Volume-Explicit Equation of State for Hard Chains, Their Mixtures, and Copolymers

Esam Z. Hamad
Chemical Engineering Dept., King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

Volume-explicit equations of states for hard chains, their mixtures, and copolymers were developed. The equations accurately represent the simulation data. They also predict the correct volume at high pressures (close packing), unlike the common pressure-explicit equations, which predict a physically unattainable volume. Entropic demixing is also predicted by the proposed equations. The developed equation can be used as the repulsive part in developing volume-explicit real polymer equations of state or excess Gibbs energy models.

Introduction

Equations of state (EOS) are valuable tools in the calculation of thermodynamic properties and phase behavior. An important result of the theoretical study of fluids and solids is that repulsive molecular forces are dominant at high densities. This result has motivated researchers to build EOS around accurate repulsive equations for small molecules (Chien et al., 1983; Tao and Mason, 1994) and polymers (Song et al., 1994b; Kiao et al., 1996).

A number of models for hard chains take advantage of the available EOS for hard spheres and small hard bodies. For small molecules, almost all the statistical-thermodynamic repulsive equations are pressure explicit. When an attractive term is added to the repulsive term to represent real polymers, an implicit equation with multiple-volume roots results. These roots have to be found numerically. The molecular weight of polymers is usually high enough to exclude a vapor phase. As such, only one volume root is physically significant. All the preceding contribute to the little attention that the statistical-thermodynamic-based polymer equations get compared to the simple and volume-explicit equations such as the Tait equation (Danner and High, 1993). However, the empirical nature of this equation inhibits its confident extension to mixtures and copolymers. It is therefore our objective in this work to use statistical thermodynamics to derive a volume-explicit EOS for hard chains, their mixtures and copolymers. Such an equation can be combined with an attractive term to describe and predict the behavior of real polymers.

Most of the thermodynamic modeling of polymers has been carried out using lattice theories because polymers usually form a dense phase, either solid or liquid. Polymer blends and solutions have also been traditionally modeled by lattice theories such as the Flory-Huggins theory (Flory, 1941; Huggins, 1941). The original theory was developed for athermal systems, and later the theory was modified by adding a semiempirical (Flory, 1954) energetic term that is proportional to the "chi parameter." This parameter, which is supposed to be independent of the state properties (it represents molecular interaction), was found to depend on composition, molecular weight, and temperature, when compared to experimental data (Schweizer and Curro, 1989). The original athermal part was also found to be an oversimplification, valid only after making a large number of simplifying assumptions (Song et al., 1994a).

Off-lattice models for polymers have been suggested to try to overcome some of the limitations of the lattice-based theories. They have the advantage of removing the artificial constraint of a lattice, which is obviously absent from real systems. Hall and coworkers (Dickman and Hall, 1986, 1988; Yethiraj and Hall, 1991) suggested the tangent hard-sphere chain model. This simple model captures two major features of real polymers, the connectivity of repeat units and the repulsive forces that dictate the structure of dense fluids and solids. This model opened the door for a number of new and relevant studies. Honnell and Hall (1991) studied mixtures of chains of the same segment size, but of different lengths. Dickman and Hall (1986) first introduced the generalized Flory theories. These theories are based on estimates of the probabilities of successfully inserting test chains into chain fluids. These theories were refined and improved over more than a decade. Versions of these theories are now available

---

Correspondence concerning this article should be addressed to E. Z. Hamad.

for homopolymers, copolymers, and polymer mixtures. Their predictive ability could be enhanced by including information on dimers (Honnell and Hall, 1989), in addition to the information on spherical units in the original theory (Dickman and Hall, 1986).

Another off-lattice approach is the first-order perturbation theory of associating fluids (TPT1), which was pioneered by Wertheim (1984, 1986). In this model, the chain is constructed by the formation of strong association bonds between two sites on each monomer (repeat unit). An advantage of this theory is that it is not restricted to spherical units. This theory was developed further by Chapman (Chapman et al., 1988; Ghonasgi and Chapman, 1994), and it was used to correlate and predict experimental results for real systems. In general, the equation of state of m repeat unit chains can be written as

$$Z = m(Z_{\text{units}} + Z_{\text{bond}}), \tag{1}$$

where the first term between the parenthesis is the compressibility factor of the unbonded units, and the second term accounts for the change in Z due to the presence of bonds between the units in a polymer chain. The general form of the theory for multicomponent mixtures and heteronuclear chains containing hard-spherical units in the canonical ensemble was given by Malakhov and Brun (1992). This TPT1 theory has been compared to the simulation results of chains of Lennard-Jones segments, with good agreement (Ghonasgi and Chapman, 1994).

Chiew (1990) used the particle–particle description for hard spheres and introduced two constraints on the contact value of the radial distribution function to force the connectivity between consecutive spheres. He then combined his results with the Percus-Yevick (PY) approximation. The structure of the resulting equations is the same as for adhesive hard spheres. Using an already existing solution for adhesive hard spheres Chiew obtained Eq. 1 with a different expression for Z_{bond}. The general form of the Z_{bond} for multicomponents and heterochains is given by Malakhov and Brun (1992). This model is limited to hard-spherical repeat units. The compressibility factor is usually underestimated by this theory.

Other work along similar lines includes that of Hu et al. (1996), Phan et al. (1993), and Chang and Sandler (1995). Resummation of the virial expansion was also used to obtain models for hard chains (Boublik et al., 1990). Sanchez and LaCambe (1976) used a modified lattice theory to derive an equation of state for polymers and their mixtures.

All the work just cited results in pressure-explicit equations. In the present work, new volume-explicit equations of state for hard chains, their mixtures, and copolymers are developed. Sound statistical thermodynamics theories are used to develop the equations to give them a wide range of applicability and predictive capability. From a practical point of view, the equations can be used to develop volume-explicit equations for pure polymers, polymer mixtures (polymer solutions and polymer blends), and copolymers.

Pure Hard Chains

The first objective of this work is the development of volume-explicit EOS for pure hard chains of tangent spheres. The development will utilize contact-pair correlation functions in the isothermal–isobaric ensemble, NPT, to form a chain out of individual monomers. The equations will be tested against simulation data.

The TPT1 (Wertheim, 1984, 1986; Chapman et al., 1988; Ghonasgi and Chapman, 1994) and the PY-Chiew (Chiew, 1990) are approximate models that were formulated in the canonical ensemble (constant volume, temperature, and number of moles). The bonding contribution in the two models is given by fairly simple expressions:

$$Z_{\text{bond}} = -\frac{m-1}{m} g_{\text{NVT}}(\sigma) \qquad \text{(PY-Chiew)} \tag{2a}$$

$$Z_{\text{bond}} = -\frac{m-1}{m}\left[1 + \rho\frac{\partial}{\partial\rho}\{\ln g_{\text{NVT}}(\sigma)\}\right] \quad \text{(TPT1)}, \tag{2b}$$

where $g_{\text{NVT}}(\sigma)$ is the canonical ensemble pair correlation function at contact for the spherical units that make up the chain molecules. Combining Eqs. 1 and 2 gives

$$Z = mZ_{\text{HS}}(T,\rho) - (m-1)g_{\text{NVT}}(\sigma) \qquad \text{(PY-Chiew)} \tag{3a}$$

$$Z = mZ_{\text{HS}}(T,\rho) - (m-1)\left[1 + \rho\frac{\partial}{\partial\rho}\{\ln g_{\text{NVT}}(\sigma)\}\right] \quad \text{(TPT1)}. \tag{3b}$$

The preceding equations are the final working equations in the canonical ensemble. They are of course approximate equations.

Approximate models such as Eqs. 2 and 3 usually behave differently in different ensembles. A good example is the PY approximation for hard spheres, where the equation of state can be obtained from the total correlation function (based on the grand canonical ensemble), or from the contact value of the pair correlation function (based on the canonical ensemble). The first route gives a more accurate equation of state. It is therefore interesting to see how well the final form of the TPT1 and the PY-Chiew approximations, Eq. 3, perform in other ensembles. Here we work in the NPT ensemble because of the practical advantages of the NPT variables, as discussed before. We will apply the final working equations of the TPT1 and the Chiew approximations because of their simplicity. A derivation from the basic approximations of the two models in the NPT ensemble, if possible, will not necessarily result in the same final working equations (see Eqs. 4 and 5 below). We will see later that the resulting equations are more accurate than the canonical ensemble equations. This is in addition to the advantage of the volume-explicit form of NPT equations.

Based on the preceding discussion we replace Z_{HS} and $g_{\text{NVT}}(\sigma)$ in Eq. 3 with their corresponding values in the NPT ensemble to get

$$Z = mZ_{\text{HS}}(T,P) - (m-1)g_{\text{NPT}}(\sigma) \tag{4}$$

and

$$Z = mZ_{\text{HS}}(T,P) - (m-1)\left[1 + P\frac{\partial}{\partial P}\{\ln g_{\text{NPT}}(\sigma)\}\right], \tag{5}$$

where $Z_{\mathrm{HS}}(T, P)$ is the volume-explicit compressibility factor for hard spheres and $g_{\mathrm{NPT}}(\sigma)$ is the pair correlation function at contact for the spherical units that make up the chain molecules in the NPT ensemble. Note that Eqs. 4 and 5 are not labeled as PY-Chiew and TPT1 because we did not derive them for these known basic approximations. To utilize these two equations, we need expressions for Z_{HS} and $g_{\mathrm{NPT}}(\sigma)$.

In the canonical ensemble the contact values for pure components and mixtures can be obtained directly from the partition function, Q, without having to find the spacial dependence of g from integral equations (Hamad, 1994):

$$g_{ij,\mathrm{NVT}}(\sigma_{ij}) = \frac{-1}{2\pi N(2-\delta_{ij})\rho x_i x_j \sigma_{ij}^2} \frac{\partial \ln Q}{\partial \sigma_{ij}}. \tag{6}$$

For pure species, the relationship reduces to

$$g_{\mathrm{NVT}}(\sigma) = \frac{-1}{4\pi N \rho \sigma^2} \frac{\partial \ln Q}{\partial \sigma} = 3\frac{Z-1}{2\pi\rho\sigma^3}. \tag{7}$$

In the isothermal-isobaric ensemble, one can derive the following equation:

$$g_{\mathrm{NPT}}(\sigma) = \frac{-kT}{4\pi N P \sigma^2} \frac{\partial \ln \Delta}{\partial \sigma} = 3RT\frac{Z-1}{2\pi P \sigma^3}, \tag{8}$$

where Δ is the NPT partition function. Equations 7 and 8 can be combined to obtain the following relationship between the two contact values:

$$g_{\mathrm{NPT}}(\sigma) = \frac{g_{\mathrm{NVT}}(\sigma)}{Z_{\mathrm{HS}}}. \tag{9}$$

An accurate equation of state for hard spheres in the isothermal-isobaric ensemble was derived recently (Hamad, 1997a), and is expressed by

$$Z_{\mathrm{HS}}(T, P) = 1 + 4\mathfrak{p} + \frac{3\mathfrak{p}}{4}\ln\left[\frac{3+\mathfrak{p}}{3+25\mathfrak{p}}\right], \tag{10}$$

where the dimensionless pressure is $\mathfrak{p} = \pi\sigma^3 P/6kT$. This equation is more accurate than the traditional Carnahan-Starling (1969) equation, especially at high pressures. The contact value of the pair correlation function can be obtained by substituting Eq. 10 in Eq. 8:

$$g_{\mathrm{NPT}}(\sigma) = 1 + \frac{3}{16}\ln\left[\frac{3+\mathfrak{p}}{3+25\mathfrak{p}}\right]. \tag{11}$$

Combining Eq. 4 with Eqs. 10 and 11 gives a simple volume-explicit equation of state for hard chains:

$$Z = 1 + 4m\mathfrak{p} + \frac{3}{16}(1 - m + 4m\mathfrak{p})\ln\left[\frac{3+\mathfrak{p}}{3+25\mathfrak{p}}\right]. \tag{12}$$

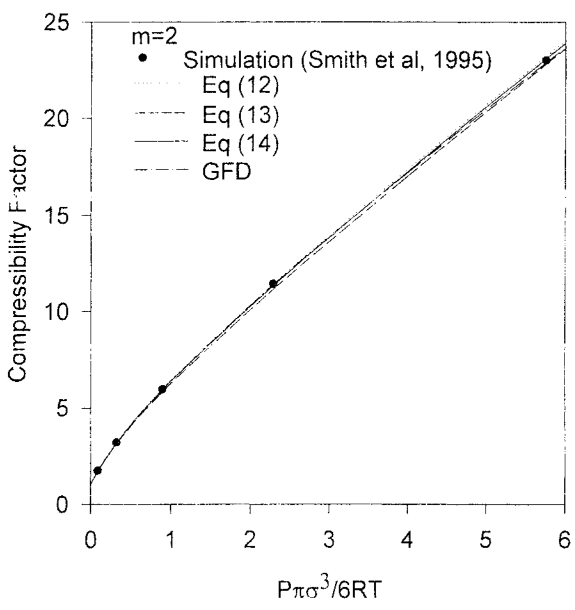

Figure 1. Compressibility factor of hard dimers vs. reduced pressure.

On the other hand, Eq. 5 yields a more complex equation,

$$Z = 1 + 4m\mathfrak{p} + \frac{3}{4}m\mathfrak{p}\ln\left[\frac{3+\mathfrak{p}}{3+25\mathfrak{p}}\right] + \frac{216(m-1)\mathfrak{p}}{(3+\mathfrak{p})(3+25\mathfrak{p})\{16+3\ln[(3+\mathfrak{p})/(3+25\mathfrak{p})]\}}. \tag{13}$$

To test the accuracy of the preceding equations, we compare their predictions with accurate simulation data (Smith et al., 1995) for hard chains with 2 to 16 repeat units. We start with hard dimers ($m = 2$). Figure 1 shows the prediction of Eqs. 12 and 13 and the generalized Flory dimer theory (GFD) (Honnell and Hall, 1989). This theory, which for $m = 2$ reduces to the Tildesley-Streett equation (Tildesley and Streett, 1980), gives a volume-implicit equation of state, and normally one that needs solving numerically for the volume. The first thing we notice is that Eqs. 12 and 13 accurately predict the compressibility factor. They are only slightly less accurate than the Tildesley-Streett equation. The second thing we notice is that the two equations are much more accurate than their counterparts in the canonical ensemble, which are shown in Figure 2. At the highest density (or pressure), the TPT1 in the canonical ensemble underestimates the compressibility factor by 3%, while the underestimation of Eq. 12 is only 0.8%. The PY-Chiew underestimates the compressibility factor by 13%, while Eq. 11 overestimates it by only 0.9%. Since Eqs. 11 and 12 bracket the simulation data, a very accurate representation of the data can be obtained by taking two-thirds of Eq. 11 and one-third of Eq. 12:

$$Z_{\mathrm{avg}} = \left[Z_{\mathrm{eq(12)}} + 2Z_{\mathrm{eq(11)}}\right]/3. \tag{14}$$

Figure 1 clearly shows the accuracy of this average equation.

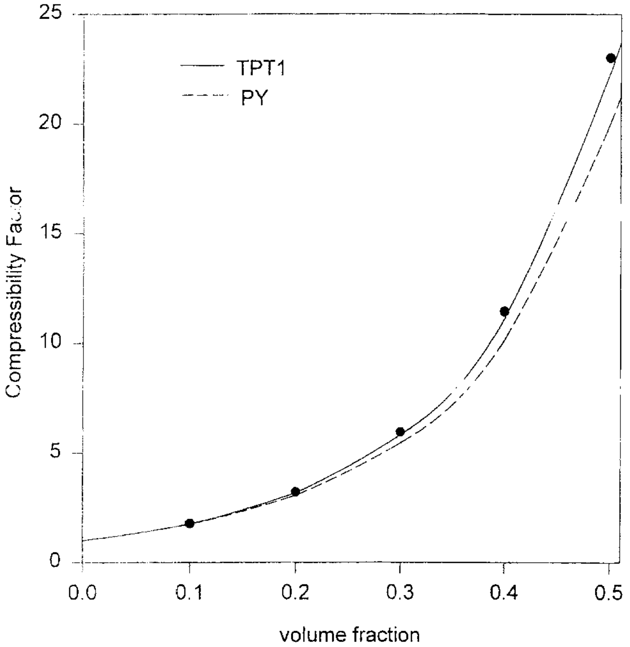

Figure 2. Compressibility factor of hard dimers vs. volume fraction.

Points are simulation data (Smith et al., 1995).

Another advantage of Eqs. 12 and 13 is illustrated in Figure 3. Here the dimer residual volume per mole of repeat units is plotted vs. pressure. At high pressures, the Tildesley-Streett and the GFD equations give a physically unattainable reduced volume, $6v/\pi\sigma^3$ of unity. On the other hand, the proposed equations give a value of 1.58, which is very close to the hard-sphere random close packing value of 1.570 (Bernal, 1965).

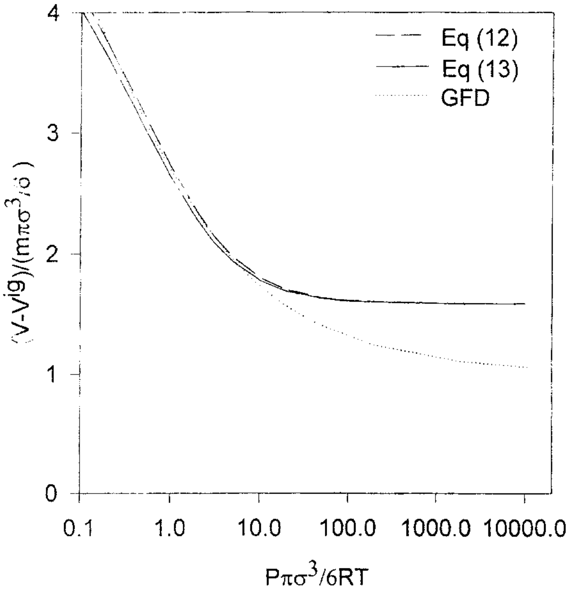

Figure 3. Hard dimers residual volume per mole of repeat units vs. pressure.

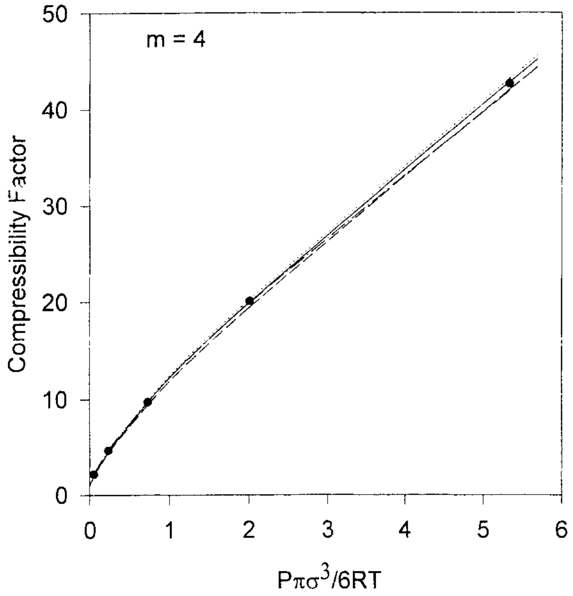

Figure 4. Compressibility factor of hard 4-mer chains.

Curves and points have the same meaning as in Figure 1.

Results for chains with 4, 8, and 16 repeat units are shown in Figures 4–6. Again the figures support the accuracy of the proposed equations. For the longest chains (16-mer), Eqs. 12 and 13 are more accurate than the GFD theory. This indicates that the proposed estimations keep their accuracy with increasing chain length, unlike some other models.

Polymer Mixtures

The preceding positive result encourages us to extend the isothermal–isobaric ensemble equations to mixtures. To do so, we will need a mixture NPT equation for hard spheres

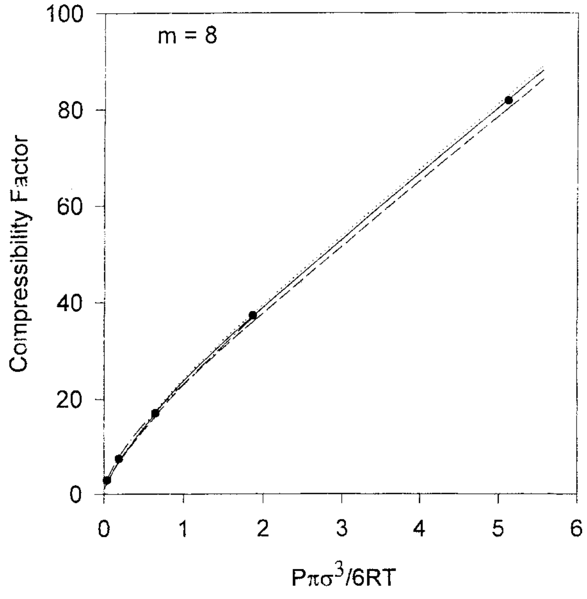

Figure 5. Compressibility factor of hard 8-mer chains.

Curves and points have the same meaning as in Figure 1.

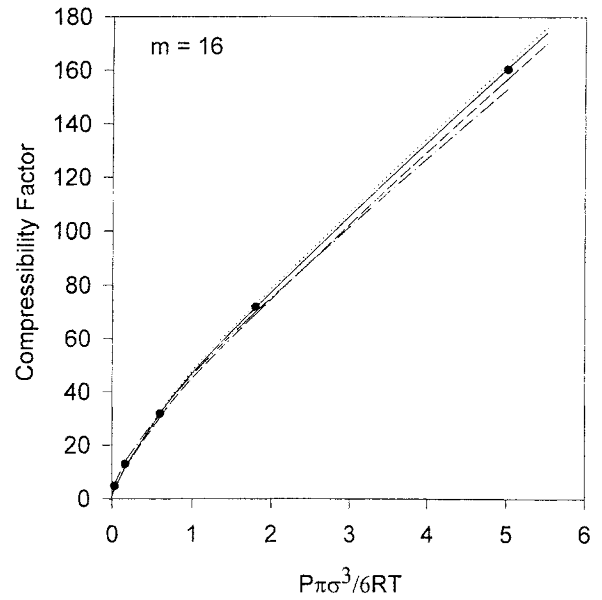

Figure 6. Compressibility factor of hard 16-mer chains.

Curves and points have the same meaning as in Figure 1.

and the contact values of the pair correlation functions. An accurate equation of state for mixtures of hard spheres in the isothermal–isobaric ensemble has been suggested (Hamad, 1997a). It is a generalization of the pure equation of state given by Eq. 10.

$$Z_{\mathrm{HS}}(T,P)=1+b_{\mathrm{P}}+\frac{3f_{\mathrm{P}}}{4}\ln\left[\frac{3+h_{\mathrm{P}}}{3+25h_{\mathrm{P}}}\right],$$

where

$$\begin{aligned} b&=3S_1S_2+S_3\\ f&=2S_2^2(3S_1^2-S_2)/h\\ h&=(5S_1S_2-S_3)/4\\ S_j&=\sum_i x_i\sigma_{ii}^j. \end{aligned}\qquad(15)$$

For the mixture contact values, accurate expressions are available for these in the canonical ensemble (Mansoori et al., 1971; Hamad, 1995). However, no such expressions are available in the isothermal–isobaric ensemble. Here we will derive the mixture contact values from a combination of exact equations (relating the contact values) and an appropriate closure. The exact equations are the extension of Eq. 8 to mixtures of additive hard spheres. Differentiating the mixture NPT partition function with respect to the size of spheres of one component and using the definition of the contact values, gives:

$$\frac{\partial(G-G^{ig})/NkT}{\partial\sigma_{ii}}=\frac{P}{12kT}x_i\sum_j x_j\sigma_{ij}^2 g_{ij,\mathrm{NPT}}(\sigma_{ij}),\qquad(16)$$

where we have used the independence of the ideal gas properties on σ_{ij} and the relationship $G/kT=-\ln\Delta$ to obtain the preceding equation. The residual Gibbs energy can be obtained by integrating the mixture equation of state, Eq. 15, according to:

$$\frac{G-G^{ig}}{NkT}=\int_0^P(Z-1)\frac{dP}{P}.\qquad(17)$$

For binary mixtures, Eq. 16 will give us two equations with three unknowns: g_{11}, g_{12}, g_{22}. A closure is needed to obtain all three contact values. A simple, yet fairly accurate closure has been suggested for the canonical ensemble (Hamad, 1997b):

$$2\sigma_{12}g_{12}=\sigma_{11}g_{22}+\sigma_{22}g_{11}.\qquad(18)$$

However, we can also use this equation in the isothermal–isobaric ensemble because the contact values in the two ensembles can be shown to be related by (as will be seen in Appendix B)

$$g_{ij,\mathrm{NPT}}=\frac{g_{ij,\mathrm{NVT}}}{Z}.\qquad(19)$$

In the previous two equations, we have dropped (σ_{ij}) from g_{ij} for simplicity. Combining the closure equation with Eq. 16 gives the individual contact values. The expressions are given in Appendix A.

Now we can develop equations for chain mixtures by using the general expression given by Eq. 1 and the values of Z_{bond} given by Malakhov and Brun (1992) in terms of the contact values. We first start with the solutions of hard chains in monomers of hard spheres. The compressibility factors for this case are

$$Z=[x_s+(1-x_s)m]Z_{\mathrm{HS}}(T,P)-(1-x_s)(m-1)g_{\mathrm{NPT},22}\qquad(20)$$

$$Z=[x_s+(1-x_s)m]Z_{\mathrm{HS}}(T,P)-(1-x_s)(m-1)\times\left[1+P\frac{\partial\ln g_{\mathrm{NPT},22}}{\partial P}\right],\qquad(21)$$

where x_s is the mole fraction of the solvent molecules, and g_{22} is the contact value of the chain spheres. Again the average Z is given by an expression similar to Eq. 14. In evaluating Z_{HS} and g_{22} one needs to supply the mole fraction of spheres of different sizes, x_1 with $x_2=1-x_1$. This mole fraction is obtained from

$$x_1=x_s/[x_s+m(1-x_s)].\qquad(22)$$

Figure 7 shows the compressibility factor of chains of 16-mer in a hard-sphere solvent. The solvent spheres are half the diameter of the chain spheres and the mole fraction is $x_s=1/2$. The simulation data are taken from the literature (Wichert et al., 1996). The figure shows the accuracy of the proposed equations, especially the average model. Figure 8 shows the results when the solvent spheres are larger than the chain spheres. The solvent spheres are now four times the diameter of the chain spheres and the mole fraction is

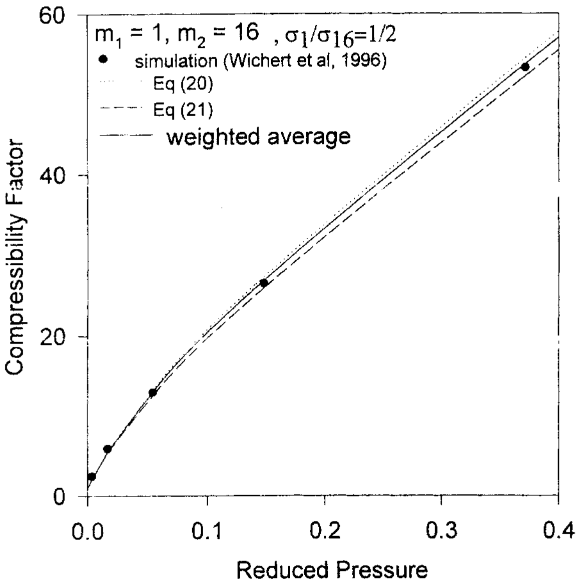

Figure 7. Compressibility factor of solutions of 16-mer chains in hard spheres for $\sigma_1/\sigma_{16} = 1/2$ and solvent mole fraction $x_s = 0.5$.

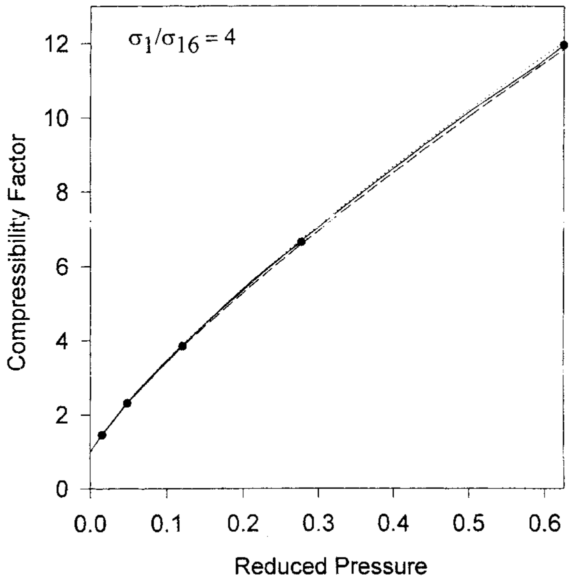

Figure 8. Compressibility factor of solution of 16-mer chains in hard spheres for $\sigma_1/\sigma_{16} = 4$ and solvent mole fraction $x_s = 0.94$.

Curves and points have the same meaning as in Figure 7.

$x_s = 0.94$. The accuracy of the three proposed equations is still very good even with this large size ratio.

Next we turn to mixtures of two hard chains, as a model for polymer blends. The compressibility factors for a mixture of two homopolymers are given by

$$Z = [x_{c1}m_1 + x_{c2}m_2]Z_{\mathrm{HS}}(T,P) - x_{c1}(m_1 - 1)g_{\mathrm{NPT},11} - x_{c2}(m_2 - 1)g_{\mathrm{NPT},22} \quad (23)$$

$$Z = [x_{c1}m_1 + x_{c2}m_2]Z_{\mathrm{HS}}(T,P) - x_{c1}(m_1 - 1) \times \left[1 + P\frac{\partial \ln g_{\mathrm{NPT},11}}{\partial P}\right] - x_{c2}(m_2 - 1)\left[1 + P\frac{\partial \ln g_{\mathrm{NPT},22}}{\partial P}\right], \quad (24)$$

where m_i is the chain length of species i, x_{ci} is the mole fraction of chains i, and g_{ii} is the contact value of spheres in chain i. The mole fraction of the spheres is given by

$$x_1 = m_1 x_{c1}/(m_1 x_{c1} + m_2 x_{c2}). \quad (25)$$

Figure 9 shows an equimolar mixture of 8-mer chains with 16-mer chains, with segments in the shorter chains half the size of segments in the longer chains, $\sigma_8/\sigma_{16} = 1/2$. The accuracy of the models is again apparent. A similar mixture with $\sigma_8/\sigma_{16} = 2/1$ is shown in Figure 10, again with accurate predictions.

Copolymers

Copolymers consist of at least two different types of chemically bonded repeat units. Here we will discuss two types of copolymers: diblock and alternating copolymers.

In diblock copolymers two types of units are arranged in two blocks. The blocks are chemically bonded together. For this type of polymer the equation of state is obtained by recasting the corresponding equations of the NVT ensemble:

$$Z = (m_a + m_b)Z_{\mathrm{HS}}(T,P) - (m_a - 1)g_{\mathrm{NPT},11} - (m_b - 1)g_{\mathrm{NPT},22} - g_{\mathrm{NPT},12} \quad (26)$$

$$Z = (m_a + m_b)Z_{\mathrm{HS}}(T,P) - (m_a - 1)\left[1 + P\frac{\partial \ln g_{\mathrm{NPT},11}}{\partial P}\right] - (m_b - 1)\left[1 + P\frac{\partial \ln g_{\mathrm{NPT},22}}{\partial P}\right] - \left[1 + P\frac{\partial \ln g_{\mathrm{NPT},12}}{\partial P}\right], \quad (27)$$

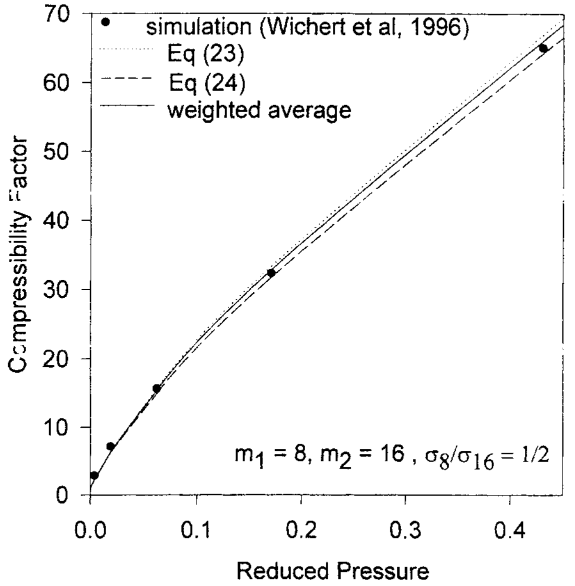

Figure 9. Compressibility factor of equimolar mixture of 8-mer and 16-mer chains: $\sigma_8/\sigma_{16} = 1/2$.

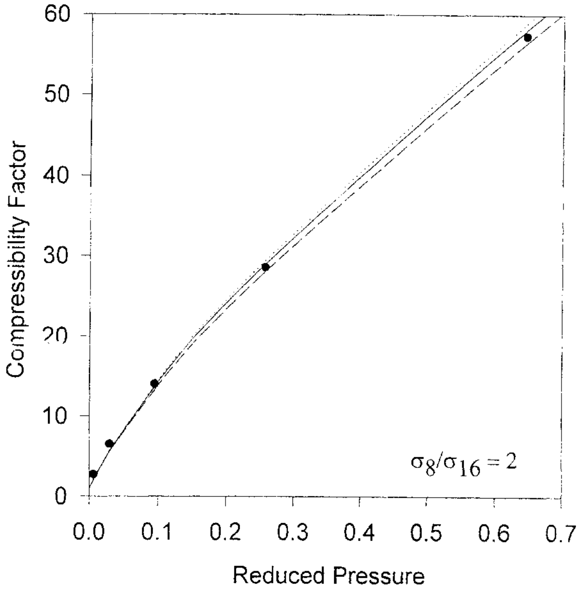

Figure 10. Compressibility factor of equimolar mixture of 8-mer and 16-mer chains: $\sigma_8/\sigma_{16} = 2$.
Curves and points have the same meaning as in Figure 9.

where m_a and m_b are the lengths of the two blocks. Figure 11 shows the compressibility factor of a 32-mer chain with two blocks of equal length. The spheres in the two blocks have a diameter ratio of 2. The predictions of the three equations are accurate when compared to the simulation data (Gulati et al., 1996).

In alternating copolymers two types of repeat units appear alternatively. For this type of polymer, only the unlike pair correlation function appears in the bonding term:

$$Z = mZ_{HS}(T,P) - (m-1)g_{NPT,12} \tag{28}$$

$$Z = mZ_{HS}(T,P) - (m-1)\left[1 + P\frac{\partial \ln g_{NPT,12}}{\partial P}\right]. \tag{29}$$

The compressibility factor of a 32-mer chain is shown in Figure 12. The values for the compressibility factor are only slightly different from the values of the diblock copolymer for the same size ratio of 2. The prediction of the three models is again accurate when compared to the simulation data (Gulati et al., 1996).

Discussion and Conclusions

In this work we have developed accurate equations of state for hard chains, their mixtures, and copolymers, in the isothermal–isobaric ensemble. The proposed equations have the advantage of being volume explicit. They also predict the correct volume at very high pressures, unlike most pressure-explicit equations. The new equations were tested for hard chains, solutions of hard chains, mixtures of hard chains, and block and alternating copolymers. All predictions were accurate when compared to simulation data. For long chains at high densities, the proposed equations are more accurate than the generalized Flory dimer theory.

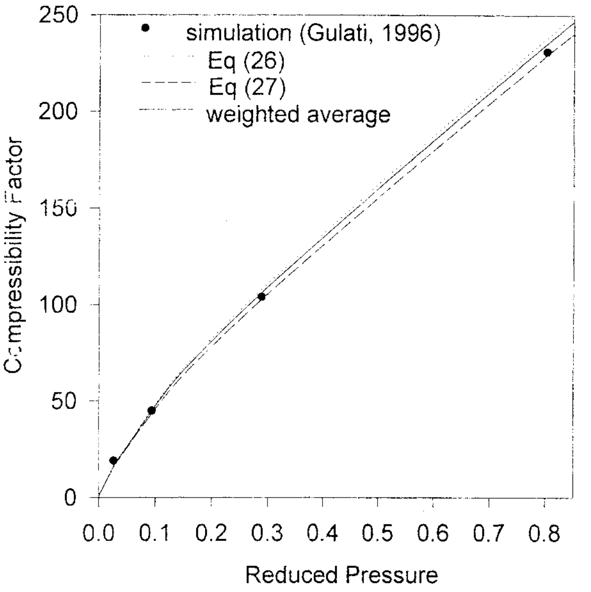

Figure 11. Compressibility factor of diblock copolymer.
Each block is 16-mer with $\sigma_a/\sigma_b = 2$.

As all the suggested equations are volume-explicit, they only have one value for the volume (one root) at any given pressure. Different phases, such as liquid and solid, will be described by equations with different pressure dependencies. These dependencies are obtained from the equations of state of the different phases. If the volume is given and one needs to solve for the pressure, then only one real root exists for the proposed equations for hard chains.

Polymer solutions and blends often show phase separation due to the small entropy of mixing. The study of the phase boundaries is very much simplified in the isothermal–isobaric ensemble equations, because the pressure appears as the in-

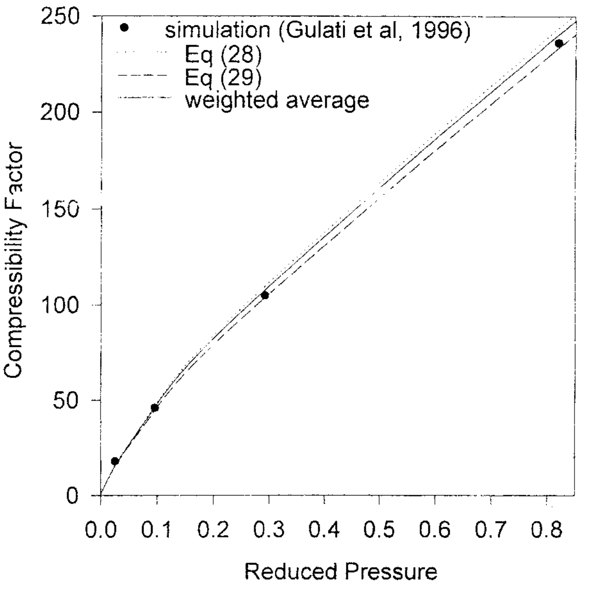

Figure 12. Compressibility factor of a 32-mer alternating copolymer with $\sigma_2/\sigma_1 = 2$.

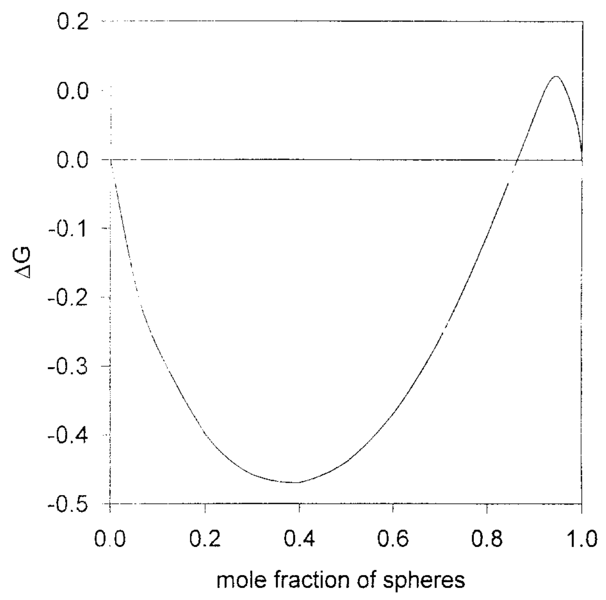

Figure 13. The Gibbs energy of mixing vs. solvent mole fraction for 16-mer chains in hard spheres.

The chain spheres are half the size of the solvent spheres. Curve was calculated from Eq. 21.

dependent variables. In the canonical ensemble the calculations are complicated by the need to numerically solve a set of complicated equations. Phase separation is characterized by the presence of a composition interval where the second derivative of the Gibbs energy of mixing ΔG is negative. In terms of the excess Gibbs energy G^E, one can write ΔG as

$$\frac{\Delta G}{NkT} = \sum_i x_i \ln(x_i) + \frac{G^E}{NkT}, \tag{30}$$

where the excess Gibbs energy is obtained from

$$\frac{G^E}{NkT} = \int_0^P \left[Z - \sum_i x_i Z_i \right] \frac{dP}{P}. \tag{31}$$

Figure 13 shows the Gibbs energy of mixing for a solution of 16-mer chains in hard spheres according to Eq. 21. The chain spheres are half the size of the solvent spheres ($\sigma_{16}/\sigma_1 = 1/2$). Equation 20 gives similar results. The figure clearly shows an immiscibility region close to solvent mole fraction of unity. The phase separation was also observed for other solutions. This phase separation is purely entropic, as there are no attractive forces. This result is consistent with the predictions of much more sophisticated models that include accurate thermodynamically consistent integral equations, density-functional theory, and computer simulation of hard-core lattice polymers (Biben and Hansen, 1991; Dijkstra and Frenkel, 1994). Experiments on colloids also support the presence of demixing. The models and the experiments suggest an entropic phase separation for solutions of very large molecules in small molecules. The demixing is found to take place in solutions of roughly equal volume fractions, as observed in our case. The existing pressure-explicit equations do not predict this phase separation because the excess Gibbs energy is always negative (Mansoori et al., 1971). This exciting result of our simple model is currently being investigated.

Acknowledgment

The author acknowledges the support of King Fahd University of Petroleum & Minerals.

Literature Cited

Bernal, J. D., *Liquids: Structure, Properties, Solid Imperfections*, T. J. Hughel, ed., Elsevier, Amsterdam (1965).

Biben, T., and J. Hansen, "Phase Separation of Asymmetric Binary Hard-Sphere Fluids," *Phys. Rev. Lett.*, **66**, 2215 (1991).

Boublik, T., C. Vega, and M. Diaz-Pena, "Equation of State of Chain Molecules," *J. Chem. Phys.*, **93**, 730 (1990).

Carnahan, N. F., and K. E. Starling, "Rigid Sphere Equation of State," *J. Chem. Phys.*, **51**, 635 (1969).

Chang, J., and S. Sandler, "The Correlation Functions of Hard-Sphere Chain Fluids: Comparison of the Wertheim Integral Equation Theory with the Monte Carlo Simulation," *J. Chem. Phys.*, **102**, 437 (1995).

Chapman, W. G., G. Jackson, and K. E. Gubbins, "Phase Equilibria of Associating Fluids: Chain Molecules with Multiple Bonding Sites," *Mol. Phys.*, **65**, 1057 (1988).

Chien, C. H., R. A. Greenkorn, and K. C. Chao, "Chain-of-Rotators Equation of State," *AIChE J.*, **29**, 560 (1983).

Chiew, Y. C., "Percus-Yevick Integral-Equation Theory for Athermal Hard-Sphere Chains," *Mol. Phys.*, **70**, 129 (1990).

Danner, R. P., and M. S. High, *Handbook of Polymer Solution Thermodynamics*, Amer. Inst. Chem. Eng., New York (1993).

Dickman, R., and C. K. Hall, "Equation of State for Chain Molecules: Continuous-Space Analog of Flory Theory," *J. Chem. Phys.*, **85**, 4108 (1986).

Dickman, R., and C. K. Hall, "High Density Monte-Carlo Simulations of Chain Molecules: Bulk Equation of State and Density Profile Near Walls," *J. Chem. Phys.*, **89**, 3168 (1988).

Dijkstra, M., and D. Frenkel, "Evidence of Entropy-Driven Demixing in Hard-Core Fluids," *Phys. Rev. Lett.*, **72**, 298 (1994).

Flory, P. J., "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.*, **9**, 660 (1941).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York (1954).

Ghonasgi, D., and W. G. Chapman, "Prediction of the Properties of Model Polymer Solutions and Blends," *AIChE J.*, **40**, 878 (1994).

Gulati, H. S., J. M. Wichert, and C. K. Hall, "Generalized Flory Equations of State for Hard Heteronuclear Chain Molecules," *J. Chem. Phys.*, **104**, 5220 (1996).

Hamad, E. Z., "Consistency Test of Mixture Pair Correlation Function Integrals," *J. Chem. Phys.*, **101**, 10195 (1994).

Hamad, E. Z., "Consistent Contact Pair Correlation Functions and Equations of State for Hard-Sphere Mixtures," *J. Chem. Phys.*, **103**, 3733 (1995).

Hamad, E. Z., "Volume-Explicit Equation of State for Hard Spheres, Disks and Mixtures of Hard Spheres," *Ind. Eng. Chem. Res.*, **36**, 4385 (1997a).

Hamad, E. Z., "Closures for Exact Relations Between Mixture Pair Correlation Integrals," *J. Chem. Phys.*, **107**, 6877 (1997b).

Honnell, K. G., and C. K. Hall, "A New Equation of State for Athermal Chains," *J. Chem. Phys.*, **90**, 1841 (1989).

Honnell, K. G., and C. K. Hall, "Theory and Simulation of Hard Chain Mixtures: Equation of State, Mixing Properties, and Density Profile Near Hard Walls," *J. Chem. Phys.*, **95**, 4481 (1991).

Hu, Y., H. Liu, and J. M. Prausnitz, "Equation of State for Fluids Containing Chainlike Molecules," *J. Chem. Phys.*, **104**, 396 (1996).

Huggins, M. L., "Solutions of Long Chain Compounds," *J. Chem. Phys.*, **9**, 440 (1941).

Kiao, R., J. M. Caruthers, and K. C. Chao, "Polymer Chain-of-Rotators Equation of State," *Ind. Eng. Chem. Res.*, **35**, 1446 (1996).

Malakhov, A. O., and E. B. Brun, "Multicomponent Hard-Sphere Heterochain Fluid: Equations of State in a Continuum Space," *Macromol.*, **25**, 6262 (1992).

Mansoori, G. A., N. F. Carnahan, K. E. Sterling, and T. W. Leland, "Equilibrium Thermodynamic Properties of Mixtures of Hard Spheres," *J. Chem. Phys.*, **54**, 1523 (1971).

Phan, S., E. Kierlik, M. Rosinberg, H. Yu, and G. Stell, "Equations of State for Hard Chain Molecules," *J. Chem. Phys.*, **99**, 5326 (1993).

Sanchez, I., and R. LaCombe, "An Elementary Molecular Theory of Classical Fluids. Pure Fluids," *J. Phys. Chem.*, **80**, 2352 (1976).

Schweizer, K. S., and J. G. Curro, "Integral Equation Theory of the Structure and Thermodynamics of Polymer Blends," *J. Chem. Phys.*, **91**, 5059 (1989).

Smith, S. W., C. K. Hall, and B. D. Freeman, "Molecular Dynamics Study of Transport Coefficients for Hard-Chain Fluids," *J. Chem. Phys.*, **102**, 1057 (1995).

Song, Y., S. M. Lambert, and J. M. Prausnitz, "Equation of State for Mixtures of Hard Sphere Chains Including Copolymers," *Macromol.*, **27**, 441 (1994a).

Song, Y., S. M. Lambert, and J. M. Prausnitz, "A Perturbed Hard-Sphere-Chain Equation of State for Normal Fluids and Polymers," *Ind. Eng. Chem. Res.*, **33**, 1047 (1994b).

Tao, F. M., and E. A. Mason, "Statistical-Mechanical Equation of State for Nonpolar Fluids: Prediction of Phase Boundaries," *J. Chem. Phys.*, **100**, 9075 (1994).

Tildesley, D. J., and W. B. Streett, "An Equation of State for Hard Dumbbell Fluids," *Mol. Phys.*, **41**, 85 (1980).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces: I. Statistical Thermodynamics," *J. Stat. Phys.*, **35**, 19 (1984).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces: IV. Equilibrium Polymerization," *J. Stat. Phys.*, **42**, 477 (1986).

Wichert, J. M., H. S. Gulati, and C. K. Hall, "Binary Hard Chain Mixtures: I. Generalized Flory Equations of State," *J. Chem. Phys.*, **105**, 7669 (1996).

Yethiraj, A., and C. K. Hall, "Square-Well Chains: Bulk Equation of State Using Perturbation Theory and Monte Carlo Simulations of Bulk Pressure and Density Profiles Near Walls," *J. Chem. Phys.*, **95**, 1999 (1991).

Appendix A: Mixture Contact Pair Correlation Functions in the NPT Ensemble

For a binary mixture, Eq. 16 gives two equations. Combining these equations with Eq. 18 and solving for the three $g_{ij,\mathrm{NPT}}$, gives

$$g_{11,\mathrm{NPT}} = 1 + \frac{\left(x_1\sigma_{11}\sigma_{12} + 2x_2\sigma_{22}^2\right)\dfrac{\partial\Gamma}{\partial\sigma_{11}} - x_1\sigma_{11}\sigma_{12}\dfrac{\partial\Gamma}{\partial\sigma_{22}}}{x_1\left(x_1^2\sigma_{11}^3\sigma_{12} + 2x_1x_2\sigma_{11}^2\sigma_{22}^2 + x_2^2\sigma_{12}\sigma_{22}^3\right)}$$

$$g_{12,\mathrm{NPT}} = 1 + \frac{x_2^2\sigma_{22}^3\dfrac{\partial\Gamma}{\partial\sigma_{11}} + x_1^2\sigma_{11}^3\dfrac{\partial\Gamma}{\partial\sigma_{22}}}{x_1x_2\sigma_{12}\left(x_1^2\sigma_{11}^3\sigma_{12} + 2x_1x_2\sigma_{11}^2\sigma_{22}^2 + x_2^2\sigma_{12}\sigma_{22}^3\right)},$$

where $g_{22,\mathrm{NPT}}$ is obtained from $g_{11,\mathrm{NPT}}$ by interchanging subscripts 1 and 2. The dimensionless residual Gibbs energy, Γ, is given by

$$\Gamma \equiv \frac{G - G^{ig}}{NkT} = b\rho + \frac{3f\rho}{4}\ln\left[\frac{3 + h\rho}{3 + 25h\rho}\right] + \frac{9f}{4h}\ln\left(1 + \frac{h\rho}{3}\right) - \frac{9f}{100h}\ln\left(1 + \frac{25h\rho}{3}\right).$$

Appendix B: Relationship Between Contact Values of Pair Correlation Function in the NVT and NPT Ensembles

The contact values for hard spheres in the NVT ensemble can be obtained from the following relationship (Hamad, 1994):

$$g_{ij,\mathrm{NVT}}(\sigma_{ij}) = \frac{-1}{2\pi N(2 - \delta_{ij})\rho x_i x_j \sigma_{ij}^2}\left[\frac{\partial \ln Q}{\partial \sigma_{ij}}\right]_{T,V}. \quad \text{(B1)}$$

A similar relationship can be written in the NPT ensemble:

$$g_{ij,\mathrm{NPT}}(\sigma_{ij}) = \frac{-kT}{2\pi N(2 - \delta_{ij})P x_i x_j \sigma_{ij}^2}\left[\frac{\partial \ln \Delta}{\partial \sigma_{ij}}\right]_{T,P}. \quad \text{(B2)}$$

Dividing the previous two equations gives

$$\frac{g_{ij,\mathrm{NVT}}(\sigma_{ij})}{g_{ij,\mathrm{NPT}}(\sigma_{ij})} = \frac{P}{RT\rho}\,\frac{\left(\partial A/\partial\sigma_{ij}\right)_{T,V}}{\left(\partial G/\partial\sigma_{ij}\right)_{T,P}}, \quad \text{(B3)}$$

where we have used the following relationships between the partition functions and thermodynamic quantities:

$$\ln Q = -A/kT$$
$$\ln \Delta = -G/kT. \quad \text{(B4)}$$

The first ratio on the righthand side of Eq. B4 is the compressibility factor Z, and we will show next that the second ratio is equal to unity. First, from the properties of partial derivatives we can write:

$$\left[\frac{\partial G}{\partial\sigma_{ij}}\right]_{T,P} = \left[\frac{\partial G}{\partial\sigma_{ij}}\right]_{T,V} + \left[\frac{\partial G}{\partial V}\right]_{T,\sigma_{ij}}\left[\frac{\partial V}{\partial\sigma_{ij}}\right]_{T,P}. \quad \text{(B5)}$$

Replacing G by $A + PV$ in the first term on the righthand side and using $dG = VdP - SdT$ in the second term, gives

$$\left[\frac{\partial G}{\partial\sigma_{ij}}\right]_{T,P} = \left[\frac{\partial A}{\partial\sigma_{ij}}\right]_{T,V} + V\left[\frac{\partial P}{\partial\sigma_{ij}}\right]_{T,V} + V\left[\frac{\partial P}{\partial V}\right]_{T,\sigma_{ij}}\left[\frac{\partial V}{\partial\sigma_{ij}}\right]_{T,P}. \quad \text{(B6)}$$

Using the differential identity

$$\left[\frac{\partial P}{\partial V}\right]_{T,\sigma_{ij}}\left[\frac{\partial V}{\partial\sigma_{ij}}\right]_{T,P}\left[\frac{\partial\sigma_{ij}}{\partial P}\right]_{T,V} = -1, \quad \text{(B7)}$$

Eq. B6 reduces to

$$\left[\frac{\partial G}{\partial\sigma_{ij}}\right]_{T,P} = \left[\frac{\partial A}{\partial\sigma_{ij}}\right]_{T,V}. \quad \text{(B8)}$$

Equation B3 now becomes

$$\frac{g_{ij,\mathrm{NVT}}(\sigma_{ij})}{g_{ij,\mathrm{NPT}}(\sigma_{ij})} = Z. \quad \text{(B9)}$$

This is Eq. 19 in the text.

Manuscript received May 19, 1998, and revision received Sept. 18, 1998.