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# Segregation of penetrable soft spheres under gravity: Mean-field approach

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ABSTRACT

We study the segregation of the additive and non-additive soft-sphere mixtures, which have the purely repulsive interactions, on the relative range of temperature, the cross-interaction between unlike species, the buoyant mass, and the layer numbers. The results show that the most segregation is found at $m_2/m_1 = 1$ and a low temperature, where $m_i$ is the mass of species $i$. The crossover point corresponding to the mixing phase is shifted toward a large mass ratio with increasing the temperature. For the non-additive soft sphere mixture, the crossover point is shifted toward a small mass ratio with increasing the cross-interaction between unlike species. The increase of gravitational strength drives the larger particles sinking to the bottom. The pressure at height $z$ has been calculated from the force balance on a slab of fluids adjacent to the wall. The pressure at the bottom decreases with decreasing the temperature, whereas the pressure at a high altitude increases because of the large particles at the top. For the mixing phase, the large pressure discontinuity is found at $z = \sigma_1$ because of the density difference between two particles. Through this work, we show that the center of mass of the species, $< z_i >$, is a proper factor for studying the particle segregation.



## 1. Introduction

The sedimentation of the colloids in a suspension shows the spatial inhomogeneous due to the symmetry breaking induced by the gravitational field. The sedimentation under gravity is very important in many technical applications such as the growth of crystals [1] and the separation in a charged colloidal systems [2,3]. Therefore, the sedimentation has been of scientific interest for a long time since early work of Jean Perrin. For example, the rise and sink phenomena of the larger particles with respect to the smaller particles in granular systems, known as the Brasil nut (BN) and reverse Brazil nut (RBN) effects, have been extensively studied [4–12]. However, almost all of the studies for the BN and RBN phenomena are limited to a hard sphere mixture, but not to a soft-sphere mixture that allows for large overlaps. There are a large amount of the soft-sphere mixtures that allow the overlaps in nature.

Kohl and Schmiedeberg [12] have recently studied the segregation process of a penetrable soft-sphere mixture under gravity through the Brownian dynamics simulation. They have reported that the overlaps of the particles influence the effective buoyancy. The sedimentation process might lead to complex configuration depending on the pressure and the dynamics of the segregation process consists of the multiple steps. However, their studies are mainly restricted on the dynamics of the segregation process for a penetrable soft-sphere mixture. The more detailed properties of the segregation for a penetrable soft-sphere mixture are needed to elucidate the nature of the segregation in the gravitational field. The purpose of this paper is to study the segregation of an additive penetrable soft-sphere mixture with a purely soft repulsive interaction and a non-additive penetrable soft-sphere mixture with a non-additive interaction between different species. Although simple, the penetrable soft-sphere models have served as the models in order to find the adequacy of different integral equation theories in statistical mechanics. They give rise to many different phase behaviors in bulk phase and nanopores. In particular, the nonadditive soft-sphere mixture shows the fluid–fluid demixing transition in bulk phase, and the layering transition and population inversion in nanopores [13–15].

The remainder of the paper is organized as follows. In Section 2, we will introduce the molecular model and describe the particle density distribution, which is based on the mean-field approximation, for studying the segregation of a soft-sphere mixture under gravity. In Section 3, we introduce the center of mass of the two species, $< z_i >$, in order to study the particle segregation. We study the segregation of a soft-sphere mixture on the relative range of temperature, the cross-interaction between unlike species, the buoyant mass, and the layer numbers. We calculate the pressure at height $z$ from the force balance on a slab of fluids adjacent to the bottom and investigate the relationship between the pressure at height $z$ and the particle segregation. We show that the crossover point, $< z_1 >/< z_2 > = 1$, is shifted toward a large mass ratio with increasing the temperature. While it is shifted

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toward a small mass ratio with increasing the cross-interaction between unlike species. In concluding remarks, we briefly discuss the weakness of the mean-field approximation employed for studying the particle segregation and the effect of a diameter ratio of the species for the particle segregation.

## 2. Model and theory

We consider a soft-sphere mixture in the gravitational field. We label the species by $i = 1, 2$, and denote the buoyant mass and penetrable diameter for species $i$ by $m_i$ and $\sigma_i$. We assume that the soft spheres interact via a purely repulsive harmonic potential

$$u_{ij}(r) = \varepsilon 2\left(1 - r\sigma_{ij}\right)^2, \quad r < \sigma_{ij} \qquad = 0, \quad r > \sigma_{ij} \tag{1}$$

where $\varepsilon$ is the energy scale [12]. The penetrable diameters of the two species are $\sigma_{11} = \sigma_1$, $\sigma_{22} = \sigma_2$, and a crossed diameter $\sigma_{12} = (\sigma_1 + \sigma_2)/2(1 + \Delta)$, where the parameter $\Delta$ denotes the deviations of the inter-species interactions from additivity. It is known that for positive non-additivity $\Delta > 0$ the system tends to segregate into two fluid phases in bulk phase as well as the population inversion in a nanopore [13–15].

Under an external potential in the $z$-direction [16,17], the intrinsic (Helmholtz) free energy $F[\rho_1(z), \rho_2(z)]$, which is a functional of the one-body particle density $\rho_i(z)$, $i = 1, 2$, is given by

$$\beta F[\rho_1(z), \rho_2(z)]A = \sum_{i=1}^{2} \int dz\ \rho_i(z)[\ln \rho_i(z) - 1] + \beta F_{ex}[\rho_1(z), \rho_2(z)] + \sum_{i=1}^{2} \int dz\ \rho_i(z) \beta u_{i,ext}(z) \tag{2}$$

where $F_{ex}[\rho_1(z), \rho_2(z)]/A$ is the excess free energy per unit of area originating from the particle interactions, $\beta = 1/k_BT$ ($k_B$ being the Boltzmann constant), and $A$ is the macroscopic horizontal area. It should be mentioned that the thermal de Broglie wavelength $\Lambda_i$ for species $i$ has been suppressed. If the bottom is a hard wall, the external potential has an additional gravitational interaction with the system particles. Then, the external potential becomes

$$\beta u_{i,ext}(z) = \beta m_i g(z - \sigma_i/2), \quad z > \sigma_i/2 \qquad = \infty, \quad z < \sigma_i/2 \tag{3}$$

where $g$ is the gravitational acceleration and $z$ is the distance from the bottom at $z = 0$. The equilibrium particle density distribution $\rho_i(z)$ of a soft-sphere mixture is determined by the minimum of the free energy functional such as

$$\ln \rho_i(z) + \beta m_i g(z) - c_i^{(1)}(z; [\rho_1(z), \rho_2(z)]) = \lambda_i, \quad i = 1, 2 \tag{4}$$

where $c_i^{(1)}(z; [\rho_1(z), \rho_2(z)]) = -\partial \beta F_{ex}[\rho_1(z), \rho_2(z)]/\partial \rho_i(z)$ is the one-particle direct-correlation function and $\lambda_i$ the Lagrange multipliers. The Lagrange multipliers $\lambda_i$ are introduced to conserve the number of particles of each species, i.e., the layer number $\mu_i$,

$$\mu_i \equiv N_i A = \int_{\sigma_i/2}^{\infty} dz\, \rho_i(z), \quad i = 1, 2 \tag{5}$$

where $N_i$ is the number of particle for species $i$.

As an approximation of the excess free energy functional $F_{ex}[\rho_1(z), \rho_2(z)]$, we have introduced the mean-field approximation, which is asymptotically exact for high densities and gives accurate results for finite densities in non-uniform phases [12–14]. In this case, $F_{ex}[\rho_1(z), \rho_2(z)]$ becomes

$$\beta F_{ex}[\rho_1(z), \rho_2(z)]A = 12 \sum_{i,j=1}^{2} \int dz\, \rho_i(z) \int dz'\, \rho_j(z') \beta u_{ij}(|z - z'|)] \tag{6}$$

where $\beta u_{ij}(z) = 2\pi \int_z^{\sigma_{ij}} dR\, R\, \beta u_{ij}(R)$ for $z \le \sigma_{ij}$. Finally, the particle density distribution $\rho_i(z)$ becomes, after some calculations,

$$\rho_i(z) = \mu_i B_i[\rho_1(z), \rho_2(z)] \exp\left[-m_i g(z - \sigma_i/2) + c_i^{(1)}(z; [\rho_1(z), \rho_2(z)])\right], \quad i = 1, 2 \tag{7}$$

with

$$B_i[\rho_1(z), \rho_2(z)] = \int_{\sigma_i}^{\infty} dz[\exp(-m_i g(z - \sigma_i) + c_i^{(1)}(z; [\rho_1(z), \rho_2(z)])] \tag{8}$$

and

$$c_i^{(1)}(z; [\rho_1(z), \rho_2(z)]) = \sum_{j=1}^{2} \int dz' \rho_j(z') \beta u_{ij}(|z - z'|). \tag{9}$$

Given the gravity and boundary condition, the particle density distribution $\rho_i(z)$ can be calculated numerically with a standard Picard iteration procedure. At an initially fixed layer number $\mu_i$, we first start an initial guess for the particle density distribution $\rho_i(z)$. The iteration procedure continues until the particle density distribution $\rho_i(z)$ and layer number $\mu_i$ have converged. Through this work, we have studied the particular case, where the diameter ratio of the species is $\sigma_2/\sigma_1 = 2$ [12]. We have used the reduced temperature $T^* \equiv k_BT/\varepsilon$, dimensionless gravitational strength (or Peclet number) $g^* \equiv (m_1\sigma_1/k_BT)g$, and dimensionless pressure $P^* = P\sigma_1^3/\varepsilon$.

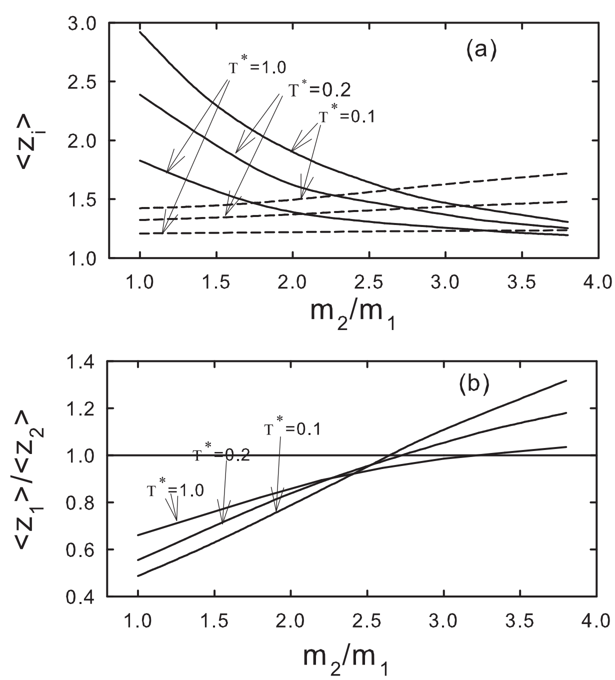


**Fig. 1.** (a) Center of mass of the species $i$. Dashed line ($< z_1 >$) and solid line ($< z_2 >$). (b) segregation parameter $< z_1 >/< z_2 >$ of a soft-sphere mixture, where $g^* = 1.5$ and $\mu_1 = \mu_2 = 2$, respectively.