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Phase behaviour of short range triangle well fluids: A comparison with lysozyme suspensions

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ABSTRACT

The phase coexistence of colloidal suspensions is studied by Monte Carlo Replica Exchange (REMC) simulations using an attractive triangle potential model of short range ($1.15\sigma \leq \lambda \leq 1.4$) in a wide temperature range. Typical liquid-vapor coexistences are found at temperatures close to the critical one, while for lower temperatures the liquid-vapor metastability is broken in favor of the vapor-solid coexistence. Structural properties are accessed through the radial distribution function and the global order parameter. The formation of a solid phase with structure belonging to the close-packed family is shown. The coexistence curves are plotted in reduced coordinates and compared with those experimentally obtained for protein suspensions (lysozyme aqueous suspensions with additives). A good qualitative agreement between experimental data and simulation results is found.

1. Introduction

The study of the phase behaviour and thermodynamic properties of colloidal systems has been a subject of great interest to the scientific community for many decades due to its wide application areas such as physics, materials science, biology, medicine among others. The colloidal systems can be considered as simple models capable of representing, to some extent, the thermodynamic behaviour of complex fluids such as protein and suspensions, and human formulated fluids as paints, drilling fluids and other type of suspensions. Therefore they have been extensively studied by different techniques including both, theoretical and experimental ones [1–7].

The presence of transitions involving a condensed phase in some protein systems is related to certain diseases [8–12], so understanding their phase behaviour is of great interest to the pharmaceutical industry. This understanding could help to develop new therapeutic products. In addition, proteins are present in a grate variety of processes which go from food to nanotechnology, passing through biotechnology [13–17], where transitions usually play an important role.

In particular, the protein called lysozyme has been widely used as a model protein to understand the phase behaviour of biocolloids in aqueous suspensions [3,4,18-21]. Lysozyme is a tightly folded globular protein, so that it takes a nearly spherical shape. This feature explains why it is considered a model protein. In recent years its behaviour has been compared to that of simple spherical potential models [18,22-26] and others where anisotropic interactions are allowed by including patches on the spherical surface (patchy particles) [20].

It has been demonstrated that protein suspensions show similar transitions to the ones observed in simple fluids. In general, this kind of transition takes place at conditions in which the interaction distance is smaller than the protein size [23,27-29]. Therefore, it is possible to model a suspension of this type, such as a simple colloidal system. The protein systems have been studied by means of theoretical approaches and molecular simulations. In both cases, the effective interaction between a couple of protein particles is given through potential models that include a repulsive hard core and an attractive term of short-range; the effect of the continuous medium is included by adjusting the potential parameters [18]. The potential models employed to capture the protein behaviour are the Lennard-Jones (LJ), Yukawa (YK), square well (SW) and Asakura-Oosawa(AO) [3-5,18,23-26,30-32]. Results from the Lennard-Jones potential have been compared to those from the experimental

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lysozyme suspensions [4]. This model can capture the experimental behaviour only in the region of high temperature, while producing significant deviations at temperatures well below the critical one. This functional form has no discontinuities although its implementation in simulations requires considering a cut-off distance or the Ewald summation formalism to deal with its long-range tail. The simple cut-off scheme is by far more frequently implemented, making the LJ model results depend on this parameter to some extent. Putting aside the cut-off, this functional shape depends only on two parameters, namely core size and attraction depth. As mentioned by Katsonis et al. [4], it is not possible to establish identical functional dependencies of interaction potentials for different proteins by modifying only the depth of attraction for a fixed core size.

The SW model is mathematically simple, constituted by a hard core plus an attractive well of constant interaction energy for a given range. Despite being a rough approximation, the SW potential has been used to represent proteins [23–26], specifically, crystalline proteins through molecular simulation; it was found that it is possible to map the results with respect to experimental data for intervals of interaction ranges shorter than 1.25σ [23] (being σ the hard-core diameter). In addition, Duda [24] found that the SW model is capable of representing experimental data of liquid-vapor coexistence (LVE) of lysozyme suspensions in reduced units, with very short interaction ranges (about 1.1σ). On the other hand, using the YK and AO model, Valadez-Pérez et al. [25] have shown that the coexistence curve is more or less independent of the detailed functional form of the interaction, but depends on the second virial coefficient.

From the simulation and theoretical points of view, to study protein systems it is necessary to use potential models that include a hard core plus an attractive region, considering short-range interactions. Therefore in this contribution a short-range triangle-well (TW) model, which has the advantage that the slope of the tail tends to zero when the intermolecular distance is increased [33-42,42-44], is used. This fact prevents the truncation problems in the potential model. Additionally, the Replica Exchange Monte Carlo simulation technique is implemented since it allows to study low temperature regions and to describe transitions different from the vapor-liquid one [45–47].

2. Methods

2.1. Pair potential

The interaction between the proteins molecules is modeled by using a triangle potential (TW), which contains a repulsive hard core and an attractive well having its larger depth at contact (see Fig. 1). This potential model has only one discontinuity, furthermore it does not introduce truncation issues, contrasting with Yukawa, Lennard-Jones and Sutherland fluids. The hard-core contribution to the pair potential does not permit the penetration between the particles, unlike soft potentials.

The TW potential is given by

$$u(x) = \begin{cases} \infty, & \text{for} \quad x \le 1, \\ \epsilon(x-\lambda)/(\lambda-1), & \text{for} \quad 1 < x \le \lambda, \\ 0, & \text{for} \quad \lambda < x, \end{cases} \tag{1}$$

where $x = r/\sigma$ is the reduced distance, σ is the hard-core diameter, ϵ is its potential depth, and λ controls the interaction range (see Fig. 1). An important characteristic of this expression is the slope of its attractive region which resembles real potentials without extending to long distances.

Results are given in dimensionless units as follows: $r^* = r/\sigma$ for distance, $T^* = k_B T/\epsilon$ for temperature, $\rho^* = \rho\sigma^3$ for density, and $\phi = \rho^*\pi/6$ for the packing fraction.

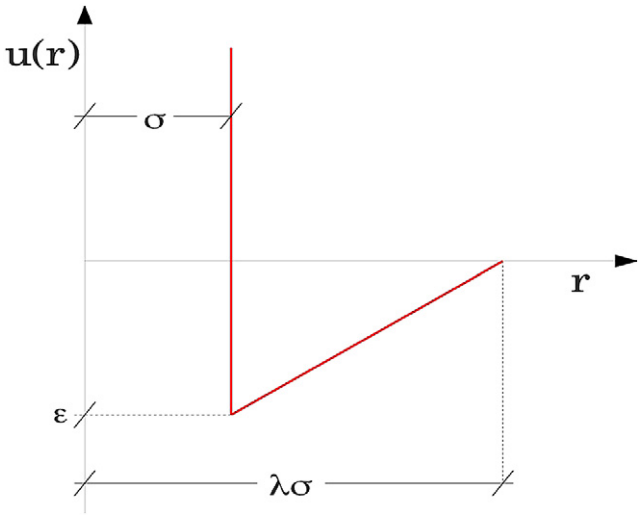

Fig. 1. Triangle model potential.

2.2. Simulation details

The simulation data were computed by means of the Replica Exchange Monte Carlo (REMC) method. The REMC technique, also known as Parallel Tempering, was derived to achieve good sampling of systems that present a free energy land-scape with many local minima [45–47]. The REMC method consists of simulating M replicas (copies) of the system at different thermodynamic conditions; the attempted swap moves are accepted or rejected according to the traditional Metropolis algorithm. Due to these exchanges, a particular replica travels through many temperatures, allowing it to overcome free energy barriers.

The method samples an expanded canonical ensemble, taking the temperature as the expansion variable. The existence of this expanded ensemble justifies the introduction of exchange trials between replicas (swap trials). The expanded 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 (NVT_i^*) canonical ensemble of the system (subensemble i) at temperature T_i^*, and volume V, with N particles. M is the number of replicas which equals the number of subensembles (each subensemble is sampled by a single replica at a time). To satisfy the detailed balance condition, the probability of acceptance of the swap trial is given by

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

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

All cells are equally set-up. They consist of rectangular boxes of dimensions $L_x = L_y = 10\sigma$ and $L_z = 4L_x$, where periodic boundary conditions in the three directions are employed. Verlet lists are implemented to improve performance. Initially, a collection of 1200 particles were randomly placed at a slab centered in the middle of the M boxes. The highest temperature is set at a value close to but below the critical temperature, while the other temperatures are established by following a decreasing geometric progression. The initial configuration is equilibrated by conducting 1×10^7 simulation