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Heat capacity of square-well fluids of variable width

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We have obtained by Monte Carlo *NVT* simulations the constant-volume excess heat capacity of square-well fluids for several temperatures, densities and potential widths. Heat capacity is a thermodynamic property much more sensitive to the accuracy of a theory than other thermodynamic quantities, such as the compressibility factor. This is illustrated by comparing the reported simulation data for the heat capacity with the theoretical predictions given by the Barker–Henderson perturbation theory as well as with those given by a non-perturbative theoretical model based on Baxter's solution of the Percus–Yevick integral equation for sticky hard spheres. Both theories give accurate predictions for the equation of state. By contrast, it is found that the Barker–Henderson theory strongly underestimates the excess heat capacity for low to moderate temperatures, whereas a much better agreement between theory and simulation is achieved with the non-perturbative theoretical model, particularly for small well widths, although the accuracy of the latter worsens for high densities and low temperatures, as the well width increases.

1. Introduction

Thermodynamic and structural properties of square-well (SW) fluids have been profusely studied both from theory and from computer simulation [1–38]. From the theoretical side, the first few virial coefficients have been obtained [1, 2, 37] and the radial distribution function has been evaluated from numerical solutions of integral equation theories, such as Percus–Yevick [6–8, 30, 38], Yvon–Born–Green [14], HNC [10], MSA [16, 30], Rogers–Young [28], ORPA [28], and HRT [35]. Simpler analytical approximations have also been proposed [11, 12, 19–22, 34]. The thermodynamic properties have been derived from the theoretical structure functions as well as from perturbation theory [3, 4, 9, 13, 23, 27]. Access to the 'experimental' properties of SW fluids has been made possible via molecular dynamics and Monte Carlo simulations [5, 10, 13, 16–18, 26, 36, 38]. Special attention has been given to the determination of the critical point of SW fluids [6–8, 13, 18, 23, 25, 26, 29, 33–35, 38], both from the theoretical and simulational viewpoints. The main reason for this wide interest lies in the fact that a SW fluid is perhaps the simplest one whose particles have attractive as well as repulsive interactions. In general, theories are easier to apply to SW fluids than to other fluids with more realistic potentials. In addition, the SW potential seems to be particularly sensitive to the performance of a theory. Therefore, this kind of fluid is an excellent testing-ground for many theories of fluids and so the study of SW fluids can be considered as a first step towards our understanding of the properties of fluids with more sophisticated interactions. There is an additional reason explaining the recent revival of interest in SW fluids. The SW potential possesses, besides the diameter of the hard core and the depth of the well, an additional parameter measuring the width of the well. This makes the SW potential with a small width especially suited to model the effective interactions among colloidal particles [16, 28, 30, 31, 38]. In this context, the glass transition [30, 31] and a solid-to-solid isostructural transition [24] have been studied for narrow SW systems.

Despite the extensive number of studies devoted to the SW fluid, relatively little attention has been paid to several thermodynamic properties. This is the case for the heat capacity. To the best of our knowledge, [5, 10] only a few simulation data of this property for SW fluids are available. Theoretical calculations of the same quantity are equally scarce [10]. In the present paper we have carried out Monte Carlo (MC) simulations of the constant-volume excess heat capacity C_V^E of SW fluids for several values of the potential width and, for each of them, for several densities and temperatures. Moreover, in order to clarify the sensitivity of this property with regard to the accuracy of a theory, the simulation data are compared with the results obtained from the Barker–Henderson (BH) [39, 40] perturbation theory and with those derived from the theoretical model

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proposed by Yuste and Santos [22], recently simplified by Acedo and Santos [34].

The paper is organized as follows. In the next section, we summarize the theoretical foundations of the MC procedure used and we describe the simulations performed and the results obtained. In section 3, we present an outline of the above-mentioned theories. Finally, in the last section the theoretical results are compared with simulation data and discussed.

2. Monte Carlo simulations

In an SW fluid, particles interact by means of a potential of the form

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

where λ is the potential width in units of the particle diameter σ and ϵ is the potential depth.

Constant-volume averaged excess heat capacity per particle in an SW fluid can be expressed in the form [5]:

$$\frac{C_V^E}{Nk} = \frac{1}{T^{*2}} \frac{\langle (M - \langle M \rangle)^2 \rangle}{N}, \tag{2}$$

where N is the number of particles, k is the Boltzmann constant, $T^* = kT/\epsilon$ is the reduced temperature and M is the number of pairs of interacting particles, that is, the number of pairs of particles whose centres lie separated by a reduced distance $r^* = r/\sigma \le \lambda$.

The averages involved in equation (2) can be calculated by MC simulations in the NVT ensemble. Therefore, we have proceeded to calculate by means of MC NVT the constant-volume averaged excess heat capacity per particle for SW fluids with well widths λ ranging from 1.1 to 1.5. For each value of λ, C_V^E has been evaluated for several densities along isotherms. To this end, a system consisting of 512 particles placed in a cubic box with periodic boundary conditions was used. Particles were initially placed in a regular configuration and then the system was allowed to equilibrate for 2×10^4 cycles, each of them consisting of an attempted move per particle, the first 10^4 cycles at a very high temperature, and the remaining ones at the desired temperature. The calculation of C_V^E was performed by averaging over the next 5×10^5 cycles, performing partial averages every 10^4 cycles with the aim of estimating the statistical error from the standard deviation. The use of such a huge number of cycles in the calculations was motivated by the need to ensure that the values of C_V^E converged to a constant value, apart from statistical fluctuations. In fact, we realized that for low values of the number of cycles used in the calculations, the values of C_V^E increase with the number of cycles used.

The results are shown in table 1. We have considered four isotherms for $\lambda = 1.1, 1.2, 1.3$ and three isotherms for $\lambda = 1.5$. The lowest temperature in each case is larger than the estimated critical temperature [13, 18, 23, 25, 26, 33–35]: $T_c^* \simeq 0.5, 0.6, 0.8, 1.2$ for $\lambda = 1.1, 1.2, 1.3, 1.5$, respectively.

Table 1. MC simulation data for C_V^E/Nk. The numbers in parentheses indicate the statistical uncertainty in the last decimal places.

ρ^*	$T^* = 0.7$	$T^* = 1.0$	$T^* = 1.5$	$T^* = 2.0$	$T^* = 2.5$
$\lambda = 1.1$					
0.1	0.527(3)	0.1731(8)	0.0580(2)		
0.2	0.94(1)	0.319(1)	0.1109(3)	0.0556(2)	
0.3	1.25(2)	0.431(3)	0.1588(8)		
0.4	1.40(2)	0.525(5)	0.1979(9)	0.1033(4)	
0.5	1.51(3)	0.603(7)	0.230(1)		
0.6	1.50(3)	0.630(7)	0.252(2)	0.1361(7)	
0.7	1.42(3)	0.612(7)	0.261(3)		
0.8	1.38(2)	0.595(6)	0.256(3)	0.142(1)	
0.9	1.15(3)	0.534(7)	0.241(4)		
$\lambda = 1.2$					
0.1		0.367(2)	0.1155(3)	0.0559(1)	
0.2	3.11(17)	0.621(7)	0.1988(6)	0.0979(3)	
0.3		0.77(1)	0.2568(9)	0.1288(6)	
0.4	3.68(22)	0.83(1)	0.282(2)	0.1463(6)	
0.5		0.82(1)	0.295(2)	0.1528(6)	
0.6	3.01(14)	0.743(9)	0.282(3)	0.1459(8)	
0.7		0.657(8)	0.253(2)	0.1351(7)	
0.8	1.35(5)	0.530(8)	0.222(2)	0.1209(9)	
0.9		0.463(6)	0.195(2)	0.111(1)	
$\lambda = 1.3$					
0.1			0.1846(6)	0.0864(2)	0.0504(1)
0.2		1.17(1)	0.303(2)	0.1423(7)	0.0834(3)
0.3			0.359(4)	0.1720(5)	0.1016(4)
0.4		1.35(2)	0.363(2)	0.178(1)	0.1060(6)
0.5			0.340(3)	0.1688(8)	0.1019(7)
0.6		0.90(2)	0.289(3)	0.151(1)	0.0918(3)
0.7			0.251(2)	0.1350(9)	0.0838(5)
0.8		0.512(8)	0.226(2)	0.126(1)	0.0807(6)
0.9			0.219(2)	0.122(1)	0.078(1)
$\lambda = 1.5$					
0.1			0.426(3)	0.1724(4)	0.0952(3)
0.2			0.705(5)	0.263(2)	0.1426(8)
0.3			0.719(9)	0.277(2)	0.1495(7)
0.4			0.563(5)	0.239(2)	0.1339(8)
0.5			0.401(6)	0.190(2)	0.1142(6)
0.6			0.295(2)	0.161(1)	0.1027(5)
0.7			0.270(2)	0.1513(6)	0.0977(6)
0.8			0.235(3)	0.136(1)	0.0894(9)
0.9			0.188(2)	0.109(2)	0.0716(6)

3. Theory

3.1. *Barker–Henderson perturbation theory*

In the second-order BH perturbation theory [39, 40], the free energy is expressed in the form

$$\frac{F}{NkT}=\frac{F_0}{NkT}+\frac{F_1}{NkT}\frac{1}{T^*}+\frac{F_2}{NkT}\frac{1}{T^{*2}}, \tag{3}$$

where F_0 is the free energy of the hard-sphere (HS) reference system and F_1 and F_2 are the first- and second-order perturbative terms, respectively. According to this theory, the constant-volume excess heat capacity per particle is given by

$$\frac{C_V^E}{Nk}=-\frac{2}{T^{*2}}\frac{F_2}{NkT}, \tag{4}$$

where

$$\frac{F_2}{NkT}=-\pi\rho kT\left(\frac{\partial\rho}{\partial P}\right)_0\int_0^\infty [u_1^*(r)]^2 g_0(r) r^2 \mathrm{d}r \tag{5}$$

in the so-called *macroscopic compressibility approximation*, whereas

$$\frac{F_2}{NkT}=-\pi\rho kT\int_0^\infty [u_1^*(r)]^2\left\{\frac{\partial[\rho g_0(r)]}{\partial P}\right\}_0 r^2\mathrm{d}r \tag{6}$$

in the so-called *local compressibility approximation*. In equations (5) and (6), $\rho=N/V$ is the number density, $u_1^*(r)=u_1(r)/\epsilon$ is the perturbative contribution to the potential function, which in an SW potential is $u_1^*(r)=-1$ for $\sigma<r<\lambda\sigma$, P is the pressure and $g_0(r)$ is the radial distribution function (rdf) of the hard-sphere reference fluid.

In recent years, several analytical and very accurate expressions for the rdf $g_0(r)$ of the HS fluid have been proposed [41–43]. They can be used to determine F_2 in expressions (5) and (6). Regarding $(\partial\rho/\partial P)_0$, which appears explicitly in expression (5) and implicitly in (6), it can be obtained from the well-known Carnahan–Starling [44] equation of state

$$Z_0=\frac{P_0V}{NkT}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \tag{7}$$

where $\eta=(\pi/6)\rho\sigma^3$ is the packing fraction.

3.2. *Yuste–Acedo–Santos model*

The internal energy can be obtained from the rdf $g(r)$ through the energy equation

$$U=\frac{3}{2}NkT+2\pi N\rho\int_0^\infty u(r)g(r)r^2\mathrm{d}r, \tag{8}$$

whence

$$\frac{C_V^E}{Nk}=\frac{2\pi\rho}{k}\int_0^\infty u(r)\left[\frac{\partial g(r)}{\partial T}\right]_V r^2 dr. \tag{9}$$

In the special case of the SW potential (1), equations (8) and (9) become

$$U=\frac{3}{2}NkT-12N\epsilon\eta\int_1^\lambda g(r^*)r^{*2}\,\mathrm{d}r^*, \tag{10}$$

$$\frac{C_V^E}{Nk}=-12\eta\int_1^\lambda\left[\frac{\partial g(r^*)}{\partial T^*}\right]_\eta r^{*2}\,\mathrm{d}r^*, \tag{11}$$

respectively. The rdf $g(r^*)$ of the SW fluid depends on the packing fraction η, the reduced temperature T^* and, parametrically, on the well width λ. In principle, one has to resort to numerical solutions of integral equation theories. On the other hand, particularly suitable for the purpose of obtaining the heat capacity is the heuristic model proposed by Yuste and Santos [22] and recently simplified by Acedo and Santos [34], which is analytical and fairly accurate. Henceforth we will refer to this model as the Yuste–Acedo–Santos (YAS) model. It is based on expressing the Laplace transform $G(t)$ of $r^*g(r^*)$ in the form

$$\begin{aligned}G(t)&=t\frac{F(t)\exp(-t)}{1+12\eta F(t)\exp(-t)}\\&=\sum_{n=1}^\infty(-12\eta)^{n-1}t[F(t)]^n\exp(-nt),\end{aligned} \tag{12}$$

where the auxiliary function $F(t)$ is assumed to have the form [22, 34]

$$F(t)=-\frac{1}{12\eta}\left\{\frac{\exp(1/T^*)+K_1t-[\exp(1/T^*)-1+K_2t]\exp[-(\lambda-1)t]}{1+S_1t+S_2t^2+S_3t^3}\right\}. \tag{13}$$

The coefficients K_1, K_2, S_1, S_2 and S_3 are *explicit* functions of η, T^* and λ determined from consistency conditions. We refer the interested reader to [22, 34] for further details. The YAS model (13) reduces to the exact solutions of the Percus–Yevick (PY) equation in the limit of hard spheres ($\lambda\to1$ or $T^*\to\infty$) [45, 46], as well as in the limit of sticky hard spheres ($\lambda\to1$ and $T^*\to0$ with $T^*\sim-1/\ln(\lambda-1)$) [47]. From that point of view, the approximation (13) can be seen as a simple extension to finite widths of Baxter's solution of the PY equation for sticky hard spheres.

Upon Laplace inversion of equation (12), the final expression of the rdf reads

$$g(r^*) = r^{*-1} \sum_{n=1}^{\infty} (-12\eta)^{n-1} f_n(r^* - n)\Theta(r^* - n), \qquad (14)$$

where the functions $f_n(r^*)$ are the inverse Laplace transforms of $t[F(t)]^n$ and $\Theta(r^*)$ is Heaviside's step function. Therefore, to determine the rdf for $r^* < n+1$ only the first n terms in the summation (14) are needed. In particular, for the values of $\lambda \leq 2$ considered in this paper, one has

$$g(r^*) = -\frac{r^{*-1}}{12\eta} \sum_{i=1}^{3} z_i \frac{\exp(1/T^*) + K_1 z_i}{S_1 + 2S_2 z_i + 3S_3 z_i^2} \times \exp[z_i(r^* - 1)], \quad 1 < r^* \leq \lambda, \qquad (15)$$

where z_i $(i = 1, 2, 3)$ are the three roots of the cubic equation $1 + S_1 t + S_2 t^2 + S_3 t^3 = 0$. Inserting equation (15) into equation (11), we finally get

$$\frac{C_V^E}{Nk} = \frac{\partial}{\partial T^*} \sum_{i=1}^{3} \frac{\exp(1/T^*) + K_1 z_i}{S_1 + 2S_2 z_i + 3S_3 z_i^2} \times \left[z_i^{-1} - 1 + (\lambda - z_i^{-1}) \exp[z_i(\lambda - 1)] \right]. \qquad (16)$$

The heat capacity can also be obtained from the YAS rdf by following the virial and compressibility routes to the equation of state. The reason for the choice of the energy route (8) is two-fold. First, it is obviously the most direct route to determine the heat capacity. Second, we have checked that the other routes yield results that present larger deviations from the simulation data. This latter observation is consistent with the case of the PY theory for sticky hard spheres [48] and for SW fluids [7, 8].

4. Results and discussion

Results obtained for C_V^E from the second-order BH perturbation theory within the local compressibility approximation as well as within the macroscopic compressibility approximation are compared in figures 1–4 with the simulation data of table 1. We can see that although the local compressibility approximation provides a better agreement with simulation data, both approximations are rather poor at low temperatures. This might be due either to the insufficient accuracy of both the local compressibility and the macroscopic compressibility approximations or to the fact that higher-order terms, beyond the second one, in the expansion of the Helmholtz free energy in power series of the inverse of the reduced temperature, have a non-negligible contribution to the heat capacity. In order to

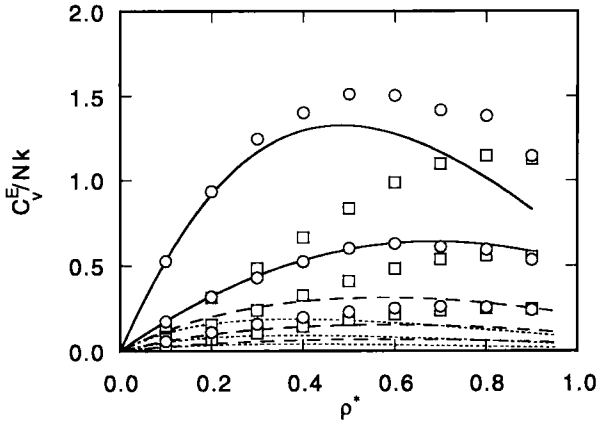

Figure 1. Constant-volume excess heat capacity for an SW fluid with $\lambda = 1.1$ as a function of the reduced density ρ^*. Circles: simulation data from table 1 for $T^* = 0.7$, $T^* = 1.0$ and $T^* = 1.5$, respectively, from top to bottom. Squares: values obtained from equation (4) using the simulation data of F_2 reported in [49]. Continuous curve: YAS model. Dashed curve: BH perturbation theory in the local compressibility approximation. Dotted curve: BH perturbation theory in the macroscopic compressibility approximation.

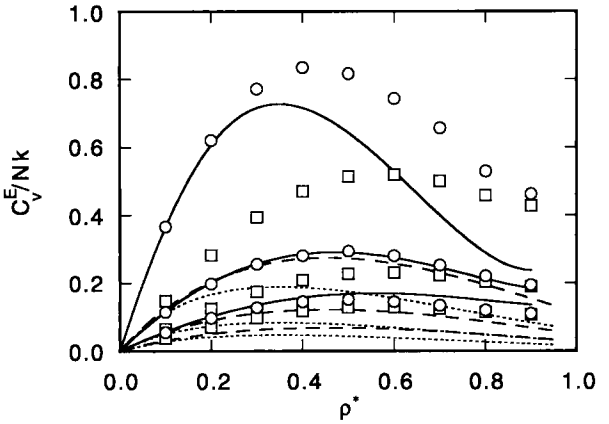

Figure 2. As in figure 1 for $\lambda = 1.2$, except that the temperatures are $T^* = 1.0$, $T^* = 1.5$ and $T^* = 2.0$, respectively, from top to bottom.

determine which of these two possibilities is the right one, we can use for F_2 in equation (4) simulation data, thus avoiding theoretical approximations. These simulations were performed by Barker and Henderson [50] who reported the results in terms of a function depending on 45 parameters for each density. These parameters were determined from a least-squares fitting of their simulation data. Since the use of that fitting is somewhat tedious, we have preferred to use directly simulation data for F_2, which are available for several densities and well widths [49], to determine C_V^E from equation (4). As one can see in figures 1–4, results thus obtained are much closer to the theoretical results

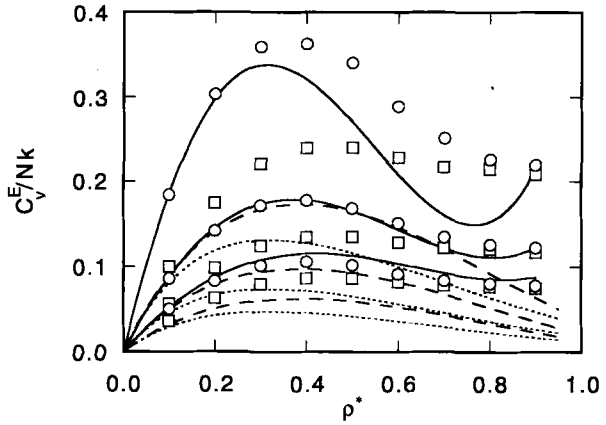

Figure 3. As in figure 1 for $\lambda = 1.3$, except that the temperatures are $T^* = 1.50$, $T^* = 2.0$ and $T^* = 2.5$, respectively, from top to bottom.

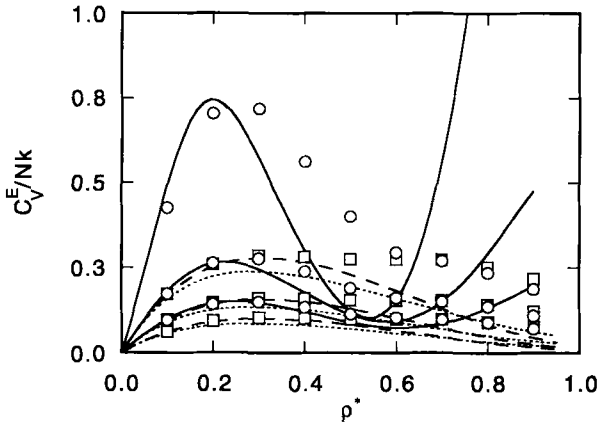

Figure 4. As in figure 1 for $\lambda = 1.5$, except that the temperatures are $T^* = 1.50$, $T^* = 2.0$ and $T^* = 2.5$, respectively, from top to bottom.

derived from the BH second-order perturbation theory than to the values of C_V^E obtained from direct simulations, except in the high density limit. This means that the main reason of the failure of the BH perturbation theory in predicting the heat capacity of SW fluids arises in the truncation of the perturbative series at the level of the second-order term, the higher-order terms having a non-negligible contribution. This is in contrast to the situation for the equation of state [39, 51], which is accurately given by the second-order BH perturbation theory even at relatively low temperatures for wide ranges of densities and potential wells. The reason is that, as pointed out before, the constant-volume excess heat capacity is a thermodynamic property particularly sensitive to the performance of a theory and therefore the influence of higher-order terms, which is small in the equation of state, may be important in the heat capacity. This is particularly true for low values of the potential width, since the lower the potential width, the slower the convergence of the BH perturbation theory at low temperatures [15].

A much better agreement is obtained with YAS theory, equation (16), at low to moderate densities, as shown in the same figures. This theory, in contrast to the BH theory, provides a better agreement with the simulation data of C_V^E as the potential width decreases. This is consistent with the fact that, as mentioned before, the YAS model is an extension to $\lambda > 1$ of the PY solution for sticky hard spheres and hence it is expected to be as accurate as the PY theory at least for small $\lambda - 1$. The structural properties predicted by the YAS model for the SW fluid also exhibit good agreement with simulation data for low values of $\lambda - 1$ whereas the accuracy worsens as λ increases [22, 34]. Figures 1–4 show that, given a well width λ, the YAS values of C_V^E are more accurate as the temperature increases and/or the density decreases.

In conclusion, we have performed Monte Carlo simulations of the constant-volume excess heat capacity of SW fluids of variable width for a wide range of densities and at several characteristic temperatures. This thermodynamic quantity vanishes for hard spheres and so it represents an important measure of the influence of attractive forces on the state of the fluid. Moreover, the heat capacity seems to provide a rather stringent test to assess the accuracy of theoretical approaches. In this paper we have compared the simulation data with the BH perturbation theory [39, 40] and with a non-perturbative theory developed by Yuste, Acedo, and Santos [22, 34]. While the former theory presents a poor performance, which can be attributed to the truncation of the perturbative series to second order rather than the inaccuracy of the theory itself, the non-perturbative theory does a fairly good job, especially for narrow wells, except at low temperatures and high densities. Although a potential well of $\lambda = 1.5$ is appropriate for many simple fluids, SW fluids with lower values of λ may be of interest because the properties of certain colloidal suspensions are well reproduced by considering SW interactions with narrow potential widths. Therefore, as several theories for SW fluids have achieved a considerable accuracy for the equation of state and the pair correlation function of SW fluids, the constant volume excess heat capacity seems to be a suitable thermodynamic property to discriminate between them. In this context, we expect that our simulation data can stimulate other studies on the heat capacity of SW fluids of variable width and can be used to check the reliability of other approximations.

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