



Molecular dynamics simulation of the free-energy expansion of the square-well fluid



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ARTICLE INFO

Available online 29 December 2012

Keywords:

Square-well
Free energy
Molecular dynamics
Short ranges
Critical point

ABSTRACT

The high-temperature expansion of the free energy of a fluid of square wells, SW, is considered. The first four terms in this expansion are calculated for SW systems of variable range $\lambda\sigma$, where σ is the diameter of the spherical hard-core. The properties were calculated via molecular dynamics, MD, for ranges $1 \leq \lambda \leq 2.5$ with special emphasis on the region of shorter ranges: $\lambda = 1.025, 1.050, 1.075, 1.100, 1.125$ and 1.150 . The principal aims are to compare these results with the previous ones obtained using the Monte Carlo, MC, method (Espíndola-Heredia et al. J. Chem. Phys. 130, 024509 (2009)) that showed large statistical noise in the higher-order terms at high densities, and to provide a benchmark to check the theoretical Short-Range Expansion of the free energy of these systems. The results have been corrected to obtain the thermodynamic limit via a change of ensemble algorithm and by simulating systems with 125, 200, 500 and 1000 particles. The MD results are much smoother than the corresponding MC data and their precision allow to determine the behavior of the series for high densities. The simulation results are used to test a theory built to write the free energy for short ranges. The position of the critical point is calculated with this theory for very short ranges.

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1. Introduction

The square-well, SW, potential is one of the simplest fluid models incorporating an attractive force that resembles the dispersion forces in real fluids, this in addition to a spherical hard-core. This interaction is defined by:

$$u(r) = \begin{cases} \infty, & r \leq \sigma, \\ -\epsilon, & \sigma < r \leq \lambda\sigma, \\ 0, & \lambda\sigma < r, \end{cases} \quad (1)$$

where σ is the hard-core diameter of the particle, $\lambda = r/\sigma$ is the reduced range of its potential well, and ϵ is its depth. The simplicity of this SW interaction, together with the flexibility of its phase diagram upon variation of its range, has spurred plentiful studies. Interest in the behavior of short-ranged SW fluids (that is, with $1 \leq \lambda \leq 1.25$) has been renewed in recent years due to their use in the modeling of protein crystallization and colloidal dispersions. Among the works concentrating on short-ranged SW fluids, we may mention the calculation of pair correlation functions [1,2], phase equilibria [3–6], and interfacial properties [7]. Also, a modification of the Monte Carlo method, appropriate to deal with short-ranged potentials, has been introduced

recently [8]. The special case of the approach of the SW fluid to the adhesive hard-sphere, AHS, limit has attracted much attention since the work of Baxter; [9] we point out to the study at very short ranges carried out by Largo et al. [10] The current state of affairs in this matter has been considered by Pini et al. [11].

The free energy is of paramount importance because its knowledge as a function of the appropriate variables permits the calculation of all thermodynamic properties of the homogeneous system, and a practical route to the free energy is the high-temperature, HT, perturbation theory developed for the SW system by Barker and Henderson [13]. Two of the main uses of the SW free-energy are in the very successful statistical associating-fluid theory, SAFT, in its variable range version [14–16], and in the discrete perturbation theory, DPT [17]. In particular, in order to treat soft-core potentials, the latter theory needs knowledge of the first HT terms of the SW fluid for short ranges. After the pioneering work of Barker and Henderson [13] and of Alder et al., [18] who calculated the first two terms in the HT series for SW of $\lambda = 1.5$, the case of several λ 's was considered by Henderson et al. [19] More extensive calculations of the first two terms were carried out by Largo and Solana by the Monte Carlo method [20], which included the cases with $\lambda = 1.1$ and 1.2 . More recently, Espíndola-Heredia and co-workers calculated the first four terms for $1.1 \leq \lambda \leq 3$, also by the Monte Carlo method, and studied the variation of the statistical uncertainties with the size of the system [21]. The results of this work for the shortest ranges, $\lambda \leq 1.2$ had however higher errors and, also, the third- and fourth-order

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terms showed large fluctuations at high densities, both effects probably due to problems with the statistical sampling.

The main purpose of this work is to provide the first few HT perturbation terms of the Helmholtz free energy for SW systems with short ranges: $\lambda = 1.025, 1.050, 1.075, 1.100, 1.125$ and 1.150 . The method is based on molecular dynamics simulations of hard-sphere systems. This information complements previous works, gives more reliable values of the free energy at high densities and allows us to check the accuracy of a theory developed some time ago for short-ranged SW fluids. This theory, named Short-Range Expansion, SRE, gives the perturbation terms as series in powers of $\lambda - 1$. The SRE can be used to obtain, among other properties, the critical points of the SW fluids at short ranges.

This work is arranged as follows: Section 2 incorporates the necessary information about the HT perturbation expansion and the SRE. Then, Section 3 describes briefly the computer simulations performed. Section 4 presents and discusses the main results of the work, and in the last section the principal conclusions are drawn.

2. Theory

2.1. High-temperature expansion of SW free energy

In this study, the main quantity of interest is the Helmholtz free energy of the SW fluid, $A(\rho, T)$, from which all static thermodynamic properties can be derived. We introduce the reduced free energy per particle as

$$a = \frac{A}{Nk_B T}, \tag{2}$$

where N is the number of particles, k_B is the Boltzmann constant, and T is the temperature. The perturbation theory for non-polar gases was originally proposed by Zwanzig [12]. Here we make extensive use of the Barker–Henderson perturbation theory that introduces a high-temperature expansion of the form [13]

$$a = a_{HS}(\rho) + \sum_{n=1}^{\infty} \frac{a_n}{T^{*n}}. \tag{3}$$

Here $a_{HS}(\rho)$ is the free energy of a reference hard-sphere, HS, system, $a_n(\rho)$ are the perturbation coefficients and $T^* = kT/\epsilon$. In these equations $\rho = N\sigma^3/V$ is the reduced particle density over the volume V . The coefficients a_n are calculated as certain averages, specified below, over the HS system [13]. Let the particles of the HS fluid be in a certain configuration, then M is the number of particle pairs in the system such that their center-to-center distance r lays within the well, that is, with $\sigma < r < \sigma\lambda$, then the first four perturbation coefficients are given by [13]

$$\begin{aligned} a_1 &= -\langle M \rangle_0 / N, \\ a_2 &= -\langle (M - \langle M \rangle_0)^2 \rangle_0 / 2N, \\ a_3 &= -\langle (M - \langle M \rangle_0)^3 \rangle_0 / 6N, \end{aligned} \tag{4}$$

and

$$a_4 = \left(\langle (M - \langle M \rangle_0)^4 \rangle_0 - 3 \langle (M - \langle M \rangle_0)^2 \rangle_0^2 \right) / 24N.$$

In these equations the subscript 0 means the averages are calculated in a hard-sphere system. The first two terms of this perturbation series have been calculated for various values of $\lambda \geq 1.2$ by several authors [20]. Recently [21], the first four terms were calculated for $1.2 \leq \lambda \leq 3$ by the Monte Carlo method. In this work we concentrate on two unresolved questions: 1) How is the behavior of the coefficients for short ranges? and 2) How is the behavior of the higher-order terms at densities higher than 0.5?

We are also interested in the compressibility factor, $Z = PV/Nk_B T$, where P is the pressure. This factor is obtained readily from the free energy

$$Z = \rho \left(\frac{\partial a}{\partial \rho} \right)_T \tag{5}$$

and has a high-temperature expansion equivalent to Eq. (3)

$$Z = Z_{HS}(\rho) + \sum_{n=1}^{\infty} \frac{Z_n}{T^{*n}}, \tag{6}$$

where Z_{HS} is the compressibility factor of the HS system and each coefficient Z_n is related to the corresponding a_n by an equation similar to 5.

Here we use for Z_{HS} the very accurate formula due to Kolafa and given by [22].

$$Z_{HS} = \frac{1 + \eta + \eta^2 - \frac{2}{3}(\eta^3 + \eta^4)}{(1 - \eta)^3}, \tag{7}$$

where the packing fraction is $\eta = \pi\rho/6$. This equation is also used below for calculating the correction due to change from the NVT ensemble to the μVT ensemble.

2.2. Short-Range Expansion of the SW free energy

The availability of reliable values of the free-energy coefficients a_1, a_2, \dots , allows to test the Short-Range Expansion, SRE, of the SW fluid free-energy introduced years ago [23]. This theory is an expansion in powers of $\lambda - 1$ of the perturbation coefficient a_i :

$$a_n(\rho, \lambda) = \sum_{m=1}^{\infty} \phi_{nm}(\rho)(\lambda - 1)^m. \tag{8}$$

To the third order in $\lambda - 1$ the functions ϕ_{nm} are expressed by

$$\begin{aligned} \phi_{11} &= f_{11} \\ \phi_{21} &= f_{21} \\ \phi_{31} &= f_{31} \\ \phi_{12} &= f_{11}/2 \\ \phi_{22} &= f_{21}/2 + f_{22} \\ \phi_{32} &= f_{31}/2 + f_{32} \\ \phi_{13} &= f_{11}/6 \\ \phi_{23} &= f_{21}/6 + f_{22} \\ \phi_{33} &= f_{31}/6 + f_{32} + f_{33} \end{aligned} \tag{9}$$

where the coefficients f_{nm} are given by terms containing contact values of the HS background correlation function $y(x) = e^{u_{HS}(x)/k_B T} g_{HS}(x)$ and its various derivatives with respect to x and packing fraction η ; here $x = r/\sigma$, and $u_{HS}(x)$ are the potentials of the HS system, and $g_{HS}(x)$ is the corresponding radial distribution function. One finds [23],

$$\begin{aligned} f_{11} &= -12 \eta y^0 \\ f_{21} &= -12 \eta y^0_x - 6 \eta y^0_{xx} \\ f_{22} &= 18 \eta^2 y^0_{\eta} - 6 \eta y^0_{xx} \\ f_{31} &= -4 \eta y^0_x - 8 \eta y^0_{xx} - 2 \eta y^0_{xxx} \\ f_{32} &= 36 \eta^2 y^0_{\eta} - 18 \eta y^0_{xx} + 18 \eta^2 y^0_{x\eta} - 6 \eta y^0_{xx} \\ f_{33} &= -10 \eta y^0_{xx} - 18 \eta^3 y^0_{\eta\eta} + 18 \eta^2 y^0_{x\eta} - 4 \eta y^0_{xxx}. \end{aligned} \tag{10}$$

In these equations, the superscript “0” means a quantity calculated at $x = 1$ with $y_{\xi} = \partial y / \partial \xi$ and $y_{\xi\xi} = \partial^2 y / \partial \xi^2$ where ξ and ζ are either η or x . The terms y^0, y^0_{η} and $y^0_{\eta\eta}$ are obtained directly from (7), whereas y^0_x, y^0_{xx} and $y^0_{x\eta}$ are obtained to good approximation [24] from the Verlet–Weis algorithm for $g_{HS}(x)$ [25].

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