Simple Equation of State for Hard-Sphere Chains

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A simplified thermodynamic perturbation theory-dimer framework is used to derive an equation of state for hard-sphere chains. The accuracy of the equation is tested against simulation data for hard-sphere chains containing up to 201 hard-sphere segments. A comparison is also presented with the results of other more sophisticated hard-sphere chain equations of state. The equation reproduces the compressibility factor of hard-sphere chains obtained from molecular simulation with a reasonable degree of accuracy. The equation can potentially form the theoretical backbone of an equation of state for real chainlike molecules. From a practical perspective, it has the advantage of being considerably simpler than alternative hard-sphere chain equations.

Introduction

Equations of state have an important role in the prediction of chemical processes and the phase behavior of fluid mixtures (Sadus, 1992). Historically, most equations of state used commonly in chemical engineering applications have been largely empirical. Empirical equations of state such as the Redlich-Kwong (1949), Peng-Robinson (1976), and Soave (1972) equations and their many variants (Sadus, 1994) are often preferred to more theoretically based equations (Sadus, 1992). Part of the appeal of these equations is that they are cubic with respect to volume (or density), and as such the volume can be obtained analytically. In contrast, at a given pressure, more theoretically based equations that involve typically the Carnahan-Starling (1969) term have six possible solutions for volume. Although the empirical approach has worked successfully for fluids of relatively simple molecules, extension of large molecular fluids such as long-chain hydrocarbons and polymers is difficult. It has been demonstrated amply that the prediction of the properties of these fluids requires a more sophisticated approach exemplified by the simplified perturbed hard-chain theory (SPHCT) (Kim et al., 1986), statistical associating fluid theory (SAFT) (Chapman et al., 1988), and statistical associating fluid theory−variable range (SAFT-VR) (Gil-Villegas et al., 1997) equations of state.

An important aspect of the development of accurate equations of state for real chainlike molecules is the development of accurate models for the hard-sphere chain. The concept of the hard-sphere chain provides the theoretical backbone for an equation of state for chainlike molecules that is analogous to the role of the hard-sphere concept for simple molecules. Several hard-sphere chain equations have been proposed (Dickman and Hall, 1986; Chapman et al., 1988; Ghonasgi and Chapman, 1994; Chang and Sandler, 1994; Sadus, 1995, 1996). The benchmark for the accuracy of hard-sphere chain equations of state is molecular simulation data, which provide essentially exact results for the hard-sphere chain model. The results of calculations (Sadus, 1995) with many of the proposed hard-sphere chain equations of state agree well with simulation data.

From a practical perspective, it would be very desirable to minimize the complexity of the equation of state while not sacrificing accuracy excessively and retaining some theoretical basis. The aim of this work is to derive a reasonably accurate but simple equation of state for hard-sphere chains.

Derivation

The starting basis for our derivation is the general relationship for the simplified thermodynamic perturbation theory−dimer (STPT−D) equation (Sadus, 1995). The STPT−D equation was derived (Sadus, 1995) from the thermodynamic perturbation theory−dimer (TPT−D) model proposed by Ghonasagi and Chapman (1994) and Chang and Sandler (1994). The TPT−D model modifies the generalized TPT model (Wertheim, 1987; Chapman et al., 1988) to include structural information on the diatomic fluid. Sadus (1995) proposed that the TPT−D equations could be simplified by proposing a general linear relationship between the hard-sphere and dimer site–site correlation functions. The resulting STPT–D equation (Sadus, 1995) is

$$Z^{m} = 1 + m(Z^{HS} - 1) + (1 - m)\eta \frac{\partial \ln g_{HS}}{\partial \eta} + \frac{\alpha\eta(2 - m)}{2\alpha\eta + 1}. \tag{1}$$

Equation 1 relates the compressibility factor (Z^{m}) of a chain of m tangent hard-sphere segments to the hard-sphere compressibility factor (Z^{HS}), the hard-sphere site–site correlation function at contact (g_{HS}), and the packing fraction defined as $\eta = \pi m \rho \sigma^{3}/6$, where ρ is the number density and σ is the hard-sphere diameter. It is valid for all chains that have $m \geq 2$. In Eq. 1, the α parameter links the hard-dimer site–site correlation function to the hard-sphere correlation function (Sadus, 1995).

Shah et al. (1994) have reported an empirical relationship for Z^{HS} that can be expressed as

$$Z^{HS} = \frac{1 + (k_0 + k_1)\eta}{(1 - k_0\eta)^{2}}, \tag{2}$$

where $k_0 = 1.2864$ and $k_1 = 2.8225$ are empirically evaluated constants (Shah et al., 1994). Comparison of the results obtained (Shah et al., 1994) from Eq. 2 with molecular simulation data for hard spheres indicates that the compressibility factor is predicted with an accuracy that is close to that of the Carnahan-Starling (1969) equation. However, because Eq. 2 has quadratic volume dependence when it is coupled to a van der Waals-like dispersion term, the resulting equation yields only four roots, one of which is always negative. Therefore, the use of the Shah et al. term in Eq. 1 instead of the Carnahan-Starling term will result in a less complicated equation of state for chains.

The hard-sphere correlation function can be obtained from the general relationship:

$$g^{HS} = \frac{1 - Z^{HS}}{4\eta}. \tag{3}$$

Therefore, substituting the righthand side of Eq. 2 into Eq. 3 yields the following relationship:

$$g_{HS} = \frac{k_0 + k_1 - k_0^{2}\eta}{4(1 - k_0\eta)^{2}}. \tag{4}$$

Substituting Eqs. 3 and 4 into Eq. 1 results in the following equation

$$Z^{m} = 1 + m\left(\frac{(k_0 + k_1)\eta - k_0^{2}\eta^{2}}{(1 - k_0\eta)^{2}}\right) + (1 - m)\left(\frac{2k_0\eta}{1 - k_0\eta} - \frac{k_0^{2}\eta}{k_0 + k_1 - k_0^{2}\eta}\right) + \frac{\alpha\eta(2 - m)}{2\alpha\eta + 1}. \tag{5}$$

We will refer to this equation as the empirical simplified thermodynamic perturbation theory–dimer (ESTPT–D) equation.

In Eq. 5, α is the only parameter whose value is unknown. Its value can be obtained from simulation data (Yethiraj and Hall, 1990), but the overall accuracy of the equation of state is improved (Sadus, 1995) by evaluating it from second virial coefficient data. The second virial coefficient (B_2) can be obtained from (Reed and Gubbins, 1973)

$$B_2 = \left(\frac{\partial Z}{\partial \rho}\right)_{\rho = 0}. \tag{6}$$

For the compressibility factor given by the ESTPT–D equation (Eq. 5), we obtain:

$$\frac{B_2}{m^{2}\sigma^{3}} = \frac{\pi}{6}\left[k_1 - k_0 + \frac{k_0^{2}}{k_0 + k_1} + \frac{1}{m}\left(2k_0 - \frac{k_0^{2}}{k_0 + k_1}\right) + \alpha\left(\frac{2}{m} - 1\right)\right]. \tag{7}$$

Comparing molecular simulation data (Yethiraj et al., 1992) for the second virial coefficients of hard-sphere chains containing up to 128 hard-sphere segments with the results obtained from Eq. 7, we find that the average absolute deviation is minimized when $\alpha = 1.2313$.

Comparison with Simulation Data and Other Equations of State

The rationale for the ESTPT–D equation is to provide a backbone for the development of equations of state to model real chainlike fluids. The equation has the advantages that it is relatively simple; it has a reasonable theoretical basis, and it can be used for any number of segments. However, it is almost inevitable that the trade-off for increased simplicity will be a reduction in accuracy. Therefore, it is important to establish how well the equation represents the properties of hard-sphere chains.

The compressibility factor predicted by the ESTPT–D equation is compared in Figure 1 with molecular simulation data for hard chains containing 4, 8, 16, 51 and 201 hard-sphere segments. The simulation data for $m \leq 16$ and $m = 32$ were obtained from Chang and Sandler (1994) and Denlinger and Hall (1990), respectively. The simulation data reported by Gao and Wiener (1989) was used for the comparison of the 51-mer and 201-mer chains. It is apparent from Figure 1 that the ESTPT–D provides a reasonable description of the hard-sphere chain for the full density range. The average absolute deviation between simulation and equation-of-state calculations ranges between 4.43% ($m = 2$) and 9.54% ($m = 51$). How does this compare with other equations of state?

Many theoretically based hard-sphere chain equations of state have been proposed and the accuracy of some of these equations have been evaluated elsewhere (Sadus, 1995). A common feature of many hard-sphere chain equations is the incorporation of structural information for the diatomic fluid in addition to contributions from hard-sphere properties. Ghonasgi and Chapman (1994) and Chang and Sandler (1994) proposed the following thermodynamic perturbation

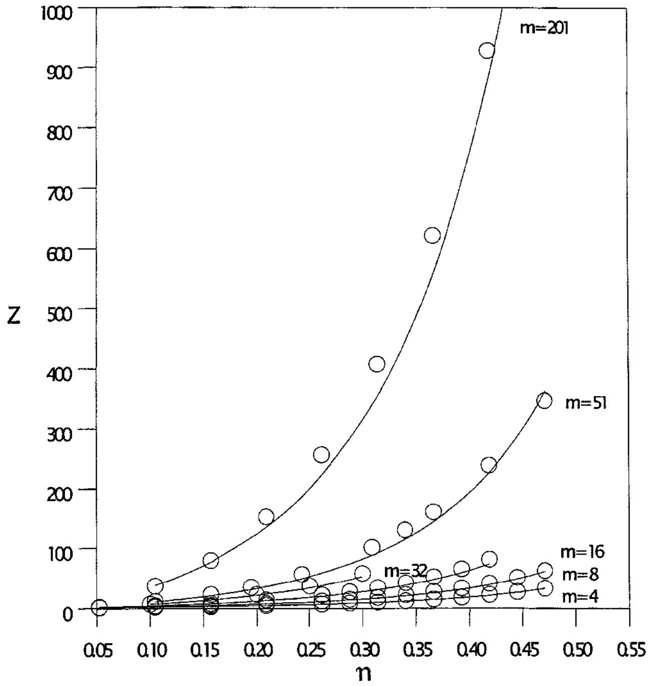

Figure 1. Compressibility factor of hard-sphere chains of different size as a function of packing fraction.

The open circles represent molecular simulation data, whereas the lines represent calculations using the ESTPT–D equation of state.

theory–dimer (TPT–D1) equation:

$$Z^m = m\left[\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right] - 0.5m\left[1+\frac{\eta(5-2\eta)}{(1-\eta)(2-\eta)}\right] - (0.5m-1)\left[1+\frac{2\eta(2+\eta)}{(1-\eta)(1+2\eta)}\right]. \tag{8}$$

Chang and Sandler (1994) also proposed an empirical improvement referred to as the TPT–D2 equation:

$$Z^m = m\left(\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right) - 0.5m\left(1+\frac{\eta(5-2\eta)}{(1-\eta)(2-\eta)}\right) - (0.5m-1)\left(1+\frac{\eta(3.498-0.24\eta-0.414\eta^2)}{(1-\eta)(2-\eta)(0.534+0.414\eta)}\right). \tag{9}$$

The simplified thermodynamic perturbation theory–dimer equation (STPT–D) proposed by Sadus (1995) has the following functional form:

$$Z^m = 1+\frac{m(4\eta-2\eta^2)}{(1-\eta)^3} + (1-m)\left(\frac{\eta(5-\eta)}{(1-\eta)(2-\eta)}\right) + \frac{0.7666\eta(2-m)}{1.5332\eta+1}. \tag{10}$$

Table 1. Average Absolute Deviation of the Calculated Compressibility Factor of m-Hard-Sphere Chains vs. Molecular Simulation Data

	AAD (%)				
m	GF–D*	TPT–D1*	TPT–D2*	STPT–D*	ESTPT–D
4	1.72	1.04	0.76	0.85	4.43
8	3.58	1.88	1.78	1.28	5.95
16	6.64	2.63	3.74	1.67	7.41
32	10.44	4.27	5.75	1.08	7.75
51	5.37	2.72	3.26	3.97	9.35
201	9.35	5.89	6.51	3.92	8.10

*From Sadus (1995).

An alternative to the thermodynamic perturbation theory approach is the generalized Flory–dimer (GF–D) equation (Honnell and Hall, 1989). The GF–D equation is

$$Z^m = \left(\frac{v_e(m)-v_e(1)}{v_e(2)-v_e(1)}\right) Z_{\text{dimer}} - \left(\frac{v_e(m)-v_e(2)}{v_e(2)-v_e(1)}\right) Z_{\text{mono}}, \tag{11}$$

where v_e is the excluded volume of an m-segment molecule, and the compressibility factor of the monomer and dimer are calculated from the Carnahan-Starling (1969) and Tildesley-Streett (1980) equations, respectively.

The average absolute deviations between simulation results and equation-of-state calculations are summarized in Table 1. It is apparent form this analysis that the TPT–D1, TPT–D2, and STPT–D equations are considerably more accurate than the ESTPT–D equation. Nonetheless, the ESTPT–D equation performs well in view of its relative simplicity. Although the quality of agreement between theory and simulation deteriorates with increasing chain length, the reduction in the quality of prediction does not represent a catastrophic failure of the equation. Indeed, it is of interest to note that in some cases the ESTPT–D equation either comes reasonably close ($m = 16$) or outperforms slightly ($m = 32$, 201) the more sophisticated GF–D equation.

Conclusions

In view of its relative simplicity, the ESTPT–D equation reproduces the simulation data for the compressibility factor of hard-sphere chains with a reasonable degree of accuracy. It can be used potentially as the backbone of a real equation for real chainlike fluids such as n-alkanes and polymers. From a practical perspective, the equation also offers the advantage that if it is used in conjunction with a typical dispersion term, the resulting equation will have only four volume roots compared with the six roots resulting from the use of other hard-sphere chain equations.

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