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Citation: [The Journal of Chemical Physics](#) **96**, 4604 (1992); doi: 10.1063/1.462796

View online: <http://dx.doi.org/10.1063/1.462796>

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Bonded hard-sphere (BHS) theory for the equation of state of fused hard-sphere polyatomic molecules and their mixtures

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(Received 15 October 1991; accepted 27 November 1991)

The bonded hard-sphere (BHS) approach originally developed for diatomic and triatomic molecules is generalized to hard-sphere polyatomic models which are formed by bonding together their constituent hard spheres. The thermodynamic properties of the polyatomic fluid are obtained from the known properties of a corresponding multicomponent mixture of different sized hard spheres with bonding sites. In the limit of complete bonding, hard-sphere polyatomic molecules are formed. As well as the general expressions for polyatomic molecules and their mixtures, the equation of state of hard-sphere chain molecules, which are simple models of homologous series such as the alkanes, perfluoroalkanes, etc., is presented. More specifically, the chain molecules are formed from two different types of hard spheres 1 and 2. Spheres of type 1 make up the backbone of the chain and, in this case, would represent the carbon atoms; spheres of type 2 represent the substituents, i.e., the hydrogen or fluorine atoms. Although the BHS theory is only strictly valid for molecules of tangent spheres, the theory can also be applied to fused hard-sphere (FHS) molecules with overlapping spheres. The latter are more realistic models of actual molecules. In the spirit of the semiempirical scaled particle theories (SPT), the properties of the FHS molecule can be related to those of an equivalent BHS molecule of tangent spheres with the same parameter of nonsphericity, α . When dealing with large polyatomic molecules, α does not need to be calculated numerically as is the case with the usual SPT approach. As an approximation one may use the analytical values of α for the diatomic segments making up the molecule. This simple approach turns out to be quite successful. The BHS equation of state has been compared with "exact" computer simulation data for homonuclear and heteronuclear FHS systems of diatomics, linear and nonlinear triatomics, and tetrahedral pentatomics, as well as mixtures of FHS molecules. Good agreement is found for all of these systems. In general, the BHS approach is more rigorous and easier to extend to larger polyatomic molecules and their mixtures than SPT.

I. INTRODUCTION

The development of an accurate thermodynamic perturbation theory has been central to the progress of theories of liquids and their mixtures. In this well-established approach, the thermodynamic properties of the fluid are related to those of a suitable reference system with purely repulsive interactions, using an expansion in powers of the attractive perturbation potential.¹ The success of the method rests in the fact that the structure of a liquid is principally determined by the repulsive forces between molecules. A knowledge of the properties of an appropriate hard-core reference is therefore sufficient to describe the behavior of the fluid. For spherical molecules the reference is simply a hard sphere with a temperature-dependent diameter which incorporates the softness of the full potential, and accurate representations of the thermodynamic and structural properties of hard-sphere systems are readily available. In the case of nonspherical polyatomic molecules, the most obvious reference models are based on hard-core potentials of fused hard spheres (FHS), where the molecules are represented by a number of overlapping hard-sphere sites. FHS models take into account the anisotropic nature of the repulsive forces. The main purpose of this work is to develop a general analytical expression for the thermodynamic properties of pure fluids and multicomponent mixtures composed of these

FHS reference molecules, which could find use in perturbation theories of polyatomic molecules.

A great deal of effort has been spent on the determination of the thermodynamic properties of FHS models. For an essentially complete account of such studies the reader is referred to a series of review articles.²⁻⁴ The so-called scaled particle theories (SPT) are by far the most useful semiempirical theories of FHS molecules.² With such an approach, the equation of state of the fluid is given in terms of a parameter of nonsphericity, α , which accounts for molecular shape and characterizes the geometry of the molecule. In the latest studies employing SPT,⁵⁻⁷ the most successful versions of the theory have been tested with computer simulation data for the equation of state of homonuclear and heteronuclear FHS diatomics, triatomics, and pentatomics, and good agreement between theory and simulation was established.

Although SPT generally provides one with a reasonable description of the properties of FHS systems, the approach suffers from a number of serious drawbacks. Firstly, SPT is not expected to be a good representation of the properties of highly-asymmetrical heteronuclear polyatomic molecules since the equations are based on either those of hard spheres, as in earlier versions of the theory,² or those of homonuclear hard-sphere chains.⁵⁻⁷ Furthermore, the parameter of nonsphericity must be calculated numerically in the case of large polyatomic molecules, especially if these are highly asym-

metrical. This means that analytical expressions for the thermodynamic properties of arbitrary FHS polyatomic molecules are not, in general, available within the SPT approach. Finally, when SPT is extended to mixtures, an effective nonsphericity parameter, α_m , for the mixture is used together with the usual pure-component equations (see, for example, Ref. 6). This approximation is equivalent to the van der Waals one-fluid (vdW1) conformal mixing rule which can be quite crude when the components of the mixture are very different in size and shape. In order to overcome the deficiencies of SPT, we generalize the alternative approach of bonded hard-sphere (BHS) theory, originally developed for diatomic⁸ and triatomic⁹ molecules, to FHS molecules and their mixtures.

The equations of state of heteronuclear diatomic and triatomic molecules formed from tangentially-bonded hard spheres of different sizes have been determined using BHS theory and computer simulation in a couple of preceding studies.^{8,9} By examining reference mixtures of hard spheres with bonding sites, theoretical expressions for the thermodynamic properties of the tangent hard-sphere molecules were obtained in the limit of complete association. A number of symmetrical and asymmetrical heteronuclear molecules were studied, and the BHS theory was found to be in excellent agreement with the simulation data over a range of densities in the fluid state.

In this work, expressions for the thermodynamic properties of arbitrary polyatomic molecules formed from fused hard spheres are presented. More specifically, the BHS equation of state of simple models for homologous series of chain molecules such as alkanes and their derivatives (perfluoroalkanes, etc.) are obtained. A general analytical expression for mixtures of polyatomic molecules formed from any number of hard-sphere sites is also given.

Although the BHS theory is strictly only rigorous for molecules formed from tangentially-bonded hard spheres, the approach is extended to deal with molecules of fused hard spheres by using simple ideas about the parameter of nonsphericity which stem from SPT. An approximate method of obtaining the thermodynamic properties of FHS polyatomics using the analytical α 's of their diatomic segments is also proposed; this circumvents the problem inherent in SPT of numerically calculating α for large molecules. Hence, the BHS expressions can be used for the more realistic FHS models of any polyatomic molecule as well as for the tangent BHS models. After presenting the theory in some detail, the adequacy of the BHS approach in describing the thermodynamic properties of a number of homonuclear and heteronuclear FHS systems including diatomics, linear and nonlinear triatomics, and tetrahedral pentatomics is examined by comparison with exact simulation data.

II. THEORY

A. Potential models

Fused hard-sphere models have been extensively used as convenient references for polyatomic molecules since these incorporate a good representation of the anisotropic repulsive forces between molecules. In such models the molecules

are represented by a number of sites interacting via hard-sphere potentials; these sites usually coincide with the individual atoms forming the molecule. The interaction potential, $u(1,2)$, for a pair of FHS molecules 1 and 2 takes the form

$$u(1,2) = \sum u_{ij}^{\text{hs}}(r_{ij}), \quad (1)$$

where

$$u_{ij}^{\text{hs}}(r_{ij}) = \begin{cases} +\infty, & \text{if } r_{ij} < \sigma_{ij} \\ 0, & \text{if } r_{ij} \geq \sigma_{ij} \end{cases} \quad (2)$$

Although the overall potential depends on the positions and orientations of the two molecules, represented by (1,2), it can be separated into a sum over all intermolecular pairs of hard-sphere sites. If any of the hard-sphere sites with diameters σ_i and σ_j are closer together than $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, then the two molecules will overlap with an infinite potential energy, i.e., $u(1,2) = u_{ij}^{\text{hs}}(r_{ij}) = +\infty$.

Initially, molecules formed from tangentially-bonded hard spheres are examined since these systems can be treated naturally within the framework of BHS theory. Various examples of diatomic, triatomic, and polyatomic chain molecules are shown in Fig. 1. Such models are just special cases of the more general FHS models with overlapping intramo-

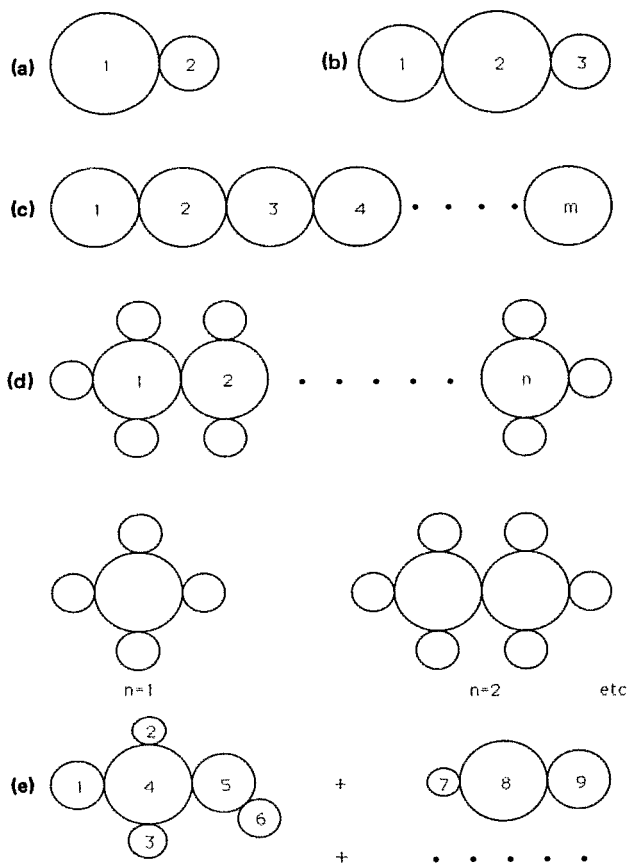


FIG. 1. The BHS models are formed from tangentially-bonded hard spheres. Examples of these are (a) heteronuclear diatomics, (b) heteronuclear triatomics, (c) homonuclear chains, (d) heteronuclear chain models of alkanes, and (e) general multicomponent mixtures.

lecular hard-sphere sites. The BHS approach is then extended to deal with FHS systems which are more accurate representations of real polyatomic molecules.

B. Bonded hard-sphere (BHS) theory

In obtaining a BHS equation of state for molecules formed from tangent hard spheres, the properties of an equivalent reference mixture of different sized spheres is used. Consequently, expressions for the thermodynamic and structural properties of hard-sphere mixtures will be reviewed first.

The compressibility factor of a multicomponent mixture of hard spheres is accurately given by the expression of Mansoori *et al.*:¹⁰

$$Z^{\text{hs}} = \frac{PV}{NkT} = \frac{6}{\pi\rho} \left(\frac{\xi_0}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} - \frac{\xi_3\xi_2^3}{(1-\xi_3)^3} \right), \quad (3)$$

where P is the pressure of the system, V is the volume, T is the temperature, N is the total number of spheres, $\rho = N/V$ is the total number density, and k is Boltzmann's constant. The appropriate reduced densities ξ_i for the hard-sphere mixture are

$$\xi_i = \frac{\pi\rho}{6} \sum_i x_i (\sigma_i)^3. \quad (4)$$

Here, $x_i = N_i/N$ is the mole fraction, N_i is the number, σ_i is the diameter of spheres of component i , and $\eta = \xi_3$ is the packing fraction of the mixture. The sum in Eq. (4) is over all the hard-sphere components.

As will become clear later, the BHS approach also requires the use of the corresponding expressions for the contact values of the mixture's hard-sphere radial distribution functions. For a pair of components i and j , the value of the radial distribution function $g_{ij}^{\text{hs}}(r_{ij})$ at hard-sphere contact, i.e., its value when the distance between the i and j spheres is $r_{ij} = \sigma_{ij} = (\sigma_i + \sigma_j)/2$, is given by¹¹

$$g_{ij}^{\text{hs}}(\sigma_{ij}) = \frac{1}{(1-\xi_3)} + 3 \left(\frac{\sigma_i\sigma_j}{\sigma_i + \sigma_j} \right) \frac{\xi_2}{(1-\xi_3)^2} + 2 \left(\frac{\sigma_i\sigma_j}{\sigma_i + \sigma_j} \right)^2 \frac{\xi_2^2}{(1-\xi_3)^3}. \quad (5)$$

The BHS equation of state for an arbitrary molecule formed from bonded hard spheres will be expressed in terms of the $g_{ij}^{\text{hs}}(\sigma_{ij})$ s for all contact pairs, and their derivatives with respect to the number density:

$$\rho \left(\frac{\partial g_{ij}^{\text{hs}}(\sigma_{ij})}{\partial \rho} \right)_{T,N} = \frac{\xi_3}{(1-\xi_3)^2} + 3 \left(\frac{\sigma_i\sigma_j}{\sigma_i + \sigma_j} \right) \frac{\xi_2(1+\xi_3)}{(1-\xi_3)^3} + 2 \left(\frac{\sigma_i\sigma_j}{\sigma_i + \sigma_j} \right)^2 \frac{\xi_2^2(2+\xi_3)}{(1-\xi_3)^4}. \quad (6)$$

It is important to note that Eq. (6) represents a derivative with respect to the total number density of spheres in the mixture.

An expression for the thermodynamic properties of diatomic molecules, formed from tangentially-bonded hard

spheres 1 and 2 of diameters σ_1 and σ_2 such that the bond length between the centers of spheres 1 and 2 is $l_{12} = (\sigma_1 + \sigma_2)/2$ [see Fig. 1(a)], was obtained in a preceding study.⁸ The corresponding BHS equation of state, given in terms of the compressibility factor, is

$$Z^{\text{di}} = \frac{PV}{N_m kT} = 2Z^{\text{hs}} - \left[1 + \frac{\rho}{g_{12}^{\text{hs}}(\sigma_{12})} \left(\frac{\partial g_{12}^{\text{hs}}(\sigma_{12})}{\partial \rho} \right)_{T,N} \right], \quad (7)$$

where N_m is now the number of diatomic molecules, and the total packing fraction of the system is given by $\eta = \xi_3 = \pi(\sigma_1^3 + \sigma_2^3)N_m/(6V)$.

In a subsequent paper,⁹ the BHS theory was extended to triatomic molecules formed from three fused hard spheres 1, 2, and 3 with diameters σ_1 , σ_2 , and σ_3 ; spheres 1 and 3 were positioned at each end with sphere 2 in the center. Generally speaking, for FHS models of triatomics, the bond lengths l_{12} from the center of sphere 1 to the center of sphere 2 and l_{23} from the center of sphere 2 to the center of sphere 3 have to be specified together with the bond angle ω . In this case, however, the hard spheres were fused tangentially to each other so that the bond lengths were $l_{12} = (\sigma_1 + \sigma_2)/2$ and $l_{23} = (\sigma_2 + \sigma_3)/2$ [see Fig. 1(b)]. The BHS equation of state for such a system is given by⁹

$$Z^{\text{tri}} = \frac{PV}{N_m kT} = 3Z^{\text{hs}} - \left[1 + \frac{\rho}{g_{12}^{\text{hs}}(\sigma_{12})} \left(\frac{\partial g_{12}^{\text{hs}}(\sigma_{12})}{\partial \rho} \right)_{T,N} \right] - \left[1 + \frac{\rho}{g_{23}^{\text{hs}}(\sigma_{23})} \left(\frac{\partial g_{23}^{\text{hs}}(\sigma_{23})}{\partial \rho} \right)_{T,N} \right], \quad (8)$$

which includes the separate contributions due to the 1-2 and 2-3 bonding contacts. The packing fraction is now $\eta = \xi_3 = \pi(\sigma_1^3 + \sigma_2^3 + \sigma_3^3)N_m/(6V)$.

Before a general BHS equation of state for arbitrary polyatomic molecules and mixtures is presented, it is instructive to develop the BHS approach for chain models of an important class of polyatomic molecules, namely the homologous series of alkanes and their derivatives (e.g., perfluoroalkanes, perchloroalkanes, etc.). The compressibility factor of a simple "united-atom" chain model formed from hard spheres of equal size [Fig. 1(c)] has already been given by Chapman *et al.*:¹²

$$Z^{\text{chain1}} = \frac{PV}{N_m kT} = m \frac{(1 + \eta + \eta^2 - \eta^3)}{(1 - \eta)^3} - (m - 1) \frac{(1 + \eta - \eta^2/2)}{(1 - \eta)(1 - \eta/2)}, \quad (9)$$

where m is the number of spheres in the chain and $\eta = \pi m \sigma^3 N_m/(6V)$ is the packing fraction. Although this equation is in good agreement with simulation data for hard-sphere chains¹² and gives reasonable agreement in describing the thermodynamic properties of alkanes (e.g., see Refs. 13 and 14), the chain model it describes is not sophisticated enough to reproduce finer details of the properties of real chain molecules. In particular, it does not describe the

anomaly in the critical pressure exhibited by the homologous series of the alkanes which is presumably due to "end effects." It is with this in mind that a second more detailed model for these chain molecules is examined.

The improved chain model is depicted in Fig. 1(d) together with the first two homologues of the series. These molecules are formed from two different types of hard spheres 1 and 2 with diameters σ_1 and σ_2 . Spheres of type 1 make up the backbone of the chain, and spheres of type 2 represent the substituent atoms. In the case of alkanes and their derivatives, spheres 1 would represent the carbon atoms and spheres 2 the substituent hydrogen, chlorine, or fluorine atoms, etc. Hence, we retain the identities of the substituent and backbone atoms, rather than treating the methyl and methylene groups as "united-atom" segments.

The starting point in the development of a BHS equation of state for such a chain model is a binary mixture of hard spheres with diameters σ_1 and σ_2 . In order to ensure the correct stoichiometry in forming the hard-sphere chains, the compositions of spheres 1 and 2 have to be $x_1 = N_1/N = n/(3n+2)$ and $x_2 = N_2/N = (2n+2)/(3n+2)$, respectively, where n is the number of spheres making up the backbone of the chain. Note that there are a total of $3n+2$ spheres in the chain molecule, n of which are spheres of type 1 (carbons) and $2n+2$ of which are spheres of type 2 (hydrogens, chlorines, fluorines, etc.). Bonding sites are then placed on the hard spheres to allow for association; in the limit of complete bonding the chain molecules are formed (see Fig. 2). Two different types of sites have to be considered, namely, one type A to allow for bonding between spheres 1 forming the backbone of the chain, and another type B to allow for bonding between the backbone and substituent spheres 1 and 2. Only A - A bonding between like spheres of types 1 and 2 are permitted, with no possibility of multiple bonding at a given site. Furthermore, all the bonding sites of a given type are taken to be equivalent, and can be represented by off-center square-well potentials, ϕ_{AA}^{bond} and ϕ_{BB}^{bond} , which are highly directional and short ranged. However, since for the systems of interest, the limiting case of complete association is being examined, the precise nature of the site-site potentials need not be specified. As will become clear later, an important assumption made in the BHS approach is that bonding at one site is independent of bonding at another site on the same sphere so that the relative positions of the sites are arbitrary. Since this assumption is most reasonable when the sites are as far apart as possible, one would expect the theory to work best when a tetrahedral geometry is adopted so that the angle between the sites on each sphere is 109° .

As has already been mentioned, the thermodynamic properties of the chain molecules formed from tangent hard spheres can be expressed in terms of the properties of a corresponding mixture of associating hard spheres in the limit of complete bonding. The properties of the latter can be obtained using a simple perturbation theory based on the approach of Wertheim¹⁵⁻¹⁸ for molecules with multiple bonding sites. The general expressions for multicomponent mixtures of associating hard spheres^{12,19} have been used to develop the BHS theory for diatomic⁸ and triatomic⁹ tangent hard-sphere molecules. In the spirit of the BHS approach, the compressibility factor of the chain molecules formed from spheres of type 1 and 2 can be written as the sum of the hard-sphere contribution, and the 1-1 and 1-2 bonding contributions:

$$Z^{\text{mix}} = \frac{PV}{NkT} = Z^{\text{hs}} + Z_{11}^{\text{bond}} + Z_{12}^{\text{bond}}. \quad (10)$$

Here, the hard-sphere term Z^{hs} is given by Eq. (3) and the bonding terms by

$$Z_{11}^{\text{bond}} = \rho \left(\frac{2n-2}{3n+2} \right) \left(\frac{\partial X_A}{\partial \rho} \right)_{T,N} \left(\frac{1}{X_A} - \frac{1}{2} \right) \quad (11)$$

and

$$Z_{12}^{\text{bond}} = \rho \left(\frac{4n+4}{3n+2} \right) \left(\frac{\partial X_B}{\partial \rho} \right)_{T,N} \left(\frac{1}{X_B} - \frac{1}{2} \right). \quad (12)$$

The factors arise because there are a total of $2n-2$ equivalent sites of type A and $4n+4$ equivalent sites of type B per chain of $3n+2$ spheres. X_A and X_B are the fractions of spheres of a given type not bonded at sites A and B , respectively. Following Wertheim's prescription these are expressed as

$$X_A = \frac{1}{1 + [\rho \Delta_{AA}/(3n+2)] X_A} \quad (13)$$

and

$$X_B = \frac{1}{1 + [\rho \Delta_{BB}/(3n+2)] X_B}. \quad (14)$$

For short-range potentials Δ_{AA} and Δ_{BB} are accurately given by²⁰

$$\Delta_{AA} = 4\pi g_{11}^{\text{hs}}(\sigma_{11}) \sigma_{11}^2 \int \langle f_{AA}(11) \rangle_{\omega_1, \omega_1} dr_{11}, \quad (15)$$

and

$$\Delta_{BB} = 4\pi g_{12}^{\text{hs}}(\sigma_{12}) \sigma_{12}^2 \int \langle f_{BB}(12) \rangle_{\omega_1, \omega_2} dr_{12}. \quad (16)$$

Here, $g_{11}^{\text{hs}}(\sigma_{11})$ and $g_{12}^{\text{hs}}(\sigma_{12})$ are the 1-1 and 1-2 contact

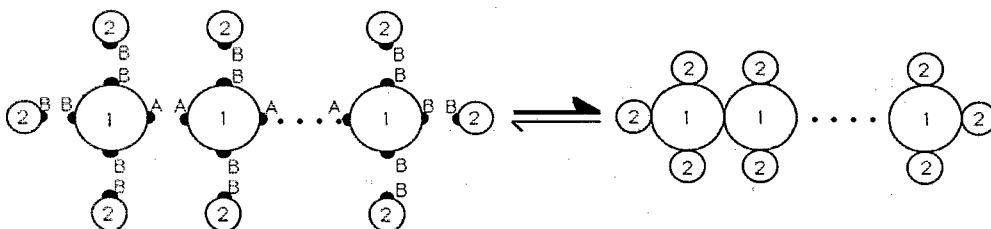


FIG. 2. The chain molecules are formed by bonding together the backbone spheres 1 and the substituent spheres 2 of the hard-sphere mixture with association sites. Only A - A and B - B bonding is allowed.

values of the radial distribution function for the hard-sphere reference mixture [see Eq. (5)], and

$$\langle f_{AA}(11) \rangle_{\omega_1, \omega_1} = \langle \exp(-\phi_{AA}^{\text{bond}}/kT) - 1 \rangle_{\omega_1, \omega_1}$$

and

$$\langle f_{BB}(12) \rangle_{\omega_1, \omega_2} = \langle \exp(-\phi_{BB}^{\text{bond}}/kT) - 1 \rangle_{\omega_1, \omega_2}$$

are the angle averages of the Mayer f function for the A - A and B - B site-site intermolecular potential over all orientations of the spheres.

The fully-bonded chain molecules are formed when the strengths of the A - A and B - B site-site interactions tend to infinity as their ranges tend to zero. If this is done so that the limiting values of Δ_{AA} and Δ_{BB} are infinite, the fractions of spheres not bonded at sites A and B tend to zero, i.e., $X_A = X_B = 0$. This effectively means that there are infinitely strong bonding spots on the surface of the spheres causing irreversible association at hard-sphere contact. Rearranging Eqs. (13) and (14) we obtain quadratic equations in X_A and X_B :

$$\left(\frac{\rho \Delta_{AA}}{3n+2} \right) X_A^2 + X_A - 1 = 0 \quad (17)$$

and

$$\left(\frac{\rho \Delta_{BB}}{3n+2} \right) X_B^2 + X_B - 1 = 0. \quad (18)$$

In the limit of complete bonding these expressions can be written as

$$\lim_{X_A \rightarrow 0} \left[\left(\frac{\rho \Delta_{AA}}{3n+2} \right) X_A^2 + X_A - 1 \right] = \left(\frac{\rho \Delta_{AA}}{3n+2} \right) X_A^2 - 1 = 0 \quad (19)$$

and

$$\lim_{X_B \rightarrow 0} \left[\left(\frac{\rho \Delta_{BB}}{3n+2} \right) X_B^2 + X_B - 1 \right] = \left(\frac{\rho \Delta_{BB}}{3n+2} \right) X_B^2 - 1 = 0, \quad (20)$$

or simply as

$$X_A^2 = \frac{3n+2}{\rho \Delta_{AA}} \quad (21)$$

and

$$X_B^2 = \frac{3n+2}{\rho \Delta_{BB}}. \quad (22)$$

Differentiating X_A and X_B with respect to the total number density of spheres and then substituting into Eqs. (11) and (12) gives

$$Z_{11}^{\text{bond}} = -\rho X_A^2 \frac{(n-1)}{(3n+2)^2} \left[\Delta_{AA} + \rho \left(\frac{\partial \Delta_{AA}}{\partial \rho} \right)_{T,N} \right] \quad (23)$$

and

$$Z_{12}^{\text{bond}} = -\rho X_B^2 \frac{(2n+2)}{(3n+2)^2} \left[\Delta_{BB} + \rho \left(\frac{\partial \Delta_{BB}}{\partial \rho} \right)_{T,N} \right]. \quad (24)$$

After substituting the limiting values Eqs. (21) and (22) into Eqs. (23) and (24), respectively, the 1-1 and 1-2 bonding contributions are given by

$$\begin{aligned} \lim_{X_A \rightarrow 0} Z_{11}^{\text{bond}} &= -\left(\frac{n-1}{3n+2} \right) \left[1 + \frac{\rho}{\Delta_{AA}} \left(\frac{\partial \Delta_{AA}}{\partial \rho} \right)_{T,N} \right] \\ &= -\left(\frac{n-1}{3n+2} \right) \left[1 + \frac{\rho}{g_{11}^{\text{hs}}(\sigma_{11})} \left(\frac{\partial g_{11}^{\text{hs}}(\sigma_{11})}{\partial \rho} \right)_{T,N} \right], \end{aligned} \quad (25)$$

and

$$\begin{aligned} \lim_{X_B \rightarrow 0} Z_{12}^{\text{bond}} &= -\left(\frac{2n+2}{3n+2} \right) \left[1 + \frac{\rho}{\Delta_{BB}} \left(\frac{\partial \Delta_{BB}}{\partial \rho} \right)_{T,N} \right] \\ &= -\left(\frac{2n+2}{3n+2} \right) \left[1 + \frac{\rho}{g_{12}^{\text{hs}}(\sigma_{12})} \left(\frac{\partial g_{12}^{\text{hs}}(\sigma_{12})}{\partial \rho} \right)_{T,N} \right]. \end{aligned} \quad (26)$$

Note that these expressions represent the contributions due to complete association. As shown, the bonding terms can also be written in terms of the contact values of the hard-sphere radial distribution functions $g_{11}^{\text{hs}}(\sigma_{11})$ and $g_{12}^{\text{hs}}(\sigma_{12})$ since these differ from Δ_{AA} and Δ_{BB} only by a multiplying factor [see Eqs. (15) and (16)]. The full equation of state of the chain molecule is obtained when the hard-sphere reference term, Eq. (3), and bonding terms, Eqs. (25) and (26), are combined in Eq. (10). The final expression for the molecular compressibility factor is given by

$$\begin{aligned} Z^{\text{chain2}} &= \frac{PV}{N_m kT} \\ &= (3n+2)(Z^{\text{hs}} + \lim_{X_A \rightarrow 0} Z_{11}^{\text{bond}} + \lim_{X_B \rightarrow 0} Z_{12}^{\text{bond}}) \\ &= (3n+2)Z^{\text{hs}} \\ &\quad - (n-1) \left[1 + \frac{\rho}{g_{11}^{\text{hs}}(\sigma_{11})} \left(\frac{\partial g_{11}^{\text{hs}}(\sigma_{11})}{\partial \rho} \right)_{T,N} \right] \\ &\quad - (2n+2) \left[1 + \frac{\rho}{g_{12}^{\text{hs}}(\sigma_{12})} \left(\frac{\partial g_{12}^{\text{hs}}(\sigma_{12})}{\partial \rho} \right)_{T,N} \right], \end{aligned} \quad (27)$$

where the expression is multiplied by the factor of $(3n+2)$ since N_m is the number of molecules and not the number of spheres.

One must ensure that this BHS equation of state has the correct limiting behavior. When there is one sphere in the chain ($n=1$) and the diameters of the substituent spheres are zero ($\sigma_2=0$), expression (27) unsurprisingly reduces to the Carnahan and Starling equation²¹ for pure hard spheres:

$$Z^{\text{hs}} = \frac{PV}{N_1 kT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (28)$$

where the molecular packing fraction is $\eta = \pi \sigma_1^3 N_1 / (6V)$. If we retain the backbone chain of n spheres with $\sigma_2=0$ for the diameters of the substituent spheres, the equation reverts to Eq. (9) for the chains of homonuclear tangent hard spheres with $m=n$. When $n=1$ but $\sigma_2 \neq 0$, the equation of

state for the first homologue in the series (e.g., methane) is obtained:

$$Z^{\text{chain2}} = 5Z^{\text{hs}} - 4 \left[1 + \frac{\rho}{g_{12}^{\text{hs}}(\sigma_{12})} \left(\frac{\partial g_{12}^{\text{hs}}(\sigma_{12})}{\partial \rho} \right)_{T,N} \right]. \quad (29)$$

In this case the equation does not include the contribution due to 1-1 contacts. This term is included in second and higher homologues ($n \geq 2$) of the series to account for the 1-1 bonds forming the backbone of the chain.

Before we continue, it is important to mention the deficiencies of Wertheim's first-order thermodynamic perturbation theory as applied to the aforementioned BHS theory of chain molecules. Since, within the theory, one assumes that each attraction site contributes independently to the thermodynamic properties of the system regardless of its position, it will fail when two sites are close enough for the hard cores to prevent simultaneous bonding at both positions. This has two major consequences as far as the chain model is concerned. The first is that the theory cannot distinguish between different configurations of the chain molecules. For the sake of brevity and to simplify the discussion, we have treated all of type *A* and *B* sites as equivalent. It would have been more rigorous to treat each sphere as a separate component with different sites in order to control the specificity of sphere-sphere bonding. In the end, however, the two routes yield the same final expressions for the equation of state. The satisfactory outcome of the simplified approach highlights the problem with the BHS approach. In effect, structural isomers of a chain molecule are treated in the same way within the BHS theory. Since all isomers have the same number of bonds of a given type, the theory predicts that their thermodynamic properties will be identical; this turns out to be a good approximation in practice. The second problem with the BHS approach has already been discussed in the context of triatomic molecules.⁹ The accuracy of the equation of state, Eq. (27), in describing the properties of the chain fluid is expected to decrease when the substituent spheres become significantly larger than the backbone spheres ($\sigma_2 \geq 3\sigma_1$). This is because 1-1 contacts are sterically excluded for chain molecules with sufficiently small central spheres, while the BHS theory implicitly includes the possibility of 1-1 contacts in the reference hard-sphere term. This having been said, the BHS approach will nevertheless prove to be very successful in accurately representing the thermodynamic properties of a large number of hard-sphere polyatomic molecules.

Following a similar procedure to that described earlier for the hard-chain polyatomic molecules, the general BHS equation of state for a multicomponent mixture of molecules formed from tangent hard spheres of different sizes is derived as

$$Z^{\text{BHS}} = \frac{PV}{N_m kT} = \sum_i x_m(i) N_s(i) Z^{\text{hs}} - \sum_i x_m(i) \sum_{\text{bonds}} \left[1 + \frac{\rho}{g_{jk}^{\text{hs}}(\sigma_{jk})} \left(\frac{\partial g_{jk}^{\text{hs}}(\sigma_{jk})}{\partial \rho} \right)_{T,N} \right]. \quad (30)$$

Here, N_m is the total number of molecules and $x_m(i)$ is the

mole fraction of molecules of type *i* comprising $N_s(i)$ hard-sphere segments. The equation of state represents two sums, one over all components *i* in the mixture, and the other over the number of bonding contacts *jk* per molecule of type *i*. For example, in the case of the arbitrary mixture depicted in Fig. 1(e), the sum would include five bonding contacts 1-4, 2-4, 3-4, 4-5, and 5-6 for the first molecule, and two bonding contacts 7-8 and 8-9 for the second molecule. The equation of state would therefore include contributions from the contact values of the radial distribution function for each of these bonds. It is important to note that in this expression ρ represents the total number density of spheres and not the number density of molecules, and that Z^{hs} is the total compressibility factor of the multicomponent hard-sphere reference mixture.

The BHS equations of state presented here for diatomic, triatomic, and chain molecules, and the general expression for mixtures of hard-sphere polyatomic molecules are compared with existing simulation data of a number of FHS systems in Sec. III.

C. BHS theory of FHS molecules

In the discussion thus far, we have focused on model molecules formed from tangentially-bonded hard spheres which can be conveniently treated with the framework of the BHS approach. FHS models formed from overlapping hard spheres are, however, more accurate representations of the repulsive intermolecular forces present in real systems. In this section we show how, by using ideas originating from SPT, the BHS theory developed earlier can be used to describe the thermodynamic properties of FHS molecules.

Central to any SPT is the parameter of nonsphericity α which accounts for molecular shape and characterizes the geometry of the molecule.² For a molecule modeled as a convex body, the parameter α is rigorously defined in terms of the molecule's surface area, S_m , volume, V_m , and $1/4\pi$ multiple of the mean-curvature integral, R_m :

$$\alpha = \frac{R_m S_m}{3V_m}. \quad (31)$$

The mean-curvature integral was originally used by Ki-hara²² to represent the shapes of convex molecules. Although FHS models are nonconvex bodies for which the mean radius of curvature is ill defined, Boublik and Nezbeda²³ have shown that by using the mean-curvature integral of an equivalent convex body enveloping the molecule, an accurate expression for α of the FHS molecule can be obtained. This value of the mean-curvature integral, together with the correct values for the surface area and volume of the FHS molecule, provides one with an SPT equation of state for the FHS fluid.

SPT equations of state are, in general, functions of the temperature, density, and α with all the molecular shape dependence included in the latter; an example of such an equation is presented in Sec. II C. The consequence of this in the context of SPT is that two molecules of different geometry but with the same value of α will have the same thermodynamic properties. The uniqueness of α in determining the effect of shape on the molecular properties is born out in

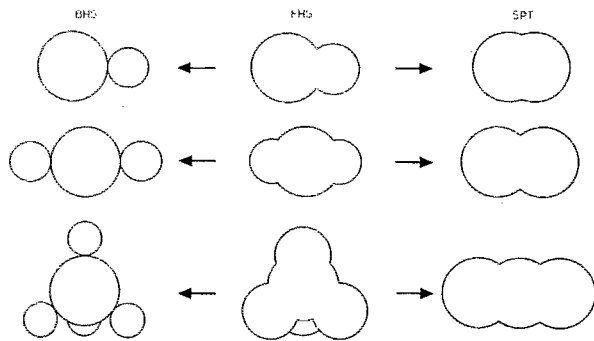


FIG. 3. In the BHS approach the FHS molecules are treated as equivalent BHS molecules formed from tangentially-bonded hard spheres, while in the latest SPT the FHS molecules are related to homonuclear chains of hard spheres. A schematic representation of this is shown for diatomic, triatomic, and pentatomic FHS molecules.

practice as shown by a number of appropriate simulation studies.² We take advantage of this to relate the properties of arbitrary FHS molecules to those of equivalent tangent hard-sphere BHS molecules which can be treated within the BHS approach.

In order to use the BHS theory to determine the thermodynamic properties of a FHS molecule formed from overlapping hard spheres, an equivalent BHS molecule with the same value of α is examined. For the FHS and BHS molecules to be equivalent, the relative sizes of hard spheres forming the BHS molecule must satisfy the following equation:

$$\alpha_{\text{FHS}} = \alpha_{\text{BHS}}. \quad (32)$$

The diameters of the hard spheres making up the BHS molecule will generally be different from those of the original FHS molecule. Typical examples of equivalent BHS molecules for diatomic, triatomic, and pentatomic FHS molecules are depicted in Fig. 3.

The parameter of nonsphericity of a diatomic FHS molecule is calculated from the molecular surface area and volume, and from the mean-curvature integral of the enveloping convex body, given by⁸

$$S_m = \frac{\pi}{2} (\sigma_1^2 + \sigma_2^2 + 2\sigma_1 a + 2\sigma_2 b), \quad (33)$$

$$V_m = \frac{\pi}{12} (\sigma_1^3 + \sigma_2^3 + 3\sigma_1^2 a + 3\sigma_2^2 b - 4a^3 - 4b^3), \quad (34)$$

and

$$R_m = \frac{1}{4} \left(\sigma_1 + \sigma_2 + l_{12} + \frac{(\sigma_1 - \sigma_2)^2}{4l_{12}} \right), \quad (35)$$

respectively. The distances a and b from the centers of spheres 1 and 2 to the intersecting plane are given by

$$a = \frac{1}{2} \left(l_{12} + \frac{\sigma_1^2 - \sigma_2^2}{4l_{12}} \right) \quad (36)$$

and

$$b = l_{12} - a. \quad (37)$$

In the particular case of BHS molecules with tangentially-fused hard spheres, $a = \sigma_1/2$, $b = \sigma_2/2$, and $l_{12} = (\sigma_1 + \sigma_2)/2$. These expressions are used in Eq. (31)

to determine α for the FHS diatomic and the corresponding BHS diatomic. The ratio of the hard-sphere diameters $\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}}$ of the BHS molecule is obtained by solving relation (32) so that the values of α for the FHS and BHS molecules are identical. The BHS compressibility factor, Eq. (7), for diatomic molecules of tangent hard spheres can then be used as the equation of state for the original FHS molecule. This procedure is employed in Sec. III to determine the equation of state of a number of homonuclear and heteronuclear FHS diatomics for which simulation data are available.

The BHS equation of state, Eq. (8), for tangent hard-sphere triatomics can be used in a similar way for FHS triatomics. As with the diatomic molecules, this requires the calculation of α for the FHS triatomic and for the equivalent BHS molecule. The surface area and volume of a linear triatomic molecule in which the end spheres 1 and 3 do not overlap, are given by⁹

$$S_m = \frac{\pi}{2} [\sigma_1^2 + \sigma_3^2 + 2a\sigma_1 + 2(b+c)\sigma_2 + 2d\sigma_3] \quad (38)$$

and

$$V_m = \frac{\pi}{12} [\sigma_1^3 + \sigma_3^3 + 3a\sigma_1^2 + 3(b+c)\sigma_2^2 + 3d\sigma_3^2 - 4(a^3 + b^3 + c^3 + d^3)]. \quad (39)$$

If $(\sigma_1 + \sigma_3)/2 > l_{12} + l_{23}$, spheres 1 and 3 overlap and the volume of the molecule is given by

$$V_m = \frac{\pi}{12} [2\sigma_1^3 + 2\sigma_3^3 + 3(a-e)\sigma_1^2 + 3(b+c)\sigma_2^2 + 3(d-f)\sigma_3^2 - 4(a^3 + b^3 + c^3 + d^3 - e^3 - f^3)]. \quad (40)$$

As for the diatomics, the distances from the centers of spheres 1 and 2 to the intersecting plane of the two spheres are a and b , respectively, where

$$a = \frac{1}{2} \left(l_{12} + \frac{\sigma_1^2 - \sigma_2^2}{4l_{12}} \right) \quad (41)$$

and

$$b = l_{12} - a. \quad (42)$$

Similarly, the distances c and d from the centers of spheres 2 and 3 to the intersecting plane of the two spheres are

$$d = \frac{1}{2} \left(l_{23} + \frac{\sigma_3^2 - \sigma_2^2}{4l_{23}} \right) \quad (43)$$

and

$$c = l_{23} - d. \quad (44)$$

For molecules with overlapping end spheres 1 and 3, the distances e and f from the centers of the spheres to the intersecting plane are given by

$$e = \frac{1}{2} \left(l_{12} + l_{23} + \frac{\sigma_3^2 - \sigma_2^2}{4(l_{12} + l_{23})} \right) \quad (45)$$

and

$$f = l_{12} + l_{23} - e, \quad (46)$$

respectively. In the case of molecules with tangentially-fused hard spheres, this contribution is not included and $a = \sigma_1/2$,

$b = c = \sigma_2/2$, $d = \sigma_3/2$, $l_{12} = (\sigma_1 + \sigma_2)/2$, and $l_{23} = (\sigma_2 + \sigma_3)/2$. There are no analytical expressions for the mean-curvature integral of the convex bodies of nonlinear FHS molecules. In the case of linear FHS triatomics, however, the analytical mean-curvature integral of the equivalent convex body with $\sigma_1 \neq \sigma_2 \neq \sigma_3$ and $\sigma_3 \leq [\sigma_2(l_{12} + l_{23}) - \sigma_1 l_{23}]/l_{12}$ is given by⁹

$$R_m = \frac{1}{4} \left(\sigma_1 + \sigma_3 + l_{12} + l_{23} + \frac{(\sigma_2 - \sigma_1)^2}{4l_{12}} + \frac{(\sigma_2 - \sigma_3)^2}{4l_{23}} \right). \quad (47)$$

When $\sigma_3 \geq [\sigma_2(l_{12} + l_{23}) - \sigma_1 l_{23}]/l_{12}$ the central sphere is included within the convex body formed by the outer spheres, and R_m is then given by

$$R_m = \frac{1}{4} \left(\sigma_1 + \sigma_3 + l_{12} + l_{23} + \frac{(\sigma_1 - \sigma_3)^2}{4(l_{12} + l_{23})} \right). \quad (48)$$

As before, these expressions for S_m , V_m , and R_m are used in Eq. (31) to determine α for the FHS triatomic and for the equivalent BHS triatomic. In the case of a symmetrical FHS triatomic with $\sigma_1 = \sigma_3$, the ratio of the end-to-middle hard-sphere diameters $\sigma_1^{\text{BHS}}/\sigma_2^{\text{BHS}} = \sigma_3^{\text{BHS}}/\sigma_2^{\text{BHS}}$ for the corresponding BHS molecule is obtained by solving relation (32). The BHS compressibility factor, Eq. (8), for triatomic molecules of tangent hard spheres is used in Sec. III as the equation of state for a number of symmetrical FHS triatomics. For asymmetrical triatomics the same method can be applied, although there is no unique solution to Eq. (32). This problem can easily be resolved by keeping the ratio of the end-sphere diameters $\sigma_3^{\text{BHS}}/\sigma_1^{\text{BHS}}$ at the constant value of σ_3/σ_1 for the FHS molecule when Eq. (32) is solved for the ratio $\sigma_1^{\text{BHS}}/\sigma_2^{\text{BHS}}$ which produces the same value of α as that of the FHS molecule.

The generalization of the BHS approach to FHS molecules discussed thus far suffers from the same central problem as SPT since both procedures require the calculation of α . As was shown earlier, α can be determined analytically for FHS diatomics and linear triatomics. However, for nonlinear FHS triatomics and larger FHS polyatomics, α has to be determined numerically.²⁴ This is by no means straightforward for large molecules of complicated shape. A considerable advantage of the BHS approach over SPT is that the method outlined earlier for diatomic molecules can be carried out for the diatomic segments making up the polyatomic molecules. Hence, although α for the polyatomic molecule cannot be determined analytically, the α 's for the separate diatomic segments can. In this way an equivalent polyatomic molecule of tangent hard spheres can be constructed, and the BHS equation of state, Eq. (30), can be used to describe the properties of the FHS polyatomic. This approximate scheme has been used quite successfully to determine the equation of state of FHS tetrahedral pentatomics in Sec. III. Hence, the method provides an analytical, albeit approximate, route to the properties of FHS polyatomics, and we feel this is one of the most attractive features of the BHS approach.

D. Scaled particle theory (SPT)

Ritchie²⁵ was the first to extend the idea of SPT, originally developed for hard-sphere fluids, to hard convex bodies, although an analytical expression for the system's thermodynamic properties was not obtained in his study. An equation of state for hard convex molecules based on SPT and incorporating α , which accounts for molecular shape, was later obtained by Gibbons.^{26,27} This equation can be used to describe the properties of nonconvex FHS models, for which α is not rigorously defined, if the correct values for the surface area and volume of the FHS molecule are used together with the mean-curvature integral of an equivalent hard convex body.²³

There have been a number of improvements to the SPT equation of state of Gibbons. In a modification often referred to as the improved scaled particle theory (ISPT), Boublik²⁸ adapted the original SPT equation so that it gives the correct hard-sphere limit, reducing to the Carnahan and Starling equation (28) when $\alpha = 1$. More recently, Boublik and co-workers^{5,6} have compared the virial coefficients for chains of hard spheres obtained from Eq. (9) with those for convex bodies obtained from SPT to obtain a linear dependence of the virial coefficients on the nonsphericity parameter. The relationship for the second virial coefficient has also been reported in a later study by Walsh and Gubbins.⁷ In so doing, the shape dependence of the equation of state incorporated in α can be related to the number of spheres m in the chain via the relation $\alpha = (m + 1)/2$. Hence, Eq. (9) for hard-sphere chains can be used as a reference SPT equation of state for FHS molecules; in essence, the FHS molecules are related to chains of an equivalent length m (see Fig. 3). The latest SPT expression for the compressibility factor is given in the Carnahan and Starling form as⁵

$$Z^{\text{SPT}} = \frac{1}{(1 - \eta)} + \frac{3\alpha\eta}{(1 - \eta)^2} + \frac{\eta^2[49\alpha - 31 - \eta(11\alpha - 7) - \eta^2(25\alpha - 21)]}{6(1 - \eta)^3}. \quad (49)$$

This expression provides a good representation of the thermodynamic properties of a number of linear and nonlinear polyatomic FHS molecules including homonuclear and heteronuclear diatomics, linear and nonlinear triatomics, tetraatomics, and tetrahedral pentatomics.⁵⁻⁷ However, a hard-sphere chain molecule may not be the most appropriate reference system for some highly-asymmetrical polyatomic molecules, and we expect the equation not to be as accurate in these cases. We shall compare the results obtained from the previously-tested SPT equation with those from the BHS equations developed in earlier sections to determine the adequacy of the latter.

III. RESULTS AND DISCUSSION

Computer simulations have played an invaluable role in studies of the structural and thermodynamic properties of FHS systems, and have now become central to statistical physics as a source of exact data for model systems. Two

TABLE I. Simulation data, Z^{sim} , for the compressibility factor of homonuclear FHS diatomics are compared with the BHS, Z^{BHS} [Eq. (7)], and SPT, Z^{SPT} [Eq. (49)], equations of state. The references to the simulation data are given in the last column.

σ_2/σ_1	l_{12}/σ_1	$\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}}$	α	η	Z^{sim}	Z^{BHS}	Z^{SPT}	Ref.
1	1/20	0.0250	1.0012	0.408	7.5	7.27	7.29	32
1	1/10	0.0501	1.0048	0.408	7.9	7.30	7.32	32
1	1/5	0.1010	1.0185	0.105	1.56	1.56	1.57	33
1	1/5	0.1010	1.0185	0.157	2.01	1.98	1.99	33
1	1/5	0.1010	1.0185	0.209	2.59	2.54	2.55	33
1	1/5	0.1010	1.0185	0.262	3.36	3.31	3.32	33
1	1/5	0.1010	1.0185	0.271	3.51	3.47	3.48	33
1	1/5	0.1010	1.0185	0.314	4.45	4.35	4.37	33
1	1/5	0.1010	1.0185	0.367	5.95	5.84	5.86	33
1	1/5	0.1010	1.0185	0.419	8.02	7.93	7.96	33
1	1/5	0.1010	1.0185	0.445	9.44	9.30	9.33	33
1	1/5	0.1010	1.0185	0.471	11.17	10.99	11.01	33
1	2/5	0.2087	1.0714	0.105	1.59	1.59	1.59	33
1	2/5	0.2087	1.0714	0.157	2.04	2.03	2.04	33
1	2/5	0.2087	1.0714	0.209	2.64	2.63	2.64	33
1	2/5	0.2087	1.0714	0.262	3.49	3.45	3.47	33
1	2/5	0.2087	1.0714	0.314	4.59	4.56	4.59	33
1	2/5	0.2087	1.0714	0.367	6.21	6.16	6.20	33
1	2/5	0.2087	1.0714	0.408	8.1	7.86	7.92	32
1	2/5	0.2087	1.0714	0.419	8.42	8.41	8.47	33
1	2/5	0.2087	1.0714	0.445	9.91	9.90	9.96	33
1	2/5	0.2087	1.0714	0.471	11.67	11.72	11.79	33
1	3/5	0.3333	1.1607	0.105	1.63	1.64	1.64	33
1	3/5	0.3333	1.1607	0.157	2.13	2.12	2.13	33
1	3/5	0.3333	1.1607	0.188	2.46	2.48	2.49	34
1	3/5	0.3333	1.1607	0.209	2.78	2.77	2.79	33
1	3/5	0.3333	1.1607	0.262	3.67	3.68	3.71	33
1	3/5	0.3333	1.1607	0.281	4.04	4.08	4.12	34
1	3/5	0.3333	1.1607	0.314	4.95	4.92	4.97	33
1	3/5	0.3333	1.1607	0.367	6.69	6.70	6.78	33
1	3/5	0.3333	1.1607	0.375	6.96	7.03	7.11	34
1	3/5	0.3333	1.1607	0.419	9.23	9.23	9.33	33
1	3/5	0.3333	1.1607	0.445	10.89	10.91	11.03	33
1	3/5	0.3333	1.1607	0.469	12.70	12.79	12.92	34
1	3/5	0.3333	1.1607	0.471	12.87	12.96	13.09	33
1	3/4	0.4514	1.2571	0.408	9.1	9.45	9.57	32
1	4/5	0.5000	1.2963	0.105	1.70	1.71	1.71	33
1	4/5	0.5000	1.2963	0.157	2.26	2.25	2.26	33
1	4/5	0.5000	1.2963	0.209	3.01	2.99	3.01	33
1	4/5	0.5000	1.2963	0.262	4.05	4.04	4.07	33
1	4/5	0.5000	1.2963	0.314	5.48	5.48	5.53	33
1	4/5	0.5000	1.2963	0.367	7.52	7.56	7.65	33
1	4/5	0.5000	1.2963	0.419	10.54	10.53	10.65	33
1	4/5	0.5000	1.2963	0.445	12.50	12.51	12.64	33
1	4/5	0.5000	1.2963	0.471	14.88	14.93	15.07	33
1	1	1.0000	1.5000	0.105	1.79	1.81	1.81	33
1	1	1.0000	1.5000	0.157	2.46	2.46	2.46	33
1	1	1.0000	1.5000	0.209	3.36	3.35	3.35	33
1	1	1.0000	1.5000	0.262	4.62	4.62	4.63	33
1	1	1.0000	1.5000	0.314	6.40	6.37	6.39	33
1	1	1.0000	1.5000	0.367	8.95	8.94	8.96	33
1	1	1.0000	1.5000	0.419	12.64	12.61	12.62	33
1	1	1.0000	1.5000	0.445	15.12	15.07	15.06	33
1	1	1.0000	1.5000	0.471	18.06	18.10	18.05	33
1	1	1.0000	1.5000	0.497	20.70	21.85	21.73	31

TABLE II. Simulation data, Z^{sim} , for the compressibility factor of heteronuclear FHS diatomics are compared with the BHS, Z^{BHS} [Eq. (7)], and SPT, Z^{SPT} [Eq. (49)], equations of state. The references to the simulation data are given in the last column.

σ_2/σ_1	l_{12}/σ_1	$\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}}$	α	η	Z^{sim}	Z^{BHS}	Z^{SPT}	Ref.
1/2	3/8	0.1151	1.0237	0.408	7.8	7.46	7.49	32
1/2	1/2	0.2251	1.0818	0.408	8.3	7.94	8.01	32
1/2	5/8	0.3457	1.1706	0.250	3.46	3.47	3.50	36
1/2	5/8	0.3457	1.1706	0.300	4.58	4.58	4.62	36
1/2	5/8	0.3457	1.1706	0.350	6.04	6.11	6.18	36
1/2	5/8	0.3457	1.1706	0.400	8.44	8.27	8.37	36
1/2	5/8	0.3457	1.1706	0.408	8.9	8.70	8.80	32
1/2	3/4	0.5000	1.2963	0.408	10.0	9.80	9.91	32
5/9	1/2	0.2423	1.0932	0.209	2.68	2.66	2.67	35
5/9	1/2	0.2423	1.0932	0.367	6.34	6.29	6.34	35
2/3	1/3	0.1390	1.0338	0.209	2.66	2.57	2.57	35
2/3	1/3	0.1390	1.0338	0.367	6.04	5.93	5.96	35
2/3	1/2	0.2679	1.1111	0.209	2.75	2.69	2.70	35
2/3	1/2	0.2679	1.1111	0.367	6.45	6.40	6.46	35
2/3	2/3	0.4202	1.2315	0.209	2.93	2.89	2.90	35
2/3	2/3	0.4202	1.2315	0.367	7.13	7.15	7.23	35
0.67	3/4	0.5205	1.3123	0.408	10.1	9.95	10.06	32
5/6	1/2	0.2820	1.1213	0.209	2.78	2.71	2.72	35
5/6	1/2	0.2820	1.1213	0.367	6.51	6.46	6.52	35
0.84	3/4	0.4985	1.2591	0.408	9.9	9.79	9.90	32

methods of simulation, namely Monte Carlo (MC) and molecular dynamics (MD), have been developed and refined over the years; for a detailed account of these the reader is referred elsewhere.²⁹ As far as FHS molecules with purely repulsive nonspherical potentials are concerned, the MC method has been overwhelmingly used since MD studies of such molecules are considerably more difficult to undertake due to the discontinuous nature of the potential. In our study, we use existing simulation data for a number of FHS systems to confirm the adequacy of the BHS approach in describing their equations of state.

The simplest and most extensively studied FHS models are the diatomic molecules. As was mentioned earlier, the adequacy of the BHS and SPT equations of state in describing the properties of heteronuclear diatomics of tangent hard spheres has previously been established.⁸ Computer simulations of homonuclear FHS diatomics with $\sigma_1 = \sigma_2$ and with bond lengths ranging from the hard-sphere limit of $l_{12} = 0$ to the tangent hard-sphere limit of $l_{12} = \sigma_1 = \sigma_2$ have been undertaken for a large number of packing fractions in the fluid state.³⁰⁻³⁴ Ample simulation data³⁴⁻³⁶ are also available for heteronuclear FHS diatomics with a range of size ratios σ_2/σ_1 and bond lengths l_{12} . The results of these studies for the compressibility factor of homonuclear and heteronuclear systems are summarized in Tables I and II, respectively. Here, the simulation data are compared with the corresponding results of the BHS equation of state for diatomics, Eq. (7), and the SPT expression, Eq. (49). In order to use the BHS approach for these FHS molecules, the procedure described in Sec. II C is employed to determine the hard-sphere diameter ratio $\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}}$ of the equivalent BHS

molecule. Although this approach is less naturally suited to homonuclear molecules, in which the hard-sphere sites are of the same size, than to heteronuclear molecules with different-sized spheres, there is excellent agreement between the BHS equation of state and the simulation data for both systems, as is clearly evident from Tables I and II. SPT also provides an accurate representation of the equation of state over the entire range of fluid densities and, in many cases, the results are indistinguishable from those of the BHS approach. The only exception to the close agreement between theory and simulation involves the MC data of Streett and Tildesley³² which seem to be of rather poor quality.

In a recent paper,⁹ we have compared the BHS equation of state, Eq. (8), with simulation data for symmetrical and asymmetrical linear triatomics of tangentially-bonded hard spheres; the BHS approach successfully described the properties of these triatomic molecules in the fluid state. The approach has not, however, been applied to FHS triatomics with overlapping hard-sphere sites. Simulation data are available for the equation of state of symmetrical FHS triatomics in both linear³⁶⁻³⁹ and nonlinear^{38,40} configurations. A comparison of these data with the BHS theory, Eq. (8), and SPT, Eq. (49), is presented in Table III. As with the diatomics, the procedure described in Sec. II C is used to apply the BHS approach to FHS triatomics; the corresponding values of the diameter ratios $\sigma_1^{\text{BHS}}/\sigma_2^{\text{BHS}} = \sigma_3^{\text{BHS}}/\sigma_2^{\text{BHS}}$ for the equivalent BHS molecule with tangent hard spheres are also given in Table III. Reasonable agreement between the BHS and SPT equations of state, and the simulation data is found for the linear molecules with a bond angle of $\omega = 180^\circ$. In the case of nonlinear triatomics, there is no analytical expression

TABLE III. Simulation data, Z^{sim} , for the compressibility factor of linear and nonlinear symmetrical FHS triatomics are compared with the BHS, Z^{BHS} [Eq. (8)] and SPT, Z^{SPT} [Eq. (49)], equations of state. The references to the simulation data are given in the last column.

$\sigma_1^{\text{BHS}}/\sigma_2^{\text{BHS}}$	α	η	Z^{sim}	Z^{BHS}	Z^{SPT}	Ref.
$\sigma_1 = \sigma_3 = \sigma_2$ $l_{12} = l_{23} = 4\sigma_1/5$ $\omega = 180^\circ$						
0.5134	1.6205	0.250	4.48	4.59	4.59	36
0.5134	1.6205	0.300	6.04	6.30	6.30	36
0.5134	1.6205	0.350	8.33	8.71	8.70	36
0.5134	1.6205	0.400	11.65	12.15	12.12	36
$\sigma_1 = \sigma_3 = \sigma_2/0.857$ $l_{12} = l_{23} = 0.4485\sigma_1$ $\omega = 180^\circ$						
0.2944	1.2658	0.470	14.84	14.41	14.53	37
$\sigma_1 = \sigma_2 = \sigma_3$ $l_{12} = l_{23} = 0.4485\sigma_1$ $\omega = 180^\circ$						
0.2571	1.2101	0.470	12.84	13.61	13.72	37
$\sigma_1 = \sigma_3 = \sigma_2/1.2$ $l_{12} = l_{23} = 0.4485\sigma_1$ $\omega = 180^\circ$						
0.1976	1.1309	0.470	12.88	12.48	12.57	37
$\sigma_1 = \sigma_2 = \sigma_3$ $l_{12} = l_{23} = \sigma_1/2$ $\omega = 180^\circ$						
0.2926	1.2632	0.453	12.88	12.80	12.92	38
$\sigma_1 = \sigma_2 = \sigma_3$ $l_{12} = l_{23} = \sigma_1/2$ $\omega = 90^\circ$						
0.2926	1.2632	0.399	8.34	8.99	9.08	38
0.2356	1.18	0.399	8.34	8.31	8.40	38
$\sigma_1 = \sigma_2 = \sigma_3$ $l_{12} = l_{23} = 0.3979\sigma_1$ $\omega = 180^\circ$						
0.2104	1.1468	0.287	4.35	4.18	4.21	39
0.2104	1.1468	0.344	5.93	5.78	5.84	39
0.2104	1.1468	0.401	8.30	8.14	8.22	39
0.2104	1.1468	0.458	12.02	11.73	11.82	39
$\sigma_1 = \sigma_3 = 3\sigma_2/5$ $l_{12} = l_{23} = 4\sigma_1/3$ $\omega = 105^\circ$						
0.6000	1.7416	0.250	4.94	4.90	4.89	40
0.6000	1.7416	0.300	6.84	6.78	6.76	40
0.6000	1.7416	0.350	9.46	9.43	9.38	40
0.6000	1.7416	0.375	11.14	11.16	11.09	40

for α so the BHS procedure used for the linear molecules cannot be directly applied. However, the expression for α corresponding to an equivalent linear molecule can be used as an approximation to that of the nonlinear molecule. The BHS and SPT results obtained in this way for the nonlinear triatomics with $\omega = 90^\circ$ and $\omega = 105^\circ$ are in good agreement with the simulation data as shown in Table III. If the numerical value of $\alpha = 1.18$ (Ref. 38) is used for the FHS triatomic with $\omega = 90^\circ$ instead of the analytical value of $\alpha = 1.2633$ for the linear molecule, even better agreement is seen.

The adequacy of BHS expressions such as Eq. (9) in representing the equation of state of chains of hard spheres has already been examined,^{12,6,7} and no further comparisons will be made in this study. The remaining single-component FHS system for which simulation data are available is the tetrahedral pentatomic model of carbon tetrachloride. Nezbeda and Vörtler⁴¹ have reported Monte Carlo data for the compressibility factor of FHS tetrahedral pentatomics with $\sigma_1 = 3.4\sigma_2/3.5$ and $l_{12} = 1.77\sigma_1/3.4$, where σ_1 and σ_2 are the diameters of the central and substituent spheres, respectively, and l_{12} is the 1-2 bond length. Molecular dynamics simulations of a similar model with slightly different molecular parameters of $\sigma_1 = 3.2\sigma_2/3.4$ and $l_{12} = 1.77\sigma_1/3.2$ have also been performed by Alejandre and Chapela.³⁹ The results of both of these studies are summarized in Table IV together with the corresponding results of the BHS equation (29). The latter, which was originally derived for systems of tangentially-bonded hard spheres, can be used to describe

FHS molecules. In this case, an equivalent BHS model has been constructed by separately determining the diameter ratios $\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}}$ for the diatomic segments making up the molecule. This entails the solution of Eq. (32) using the analytical expression of α for each of the diatomic segments. Moderate agreement with simulation is seen, with the BHS theory overestimating the exact simulation data by about 7–

TABLE IV. Simulation data, Z^{sim} , for the compressibility factor of tetrahedral FHS pentatomics are compared with the BHS equation of state, Z^{BHS} [Eq. (29)]. The references to the simulation data are given in the last column.

$\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}}$	η	Z^{sim}	Z^{BHS}	Ref.
$\sigma_1 = 3.2\sigma_2/3.4$ $l_{12} = 1.77\sigma_1/3.2$ $\omega = 109^\circ$				
0.2892	0.300	5.57	5.97	39
0.3229	0.300	5.57	6.41	39
0.2892	0.400	10.50	11.42	39
0.3229	0.400	10.50	12.41	39
0.2892	0.480	17.40	19.93	39
0.3229	0.480	17.40	21.83	39
$\sigma_1 = 3.4\sigma_2/3.5$ $l_{12} = 1.77\sigma_1/3.4$ $\omega = 109^\circ$				
0.2757	0.200	2.94	3.15	41
0.3048	0.200	2.94	3.30	41
0.2757	0.300	5.39	5.80	41
0.3048	0.300	5.39	6.17	41
0.2757	0.356	7.70	8.27	41
0.3048	0.356	7.70	8.85	41
0.2757	0.400	10.26	11.03	41
0.3048	0.400	10.26	11.87	41

TABLE V. Simulation data, Z^{sim} , for the compressibility factor of binary mixtures of linear homonuclear FHS molecules, formed from tangentially-fused spheres of the same size, are compared with the BHS equation of state, Z^{BHS} [Eq. (30)]. The simulation data for the mixtures of (a) hard spheres and (b) diatomics are those of Graham and Jackson (Ref. 43) and the data for the mixtures of (a) diatomics and (b) tetratomics are those of Boublik *et al.* (Ref. 6).

$x_b = 0.10$			$x_b = 0.50$			$x_b = 0.90$		
η	Z^{sim}	Z^{BHS}	η	Z^{sim}	Z^{BHS}	η	Z^{sim}	Z^{BHS}
(a) hard spheres + (b) diatomics								
0.099	1.57	1.54	0.102	1.61	1.66	0.100	1.73	1.74
0.147	1.99	1.92	0.153	2.09	2.17	0.152	2.28	2.34
0.196	2.53	2.43	0.201	2.77	2.81	0.202	3.07	3.13
0.242	3.30	3.07	0.253	3.64	3.75	0.252	4.14	4.22
0.295	4.22	4.05	0.306	4.81	5.08	0.304	5.57	5.79
0.346	5.55	5.36	0.356	6.49	6.85	0.353	7.65	7.88
0.394	7.45	7.08	0.407	8.87	9.43	0.403	10.60	10.90
0.445	10.11	9.69	0.455	12.37	12.92	0.450	14.97	14.98
(a) diatomics + (b) tetratomics								
			0.200	3.94	3.94			
			0.300	7.70	7.70			
			0.350	10.65	10.81			

10 %. Alternatively, an equivalent BHS molecule can be obtained by examining the triatomic segments of the pentatomic molecule using the analytical expression of α for linear triatomics. After solving Eq. (32) for the triatomic segments, $\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}}$ for the equivalent BHS molecule is obtained. The values of the BHS compressibility factor determined in this way are also shown in Table IV as the second line of results for each state point. The results obtained using the molecule's diatomic segments are in better agreement with simulation data than the results obtained using the triatomic segments. In the spirit of Rigby's prescription,⁴² we have also attempted to equate the volume of the FHS pentatomic with an equivalent BHS molecule to obtain the molecular parameters of the latter. The agreement between theory and simulation was, however, quite poor and the corresponding results are not reported.

The BHS approach can easily be generalized to mixtures, as shown in Sec. II B. An important class of FHS mixtures involving binary mixtures of linear homonuclear molecules formed from tangent hard spheres of equal size is examined next. The BHS approach is expected to be a good representation of these mixtures since it was developed for tangent hard-sphere molecules. The simplest system of this type is a mixture of (a) hard spheres of diameter σ and (b) homonuclear FHS diatomics with $\sigma_1 = \sigma_2 = \sigma$ and $l_{12} = \sigma/2$. In Table V we compare isothermal-isobaric Monte Carlo (MC-NPT) simulations data⁴³ for three compositions, $x_b = 0.1, 0.5$, and 0.9 , of this mixture with the results of the BHS equation of state, Eq. (30). Note that for this particular system the BHS expression (30) reduces to the expression of Wertheim.⁴⁴ The simulation data⁶ for equimolar $x_a = x_b = 0.5$ mixtures of (a) diatomics and (b) linear tetratomics formed from tangentially-bonded hard spheres of the same size σ are also given in Table V. As for the former mixture, excellent agreement between the BHS equation (30) and the simulation results is seen.

Simulation data have been reported for a number of binary mixtures of FHS molecules.^{36,45-47} The BHS approach can also be used to describe the thermodynamic properties of such mixtures by following the procedure of Sec. II C for

each of the mixture's components. In this way the BHS equation of state (30) for an equivalent mixture of molecules formed from tangent hard spheres is used to describe the original FHS mixture. It is important to note that the ratio of the hard-sphere diameters for the various FHS components of the mixture will be different from those of the equivalent BHS mixture. However, the diameters of the largest spheres of the equivalent BHS molecules are taken to be the same as those of the corresponding FHS molecules; the relationships between the sizes of the hard-sphere sites for the different components of the FHS mixture are also retained.

A comparison of the simulation data⁴⁶ and BHS theory for mixtures of homonuclear FHS diatomics is presented in Table VI, and excellent agreement is seen. These mixtures are composed of diatomics with $\sigma_1 = \sigma_2$ and $l_{12}/\sigma_1 = 1, 0.6, 0.3$, and 0 ; the diameter ratios of the equivalent tangent hard-sphere molecules are $\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}} = 1, 0.3333, 0.1535$, and 0 , respectively. The simulation data of Aviram and Tildesley⁴⁵ for similar mixtures were found to be in very poor agreement with the BHS results for no apparent reason, and in some cases the differences were as large as 30%. Furthermore, these data are significantly different from the data of Wojcik and Gubbins⁴⁶ for almost identical systems. Nezbeda *et al.*⁴⁸ have shown that the results of a related study by Aviram *et al.*⁴⁹ for pure homonuclear FHS diatomics are incorrect. Presumably, the simulation data for the mixtures are also incorrect and, consequently, we are not including these results in our comparisons.

The simulation data for mixtures of (a) hard spheres and (b) heteronuclear diatomics, and of (a) hard spheres and (b) linear homonuclear triatomics are compared with the BHS theory, Eq. (30), in Tables VII and VIII, respectively. Clearly, the BHS theory gives an accurate representation of the thermodynamic properties of such mixtures. In the case of the first class of mixtures, diatomic components with $\sigma_1 = 2\sigma_2$ and bond lengths of $l_{12} = 5\sigma_1/8$ are examined. The BHS molecule corresponding to this diatomic molecule has tangentially-fused hard spheres with a diameter ratio of $\sigma_2^{\text{BHS}}/\sigma_1^{\text{BHS}} = 0.3457$. The linear triatomic molecules in the mixtures of Table VIII have molecular param-

TABLE VI. The simulation data of Wojcik and Gubbins (Ref. 46), Z^{sim} , for the compressibility factor of mixtures of homonuclear FHS diatomics are compared with the BHS equation of state, Z^{BHS} [Eq. (30)].

η	$x_a = 0.25$		$x_a = 0.50$		$x_a = 0.75$	
	Z^{sim}	Z^{BHS}	Z^{sim}	Z^{BHS}	Z^{sim}	Z^{BHS}
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = 0.6\sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0$ $\sigma_1^a = \sigma_1^b$				
0.300			4.20	4.25		
0.450	9.78	9.84	10.15	10.30	10.76	10.78
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = \sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0$ $\sigma_1^a = \sigma_1^b$				
0.300			4.88	4.91		
0.350	5.95	5.91			7.26	7.31
0.430	9.74	9.62	11.06	10.94	12.31	12.27
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = 0.6\sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0.3\sigma_1^b$ $\sigma_1^a = \sigma_1^b$				
0.300			4.31	4.33		
0.450			10.52	10.55		
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = \sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0.6\sigma_1^b$ $\sigma_1^a = \sigma_1^b$				
0.450	12.26	12.32	13.33	13.40	14.46	14.49
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = 0.6\sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0$ $V_m^a = V_m^b$				
0.300			4.25	4.15		
0.450	9.76	9.63	10.27	9.98	10.82	10.49
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = \sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0$ $V_m^a = V_m^b$				
0.300			4.83	4.82		
0.430			10.71	10.68		
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = 0.6\sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0.3\sigma_1^b$ $V_m^a = V_m^b$				
0.300			4.30	4.31		
0.450			10.52	10.49		
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = \sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0.6\sigma_1^b$ $V_m^a = V_m^b$				
0.450	12.14	12.34	13.27	13.43	14.37	14.51
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = 0.6\sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0$ $V_m^a = 2V_m^b/3$				
0.300			4.19	4.03		
0.450	9.63	9.40	10.06	9.58	10.60	10.07
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = \sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0$ $V_m^a = 2V_m^b/3$				
0.300			4.63	4.68		
0.430			10.24	10.28		
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = \sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0.6\sigma_1^b$ $V_m^a = 2V_m^b/3$				
0.450	11.86	12.31	12.92	13.38	13.94	14.48
		(a) $\sigma_1^a = \sigma_2^a l_{12}^a = 0.6\sigma_1^a +$ (b) $\sigma_1^b = \sigma_2^b l_{12}^b = 0.3\sigma_1^b$ $V_m^a = 0.64V_m^b$				
0.300			4.27	4.22		
0.450			10.25	10.19		

TABLE VII. Simulation data, Z^{sim} , for the compressibility factor of mixtures of (a) hard spheres and (b) heteronuclear FHS diatomics are compared with the BHS equation of state, Z^{BHS} [Eq. (30)]. The simulation data for the equimolar systems are those of Nezbeda *et al.* (Ref. 36) and the data for the other systems are reported in the review article of Boublik and Nezbeda (Ref. 2). *, we suspect that this value is erroneous.

η	$x_a = 0.25$		$x_a = 0.50$		$x_a = 0.75$	
	Z^{sim} (Ref. 2)	Z^{BHS}	Z^{sim} (Ref. 36)	Z^{BHS}	Z^{sim} (Ref. 2)	Z^{BHS}
		(a) $\sigma^a +$ (b) $\sigma_1^b = 2\sigma_2^b l_{12}^b = 5\sigma_1^b/8$ $\sigma^a = \sigma_1^b$				
0.250	3.40	3.37	3.26	3.27	3.19	3.17
0.300	4.45	4.42	4.26	4.27	4.17	4.12
0.350	5.88	5.88	5.66	5.65	5.50	5.42
0.400	7.96	7.92	7.73	7.58	7.35	7.25
		(a) $\sigma^a +$ (b) $\sigma_1^b = 2\sigma_2^b l_{12}^b = 5\sigma_1^b/8$ $\sigma^a = \sigma_2^b$				
0.250	3.21	3.22	2.94	2.99	2.77	2.82
0.300	4.22	4.20	3.84	3.86	3.58	3.60
0.350	4.61*	5.56	5.04	5.05	4.64	4.67
0.400	7.61	7.47	6.63	6.72	6.09	6.16
		(a) $\sigma^a +$ (b) $\sigma_1^b = 2\sigma_2^b l_{12}^b = 5\sigma_1^b/8$ $V_m^a = V_m^b$				
0.250	3.37	3.36	3.26	3.26	3.21	3.17
0.300	4.48	4.41	4.33	4.26	4.14	4.11
0.350	5.88	5.87	5.57	5.63	5.46	5.41
0.400	7.91	7.91	7.54	7.56	7.30	7.23

TABLE VIII. Simulation data, Z^{sim} , for the compressibility factor of mixtures of (a) hard spheres and (b) linear homonuclear FHS triatomics are compared with the BHS equation of state, Z^{BHS} [Eq. (30)]. The simulation data for the equimolar systems are those of Nezbeda *et al.* (Ref. 36) and the data for the other systems are reported in the review article of Boublik and Nezbeda (Ref. 2).

η	$x_a = 0.25$		$x_a = 0.50$		$x_a = 0.75$	
	Z^{sim} (Ref. 2)	Z^{BHS}	Z^{sim} (Ref. 36)	Z^{BHS}	Z^{sim} (Ref. 2)	Z^{BHS}
	(a) $\sigma^a +$ (b) $\sigma_1^b = \sigma_2^b = \sigma_3^b$ $l_{12}^b = l_{23}^b = 4\sigma_1^b/5$ $\omega = 180^\circ$ $\sigma^a = \sigma_1^b$					
0.250	4.11	4.19	3.69	3.80	3.36	3.43
0.300	5.56	5.68			4.50	4.51
0.350	7.68	7.77	6.68	6.87	5.98	6.01
0.400	10.44	10.75			8.01	8.13
	(a) $\sigma^a +$ (b) $\sigma_1^b = \sigma_2^b = \sigma_3^b$ $l_{12}^b = l_{23}^b = 4\sigma_1^b/5$ $\omega = 180^\circ$ $V_m^a = V_m^b$					
0.250	4.03	3.89			3.35	3.25
0.300	5.46	5.22			4.40	4.23
0.350	7.52	7.07			5.92	5.59
0.400	10.36	9.71			7.95	7.50

eters of $\sigma_1 = \sigma_2 = \sigma_3$, $l_{12} = l_{23} = 4\sigma_1/5$, and $\omega = 180^\circ$; the diameter ratios for the equivalent BHS triatomic are $\sigma_1^{\text{BHS}}/\sigma_2^{\text{BHS}} = \sigma_3^{\text{BHS}}/\sigma_2^{\text{BHS}} = 0.5134$. The simulation data for the equimolar mixtures of hard spheres with diatomics and triatomics are quoted from the study by Nezbeda *et al.*³⁶ It must be noted that although the original reference for the data corresponding to the hard-sphere mole fractions of $x_a = 0.25$ and 0.75 has been impossible to trace, the data is reported in the review article of Boublik and Nezbeda.²

In their study of FHS mixtures, Nezbeda *et al.*³⁶ also examined an equimolar mixture of the diatomic and triatomic molecules which were separate components of their two earlier mixtures. The results of their simulations are given in Table IX together with the corresponding values from the BHS equation of state, Eq. (30). The latest simulations of mixtures of FHS molecules were undertaken in a subsequent

study by Vörtler *et al.*⁴⁷ Equimolar mixtures of heteronuclear diatomics with nonlinear symmetrical triatomics were simulated, and data for a mixture of linear and nonlinear triatomics were also reported. These results are summarized in Table IX and, as before, excellent agreement between the simulation data and the BHS theory is seen. Since the diatomic and linear triatomics components of these mixtures are the same as those of the previous study by Nezbeda *et al.*,³⁶ the molecules can be represented by the same equivalent BHS molecules. The nonlinear triatomic with $\sigma_1 = \sigma_3 = 3\sigma_2/5$, $l_{12} = l_{23} = 4\sigma_1/3$, and $\omega = 105^\circ$ is already a BHS model with tangentially-bonded hard spheres, i.e., $\sigma_1^{\text{BHS}}/\sigma_2^{\text{BHS}} = \sigma_3^{\text{BHS}}/\sigma_2^{\text{BHS}} = 3/5$.

We have now compared the BHS theory with all the available simulation data for FHS molecules and their mixtures. All in all, very good agreement is found, confirming

TABLE IX. Simulation data, Z^{sim} , for the compressibility factor of equimolar FHS mixtures of (a) diatomics and (b) triatomics, and of (a) linear and (b) nonlinear triatomics are compared with the BHS equation of state, Z^{BHS} [Eq. (30)]. The references to the simulation data are given in the last column.

η	Z^{sim}	Z^{BHS}	Ref.
	(a) diatomics + (b) triatomics		
	(a) $\sigma_1^a = 2\sigma_2^a$ $l_{12}^a = 5\sigma_1^a/8 +$ (b) $\sigma_1^b = \sigma_2^b = \sigma_3^b$ $l_{12}^b = l_{23}^b = 4\sigma_1^b/5$ $\omega = 180^\circ$ $\sigma_1^a = \sigma_2^b$		
0.250	3.69	4.02	36
0.300	4.92	5.42	36
0.350	6.70	7.38	36
0.400	9.20	10.16	36
	(a) $\sigma_1^a = 2\sigma_2^a$ $l_{12}^a = 5\sigma_1^a/8 +$ (b) $\sigma_1^b = \sigma_3^b = 3\sigma_2^b/5$ $l_{12}^b = l_{23}^b = 4\sigma_1^b/3$ $\omega = 105^\circ$ $\sigma_1^a = \sigma_2^b/2$		
0.308	5.34	5.43	47
0.375	8.24	8.23	47
	(a) $\sigma_1^a = 2\sigma_2^a$ $l_{12}^a = 5\sigma_1^a/8 +$ (b) $\sigma_1^b = \sigma_3^b = 3\sigma_2^b/5$ $l_{12}^b = l_{23}^b = 4\sigma_1^b/3$ $\omega = 105^\circ$ $\sigma_1^a = 2\sigma_2^b$		
0.257	3.50	3.58	47
0.374	7.23	7.01	47
	(a) $\sigma_1^a = 2\sigma_2^a$ $l_{12}^a = 5\sigma_1^a/8 +$ (b) $\sigma_1^b = \sigma_3^b = 3\sigma_2^b/5$ $l_{12}^b = l_{23}^b = 4\sigma_1^b/3$ $\omega = 105^\circ$ $V_m^a = V_m^b$		
0.285	5.26	5.11	47
0.378	8.92	9.16	47
	(a) nonlinear triatomic + (b) linear triatomic		
	(a) see triatomic above + (b) $\sigma_1^b = \sigma_2^b = \sigma_3^b$ $l_{12}^b = l_{23}^b = 4\sigma_1^b/5$ $\omega = 180^\circ$ $\sigma_1^a = 2\sigma_2^b$		
0.276	5.11	4.82	47
0.368	8.94	8.58	47

the accuracy of the BHS approach in representing the thermodynamic properties of such systems. For all of the systems in which comparisons were made, the BHS equation of state gave comparable results to the most up-to-date and widely-tested version of SPT.

IV. CONCLUSION

In this paper, we present a general equation of state for FHS models of polyatomic molecules and mixtures. A simple method of extending the BHS theory to FHS molecules is proposed, and considerable success is achieved in describing the properties of these systems. We feel that the BHS theory has a number of advantages over SPT. Firstly, the BHS approach has a firm footing in statistical mechanics in that it incorporates the structure of the reference hard-sphere system for which the properties are accurately known. Hence, the theory can easily be extended to large polyatomics and mixtures. An approximate scheme can be used together with the BHS approach to describe the properties of large polyatomics in terms of the shape factors of the diatomic segments making up the molecule. This overcomes the nontrivial problem of numerically calculating α when SPT is applied to the same FHS molecules. Furthermore, since each intramolecular bonding contact is treated independently within the BHS theory, it is an ideal framework on which to build a rigorous group contribution approach for polyatomics. It is hoped that BHS theory will be used in future perturbation theories of more realistic polyatomic molecules.

¹ J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).

² T. Boublik and I. Nezbeda, *Coll. Czech. Chem. Commun.* **51**, 2301 (1986).

³ I. Nezbeda, S. Labík, and A. Malijevský, *Coll. Czech. Chem. Commun.* **54**, 1137 (1989).

⁴ C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon, Oxford, 1991), Vol. 2.

⁵ T. Boublik, *Mol. Phys.* **68**, 191 (1989).

⁶ T. Boublik, C. Vega, and M. Diaz-Peña, *J. Chem. Phys.* **93**, 730 (1990).

⁷ J. M. Walsh and K. E. Gubbins, *J. Phys. Chem.* **94**, 5115 (1990).

⁸ A. L. Archer and G. Jackson, *Mol. Phys.* **73**, 881 (1991).

⁹ M. D. Amos and G. Jackson, *Mol. Phys.* **74**, 191 (1991).

¹⁰ G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys.* **54**, 1523 (1971).

¹¹ T. Boublik, *J. Chem. Phys.* **53**, 471 (1970).

¹² W. G. Chapman, G. Jackson, and K. E. Gubbins, *Mol. Phys.* **65**, 1057 (1988).

¹³ G. Jackson and K. E. Gubbins, *Pure Appl. Chem.* **61**, 1021 (1989).

¹⁴ W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem. Res.* **29**, 1709 (1990).

¹⁵ M. S. Wertheim, *J. Stat. Phys.* **35**, 19 (1984).

¹⁶ M. S. Wertheim, *J. Stat. Phys.* **35**, 35 (1984).

¹⁷ M. S. Wertheim, *J. Stat. Phys.* **42**, 459 (1986).

¹⁸ M. S. Wertheim, *J. Stat. Phys.* **42**, 477 (1986).

¹⁹ G. Jackson, *Mol. Phys.* **72**, 1365 (1991).

²⁰ G. Jackson, W. G. Chapman, and K. E. Gubbins, *Mol. Phys.* **65**, 1 (1988).

²¹ N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).

²² T. Kihara, *Adv. Chem. Phys.* **5**, 147 (1963).

²³ T. Boublik and I. Nezbeda, *Chem. Phys. Lett.* **46**, 315 (1977).

²⁴ J. Alejandre, S. E. Martinez-Casas, and G. A. Chapela, *Mol. Phys.* **65**, 1185 (1988).

²⁵ A. B. Ritchie, *J. Chem. Phys.* **46**, 618 (1967).

²⁶ R. M. Gibbons, *Mol. Phys.* **17**, 81 (1969).

²⁷ R. M. Gibbons, *Mol. Phys.* **18**, 809 (1970).

²⁸ T. Boublik, *J. Chem. Phys.* **63**, 4084 (1975).

²⁹ M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Clarendon, Oxford, 1987).

³⁰ B. C. Freasier, *Chem. Phys. Lett.* **35**, 280 (1975).

³¹ B. C. Freasier, D. Jolly, and R. J. Bearman, *Mol. Phys.* **31**, 255 (1976).

³² W. B. Streett and D. J. Tildesley, *J. Chem. Phys.* **68**, 1275 (1978).

³³ D. J. Tildesley and W. B. Streett, *Mol. Phys.* **41**, 85 (1980).

³⁴ B. C. Freasier, *Mol. Phys.* **39**, 1273 (1980).

³⁵ D. Jolly, B. C. Freasier, and R. J. Bearman, *Chem. Phys. Lett.* **46**, 75 (1977).

³⁶ I. Nezbeda, M. R. Reddy, and W. R. Smith, *Mol. Phys.* **55**, 447 (1985).

³⁷ W. B. Streett and D. J. Tildesley, *Discuss. Faraday Soc.* **66**, 27 (1978).

³⁸ T. Boublik, *Czech. J. Phys. B* **33**, 121 (1983).

³⁹ J. Alejandre and G. A. Chapela, *Mol. Phys.* **61**, 1119 (1987).

⁴⁰ S. Labík and I. Nezbeda, *Mol. Phys.* **48**, 97 (1983).

⁴¹ I. Nezbeda and H. L. Vörtler, *Mol. Phys.* **57**, 909 (1986).

⁴² M. Rigby, *Mol. Phys.* **68**, 687 (1989).

⁴³ K. Graham and G. Jackson (unpublished).

⁴⁴ M. S. Wertheim, *J. Chem. Phys.* **85**, 2929 (1986).

⁴⁵ I. Aviram and D. J. Tildesley, *Mol. Phys.* **35**, 365 (1978).

⁴⁶ M. Wojcik and K. E. Gubbins, *Mol. Phys.* **49**, 1401 (1983).

⁴⁷ H. L. Vörtler, J. Kolafa, and I. Nezbeda, *Mol. Phys.* **68**, 547 (1989).

⁴⁸ I. Nezbeda, W. R. Smith, and T. Boublik, *Mol. Phys.* **37**, 985 (1979).

⁴⁹ I. Aviram, D. J. Tildesley, and W. B. Streett, *Mol. Phys.* **34**, 881 (1977).