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Structures and Phase Transitions in Colloidal Dispersions from Theory and Simulation[1]

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Equilibrium properties of uncharged colloidal dispersions with particles interacting via harsh short-ranged repulsive forces and strong short-ranged attractive forces are determined by means of an approach in which colloids are treated as supramolecular versions of simple fluids. The interparticle interactions are represented by short-ranged square-well potentials. Structure factors and phase diagrams for the dispersions are determined analytically by mapping the square-well potential onto the adhesive-hard-sphere model by equating the respective second virial coefficients. Theoretical predictions are compared with molecular simulation results for the conditions relevant to real colloidal dispersions. Our results show that the adhesive-hard-sphere model can describe accurately structure factors and phase diagrams of nonionic microemulsions and inverted micellar systems containing AOT surfactant dispersed in oil. Both upper-critical and lower-critical consolute points in colloidal dispersions dominated by short-ranged attractive forces can be described using the same formalism.

KEY WORDS: adhesive hard spheres; colloidal dispersions; interparticle interactions; micellar systems; microemulsions; phase transitions.

1. INTRODUCTION

Recently, we [1] presented Monte Carlo simulation results for structure factors of monodispersed uncharged colloidal systems in which particles interact via short-ranged square-well (SW) potentials. These results were used to examine the adequacy of analytical results based on the so-called adhesive-hard-sphere (AHS) model, which depends on a single parameter

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known as the "adhesiveness" parameter (in addition to the density of the system). Structure factors and the equation of state for this model can be obtained analytically with sufficient accuracy in the Percus–Yevick (PY) approximation [2]. The adhesiveness parameter can be determined by mapping the SW potential onto the AHS model, by equating their respective second virial coefficients. Detailed comparisons of theoretical predictions with simulations show that the AHS model is sufficiently accurate to describe structure factors of the SW fluids over a range of volume fractions when the range of the square-well attraction is less than about one-fifth of the particle diameter.

The purpose of the present work is to illustrate the adequacy of the analytical solution of the AHS model for describing both structure factors and phase diagrams of square-well fluids. To meet this goal, comparisons of theoretical predictions with Monte Carlo simulation results for SW fluids under conditions relevant to real colloidal dispersions [3, 4] are presented.

2. THEORY

We consider interparticle interactions of the following form

$$\beta u_{\mathrm{SW}}(r)=\begin{cases}\infty, & R=r/d<1\\ -\Gamma_{\mathrm{SW}}, & 1\leqslant R<R_{\mathrm{SW}}\\ 0, & R\geqslant R_{\mathrm{SW}}\end{cases}\tag{1}$$

where r is the center-to-center separation distance between particles of diameter d and $\beta=1/k_{\mathrm{B}}T$, k_{B} being the Boltzmann constant and T the absolute temperature. The parameters R_{SW} and Γ_{SW} are, respectively, the range and the depth of the above square-well potential.

The AHS potential is a limiting case of the SW potential and its interparticle potential is given by [2]

$$\beta u_{\mathrm{AHS}}(r)=\begin{cases}\infty, & R<1\\ \ln[12\tau(R_{\mathrm{AHS}}-1)/R_{\mathrm{AHS}}], & 1<R<R_{\mathrm{AHS}}\\ 0, & R>R_{\mathrm{AHS}}\end{cases}\tag{2}$$

where $(R_{\mathrm{AHS}}-1)$ is the range of the pair potential and τ is a dimensionless parameter known as the *adhesiveness parameter*, which is often assumed to be directly proportional to the temperature T. However, one can also take τ to be an arbitrary function of T and, in the case of colloidal systems, it can in addition be a function of salt concentration, pH of the solution, concentration of polymer additives (if any), etc. The values of τ and ϕ at the critical point of the AHS fluid are $\tau_c = 0.098$ and $\phi_c = 0.12$. In our calculations, τ is determined analytically by equating the second virial coefficient of the AHS fluid to that of the SW fluid by means of the relation $\tau^{-1} = 4\{(R_{SW}^3 - 1)[\exp(\Gamma_{SW}) - 1]\}$, as already discussed in detail in Ref. 1.

The structure factor $S(q)$ of the SW fluid can be written as

$$S(q) = [1 - (6/\pi)\,\phi C_{SW}(q)]^{-1} \tag{3}$$

where C_{SW} is the direct correlation function of the SW fluid in q-space, q being the magnitude of the wave-vector $\mathbf{q}$, and ϕ is the volume fraction of the particles, i.e., $\phi = (\pi/6)\,\rho d^3$, with ρ the number density. The static structure factor $S(q)$ can be measured by radiation scattering.

Previous theoretical studies suggest that the values of R_{SW} and Γ_{SW} appropriate in the case of many uncharged colloidal dispersions (and in particular in nonionic reverse micelles) lie in the following ranges: $1.01 < R_{SW} < 1.2$ and $1 < \Gamma_{SW} < 4$ [4–6]. Accurate analytical solutions for the correlation function and thermodynamic properties of SW fluids are not available in the above ranges of R_{SW} and Γ_{SW}. However, our previous study [1] suggests that the AHS model can represent the structure factor and thermodynamic properties of SW fluids adequately when the SW interaction is short-ranged. The structure factor and the equation of state for the AHS model can be obtained accurately in *closed analytical* forms by means of the Percus–Yevick approximation [1, 2]. Therefore, we approximate Eq. (3) by

$$S(q) = [1 - (6/\pi)\,\phi C_{AHS}(q)]^{-1} \tag{4}$$

where C_{AHS} is the direct correlation function of the AHS model in q-space and can be obtained analytically [1].

3. MONTE CARLO SIMULATIONS

We have performed canonical-ensemble Monte Carlo simulations for the structure factor of SW fluids in order to test the adequacy of the theoretical predictions. Details of the simulation method are presented elsewhere [1, 7, 8]. In these simulations, the number of particles, N, is fixed at 500 in a cubic box of length $L = (\pi N/6\phi)^{1/3}$. The usual periodic boundary conditions are used, and the initial configurations of the particles are chosen randomly or are obtained from previous runs. In each simulation, at least four million initial configurations are rejected to eliminate the effects of the starting configurations. The structure factor $S(q)$ is then calculated from appropriate averages over two to three million configurations.

Results for the phase equilibria are obtained from our own Monte Carlo simulations and from molecular dynamics simulations available in the literature. The Monte Carlo results are based on Gibbs-ensemble simulations [9–11] in which the two coexisting homogeneous phases are simulated simultaneously in two separate boxes (thus avoiding interfaces). The details of this method may be obtained from the original references cited above. It suffices to note here that these simulations lead to a fairly high level of accuracy in the results. The molecular dynamics results for phase equilibria are obtained by constructing an equation of state from the results of the simulations [12], from which free energies are computed by means of standard techniques.

4. RESULTS AND DISCUSSION

4.1. Structure Factors

In a recent study, Huang et al. [4] have shown that microemulsions and inverted micellar solutions consisting of aerosol-OT (AOT) surfactants dispersed in oil can be described well by the SW potential. Using a random-phase approximation (RPA) in combination with a square-well potential, they fitted the structure factors of the above microemulsion and micellar systems at $\phi = 0.07$ and found that the appropriate SW parameters are $R_{SW} = 1.02$, $\Gamma_{SW} = 3.83$ for the microemulsions, and $R_{SW} = 1.1$, $\Gamma_{SW} = 0.92$ for the micellar system. We use these sets of values of the square-well parameters in order to test the validity of the AHS approximation.

In the case of the microemulsion, our present method of determining τ shows that the values of the SW parameters ($R_{SW} = 1.02$, $\Gamma_{SW} = 3.83$) correspond to an equivalent τ value of 0.0906. Since the AHS fluid with the above value of τ is in a two-phase state at the volume fraction reported in Huang et al. ($\phi = 0.07$), we take a slightly lower value for the contact potential, i.e., $\Gamma_{SW} = 3.7$, so that a new value of τ, equal to 0.1035, is obtained for the AHS model. The PY solution of the AHS model can now be obtained at $\tau = 0.1035$ for the structure factor. We have also performed Monte Carlo simulations for $S(q)$ at $\phi = 0.07$ using the new values of the SW parameters ($R_{SW} = 1.02$, $\Gamma_{SW} = 3.7$), under the assumption that the effect of such a small difference in the two values of Γ_{SW} on the structure is negligible. The validity of this assumption is confirmed by the results shown in Fig. 1, where the Monte Carlo results of Huang et al. for the original parameter set ($R_{SW} = 1.02$, $\Gamma_{SW} = 3.83$) are also given. The two MC results agree well within statistical errors, thereby establishing the negligible influence of the small change in Γ_{SW}. The prediction of the AHS model is also shown in Fig. 1. It is clear that the AHS model is in excellent

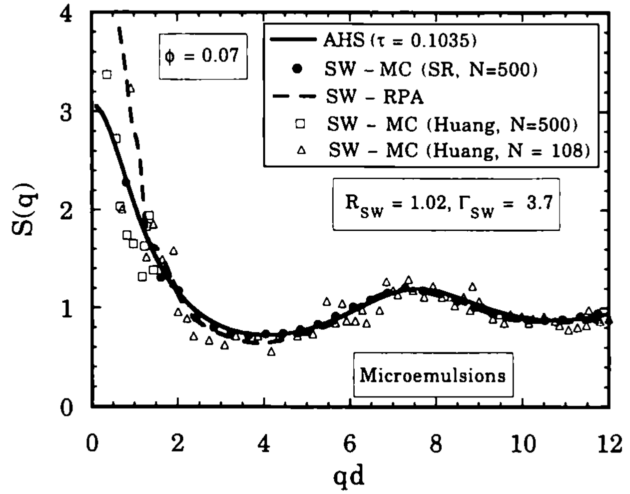

Fig. 1. Comparison of structure factors for the microemulsions predicted by the AHS model, SW-RPA [4], and Monte Carlo simulation at $\phi = 0.07$ and $R_{SW} = 1.02$, $\Gamma_{SW} = 3.7$. SR denotes present simulation results. "Huang" denotes simulation results of [4]. SW-RPA and Monte Carlo simulation results of Ref. 4 are at $\Gamma_{SW} = 3.83$.

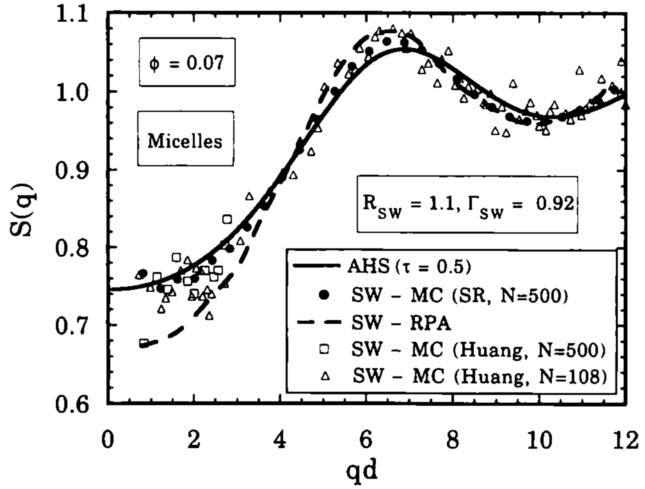

Fig. 2. Comparison of structure factors for the inverted micellar system predicted by the AHS model, SW-RPA [4], and Monte Carlo simulation at $\phi = 0.07$ and $R_{SW} = 1.1$, $\Gamma_{SW} = 0.92$. SR denotes present simulation results. "Huang" denotes simulation results of [4].

agreement with our Monte Carlo simulations over the entire range of q. Also shown in the figure are the results obtained from the SW-RPA theory [4], from Fig. 3b of Ref. 4. These results show that (i) the SW-RPA approximation is inaccurate in the low-q limit, and (ii) the AHS approximation offers a convenient and highly accurate estimate for the structure for the microemulsion.

In Fig. 2 we present results for the structure factors of an inverted micellar solution also investigated by Huang et al. [4]. The volume fraction for this system is again $\phi = 0.07$, but the square-well parameters differ significantly ($R_{SW} = 1.1$ and $\Gamma_{SW} = 0.92$) and correspond to 0.5 for τ in the AHS model. The comparison between the predictions of the AHS model and the results of the simulation in Fig. 2 shows again that the AHS model agrees very well with the exact results from our Monte Carlo simulations (which are more accurate than the results presented by Huang et al.). Moreover, as in the case of the microemulsion system, the SW-RPA fails to reproduce simulation results.

4.2. Phase Diagrams

Figure 3 shows the phase diagram predicted by the AHS model for the two values of R_{SW}; the correspondence between the set $\{R_{SW}, \Gamma_{SW}\}$ and the adhesiveness parameter τ is described in Section 2. Also included in the figure are the results for the square-well model based on Monte Carlo simulations for $R_{SW} = 1.25$ [9–11] and molecular dynamics simulations for $R_{SW} = 1.5$ [12]. As can be seen, the AHS model is better in the case of the shorter-ranged ($R_{SW} = 1.25$) SW potential than in the case of the one with the longer range ($R_{SW} = 1.5$). In both cases, however, the phase diagrams are consistent with the theory. These comparisons indicate that for smaller values of R_{SW} [i.e., $(R_{SW} - 1) < 0.2$, appropriate for several colloidal systems with short-range attraction] the phase stability for the square-well-type potential can be described adequately by mapping the SW potential onto the AHS model.

In the above comparisons the adhesiveness parameter τ has been treated as being proportional to the temperature. However, applications of the AHS model to analyze experimental data on structure factors and phase diagrams of nonionic micellar systems show that τ can be inversely proportional to the temperature. For example, such an application of the model for describing phase separation in a micellar system has been given recently by Menon et al. [13], using the experimental data of Zulauf and Rosenbusch [14] for the phase diagram for a surfactant/water mixture ($C_8E_5 + H_2O$) beyond the critical micelle concentration (cmc). This system shows a phase separation beyond the cmc as a function of temperature T,

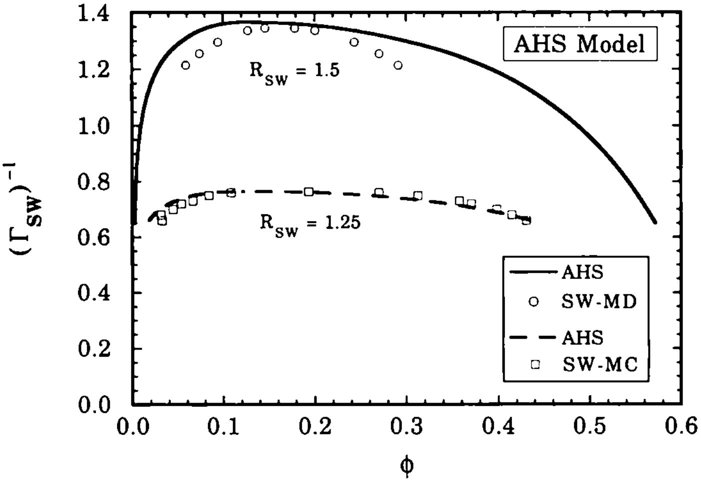

Fig. 3. Phase diagram predicted by adhesive-hard-sphere model for the square-well model. Simulation results for the square-well model are from Refs. 9–12.

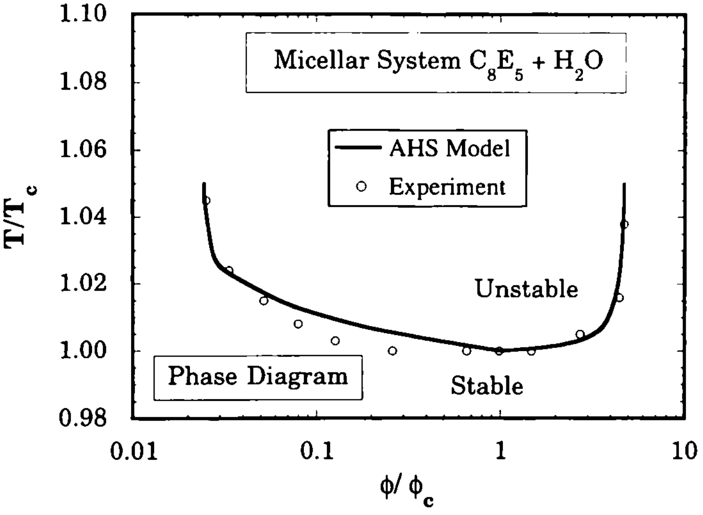

Fig. 4. Phase diagram predicted by adhesive-hard-sphere model for a nonionic micellar system $C_8E_5 + H_2O$ following Ref. 13. Experimental data are from Ref. 14.

with one phase consisting of a dilute micellar solution with monomeric surfactants and the other with a dense micellar phase. This T vs. ϕ phase diagram has been fitted with the AHS model, and the result is shown in Fig. 4. Since the parameter τ obtained from such a fit is found to be inversely proportional to T, it gives rise to a lower-critical phase diagram in the T vs. ϕ domain. These results show that the AHS model is a reasonably good approximation for describing phase separation in colloids under appropriate conditions and that both lower-critical and upper-critical phase behavior may be predicted, depending on the relationship between the AHS parameter τ and the physicochemical properties of the dispersions.

5. CONCLUSIONS

Comparisons of the predictions of the AHS model with Monte Carlo results for *structure factors* are made for nonionic microemulsions and inverted micellar systems consisting of the AOT surfactant dispersed in oil. The comparisons show that the AHS model describes the $S(q)$ of these systems accurately, and represents a significant improvement over the SW-RPA theory [4], especially in the compressibility limit (the low-q region) of the structure factor.

Comparisons of theoretical predictions with simulation results for the *phase diagrams* show that the SW potential can be replaced by an AHS potential with the same second virial coefficient if the range of attraction of the SW potential is sufficiently short, i.e., if $R_{SW} < 1.2$. In general, the above results indicate that the AHS model can be quite useful for describing phase separation in colloidal dispersions.

The present mapping of the SW potential onto the AHS model based on the second virial coefficients shows that τ is directly proportional to the contact potential Γ_{SW} for fixed values of the range of interaction. Since the contact potential Γ_{SW} is assumed to be independent of temperature T, τ becomes directly proportional to T. Consequently, the AHS model predicts an upper-critical stability region on the $(\Gamma_{SW})^{-1}$ vs. ϕ plane as evident from Fig. 3. When τ is inversely proportional to T, in the Γ_{SW} vs. ϕ plane, Fig. 3 will correspond to a lower-critical phase separation. Such a behavior is seen in Fig. 4 for the nonionic micellar solution. Therefore, the AHS model can describe both upper-critical and lower-critical phase diagrams on the T vs. ϕ plane (or in other parameter spaces), depending on how Γ_{SW} is affected by the change in the temperature, volume fraction, and other parameters.

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