$x_{19}/T^2$	...

$$G_i = - \frac{F \rho^{2(i-1)} - 2(i-1)G_{i-1}}{2\gamma} \quad (\text{A3})$$

with the first term given by  $G_1 = (1-F)/(2\gamma)$ . The parameters obtained for the fit are collected in Table III.

Contrary to the approach of Johnson, Zollweg, and Gubbins, we calculate the thermodynamics using the RHNC theory, rather than computer simulations. In this way we are able to save several orders of magnitude of CPU time. The effective diameter required in the RHNC equation is determined as suggested by Lado, Foiles, and Ashcroft,<sup>52</sup> while the effective hard sphere bridge function is calculated from the parametrization of Labik and Malijevsky.<sup>66,67</sup>

Also required is the associating strength  $\delta$  of the fluid. This is obtained by solving Eq. (37) for each of the 756 state points. Rather than fitting  $\delta$ , which is a difficult task, as it varies several orders of magnitude in the range  $1.1 \leq T \leq 6.0$ , we fit the dimensionless ratio  $\delta(\rho)/\delta(\rho=0)$ . The actual functional form used is

$$\delta/\delta_0 = 1 + \sum_{i=1}^5 \sum_{j=1}^5 a_{ij} \rho^i T^{(1-j)}. \quad (\text{A4})$$

The parameters for this fit are gathered in Table IV.

TABLE III. Parameters for the fit of the RHNC data to the modified Benedict–Webb–Rubin equation of state. The notation is the same as in Ref. 65. The nonlinear parameter is set to  $\gamma=3$ .

$i$	$x_i$	$i$	$x_i$
1	0.421 192 000D+00	17	-0.107 917 493D+03
2	0.476 645 300D+01	18	0.946 452 266D+03
3	-0.915 420 500D+01	19	-0.661 602 970D+03
4	0.161 011 000D+01	20	0.117 245 702D+03
5	-0.152 328 700D+01	21	-0.348 234 700D+01
6	0.205 245 400D+01	22	0.415 445 097D+03
7	-0.348 800 300D+01	23	0.325 092 260D+02
8	0.459 058 600D+01	24	0.136 021 606D+04
9	-0.111 109 576D+03	25	-0.672 466 920D+03
10	-0.683 045 000D+00	26	-0.114 228 784D+03
11	0.106 678 670D+02	27	0.602 317 138D+03
12	-0.243 251 130D+02	28	0.185 990 661D+03
13	0.193 579 400D+02	29	-0.116 953 259D+04
14	-0.196 790 929D+03	30	0.607 836 000D+00
15	-0.172 144 369D+03	31	0.656 689 000D+00
16	0.262 199 061D+03	32	0.588 415 000D+00

TABLE IV. Parameters  $a_{ij}$  for the fit to  $\delta/\delta_0$  [Eq. (A4)] as obtained from the RHNC integral equation.

$i$	$j=1$	$j=2$	$j=3$	$j=4$	$j=5$
1	0.496 554 000D+00	0.129 871 000D+01	-0.595 011 800D+01	0.860 280 100D+01	-0.452 759 900D+01
2	0.101 561 200D+01	-0.967 002 900D+01	0.677 884 460D+02	-0.950 135 670D+02	0.471 191 210D+02
3	-0.604 253 400D+01	0.411 972 640D+02	-0.252 396 610D+03	0.376 561 440D+03	-0.178 2499 74D+03
4	0.622 698 400D+01	-0.680 522 730D+02	0.391 425 109D+03	-0.605 492 785D+03	0.292 582 291D+03
5	-0.691 995 000D+00	0.357 118 100D+02	-0.218 469 635D+03	0.348 511 635D+03	-0.171 957 868D+03

## APPENDIX B: THE PERTURBATION THEORY OF TANG AND LU

In order to describe the thermodynamics of the reference fluid we perform a Barker–Henderson decomposition of the monomer fluid pair potential such that  $u_0$  is described in terms of a repulsive reference potential  $w_{\text{ref}}$ , which is made of the positive region of  $u_0$  and a perturbation,  $w_{\text{per}}$ , which is made of the negative part of the potential.<sup>55,54</sup>

$$w_{\text{ref}}(r) = \begin{cases} u_0(r) & r \leq t\sigma \\ 0 & r > t\sigma \end{cases}$$

and

$$w_{\text{per}}(r) = u_0(r) - w_{\text{ref}}(r) = \begin{cases} 0 & r \leq t\sigma \\ u_0(r) & r > t\sigma \end{cases}, \quad (\text{B1})$$

where  $t=1.0013$  defines the value of  $r$  where  $u_0$  becomes negative (recall that we are considering a cut and shifted potential). We now couple the perturbation potential to the reference potential with a coupling parameter,  $\lambda$ , so that the actual potential is recovered for  $\lambda=1$ :

$$w(r;\lambda) = w_{\text{ref}}(r) + \lambda w_{\text{per}}(r). \quad (\text{B2})$$

At this stage we recall the fundamental functional expression that relates the Helmholtz free energy with the radial distribution function,<sup>68</sup>

$$\frac{\delta A}{\delta w(r;\lambda)} = \frac{1}{2} N \rho g(r;\lambda). \quad (\text{B3})$$

Integration of this equation, following the rules of functional calculus,<sup>68</sup> leads to an expression relating the free energy of the monomer fluid with that of the reference fluid:

$$\frac{A}{N} - \frac{A_{\text{ref}}}{N} = \frac{1}{2} \rho \int_{t\sigma}^{\lambda=1} \int_{t\sigma}^{\infty} g(r;\lambda) w_{\text{per}} 4\pi r^2 dr d\lambda. \quad (\text{B4})$$

It is then assumed that the radial distribution function may be expanded as a series in powers of  $\lambda$  of the form  $g(r;\lambda) = g_0(r) + g_1(r)\lambda + \dots$ . Truncation of the series to first order then yields

$$\begin{aligned} \frac{A}{N} - \frac{A_{\text{ref}}}{N} &= \frac{1}{2} \rho \int_{t\sigma}^{\infty} g_0(r) w_{\text{per}}(r) 4\pi r^2 dr \\ &+ \frac{1}{4} \rho \int_{t\sigma}^{\infty} g_1(r) w_{\text{per}}(r) 4\pi r^2 dr. \end{aligned} \quad (\text{B5})$$

Following Barker and Henderson<sup>55</sup> we now choose to describe the reference potential by means of a hard sphere fluid of appropriate hard sphere diameter,  $d$ . This choice is justifi-

fied because the reference potential is made essentially of the repulsive part of the potential. In this way,  $\beta A_{\text{ref}}/N$  and  $g_0$  may be considered to be the free energy and radial distribution function of an effective hard sphere fluid, while  $g_1$  may be solved using the MSA closure.<sup>57</sup> However, the integrals appearing in Eq. (B5) are still quite tedious to calculate and a further approximation allows one to get fully analytical results. This is done by fitting the actual monomer potential,  $u_0$ , to a two Yukawa potential, following the procedure of Ref. 58:

$$u(r)^{\text{TY}} = -k_0 \epsilon \frac{e^{-z_1(r-t\sigma)}}{r} + k_0 \epsilon \frac{e^{-z_2(r-t\sigma)}}{r}. \quad (\text{B6})$$

Actually, the fit needs to be performed only for values of  $r$  greater than  $d$  and the resulting function (with  $k_0=2.4405$ ,  $z_1=3.492456$  and  $z_2=13.109857$ ) is virtually identical to the true potential. However, substitution of Eq. (B6) in the first- and second-order contributions of Eq. (B5) and solving  $g_1$  for  $u^{\text{TY}}$  rather than for  $u_0$ , a very accurate expression for Eq. (B5) may be obtained which is fully analytic.

This is done by rearranging Eq. (B5) into the form:

$$\frac{\beta A}{N} = a_0 + a_1 + a_2, \quad (\text{B7})$$

where  $a_0$  is given by the Carnahan–Starling equation of state:

$$a_0 = \frac{4\eta - 3\eta^2}{(1-\eta)^2}, \quad (\text{B8})$$

while

$$\begin{aligned} a_1 &= \frac{1}{2} \rho \int_d^{\infty} (g_0 - 1) w_{\text{per}}^{\text{TY}} 4\pi r^2 dr + \frac{1}{2} \rho \int_d^{\infty} w_{\text{per}} 4\pi r^2 dr \\ &+ g_0(d) \int_{t\sigma}^d w_{\text{per}} 4\pi r^2 dr \end{aligned} \quad (\text{B9})$$

and

$$\begin{aligned} a_2 &= \frac{1}{4} \rho \int_d^{\infty} g_1(r) w_{\text{per}}^{\text{TY}} 4\pi r^2 dr \\ &+ \frac{1}{4} \rho g_1(d) \int_{t\sigma}^d w_{\text{per}} 4\pi r^2 dr. \end{aligned} \quad (\text{B10})$$

In Eqs. (B9) and (B10) it is understood that  $w_{\text{per}}^{\text{TY}}$  is the perturbation potential when expressed as in Eq. (B6); the actual  $w_{\text{per}}$  potential is used wherever possible;  $g_0=1$  and  $g_1=0$  beyond the cutoff distance of the potential while  $g_0$  and  $g_1$  are considered to remain constant in the range  $[d, t\sigma]$ . The

only difference between the above-mentioned expressions and those obtained by Tang and co-workers<sup>58,59</sup> for the true Lennard-Jones potential are found in the trivial integrals of the form  $\int w_1 4\pi r^2 dr$  because both the integration limits and the perturbation potential differ. Solving  $a_1$  and  $a_2$  yields

$$a_1 = -\frac{12\eta\beta\epsilon}{d^3} \left[ k_1 \left( \frac{L(z_1 d)}{z_1^2(1-\eta)^2 Q(z_1 d)} - \frac{1+z_1 d}{z_1^2} \right) - k_2 \left( \frac{L(z_2 d)}{z_2^2(1-\eta)^2 Q(z_2 d)} - \frac{1+z_2 d}{z_2^2} \right) \right] + 48\eta\beta\epsilon W_{cs}(r_c, d) - 48\eta\beta\epsilon g_0(d) W_{cs}(t\sigma, d), \quad (\text{B11})$$

$$a_2 = -\frac{6\eta\beta^2\epsilon^2}{d^3} \left[ \frac{k_1^2}{2z_1 Q^4(z_1 d)} + \frac{k_2^2}{2z_2 Q^4(z_2 d)} - \frac{2k_1 k_2}{(z_1+z_2) Q^2(z_1 d) Q^2(z_2 d)} \right] - 24\eta\beta^2\epsilon^2 \left[ \frac{k_1/d}{Q^2(z_1 d)} - \frac{k_2/d}{Q^2(z_2 d)} \right] W_{cs}(t\sigma, d), \quad (\text{B12})$$

where  $\eta = \pi/6 d^3 \rho$  and  $k_i = k_0 e^{z_i(t\sigma-d)}$ . The Barker-Henderson diameter, defined as

$$d = \int_0^\infty (1 - e^{-\beta w_{\text{ref}}(r)}) dr, \quad (\text{B13})$$

is parametrized using the formula proposed in Ref. 69:

$$d/\sigma = 2^{1/6} \left[ 1 + \left( 1 + \frac{T + c_2 T^2 + c_3 T^4}{c_1} \right)^{1/2} \right]^{-1/6}, \quad (\text{B14})$$

where  $c_1 = 1.150167$ ,  $c_2 = -0.046498$ , and  $c_3 = 0.0004477054$ .

On the other hand,  $Q$  is defined as

$$Q(t) = \frac{S(t) + 12\eta L(t)e^{-t}}{(1-\eta)^2 t^3}, \quad (\text{B15})$$

where

$$S(t) = (1-\eta)^2 t^3 + 6\eta(1-\eta)t^2 + 18\eta^2 t - 12\eta(1+2\eta) \quad (\text{B16})$$

and

$$L(t) = (1+\eta/2)t + 1 + 2\eta. \quad (\text{B17})$$

The reference radial distribution at contact is given by

$$g_0(d) = \frac{1+\eta/2}{(1-\eta)^2}, \quad (\text{B18})$$

while  $W_{cs}$  is (to constant factors) the definite integral of the perturbation potential,  $w_{\text{per}}$ :

$$W_{cs}(x, y) = \left\{ \frac{1}{3} \left[ \left( \frac{\sigma}{x} \right)^3 - \left( \frac{\sigma}{y} \right)^3 \right] - \frac{1}{9} \left[ \left( \frac{\sigma}{x} \right)^9 - \left( \frac{\sigma}{y} \right)^9 \right] - \frac{1}{3} \left[ \left( \frac{\sigma}{r_c} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^6 \right] \left[ \left( \frac{x}{\sigma} \right)^3 - \left( \frac{y}{\sigma} \right)^3 \right] \right\} \frac{\sigma^3}{d^3}. \quad (\text{B19})$$

The compressibility factor may be determined by density differentiation of the free energy, which leads to

$$Z = \frac{pV}{NkT} = Z_0 + Z_1 + Z_2, \quad (\text{B20})$$

where

$$Z_0 = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \quad (\text{B21})$$

$$Z_1 = a_1 - \frac{12\eta^2\beta\epsilon}{d^3} \left[ k_1 \left( \frac{(5/2+\eta/2)z_1 d + 4 + 2\eta}{z_1^2(1-\eta)^3 Q(z_1 d)} - \frac{L(z_1 d) Q'_\eta(z_1 d)}{z_1^2(1-\eta)^2 Q^2(z_1 d)} \right) - k_2 \left( \frac{(5/2+\eta/2)z_2 d + 4 + 2\eta}{z_2^2(1-\eta)^3 Q(z_2 d)} - \frac{L(z_2 d) Q'_\eta(z_2 d)}{z_2^2(1-\eta)^2 Q^2(z_2 d)} \right) \right] - 16\eta\beta\epsilon d \frac{\partial g_0(d)}{\partial d} W_{cs}(t\sigma, d), \quad (\text{B22})$$

$$Z_2 = a_2 + \frac{12\eta^2\beta^2\epsilon^2}{d^3} \left[ \frac{k_1^2 Q'_\eta(z_1 d)}{z_1 Q^5(z_1 d)} + \frac{k_2^2 Q'_\eta(z_2 d)}{z_2 Q^5(z_2 d)} - \frac{2k_1 k_2 [Q'_\eta(z_1 d) Q(z_2 d) + Q(z_1 d) Q'_\eta(z_2 d)]}{(z_1+z_2) Q^3(z_1 d) Q^3(z_2 d)} \right] + 48\eta^2\beta^2\epsilon^2 \left[ \frac{k_1/d}{Q^3(z_1 d)} Q'_\eta(z_1 d) - \frac{k_2/d}{Q^3(z_2 d)} Q'_\eta(z_2 d) \right] W_{cs}(t\sigma, d), \quad (\text{B23})$$

while

$$d \frac{\partial g_0(d)}{\partial d} = \frac{3\eta(5+\eta)}{2(1-\eta)^3}, \quad (\text{B24})$$

and

$$Q'_\eta(t) = \frac{6(1-\eta)t^2 + 36\eta t - 12(1+5\eta) + 12[(1+2\eta)t + 1 + 5\eta]e^{-t}}{(1-\eta)^3 t^3}. \quad (\text{B25})$$

In order to calculate the associating strength,  $\delta$ , the radial distribution function could have been assumed to be  $g = g_0 + g_1$ , which is already a rather good approximation.<sup>58</sup> However, we use the simplified exponential approximation, which considerably improves the estimate of  $g$  around  $\sigma$  with no additional information.<sup>59</sup> According to this approximation,  $g = g_0 e^{g_1}$ . Once  $g$  is known,  $\delta$  is calculated directly by invoking Eq. (37). The integral must be performed numerically but would have been analytic if the bond length was held fixed.

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