

Entropically driven ordering in a binary colloidal suspension near a planar wall

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The local ordering of a binary hard-sphere mixture with a size ratio 1:10 near a planar wall is investigated by means of integral equation theory. We find that when the bulk volume fraction of the smaller particles is greater than 15%, the larger particles (at a bulk volume fraction of 1% and higher) become highly localized on the wall surface, forming a quasi-two-dimensional surface-localized monolayer. Our results are discussed and compared against computer simulation data with an effective one-component Hamiltonian that is based on sphere-sphere and sphere-wall depletion potentials.

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For many years, it has been believed that the hard-core interaction is only a purely theoretical prototype that does not exist in reality. It now appears that this situation is changing. To a good approximation, charge-stabilized polystyrene spheres with a high degree of screening behave essentially as hard-sphere (HS) colloidal particles. Due to this, in recent years the HS fluid is a subject that unites computational and experimental efforts. Well-characterized colloidal dispersions have become useful theoretical and laboratory models for the understanding of self-organization and structural phase transitions of matter in three-dimensional (3D) and 2D geometries [1].

Recently, the phase diagram of mixtures of charge-stabilized polystyrene spheres of two different sizes has been investigated by Kaplan *et al.* [2] and Dinsmore, Yodh, and Pine [3]. These authors have observed a bulk phase separation that is in qualitative agreement with the theoretical predictions [4–6], and found a new phase transition that involves coexistence between the bulk disordered phases and an ordered phase located on the walls. They suggested that the surface induced phase separation, similar to bulk separation, is promoted by an entropic “excluded-volume” effect. At present, there is a semiquantitative explanation of this effect, which is argued by the increase of the volume accessible to the smaller (*S*) particles when the larger (*L*) sphere is brought into contact with other larger sphere or is adsorbed on the wall. When the smaller spheres sufficiently outnumber the larger spheres, the gain in entropy of the system causes an effective attraction between two larger spheres and larger spheres and the wall. The predicted estimate of the magnitude of the attraction energy is as much as 10 kT between two larger spheres [7] and approximately twice as great between a larger sphere and a planar wall [2]. In a separate publication, Dinsmore, Yadh, and Pine [8] have shown how similar effects can be used to position the larger particles of a binary mixture on a substrate, or to move them in a predetermined way. The phenomenon of bimodal par-

ticle structuring near the wall is also a suitable model to understand the mechanism of pollutant removal from solid surfaces, the wetting of solids by micellar solutions, etc.

The nontrivial statistical mechanics model of the system in which we are interested can be imagined as a huge vessel of volume *V* filled by a bidisperse suspension that is a two-component mixture of larger and smaller neutral HS balls of the diameters *D* and *d*, respectively. The size ratio, *D*:*d*, is fixed to be 10:1. The walls (*W*) of the vessel are made from the same material as the colloidal particles, i.e., they are an impenetrable and a structureless confinement that interact with the suspension species through a hard-core potential, φ_{iW} [*i* = *S*, *L*]. Far from the walls, i.e., the middle part of the vessel, the fluid is homogeneous and we refer to this as the bulk (*b*). The number density of the smaller component in the bulk is ρ_S^b , which has a volume fraction $\phi_S = \pi\rho_S^b d^3/6$, whereas the larger component has a number density ρ_L^b and its bulk volume fraction is $\phi_L = \pi\rho_L^b D^3/6$. The behavior of the colloidal suspensions is normally studied at fixed pressure and temperature by changing the composition, i.e., ϕ_L or ϕ_S . To design such conditions in our study, we used the osmotic equilibrium approach [5]. According to this, one of the walls has been replaced with the osmotic membrane providing the thermodynamic contact between the vessel and reservoir. The membrane is permeable to the smaller species and their number density and volume fraction in the reservoir are ρ' and ϕ' , respectively, with the same chemical potential throughout.

The bulk part of this model has been intensively studied by means of integral equations (IE) and density functional theories as well as by computer simulations (see Ref. [6] and references cited there in). However, for some reason the relevant studies [9–11] that we have found published in the literature for the inhomogeneous part have been limited to relatively low size asymmetries only, namely, size ratios *D*:*d* that do not exceed 3:1 [usually, 10:1 has been used for the bulk]. Only simple intuitive models to explain experimental data for colloidal bidispersion confined to the plane substrate have been reported so far [3,12].

The main goal of this note is to obtain a microscopically motivated treatment of the local ordering in a binary colloidal

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dal suspension near a flat wall. To realize our intention, we used the IE approach that has been derived originally for the single-component HS fluid near a planar wall by Henderson, Abraham, and Barker [13]. To extend this to the case of a bidisperse system, the Ornstein-Zernike relation has been written for the three-component mixture of smaller, larger, and wall species. The so-called ‘‘wall limit’’ (the number density of the wall species tends to zero whereas their diameter tends to infinity) leads to the singlet-level description of the local density in a binary mixture close to a planar wall.

The question of what is an appropriate approximation for use in an IE approach is both controversial and unresolved [14]. However, the evidence indicates [15] that IE using the Percus-Yevick (PY) closure is reasonably reliable for the task outlined here. By applying the PY closure for the particle-wall correlations, the equation for the local density suitable for numerical work is written as follows:

$$y_i W(z) = 1 + 2\pi \sum_{k=S,L} \rho_k^b \int_{z-\sigma_{ik}}^{z+\sigma_{ik}} S_{ik}(|z_1-z|) \times [y_k W(z_1) e^{-\varphi_i W(z_1)/kT} - 1] dz_1, \quad (1)$$

where z is the separation of the particle center from the wall, $y_{iW}(z) = g_i(z) e^{\varphi_i W(z)/kT}$ with $g_i(z) = \rho_i(z)/\rho_i^b$ being the normalized density profile, and $\sigma_{SS} = d$, $\sigma_{LL} = D$, $\sigma_{SL} = \sigma_{LS} = (d+D)/2$. The key element of the entire scheme is the function $S_{ij}(|z|) = \int_{|z|}^{\infty} r c_{ij}^b(r) dr$, where $c_{ij}^b(r)$ is the direct correlation function between a pair of suspension particles in a bulk [16,17].

We have performed a set of ‘‘experiments,’’ each starting with a monodisperse suspension of smaller particles but at different initial bulk volume fractions ϕ_S^0 . The latter has been varied from 5% to 30%. At this initial stage, the volume fraction in the bulk part of the vessel equals that in the reservoir, $\phi_S = \phi^x \equiv \phi_S^0$, and the suspension behaves as a pure monodisperse adsorbate of the smaller particles. The relevant monodisperse local density $g_S(z)$ at $\phi_S = 0.20$ is shown in Fig. 1. This density distribution reflects the well-known particle layering phenomena in a monodisperse adsorbate and the PY approximation (solid lines) reproduces this rather well, compared with the Monte Carlo (MC) data (open squares). The particle layers are well defined though they are not perfectly organized, i.e., they are diffuse with the actual thickness extending until around one and a half particle diameters. We note that the same is valid for monodisperse suspension of only larger particles, which is illustrated in Fig. 1 as well.

In order to monitor the effect of bidispersity on the local ordering in the vicinity of the wall the larger particles have been added step by step to the bulk of monodisperse suspension of the smaller particles. Equilibrium between the osmotic pressure of the reservoir, Π^r , and that of the bidisperse suspension, Π , has been reached in each step at the reservoir volume fraction ϕ^r maintained at the initial monodisperse value, $\phi^r \equiv \phi_S^0$. The equilibrium bulk volume fraction of the smaller particles used in the solution of Eq. (1), is calculated

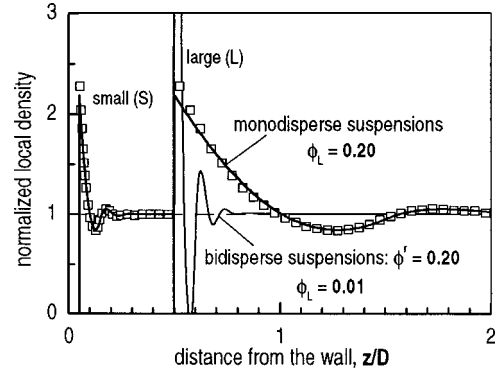


FIG. 1. Normalized local density of the small and large particles with a size ratio $d:D = 1:10$ near a planar wall. Solid lines and open squares are PY results and MC data, respectively, for pure monodisperse suspensions of only small and only large particles at bulk volume fraction $\phi = 0.20$ in each case. The dotted line is the PY result for the bidisperse suspension at a reservoir volume fraction $\phi^r = 0.20$ and a bulk volume fraction of the large particles, $\phi_L = 0.01$; the density distribution of the small particles in this case is unaffected and remains the same as in the monodisperse case.

from the equation of state derived by Lekkerkerker and Stroobants [5] within the framework of a free volume approach,

$$\rho_S^b = \alpha \rho^r (1 - \Pi_L^0 / g \Pi^r), \quad (2)$$

where Π_L^0 is the osmotic pressure of the pure larger-particle suspension and α is the fraction of the volume in the bidisperse system in which the smaller particles can move. Osmotic pressures Π_L^0 , Π^r , and free volume fraction α , have been calculated within the PY approximation and the resulting ρ_S^b has been shown to agree well with the MC data [6].

Proceeding in this way, new features in the ordering of the mixture of the larger and smaller particles near a planar wall were found. First of all we can see that at reservoir volume fraction $\phi^r = 0.20$ the low amount of larger particles (up to 5% of the volume fraction) being added to the bulk, forms the thin sublayer structuring near the wall with a well-defined surface-localized monolayer (dotted line in Fig. 1). The number of sublayers decreases if the reservoir volume fraction becomes smaller; however, the surface monolayer still is well defined even at low reservoir volume fraction, such as $\phi^r = 0.05$ (dotted line in Fig. 2). If the reservoir volume fraction does not exceed $\phi^r = 0.15$, further increasing of the volume fraction of the larger particles in bulk region starts to destroy their sublayer structuring near the wall and finally turns the local ordering to that we already observed for the monodisperse case (compare solid lines for the larger particles in Figs. 1 and 2). However, if the volume fraction of the smaller particles is substantial, i.e., $\phi^r \geq 0.15$, the sublayer structuring of the larger particles near the wall becomes irreversible and is preserved even if volume fraction of the larger particles is high (solid line in Fig. 3). Summarizing, we have confirmed the conclusions obtained from the observations [2,3] that the presence of the smaller particles becomes crucial and has strong impact on the ordering of the larger species near a planar wall. No layering phenomena

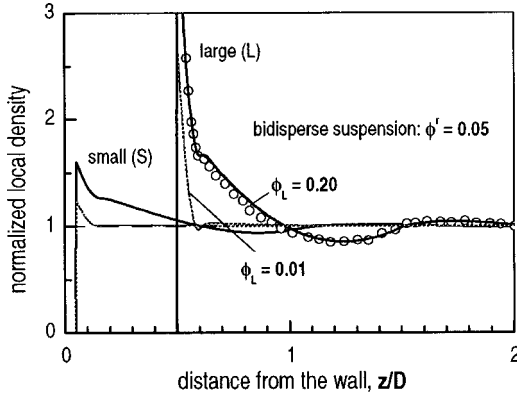


FIG. 2. Normalized local densities for the bidisperse suspension of the small and large particles with a size ratio $d:D=1:10$ near a planar wall. Reservoir volume fraction $\phi^r=0.05$. The dotted and solid lines are PY results for true bidisperse suspension at a bulk volume fraction of the large particles, $\phi_L=0.01$ and 0.20 , respectively. Open circles correspond to MC data for an effective bidisperse suspension at the same composition as in the case of the solid line.

near the wall at a low concentration of the larger particles in a bulk and no sublayer structuring near the wall are observed in monodisperse suspensions.

Although our main intention was not so much to obtain extremely accurate results for local densities but rather to give a theoretical groundwork and interpretation of the bidispersity effect on local ordering near the wall, to have some estimate for the accuracy of our conclusions we test our theoretical results against computer simulation data. Since direct simulations of a highly asymmetric binary mixture are prohibited by slow equilibration when the volume fraction of the smaller species becomes high, we applied a strategy [6], which is based on employing an effective one-component Hamiltonian H^{eff} . Using for H^{eff} the so-called depletion po-

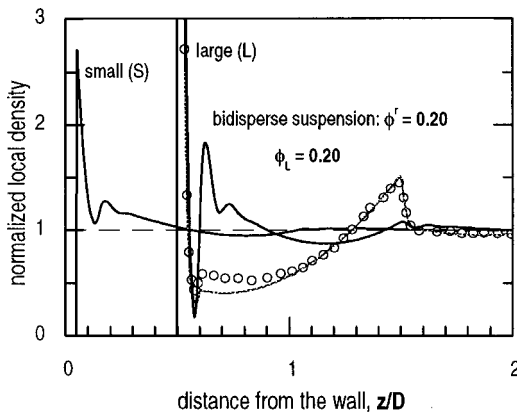


FIG. 3. Normalized local densities for the bidisperse suspension of the small and large particles with a size ratio $d:D=1:10$ near a planar wall. Reservoir volume fraction $\phi^r=0.20$ and bulk volume fraction of the large particles, $\phi_L=0.20$. The solid lines are the PY result for a true bidisperse suspension while the open circles and dotted line correspond to MC data and the PY result, respectively, for an effective bidisperse suspension at the same composition as in the case of true suspension.

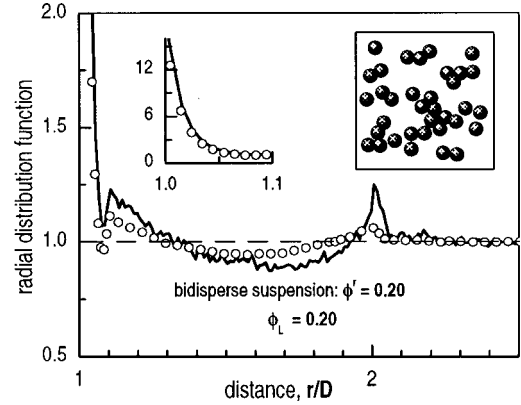


FIG. 4. The bulk (open circles) and in-surface monolayer (solid line) radial distribution functions between the large particles from the MC simulations for an effective bidisperse suspension. The left inset shows $g_{L1}(r)$ near contact. The right inset presents the typical configuration of the large particles within the surface monolayer.

tential u^{dep} [18], which arises between a pair of larger spheres in a background of smaller spheres, Dijkstra, Raij, and Evans [6] successfully simulated the phase behavior of such an *effective* bidisperse mixture and claimed remarkably good agreement with the available simulation data for the *true* binary mixture. In the present paper, following the Derjaguin approximation, we supplemented H^{eff} by the term $2u^{\text{dep}}$ for the larger sphere-wall interaction and employed this in MC simulations of the effective bidisperse suspension near a planar wall. The comparison of the resulting MC data with the PY results for the true bidisperse suspension is illustrated in Figs. 2 and 3. Up to a 10–15% reservoir volume fraction there is good agreement for the local density of larger particles obtained from the two approaches; the agreement becomes remarkably good if the concentration of the smaller species is low (Fig. 2). As the concentration of smaller particles becomes substantial, the MC data confirms the PY prediction for the stable surface-localized monolayer (Fig. 3); however, the two approaches lead to the different shapes of the density profiles of the larger particles behind the surface monolayer. This disagreement between PY results and MC data should not be attributed to the failure of the PY approximation. When Eq. (2) is applied for the effective Hamiltonian as that in MC simulations, both approaches produce almost identical results (dotted line in Fig. 3). Our preliminary calculations trace the observed difference between the PY calculations for true bidisperse suspension and MC data generated with effective Hamiltonian, to the empirical form of depletion potential [6] that neglects the interactions behind the depletion range.

The most striking prediction from the present study is concerned with the existence a surface-localized monolayer of larger particles. We should perhaps note a very evident correlation between the bulk composition, i.e., bulk volume fractions ϕ_L and ϕ_S when the surface monolayer of larger particles becomes well defined and stable with the similar compositions at which a surface crystalline phase was observed [2,3]. As the density of the larger species in the monolayer increases, a question is raised: what is the lateral

structure of the larger particles on the wall surface? The singlet level of the IE theory does not give information about the in-layer correlation functions and, obviously, we cannot answer the above question definitely. Nevertheless, we still can evaluate some information by analyzing the calculated local density variations for the true binary mixture near the wall superimposed with MC data for the effective bidisperse suspension. Both approaches estimate the average number density of the larger species in a monolayer as 3–4 per surface area of ten larger particles for the composition conditions corresponding to Fig. 3. Thus, it is very unlikely that crystalline order of the larger particles can be formed within the monolayer [19]. In Fig. 4 we plot the MC data for the radial distribution functions, $g_{LL}(r)$, between the larger particles within the surface monolayer and the same in the bulk. The very sharp nearest-neighbor peak at $r=D$ gives clear evidence of the clustering of the larger spheres; the weaker but still pronounced sharp peak for in-layer $g_{LL}(r)$ at $r=2D$ indicates a larger size of clusters in the surface monolayer than in the bulk. The right inset of the Fig. 4 shows the snapshot of the typical monolayer configurations of the larger particles during MC simulations. Although the size of

simulation system does not allow us to see big clusters, those we observed indeed do not show crystalline order. At the same time, the surface coverage provided by the smaller particles in the vicinity of the wall is quite high (≈ 240 smaller particles per surface area of one larger particle for the same composition conditions). In conjunction with the strong larger-particle-wall attraction, such a density distribution of smaller particles will limit the movement of larger spheres on the wall [20] forming an effective atomically structured or corrugationlike coverage of the adsorbent surface. This allows us to speculate that the remaining larger particles that are adsorbed on such structured substrate will grow into the crystallites in the direction normal to the wall that are observed experimentally. In this case the formation of the surface monolayer of the larger particles, revealed by the present calculations, might be the necessary condition and physical reason that can explain why surface phase transitions foreshadow the phase transitions in the bulk.

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