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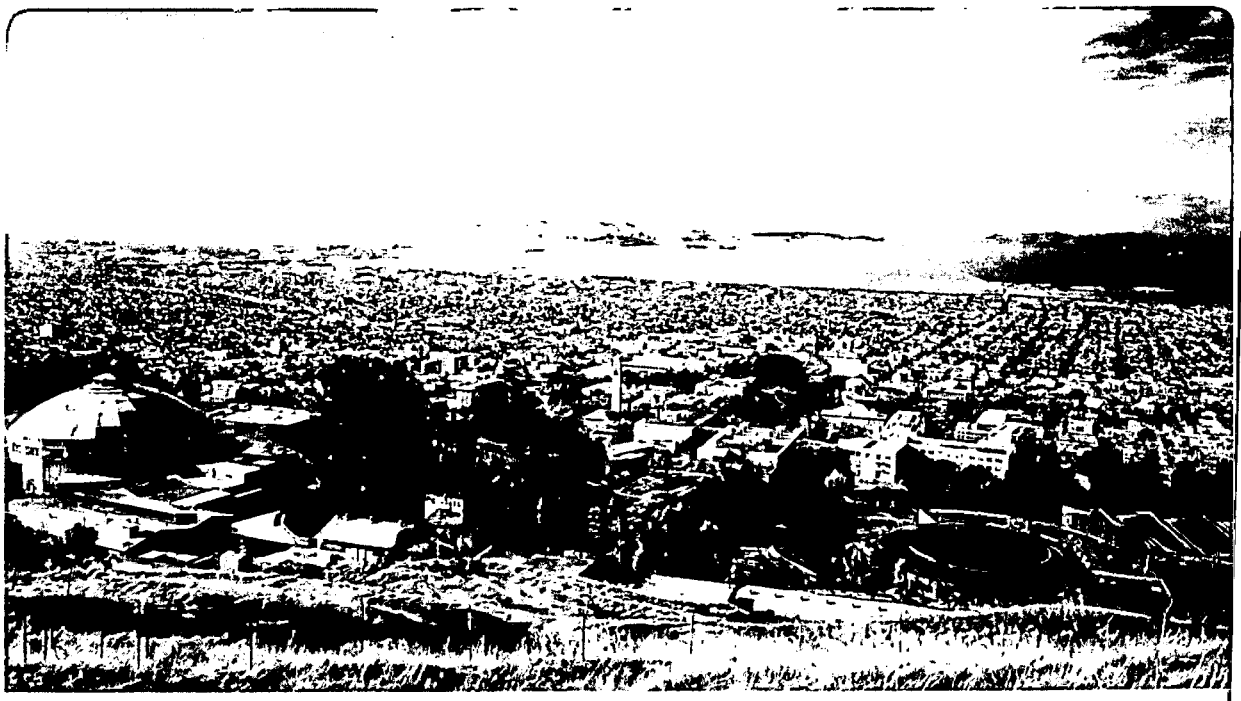

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A Perturbed Hard-Sphere-Chain Equation of State for Normal Fluids and Polymers

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ABSTRACT

A perturbed hard-sphere-chain (PHSC) equation of state is presented which uses the modified Chiew equation of state for hard-sphere chains as the reference term, a van der Waals type perturbation term and the Song-Mason method to relate equation-of-state parameters to the intermolecular potential. The PHSC equation requires three parameters to describe a pure fluid: the number of effective hard-spheres per molecule, the segmental diameter, and the intermolecular potential-well depth between a nonbonded pair of segments. The PHSC equation reproduces the thermodynamic properties of a wide variety of normal fluids including polymers. Regressed parameters are related to characteristic molecular properties calculated from group contributions based on chemical structure.

Introduction

Since the pioneering work of van der Waals (Rowlinson, 1988), numerous authors have participated in a quest for a simple analytical equation of state applicable to a wide variety of molecular fluids. Several hundred variations of the van der Waals equation as well as hundreds of empirical equations of state have been proposed for practical application. Amongst the most popular are the Redlich-Kwong equation (Redlich and Kwong, 1949), the Soave-Redlich-Kwong equation (Soave, 1972) and the Peng-Robinson equation (Peng and Robinson, 1976) which are widely used for engineering applications. However, none of these are applicable to fluids whose molecular size ranges from a single atom to a polymer.

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There have been many attempts to develop *analytical* equations of state for molecular fluids from statistical-mechanical theories; a few examples include the generalized van der Waals equations (Rigby, 1972; Svejda and Kohler, 1983), the chain-of-rotators equation (Chien, et al., 1978), the perturbed-hard-chain equation (Beret and Prausnitz, 1975b; Donohue and Prausnitz, 1978), and the statistical-mechanical perturbation equations (Song and Mason, 1989; 1990; Sowers and Sandler, 1992). Although many of the details are different, these theoretically-based equations of state share a common premise first suggested by van der Waals over one hundred years ago, namely, that the structure of a molecular fluid is determined primarily by repulsive forces; therefore, fluids of athermal hard bodies (spherical or non-spherical) can serve as useful reference systems. Because the influence of attractive forces on fluid structure is weak, perturbation methods can be used to describe their contribution to the equation of state.

To represent the compressibilities of dense liquids, including polymers, equations of state (EOS) have been developed from both phenomenological or theoretical bases; comprehensive and comparative reviews are presented by Rodgers (1993) and Vimalchand and Donohue (1989). A widely used phenomenological equation is the Tait equation (MacDonald, 1966) which is based on the observation that the reciprocal of compressibility is nearly linear in pressure. Theoretical equations of state include those of Prigogine, et al. (1957), Hijmans (1961), Flory (1970) and Patterson and Delmas (1970) which are all based on Prigogine's simplifying assumption that at high densities, all density-dependent degrees of freedom can be treated as equivalent translational degrees of freedom. These equations of state are suitable for polymers and restricted to liquid-like densities. These equations are inappropriate at low densities because they do not approach the ideal gas law in the limit of zero density. An equation of state which avoids these restrictions is that based on the Lattice Fluid (LF) theory which models a pure fluid as a binary mixture of a lattice chains with vacancies (Sanchez and Lacombe, 1976; 1978). When comparing the above equations of state, Rodgers (1993) notes that the LF EOS and the Flory EOS provide the least accurate correlation of polymer *pVT* properties.

During the last 10 years, there has been increased interest in developing analytical EOS for fluids with chain-like molecules based on a relatively simple model: athermal hard-sphere chains, where a chain molecule is modeled by a series of freely-jointed tangent hard spheres (Boublik, 1989; Boublik, et al., 1990; Chapman, et al., 1988; Chiew, 1990; Dickman and Hall, 1986; Honnell and Hall, 1989; Wertheim, 1987). A hard-sphere chain EOS can be used as the reference system in place of the hard-sphere reference used in most equations of state for simple spherical fluids. Despite their simplicity, the properties of hard-sphere-chain models take into account some significant features of real chain-like fluids such as excluded-volume effects and chain connectivity. A number of methods have been developed to obtain equations of state for hard-sphere chains, including the Generalized Flory and Generalized Flory-Huggins theories (Dickman and Hall, 1986), the Generalized Flory-Dimer theory (Honnell and Hall, 1989), and the thermodynamic perturbation theory of polymerization (Chapman, et al., 1988; Wertheim, 1987).

A particularly elegant, yet simple, method has been presented by Chiew (1990) who solved the Percus-Yevick integral equation coupled with chain connectivity for hard-sphere chains and mixtures. Analytical equations of state were obtained. A significant modification and generalization of Chiew's result has been made through the Carnahan-Starling radial distribution functions for hard-spheres and mixtures at contact for both the bonding and non-bonding terms (Song, et al., 1993a). Compared to Chiew's original equation of state, the new equation of state for hard-sphere chains and their mixtures are expressed more succinctly, making them more convenient for application.

In this paper we present a perturbed hard-sphere-chain (PHSC) equation of state applicable to real, pure molecular fluids; real mixtures are considered in a separate publication. The modified work of Chiew for hard-sphere chains is the reference system and the van der Waals attractive term is the perturbation. Our goal is to establish a theoretically-based and engineering-oriented equation of state, applicable to simple fluids and polymers over the entire fluid range of density and temperature. Normal fluids, including polymers, are characterized by three parameters: segment number

r (number of single hard spheres per chain molecule), segment size σ, and non-bonded segment pair interaction energy ε. These molecular parameters are obtained from readily available data for thermodynamic properties such as vapor pressures, densities, and compressibilities.

The PHSC equation of state presented here is similar in form to the Statistical Associating Fluid Theory (SAFT) (Chapman, et al., 1990; Huang and Radosz, 1990) which is based on the thermodynamic perturbation theory of polymerization (Chapman, et al., 1988; Wertheim, 1987) but differs in four ways. First, our reference equation of state is a generalization based on an essentially exact result within the assumptions of the Percus-Yevick theory coupled with chain connectivity, while the SAFT reference equation of state is a first-order perturbation of the cluster expansion. The reference equation developed by Song et al. (1993a) has been shown to be more accurate than the SAFT reference equation when compared with computer simulation results. Second, the PHSC equation of state is computationally much simpler. Third, the algorithms for calculating the effective hard-sphere diameter and the attractive-energy parameter are based on different statistical-mechanical perturbation theories. Finally, the PHSC equation is applicable to molecules consisting of segments of differing size, as found in copolymers. Later, we compare our calculations for pure fluids with the SAFT and Lattice-Fluid equations of state which also require three molecular parameters.

Theoretical Development

Equation of State

Equations of state of the van der Waals type follow a first-order statistical-mechanical perturbation theory based on a reference system plus a van der Waals attractive perturbation term (McQuarrie, 1976). The general form of a van der Waals-type EOS is

$$\frac{p}{\rho kT} = \left(\frac{p}{\rho kT}\right)_{ref} + \left(\frac{p}{\rho kT}\right)_{pert} \tag{1}$$

where p is the pressure, $\rho = N/V$ is the number density, N is the number of molecules, V is the volume of the system, k is Boltzmann's constant, and T is the absolute temperature. In Eq. (1), the first term represents the reference equation of state, here taken as a fluid of hard-sphere chains, and the second term is a van der Waals perturbation to account for attractive forces. The simplest van der Waals attractive form is used here:

$$\left(\frac{p}{\rho kT}\right)_{pert} = -\frac{r^2 a \rho}{kT} \tag{2}$$

where a reflects the attractive forces between two nonbonded segments.

The derivation of the reference equation of state for hard-sphere chains is presented elsewhere (Song, et al., 1993a); the result is

$$\left(\frac{p}{\rho kT}\right)_{ref} = 1 + r^2 b \rho g(d^+) - (r-1)\left[g(d^+) - 1\right] \tag{3}$$

where b is the van der Waals covolume per segment or the second virial coefficient of (nonbonded) hard spheres, $g(d^+)$ is the pair radial distribution function of hard spheres at contact, and d is the hard-sphere diameter. In Eq. (3), the first two terms are the nonbonding contributions and the last term reflects chain connectivity.

To obtain an explicit equation of state from Eq. (3) for hard-sphere chains, we require a suitable mathematical form for $g(d^+)$. The best analytical expression for $g(d^+)$ is that from the Carnahan-Starling equation,

$$g(d^+) = \frac{1 - \eta/2}{(1-\eta)^3} \tag{4}$$

where η is the packing fraction given by

$$\eta = \frac{rb\rho}{4} \tag{5}$$

and

$$b = \frac{2\pi}{3}d^3 \quad . \tag{6}$$

Eqs. (2) and (3), are combined to obtain the complete equation of state

$$\frac{p}{\rho kT} = 1 + r^2 b\rho g(d^+) - (r-1)\left[g(d^+)-1\right] - \frac{r^2 a\rho}{kT} \tag{7}$$

In addition to r, Eq. (7) contains two segment-based parameters b and a which posses clear physical meaning. For nonbonded spheres (i.e., $r = 1$), Eq. (7) reduces to the original van der Waals equation of state if $g(d^+)$ is crudely approximated as $(1-b\rho)^{-1}$. Eq. (7) obeys the ideal-gas limit as $\rho \to 0$.

To apply Eq. (7) to real molecular fluids, we require a procedure wherein the hard-sphere diameter in the reference part, d [which is related to b by Eq. (6)], and the attractive energy parameter in the perturbation, a, are expressed in terms of constants associated with intermolecular forces. We do so first for simple fluids which can be represented by a single effective hard sphere (i.e., $r = 1$). Later, we consider molecular fluids which can be described as effective hard-sphere chains ($r > 1$). The result of this procedure (described in the next section) is that hard-sphere diameter d becomes an "effective" hard-sphere diameter which depends on temperature. Since b and a are related by the second virial coefficient, a also becomes temperature-dependent.

Relating Parameters a and b to the Intermolecular Potential

Simple Fluids ($r = 1$)

Several well-established procedures are available to obtain an effective hard-sphere diameter through statistical-mechanical perturbation theories for simple fluids (Barker and

Henderson, 1967; Weeks, et al., 1971). The Weeks-Chandler-Andersen (WCA) theory (Weeks, et al., 1971) provides the most accurate procedure; however, it is difficult to implement in practice because the effective hard-sphere diameter depends on both temperature and density. A novel method for calculating the effective hard-sphere diameter in the WCA framework was given by Song and Mason (1989). Using this method, the effective hard-sphere diameter depends only on temperature; it can be calculated from a simple quadrature if the intermolecular potential is known.

The effective hard-sphere diameter d can be expressed in terms of the effective van der Waals covolume b which in the Song-Mason theory is given by (Song and Mason, 1989)

$$b(T) = \frac{2\pi}{3} d^3(T) = 2\pi \int_0^{\sigma} \left[1 - \left(1 + \frac{u_o}{kT} \right) e^{-u_o/kT} \right] R^2 dR \tag{8}$$

where $u_o(R)$ is the repulsive part of the pair potential $u(R)$

$$u_o(R) = \begin{cases} u(R) + \varepsilon, & R < \sigma \\ 0, & R > \sigma \end{cases} \tag{9}$$

where R is the center to center distance and ε is the depth of the potential well at $R = \sigma$. Dividing the pair-potential at the point where the forces between two molecules is zero is the Weeks-Chandler-Andersen decomposition (Weeks, et al., 1971) shown in Fig. 1. Eq. (8) obeys the same limits as those in WCA theory for the effective hard-sphere diameter at both high and low temperatures; it behaves smoothly at intermediate temperatures. According to Eq. (8), the physical meaning of b is the effective van der Waals covolume (or excluded volume) due exclusively to repulsive forces.

For $r = 1$, the attractive energy parameter $a(T)$ is related to the second viral coefficient $B(T)$, the van der Waals covolume $b(T)$, and the intermolecular pair-potential $u(R)$:

$$B(T) = b - \frac{a}{kT} = 2\pi \int_0^{\infty} \left[1 - e^{-u(R)/kT} \right] R^2 dR \quad . \tag{10}$$

Substitution of Eq. (8) into Eq. (10) yields

$$\frac{a(T)}{kT} = 2\pi\int_0^{\sigma}\left[1-\left(1+\frac{u_0}{kT}\right)e^{-u_0/kT}\right]R^2dR - 2\pi\int_0^{\infty}\left[1-e^{-u/kT}\right]R^2dR \quad . \qquad (11)$$

Eqs. (8) and (11) give the expressions required to calculate b and a, respectively, from the pair-potential. In practice, accurate knowledge of the full pair-potential is seldom available; fortunately, Song and Mason have shown that $b(T)$ is insensitive to the detailed shape of the pair potential. Since the pair potential can be scaled by two parameters, σ and ε, $b(T)$ can be scaled by these same two parameters and Eq. (8) expressed as

$$b(T) = \frac{2\pi}{3}d^3(T) = \frac{2\pi}{3}\sigma^3\mathcal{F}_b\,(kT/\varepsilon) \qquad (12)$$

where $\mathcal{F}_b$, a universal function only of the scaled temperature kT/ε, is applicable to all simple fluids. The universal function represents the integral in Eq. (8) after the pair potential and distance have been appropriately scaled by ε and σ, respectively.

By expanding Eq. (11) according to the Weeks-Chandler-Andersen procedure, $a(T)$ can be shown to behave in a similar manner:

$$\frac{a(T)}{kT} = 2\pi\int_0^{\sigma}\left(\frac{\varepsilon}{kT}-\frac{u_0}{kT}+\cdots\right)e^{-u_0/kT}R^2dR - 2\pi\int_{\sigma}^{\infty}\left(\frac{u}{kT}+\cdots\right)R^2dR \quad . \qquad (13)$$

Again, since the pair potential can be scaled by two parameters, σ and ε, $a(T)$ can be scaled by these same two parameters and Eq. (13) can be expressed as

$$a(T) = \frac{2\pi}{3}\sigma^3\,\varepsilon\,\mathcal{F}_a\,(kT/\varepsilon) \qquad (14)$$

where $\mathcal{F}_a$, another universal function of the scaled temperature kT/ε, is applicable to all simple fluids. When $r=1$, Eq. (7) must follow a two-parameter (σ and ε) correlation or principle of corresponding states. Consequently, the scaled critical temperature kT_c/ε is the same for simple fluids and determined to be $kT_c/\varepsilon = 1.1020$ by applying the critical conditions to Eq. (7).

In principle, any configurational thermodynamic property of a simple fluid can be used to determine both universal functions $\mathcal{F}_b$ and $\mathcal{F}_a$ if σ and ε are accurately known. Such is the case for argon and methane; accurate experimental data for the thermodynamic properties of both fluids are plentiful (Stewart and Jackobsen, 1989; Younglove and Ely, 1987). Further, precise experimental values for σ and ε are available (Aziz and Slaman, 1986; Reid, et al., 1985); these are listed in Table I. Both $\mathcal{F}_b$ and $\mathcal{F}_a$ are determined by fitting the vapor pressure and the densities of the saturated liquid and vapor. As shown in Fig. 2, $\mathcal{F}_b$ and $\mathcal{F}_a$ for methane and argon obey the same function of scaled temperature. These two "universal" functions can be represented accurately by the following empirical relations (Song, 1991):

$$\mathcal{F}_a(kT/\varepsilon) = \alpha_1 + \alpha_2 e^{-\alpha_3(kT/\varepsilon)} \tag{15}$$

$$\mathcal{F}_b(kT/\varepsilon) = \beta_1 e^{-\beta_2(kT/\varepsilon)} + (1-\beta_1)\left[1-e^{-\beta_3(kT/\varepsilon)^{-1/4}}\right] \tag{16}$$

where α_i and β_i are universal constants given in Table II. Since both universal functions must obey the correct limits at high and low temperature, these limits have been incorporated into the functional forms of Eqs. (15) and (16).

Molecular Fluids ($r > 1$)

When $r = 1$, Eq. (7) is essentially a two-parameter equation of state for simple fluids (spherical molecules) with segment-size parameter σ and energy parameter ε, both independent of temperature. However, molecular fluids (non-spherical or chain-like molecules) need an additional parameter r, representing the segment number per molecule, to describe molecular size.

Increasing the chain length raises the scaled critical temperature, kT_c/ε, of the r-mer fluid. Therefore, both functions $\mathcal{F}_b$ and $\mathcal{F}_a$ in terms of kT/ε are not directly applicable to molecular fluids. To circumvent this restriction, we replace the scaled temperature kT/ε by $kT/\varepsilon s$ where s is a parameter reflecting effects of chain connectivity on the temperature scaling of the universal functions. Hence, s should depend only on r and reduce to unity when r is unity (monomer). Both

$\mathcal{F}_b$ and $\mathcal{F}_a$ become universal functions of the scaled temperature $kT/\varepsilon s$ for all normal fluids (including polymers) having r greater than or equal to unity. Consequently, the scaled critical temperature $kT_c/\varepsilon s$ is a constant for all molecular fluids and equal to that for simple fluids, which was determined to be $kT_c/\varepsilon s = 1.1020$. This result uniquely determines s as a function of r. The behavior of $s(r)$ is shown in Fig. 3. Rather than attempting to represent $s(r)$ by an empirical analytical expression, we tabulated numerous values of s and constructed a simple interpolation computer program which evaluates $s(r)$ with high precision.

In summary, the scaled temperature for r-mer fluids is modified such that the universal functions $\mathcal{F}_b$ and $\mathcal{F}_a$ become

$$\mathcal{F}_a(kT/\varepsilon s) = \alpha_1 + \alpha_2 e^{-\alpha_3 (kT/\varepsilon s)} \tag{17}$$

$$\mathcal{F}_b(kT/\varepsilon s) = \beta_1 e^{-\beta_2 (kT/\varepsilon s)} + (1-\beta_1)\left[1 - e^{-\beta_3 (kT/\varepsilon s)^{-1/4}}\right] \tag{18}$$

where s is the unique function of r shown in Fig. 3 and constants α_i and β_i are given in Table II. Parameters a and b are given by

$$a(T) = \frac{2\pi}{3}\sigma^3 \varepsilon \mathcal{F}_a(kT/\varepsilon s) \tag{19}$$

$$b(T) = \frac{2\pi}{3}\sigma^3 \mathcal{F}_b(kT/\varepsilon s) \quad . \tag{20}$$

A loose analogy exists between s and the quantity q/c in the Perturbed-Hard-Chain equation of state (Beret and Prausnitz, 1975b); both quantities describe effects of molecular size on the scaling factor between temperature and the intermolecular potential-well depth. In the Perturbed-Hard-Chain equation of state, the reduced temperature is defined as $ckT/\varepsilon q$ where q is the external surface area and c is a parameter reflecting external molecular degrees of freedom. For spherical molecules (monomers), $q/c = 1$ ($q = c = 1$); for all other molecules, $q/c > 1$ ($q > c > 1$) and approaches an asymptotic value for large chains such as linear polymers. In these respects, q/c and $s(r)$ behave in a similar manner. However, a distinct difference is that both q and c are

usually adjustable parameters obtained from fitting thermodynamic properties of a given substance. Parameter s, on the other hand, is related to the calculated (scaled) critical properties of an r-mer fluid; s is not an adjustable parameter once r is fixed.

Eq. (7) is not directly applicable to associating fluids, such as water and alcohols, for which specific interactions (e.g., hydrogen-bonding) play an important role in their structure and thermodynamic properties. Specific (or oriented) forces are inconsistent with one of the basic assumptions of the PHSC theory, that the structure of a liquid is dominated by repulsive forces. Despite this inconsistency, two common methods can be used to extend equations of state to associating fluids. One method is to add an association term to the equation of state

$$\frac{p}{\rho kT} = \left(\frac{p}{\rho kT}\right)_{ref} + \left(\frac{p}{\rho kT}\right)_{pert} + \left(\frac{p}{\rho kT}\right)_{assoc} . \tag{21}$$

A recent example of such addition is the SAFT equation of state (Chapman, et al., 1990; Huang and Radosz, 1990) where the association term is derived from a statistical mechanical perturbation theory for spheres with "sticky" bonding sites. Lattice-fluid equations of state also have included association terms based on "quasichemical" arguments (Panayiotou and Sanchez, 1991a) and chemical-equilibria arguments (Panayiotou and Sanchez, 1991b). A second method is to distinguish between ordinary and oriented segment-segment interactions and to describe the relative frequencies of these interactions using Boltzmann statistics (Hino, et al., 1993; Sanchez and Balazs, 1989; ten Brinke and Karasz, 1984). The net effect of this second method is to give a temperature dependence to parameter ε.

Determining Molecular Parameters from Thermodynamic Properties of Real Fluids

In this section we discuss how to use the equation of state to correlate the properties of pure liquids. We focus on the liquid phase since our ultimate goal is to use the equation of state to

describe vapor-liquid and liquid-liquid equilibria of mixtures containing polymers (Song, et al., 1993b). The discussion is facilitated by introducing characteristic quantities which scale the variables in the equation of state.

Normal Fluids

The following characteristic quantities are proposed to scale the density, temperature and pressure, respectively, in Eq. (7):

$$v^* = \frac{1}{\rho^*} = \frac{2\pi}{3} r\sigma^3; \qquad T^* = \frac{\varepsilon}{k}; \qquad p^* = \frac{3\varepsilon}{2\pi\sigma^3} \quad . \tag{22}$$

These lead to the following scaled variables

$$\tilde{\rho} = \rho v^* = \rho/\rho^*; \qquad \tilde{T} = T/T^*; \qquad \tilde{p} = p/p^* \quad . \tag{23}$$

When substituted into Eq. (7) we obtain a scaled equation of state for normal liquids, including polymers:

$$\tilde{p} \;=\; -\tilde{\rho}^2 \mathfrak{F}_a(\tilde{T}/s) \;-\; \tilde{T}\left[\left(1-\frac{1}{r}\right)\tilde{\rho} g(d^+) - \tilde{\rho} - \tilde{\rho}^2 \mathfrak{F}_b(\tilde{T}/s) g(d^+)\right] \quad . \tag{24}$$

In Eq. (4), the packing fraction $\eta = \tilde{\rho}\mathfrak{F}_b(\tilde{T}/s)/4$. Since the chain length appears explicitly, it can be calculated from one of the following equations, each appropriate for a set of units used for the characteristic volume:

$$r = \frac{p^* v^*}{kT^*} \quad (v^* = \text{molecular volume}) \tag{25}$$

$$r = \frac{p^* v^*}{R_g T^*} \quad (v^* = \text{molar volume}) \tag{26}$$

$$r = \frac{p^* v^* M}{R_g T^*} \quad (v^* = \text{specific volume}) \tag{27}$$

where R_g is the gas constant and M is the molecular weight of the fluid.

For a pure volatile fluid, the three temperature-independent molecular parameters (r, σ and ε/k) are regressed from the properties of the saturated liquid, i.e., the vapor pressure and the density of the saturated liquid as a function of temperature. Since experimental saturated vapor densities are available only for a limited number of fluids, they are not used here. The DIPPR data compilation (Daubert and Danner, 1989) was used to obtain "experimental" vapor pressures and saturated liquid densities as a function of temperature. Fifty equally-spaced temperatures between the triple point and 0.9 times the critical temperature were used for each fluid. Non-linear least-squares regression was used to find a set of the three molecular parameters which minimizes the objective function, F, defined as the sum of squares of the relative deviation between calculated and experimental properties

$$F = \sum_{i=1}^{50}\left(\frac{\rho_{liq}^{\text{calc}}(T_i)-\rho_{liq}^{\text{expt}}(T_i)}{\rho_{liq}^{\text{expt}}(T_i)}\right)^2 + \sum_{i=1}^{50}\left(\frac{p_{sat}^{\text{calc}}(T_i)-p_{sat}^{\text{expt}}(T_i)}{p_{sat}^{\text{expt}}(T_i)}\right)^2. \tag{28}$$

Parameters were regressed for a wide variety of pure, non-associating fluids such as normal alkanes, branched alkanes, normal alkenes, cyclic alkanes, aromatics, ethers, ketones and chlorinated hydrocarbons; in this regression, equal weight was given to vapor-pressure data and to liquid-density data. Results are given in Table III. The root-mean-square relative deviation between calculated and "experimental" values for the liquid density and vapor pressure are given by

$$\%\text{ rms deviation } \rho_{liq} = \sqrt{\frac{1}{50}\sum_{i=1}^{50}\left(\frac{\rho_{liq}^{\text{calc}}(T_i)-\rho_{liq}^{\text{expt}}(T_i)}{\rho_{liq}^{\text{expt}}(T_i)}\right)^2}\times 100 \tag{29}$$

$$\%\text{ rms deviation } p_{sat} = \sqrt{\frac{1}{50}\sum_{i=1}^{50}\left(\frac{p_{sat}^{\text{calc}}(T_i)-p_{sat}^{\text{expt}}(T_i)}{p_{sat}^{\text{expt}}(T_i)}\right)^2}\times 100 \quad . \tag{30}$$

Excluding the critical region, these deviations are less than 1% for most fluids. Figs. 4-6 compare the ability of the PHSC equation to correlate the vapor pressure and vapor-liquid coexistence curve with other three-parameter equations of state such as the Lattice-Fluid (LF) and SAFT equations of

state. The entire liquid regime is shown in these figures, i.e., the temperature ranges from the triple point to the critical point. Calculations using the SAFT and LF equations of state were also performed using the same data-reduction method described above. Predicted vapor-phase densities give good agreement with experimental vapor-phase densities, except near the critical region. [In Figs. 4-6, experimental vapor-liquid coexistence data were obtained from Smith and Srivastava (1986) and experimental vapor-pressure data were calculated from the DIPPR correlation (Daubert and Danner, 1989).] The PHSC and LF equations of state give excellent correlation of the vapor pressure and reasonable correlation of the vapor-liquid coexistence curve, except near the critical point, which is not surprising since all are analytical equations of state. SAFT gives a surprisingly poor correlation, especially for the vapor pressure, when fitting is attempted to temperatures as low as the triple point.

Our goal here is not precise fitting of these properties; instead, it is to show that regression of pure-fluid properties using the PHSC equation yields parameters which reflect the size, shape and energetic interactions characteristic of the chemical composition of these fluids. Fig. 7 shows that combinations of the three molecular parameters r, ε and σ are correlated with related quantities which, in part, are obtained from group contributions. A characteristic volume, V^*, can be constructed from multiplying the "hard-core" volume of a spherical segment by the total number of segments,

$$V^* = \frac{\pi}{6} r \sigma^3 N_A \tag{31}$$

where N_A is Avagodro's constant. A characteristic surface area, A^* can be constructed in a similar manner as

$$A^* = \pi r \sigma^2 N_A \quad . \tag{32}$$

A characteristic "cohesive" energy, E^*, can be constructed by multiplying the potential well depth between two nonbonded segments of a molecule by the total number of segments per molecule:

$$E^* = r(\varepsilon/k)R_g \quad . \tag{33}$$

Quantities analogous to V^*, A^*, and E^* are, respectively, the van der Waals volume, V_{VDW}, van der Waals area, A_{VDW}, and the cohesive energy, $E_{coh} = \int_{V_{liq}}^{\infty} (\partial E/\partial V)_T \, dV$ which is approximated by $\Delta H^{vap} - R_g T$ at pressures below critical; here V_{liq} is the volume of the saturated liquid and ΔH^{vap} is the enthalpy of vaporization. The first two can be estimated from group contributions (Bondi, 1968). The cohesive energy can be computed from the enthalpy of vaporization (Daubert and Danner, 1989) at a specified reduced temperature, chosen here to be $T_r = 0.6$. Fig. 7 shows the correlations for V^*, A^*, and E^*. These correlations provide estimates for EOS parameters when adequate experimental data are not available.

Polymers

Molecular parameters for polymer liquids can be determined from experimental *pressure-volume-temperature* (*pVT*) data. However, for sufficiently high molecular weight polymers, *pVT* data are usually insensitive to the molecular weight, as shown in Eq. (24) where the $(1-1/r)$ term becomes essentially unity and by Fig. 3, where s reaches an asymptotic value for large r. To obtain parameters σ and ε from experimental data for polymers, we use the EOS in the limit $r \to \infty$:

$$\tilde{p} = -\tilde{\rho}^2 \mathcal{F}_a(\tilde{T}/s_\infty) - \tilde{T}\left[\tilde{\rho} g(d^+) - \tilde{\rho} - \tilde{\rho}^2 \mathcal{F}_b(\tilde{T}/s_\infty) g(d^+)\right]. \tag{34}$$

where s_∞ is $s(r)$ in the limit that $r \to \infty$, determined to be 7.0701. Our data-reduction procedure is the same as that used with the Lattice-Fluid equation of state (Sanchez and Lacombe, 1978). Although r is assumed to be large, it does not follow that a characteristic quantity has been eliminated. Typically, mass densities (or specific volumes) of polymer liquids are the quantity measured experimentally; consequently, the appropriate relationship between v^*, T^* and p^* is that given by Eq. (27) which identifies the alternate characteristic quantity r/M. Although r and M are

assumed to be large, the ratio r/M remains finite. This ratio provides a characteristic quantity of the polymer in addition to σ and ε/k.

Using Eq. (28), non-linear least-squares regression was used to find a set of the three molecular parameters which minimizes the objective function F' defined as the sum of squares of relative deviation between calculated and experimental polymer densities at a specified temperature and pressure,

$$F' = \sum_{i=1}^{n}\left(\frac{\rho_{liq}^{\text{calc}}(p_i,T_i)-\rho_{liq}^{\text{expt}}(p_i,T_i)}{\rho_{liq}^{\text{expt}}(p_i,T_i)}\right)^2 \tag{35}$$

where n is the number of experimental data points. Table IV gives parameters regressed for several polymers. The root-mean-square relative deviation between calculated and experimental polymer liquid densities is

$$\%\text{ rms deviation } \rho_{liq} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\rho_{liq}^{\text{calc}}(p_i,T_i)-\rho_{liq}^{\text{expt}}(p_i,T)}{\rho_{liq}^{\text{expt}}(p_i,T)}\right)^2}\times 100 \quad . \tag{36}$$

In general this deviation is on the order of 0.01%, most likely within experimental uncertainty. Figs. 8-10 illustrate the quality of the correlation for three common polymers, polystyrene, high-density polyethylene and poly(vinyl acetate). The PHSC equation of performs much better than the LF EOS (especially at high pressures) and equally as well or slightly better than the SAFT EOS.

Characteristic quantities like those derived for solvents can also be obtained for polymers or, more precisely, for the polymer repeat unit. An effective chain length per polymer repeat unit can be found by multiplying r/M by the molecular weight of the repeat unit, M_0. Combining this effective chain length per polymer repeat unit with the effective "hard-core" diameter of a segment yields a characteristic volume of the polymer repeat unit,

$$V_0^* = \frac{\pi}{6}\left(\frac{r}{M}\right)M_0\sigma^3 N_A \quad . \tag{37}$$

Similarly, the characteristic surface area and characteristic cohesive energy of the polymer repeat unit are, respectively,

$$A_0^* = \pi\left(\frac{r}{M}\right)M_0\sigma^2 N_A \tag{38}$$

$$E_0^* = \left(\frac{r}{M}\right)\left(\frac{\varepsilon}{k}\right)M_0 R_g \quad . \tag{39}$$

Similar to normal liquids, V_0^* correlates very well with the van der Waals volume of the polymer repeat unit calculated from group contributions (Bondi, 1968; Van Krevelen, 1990) as shown in Fig. 11(a). The characteristic surface area, shown in Fig. 11(b), correlates well with the van der Waals surface area except for polymers with very large repeat units, such as poly(ethylene terephthalate), poly(carbonate), poly(sulfone) and poly(ether ether ketone). In Fig. 11(c) the characteristic cohesive energy, E_0^*, is compared with the cohesive energy calculated using the group-contribution method of Fedors (Fedors, 1974; Van Krevelen, 1990) [poly(sulfone) is not included in Fig. 11(c) because this polymer's repeat unit contains a group not provided]. Only a rough correlation is obtained, most likely because it is very difficult to determine precisely the cohesive energy of a polymer and its counterpart, the solubility parameter. In general, the correlations appear best for polymers with repeat units having $M_0 \sim 30-150$ g/mol. Since pVT data for polymers are often available only at atmospheric pressure, or not at all, correlations like those shown in Fig. 11 provide estimates for EOS parameters.

Conclusions

The perturbed hard-sphere-chain (PHSC) equation of state uses the modified Chiew equation of state for hard-sphere chains (Chiew, 1990; Song, et al., 1993a) as the reference system, a van der Waals type perturbation term and the Song-Mason method (Song and Mason, 1989) to relate EOS parameters to the intermolecular segment-segment potential. Three

temperature independent parameters characterize a pure fluid: segment number r (number of single hard spheres per chain molecule), segment size σ, and nonbonded segment pair interaction energy ε. For normal fluids, these parameters can be found from experimental thermodynamic properties of the saturated liquid. For polymers, these parameters can be found from experimental *pressure-volume-temperature* data. The PHSC fits the properties of normal fluids better than the SAFT EOS, but essentially as well as the Lattice-Fluid EOS. Conversely, the PHSC equation of state fits polymer *pVT* data much better than the Lattice-Fluid EOS and slightly better than the SAFT EOS.

The molecular parameters can be combined to give characteristic quantities that correlate with comparable quantities estimated from group contributions or readily available experimental data. Correlations of these type relate EOS parameters to the chemical structure of a fluid.

Future application of the PHSC equation of state is directed towards the extension to mixtures, inclusion of specific interactions, and copolymers.

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Notation

Upper Case

A	=	surface area
B	=	second virial coefficient
E	=	energy
M	=	molecular weight
N	=	total number of molecules
N_A	=	Avagodro's number
R	=	intermolecular distance
R_g	=	gas constant
T	=	temperature
$\tilde{T}$	=	scaled temperature
V	=	volume
ΔH^{vap}	=	enthalpy of vaporization
$\mathfrak{F}_a$	=	universal function used to calculate $a(T)$
$\mathfrak{F}_b$	=	universal function used to calculate $b(T)$

Lower Case

a	=	equation-of-state parameter
b	=	equation-of-state parameter
d	=	effective hard-sphere diameter
$g(d^+)$	=	radial distribution function of hard spheres at contact
k	=	Boltzmann's constant
n	=	number of data points used in regression of polymer pVT data
p	=	pressure
$\tilde{p}$	=	scaled pressure
r	=	number of effective hard spheres per molecule
$s(r)$	=	parameter used to scale temperature in the universal functions
$u(R)$	=	intermolecular pair potential
$u_0(R)$	=	repulsive part of the intermolecular pair potential
v	=	molecular, molar, or specific volume

Greek Letters

α_i	=	constant in Eq. (17)
β_i	=	constant in Eq. (18)

ε	=	depth of the pair potential at its minimum
η	=	packing fraction
ρ	=	number density
$\tilde{\rho}$	=	scaled density
σ	=	separation distance at the minimum in the pair potential

Subscripts

assoc	=	association
c	=	critical property
coh	=	cohesive
liq	=	refers to the saturated liquid
pert	=	perturbation
ref	=	reference
sat	=	refers to the saturated liquid
VDW	=	van der Waals
0	=	refers to the polymer repeat unit

Superscripts

calc	=	calculated
expt	=	experimental
*	=	denotes a characteristic quantity

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Table I. Pair potential parameters used to determine universal functions in Eqs. (13) and (14)

	σ (Å)[b]	ε/k (K)	Reference
Argon	3.7565	143.224	(Aziz and Slaman, 1986)
Methane[a]	4.1257	182.125	(Reid, et al., 1985)

[a]The values listed here have been slightly adjusted (within experimental uncertainty) to produce a better fit.

[b]The definition of σ used here is the separation distance at the minimum of the potential; in the above references the symbol r_m is used for this quantity.

Table II. Constants used in Eqs. (17) and (18)

Eq. (17)		Eq. (18)	
α_1	0.7170	β_1	0.5849
α_2	1.9003	β_2	0.4772
α_3	0.5152	β_3	1.0669

Table III. PHSC equation-of-state parameters for some normal fluids

Substance	r	σ (Å)	ε/k (K)	% rms deviation ρ_{liq}	% rms deviation p_{sat}
normal alkanes					
ethane	1.757	3.768	201.4	0.28	0.57
propane	2.142	3.863	218.8	0.35	1.0
butane	2.977	3.657	206.9	0.36	0.64
pentane	3.942	3.482	197.2	0.55	0.47
hexane	4.782	3.394	194.4	0.61	0.48
heptane	5.460	3.374	195.4	0.66	0.49
octane	5.668	3.467	204.4	0.57	0.99
nonane	6.199	3.476	206.4	0.56	1.2
decane	7.083	3.400	202.7	0.60	1.3
undecane	8.409	3.270	195.0	0.74	0.65
dodecane	8.814	3.303	198.5	0.70	0.77
tridecane	8.959	3.381	203.4	0.57	1.2
tetradecane	10.82	3.181	193.6	0.99	0.66
pentadecane	11.86	3.152	191.2	0.87	0.67
hexadecane	11.84	3.233	196.6	0.75	0.92
heptadecane	14.07	3.060	187.4	1.1	1.0
octadecane	13.14	3.215	197.5	0.77	0.30
nonadecane	13.62	3.235	198.3	0.84	0.74
eicosane	14.27	3.234	199.4	0.81	1.4
branched alkanes					
isobutane	3.102	3.615	192.5	0.51	0.16
isopentane	3.136	3.829	219.7	0.42	0.66
neopentane	3.475	3.651	192.7	0.25	0.14
2,2-dimethylbutane	3.575	3.819	215.6	0.46	0.32
2,3-dimethylbutane	3.691	3.769	217.7	0.47	0.36
cyclopentane	3.129	3.591	241.5	0.38	0.49
methylcyclopentane	3.524	3.680	237.0	0.54	0.63
ethylcyclpentane	4.052	3.668	236.8	0.66	0.61
propylcyclopentane	4.436	3.703	240.0	0.63	0.77
cyclohexane	3.689	3.548	238.6	0.39	0.32
methylcyclohexane	3.967	3.688	238.0	0.61	0.33
ethylcyclohexane	4.056	3.825	253.3	0.57	0.64
propylcyclohexane	4.639	3.775	247.8	0.60	0.64
butylcyclohexane	5.218	3.732	244.4	0.67	0.67
alkenes					
ethylene	1.625	3.733	196.0	0.94	0.34
propylene	2.173	3.722	212.9	0.18	0.49
1-butene	3.016	3.563	203.1	0.43	0.79
trans-2-butene	3.075	3.521	205.8	0.28	0.35
cis-2-butene	3.157	3.466	205.4	0.37	0.25
1-pentene	3.719	3.516	200.5	0.52	0.21
1-hexene	3.907	3.652	215.3	0.47	0.63

aromatics					
benzene	3.558	3.394	248.0	0.30	0.16
toluene	3.765	3.569	256.9	0.38	0.44
ethylbenzene	4.245	3.588	253.2	0.44	0.52
propylbenzene	4.809	3.587	247.2	0.47	0.53
o-xylene	4.461	3.493	251.9	0.43	0.38
m-xylene	4.398	3.535	249.8	0.42	0.54
p-xylene	4.445	3.516	248.1	0.31	0.25
chlorobenzene	3.403	3.680	290.3	0.32	0.89
fluorobenzene	3.675	3.421	245.2	0.36	0.43
styrene	4.400	3.460	256.2	0.49	0.13
acetates					
methyl acetate	4.455	2.978	204.3	0.43	0.56
vinyl acetate	4.203	3.222	218.6	0.34	1.3
ethyl acetate	5.170	3.022	196.5	0.48	0.62
propyl acetate	5.876	3.051	194.1	0.61	0.43
butyl acetate	5.866	3.217	205.3	0.46	0.82
pentyl acetate	6.774	3.171	200.7	0.62	1.1
ethers					
dimethyl ether	2.637	3.355	210.6	0.20	0.82
diethyl ether	4.157	3.165	195.0	0.64	0.23
ethylene oxide	2.718	3.028	245.6	0.39	0.26
1,3-propylene oxide	3.031	3.245	254.3	0.08	0.17
tetrahydrofuran	3.534	3.309	240.0	0.47	0.22
ketones					
acetone	3.578	3.182	232.7	0.13	0.65
methyl ethyl ketone	3.906	3.303	232.8	0.21	0.57
diethyl ketone	4.675	3.255	221.2	0.29	0.57
2-pentanone	3.826	3.555	248.0	0.13	1.4
2-hexanone	5.640	3.196	211.9	0.46	0.80
chlorinated hydrocarbons					
methyl chloride	2.388	3.243	230.4	0.09	0.23
dichloromethane	3.428	3.067	229.9	0.29	0.12
chloroform	3.760	3.197	228.0	0.36	0.21
carbon tetrachloride	3.221	3.628	258.4	0.30	0.17

Table IV. PHSC Equation-of-state parameters for common polymers

Polymer	r/M (mol/g)	σ (Å)	ε/k (K)	% rms deviation n	% rms deviation ρ_{liq}	Ref.
high density poly(ethylene)	0.03542	3.860	384.9	67	0.014	a
low density poly(ethylene)	0.04945	3.413	336.7	61	0.016	a
iso-poly(propylene)	0.01410	5.456	551.4	45	0.029	b
iso-poly(1-butene)	0.02140	4.663	485.0	45	0.038	b
poly(isobutene)	0.01019	6.030	779.5	55	0.015	c
poly(4-methyl-1-pentene)	0.02113	4.687	446.1	126	0.022	d
poly(styrene)	0.01117	5.534	724.7	69	0.015	e
poly(*o*-methylstyrene)	0.01191	5.446	731.4	50	0.008	e
cis-1,4-poly(butadiene)	0.01499	5.264	611.8	156	0.004	f
poly(vinyl chloride)	0.00981	5.271	736.9	87	0.020	g
poly(ethylene glycol)	0.02981	3.766	405.7	68	0.015	h
poly(vinyl alcohol)	0.08469	2.531	357.7	105	0.014	i
poly(vinyl acetate)	0.02044	4.242	477.2	110	0.002	j
poly(methyl methacrylate)	0.01432	4.850	655.9	41	0.004	a
iso-poly(methyl methacrylate)	0.01580	4.662	629.4	93	0.013	a
poly(butyl methacrylate)	0.01899	4.550	510.8	168	0.014	a
poly(cyclohexyl methacrylate)	0.01482	4.889	607.2	90	0.012	a
poly(ethylene terephthalate)	0.05437	2.798	350.3	121	0.035	k
poly(carbonate)	0.02628	3.828	479.5	107	0.017	l
poly(ether ether ketone)	0.06690	2.580	322.8	126	0.042	m
poly(sulphone)	0.02401	3.912	530.5	149	0.009	n
poly(tetrafluoroethylene)	0.03753	2.516	192.8	21	0.064	o
poly(tetrahydrofuran)	0.01708	4.843	531.0	47	0.011	h

References: (a) Olabisi and Simha, 1975, (b) Zoller, 1979, (c) Beret and Prausnitz, 1975a, (d) Zoller, 1977, (e) Quach and Simha, 1971, (f) Barlow, 1978, (g) Rodgers, 1993, (h) Tsujita, et al., 1973, (i) Lucchelli, et al., 1988, (j) McKinney and Goldstein, 1974, (k) Zoller and Bolli, 1980, (l) Zoller, 1982, (m) Zoller, et al., 1989, (n) Zoller, 1978b, (o) Zoller, 1978a.

Figure Captions

Figure 1. The Weeks-Chandler-Andersen decomposition of the pair potential.

Figure 2. Universal functions $\mathcal{F}_a$ and $\mathcal{F}_b$ as determined from the vapor pressures and vapor and liquid densities of methane and argon. The symbols are from experimental data and the curves are the fit using Eqs. (15) and (16).

Figure 3. Parameter s as a function of r, used to scale the temperature in the universal functions $\mathcal{F}_a$ and $\mathcal{F}_b$ for a fluid where r is greater than unity. When r is unity, s is unity; s approaches an asymptotic value as r becomes infinite. (Note logarithmic scale on horizontal axis.)

Figure 4. The thermodynamic properties of saturated hexane: (a) vapor pressure and (b) vapor-liquid coexistence curve. The symbols are experimental data and curves are fits using the Perturbed Hard-Sphere-Chain (PHSC), the Lattice-Fluid (LF) and the Statistical Associating Fluid Theory (SAFT) equations of state.

Figure 5. The thermodynamic properties of saturated benzene: (a) vapor pressure and (b) vapor-liquid coexistence curve. The symbols are experimental data and curves are fits using the Perturbed Hard-Sphere-Chain (PHSC), the Lattice-Fluid (LF) and the Statistical Associating Fluid Theory (SAFT) equations of state.

Figure 6. The thermodynamic properties of saturated acetone: (a) vapor pressure and (b) vapor-liquid coexistence curve. The symbols are experimental data and curves are fits using the Perturbed Hard-Sphere-Chain (PHSC), the Lattice-Fluid (LF) and the Statistical Associating Fluid Theory (SAFT) equations of state.

Figure 7. Correlation of characteristic quantities calculated from molecular parameters for pure solvents in Table 3 with (a) van der Waals volume, (b) van der Waals area and (c) cohesive energy. The van der Waals volume and area were calculated from group contributions.

Figure 8. The pVT properties of polystyrene. The symbols are experimental data and curves are fits using the Perturbed Hard-Sphere-Chain (PHSC), the Lattice-Fluid (LF) and the Statistical Associating Fluid Theory (SAFT) equations of state.

Figure 9. The *pVT* properties of polyethylene (HDPE). The symbols are experimental data and curves are fits using the Perturbed Hard-Sphere-Chain (PHSC), the Lattice-Fluid (LF) and the Statistical Associating Fluid Theory (SAFT) equations of state.

Figure 10. The *pVT* properties of poly(vinyl acetate). The symbols are experimental data and curves are fits using the Perturbed Hard-Sphere-Chain (PHSC), the Lattice-Fluid (LF) and the Statistical Associating Fluid Theory (SAFT) equations of state.

Figure 11. Correlation of characteristic quantities calculated from molecular parameters for polymers in Table 4 with (a) van der Waals volume, (b) van der Waals area and (c) cohesive energy calculated from group contributions.

Figure 1

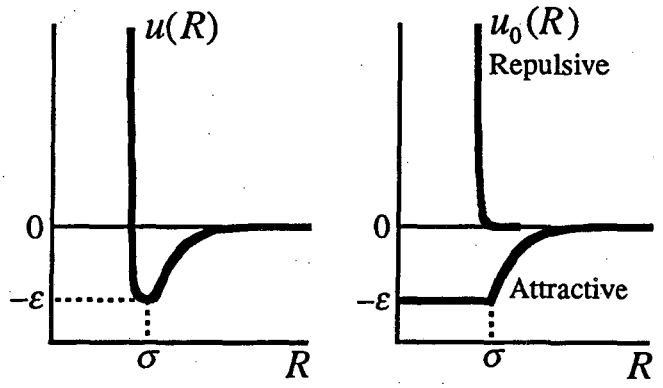

$u(R)$
0
$-\varepsilon$
σ
R
$u_0(R)$
Repulsive
0
$-\varepsilon$
Attractive
σ
R

Figure 2

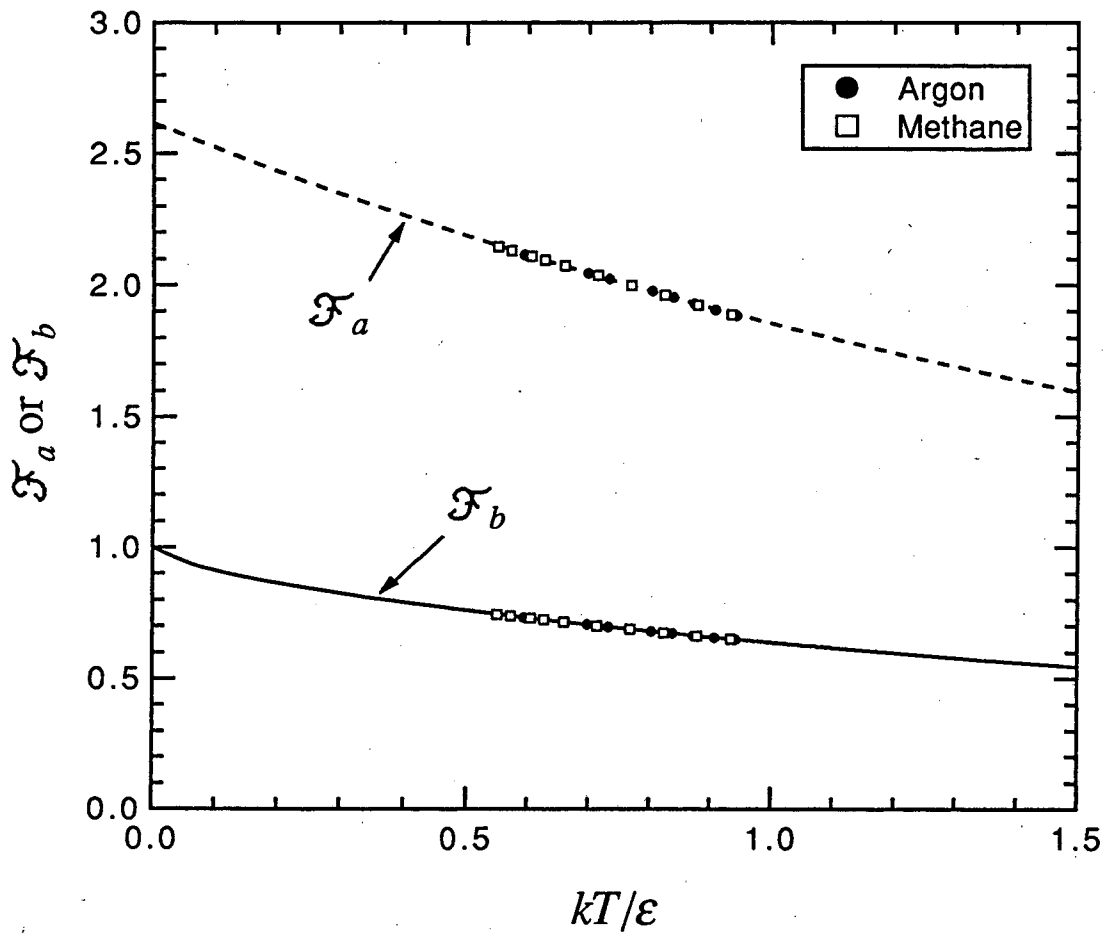

3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
Argon
Methane
$\mathcal{F}_a$
$\mathcal{F}_b$
$\mathcal{F}_a$ or $\mathcal{F}_b$
kT/ε

Figure 3

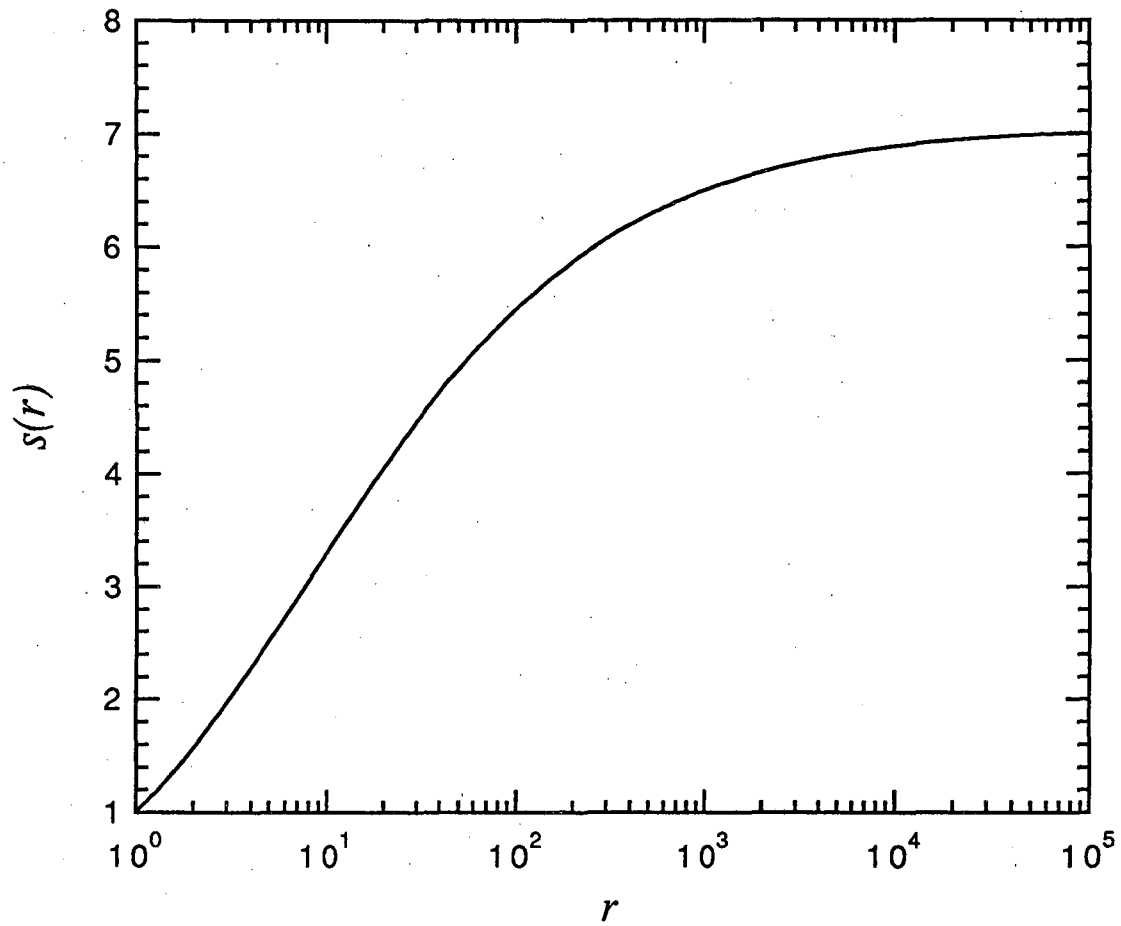


Figure 4

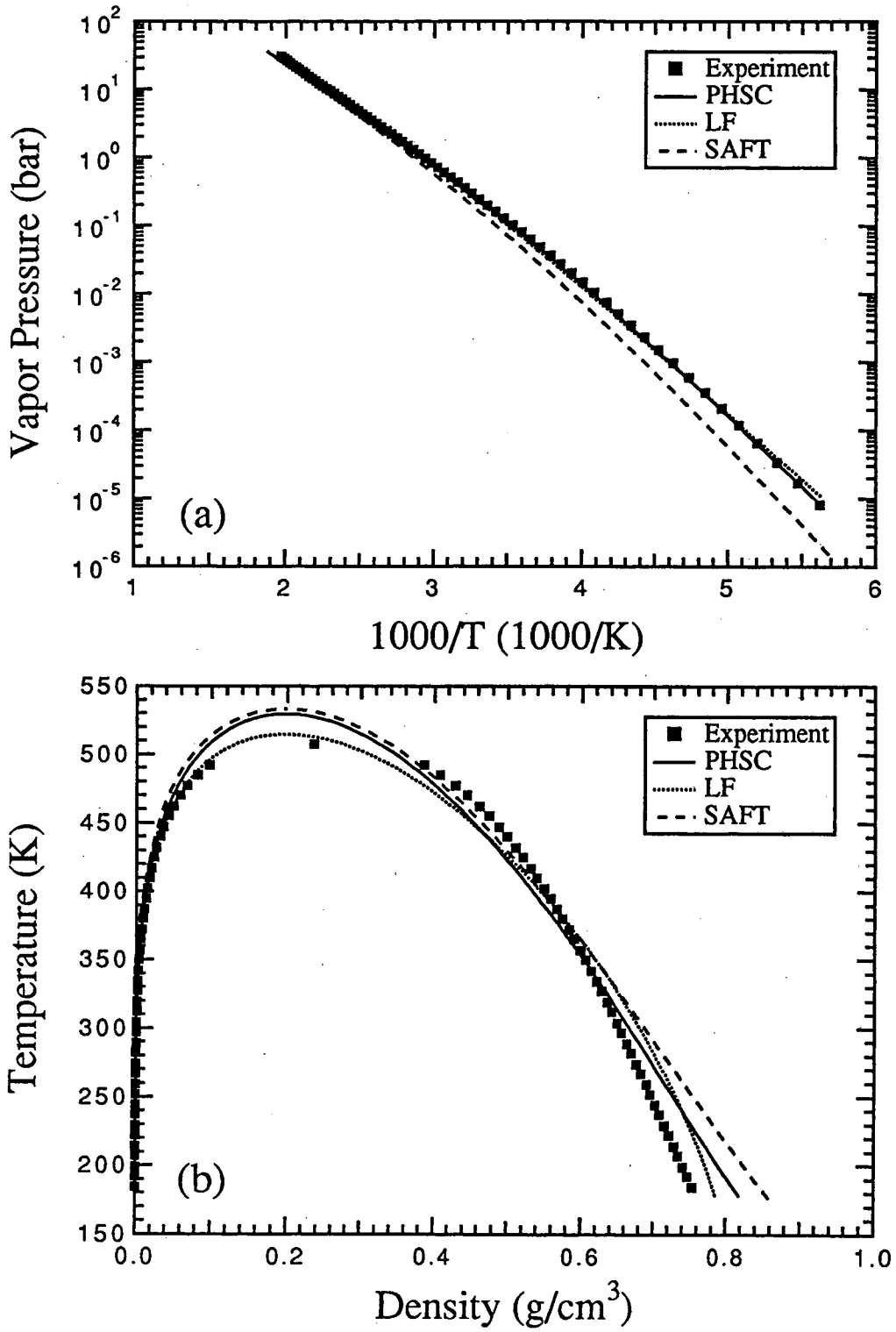
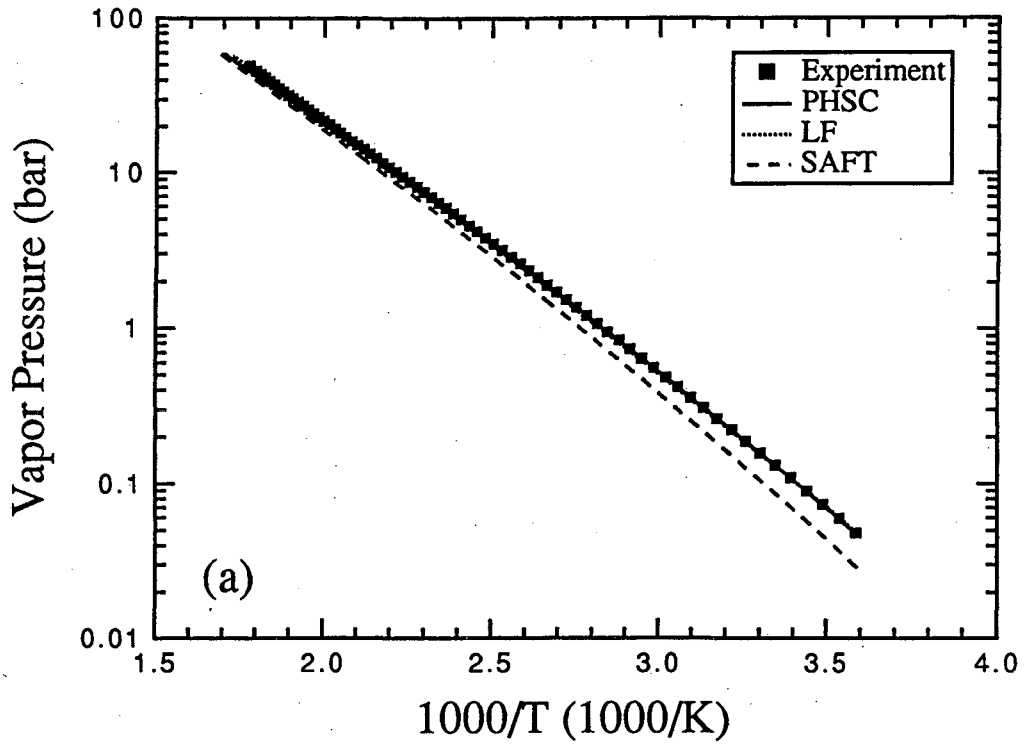

Vapor Pressure (bar)
1000/T (1000/K)
Experiment
PHSC
LF
SAFT
(a)
Temperature (K)
Density (g/cm3)
Experiment
PHSC
LF
SAFT
(b)

Figure 5


Vapor Pressure (bar)
100
10
1
0.1
0.01
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1000/K)
Experiment
PHSC
LF
SAFT
(a)

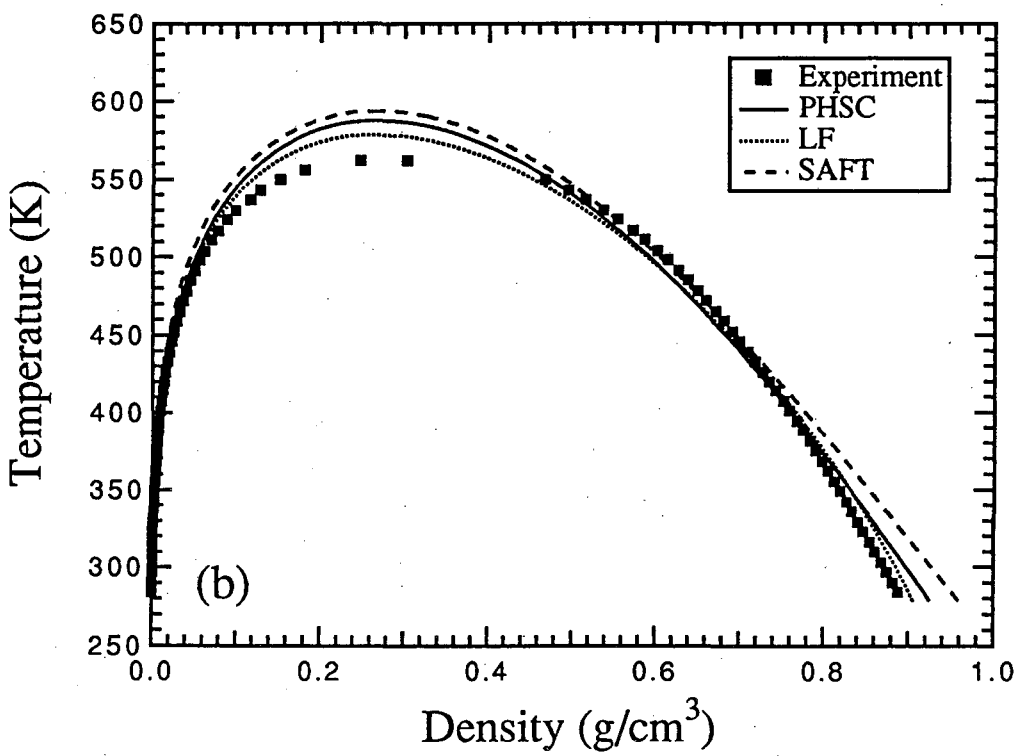

Temperature (K)
650
600
550
500
450
400
350
300
250
0.0
0.2
0.4
0.6
0.8
1.0
Density (g/cm3)
Experiment
PHSC
LF
SAFT
(b)

Figure 6

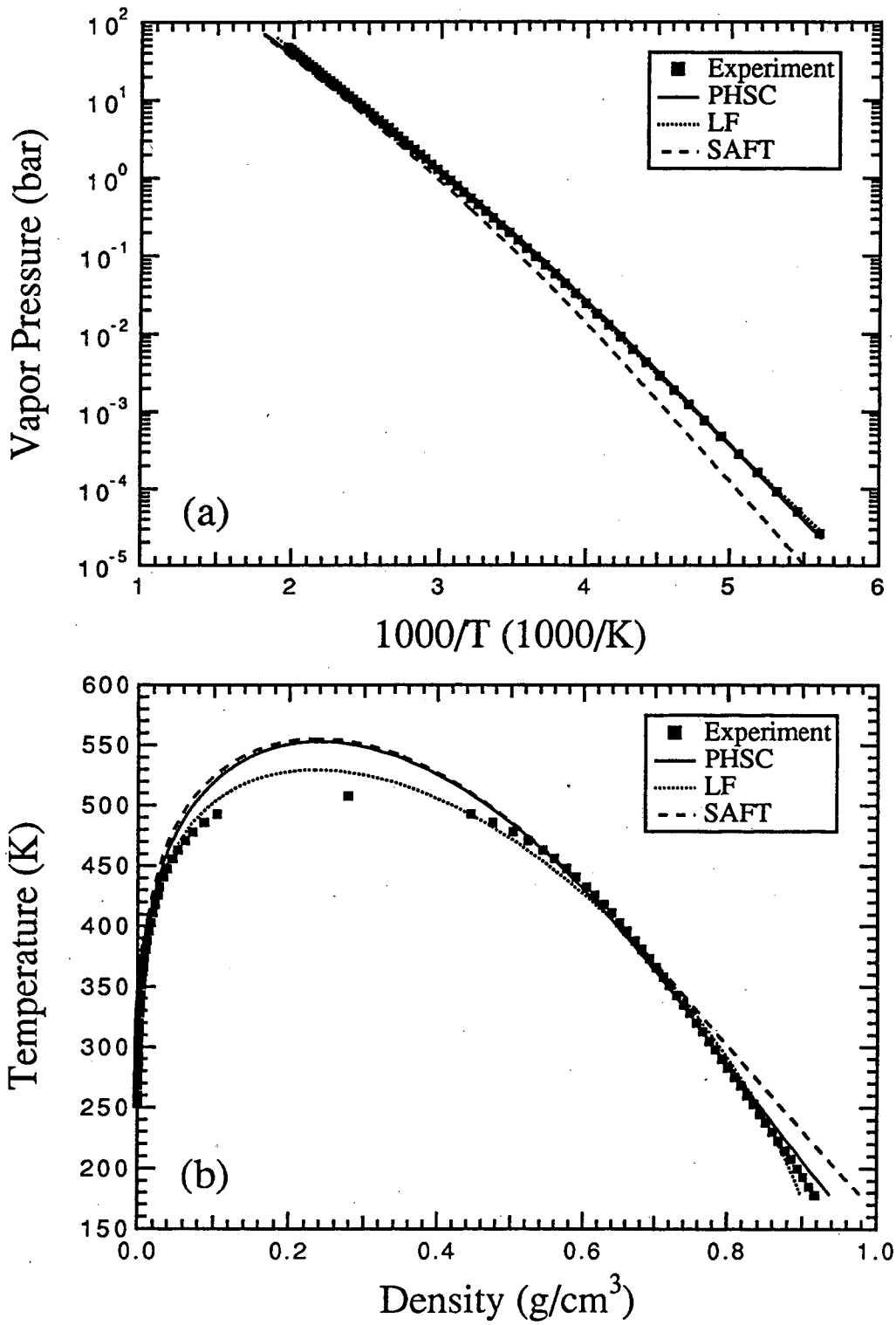

Vapor Pressure (bar)
1000/T (1000/K)
Experiment
PHSC
LF
SAFT
(a)
Temperature (K)
Density (g/cm3)
(b)

Figure 7

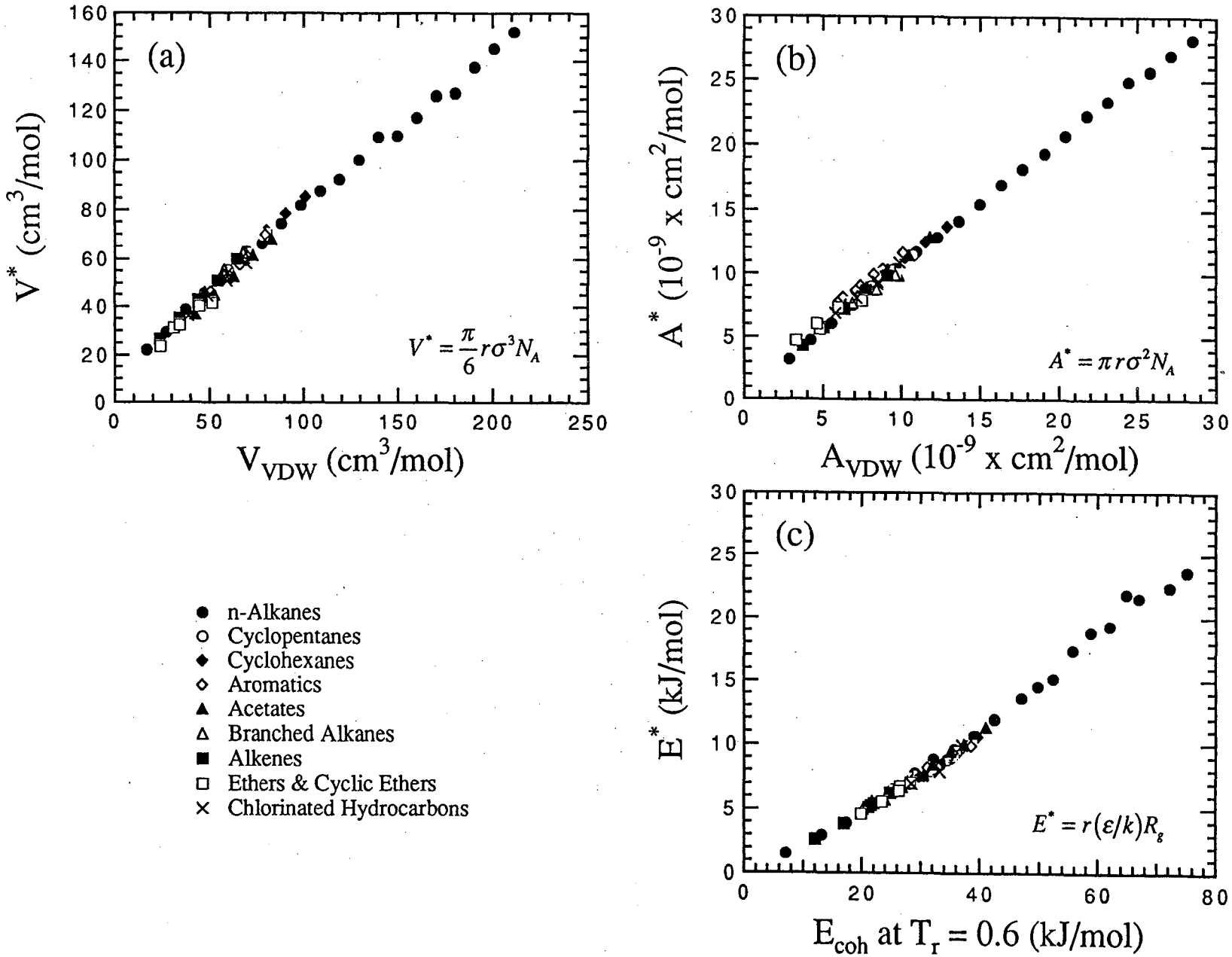

(a)
$V^* = \frac{\pi}{6} r\sigma^3 N_A$
V^* (cm^3/mol)
V_{VDW} (cm^3/mol)
(b)
$A^* = \pi r\sigma^2 N_A$
A^* (10^{-9} x cm^2/mol)
A_{VDW} (10^{-9} x cm^2/mol)
(c)
$E^* = r(\varepsilon/k)R_g$
E^* (kJ/mol)
E_{coh} at T_r = 0.6 (kJ/mol)
n-Alkanes
Cyclopentanes
Cyclohexanes
Aromatics
Acetates
Branched Alkanes
Alkenes
Ethers & Cyclic Ethers
Chlorinated Hydrocarbons

Figure 8

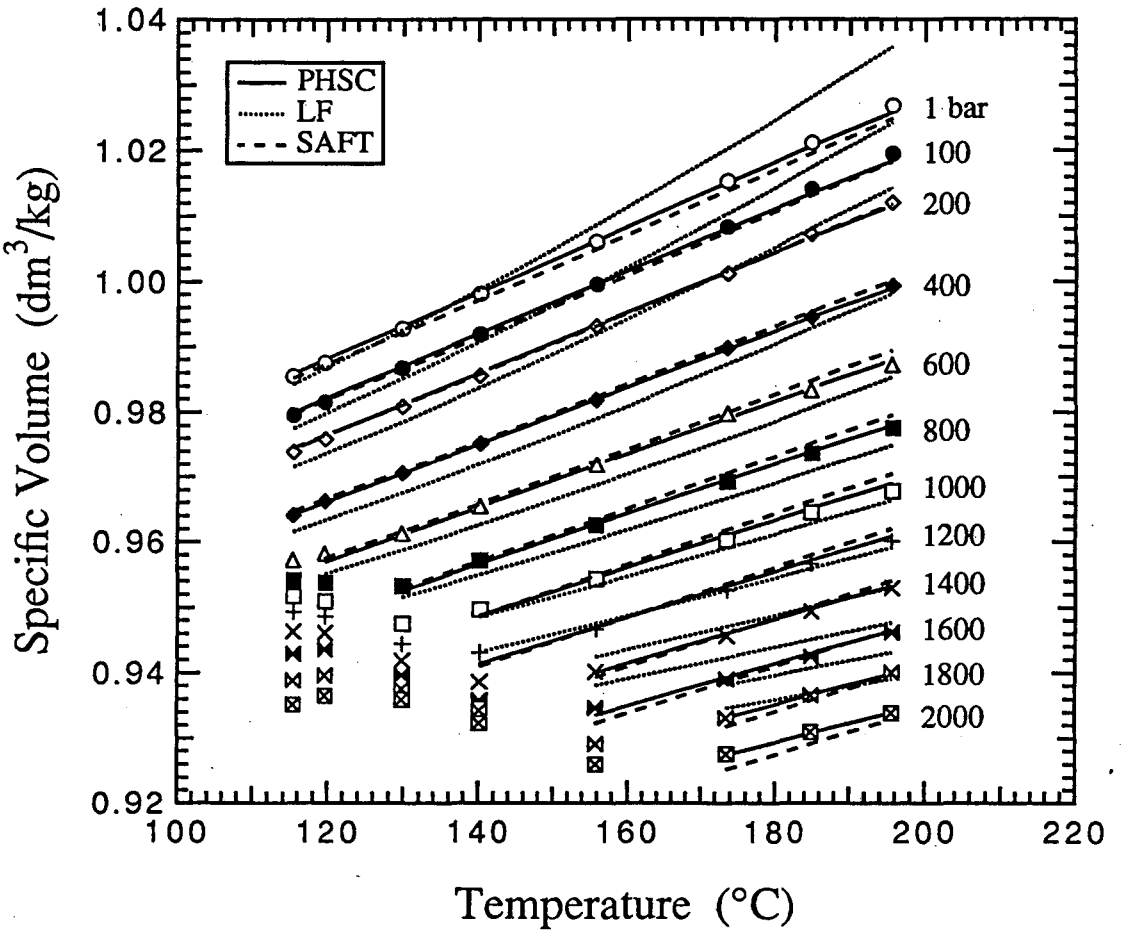

PHSC
LF
SAFT
1 bar
100
200
400
600
800
1000
1200
1400
1600
1800
2000
Specific Volume (dm^3/kg)
Temperature (°C)
1.04
1.02
1.00
0.98
0.96
0.94
0.92
100
120
140
160
180
200
220

Figure 9

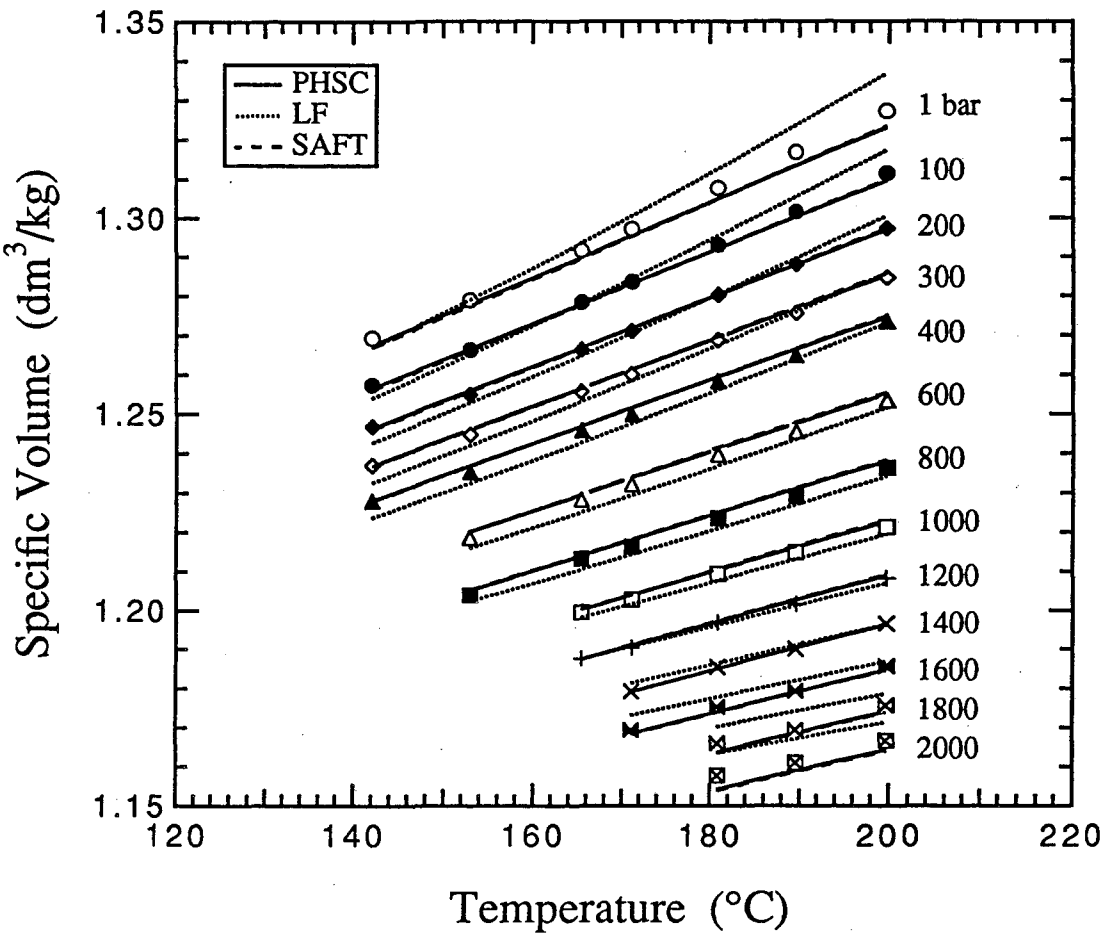

PHSC
LF
SAFT
1 bar
100
200
300
400
600
800
1000
1200
1400
1600
1800
2000
1.35
1.30
1.25
1.20
1.15
120
140
160
180
200
220
Specific Volume (dm^3/kg)
Temperature (°C)

Figure 10

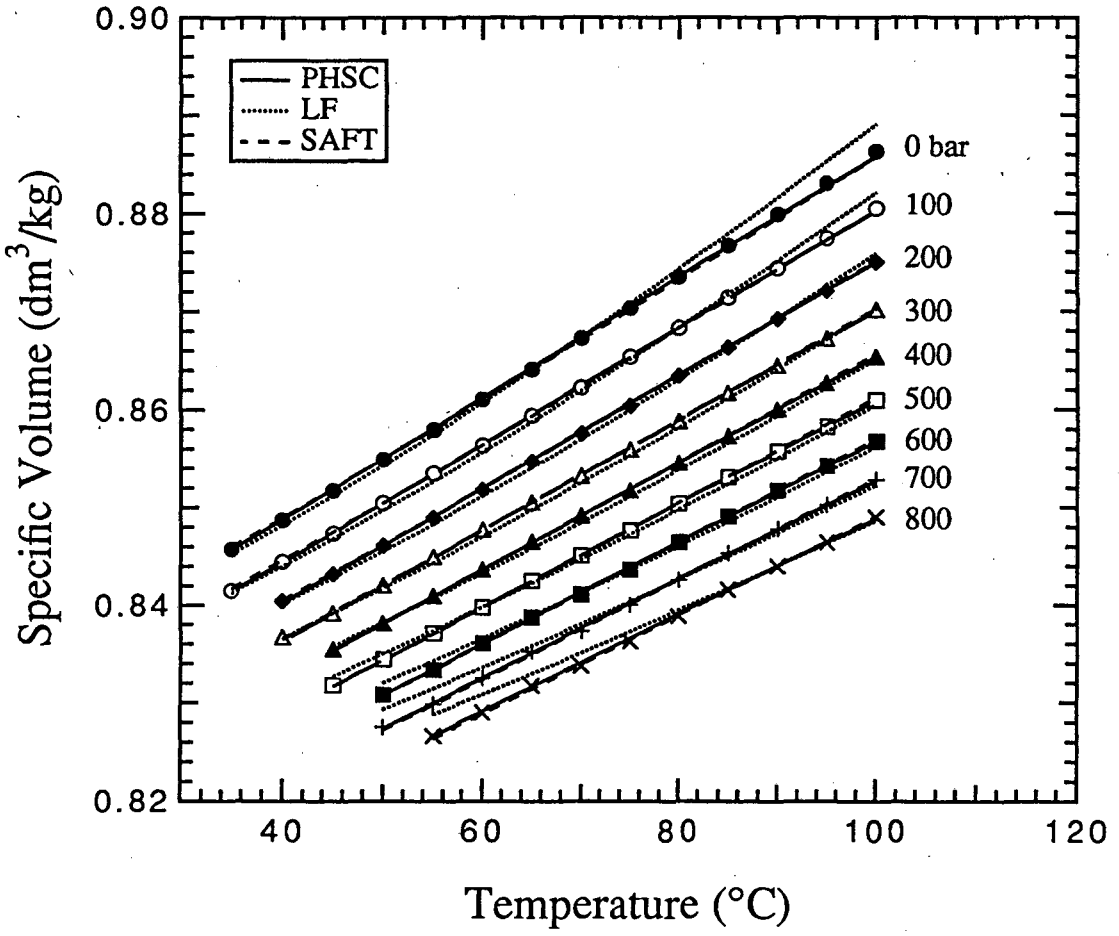
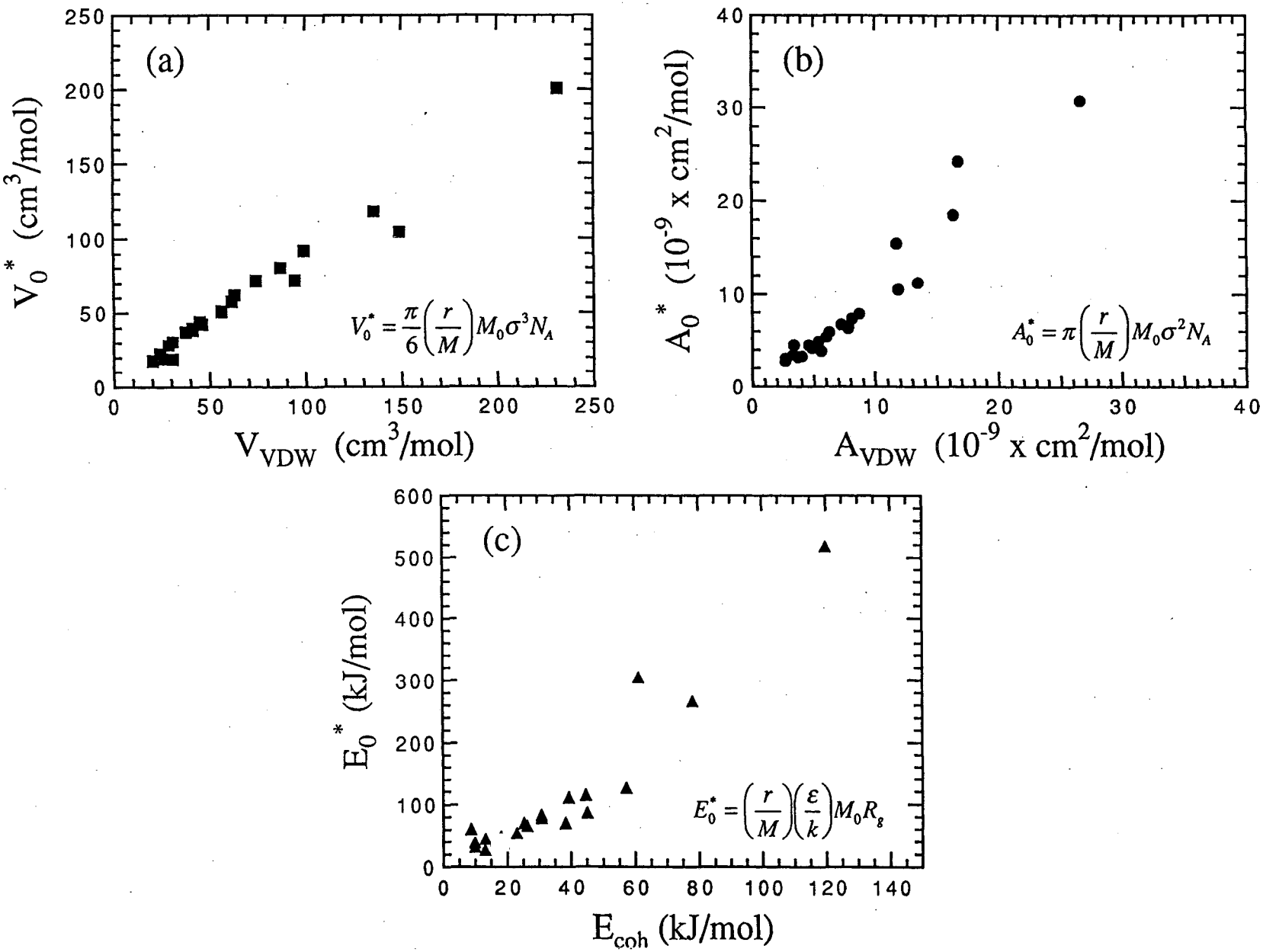

PHSC
LF
SAFT
0 bar
100
200
300
400
500
600
700
800
0.90
0.88
0.86
0.84
0.82
40
60
80
100
120
Specific Volume (dm^3/kg)
Temperature (°C)

Figure 11


(a)
$V_0^* = \frac{\pi}{6}\left(\frac{r}{M}\right)M_0\sigma^3 N_A$
V_0^* (cm^3/mol)
V_{VDW} (cm^3/mol)
(b)
$A_0^* = \pi\left(\frac{r}{M}\right)M_0\sigma^2 N_A$
A_0^* (10^{-9} x cm^2/mol)
A_{VDW} (10^{-9} x cm^2/mol)
(c)
$E_0^* = \left(\frac{r}{M}\right)\left(\frac{\varepsilon}{k}\right)M_0 R_g$
E_0^* (kJ/mol)
E_{coh} (kJ/mol)

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