MACROIONS UNDER CONFINEMENT

Computer modelling of a layering phenomenon

A.D. Trokhymchuk, D. Henderson, D.T. Wasan, A. Nikolov

1 Institute for Condensed Matter Physics
National Academy of Sciences of Ukraine
79011 Lviv, Ukraine

2 Department of Chemistry and Biochemistry
Brigham Young University
Provo, Utah 84602, USA

3 Department of Chemical Engineering
Illinois Institute of Technology
Chicago, Illinois 60616, USA

Abstract

The layering of like-charged particles or macroions confined by two plane-parallel and two inclined surfaces is studied using a canonical Monte Carlo method combined with a simulation cell that contains both the confined and bath regions. The macroion solution is modelled within a one-component fluid approach that in an effective way incorporates a conventional double layer repulsion due to the ions of suspending electrolyte as well as an extra contribution due to the discrete nature of an aqueous solvent. The plane parallel and wedge-shaped geometries mimic the confinements that naturally occur in large number of systems widely known as colloidal dispersions. The effects of macroion charge, macroion and electrolyte concentrations on the particle layering and in-layer structuring are analyzed. The relation of obtained results to experiments on confined ionic micelle solutions and suspensions of charged polystyrene spheres is discussed.

Keywords: Macroions, layering, thin colloidal films, solvent excluded volume effects, structural interactions, wedge confinement

1. Introduction

Charged colloids, or macroions, are very important ingredients of a large number of chemicals and consumer products widely used in material science, electronics as well as in everyday life. Some other examples of matter comprised macroions, including biological systems, can be found in two preceding chapters presented by Vlachy et al. and Ballauff, where the theoretical and
experimental aspects of the bulk polyelectrolyte solutions are discussed. We are interested in the confined macroions and more precisely in the macroion layer structuring next to a single macroscopic surface and/or between a pair of macrosurfaces.

The particle layering in the form of the step-wise stratification in thinning films formed from macroion solutions have been observed for some time [1–5]. The film stratification is a manifestation of the nontraditional structural forces acting between confining surfaces while the macroion films become a natural tool to probe these forces in colloidal dispersions [6–10]. From applied perspective, the phenomenon of macroion or nanocolloid layering has received considerable attention because it offers a new mechanism for stabilizing colloidal dispersions. The role of the confinement-induced structural forces in colloidal macrodispersions such as foams, emulsions, and particle suspensions has been reviewed by us recently [11]. From another side, special attention has been given to the layering phenomenon after the earlier experimental observations of ordering in some biological [12] and latex [13] suspensions. The presence of order-disorder transitions above a certain concentration in these systems was attributed exclusively to the fact that the macroions are enclosed in a restricted environment, i.e. are confined.

From the perspective of theoretical modelling, colloids dispersed in a macroion solution represent a complex material system governed by the interplay of structural forces and long-range electrostatic effects acting on different length scales. A powerful tool to study such systems is computer simulation. The purpose of this chapter is to discuss the application of computer simulations to the modelling of layering phenomenon in confined macroion solutions and to bring more understanding into nature of the processes that occur in complex colloidal systems. In doing this, besides the physical conclusions, we also summarize some methodological and modelling approaches that have been undertaken in our recent computer simulation studies regarding macroion structuring under the plane-parallel and wedge confinements [14–16]. First of all, we point out the correspondence between the thermodynamic parameters of the confined macroion suspension and those of the homogeneous or bulk reservoir. We deal with this issue by performing a canonical ensemble Monte Carlo (MC) calculations combined with a simulation cell that contains both the film region and bulk suspension.

Another important issue are the potential functions or potential model that are suitable to describe the macroion solution under confinement. These potential functions further are employed in a Metropolis algorithm to explore the configurational space during MC procedure to reach the thermodynamic equilibria in the entire system as well as to collect the ensemble averages. Because of the large size asymmetry of the species comprising a real macroion solution, the most widely used potential model is based on the one-component