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A New Equation of State for Square-Well Molecules[1]

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This paper presents a new equation of state for the square-well fluid based on perturbation theory. This equation has the exact second virial coefficient behavior, converges to the correct mean-field behavior at high densities, and accurately interpolates between the two limits. Monte Carlo simulations were performed to evaluate the limiting behavior of the theory in the dilute-gas regime. Comparison of the theory with the simulation results shows excellent agreement between the equation-of-state predictions and the data.

KEY WORDS: equation of state; molecular simulation; perturbation theory; second virial coefficient; square-well molecules.

1. INTRODUCTION

There are two very different regimes in equation-of-state behavior. One is the low-density region where the virial equation provides the exact limiting behavior. In this region, the energies are Boltzmann-weighted and the thermodynamic properties (compressibility factor, Helmholtz free energy, and internal energy) depend exponentially on inverse temperature. The other regime is at liquid-like densities. At these conditions, the behavior approaches mean-field behavior and the thermodynamic properties can be calculated very accurately by perturbation theory.

In this paper, we present a relatively simple, closed-form equation of state that represents the properties of square-well spherical molecules accurately. This new equation reduces to the exact second virial coefficient at low densities, it gives nearly exact mean-field behavior at high densities and interpolates between these two limits with remarkable accuracy.

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2. EQUATIONS OF STATE FOR THE ATTRACTIVE TERM

The square-well potential, despite its unrealistic discontinuities, has been investigated extensively due to its simplicity and due to the fact that it captures the essential characteristics of a fluid. A great amount of computer simulation work [1–3] for systems whose molecules interact via the square-well potential has provided a basis for comparison and testing of the various theories that have been developed.

In 1972, Alder et al. [1] performed molecular dynamics simulations to calculate the thermodynamic properties of the square-well fluid (internal energy and pressure) over a large range of temperature and density. They also developed an equation to describe the Helmholtz free energy for the square-well fluid based on the perturbation expansion of the free energy of a fluid of hard spheres with added attractive (square-well) potentials. For this purpose, they derived an equation for square-well molecules by taking the Taylor-series expansion of the reduced excess Helmholtz free energy about the infinite temperature (hard-sphere) limit. They also derived a statistical mechanical expansion equivalent to the Taylor-series expansion, in which the individual terms contain moments of the perturbing potential averaged over hard-sphere distribution functions. Corresponding coefficients in the two expansions provide separate but identical methods for the calculation of the coefficients in the free energy expansion. Alder et al. [1] evaluated the first four terms of the perturbation expansion as a function of density by fitting the expressions to their molecular dynamic simulation results. The resulting expression has the form

$$\begin{aligned}\frac{A^{\text{att}}}{NkT} &= \frac{\varepsilon}{kT}A_1 + \left(\frac{\varepsilon}{kT}\right)^2 A_2 + \left(\frac{\varepsilon}{kT}\right)^3 A_3 + \left(\frac{\varepsilon}{kT}\right)^4 A_4 \\ &= \sum_{n=1}^{4} \sum_{m=0}^{9} A_{nm}\tilde{\rho}^m \left(\frac{\varepsilon}{kT}\right)^n \qquad (1)\end{aligned}$$

where A^{att} is the attractive contribution to the Helmholtz free energy, ε is the depth of the square-well potential, $\tilde{\rho} = \rho\sigma^3/\sqrt{2}$ (σ is the molecular diameter and $\rho = N/V$, N is the number of molecules, and V is the volume), k is Boltzmann's constant, T is the temperature, A_1, A_2, A_3, and A_4 are the first-, second-, third-, and fourth-order perturbation terms, respectively, and are functions only of density, and A_{nm} are 27 universal constants in the density polynomials of A_1, A_2, A_3, and A_4 (A_{nm} were evaluated by fitting molecular dynamics simulations [1]). This expression is in excellent agreement with the simulations (at last in the range of the fit of the simulation data) and has been used extensively by many researchers as a basis for testing new models.

There are two disadvantages associated with Eq. (1). First, it contains three zeroth-order elements, that is, three A_{n0} terms ($A_{20} = -0.12495816 \times 10^{-3}$, $A_{30} = -0.51235572 \times 10^{-4}$, $A_{40} = +0.25364174 \times 10^{-2}$). These nonzero, zeroth-order elements are artifacts of the approximate fitting routine used and they have no effect on the pressure. Nevertheless, their finite values are unrealistic, since they result in a nonzero Helmholtz free energy at the zero-density limit. Second, the second virial coefficient calculated from Eq. (1), although quite accurate, is not exact. The exact second virial coefficient for the square-well potential is known, and given by [4]

$$B = \frac{2\pi\sigma^3}{3} - \frac{2\pi\sigma^3}{3}(R^3 - 1)(e^{\varepsilon/kT} - 1) \tag{2}$$

where B is the second virial coefficient and $R - 1$ is the range of the square-well attraction (R is taken here to be 1.5, as also is the case with the simulation data of Alder et al. [1] and, therefore, in Eq. (1)). A series expansion of the exponential in the second (attractive) term of Eq. (2) leads to

$$B^{\text{att}} = -\frac{2\pi\sigma^3}{3}(R^3 - 1) \times \left[\frac{\varepsilon}{kT} + 0.5\left(\frac{\varepsilon}{kT}\right)^2 + 0.1667\left(\frac{\varepsilon}{kT}\right)^3 + 0.04167\left(\frac{\varepsilon}{kT}\right)^4 + \cdots\right] \tag{3}$$

The second virial coefficient can be evaluated from Alder's expression [1] by taking the density derivative of Eq. (1) at the limit of zero density. This procedure results in

$$B^{\text{att}} = -\frac{2\pi\sigma^3}{3}(R^3 - 1) \times \left[\frac{\varepsilon}{kT} + 0.4693\left(\frac{\varepsilon}{kT}\right)^2 + 0.1687\left(\frac{\varepsilon}{kT}\right)^3 + 0.07355\left(\frac{\varepsilon}{kT}\right)^4\right] \tag{4}$$

A comparison of Eqs. (3) and (4) shows that Alder's [1] expression gives the exact coefficient for the first-order term; however, for the subsequent terms this is not the case. There is a −6.1% error in the second-order coefficient, a 1.2% error in the third-order coefficient, and a 76.5% error in the fourth-order coefficient, while the higher-order terms are ignored completely. Of the above errors, the most essential for the calculated second virial coefficient is that for the second-order coefficient (0.4693, as opposed to the exact value of 0.5). This error occurs because of the approximate way of fitting the perturbation terms [1], which ignored the correct limiting behavior. In particular, the error in the second-order coefficient in Alder's [1] expansion is due to the fact that the constant A_{21} is not exactly one-half the value of A_{11} as it should be but, rather, $\sim 0.47 A_{11}$. This also is the reason for the errors in the third- and fourth-order coefficients. These errors result in a small but significant discrepancy of Eq. (4), especially at low temperatures. [At high temperatures the first-order term dominates and Eq. (4) becomes very accurate.]

Here we propose a new way of normalizing the Boltzmann factors [5], which uses Alder's [1] first- and second-order perturbation terms to describe the dilute-gas region and the mean-field behavior at high densities and to interpolate between these two limiting behaviors. This expression has the form [5]

$$\frac{U}{N\varepsilon} = U_1 \exp\left(\frac{U_2}{U_1}\frac{\varepsilon}{kT}\right) \tag{5}$$

where U_1 and U_2 are the first- and second-order perturbation terms for the internal energy. The expression for the excess (attractive) Helmholtz free energy can be obtained by integrating the expression for U with respect to inverse temperature. This process yields

$$\frac{A^{\mathrm{att}}}{NkT} = U_1 \frac{U_1}{U_2}\left[\exp\left(\frac{U_2}{U_1}\frac{\varepsilon}{kT}\right) - 1\right] \tag{6}$$

A series expansion of Eq. (6) gives

$$\frac{A^{\mathrm{att}}}{NkT} = U_1\left[\frac{\varepsilon}{kT} + \frac{U_2}{U_1}\left(\frac{\varepsilon}{kT}\right)^2 + \left(\frac{U_2}{U_1}\right)^2\left(\frac{\varepsilon}{kT}\right)^3 + \left(\frac{U_2}{U_1}\right)^3\left(\frac{\varepsilon}{kT}\right)^4 + \cdots\right] \tag{7}$$

Equation (6) gives the exact second virial coefficient if U_2/U_1 is unity at the zero density limit. The use of Eqs. (6) and (7) requires expressions for U_1 and U_2 as functions of density. While we could use the polynomials given by Alder et al. [1], the equation of state is much simpler if the ratio U_2/U_1 is written as a single function of density rather than as a ratio of two polynomials. Therefore, we write the ratio U_2/U_1 as a polynomial of the form

$$\frac{U_2}{U_1} = 1 + \sum_k C_k \eta^k \tag{8}$$

Table I. Constants in the Polynomial Functions $U_1(\eta)$ and $U_2/U_1(\eta)$

	$k=$						
	1	2	3	4	5	6	7
D_k	−9.50005	−13.2655	−3.08360	20.2318	30.5450	10.3126	0.0
C_k	−5.41651	8.41582	6.67298	−19.3900	2.04454	−9.92956	11.9460

where η is the reduced density ($\eta = \pi\rho\sigma^3/6$). The expression for U_1 is given by Alder et al. [1], and in terms of a polynomial in η it has the form

$$U_1 = \sum_{k=1}^{6} D_k \eta^k \tag{9}$$

To evaluate the coefficients C_k, we fit Eq. (6) to Alder and co-workers' [1] expression for the Helmholtz free energy [Eq. (7)]. We used the original U_1 expression [Eq. (9)] and Eq. (8) for the ratio U_2/U_1. The resulting C_k coefficients are given in Table I, together with the D_k coefficients for U_1 (both quantities are given as polynomials of η). Equation (5), and therefore Eq. (6), has the exact second virial coefficient behavior. Table II presents the first four coefficients in the second virial coefficient expression for Eq. (6) and Alder's fourth-order perturbation expansion; the exact values for the square-well potential also are included for comparison.

Figure 1 shows a plot of the higher-order perturbation terms, A_2, A_3, and A_4, as functions of the reduced density, η. The symbols represent molecular simulation data [1]; error bars for some data points also are shown. The dashed lines represent calculations from Alder's expression, while the solid lines represent the new expressions for these perturbation terms. It is seen that the predictions of the proposed model for A_2, A_3, and A_4 are close to Alder's calculations and lie nearly within the error bars of the simulation data. However, it is important to note that at moderate

Table II. First Four Constants in the Second Virial Coefficient Expansion

Constant	Exact (SW)	Alder et al. [1]	Our work
1st	1.0	1.0	1.0
2nd	0.5	0.4693	0.5
3rd	0.1667	0.1687*	0.1667
4th	0.04167	0.07355	0.04167

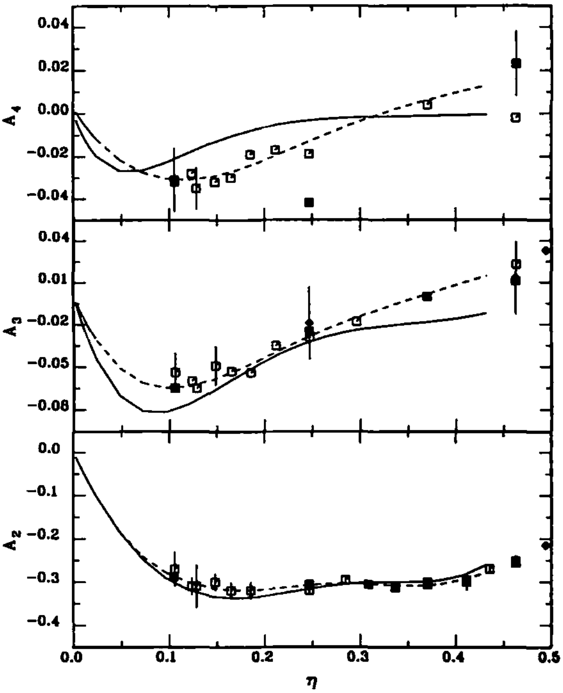

Fig. 1. Plot of the second-, third-, and fourth-order perturbation terms calculated with Alder's expressions (dashed lines) and the expressions from the proposed model [Eq. (7); solid lines]. The filled symbols correspond to hard-sphere fluctuation averages (squares, 108 molecules; diamonds, 500 molecules), and the open squares correspond to extrapolation of square-well internal energy data (108 molecules).

and high densities, the higher-order terms are negligible in comparison to the first-order term; therefore, the slight deviation of our model with Alder and co-workers' [1] expression does not introduce any observable error at these densities. At low densities, our model [Eq. (5)] is more accurate than Alder et al.'s [1] expansion, since it reduces to the exact second virial coefficient limit.

In Fig. 2, we plot the ratio U/U_1 versus η using Alder's [1] perturbation expansion and the model proposed in this paper [Eq. (5)]. The filled squares on the ordinate represent the exact zero-density limiting behavior (Boltzmann weighted energies). The two models are nearly identical, except at the dilute-gas region. In these low densities, our equation reduces to the correct second virial coefficient limit, whereas Alder's model has an

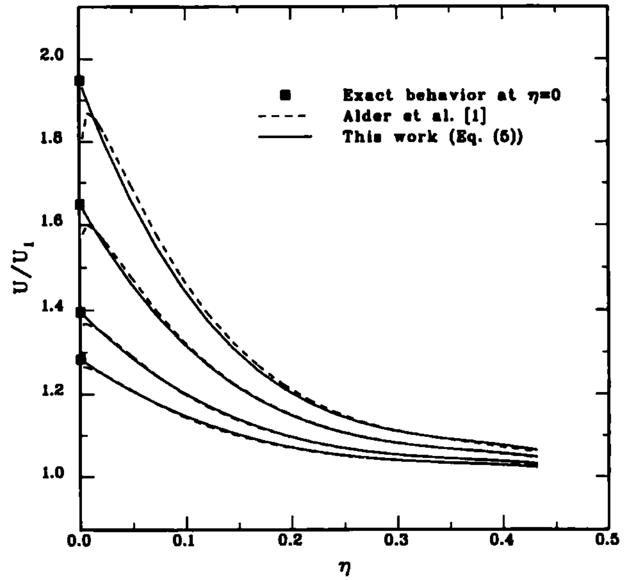

Fig. 2. Plot of the ratio of internal energy over the mean-field value (U_I) as a function of the reduced density for reduced temperatures $kT/\varepsilon = 1.5$, 2.0, 3.0, and 4.0. Dashed lines correspond to Alder et al.'s [1] expansion; solid lines correspond to the proposed model [Eq. (5)], and the filled squares on the ordinate correspond to the exact zero-density limiting behavior.

erroneous behavior (the intercept of the solid lines in Fig. 2 correspond to the second virial coefficients). In addition, our equation converges to mean-field behavior as density increases at the correct rate, as shown in Fig. 2.

3. COMPARISON WITH SIMULATIONS

A large number of simulations for the square-well fluid can be found in the literature; however, we were specifically interested in investigating the behavior of the model proposed in this paper compared with Alder et al.'s expression [1] in the dilute-gas region, where, to our knowledge, no simulation data exist. Therefore, we performed NVT (canonical ensemble) Monte Carlo simulations of square-well spherical molecules, at number densities $\rho\sigma^3 = 0.005$, 0.075, 0.010, 0.020, and 0.030. For each value of the density, temperature values $kT/\varepsilon = 1.3$, 1.5, 1.75, 2.0, 2.5, and 3.0 were studied.

The simulation cell was a cube with size 30 times the molecular diameter (this was found to be a sufficiently large size, so that the results become independent of the size of the cell). The number of molecules was adjusted to achieve the desired density, and periodic boundary conditions were employed in all three dimensions. Each simulation consisted of three phases: initial configuration, equilibration, and simulation (averaging) [6]. At each value of the number density, the initial configuration at the lowest temperature ($kT/\varepsilon = 1.3$) was generated by random insertion of the molecules, so that a configuration free of overlaps was produced. For the higher temperatures (of the same density), the initial configurations were taken from the final configuration of the system at the immediately lower temperature. Once the initial configuration was generated, the system was further equilibrated using the Metropolis algorithm [7], to ensure that the average properties of the system are independent of the initial configuration.

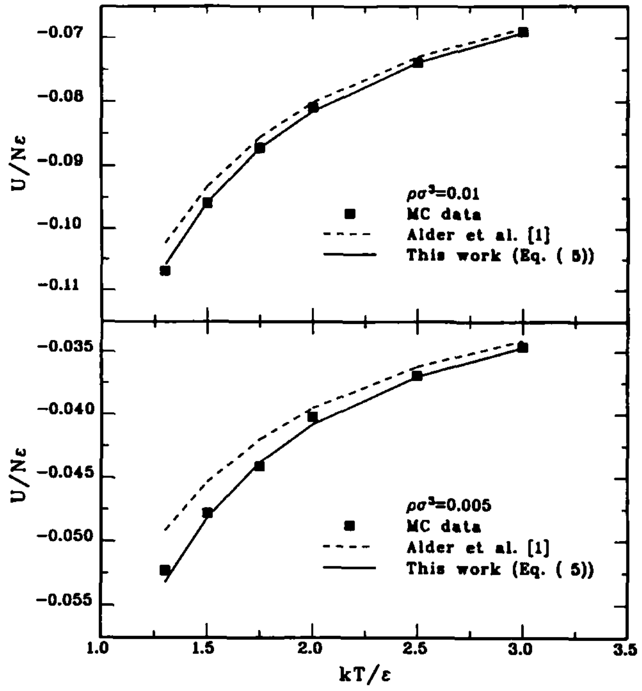

Fig. 3. Comparison of the internal energy predicted by Alder et al.'s perturbation expansion [1] (dashed lines) and by the proposed closed-form expression [Eq. (5); solid lines], at number densities $\rho\sigma^3 = 0.005$ and 0.01. Monte Carlo simulation data (filled squares) are also included.

Two million equilibration steps were used for the low temperature, and 1 million steps at the higher temperatures. Finally, the simulation (averaging) part consisted of 2 million attempted moves after each system had equilibrated.

The simulation results, as well as predictions with the theories discussed in this paper, are illustrated in Fig. 3, where a plot of $U/N\varepsilon$ versus kT/ε is presented. Monte Carlo data and equation-of-state calculations are plotted for two densities, $\rho\sigma^3 = 0.005$ and 0.01. The Alder et al. [1] fourth-order perturbation expansion is not as accurate as one would like, especially at low temperatures, where errors are of the order of 6–7%. However, the equation proposed here is in excellent agreement with the simulations over the entire temperature range.

4. CONCLUSIONS

In this paper, the thermodynamic properties of square-well spherical molecules are investigated using perturbation theory. The performance of the Alder et al. fourth-order perturbation expansion is evaluated. This equation is very accurate, except at the second virial coefficient limit, where there are deviations between the model and the exact behavior for the square-well fluid.

A new model is proposed to normalize the low-density Boltzmann-weighted behavior with increasing density. This approach involves the first two terms of perturbation theory and results in a simple, closed-form equation of state for the square-well fluid. The advantage of this new equation is that it has the exact second virial coefficient behavior, and it converges to the mean-field behavior at the correct rate. We performed Monte Carlo simulations at the dilute-gas region to evaluate the limiting behavior of our new model and compare it with the other methods. We found that the equation proposed in this paper is in excellent agreement with the data over the entire temperature range.

This new model can be extended to chain molecules easily, using the method of the density-dependent shape parameters for the repulsive and the attractive terms, as described by Bokis et al. [8]. The resulting chain equation of state is expected to be in very good agreement with computer simulation data for square-well chain molecules. In addition, we are planning to extend this new model to mixtures of square-well molecules of different sizes and/or interaction energies. In doing so, we will use mixing rules from statistical mechanics, which will retain the quadratic composition dependence of the mixture second virial coefficient and, at the same time, give accurate liquid-phase calculations.

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