PHYSICAL REVIEW E **67**, 066112 (2003)

Generalized van der Waals theory for the thermodynamic properties of square-well fluids

J. Largo and J. R. Solana*
Departamento de Física Aplicada, Universidad de Cantabria, 39005 Santander, Spain

(Received 27 January 2003; published 20 June 2003)

A theory previously developed for the coordination number of square-well fluids is used within the context of a generalized van der Waals theory to obtain the compressibility factor and the internal energy of these fluids. Results are compared with computer simulations for several densities, temperatures, and potential widths, which are also reported.

DOI: 10.1103/PhysRevE.67.066112 PACS number(s): 05.10.Ln, 05.70.Ce, 64.10.+h

I. INTRODUCTION

The square-well (SW) potential

$$u(r)=\begin{cases}\infty & \text{if} \quad r<\sigma\\ -\varepsilon & \text{if} \quad \sigma\leqslant r\leqslant\lambda\sigma\\ 0 & \text{if} \quad r>\lambda\sigma,\end{cases} \tag{1}$$

where σ is the diameter of the particles, $-\epsilon$ the potential depth, and $\lambda\sigma$ the range or potential width, has been widely used as a simple model of the potential of real fluids with spherically symmetric interactions. The reason is that it is the simplest potential model to deal with, from a theoretical viewpoint, whereas it is able to reproduce, at least in a qualitative way, most of the properties of fluids having more realistic interactions, including the vapor-liquid equilibria.

One of the most successful theories of liquids is the Barker-Henderson (BH) [1] perturbation theory which is analytical for SW fluids, provided that analytical expressions for the radial distribution function (r.d.f.) [2] and the equation of state [3] of the reference hard-sphere (HS) fluid are available. However, this theory converges slowly for short-ranged SW potentials [4], so that it is unable to accurately reproduce the thermodynamic properties of SW fluids for low values of λ.

The Barker-Henderson perturbation theory is within the spirit of the van der Waals (vdW) theory, which, in fact, can be derived on the basis of a first-order perturbation theory. van der Waals theories have experienced recently [5,6] a renaissance in the form of the so-called *generic van der Waals* equation of state. For a SW fluid this equation reduces to the form of the classical vdW one at high temperatures.

One of the most promising theories developed for SW fluids, within the scope of the vdW-type theories, is the generalized van der Waals (GvdW) theory [7–13] which derives the thermodynamic properties of SW fluids from the *coordination number* (which is the average number of particles within the potential well). It is defined in the form

$$N_c=4\pi\rho^*\int_1^\lambda g(r^*)r^{*2}dr^*, \tag{2}$$

where $r^*=r/\sigma$, $\rho^*=\rho\sigma^3$ ($\rho=N/V$ is the number density), and $g(r)$ is the r.d.f. of the SW fluid. Note that the basis of the BH perturbation theory for a SW fluid consists in changing in Eq. (2) the r.d.f. of the SW fluid by that of the reference hard-sphere fluid.

To determine the coordination number N_c of SW fluids, a number of theoretical models for N_c have been developed [9,10,13]. However, results from these models are not, in general, accurate enough and, therefore, use is made of parametrizations of the simulation data.

In a recent paper [14], we developed a theoretical model for the coordination number of SW fluids, which provides excellent agreement with simulation data for a wide range of densities, temperatures, and potential widths. In the present paper, we will test the performance of the model, used within the context of the generalized van der Waals theory, to predict the equation of state and the internal energy of SW fluids.

The paper is organized as follows. Section II summarizes the coordination number model. The generalized van der Waals model is summarized in Sec. III. Finally, in Sec. IV, Monte Carlo simulation data for SW fluids with different temperatures, densities, and well widths are presented and then used to compare with the results obtained from the GvdW theory.

II. COORDINATION NUMBER MODEL FOR SQUARE-WELL FLUIDS

Several theoretically based coordination number models for SW fluids have been derived on the basis of the quasichemical approximation. Among these, we will mention here the following expression derived by Heyes [13]:

$$N_c=\frac{z\rho^* e^{\varepsilon/kT}}{\rho^*_{\max}+\rho^*(e^{\varepsilon/kT}-1)}. \tag{3}$$

In this expression, $\rho^*_{\max}$, the maximum reduced density, is set to 1, very close to the value 0.9428 which corresponds to the density of the hard-sphere fluids, in equilibrium with the corresponding solid, whereas z, the lattice coordination number, is determined from the exact low density limit $\rho\rightarrow 0$ of the r.d.f. $g(r)=e^{-\beta u(r)}$ in combination with Eq. (2) and the low density expansion of Eq. (3). This gives

$$z=\tfrac{4}{3}\pi(\lambda^3-1). \tag{4}$$

---

*Author to whom correspondence should be addressed. Electronic address: solanajr@unican.es

With this expression for z, Eq. (3) yields the correct low density behavior of the coordination number, but departs markedly from simulation data at higher densities [14].

Let us return to Eq. (3). In the high temperature limit $T \to \infty$, it reduces to

$$N_c(T=\infty)=\frac{\rho^*}{\rho^*_{\max}} z. \tag{5}$$

In this limit the SW fluid behaves as a hard-sphere fluid, for which the average number N_c^{HS} of particles, up to a reduced distance λ of a given particle, is given in Eq. (2) by taking for the r.d.f. $g(r)$ the r.d.f. corresponding to a hard-sphere fluid $g^{HS}(r)$. Therefore, we can write

$$z(T=\infty)=\frac{\rho^*_{\max}}{\rho^*} N_c^{HS}. \tag{6}$$

We will assume that this expression of z holds at any temperature.

On the other hand, the maximum density a HS system can reach is $\rho^*_{\max}=\sqrt{2}$, which corresponds to the *regular close packed volume* V_0. This is also the upper density limit for SW systems. However, for more irregularly packed systems, other limiting values of the density of the HS system are possible [15–17]. In fact, computer simulations for the hard-sphere fluid have shown [16] that starting from an equilibrium configuration at a given density and compressing the system up to the closest packing, with the system constrained to remain in the same *inherent structure* throughout the process, limiting densities $\rho^*_{\max}$ ranging from about 1.01 to 1.2389 are obtained, depending on the starting equilibrium density. The last of these two values corresponds to the so-called *random close packing density* but other higher density packings, partially ordered, can be attained [17] with a limiting density $\rho^*_{\max}=\sqrt{2}$, corresponding to the regular close packing of a face-centered cubic (fcc) lattice.

A similar situation is expected to arise in SW systems, but for the fact that the close-packing density may depend on the range λ in addition to the density ρ^*. To obtain some insight into this dependency, let us consider the infinity range limit $\lambda \to \infty$ of Eq. (3), with z given by Eq. (6). In this limit, particles move in a uniform background and the potential well has no effect on the coordination number, that is, $N_c(\lambda=\infty)=N_c^{HS}=N$. From Eqs. (3) and (6), this requires that $\rho^*_{\max}=\rho^*$ in this limit. In the opposite limit $\lambda=1$ the width of the potential well is zero, but particles can stick to other particles so that $N_c \neq N_c^{HS}$ except in the limit $T\to\infty$ or in the limit $\rho^*=\rho^*_{\max}$. The last situation requires that $\rho^*_{\max}=\sqrt{2}$ for $\lambda=1$. A simple interpolation of $\rho^*_{\max}$ between the two extreme values of λ yields

$$\rho^*_{\max}=\rho^*+\frac{1}{\lambda^3}(\sqrt{2}-\rho^*). \tag{7}$$

From Eqs. (3) and (6), the expression of the coordination number we proposed [14] is

$$N_c=\frac{\rho^*_{\max} N_c^{HS} e^{\varepsilon/kT}}{\rho^*_{\max}+\rho^*(e^{\varepsilon/kT}-1)}, \tag{8}$$

with $\rho^*_{\max}$ given by Eq. (7). Note that although $\rho^*_{\max}$ is expected to depend on density for the reasons given above, its limiting value ρ^* for $\lambda\to\infty$ cannot be justified only on this basis. The fact is that the lattice model which constitutes the basis for the derivation of many coordination number models, in particular, Eq. (3) and subsequently Eq. (8), is not exact, which yields an incorrect density dependency of the coordination number. This is corrected, to some extent, by the density dependency of $\rho^*_{\max}$, which results from the limiting conditions imposed on N_c.

III. GENERALIZED VAN DER WAALS THEORY

The canonical partition function of a monatomic system is given by

$$Q=\frac{\Lambda^{-3N}}{N!} Q_c, \tag{9}$$

where $\Lambda=(h^2/2\pi mkT)^{1/2}$ is the thermal wavelength and

$$Q_c=\int_V \cdots \int_V e^{-\beta\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N)} d\mathbf{r}_1,\ldots,d\mathbf{r}_N \tag{10}$$

is the configurational partition function with $\beta=1/kT$ and $\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ the potential energy of the system for the particular configuration $(\mathbf{r}_1,\ldots,\mathbf{r}_N)$.

Once the partition function is known, the thermodynamic properties can be obtained by means of well-known relations. Thus, the free energy

$$F=-kT\ln Q, \tag{11}$$

the internal energy

$$U=kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}, \tag{12}$$

and the pressure

$$P=-\left(\frac{\partial F}{\partial V}\right)_{N,T}=kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}. \tag{13}$$

The corresponding excess properties over the ideal gas can be obtained from the configurational partition function in a similar way. In particular, the excess internal energy U^E is

$$U^E=kT^2\left(\frac{\partial \ln Q_c}{\partial T}\right)_{N,V}. \tag{14}$$

If the potential energy of the system is pairwise additive, and the intermolecular potential is spherically symmetrical, the excess energy of the system can be expressed in the form

$$U^E=2\pi N\rho\int_0^\infty u(r)g(r)r^2 dr. \tag{15}$$

Therefore, if the r.d.f. is known, we can obtain the excess energy U^E and, integrating Eq. (14), the configuration partition function in the form

$$\ln Q_c = \ln Q_c(T=\infty) + \int_\infty^T \frac{U^E}{kT^2} dT \tag{16}$$

or

$$F_c = F_c(T=\infty) + \tfrac{1}{2} N\psi, \tag{17}$$

where

$$\begin{aligned}\psi &= -\frac{2kT}{N}\int_\infty^T \frac{U^E}{kT^2} dT \\ &= -4\pi kT\rho \int_\infty^T \frac{1}{kT^2}\left[\int_0^\infty u(r)g(r)r^2 dr\right] dT. \end{aligned}\tag{18}$$

If the intermolecular potential $u(r)$ has a (spherical) hard core, then $F_c(T=\infty) = (V_f/V)^N$, where V_f is the *free volume* of a hard sphere fluid, so that, including the ideal gas contribution to the partition function $\Lambda^{-3N}V^N/N!$ and to the free energy, we finally obtain [8]

$$Q = Q^{HS} e^{-N\psi/2kT} \tag{19}$$

and

$$F = F^{HS} + \tfrac{1}{2} N\psi. \tag{20}$$

From these expressions, the pressure and the internal energy are obtained in the usual way, with the result

$$P = P^{HS} - \frac{1}{2} N\left(\frac{\partial\psi}{\partial V}\right)_{N,T} \tag{21}$$

or

$$Z = Z^{HS} - \frac{1}{2}\frac{V}{kT}\left(\frac{\partial\psi}{\partial V}\right)_{N,T}, \tag{22}$$

and

$$U = \frac{3}{2}NkT + U^E = \frac{3}{2}NkT - \frac{1}{2}NkT^2\left[\frac{\partial(\psi/kT)}{\partial T}\right]_{N,V}. \tag{23}$$

For the particular case of a fluid of particles interacting by means of a SW potential of the form (1),

$$U^E = -2\pi N\rho\varepsilon \int_\sigma^{\lambda\sigma} g(r) r^2 dr = -\frac{N}{2}\varepsilon N_c \tag{24}$$

and

$$\psi = kT\varepsilon \int_\infty^T \frac{N_c}{kT^2} dT. \tag{25}$$

IV. RESULTS AND DISCUSSION

We have performed Monte Carlo NVT simulations of the compressibility factor and the internal energy of SW fluids for wide ranges of densities and temperatures and several potential widths. The system consisted of 512 particles, initially placed in a regular configuration in a cubic volume with periodic boundary conditions, with fixed temperature and density. The system was allowed to equilibrate for 2×10^4 cycles, each of them consisting of an attempted move per particle, with the first 4×10^3 cycles performed at a very high temperature and the remaining at the desired temperature. After equilibration, the equation of state and the internal energy were determined from measurements performed over the next 5×10^4 cycles. Results are reported in a separate electronic file [18]. They are consistent with those from other authors for the cases where the latter are available.

These data will be used here to compare the theoretical predictions for the compressibility factor Z and the internal energy U from Eqs. (22) and (24), respectively, together with Eqs. (7), (8), and (25). For N_c^{HS} we have used an analytical expression derived by Chang and Sandler [2] on the basis of the Percus-Yevick integral equation theory. This gives rise to analytical expressions of Z and U. For the equation of state of the HS fluid, we have used the well-known Carnahan-Starling equation [3]

$$Z^{HS} = \frac{P^{HS}V}{NkT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \tag{26}$$

where $\eta = (\pi/6)\rho^*$ is the packing fraction.

Results are shown, for several values of λ, in Fig. 1 for the equation of state, and in Fig. 2 for the excess internal energy. From these figures, we can conclude that the theoretical predictions for both properties are very accurate, except perhaps for very short ranges and very low temperatures. It is to be noted that all temperatures studied are supercritical. Probably for subcritical temperatures the accuracy of the theory would be worse.

In the same figures we have included the results obtained using expression (3) for N_c, with z given by Eq. (4), instead of our expression (8). It is clear from these figures that our expression provides a remarkable improvement over Eq. (3), especially for low values of λ and high densities.

We could think that using a more accurate expression for the r.d.f. of the HS fluid than that obtained from the Percus-Yevick theory, such as those derived in Refs. [19–21], to obtain N_c^{HS}, would improve the results. However, we have found that this results in an increased complexity in the calculations, without any significant difference in the results. Therefore, expression (8) itself needs to be improved, especially for subcritical temperatures, in order to obtain more accurate results for the thermodynamic properties.

It is to be noted that expression (8) is not appropriate for the limiting case of sticky hard spheres. Even if the Percus-Yevick theory, used to determine N_c^{HS}, is not accurate enough at short distances and high densities. Certainly, Eq. (8) yields the right low density behavior for sticky hard spheres, as it leads to the right second virial coefficient when

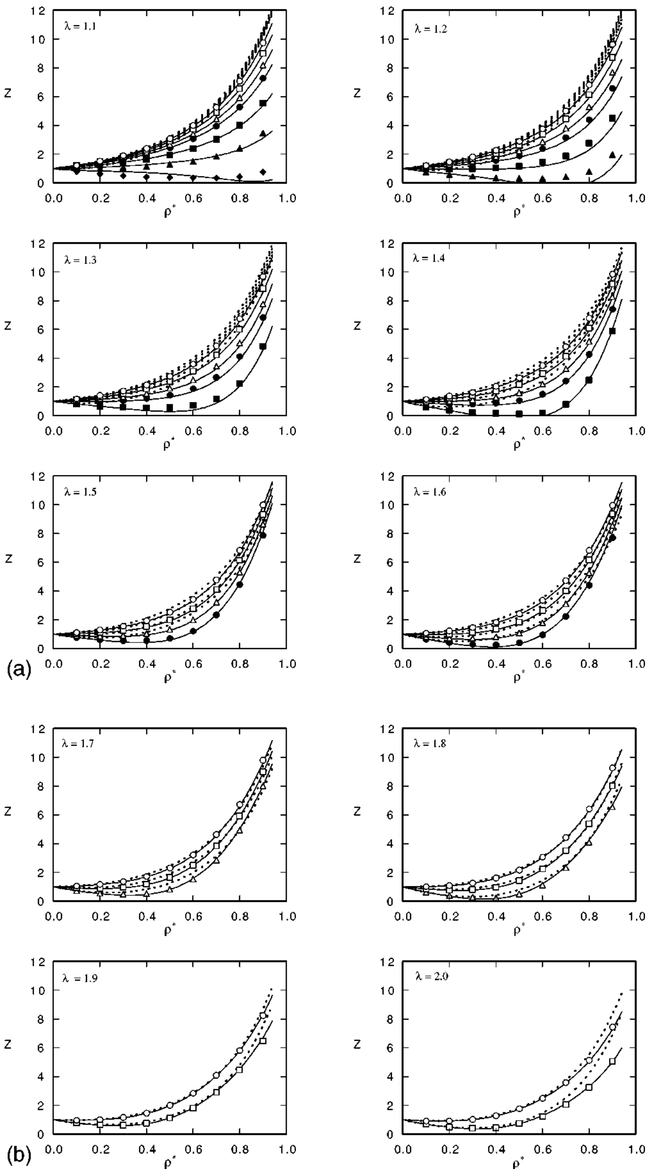

FIG. 1. Compressibility factor $Z=PV/NkT$ for square-well fluids as a function of the reduced density $\rho^*=\rho\sigma^3$ and reduced temperature $T^*=kT/\epsilon$, for different values of λ. Curves: Eq. (22) together with Eq. (25), with N_c given by Eq. (8) (continuous curves) or N_c given by Eq. (3) (dotted curves). Points: simulation data from Ref. [18]. Filled symbols: $T^*=0.5$ (diamonds), $T^*=0.7$ (triangles), $T^*=1.0$ (squares), and $T^*=1.5$ (circles). Open symbols: $T^*=2.0$ (triangles), $T^*=3.0$ (squares), and $T^*=5.0$ (circles).

used in combination with Eq. (22). However, a detailed analysis of the performance of Eq. (8) for sticky hard spheres at moderate to high densities is beyond the scope of the present paper.

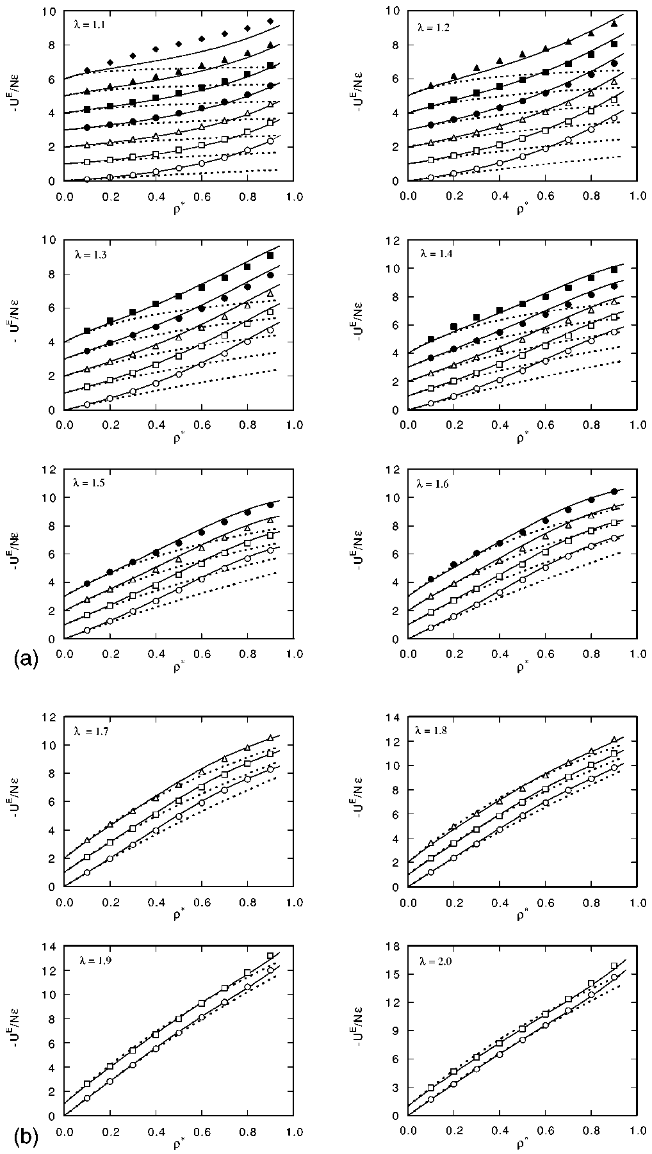

FIG. 2. Excess internal energy $-U^E/N\epsilon$ for square-well fluids as a function of the reduced density $\rho^*=\rho\sigma^3$ and reduced temperature $T^*=kT/\epsilon$ for different values of λ. Curves: Eq. (24), with N_c given by Eq. (8) (continuous curves) or N_c given by Eq. (3) (dotted curves). Points have the same meaning as in Fig. 1. For clarity, the curves for each temperature, and the simulation data, have been shifted upwards by an amount of 1 with respect to that immediately below.

ACKNOWLEDGMENT

We are grateful to the Spanish "Dirección General de Investigación" (DGI) for the financial support under Grant No. BFM2000-0014.

[1] J.A. Barker and D. Henderson, J. Chem. Phys. **47**, 2856 (1967).

[2] J. Chang and S.I. Sandler, Mol. Phys. **81**, 735 (1994).

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

[4] J. Largo and J. R. Solana (unpublished).

[5] B.C. Eu and K. Rah, Phys. Rev. E **63**, 031203 (2001).

[6] B.C. Eu, J. Chem. Phys. **114**, 10 899 (2001).

[7] J.H. Vera and J.M. Prausnitz, Chem. Eng. J. **3**, 1 (1972).

[8] S.I. Sandler, Fluid Phase Equilib. **19**, 233 (1985).

[9] K.-H. Lee, M. Lombardo, and S.I. Sandler, Fluid Phase Equilib. **21**, 177 (1985).

[10] K.-H. Lee, S.I. Sandler, and N.C. Patel, Fluid Phase Equilib. **25**, 31 (1986).

[11] R.J. Lee and J.C. Chao, Mol. Phys. **65**, 1253 (1988).

[12] M. Guo, W. Wang, and H. Lu, Fluid Phase Equilib. **60**, 37 (1990).

[13] D.M. Heyes, J. Chem. Soc., Faraday Trans. **87**, 3373 (1991).

[14] J. Largo and J.R. Solana, Fluid Phase Equilib. **193**, 277 (2002).

[15] L.V. Woodcock, Ann. N.Y. Acad. Sci. **371**, 274 (1981).

[16] R.J. Speedy, J. Phys.: Condens. Matter **10**, 4185 (1998).

[17] S. Torquato, T.M. Truskett, and P.G. Debenedetti, Phys. Rev. Lett. **84**, 2064 (2000).

[18] See EPAPS Document No. EPAPS E-PLEEE8-67-132306 for the results of our Monte Carlo NVT simulations of the compressibility factor and the internal energy of SW fluids for a range of densities, temperatures, and potential widths. A direct link to this document may be found in the online article's HTML reference section. This document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

[19] Y. Tang and B.C.-Y. Lu, J. Chem. Phys. **103**, 7463 (1995).

[20] S. Bravo Yuste and A. Santos, Phys. Rev. A **43**, 5418 (1991).

[21] S. Bravo Yuste, M. López de Haro, and A. Santos, Phys. Rev. E **53**, 4820 (1996).