Sedimentation equilibrium of suspensions of colloidal particles at finite concentrations

M. Martin1), M. Hoyos1), and D. Lhuillier2)

1) Ecole Supérieure de Physique et Chimie Industrielles, Laboratoire de Physique et Mécanique des Milieux Hétérogènes (URA CNRS 857) Paris, France
2) Université Pierre et Marie Curie, Laboratoire de Modélisation en Mécanique (URA CNRS 229). Paris, France

Abstract: Equilibrium concentration profiles of non-dilute colloidal suspensions are calculated by means of the Carnahan-Starling expression for the osmotic compressibility of hard sphere liquids. The profiles depend on the average volume fraction of the suspension, \( \langle \phi \rangle \), and on the field interaction parameter, \( \lambda_0 \) (reciprocal of the Péclet number at infinite dilution). Profiles are computed for values of \( \langle \phi \rangle \) and \( \lambda_0 \) typical of those encountered in sedimentation field-flow fractionation experiments. It is found that, in most cases, the volume fraction at the depletion wall is negligibly small and that the volume fraction at the accumulation wall, \( \phi_0 \), depends on the ratio \( \langle \phi \rangle / \lambda_0 \) only. An inflexion point is found in the concentration profile if \( \phi_0 \) is larger than 0.13, whatever the value of \( \lambda_0 \).

Key words: Sedimentation equilibrium – colloidal particles – hard spheres – finite concentrations

Introduction

The sedimentation of particulate materials is a ubiquitous and important phenomenon of environmental, biological, and industrial relevance. In a batch sedimentation process of an initially uniform suspension, one usually encounters three zones, both in transient and equilibrium conditions [1]. At the bottom of the vessel, a sedimentation cake is formed with a volume fraction which somewhat depends on the compressibility of the packing and is about 0.6. Above that sediment layer, one finds a transition layer, the height of which varies during the settling process and depends on the diffusivity of the particles. Then, a clear liquid is found above that layer. The relative importance of the three zones depends on the average volume fraction of the suspension, but also on the height of the sedimentation vessel. Many studies have focussed on the dynamics of the sedimentation process in situations where the height of the sedimentation vessel is large enough for a sediment to be formed. The theory of the transient batch settling for noncolloidal particles was first formulated by Kynch [2]. This theory has been recently extended by Davis and Russell [3] to account for the influence of the Brownian motion of the particles on the transition layer above the sediment.

There are situations, however, where the vessel height is so small that a compact sediment is never obtained in spite of the relatively large average volume fraction of the suspension. Such is the case, for instance, in field-flow fractionation (FFF) experiments. FFF is an analytical method for separation and characterization of supramolecular materials. The separation occurs during the transportation, by means of a carrier liquid, of the particulate sample through a thin, ribbon-like channel under the influence of an external field applied perpendicularly to the main plates of the channel [4]. In usual operating conditions, the carrier flow velocity is small and the mean residence time of the particles depends on the
equilibrium concentration distribution in the field direction. It is therefore of major interest to know this distribution for separation optimization as well as for particle characterization.

When the suspension is highly dilute and the field is constant throughout the channel thickness, the concentration decreases exponentially from the accumulation plate [5]. For less dilute suspensions, the volume fraction near the accumulation plate can be large enough for deviations from the exponential profile to occur.

The objective of the present study is to determine the equilibrium concentration profile for a suspension submitted to a constant field when the volume fraction near the accumulation wall is large enough for interactions between particles to be significant. This is the case of most FFF experiments with not too dilute samples.

Theory

One considers a suspension of identical Brownian particles in a quiescent fluid enclosed in a vessel between two parallel plates (the plates are assumed to be large enough for side wall effects to be negligible). A gravitational field is applied in the direction perpendicular to the plates. The acceleration of this gravitational field, \( G \), is assumed to be constant throughout the vessel. This assumption is obviously correct for experiments performed with the Earth’s gravitational field. It is mostly correct for centrifugal FFF experiments since the distance between the two rotating plates is much smaller than their mean distance to the rotation axis (in typical instruments, the variation of \( G \) through the channel thickness is less than 0.2%). For the same reason, the centrifugal sedimentation can be assumed to be a one-dimensional problem as in the Earth gravitational experiment.

General expression of the volume fraction profile

The effective force, \( F_{\text{ext}} \), exerted by the gravitational field on a particle of volume \( V_p \) is the body force corrected by the Archimedes force:

\[
F_{\text{ext}} = v_p \rho_p G - V_p V_p
\]

where \( \rho_p \) is the mass per unit volume of particles and \( V_p \), the hydrostatic pressure gradient in the suspension, given by:

\[
V_p = [\phi \rho_p + (1 - \phi) \rho_f] G ,
\]

\( \rho_f \) is the mass per unit volume of the suspending fluid, and \( \phi \) is the volume fraction of the particles. Here, bold-face symbols represent vectorial quantities. Combining Eqs. (1) and (2) and defining \( \Delta \rho = \rho_p - \rho_f \), one finds:

\[
F_{\text{ext}} = (1 - \phi) v_p \Delta \rho G .
\]

Each particle is also submitted to a thermodynamic force, \( F_{\text{th}} \), linked to the gradient of the chemical potential per particle, \( \mu_p (p, T, \phi) \). This chemical potential is the sum of two contributions: the bare particle contribution, \( \mu_b (p, T) \), at the same pressure and temperature as the suspension, and the excess (or mixing) chemical potential \( \Delta \mu_p (p, T, \phi) \). For rigid particles with hard-core interactions, \( \Delta \mu_p \) depends only on the particle volume fraction. When \( \phi \) is not uniform over the suspension, the force acting on a particle is:

\[
F_{\text{th}} = - \frac{\partial \Delta \mu_p}{\partial \phi} \nabla \phi .
\]

The chemical potential of a fluid molecule, \( \mu_f \), can also be written as the sum \( \mu_f = \mu_b + \Delta \mu_f \). As a consequence of the Gibbs–Duhem relationship between \( d \mu_p \), \( d \mu_f \), \( dp \) and \( d T \), the variations with \( \phi \) of \( \Delta \mu_f \) and \( \Delta \mu_p \) are related by [6a]:

\[
c_p \frac{\partial \Delta \mu_p}{\partial \phi} + c_f \frac{\partial \Delta \mu_f}{\partial \phi} = 0 ,
\]

where \( c_p \) and \( c_f \) are the numbers of particles and of fluid molecules per unit volume of suspension, respectively. It is usual to express \( F_{\text{th}} \) as a function of the osmotic pressure, \( \Pi \), a quantity simply related to the fluid excess chemical potential as [6b]:

\[
\frac{\partial \Delta \mu_f}{\partial \phi} = - v_f \frac{\partial \Pi}{\partial \phi} ,
\]

where \( v_f \) is the volume of a fluid molecule. Noting that \( c_p v_p = 1 - \phi \) and \( c_p v_f = \phi \), one can combine Eqs. (4) to (6) to obtain:

\[
F_{\text{th}} = - \frac{1 - \phi}{\phi} v_p \frac{\partial \Pi}{\partial \phi} \nabla \phi .
\]