

Static structure of polydisperse colloidal monolayers

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A generalization of integral equation theory of simple liquids is used to study the structure and thermodynamics of a monolayer of spherical colloidal particles having a continuous distribution $f(\sigma)$ of diameters σ . The quasi-two-dimensional fluid is modeled using both a repulsive Yukawa potential to represent charged hard spheres (with attendant charge polydispersity) and a Lennard-Jones potential to represent soft spheres with an effective attractive well. The numerical solution of the integral equations makes essential use of polynomials that are orthogonal with weight function $f(\sigma)$, which is taken here to be a Schulz distribution. © 1998 American Institute of Physics. [S0021-9606(98)51715-1]

I. INTRODUCTION

Colloidal particles, at the boundary of the microscopic and macroscopic worlds, provided the first direct evidence for the atomic hypothesis through Einstein's 1905 explanation of Brownian motion and thereby gave credibility to the new techniques of statistical mechanics then being applied to the hypothetical atoms. It seems fitting that nearly a century later colloidal suspensions should also offer a visible model for the application of the most elementary statistical technique of all, namely *counting*, to determine a fluid structure akin to that of atoms. *Digital video microscopy*¹ makes possible the direct measurement of the averaged structure of a colloidal fluid,^{2–6} a sort of real-world “molecular dynamics simulation.” For suspensions narrowly confined between parallel glass plates, the particles form a quasi-two-dimensional fluid. The direct measurement of the structure of a monolayer of charged polystyrene spheres of micrometer scale in a confined aqueous solution can then be made to yield an effective pair potential. Kepler and Fraden⁵ and Carbaljal *et al.*⁶ found in this way a potential that is short ranged with a significant attractive component, in contrast to the essentially repulsive interaction between unconfined charged colloidal spheres, while Crocker and Grier⁴ determined a repulsive interaction with a notably smaller Debye-Hückel screening length than that of an unconfined suspension. From the theoretical side, two-dimensional models of colloidal fluids with repulsive potentials have been studied using both simulation^{7–9} and integral equations.^{9–11}

All of these calculations have been for monodisperse colloidal suspensions. In this paper, we use integral equations to study the effects of size and charge polydispersity on two-dimensional fluids. The effective potential that arises in confined suspensions being still uncertain, we use two familiar interaction models: (a) the repulsive part of the Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction^{12–14} and (b) the Lennard-Jones 12-6 interaction.¹⁵

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II. INTEGRAL EQUATION FORMALISM FOR A MONOLAYER OF POLYDISPERSE SPHERES

We consider a uniform monolayer of N polydisperse colloidal spheres occupying a plane area A at temperature T . The density of particles at point \mathbf{r} with diameter σ is given by the one-body density function

$$\rho^{(1)}(\mathbf{r}, \sigma) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\sigma - \sigma_i) \right\rangle = \rho f(\sigma), \quad (1)$$

where $\rho = N/A$ and $f(\sigma)$ is the fixed distribution of particle diameters σ . The two-body density function

$$\begin{aligned} \rho^{(2)}(\mathbf{r}, \sigma, \mathbf{r}', \sigma') &= \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\sigma - \sigma_i) \delta(\mathbf{r}' - \mathbf{r}_j) \delta(\sigma' - \sigma_j) \right\rangle \\ &= \rho^2 f(\sigma) f(\sigma') g(|\mathbf{r} - \mathbf{r}'|, \sigma, \sigma') \end{aligned} \quad (2)$$

then defines the generalized pair distribution function $g(r, \sigma, \sigma')$, which is the key quantity needed for a complete description of the structure and thermodynamics of the colloidal monolayer. In these expressions, \mathbf{r}_i is the location of particle i in the plane and σ_i its diameter; the angular brackets denote a canonical ensemble average.

In classical liquid state theory, the pair distribution function is obtained from the Ornstein-Zernike (OZ) equation combined with a closure relation.¹⁵ The first of these, generalized for polydispersity, reads

$$\begin{aligned} \gamma(r_{12}, \sigma_1, \sigma_2) &= \rho \int d\mathbf{r}_3 d\sigma_3 f(\sigma_3) [c(r_{13}, \sigma_1, \sigma_3) \\ &\quad + \gamma(r_{13}, \sigma_1, \sigma_3)] c(r_{32}, \sigma_3, \sigma_2) \end{aligned} \quad (3)$$

for the indirect correlation function $\gamma = g - 1 - c$, where c is the direct correlation function. The second, or closure, relation expresses c back in terms of γ and the pair interaction ϕ ,

$$\begin{aligned} c(r, \sigma_1, \sigma_2) &= \exp[-\beta\phi(r, \sigma_1, \sigma_2) + \gamma(r, \sigma_1, \sigma_2) \\ &\quad + b(r, \sigma_1, \sigma_2)] - 1 - \gamma(r, \sigma_1, \sigma_2), \end{aligned} \quad (4)$$