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STICKY SPHERES IN PORES: THE EFFECT OF WALL-FLUID ATTRACTION ON SEDIMENTATION EQUILIBRIUM[#]

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Abstract

The sedimentation equilibrium of adhesive spheres mimicking a system of interacting spherical colloidal particles in suspensions in planar pores with adhesive (adsorbing) walls was studied on the basis of the solution to the hypernetted chain/Ornstein Zernike equation. The increasing interparticle adhesive attraction together with the gravity lead to the overall effect on particles to occupy the region of lower altitudes in the pore. It is found that at sufficiently strong stickiness the dense “substrate” being formed at the bottom of the pore behaves as a "condensation nucleus" for the condensation of particles from the bulk phase, the effect predominating the natural tendency of strongly adhesive particles to avoid the confined system. In the case of strongly adsorbing walls, the density profiles show a discontinuity in the slope at a distance of one particle diameter from the wall-fluid contact planes as a consequence of the exclusion volume of adsorbed monolayers. Due to gravity, this and other features are much more pronounced at the lower wall than at the upper one of the same adhesiveness.

Introduction

Theoretical research on the properties of colloidal suspensions in sedimentation equilibrium has received much attention in the recent literature [1-6]. These studies

[#]Dedicated to Prof. Drago Leskovšek on the occassion of his eightieth birthday.

include the application of various molecular models, and the density profiles of colloidal particles in the gravitational field have been determined by using various statistical mechanical approaches [7]. A common feature observed in all cases was the spatially inhomogeneous structure along the direction of action of the external field.

In our previous papers [5,6] we studied the sedimentation equilibrium of a model fluid with an adhesive-sphere (AS) interaction potential [8] mimicking a system of interacting spherical colloidal particles in a planar gap. The wall-fluid distribution function was calculated by the Ornstein-Zernike (OZ) equation [7] in the form suitable for inhomogeneous systems [9-11], supplemented by the hypernetted chain (HNC) approximation for the wall-fluid correlation. It was found that in the presence of gravity, the interparticle adhesive attraction additionally forces the particles toward lower altitudes in the pore. It was also observed that at sufficiently strong stickiness the adhesive fluid accumulated at the bottom of the gap behaved as a “condensation nucleus” for the condensation of particles from the bulk phase, the effect predominating over the natural tendency of strongly adhesive particles to avoid the confined system. This “unexpected” behavior was a consequence of the common effect of gravity plus the interparticle attraction. The same system in the absence of gravity has never shown such behavior [12,13].

The objective of the present paper was to extend these investigations to the case of an adhesive fluid in a planar gap with adhesive walls, a problem which in the absence of gravity has been already extensively treated [14]. The structure of the fluid in the pore and its distribution between the bulk and confined phase are thus affected by an interesting interplay of various interactions, i.e. steric effects, gravity, and the competitive particle-particle and particle-wall adhesion. The details of the model and the method are given in Section 2. In Section 3, the effects of the wall-fluid adhesion on the “condensation” behavior [5] of the fluid in the pore is estimated. The calculated density profiles of adhesive colloidal particles in "closed" pores, i.e. for a constant total amount of fluid in the pore, are presented. The effects of the wall-fluid attraction on the density profiles of sticky particles at different widths of the pore are discussed.

Model and methods

The model used here is similar to that described in our previous articles [5,6]. The sticky hard sphere fluid [8] (denoted by 2), mimicking a system of interacting spherical colloidal particles, is confined between parallel smooth hard plates (1) with lateral dimensions much bigger than the separation between the walls. The only difference is in also considering the short-ranged attraction in the wall-fluid potential of interaction. The fluid confined in the pore is in contact with a reservoir of bulk fluid at the prescribed number density ρ_b. The walls are parallel to the plane $(0,y,z)$, the lower one being located at $x = 0$ and the upper one at $x = L$. The diameter of the spheres is R, so only the width $L' = L-R$ is available to their centers. The particles interact among themselves through the square-well potential $\phi_{22}(r)$ in the limit of an infinitely strong and infinitesimally short ranged attraction [8] in which the Boltzmann factor $\exp[-\beta\phi_{22}]$ becomes

$$\exp\left[-\beta\phi_{22}(r)\right] = \frac{R}{12\tau}\delta\left(r - R^{-}\right) + \Theta(r - R) \tag{1}$$

Here, $\beta = 1/kT$, k is the Boltzmann constant and T the temperature, Θ and δ are the step and the Dirac δ functions, respectively, and τ is the stickiness parameter related to the strength of adhesion and to the temperature of the system [15].

The external potential is given by the gravitational part

$$\phi_{12}(x) = mgx + C, \quad (R/2) < x < L - (R/2) \tag{2}$$

where m is the mass of a particle, g the acceleration due to gravity, and C a constant defining the energy at the bottom of the pore, together with the wall-fluid adhesive potential [14], leading to the following form of the Boltzmann factor $\exp[-\beta\phi_{12}]$:

$$\exp[-\beta\phi_{12}(x)] = \begin{cases} A\delta[x-(R/2)], & x \le (R/2) \\ A\delta[x-(L-(R/2))], & x \ge L-(R/2) \end{cases} \tag{3}$$

corresponding to a finite probability of configurations with particles of the fluid touching the walls of the pore. The parameter A is a measure of the strength of the wall-particle adhesiveness.

The distribution of sticky colloidal particles (2) in the slit (1) is determined by the Ornstein-Zernike (OZ) equation

$$h_{12}(x) = c_{12}(x) + \rho_b \int h_{12}(|\mathbf{x}-\mathbf{x}'|)\, c_{22}(\mathbf{x}')\, d\mathbf{x}' \tag{4}$$

supplemented by the combined hypernetted chain/Percus-Yevick (HNC/PY) approximation in which the HNC closure [7]

$$c_{12}(x) = -\beta\phi_{12}(x) + h_{12}(x) - \ln g_{12}(x) \tag{5}$$

is used in the OZ equation for the wall-fluid correlations, whereas the PY expression is retained for the direct correlation function c_{22} for the adhesive fluid in a homogeneous phase, the corresponding analytical expression being found in the original paper of Baxter [8]. Above, $h_{ij} = g_{ij} - 1$ is the total correlation function.

The impulse character of the wall-fluid potential of interaction, Eq. (3), gives rise to the development of the δ-function peak in $h_{12}(x)$ at x = ½R and $x = L$ - ½R. The corresponding relation for the adhesive-hard wall-fluid correlation thus reads

$$h_{12}(x)] = \begin{cases} -1 + B_{low}\delta[x-(R/2)], & x \le (R/2) \\ -1 + B_{upp}\delta[x-(L-(R/2))], & x \ge L-(R/2) \end{cases} \tag{6}$$

where the amplitudes of the δ -function peaks B_{low} and B_{upp} represent a measure of the adsorption of the fluid particles on the lower and on the upper wall of the pore. The numerical solution of Eq. (4), based on the Picard iteration, is described in detail in Refs. 12 and 14. During the iteration, the flat profile $h = 0$ at $(R/2) < x < L - (R/2)$ and the values of the coefficient of the δ-function peak $B_{\mathrm{low}} = 0$ at $x = (R/2)$ and $B_{\mathrm{upp}} = 0$ at $x = L - (R/2)$ were used as the initial approximation. In each iteration, the profile $h(x)$ and the values B_{low} and B_{upp} from the preceding step were used for a set of discrete points within the interval $(R/2) \le x \le L - (R/2)$.

The constant C in Eq. (2) was chosen so that the average density in the pore $<\rho>$, taken over the accessible region L-R, equalled the density of the fluid in the reservoir, or equivalently [5]:

$$\frac{1}{L-R}\int_{R/2}^{L-R/2}[h_{12}(x)+1]\,dx = 1 \tag{7}$$

Results and discussion

The gravitational effects on the properties of the fluid in the pore are dependent on the strength of the gravitational field relative to the thermal energy kT. These effects are therefore characterized by the dimensionless parameter $k_1^* = mgR/kT$, using the diameter of the particles R as a length unit. The reduced value of the energy at the bottom of the pore is then $k_2^* = C/kT$. The average density in the pore $<\rho>$ is expected to decrease with increasing strength of the attractive interactions among the particles due to the tendency of the sticky particles to avoid the confined system. In our recent study [5] we found, however, that the system showed such behavior only in the case of weak to moderate interparticle attraction. $<\rho>$ first decreased with reducing τ, at a certain τ reached a minimum, and then rapidly grew with further decrease of τ. Namely, in the presence of gravity, the particles are forced to occupy the region of lower altitudes in the pore, the effect being even enhanced with increasing strength of the attraction among the particles. At the bottom of the pore, a dense and highly layered "substrate" of strongly adhesive particles is formed, and as such, acts as a "condensation" nucleus for the condensation of particles from the bulk phase. In the presence of the wall-fluid adhesion, the particles are more likely to occupy the interior of the pore, thus giving rise to an increase in <ρ>. This is illustrated in Fig. 1 where the dependence of the average reduced density <$\rho^* = \rho R^3$> in the pore on the strength of

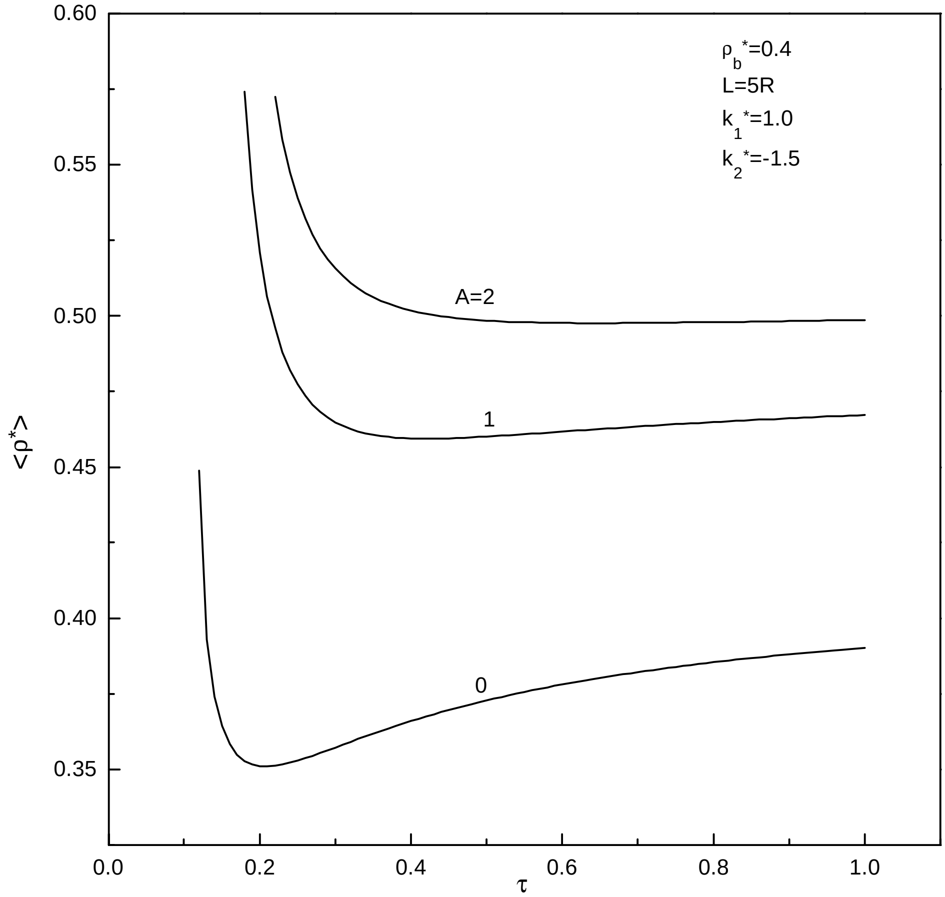

Figure 1. The average density <$\rho^* = \rho R^3$> in a gap of width L=5R as a function of the stickiness parameter τ at the values of gravitational parameters $k_1^* = mgR/kT = 1$ and $k_2^* = C/kT = -1.5$, and at different values of the strength of the wall-fluid adhesion A. The system is in equilibrium with the bulk fluid phase of density $\rho_b^* = \rho_b R^3 = 0.4$.

attraction among the particles at the reduced bulk density $\rho_b^* = \rho_b R^3 = 0.4$, $k_1^* = 1$, $k_2^* = -1.5$, $L = 5$, and at different values of the wall adhesiveness A, is presented. At higher A, as expected, weaker attractive interactions among the particles are needed for condensation to start, leading to the shift of the minimum of $<\rho^*>$ to higher τ.

In Figs. 2 and 3 we present the one-particle distribution function $g(x) = \rho(x)/\rho_b$ of the adhesive particles in the gap with adhesive (adsorptive) walls at two different

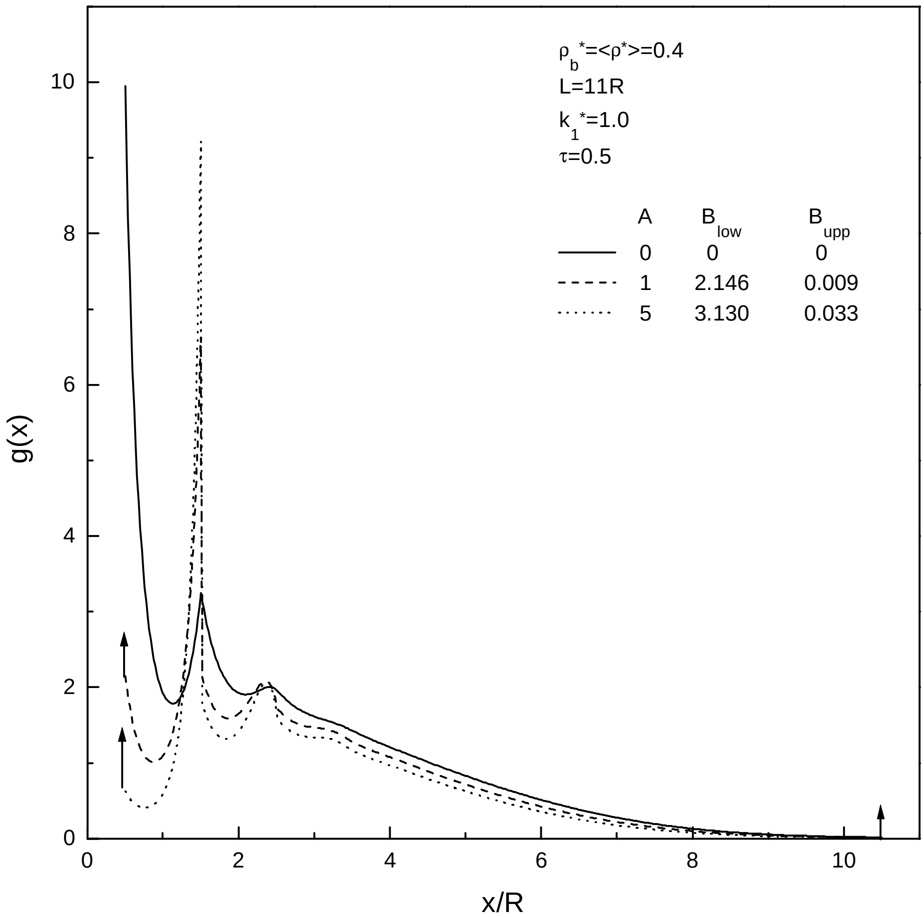

Figure 2. One-particle distribution function $g(x) = \rho(x)/\rho_b$ versus altitude for a system of adhesive spheres in a gap of width $L = 11R$, at values of the gravitational parameter $k_1^* = 1$, the stickiness parameter $\tau = 0.5$, and at different values of the wall adhesiveness A . At each set of parameters, the parameters k_2^* are obtained from the normalization condition (7) providing for the equality $<\rho^*> = \rho_b^* = 0.4$. $B_{\rm low}$ and $B_{\rm upp}$ are the amplitudes of the δ-function peak in the wall-fluid correlation function $h(x)$ at the wall-fluid contact. The coverage of the walls is noted by the arrows at the planes of closest approach to the walls.

widths, $L = 11R$ and $L = 5R$. For the sake of comparison, the bulk density $\rho_b^* = 0.4$ and the gravitational parameter $k_1^* = 1$ are the same as used in our previous work [5]. The interparticle stickiness parameter $\tau = 0.5$ is chosen corresponding to moderately sticky attraction. The wall adhesive strength parameter A varies from 0 to 5, the former

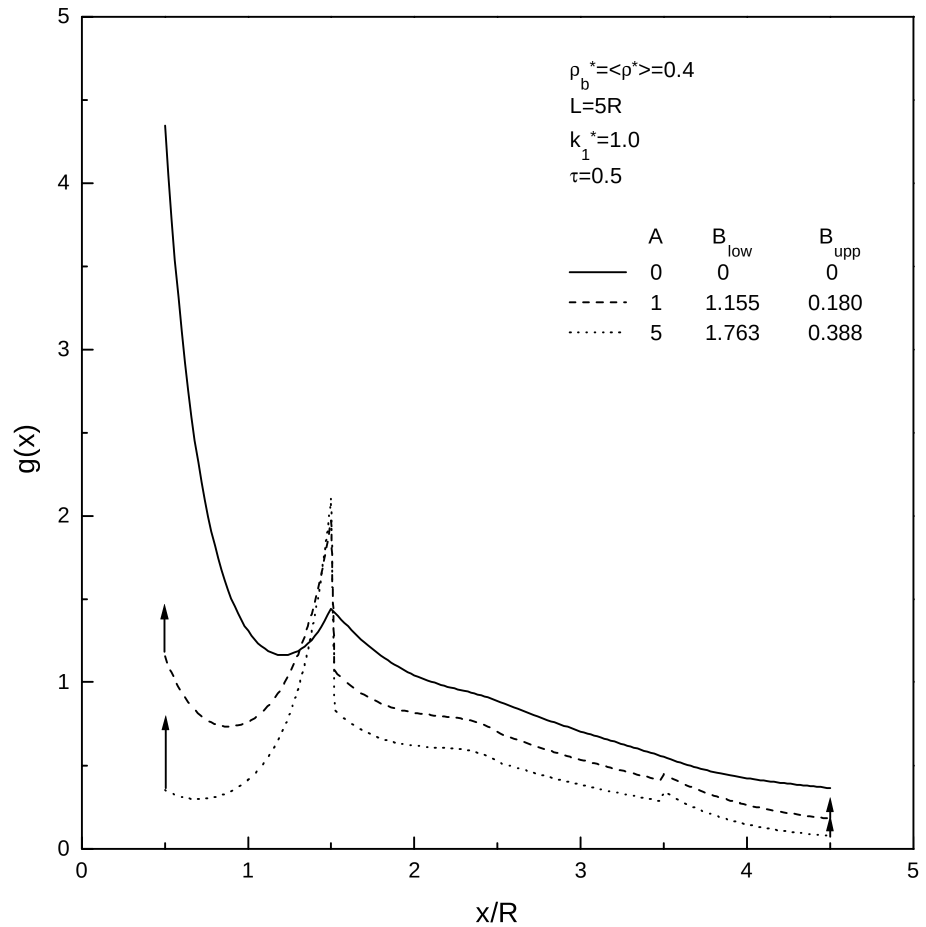

Figure 3. Same as Fig. 2 but for a gap of width $L = 5R$.

corresponding to the hard wall case, studied in more detail in our preceding work [5], and the latter to strongly adsorptive walls. Because of gravity, the profiles consist of an oscillatory part near the bottom, revealing the existence of molecular layers, and a non-oscillatory tail at higher altitudes [5,6]. In the hard wall case, $A = 0$, a region of increased fluid density forms; mainly adjacent to the lower wall due to the steric shielding effects. When an adhesive wall-fluid attraction is introduced, adsorbed monolayers of particles at the walls are formed, the measure of the two-dimensional coverage being the amplitudes of the δ -function peaks B_{low} and B_{upp} in $h_{12}(x)$ at $x = (R/2)$ and $x = L - (R/2)$, respectively. The ordered two-dimensional monolayers of particles partly cover the walls, thus giving rise to the partial exclusion of particles from the domain occupied by the particles of the adsorbed "subphase", the result being a decrease of fluid density in the close vicinity to the walls. The adsorbed monolayers adhere the non-adsorbed particles. As a result, sharp peaks at $x = (3R/2)$ and $x = L - (3R/2)$ evolve and the densities at infinitesimally larger distances from the walls distinctively decrease, a feature similar to that found for the adsorption of the first layers. The occurence of peaks and minima at larger distances from the walls is again a consequence of adhesive attraction between successive molecular layers. These effects are, of course, much more pronounced at the lower wall, in contrast to the situation in similar systems without gravity [14]. Accordingly, the amplitude B_{low} is higher than B_{upp}, the difference being, clearly, more pronounced in wider pores due to the stronger effects of gravity at larger altitudes x. In the case of the wider gap $L = 11R$ (Fig. 2), the tails of the curves vanish upon approaching the top of the pore. Though the fluid is present in a negligible amount in the vicinity of the upper wall, the strongly attractive wall with the highest adhesiveness $A = 5$ causes a rather large number of particles to "hang" on its surface, as can be concluded from the relatively high value of the amplitude of the δ-function peak B_{upp}.

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Povzetek

Sedimentacijsko ravnote□je inte ragirajoèih koloidnih delcev v disperziji obravnavamo na osnovi rešitve hypernetted chain / Ornstein-Zernikove integralske enaèbe za sistem togih kroglic z adhezivnim potencialom v planarni pori z adhezivnima (adsorbirajoèima) stenama. Gravitacija ter privlaène sile med koloidnimi delci vodijo do tvorbe gostega "substrata" na dnu pore. Izka□e se, da v primeru moène adhezivnosti med koloidnimi delci, ta deluje kot "kondenzacijsko jedro" za kondenzacijo delcev iz ravnote□nega sistema v poro - pojav, ki prevlada nad naravno te□njo mo èno adhezivnih delcev, da bi se izognili omejenemu sistemu. V primeru adhezije med stenama ter delci se ob stenah tvorita monoplastni oblogi delcev. Njihov izkljuèeni volumen povzroèa nezveznosti v gostotnem profilu na razdaljah enega premera delca od kontaktnih ravnin pri obeh stenah. Zaradi gravitacije so navedeni pojavi veliko bolj izraziti na dnu pore kot pri zgornji steni iste adhezivnosti.