

## Measuring the equation of state of a hard-disc fluid

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**Abstract.** – We use video microscopy to study a two-dimensional (2D) model fluid of charged colloidal particles suspended in water and compute the pressure from the measured particle configurations. Direct experimental control over the particle density by means of optical tweezers allows the precise measurement of pressure as a function of density. We compare our data with theoretical predictions for the equation of state, the pair-correlation function and the compressibility of a hard-disc fluid and find good agreement, both for the fluid and the solid phase. In particular, the location of the transition point agrees well with results from Monte Carlo simulations.

Hard-disc (HD) fluids play a prominent role in liquid-state theories. This is due to the fact that, first, they often serve as reference systems in perturbation theories of two-dimensional (2D) liquids (just as hard-sphere fluids do for liquids in three dimensions), and that, secondly, at high densities the behavior of every 2D fluid is dominated by excluded-volume effects, which in turn depends just on the short-ranged hard-core part of the interparticle potential. Mainly for these two reasons, the HD equation of state (EOS) appears also in many theories on monolayer adsorption on solid surfaces [1, 2], an aspect illustrated, for example, in ref. [3], where the HD EOS is used in statistical mechanical theories modeling the binding of peripheral globular proteins on lipid membranes. The important role of the HD system explains the overwhelming number of theoretical studies on the EOS of a HD fluid, starting as early as 1959 with the presentation of results from scaled particle theory [4]. Most of all approaches to the EOS are based on particular resummations of the virial series and the construction of sophisticated Padé approximants [5–7], others use results from integral equation theories [8], or from theories based on overlap volume functions [9]. Not only the EOS, but also the structure of a hard-disc fluid has been explored in detail and is to date well understood [7–10]. Hard discs are popular also as model system to test advanced density functional theories [11, 12], used, for instance, to study discs in cavities [13], or induced freezing and re-entrant melting [14]. Many computer simulation studies of HD systems are available [1, 15, 16], of which the more recent ones have focused mainly on the melting properties of HD solids [16].

All these theoretical efforts contrast with the situation on the experimental side. To our knowledge, the HD EOS has never been tested with experimental data. The present letter aims at closing this gap. We report on experiments with a 2D model liquid of charged colloidal particles suspended in water. Correlation functions computed from real-space images, together with the virial equation, are used to calculate the pressure  $p$  of the 2D liquid as a function of the 2D particle density  $\rho$ , which in our experiment can be conveniently varied by means of optical tweezers. We have thus realized a 2D colloidal model fluid for which the EOS, *i.e.* the  $p(\rho)$  diagram, can be determined directly. Comparing the experimental to the theoretical

EOS of HDs, we find the colloidal liquid to behave as a 2D fluid of HDs over a wide density range from the fluid to the solid phase.

We should remark that monolayers of atoms adsorbed on solid surfaces behave in certain cases also as 2D fluids [1, 2]. In order to obtain experimental EOSs in these atomic systems, one has to transform measured isotherms to  $p(\rho)$  diagrams. This has been done by Glandt *et al.* [17], who compared various theoretical EOSs for a 2D Lennard-Jones (LJ) fluid with the 2D pressure of argon and krypton, adsorbed on graphitized carbon black [18]. Still, treating adsorbed monolayers as 2D fluids remains an idealization which is rarely justified because the 2D system is usually not isotropic due to the natural corrugation of the substrate surface [2, 14, 19].

Contrary to atomic systems, where one is simply stuck with the interaction dictated by the electronic structure of the atoms, the interactions between colloidal particles can be externally controlled and thus adapted to the problem one wants to study. To experimentally realize a hard-disc system with colloidal particles, it is important to assure that the inter-particle potential is extremely short ranged and that no attractive parts in the potential exist. We have decided not to work with sterically stabilized colloidal particles as this stabilization usually leads to a structured pair potential in the distance region where the polymer brushes start to overlap [20]. Rather, we chose to use charge-stabilized colloids at moderate salt concentrations. A screening length  $\kappa^{-1}$  between 100 nm and 200 nm yielded optimal results. Higher salt concentrations resulted in an increased unfavorable particle substrate interaction and a pronounced attractive van der Waals contribution in the interparticle potential. For the same reason it proved unpractical to use very thin sample cells, as this is known to also induce an attractive part in the pair potential [21]. The colloidal system employed consisted of charged sulphate-terminated polystyrene spheres of  $\sigma_0 = 3 \mu\text{m}$  diameter (IDC Cooperation) and of charged sulphate-terminated silica particles of  $2.4 \mu\text{m}$  diameter (polydispersity  $< 4\%$ ). The suspension was injected into a sample cell made of fused silica plates with  $200 \mu\text{m}$  spacing. We performed measurements at high and at low salt concentration, *i.e.* at  $\kappa\sigma_0 = 20.0$  and  $\kappa\sigma_0 = 6.9$ , using the  $2.4 \mu\text{m}$  spheres in the high-salt and the  $3 \mu\text{m}$  spheres in the low-salt measurement. In order to confine the particles to two dimensions, the widened beam of a frequency-double Nd:YV0<sub>4</sub> laser was directed from above into the sample cell, exerting a vertical light pressure on the particles and pushing them towards the bottom plate of the sample cell. The light pressure and gravity on the one side and the electrostatic particle-wall repulsion on the other side create a sharp potential minimum in the vertical direction in which the particles are trapped and thus effectively confined to two dimensions. We have varied the intensity of the laser beam over a wide range and observed no influence on the particle structure. Therefore, light-induced effects on the pair interaction can be ruled out. In contrast to the above-mentioned 2D LJ fluids, realized by adsorbed atoms on solid surfaces, we here do not need to make special assumptions concerning the properties of the substrate surface. It can be safely ruled out in our experiment that the particles' mobility in 2D is in any way hindered by a possible periodicity of the substrate surface. Our system is almost perfectly two-dimensional with vertical out-of-plane fluctuations of less than 250 nm. An important component of our set-up, which is indispensable for measuring  $p(\rho)$  diagrams, is our method to vary the particle density  $\rho$ . This was achieved by a scanned optical laser tweezers briefly described in the following. The beam of a laser was reflected from a computer-controlled system of mirrors and focused into the 2D system plane. By means of these mirrors the tweezers were repeatedly (200 Hz) scanning a line having the form of a rectangular box, which results in an optical line trap for the particles along the contour of the box. Trapped particles arrange like a pearl-necklace along this contour and, due to the repulsive inter-particle potential, prevent other particles from escaping the box, thus defining a system (all particles

in the box) with a certain number of particles (1000 to 3000). The box size can be changed via the control unit of the mirror system which allows precise adjustment of the particle density in the system. For each system at density  $\rho$ , digital video microscopy measurements were made using a high-aperture long-distance microscope objective (Zeiss Achroplan 63 $\times$ ) with dark-field illumination. The particle positions were determined with an accuracy of better than 50 nm. From statistical averages of the particle positions, we computed pair correlation functions  $g(r)$ . Further details about the experimental set-up and the data analysis can be found in our previous papers [22, 23].

Having the pair-correlation function at density  $\rho$ , the pressure can be computed from the virial equation which for an isotropic 2D system reads

$$\beta p \sigma^2 = \rho \sigma^2 - \frac{\pi \rho^2 \sigma^2}{2} \int_0^\infty dr r^2 \beta u'(r) g(r), \quad (1)$$

where  $\beta = 1/kT$ .  $u'(r)$  is the derivative of the interparticle potential  $u(r)$  with respect to the distance  $r$ ; this potential is not known *a priori*, but may be derived from the structural data, *e.g.* from inverting  $g(r)$ . This was done by means of the Ornstein-Zernike equation and appropriate closure relations (Percus-Yevick and HNC), a method described and tested in [22], see also [24]. Performing then this integral for all measured  $g(r)$ 's, we obtain  $p(\rho)$ , the desired EOS. For the  $\kappa\sigma_0 = 20.0$  measurement, we obtained, from the inversion, almost perfect Yukawa potentials ( $u(r) \sim e^{-\kappa r}/r$ ) which were —within the error bars specified below— identical, regardless at what density we analyzed the pair-correlation function, while for the low-salt measurement we obtained, for all  $g(r)$ 's, Yukawa potentials with almost identical prefactors and screening constants  $\kappa$ , but with a density-dependent truncation at large distances and high densities. This density-dependent truncation has been interpreted in terms of many-body interactions [22, 23]. The fact that in both measurements the  $\kappa$  resulting from the inversion procedure do not show any dependence on  $\rho$  clearly indicates that the salt-ions dominate the screening behavior and that the contribution of counter-ions to the screening can be neglected. Due to the double layers around the particles, the effective hard-core diameter  $\sigma$  is larger than the actual particle diameter  $\sigma_0$ . Similar to [25], we determined  $\sigma$  by first evaluating the second virial coefficient

$$B_2 = -\pi \int_0^\infty r (e^{-\beta u(r)} - 1) dr \quad (2)$$

using the interparticle potential  $u(r)$  obtained from the measured  $g(r)$ 's, and by then identifying  $B_2$  with the second virial coefficient of a pure HD system,  $B_2^{(\text{HD})} = \pi\sigma^2/2$ . We obtain  $\sigma = 1.084\sigma_0$  for the  $\kappa\sigma_0 = 20.0$  measurement, and  $\sigma = 2.16\sigma_0$  for the  $\kappa\sigma_0 = 6.9$  measurement.

Figure 1 shows the pressure as a function of  $\rho\sigma^2$ , for both measurements. The precision of our procedure is limited mainly by errors made in the determination of  $u(r)$ ; they lead to small variations in the computed pressure, but also in the effective hard-core radii. Therefore, the error bars appear tilted in fig. 1. The measured EOS is compared with Monte Carlo (MC) data from [12], and with an expression proposed by Baus and Colot [7] for the EOS of a fluid HD system,

$$\beta p / \rho = \frac{1 + \sum_{n=1}^6 c_n \eta^n}{(1 - \eta)^2} \quad (3)$$

with  $\eta = \pi\rho\sigma^2/4$  and  $c_1 = 0$ ,  $c_2 = 0.128$ ,  $c_3 = 0.0018$ ,  $c_4 = -0.0507$ ,  $c_5 = -0.0533$ ,  $c_6 = -0.0410$ . The agreement between our high-salt data and the HD EOS is almost perfect, both on the fluid and the solid side of the phase transition, but also with regard to the

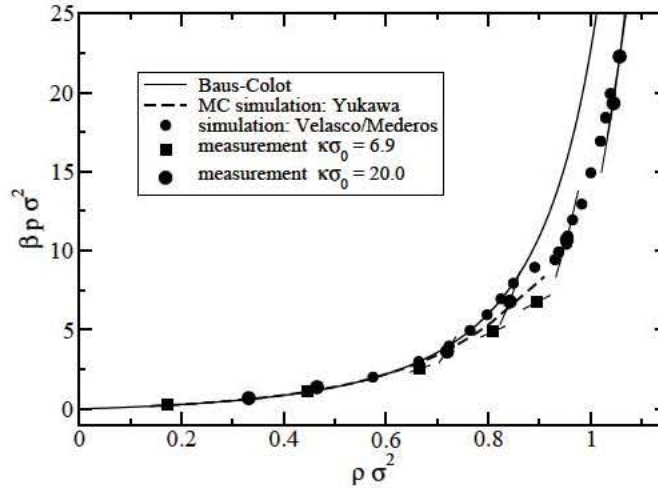


Fig. 1 – Equation of state of a hard-disc system in the fluid and the solid density range. Theoretical predictions for the fluid branch (Baus/Colot [7]) and the solid branch (Velasco/Mederos [12]) are compared with experimental data, measured in high-salt (filled circles) and low-salt (filled squares) colloidal suspensions. Error bars (solid short lines attached to the filled symbols) are inclined for reasons explained in the text. Monte Carlo data for a Yukawa fluid (dashed line) are provided to interpret the  $\kappa\sigma_0 = 6.9$  measurement.

location of the transition point itself. A much simpler EOS [6] ( $c_2 = 0.125$  and  $c_n = 0$  for  $n = 1, n > 2$  in eq. (3)) agrees equally well and also the density-functional theory by Velasco and Mederos [12] (data not shown here). Surprisingly, even for low-salt concentration ( $\kappa\sigma_0 = 6.9, \sigma/\sigma_0 = 2.16!$ ), the colloidal system can still be successfully mapped to a HD fluid, at least for low densities. For  $\rho\sigma^2 > 0.7$ , there are marked deviations from the HD EOS. We performed MC simulations to compute pair-correlation functions of a quasi-2D fluid system, using the Yukawa part of  $u(r)$  of the  $\kappa\sigma_0 = 6.9$  measurement. The pressure curve, computed with eq. (1) from the MC-generated pair-correlation functions, is plotted as dashed line in fig. 1. It is evident that this line differs, as expected, from the HD EOS, but also from the experimental values of the  $\kappa\sigma_0 = 6.9$  measurement, a difference which hence must be due to deviations of the experimental pair potential from the assumed Yukawa form. As pointed out in [22, 23] the experimental pair potential shows a density-dependent truncation in  $u(r)$ , which has been ignored in the MC simulation.

Baus and Colot [7] have suggested a semiempirical expression for the direct correlation function of a HD fluid which can be related to  $g(r)$  via the Ornstein-Zernicke equation. Figure 2 shows the resulting pair-correlation functions (solid lines) for various densities and compares them with our measured  $g(r)$ . We emphasize that after matching the second virial coefficient no free parameter was used. While in the case of high-salt concentration excellent agreement is found, differences are observed for the  $\kappa\sigma_0 = 6.9$  measurement, mainly for small particle separations where the first peak is less pronounced compared to that of the HD fluid, due to the softer pair potential. For larger distances, packing effects dominate, and the agreement is again good.

From the recorded particle positions we can also compute the particle number fluctuation  $\langle \Delta N^2 \rangle / \langle N \rangle$  with  $\Delta N = N - \langle N \rangle$ ,  $\langle N \rangle$  being the mean number of particles. This quantity, which is related to the isothermal compressibility,  $\chi_T k T \rho = \langle \Delta N^2 \rangle / \langle N \rangle$ , is plotted as open symbols in fig. 3. Alternatively, we can calculate  $\chi_T$  from the density derivative of the pres-

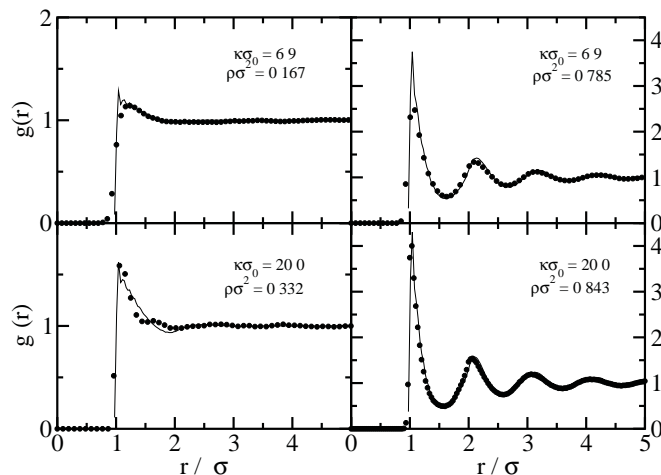


Fig. 2 – Comparison between theoretical [7] (solid line) and experimental (filled circles) pair-correlation functions for a hard-disc fluid at different densities, experimentally realized with low-salt ( $\kappa\sigma_0 = 6.9$ ) and high-salt ( $\kappa\sigma_0 = 20.0$ ) colloidal suspensions.

sure,  $\chi_T kT\rho = (\beta\partial p/\partial\rho)^{-1}$ , which we did in fig. 3 (filled symbols) computing the differences between neighboring experimental values in fig. 1. The compressibilities, calculated in both ways, are compared with the derivative of Henderson's EOS [6],

$$\rho kT\chi_T = \left[ \frac{1 + \eta^2/8}{(1 - \eta)^2} + \eta \frac{\eta + 8}{4(1 - \eta)^3} \right]^{-1}, \quad (4)$$

plotted in fig. 3 as solid line. While the density derivatives of the experimental pressure values agree nicely with the theoretical prediction of eq. (4),  $\langle\Delta N^2\rangle/\langle N\rangle$  shows deviations, especially

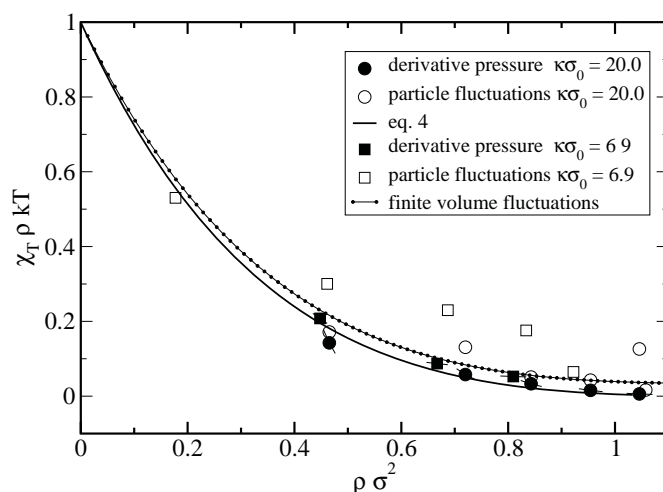


Fig. 3 – Compressibility of a hard-disc fluid, as obtained from density derivatives of the  $p(\rho)$  curves of fig. 1 and the particle number fluctuations  $\langle\Delta N^2\rangle/\langle N\rangle$ . Symbols for the experimental values, lines for theoretical predictions for an infinite system, eq. (4), and a finite system [26].

for the low-salt measurement. One reason for this discrepancy might be a finite-size effect. To estimate this effect, we used the pair-correlation functions, suggested by Baus and Colot for the infinite system, to calculate the particle number fluctuation in a finite subvolume ( $V = \pi r_0^2$ ,  $r_0 = 10\sigma_0$ ) of a hard-disc fluid composed of a fixed number of particles (1000 particles), in a way described in detail by Roman *et al.* [26]. The result is plotted in fig. 3 and the small correction illustrates that, at least for the high-salt measurement, the observed differences can be explained with a finite-size effect. For the low-salt measurement, the remaining differences are probably due to insufficient sampling.

To obtain more information on the character of the different phases in fig. 1, we also examined the orientational correlation function  $g_6(r)$  [27] for the high-salt measurement. Up to a density of  $\rho\sigma^2 = 0.85$ , the system exhibits a pure liquid phase as confirmed by the isotropic pair-correlation function  $g(r)$  and the exponentially decaying  $g_6(r)$ . On the other hand, at densities above  $\rho\sigma^2 = 0.95$  the system is in stable crystalline state, with a slow algebraically decaying pair correlation function and a constant orientational correlation function. However, in between, *i.e.* for  $0.85 < \rho\sigma^2 < 0.95$ , there is a transition region, in which  $g_6(r)$  decays more slowly than exponentially and a local hexagonal order can be observed. At present it cannot be decided whether this is the hexatic phase or a very polycrystalline state. In contrast to the measurement of Marcus and Rice [20] no pronounced liquid-hexatic and hexatic-solid coexistence region has been observed, which is most likely due to the fact that their pair-potentials had weak attractive parts, while ours are purely repulsive.

We close with a few comments and summarizing remarks. i) Similar hard-disc-like fluids have been experimentally realized also by Murray *et al.* [28] and by Marcus *et al.* [20] using colloidal suspensions in confined geometries. While these authors concentrated on the melting properties of 2D systems, it has been the focus of the present work to study the EOS of the 2D system which naturally requires a convenient experimental tool to vary the density, realized here with optical line tweezers. ii) To experimentally realize a HD system, it is decisive to choose the right salt concentration, as salt tunes the inter-particle potential but also the interaction between particle and wall. Too much salt leads to an attraction in the interparticle potential and makes the wall-particle interaction more short-ranged (so that the 2D system plane is shifted too close to the wall), while too little salt results in a very soft repulsive potential. In both cases, the colloidal system can no longer be interpreted as a hard disc system. The extent of the deviation between the experimental and the HD system caused by a very soft pair potential ( $\kappa\sigma_0 = 6.9$ ) has been shown above. iii) 2D colloidal suspensions can indeed be considered as a hard-disc system. This applies both to the structure as well as to the thermodynamics. The effective HD radius of the colloidal particles is correctly defined by simply demanding the second virial coefficient to be equal in both descriptions. iv) On the atomic level, the EOS of 2D fluids can be derived from adsorption isotherms [2]. As opposed to these experiments, we here have the full structural information, controllable substrate-particle interactions and tunable inter-particle potentials. In adsorbed monolayer films [18] the phase behavior can be deduced only via averaged quantities and there is a certain ambiguity about the emergence of multi-layer adsorption at higher densities. This highlights once again the power of colloids as a model system in statistical mechanics.

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