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Structure and coexistence properties of shoulder–square well fluids

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ABSTRACT

Shoulder–square well fluids are studied for different heights and locations of the shoulder. The vapor–liquid metastable coexistence is accessed by combining the slab technique and the replica exchange Monte Carlo method. Phase diagrams and structural properties are reported. It was shown that the shoulder height as well as its location plays an important role on the shape of the phase diagrams. The shoulder acting as a barrier always produces denser liquid and solid states in coexistence with less dense vapors. A shift of the shoulder position to larger distances leads to lower critical temperatures and higher critical densities.

1. Introduction

There are several examples of common substances showing complex thermodynamic behaviors [1–3]. These are, among others, water, phosphorus, carbon, metal crystals (cerium and cesium), micellar structures, silica, granular materials, proteins, and colloids (see Ref. [4] and references therein). In particular, water, in addition to its well known melting curve with negative slope, shows a second critical point at high pressures, as well as a liquid–liquid transition at high pressures and temperatures [5,2]. Of course, this rich behavior is a consequence of the nontrivial collective interaction between the system entities, and therefore, such systems have attracted a great deal of attention. On the one hand, there is a large number of works devoted to developing detailed models for quantitatively reproducing all thermodynamic properties [6–8], and on the other hand, several works deal with the simplest models capable of qualitatively capturing some characteristics of this complex behavior [9–11]. In this last context, a combination of square shoulder and square well potentials, which have been widely studied in the literature [12–16], captures real substance complex behaviors such as the presence of several critical points. The combination of the square shoulder and the square well potentials results in the interaction pair known as shoulder–square well (SSW) [1,4,17–21].

Using different techniques such as molecular dynamics, Monte Carlo (MC) simulations, and perturbation theory, it was shown that the SSW model can yield anomalies in the phase diagram [1,4,17–24]. Depending on the parameter values defining the SSW, one can find different kinds of phase transitions [25]. For instance, Skibinsky et al. [4], Cervantes et al. [19], and Rzysko et al. [20] reported the existence of more than one critical point and fluid–fluid transitions. That is, the phase diagram may show a vapor–liquid critical point and/or a liquid–liquid critical point. Despite the simplicity and the importance of the SSW potential, so far there are mostly theoretical studies dealing with its coexistence and structural properties. However, to the best of our knowledge, the SSW has been poorly studied by using computer simulations.

In a recent study [26] we analyzed the shoulder–square well potential where the shoulder is placed at contact with the hard-sphere discontinuity. In this case, we focus our attention on a single vapor–liquid critical point, and on how higher energy shoulders produce a lower proportion of short bonding distances. Likewise, at very low temperatures the crystallization was observed to occur more easily by restricting the bonding distances. Furthermore, we reported the formation of a gel-like phase for certain conditions. In this work we also studied the phase diagram region below the vapor–liquid critical point, but in this case we considered both, a shoulder placed at contact with the hard-sphere discontinuity and followed by a square well, and a square well followed by a shoulder (acting as a barrier). Hence, the main purpose of this work is to show the effect of the height and location of the shoulder on the vapor–liquid coexistence and structural properties of SSW fluids.

2. Potential models

A system composed by N spherical particles with diameter σ was considered. The particles interact via a discrete potential known as shoulder–square well, which is defined by

$$U(r) = \begin{cases} \infty, & \text{for } r \le \sigma, \\ \epsilon_1, & \text{for } \sigma < r \le \lambda_1, \\ \epsilon_2, & \text{for } \lambda_1 < r \le \lambda_2, \\ 0, & \text{for } r > \lambda_2, \end{cases} \quad (1)$$

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where r is the interparticle distance, λ_1 and λ_2 define the shoulder and well widths, and ϵ_1 and ϵ_2 are the corresponding energy values (see Fig. 1). In case a) of Fig. 1, λ_1 and ϵ_1 correspond to the shoulder whereas λ_2 and ϵ_2 define the attractive well. Conversely, in case b), λ_1 and ϵ_1 correspond to the attractive well while λ_2 and ϵ_2 define the shoulder (acting as a barrier).

As mentioned in the Introduction, the location and the height of the shoulder are varied. This is done by selecting six series of parameters as shown in Table 1, where $\lambda_1 = 1.25$ and $\lambda_2 = 1.5$ are kept constant.

Table 1
Parameters of SSW potential for the different cases studied. Energy units are given in k_BT.

Case	ϵ_1	ϵ_2
1a	1	−1
1b	−1	1
2a	0.5	−1
2b	−1	0.5
3a	−0.5	−1
3b	−1	−0.5

3. Simulation details

The replica exchange Monte Carlo (REMC) simulation method [27–29] is used to obtain the coexistence and structure properties of shoulder–square well fluids. This method was derived to achieve good sampling of systems presenting a free energy landscape with several local minima. The method consists of simulating M replicas of the system in parallel, each being at different thermodynamic conditions, while performing exchange (swap) trials between them. Due to these exchanges, a particular replica travels through different thermodynamic conditions, allowing it to overcome free energy barriers.

The REMC is set to sample an extended canonical ensemble taking the temperature as the expansion thermodynamic variable. The existence of this extended ensemble justifies the introduction of swap trials between replicas, with the restriction that the detailed balance condition is fulfilled. This technique allows exploring efficiently the regions of coexistence at low temperatures where traditional simulation methods tend to get trapped at local, free energy minima. The extended canonical ensemble is defined as

$$Q_{ext} = \prod_{i=1}^{M} Q_{NVT_i}, \tag{2}$$

where Q_{NVT_i} is the partition function of the canonical ensemble of the system at temperature T_i, V is the volume of the cell, and N is the number of particles at each replica. M is the number of system replicas, which matches the number of different temperatures. To satisfy the detailed balance condition, the probability of acceptance of the exchange is given by

$$P_{ac} = \min\left(1, \exp\left[\left(\beta_j - \beta_i\right)\left(U_i - U_j\right)\right]\right), \tag{3}$$

where $U_i - U_j$ is the potential energy difference between replicas i and j and $\beta_j - \beta_i$ is the difference between the corresponding reciprocal temperatures.

We set rectangular simulation boxes of dimensions $L_x = L_y = 8\sigma$ and $L_z = 50\sigma$. Periodic boundary conditions are set in the three directions. Verlet lists are implemented to improve performance. A collection of 800 particles were randomly placed at a slab centered [30] inside the $M = 12$ boxes (the center of mass of the system is kept at the cell center). This is appropriate for capturing the vapor–liquid metastable coexistence. Different initial conditions should be set in order to capture other coexistences. The highest temperature was set at a value very close to the critical temperature of the system, while the other temperatures were established following a decreasing geometric progression. The initial configuration is equilibrated by conducting 10^7 MC simulation steps. All results were calculated over additional 4×10^7 configurations.

To detect crystal structures, the order parameter (Q_6) was calculated at the dense phase. This parameter is a quantitative measure of the bond order of the system, and it is achieved through defining a set of bonds that connect pairs of neighbors. It is defined as [31]

$$Q_6 = \left(\frac{4\pi}{13}\sum_{-6}^{6} \left|\langle Y_{6m}(\theta,\phi)\rangle\right|^2\right)^{1/2}, \tag{4}$$

where $\langle Y_{6m}(\theta,\phi)\rangle$ is the ensemble average of all bonds of the spherical harmonics of the orientation angles θ and ϕ (which are the polar angles with respect to a fixed coordinates system). The value of Q_6 tends to zero for a completely random system of a large number of bonds, $1/\sqrt{NN_n/2} \pm 1/\sqrt{13NN_n}$, whereas it increases when bonds show angular correlations [31].

The densities of the coexistence phases were obtained by ensemble averaging from the corresponding regions. The coexistence curves are obtained from these data. The critical density and temperature were calculated by using the rectilinear diameters law and the universal value of $\beta = 0.325$ [32]. All results are presented in dimensionless units, i.e., $r^* = r/\sigma$ for distance, $T^* = k_BT/\epsilon_2$ for temperature, and $\rho^* = \rho\sigma^3$ for density.

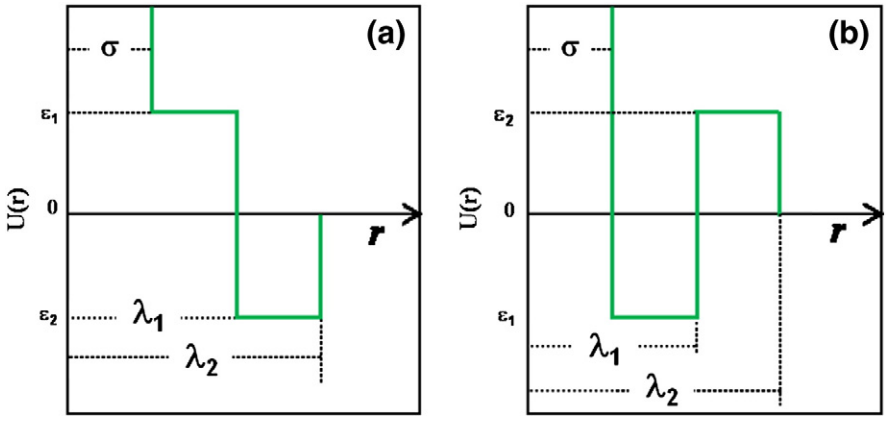

Fig. 1. Schematic diagram of SSW potential for $\lambda_1 = 1.25$, and $\lambda_2 = 1.5$ (these values are set constant along this work). a) Shoulder placed at contact with the hard-sphere discontinuity and followed by a square well. b) Square well followed by a shoulder (acting as a barrier).