Hard-core Yukawa model for charge-stabilized colloids

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The hypernetted chain approximation is used to study the phase diagram of a simple hardcore Yukawa model of a charge-stabilized colloids. We calculate the static structure factor, the pair distribution function, and the collective mode energies over a wide range of parameters, and the results are used for studying the freezing transition of the system. The resulting phase diagram is in good agreement with the known estimates and the Monte Carlo simulations.

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I. INTRODUCTION

The phases of the charge-stabilized colloids have become a subject of growing interest in many recent experimental and theoretical investigations [1–5]. However, it is fair to say that our understanding of charge-stabilized colloids is very far from complete, and even some basic questions such as what is the form of interactions between strongly charged colloidal particles still remains controversial [6–8]. On the other hand, it seems to be quite well-known that when the concentration of colloids is sufficiency large it freezes into a crystal. Both body-centered-cubic (bcc) and face-centered-cubic (fcc) crystals have been found. Therefore, the full phase diagram consists of two melting lines (liquid-bcc solid and liquid-fcc solid) and a structural (bcc-fcc) transition, depending on the effective temperature and inverse screening length [4].

There have been a number of approaches for studying the phase diagram of the charge-stabilized colloids using a variety of analytical and simulation studies [4–11]. Most approaches rely on using a one-component system of spherical particles interacting via a simple pair potential, consisting of a hard sphere interaction plus a repulsive Yukawa term, called hard-core Yukawa (HCY) potential. Since this potential is purely repulsive, it can give rise to a single fluid phase that can freeze into a solid with either an fcc or a bcc structure [4].

The phase diagram of particles interacting via a Yukawa potential is of special interest, since it has been applied to a wide range of the physical systems, and also it provides a good testing ground for theories of the phase transitions [6,12]. There are a number of theoretical and Monte Carlo studies to discuss the freezing behavior of the particles interacting via a pure Yukawa potential [2,7,8,13,14]. On the other hand, various theoretical and numerical works have studied the phase behavior of the HCY model [9,11,15–18]. The later case (which we study in this paper) may provide an understanding of the phase diagram of the charged-stabilized colloidal particles for which the colloid-colloid interactions can to some extent be represented by this HCY model. Here, the hardcore term represents the finite size of the colloidal particles while the Yukawa terms represents the repulsive electrostatic interaction.

Kloczkowski and Samborski [15] studied the freezing of hard spheres with a Yukawa attractive or repulsive potential in the mean spherical approximation by using the density functional theory. A simple theory was proposed in Ref. [8] to find the location of the phase boundary of the repulsive Yukawa potential. The thermodynamics of the fluid and solid one-component plasma with the Yukawa potential has been also studied in detail from molecular dynamics in Ref. [14]. On the other hand, many works have discussed the HCY potential. The phase diagram of the HCY mixtures, constituted of equal-sized hard spheres, determined in the Ref. [10] by means of Gibbs ensemble Monte Carlo simulations, semi-grand canonical Monte Carlo simulations, and through the modified hypernetted-chain theory. The self-consistence Ornstein-Zernike approximation, the generalized mean spherical approximation, the modified hypernetted-chain approximation, and the hierarchical reference theory were applied to the determination of thermodynamics and structural properties, and the phase diagram of the HCY fluid by Caccamo *et al.* [13] Thermodynamically self-consistent integral equation theories supplemented by a one-phase freezing criterion, and Monte Carlo simulations were used in Ref. [18] to investigate the thermodynamics and structural properties, and phase diagram of the HCY fluid. The results of Monte Carlo simulations and an analytical theory for HCY fluids of variable range was presented by Shukla [11]. A two-dimensional Clapeyron integration was used in Ref. [9] for the HCY potential of variable range to compute the line of triple points. The results for the triple point of the Yukawa system are also given in the Ref. [19].

In this paper, we use the well-tested and widely applied hypernetted-chain (HNC) formalism [20,21] to study the freezing transition of the charge-stabilized colloidal particles interacting via HCY potential. Our primary aim is to clarify how well the HNC approach models the static properties of the HCY particles. To this end, we calculate the static structure factor and the pair correlation function for different densities and temperatures. The results are often compared with the available Monte Carlo simulations, from which a good agreement between the results are observed. We also discuss

the collective mode of the energies as the system approaches freezing transition.

The behavior of physical quantities may be used to extract information on the phase diagram and the phase transition can be detected by looking at their behavior in a fixed temperature (density) but varying the density (temperature). To give an estimation of the freezing transition, we use the Hansen-Verlet criterion [22], from which the transition is determined by evaluating the peak value of the structure factor. The results for the transition temperatures are compatible with recent Monte Carlo simulations [4]. The tendency of the colloidal system toward an ordered phase by fixing the density (temperature) and varying the temperature (density) can be also observed in the behavior of the collective modes of the energies.

The rest of this paper is organized as follows. In Sec. II, we shortly review the model and HNC formalism. The numerical results are presented and discussed in the Sec. III, and conclusions appear in Sec. IV.

II. THEORY

A. Hard-core Yukawa model

The charge-stabilized colloids consist of mesoscopic particles with surface charges that are dispersed in a solvent with counterions. In the first approximation, the interactions between particles are described by the Yukawa potential $\beta U(r) \approx \beta\lambda \exp(-\kappa r)/r$, where κ and λ are the inverse screening length and the interaction strength, respectively [23], and $\beta = 1/(k_B T)$ is the inverse temperature. In the limit of $\kappa \to 0$, one recovers the Coulomb potential.

However, the Yukawa model neglects the effect of the size of the particles. In order to consider this effect, we use the modified Yukawa model with the hard-core part [24]:

$$\beta U(r) = \begin{cases} \infty & \text{for } r < \sigma \\ \beta\lambda \dfrac{\exp[-\kappa(r-\sigma)]}{r/\sigma} & \text{for } r > \sigma, \end{cases} \quad (1)$$

where σ is the diameter of particles. We present the results of this HCY potential with the inverse screening length fixed at $\kappa\sigma = 5$ (for a ready comparison of our results with the Monte Carlo simulation of Ref. [4]) in Sec. III.

B. HNC formalism

Given the HCY potential of interaction between charge-stabilized colloids, the evaluation of correlation functions reduces to a problem in classical liquid-state theory [20]. One of the basic quantities is the pair distribution function defined by

$$g(|\mathbf{r}-\mathbf{r}'|) = \left\langle \sum_{i=1}^{N} \sum_{j\neq i}^{N} \delta(\mathbf{r}-\mathbf{r_i})\delta(\mathbf{r}'-\mathbf{r_j})/\rho^2 \right\rangle, \quad (2)$$

where ρ is the density of the liquid. Other basic quantities are the pair correlation function $h(r) = g(r) - 1$ and the static structure factor defined by

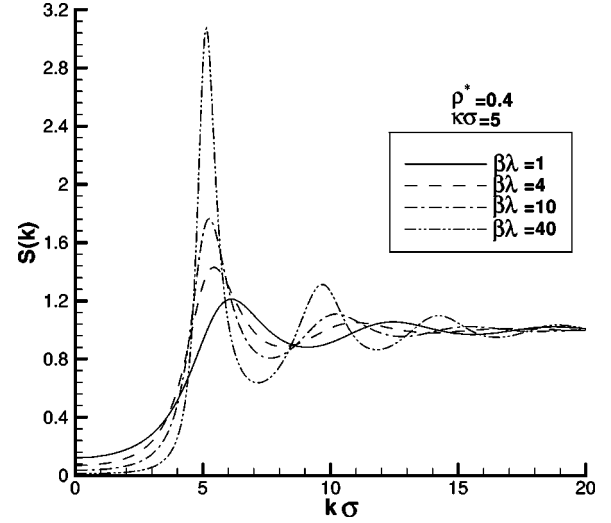$$S(q) = 1 + \rho \int d^d r\, h(r)\exp(i\mathbf{q}\cdot\mathbf{r}). \quad (3)$$

FIG. 1. The static structure factor in terms of $k\sigma$ for $\rho^* = 0.4$ and different values of $\beta\lambda$.

The pair correlation function for a simple, isotropic fluid can be decomposed as the Ornstein-Zernike relation [20,21]

$$h(r) = C(r) + \rho \int d^d r'\, C(|\mathbf{r}-\mathbf{r}'|)\mathbf{h}(\mathbf{r}'), \quad (4)$$

where $C(r)$ is called the direct correlation function and can be related to the structure factor through $S(q) = 1/[1 - \rho C(q)]$. A closure relation between $h(r)$ and $C(r)$ is needed to supplement the Ornstein-Zernike relation. In the HNC approach, it is given by [20,21]

$$C(r) = \exp[-\beta U(r) + Y(r)] - 1 - Y(r), \quad (5)$$

where $U(r)$ is the interparticle pair potential and $Y(r) = h(r) - C(r)$. The self-consistent solution of Eqs. (4) and (5) gives the calculations of the correlations in the liquid state within the HNC scheme. In the next section, we present numerical results for various quantities of interest.
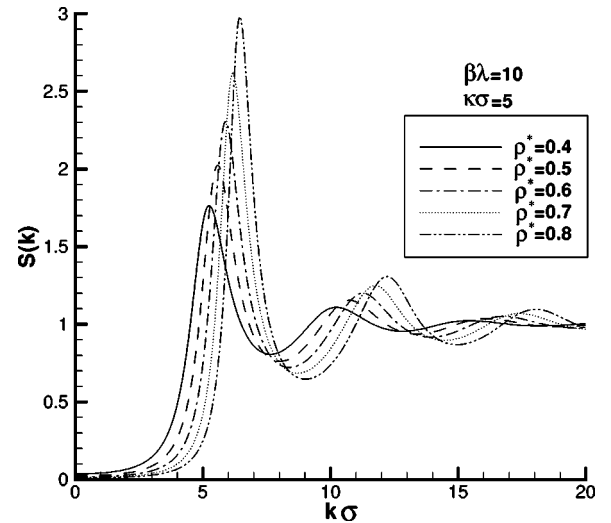

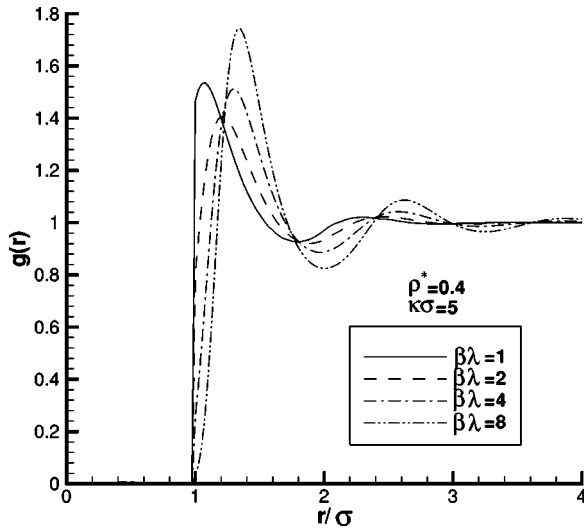FIG. 2. The static structure factor for $\beta\lambda = 10$ and various densities.

FIG. 3. The pair-distribution function for $\rho^*=0.4$ and different values of $\beta\lambda$.

III. NUMERICAL RESULTS AND DISCUSSION

In this section, we present the results of the numerical calculations for the quantities of physical interest. We numerically solve the set of Eqs. (2), (3), (4) and (5) with the potential defined in Eq. (1), and find the static structure factor and the pair distribution function. The numerical calculations are done for a fixed $\kappa\sigma=5$ for different values of $\lambda\beta$ and $\rho^*=\rho\sigma^3$.

One of our numerical results that was developed by iterating the above-mentioned set of equations is the behavior of the static structure factor that is shown in Fig. 1 for a fixed $\rho^*=0.4$ and different values of $\beta\lambda$. It indicates that the peak of the structure factor increases with increasing $\beta\lambda$ (decreasing temperature), and shows a tendency toward the formation of an ordered structure.

We can also see the freezing transition by fixing $\beta\lambda$ and varying the density. The results for $\beta\lambda=10$ and different values of ρ^* are shown in Fig. 2. The same scenario of the transition can also be discussed by studying the behavior of
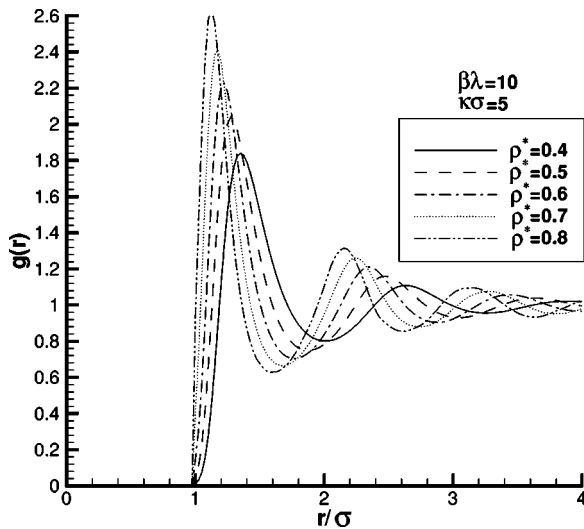

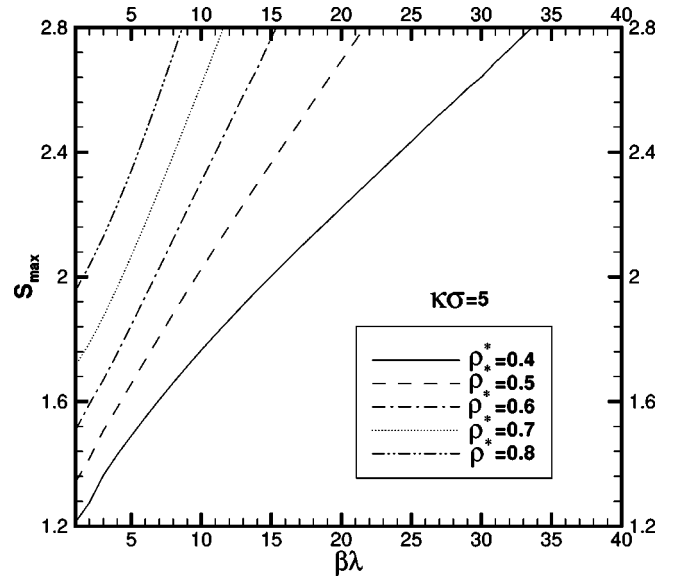FIG. 4. The pair-distribution function for $\beta\lambda=10$ and different values of ρ^*.

FIG. 5. The behavior of the S_{max} in terms of $\beta\lambda$ for various values of ρ^*.

the pair-distribution function. The results of $g(r)$ for a fixed temperature (density) and with different densities (temperatures) are plotted in Figs. 3 and 4.

The results of the static structure factor and the pair-distribution function are in good qualitative agreement with the expected results of the phase diagram of the charge-stabilized colloids.

To obtain some quantitative description of the transition point, we use the Hansen-Verlet criterion [22] that states that the maximum peak height of the S_{max} in the fluid structure factor $S(k)$ should reach a fixed value at melting. The results for S_{max} are shown in Fig. 5.

By comparing with the results of Monte Carlo simulations, we assume that the transition appears when the peak of $S(q)$ reaches the value $S_{max}\approx3$, and extract the phase transition point based on this criterion. The resulting phase diagram is plotted in Fig. 6. To compare, we have also plotted
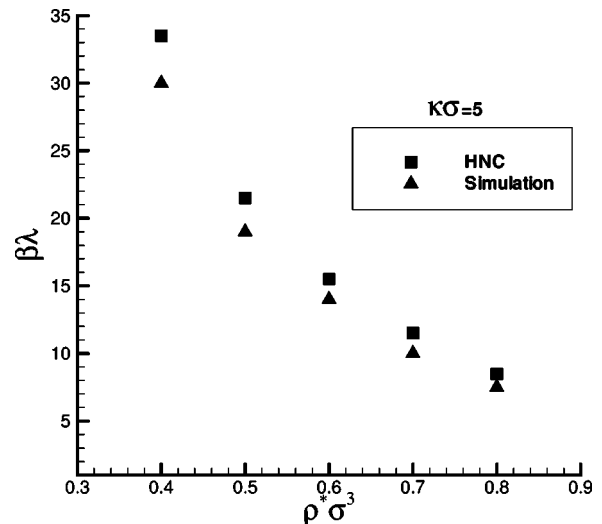

FIG. 6. The phase diagram of the $\kappa\sigma=5$ HCY system. Squares are the results of HNC calculations and triangles are results of the Monte Carlo simulation extracted from Ref. [4].
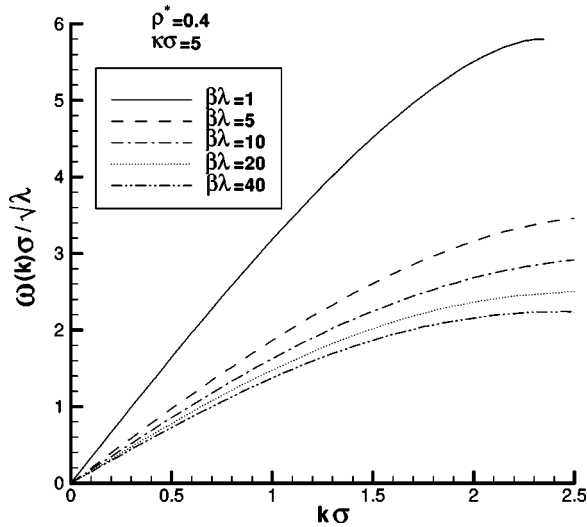
FIG. 7. The collective mode energies as a function of $k\sigma$ at $\rho^*=0.4$ for various values of $\beta\lambda$.

FIG. 8. The collective mode energies as a function of $k\sigma$ at $\beta\lambda=10$ for various values of ρ^*.

the results of the Monte Carlo simulation extracted from Fig. 3 of Ref. [4].

Finally, we calculate the dispersion of the collective modes of the colloidal system in the liquid phase and as it approaches the freezing transition. The dielectric function of the system within the generalized random-phase approximation [25] is given by

$$\varepsilon(q,\omega)=1+\beta\rho\,V_{eff}(q)W[\,\omega/(q\sqrt{T})\,],\qquad(6)$$

where

$$W(x)=\frac{1}{\sqrt{2\pi}}\int dy\,y\,\frac{e^{-y^2/2}}{x-y+i\eta},\qquad(7)$$

is the plasma dispersion function, and $V_{eff}(q)$ is the effective interaction between the particles. The frequency integral over the fluctuation-dissipation theorem allows us to write the following relation:

$$S(q)=\frac{1}{1+\beta\rho V_{eff}(q)},\qquad(8)$$

between the effective interaction and the static structure factor. We use the converged HNC results for $S(q)$ to determine $V_{eff}(q)$. The collective mode energies calculated from the roots of $\varepsilon(q,\omega)=0$ are shown in Figs. 7 and 8. In the long-wavelength limit $\omega(k)\sim k$, corresponding to sound waves [26]. For a fixed ρ^*, the system moves toward an ordered phase as $\beta\lambda$ increases, while the collective modes soften. Mode dispersions also show flattening at larger wave vectors with increasing $\beta\lambda$. At a fixed value of $\beta\lambda$, the sys-
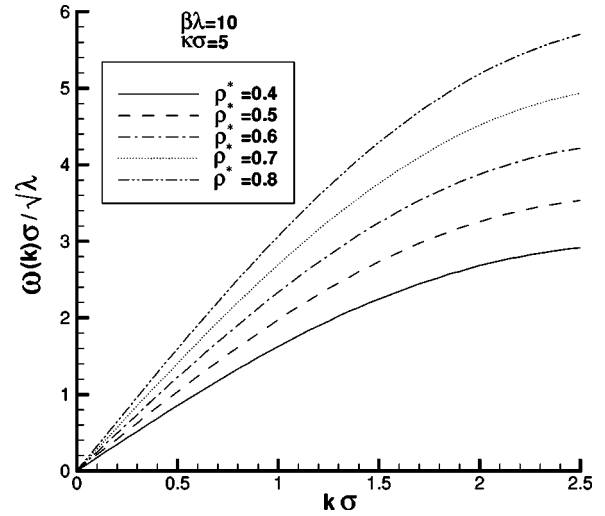
tem is driven to the ordered phase with increasing ρ^*. In this case, the mode energies increase as ρ^* is increased.

IV. CONCLUSIONS

In this paper, we studied the hard-core Yukawa model for charge-stabilized colloids in the HNC approximation. In spite of the fact that the Yukawa model is an approximate model for real charge-stabilized colloids, it has been used by many authors [4,6–8] and reasonable results are obtained describing the liquid-solid and solid-liquid phase transition of the system. On the other hand, the HNC method is tested and widely applied for different models, and one expects that the results be compatible with Monte Carlo simulations. Therefore, we found the static structure factor and the pair-distribution function for different values of the temperature and density based on this approach. We discussed how the results of these quantities may be applied for the qualitative explanation of the phase diagram. We also invoked the behavior of the peak of structure factor combined with the Hansen-Verlet criterion to estimate the freezing temperature, from which the resulting phase diagram supports the Monte Carlo simulations quite well. The behavior of the collective mode dispersions also exhibits the expected behavior as the colloidal system approaches freezing transition.

ACKNOWLEDGMENTS

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