

## Microscopic structure and dynamics of a dense fluid near a smooth wall-video microscopy of colloidal spheres

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# Microscopic structure and dynamics of a dense fluid near a smooth wall—video microscopy of colloidal spheres

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**Abstract.** We measure the instantaneous atomic structure and dynamics of a three dimensional (3D) fluid near crystallization in contact with a smooth wall. Our 'atoms' are monodisperse, highly charged submicrometre spheres in colloidal suspension in water. We simultaneously follow the positions of about 2000 spheres using video microscopy, taking snapshots at intervals close to the collision time of the fluid. We find that the dense fluid is layered in the direction perpendicular to the wall, with at least four distinct layers. We compare the microscopic particle dynamics of the first layer of fluid with those of a two dimensional (2D) layer of spheres at the same density but rigidly confined between two smooth walls, on a time scale at which over 96% of the spheres remain in the first 3D layer. We find dramatic differences in the correlation lengths and times, the defect structure and dynamics, the particle trajectories and the self-diffusion times for the two cases.

## 1. Introduction

We have studied the influence of a hard wall on microscopic structure and dynamics in real space and time for a fluid very close to freezing. The sample is a monodisperse colloidal dispersion in water of polystyrene sulphate latex spheres with diameter  $d = 0.305 \pm 0.006 \mu\text{m}$  with surface charge  $\approx 4 \times 10^5$  electronic charges [1]. The colloidal spheres are maintained in intimate contact with H and OH ion exchange resin and held at temperature  $T = 29 \pm 0.1 \text{ }^\circ\text{C}$ . The spheres interact with a combination of repulsive screened Coulomb, hard sphere, van der Waals, and hydrodynamic forces [2]. The spheres are strongly repelled by the glass walls of the cell, as the walls have a comparable surface charge density to that of the spheres [3]. The spheres exhibit Brownian motion, and so have a true thermodynamic temperature. They crystallize into 3D FCC and 2D triangular crystal structures at a nearest neighbour separation  $a = 1.35 \mu\text{m}$  [4]. In previous experiments [4], we observed a very gradual melting transition in a 2D colloidal crystal confined between two smooth glass plates as its density is varied. In contrast, a 3D FCC colloidal crystal near a smooth wall exhibits an abrupt melting transition at the

same in-plane density. In this paper, we contrast the structure and dynamics of high density 3D and 2D fluids just before crystallization.

## 2. Experiment and results

### 2.1. Experimental geometry

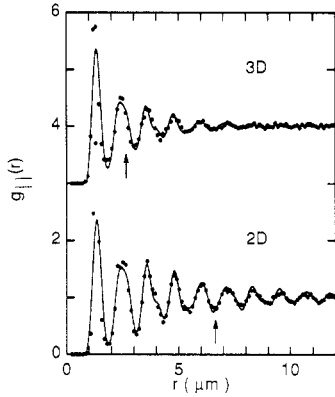
Details of the experiment are given elsewhere [4–6]. The total thickness of the 3D colloid for these runs was  $\approx 500 \mu\text{m}$  along  $z$ , perpendicular to a smooth glass wall in the  $x, y$  plane. In the 2D experiment, the sample geometry is the same, except that a second glass plate is brought to within  $z = 2\text{--}2.5 \mu\text{m}$  of the first. The 2D sample is rigidly 2D: it has root-mean-square fluctuations out of plane (along  $z$ ) smaller than  $0.03a$  as the in-plane density is changed from that of the fluid until that of the crystal just past freezing [3, 4]. The 3D fluid just before freezing has an in-plane density  $n = 0.0562 \pm 0.0004$  (in units of inverse diameters squared) about 6% lower than  $n_c$ , that of the FCC (111) face of the crystal which nucleates at the glass surface [4]. We image a region of size  $\Delta x \times \Delta y \times \Delta z = 59 \mu\text{m} \times 46 \mu\text{m} \times 0.4 \mu\text{m}$  in the centre of a sample that is  $10^{2-3}$  times larger in linear extent. The depth of focus of the objective lens,  $\pm 0.2 \mu\text{m}$ , is comparable to a sphere diameter, making it possible to image a single layer of spheres.

### 2.2. Density profile of the 3D fluid perpendicular to a wall

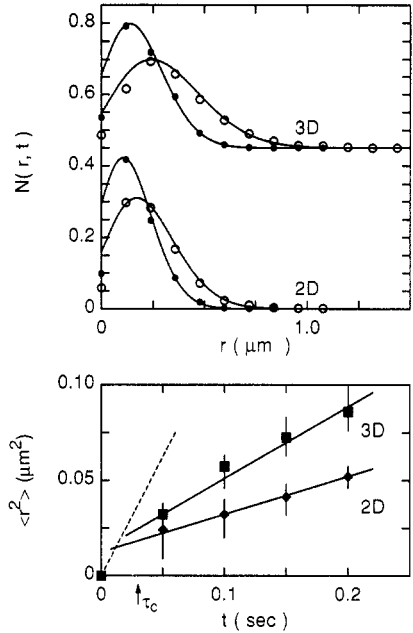
We have previously shown [5] that the variance about the mean of image intensity, a measure of image contrast, is directly proportional to average sphere density in rigid 2D layers. We observe sharp distinct peaks in the variance of images of an FCC crystal very close to melting as we translate the focus of the lens in the  $z$  direction away from the glass wall. We also find at least four distinct layers in the 3D fluid near the smooth wall. We will discuss our results at length elsewhere [6]. Fluid layering near a hard wall has been observed in both simulations [7] and density functional theories [8]. What is surprising in our experiment is the sharpness of the fluid layers in the  $z$  direction, with root mean square deviation  $\approx 0.1a$  comparable to that of the bulk crystal; their separation, that of the crystal planes; and a growing correlation length perpendicular to the wall very close to the freezing transition. At the same time, the fluid in-plane correlations remain very short ranged, with a correlation length of  $\approx 2a$  even for the first layer of the fluid just before freezing, upon which we will now focus our attention. As the 3D first layer is so sharp, it is interesting to contrast its structure and microscopic particle dynamics to a rigid 2D layer at the same in-plane density.

### 2.3. In-plane microscopic structure of the first 3D fluid layer—comparison with 2D

The particle center locations in each video frame are used to determine in-plane density, correlation functions, structure factors, and topological defects [3–5]. The 2D layer has 84% perfect sixfold coordination, while the 3D first layer has only 67% sixfold coordination. The contrast in defect densities in the 2D and 3D layers is apparent in their



**Figure 1.** In-plane pair correlation functions for the first 3D fluid layer with in-plane density  $n = 0.94n_c$  (shifted +3 vertically) and a 2D layer with the same in-plane density. The lines through the data points are fits to an exponentially decaying broadened perfect hexagonal  $g(r)$ . The in-plane correlation length  $\xi$  is marked by the arrows for each curve.



**Figure 2.** Top: distributions  $N(r, t)$  normalized to the total number of spheres for  $t = 0.05$  s (full circles) and  $0.2$  s (open circles) for the first 3D fluid layer with  $n = 0.94n_c$ , displaced vertically by  $0.45$ ; and for the 2D layer with the same density. Bottom: mean squared in-plane distance moved versus time for the 3D and 2D layers. The broken line depicts a slope of  $2D_0 = 2 \times 0.89D_{\text{Stokes}}$ . The full lines have slopes  $2D_{3D} = 2 \times 0.29D_0$  and  $2D_{2D} = 2 \times 0.16D_0$ .

in-plane pair correlation functions, shown in figure 1. The 3D in-plane correlation length  $\xi_{3D} \approx 2a$ , while the 2D correlation length  $\xi_{2D} \approx 5a$ . At this density, the 2D sample is just inside the intermediate region or hexatic phase at the fluid–hexatic border [4].

#### 2.4. Dynamics of the first 3D fluid layer—comparison with 2D

The time decay of the first ring at  $K = K_0$  of the in-plane intermediate scattering function  $F(K, t)$  gives an estimate of the lifetime of fluctuations with sixfold order at the crystal row spacing  $\sqrt{3a/2} = 2\pi/K_0$ . These fluctuations are roughly the size of the correlation length  $\xi$  determined from  $g(r)$ . We take for an ‘atomic’ or sphere–sphere collision time for this Brownian dynamical system  $\tau_c = (0.1a)^2/D_0 = 0.03$  s in our case, where  $D_0$  is the Stokes self-diffusion coefficient for a single sphere moving parallel to a hard wall a distance of four sphere diameters away [9]. We define a ‘correlation time’  $\tau$  as the lifetime of the ordered patches determined from the slope of  $\log F(K_0, t)$  versus  $t$  for  $0 \leq t \leq 0.2$  s. We find  $\tau_{3D} \approx 0.25$  s and  $\tau_{2D} \approx 1$  s or 8–30 collision times for the 3D and 2D layers, respectively.

For both samples, the in-plane displacement distributions,  $N(r, t)$ , of  $\approx 1400$  interior spheres in our imaging region after a time interval  $t$  are well represented by the Brownian

form  $r \exp(-r^2/(4D(t)t))$  in the time intervals  $t = M \times 0.05$  s,  $M = 1-4$ , as shown in figure 2. For  $t = 0.2$  s, 3.8% of the spheres in the 3D first layer have hopped to or from the second layer. Also shown in figure 2 are the mean square in-plane displacements  $\langle r^2(t) \rangle \equiv 2D(t)t$  of the spheres, determined from the fits to  $N(r, t)$ , with  $D(t)$  the (time dependent) self-diffusion coefficient. The mean square displacements are linear in time to within experimental error after approximately one collision time  $\tau_c$ , marked on the graph. Thus we see the 'cage effect' on the self-diffusion of these dense fluids [10] in roughly one collision time. From the subsequent slopes of the mean squared displacements, we estimate the later time self-diffusion coefficients to be  $D_{3D} = 0.18 \pm 0.02 \mu\text{m}^2 \text{s}^{-1} = 0.29 D_0$ , and  $D_{2D} = 0.10 \pm 0.01 \mu\text{m}^2 \text{s}^{-1} = 0.16 D_0$ . Since the in-plane densities of the two samples are identical, and the vast majority (96%) of the 3D spheres remain in the first layer on this timescale (with root mean fluctuations out of plane  $\sim 0.1a$  in comparison to  $\sim 0.03a$  for the 2D layer), the factor of four difference in correlation time and nearly factor of two difference in the self-diffusion coefficients in the first 3D layer and the 2D layer must arise from the high degree of in-plane order of the 2D fluid compared to that of the 3D layer.

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### References

- [1] A review on the use of colloidal spheres to study condensed matter physics is given in Pieranski P 1983 *Contemp. Phys.* **24** 25
- [2] Hess W and Klein R 1983 *Adv. Phys.* **32** 173
- [3] Murray C A and Van Winkle D H 1987 *Phys. Rev. Lett.* **58** 1200  
Murray C A, Van Winkle D H and Wenk R A 1990 *Phase Trans.* **21** 93
- [4] Murray C A and Wenk R A 1990 *Phys. Rev. B* **42** 688
- [5] Van Winkle D H and Murray C A 1988 *J. Chem. Phys.* **89** 3885
- [6] Murray C A, Sprenger W O and Wenk R A to be published
- [7] Magda J J, Tirrell M and Davis H T 1985 *J. Chem. Phys.* **83** 1888 and references therein
- [8] Evans R 1989 Microscopic theories of simple fluids and their interfaces *Liquids at Interfaces (Les Houches Session XLVIII, 1988)* ed J Charolin, J F Joanny and J Zinn-Justin (Amsterdam: Elsevier) ch 1, and references therein
- [9] Happel J and Brenner H 1973 *Low Reynolds Number Hydrodynamics* 2nd edn (Dordrecht: Nijhoff) ch 7
- [10] Pusey P N and Tough R J A 1982 *J. Phys. A: Math. Gen.* **15** 1291  
Nagele G, Medina-Noyola M, Klein R and Arauza-Lara J L 1988 *Physica A* **149** 123