Structural study of emulsions stabilized by charged nanoparticles

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Abstract.The aim is a quantitative study of the structure of the Pickering emulsionsthat are stabilized by charged nanoparticles. We assume that the interaction potential between droplets is of Sogami type. First, we compute the structural properties using the *Integral Equation Method* with the so-called *hybridized-mean spherical approximation* (HMSA). Finally, the validity of this method is tested by confronting the results of the correlation functions found by HMSA integral equation with those from Molecular Dynamics (MD) simulations.

1. Introduction

Very often, an emulsion presents in the form of oil droplets in water or water droplets in oil, but in both cases the droplets need to be stabilized to prevent them from re-coalescing, because when two droplets come into contact, they naturally coalesce to minimize the surface energy. Emulsion droplets stabilization is often achieved through the addition of amphiphilic molecules such as surfactants, which act by decreasing the interfacial tension between the phases. In addition to molecular surfactants, solid particles having intermediate wetting properties can also be used to stabilize emulsions. In fact, the solid particles form a shell protecting the emulsion droplets against coalescence. Emulsions stabilized by solid particles are known as Pickering emulsions [1, 2],in which emulsifiers irreversibly adsorb at the oil–water interface and require a much higher energy for desorption as compared to conventional surfactants [3]. In addition to the high stability of Pickering emulsions, the stabilization of emulsions by solid particles gives the possibility to control the size of the droplet of the emulsion, because the solid stabilizing particles are necessarily smaller than the emulsion droplets. Solid particles of nanometric size allow the stabilization of droplets as small as few micrometers diameter. Micron-sized solid particles can stabilize larger droplets, the diameter of which possibly reaching few millimeters [4].

The Pickering emulsions have a complex structure which is present in the form of a core with discrete spherical particles arranged on a (spherical) surface. Therefore, simple models that may have a crude resemblance to the structures are often considered. The most frequently used model for these systems is to assume a core–shell structure, where the shell has a homogenous density and thickness [5, 6]. This approach is not strictly appropriate but may often be valid if the preparing conditions (such as wettability, charge, concentration, shape and size of particles, etc.) are right.

In this work, using the model of core-shell supra-colloids that we assume interacting via Sogami and Ise potential, we investigate the structural properties of Pickering emulsions, stabilized by charged nanoparticles, i.e. formed by micrometer-sized droplets, through the use of the so-called integral equation method. We validate the use of this method by MD simulation.

This paper is organized as follows. In Sec. 2, we present the useful theoretical backgrounds. Results and discussion are the aim of Sec. 3. Finally, some concluding remarks are drawn in the last section.

2. Theoretical backgrounds

2.1. Interaction Potential

We consider a system of supra-colloids of diameter σ, interacting via the Sogami and Ise potential which has usual screened Coulomb repulsion and also an attractive part leading to a secondary minimum [7, 8], defined as

$$U_s(r) = \frac{Z^2 e^2}{2\varepsilon}\left[\frac{\sin(\kappa\sigma/2)}{(\kappa\sigma/2)}\right]^2 \left[\frac{2+\kappa\sigma\,\coth(\kappa\sigma/2)}{r} - \kappa\right] exp(-\kappa r), (1)$$

wherer is the inter-particle distance, and κ is the inverse screening length that is given by

$$\kappa^2 = \frac{4\pi}{\varepsilon k_B T}(\rho Z e^2 + C_s). \qquad (2)$$

Here ρ is the number density of droplets, each having a surface charge Ze , C_s is the salt concentration, ε is the relative dielectric constant of water and k_B is the Boltzmann's constant. The absolute temperatureT is fixed to the value 298°K. Then, the chosen potential depends on seven parameters:$(Z, \sigma, \kappa, \varepsilon, \rho, C_s, T)$. The above potential exhibits a minimum point for

$$r_m = \frac{\frac{\kappa\sigma}{2}\coth\left(\frac{\kappa\sigma}{2}\right)+1+\left[\left(\frac{\kappa\sigma}{2}\coth\left(\frac{\kappa\sigma}{2}\right)+1\right)\left(\frac{\kappa\sigma}{2}\coth\left(\frac{\kappa\sigma}{2}\right)+3\right)\right]^{1/2}}{\kappa}. (3)$$

2.2. Theory and simulation details

The static description of the homogenous classical liquids, whose particles are taken to interact through an effective pair potential, can be obtained from the exact Ornstein-Zernike (OZ) [9] equation which represents the starting point of the Integral Equation Theory (IET).

$$h(r) = c(r) + \gamma(r) = c(r) + \rho \int c(r')h(|r-r'|)dr' \qquad (4)$$

The total correlation function $h(r)$ is a sum of two contributions. The first contribution is the direct correlation function, $c(r)$, which represents the correlation between a particle of a pair with its closest neighbor separated by a distance r. The second contribution is the indirect correlation function, $\gamma(r)$, which represents the correlation between the selected particles of the pair with the rest of the fluid constituents. To solve equation (4), an approximation (closure) relation which relates the correlation function $c(r)$ and $h(r)$ to the pair-potential should be added. In this study, we will use HMSA,

$$g^{HMSA}(r) = \exp(-\beta u_o(r))\left\{1 + \frac{\exp\{f(r)[g(r)-1-c(r)-\beta u_1(r)]\}-1}{f(r)}\right\}, \quad (5)$$

where$u_o(r)$ and $u_1(r)$are respectively the short-range and the long-range contributions of the potential according to Weeks *et al.* [10],

$$u(r) = u_o(r) + u_1(r), (6)$$

where

$$u_o(r) = \begin{cases} u(r) - u(r_m), & r < r_m \\ 0, & r > r_m, \end{cases} (7)$$

and

$$u_1(r) = \begin{cases} u(r_m), & r < r_m \\ u(r), & r > r_m. \end{cases} (8)$$

Here, r_m denotes the position of the minimum of the potential, and $f(r)$ is the mixing-function, proposed by Bretonnet and Jakse [11], which ensures the requirement of the thermodynamic consistency, in calculating the isothermal compressibility by two different routes.

Within the framework of MD method, the equations of motion are solved in the microcanonical ensemble using the velocity Verlet algorithm [12] with the thermostat of Berendsen [13], in order to keep the temperature constant. Periodic boundary conditions are applied to remove the surface effects and simulate an infinite system. In the following, we will use dimensionless units, where the length unit is σ, time in units of $\sigma\sqrt{m/\epsilon}$, where ε is the depth of the interaction potential and m is the droplet mass, $k_B T$ is the energy unit, and $L_0 = \sqrt[3]{6V/\pi N} \times N$ is the box size, where N is the number of droplets and V is the volume of simulation box (in periodic conditions). MD simulations where carried out with 1728 particles and the (reduced) time step for the velocity Verlet algorithm is chosen to be 0.01.

3. Results and discussions

We start by comparing the theoretical results for the correlation functions **g(r)** calculated from HMSA approximation and MD simulation. From the figure 1(a)-(b) we particularly note that the peaks in the correlation functions from molecular dynamics simulations are in good agreement with the corresponding values calculated from the integralequation. Thus, HMSA solution of OZ relation provides a very accurate description of our system.
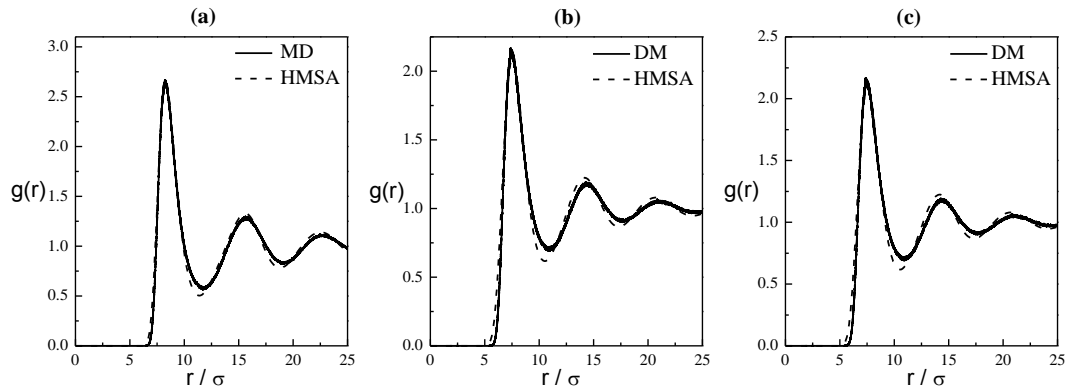

Figure 1.Comparison for the correlation function calculated from HMSA approximation and from MD simulation, (a) at $Z = 2000$ and $\rho^* = 0.0020$ and $\sigma = 20000$Å, (b) at $Z = 2000$ and $\rho^* = 0.0025$ and $\sigma = 20000$Å, (c) at $Z = 2000$ and $\rho^* = 0.0025$ and $\sigma = 30000$Å.

3.1. The density effect

In this section, we study the effect of the increasing density of the supra-colloids, at fixed $\sigma = 20000$Å and $Z = 2000$. Figure 2shows the correlation function for different densities obtained by the HMSA closure. It is clear from this figure, on the one hand, that as the density of supra-colloids increases, the height of the main peak of $g(r)$ steadily increases (1.33 for $\rho^* = 0.0010$ to 2.09 for $\rho^* = 0.0025$) and the peak positions steadily decreases in r.Such a result indicates that, when the number density is increased, the local density around a droplet, taken as origin, also increases. The decreasing peak position in the structure factor (figure 3) with the increasing density of supra-colloids is also consistent with this feature. On the other hand, the height of the second peak increases at increasing density and is absent at$\rho^* = 0.0010$. Thus, a local structural order is established, represented by the first and second peak, and the local density increases (height of the main peak), when the supra-colloid density increases.
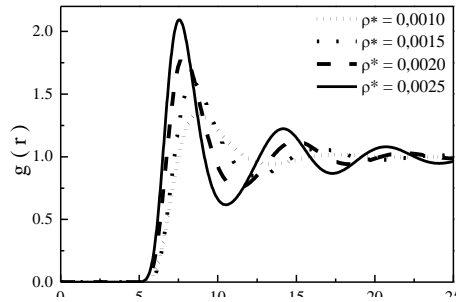
Figure 2. Variation of the correlation functionwith the reduced density ($\rho^* = \rho\sigma^3$) of supra-colloids, at fixed charge ($Z = 2000$) and fixed size ($\sigma = 20000$Å).
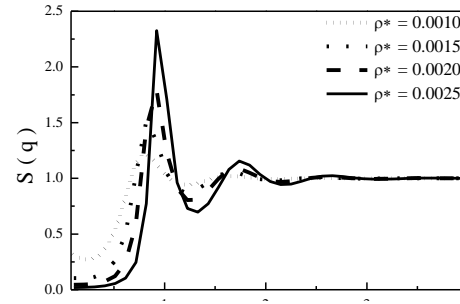
Figure 3. Variation of the factor structure with the reduced density of supra-colloids at fixed charge ($Z = 2000$) and fixed size ($\sigma = 20000$Å).

3.2. The charge effect

The charge of the supra-colloids is varied from 500 to 2000 at fixed $\boldsymbol{\sigma = 20000}$Å and $\boldsymbol{\rho^* = 0.0020}$. The effective pair-potential is shown in figure 4. It explains that as the charge of particles is increased, the potential depth is diminished. Thus, the effective interaction between the supra-colloids becomes less and less attractive as the charge increases and finally it becomes repulsive. This tendency is confirmed in figure 5 and figure 6 that represent the correlation function and structure factor, respectively. In fact, we remark that the position of the principal peak of the correlation function is shifted towards the higher values by an increasing of the charge. In contrast, the main peak of the factor structure is shifted towards smaller distances as the charge of particles increases.
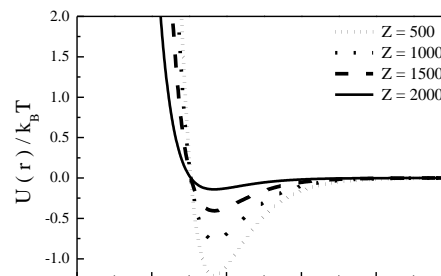

Figure 4. Variation of the effective pair-potential with the charge of supra-colloids, at fixed density ($\rho^* = 0.0020$) and fixed size ($\sigma = 20000$Å).
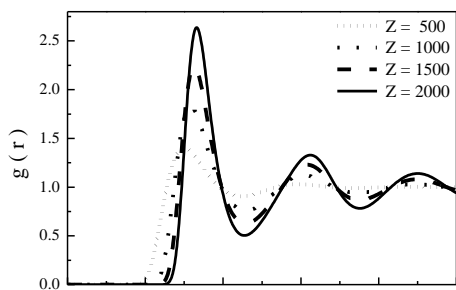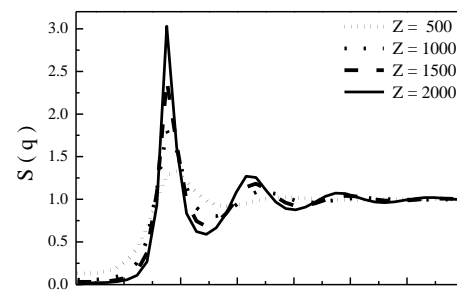

Figure 5. Variation of the correlation function with the charge of supra-colloids at fixed density ($\boldsymbol{\rho^* = 0.0020}$) and fixed size ($\boldsymbol{\sigma = 20000}$Å).

Figure 6. Variation of the factor structure with the charge of supra-colloids at fixed density ($\boldsymbol{\rho^* = 0.0020}$) and fixed size ($\boldsymbol{\sigma = 20000}$Å).

3.3. The size effect

In this section, the effect of the variation of the size of the supra-colloids on the structure is studied at $\rho^* = 0.0020$ and $Z = 2000$. The variation of the effective pair-potential (figure 7) is very much similar to that of the charge variation, i.e. as the size increases; the effective interaction between the supra-colloids becomes less and less attractive. The figure 8 shows that the height of the principal peak of the correlation-function decreases progressively, and its position is shifted to higher values, as the droplet size is increased. This means that the size of the local ordered region made of first neighbors (around some droplet) increases with increasing droplet diameter.This result is confirmed by the variation of the factor structure shown in figure 9.
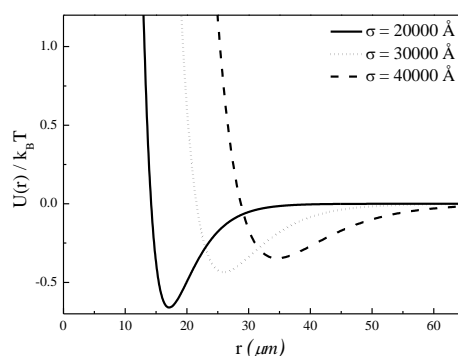

Figure 7. Variation of the effective pair-potential with the size of supra-colloids at fixed density ($\rho^* = 0.0020$) and fixed charge ($Z = 2000$).
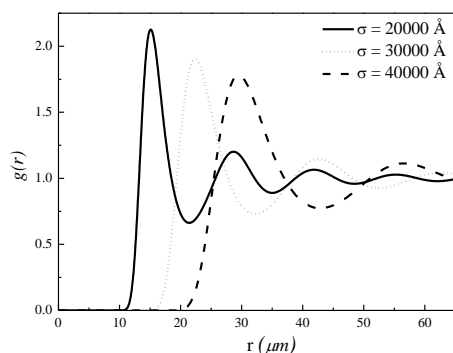

Figure 8. Variation of the correlation function with the size of supra-colloids at fixed density ($\rho^* = 0.0020$) and fixed charge ($Z = 2000$).
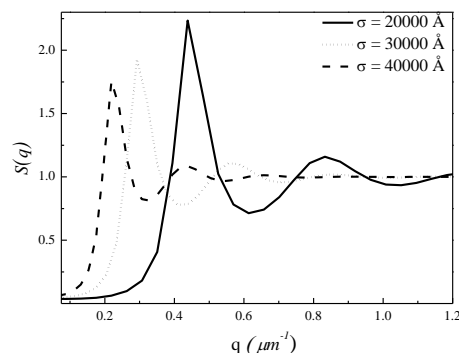
Figure 9. Variation of the factor structure with the size of supra-colloids, at fixed density$\rho^* = $ **0.0020**and fixed charge ($Z=2000$).

4. Conclusion

The structure of Pickering emulsions, using the model of supra-colloids, is studied through of the use of the integral equation method. We find a systematic variation in correlation functions, the structure factors and the effective pair-potentials as the density, the charge and the size of supra-colloid are varied.

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