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Sedimentation in nano-colloidal dispersions: Effects of collective interactions and particle charge

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Abstract

This is a review paper summarizing the progress of the development of colloidal sedimentation models for monodisperse, bidisperse, and polydisperse nanoparticle dispersions. This topic is of considerable interest because the sedimentation behavior of nanoparticles plays an important role in many practical systems, such as industrial coatings, optical products, ceramics, paints, dyes, and cosmetics. The limitations of various models are discussed. Multi-particle systems are highlighted, with a focus on the collective thermodynamic interactions resulting in the attractive depletion and repulsive structural forces. The effects of the particle concentration, particle charge, polydispersity in size, and electrolyte concentration on the sedimentation process are briefly summarized. Our contributions to this subject are reviewed.

Keywords: Sedimentation; Collective interaction; Nanoparticles; Colloidal dispersion; Particle charge

Contents

1. Introduction

The sedimentation process of nano-colloidal suspensions has been intensively studied; it is found in many common practical applications such as solid–fluid separations in gravity settling and purification processes involving particulate slurries and sludge. Other industrial applications include enhancing the shelf life of various products like foods, pharmaceuticals, cosmetics, consumer products, paints, coating products, and nano-structured materials. The concentration dependence of the sedimentation velocity on the particle–particle and particle–fluid interactions is of interest because of its application in determining the stability and quality of the dispersions.

2. Phenomenological models of sedimentation

Sedimentation under gravity is one of the oldest technologies used in phase separation. The balance between the buoyancy and frictional forces drives the particle separation rate from the fluid. Stokes' law [1] first relates the sedimentation velocity of a

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single spherical particle (U_0) to the gravitational force and the friction drag forces. Stokes' velocity, U_0, is frequently used as a scaling factor in determining the sedimentation rates.

Based on an experimental study, Richardson and Zaki [2] found that the sedimentation velocity (U) for particle concentrations up to and around 40 vol.% is described by the following equation:

$$\frac{U}{U_0} = (1-\phi)^n \cong 1 - n\phi + \frac{n^2\phi^2}{2} + \cdots \tag{1}$$

where the value of n is close to 5 and ϕ is the particle volume fraction.

Kynch [3] proposed a model of sedimentation by introducing the particle flux ($f=\phi U$) of a number of particles moving downward per unit of area per unit of time. The continuity equation along the vertical height, z, and time, t, obtained by the material balance was derived as:

$$\frac{\partial\phi}{\partial t} + \frac{\partial f}{\partial z} = 0 \tag{2}$$

However, Kynch's theory of sedimentation does not apply to the compression region [4] where the particles accumulate and become concentrated. The excluded volume due to multi-particle collective interactions in the compressed zone becomes important and needs to be incorporated into the model.

The sedimentation velocity of hard-sphere particles has been studied for dilute monodisperse suspensions and Batchelor [5] presented theoretical equations. According to Batchelor, the sedimentation velocity, corrected to the order of the particle volume fraction, ϕ, with the contribution from the near-field two-body hydrodynamic backflow varies with ϕ as

$$\frac{U}{U_0} = 1 + K\phi \tag{3}$$

where K is defined as the sedimentation coefficient. According to Batchelor, the value of K was -6.55 for monodisperse hard sphere systems with consideration to two-body hydrodynamic interactions. However, values of K determined experimentally by investigators deviate from the value of -6.55 [6]. As shown in Fig. 1, the sedimentation rate normalized by the Stokes velocity is plotted as a function of the particle volume fraction for various particle systems. The departure of the sedimentation coefficient (K) from the theoretical value (-6.55) is observed at particle concentrations greater than 10 vol.%. The value of K gradually decreases to -4.7 as the particle concentration increases.

Buscall et al. [7,8] and Barker et al. [9,10] proposed the generalized continuous approach, which can be used for more concentrated systems by combining the force and flux balance equations giving,

$$\frac{\Delta\rho\phi g u}{U(\phi)} - \Delta\rho\phi g + \left|\frac{\partial P}{\partial z}\right| = 0 \tag{4}$$

where the first term arises from the viscous drag on the particle density difference ($\Delta\rho$) for particles moving with velocity u. The velocity function $U(\phi)$ accounts for the hindered settling.

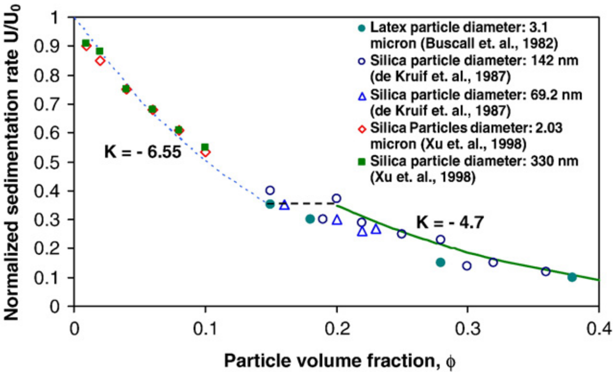

Fig. 1. Comparison of the normalized sedimentation rate U/U_0 as a function of particle volume fraction with the prediction by Eq. (8); ··· with $K=-6.55$, − $K=-4.7$.

The second term represents the effect of the gravitational field. The particle pressure gradient, $\frac{\partial P}{\partial}$, is related to the osmotic pressure or particle network structure.

The expression for the sedimentation velocity u that accounts for the particle interactions is:

$$u = U\left(1 - \frac{1}{\Delta\rho\phi g}\left|\frac{\partial P}{\partial z}\right|\right) \tag{5}$$

Buscall's generalized continuous model only accounts for the particle interactions through the osmotic pressure and does not directly account for the collective thermodynamic interactions of the sediment particles.

Davis and Russel [11] proposed an extension model of Kynch's batch sedimentation theory by introducing a diffusion term which relates to the osmotic pressure. It was found that the diffusion term smoothes the discontinuities of the Kynch's theory. However, the model was generally formulated to account for the collective interactions based on Buscall's generalized continuous approach.

3. Collective interactions

3.1. Monodisperse particle systems

Particle interactions in the presence of surrounding particles are different from the interactions between only two particles in the absence of other particles. The role of collective interactions (the presence of many particles) on the sedimentation velocity and dispersion microstructure has received attention in several recent studies [6,12,13]. Collective interactions include hydrodynamic interactions and thermodynamic interactions. Hydrodynamic interactions retard the backflow, which is the reverse flow of fluid to compensate for the movement of the settling particles. Thermodynamic interactions are due to the attractive self-depletion and repulsive structural forces in concentrated dispersions [6,13–16].

It was pointed out in a series of papers published by Beenakker and Mazur [17,18] that the collective hydrodynamic interactions between two particles in the presence