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LETTER TO THE EDITOR

Barometric equilibrium as a probe of the equation of state of colloidal suspensions

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Abstract. Measured density profiles of colloidal suspensions in the gravitational field may be inverted, within the local density approximation, to yield the osmotic equation of state. The feasibility of the procedure is tested by Monte Carlo simulations of the density profiles for two simple models of interacting colloidal particles.

In 1910 Jean Perrin [1] measured the density profile of dilute suspensions of Brownian particles subjected to gravity, and by identification with the barometric law, which holds for non-interacting particles, was able to obtain an estimate of Avogadro's number. Here we investigate theoretically the case of concentrated suspensions of interacting colloidal particles to examine which information may be extracted from a measurement of the density profile $\rho(z)$ as a function of the altitude z . We have calculated the density profiles for two simple models of interacting Brownian particles by Monte Carlo (MC) simulations, and show that, after suitable coarse-graining, these 'experimental' data are accurately reproduced, from a knowledge of the osmotic equation of state (EOS) of the homogeneous suspension, within the local density approximation (LDA). This direct test of the LDA lends support to the inverse procedure, which uses the equivalent hydrostatic equilibrium condition to extract the unknown osmotic EOS from laboratory measurements of the density profile [2].

The two models of interacting particles that we consider are: (a) a system of hard spheres of diameter σ as a model for sterically stabilized colloids [3] and (b) a system of particles interacting via a screened Coulomb potential, $v(r) = (U_0\lambda/r)\exp(-r/\lambda)$ (where U_0 is the energy scale and λ the screening length) as a crude model for charge-stabilized colloids [4]. Apart from their mutual interactions the particles of buoyant mass m are subjected to the gravitational potential $\phi(z) = mgz$, and their vertical coordinate is restricted to $0 \leq z \leq \infty$, i.e. the particles occupy a semi-infinite container. There is no upper limiting surface, and confinement is therefore ensured by gravity. For a given temperature T , an equilibrium state of the inhomogeneous colloidal suspension is characterized by the parameters $\alpha = mg/k_B T$ and n_s , the number of particles per unit area of the horizontal (x, y) bottom plane. For colloidal particles with a diameter σ of a few hundred nanometres, the dimensionless parameter $\alpha\sigma$ is typically of the order of one at room temperature.

We have computed the density profiles $\rho(z)$ for both models from Monte Carlo (MC) simulations, using the standard Metropolis algorithm [5], with a vertical downward bias controlled by the Boltzmann factor $\exp(-mgz/k_B T)$, and runs extending over tens of thousands of cycles (a cycle involves one trial move for each of the N particles, with $N \simeq 10^3$). Periodic boundary conditions were adopted in the horizontal plane. The calculated density profiles $\rho(z)$ exhibit marked oscillations near $z = 0$, indicative of layering of the particles near the bottom. By convoluting $\rho(z)$ with a triangular resolution function of width comparable to the particle size, a smooth, essentially monotonic profile $\bar{\rho}(z)$ results. Examples are shown in figure 1.

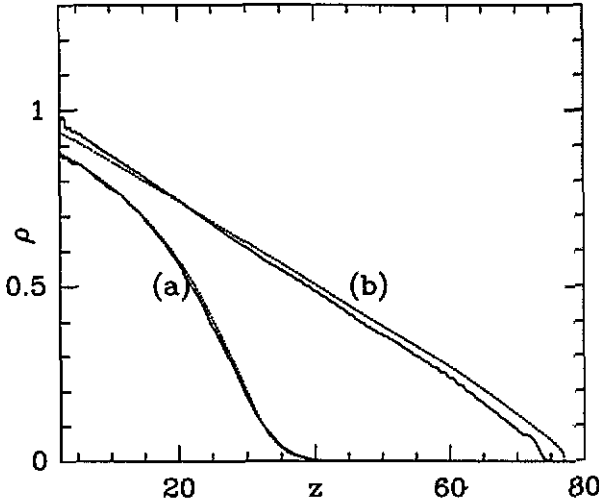


Figure 1. Density profiles for (a) the hard-sphere potential and (b) a screened Coulomb potential with $U_0 = 200k_B T$. The full curves are the smoothed MC profiles $\bar{\rho}(z)$, the dashed curves are results from the LDA. In case (a), the unit of length is the hard-sphere diameter σ and the parameters are $\alpha = 0.5\sigma^{-1}$, $n_s = 20\sigma^{-2}$. In case (b), the unit of length is the screening length λ , and the parameters are $\alpha = 17\lambda^{-1}$, $n_s = 40\lambda^{-2}$. This choice of parameters results in densities ρ_0 at the bottom that are close to the crystallization density for both systems.

Alternatively, the profile may be calculated from density functional theory [6]. For profiles varying slowly over length scales comparable to the particle size, the local density approximation (LDA) should be adequate. Note that the coarse-grained profiles $\bar{\rho}(z)$ vary significantly only over length scales much larger than the scale α^{-1} characteristic of non-interacting particle profiles. In the present situation it is easily shown that the LDA is equivalent to the expression for local hydrostatic equilibrium, namely:

$$dP(z)/dz = -mg\rho(z) \quad (1)$$

where $P(z) = P(\rho(z))$ is the osmotic pressure of the isothermal suspension at altitude z . In the LDA this pressure is equal to that of a homogeneous suspension of density $\rho = \rho(z)$. If $Z(\rho) = P(\rho)/\rho k_B T$ denotes the corresponding dimensionless EOS, straightforward integration of (1) leads to:

$$z = \frac{1}{\alpha} \left(\int_{\rho}^{\rho_0} \frac{Z(\rho')}{\rho'} d\rho' + Z(\rho_0) - Z(\rho) \right) \quad (2)$$

where $\rho_0 = \rho(z = 0)$. Thus a knowledge of the density dependence of Z for the homogeneous suspension leads directly to $z(\rho)$, and by inversion to the desired density profile. The constant ρ_0 follows directly from integration of (1) between $z = 0$ and $z = \infty$, the normalization of $\rho(z)$, and the boundary condition $P(\infty) = 0$, with the result:

$$\rho_0 Z(\rho_0) = \alpha n_s. \quad (3)$$

The LDA density profiles calculated from (2) and (3) using the Carnahan–Starling EOS for the hard-sphere fluid [7] and the mean spherical approximation (MSA) EOS for the screened Coulomb interaction [8] are also shown in figure 1. The density profile for hard spheres may in fact be derived from equation (1) in closed form [9]. The agreement with the ‘exact’ MC data for $\bar{\rho}(z)$ is seen to be excellent, and this agreement is maintained for other values of the parameters α and n_s , provided the resulting bottom density ρ_0 , calculated from (3), does not exceed the crystallization density. The slightly larger discrepancy between MC and LDA results in the case of the screened Coulomb potential probably originates from the lesser accuracy of the approximate EOS used to solve the LDA equations. It is worth pointing out that density functional theory provides a powerful framework to improve upon the macroscopic hydrostatic equilibrium description in situations where the density profile varies rapidly (in particular for heavier Brownian particles), e.g. by adding appropriate gradient corrections to the LDA [6].

This excellent agreement between LDA and MC results suggests inverting the whole procedure. Starting from the measured density profile $\bar{\rho}(z)$, one may integrate (1) numerically to determine $P(z)$, and then eliminate the altitude z between $P(z)$ and $\bar{\rho}(z)$ to extract the EOS $Z(\rho)$ of the homogeneous colloidal fluid. Results of this inversion procedure using the MC-generated profiles $\bar{\rho}(z)$ are shown in figure 2. The EOS obtained agree remarkably well with the approximate analytical results [7, 8]. This suggests two applications. Firstly, a calculation of the density profile for particles in a gravitational field determines in principle the EOS along a complete isotherm (from $\rho = 0$ to $\rho = \rho_0$) in a single MC simulation. In fact, for runs corresponding to values of ρ_0 higher than the crystallization density ρ_c , we were even able to locate the horizontal tie-line for fluid–solid coexistence on the $P(\rho)$ isotherm. However, for practical purposes, the method is limited in accuracy, since the establishment of a stable density profile in a simulation is a fairly slow process and requires for equilibration a much larger number of cycles than standard simulations on homogeneous systems. Thus the method would require a computational effort comparable to that needed to explore many individual state points of the corresponding homogeneous suspension, in order to achieve a high degree of accuracy; the present method remains, however, useful for a quick, semi-quantitative determination of the entire EOS in a single run.

More importantly, the inversion procedure may be applied to analyse experimental density profiles, determined e.g. by measuring light or x-ray absorption coefficients as a function of altitude. Proceeding once more from equation (1) would lead directly to the osmotic EOS of the colloidal suspension, thus providing an indirect but accurate measurement of the osmotic pressure which is generally too weak to be directly measurable [2]. (P is of the order of 1 Pa for a room temperature suspension of particles of a few hundred nanometres, even for a packing fraction as large as 0.5.) A good knowledge of the osmotic EOS would be of considerable

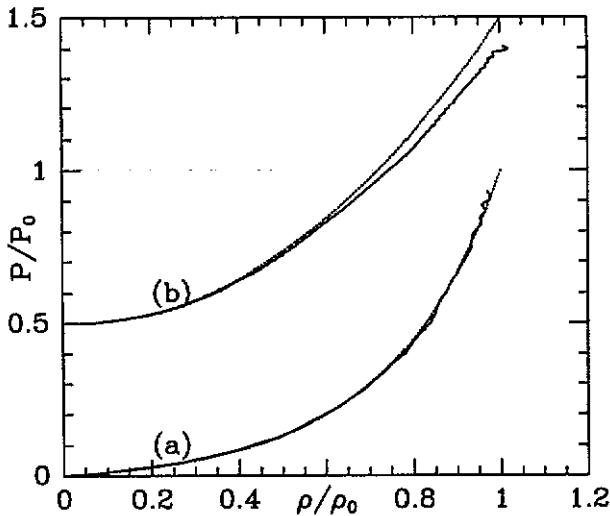


Figure 2. Equation of state obtained from the density profiles presented in figure 1 by following the inversion procedure described in the text. The pressure and densities have been scaled by their values at the bottom and the results for the screened Coulomb potential (b) have been vertically shifted. The dashed curves are analytical approximations to the EOS from [7] (system (a)) and [8] (system (b)). The MSA approximation for system (b) is known to be less accurate than the nearly exact Carnahan-Starling EOS for system (a).

interest because the latter contains significant, though indirect information on the direct interactions between colloidal particles, since the pressure variation with density depends sensitively on the nature of the interactions. This sensitivity is illustrated in figure 1, where it is seen that the two potentials studied, although both are purely repulsive, lead to density profiles with markedly dissimilar shapes. The experiments could alternatively be carried out in a rotating horizontal cylinder so that the radial density profile would build up under the effect of the centrifugal force rather than gravity. The advantage of this set-up is that the centrifugal force could be tuned by varying the frequency of rotation of the cylinder.

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