Direct observation of hydrodynamic instabilities in driven non-uniform colloidal dispersions

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Particulate dispersions have long been subjected to external fields as a means to separate different constituents; in particular, sedimentation is important not only for analytical but also for preparative purposes [1]. For bulk systems, successful separation depends crucially upon avoiding hydrodynamic instabilities. The development of microfluidics [2] has made it possible to exploit the suppression of turbulence at small length scales in order to design novel separation devices [3]; on the other hand, this significantly increased stability against mechanical perturbations severely limits mixing needed for many ‘lab-on-a-chip’ applications. Often strong external fields [4] or complex fabrication [5] are required to produce hydrodynamic instabilities required for efficient mixing.

Experiments [6, 7] and computer simulations [8] which study velocity fluctuations have played a crucial role in our understanding of how dispersions respond to external driving fields, in particular to gravity. The motion of a solute particle is characterised by a Peclet number $Pe = \tau_D/\tau_S$, which is the ratio between the time $\tau_D$ it takes a particle to diffuse its own radius and the time $\tau_S$ it takes to sediment the same distance. A Peclet number of order unity is the dividing line between colloidal ($Pe \lesssim 1$) and granular systems ($Pe \gg 1$), i.e. $Pe$ measures the importance of Brownian motion. All attempts at a quantitative description of sedimentation to date considered a homogenously distributed dispersion as the initial state. For preparative purposes, on the other hand, starting with a particle-rich layer on top of pure solvent is more relevant as it enables the separation of particles depending on their sedimentation coefficient. However, this configuration is unstable with respect to gravity. The particle velocities become correlated, which leads to emergent density fluctuations and consequently more rapid sedimentation than Stokes’ flow alone. It is well known that many practical particle concentrations develop this Rayleigh-Taylor (RT) instability. This provides an avenue by which the system may be successfully mixed on the one hand, conversely this very mixing, leads, chaotically, to a scenario in which separation does not occur. For stable separation, it is essential to avoid the RT instability. It is possible to use a density gradient to counteract the instabilities [1].

The ‘original’ Rayleigh-Taylor instability, which occurs if a heavy, immiscible fluid layer is placed on top of a lighter one has been intensively studied for the case of a simple Newtonian fluid both by theory [9], simulation [10] and experiment, and is observed in granular matter [11], in surface-tension dominated colloid-polymer mixtures [12] and in a suspension of dielectric particles exposed to an ac electric field gradient [13].

Here we consider a suspension of colloidal hard spheres (without surface tension) of microfluidic dimensions, in which we have access to all relevant length scales, from the single particle level to the full system. A systematic study of sedimentation in an inhomogeneous system is presented. We employ three approaches: experiment, computer simulation and theory. The experimental realisation is provided by confocal microscopy at the single-particle level [13], while the simulation is a particle-based mesoscale technique [14] which captures the direct interactions between the colloidal particles, and, crucially, the solvent which mediates the hydrodynamic interactions and whose backflow drives the RT instability. Our
results at short times are modelled with a linear stability analysis [9].

The RT instability is thought of as a fluctuation in the interface between two fluids. Since in a hard-sphere suspension there is no phase separation, we consider a continuous density profile, albeit rapidly varying. To capture the lateral fluctuations, we consider the stability of this density and associated pressure profile against fluctuations of wavelength $\lambda$ in a horizontal plane perpendicular to gravity. We consider a slit geometry of height $L$ which is sketched in Fig. 1a. In the absence of surface tension, the fluctuations of all wavelengths are in principle unstable, but short wavelength fluctuations are washed out by diffusion of the colloidal particles and so do not grow exponentially [14, 18].

Our linear stability analysis, which reveals the stable and fast-growing wavelengths of fluctuations, is based on a continuum hydrodynamics approach where the colloidal dispersion is considered as an incompressible one-component fluid with inhomogeneous mass density $\rho(x)$ and corresponding kinematic viscosity $\nu(x)$ as obtained from the Saito representation [19]. The spatially varying density profile is given by $\rho(x) = \phi(x)\rho_c + (1 - \phi(x))\rho_s$, where $\rho_c$ and $\rho_s$ are the mass densities of the colloidal particles and the solvent. The colloidal packing fraction profile $\phi(x)$ is an input from an equilibrated simulation for inverted gravity. The stability of the initial density $\rho(x)$ and pressure $p(x)$ profiles against perturbations $\delta \rho \propto \delta p \propto \exp(i(k_0 y + k_2 z) + n(kt))$ with wave number $k = (k_x^2 + k_2^z + k_3^z)^{1/2}$ in the $yz$ plane and growth rate $\eta$ is calculated via the linearized Navier-Stokes equations [6] resulting in the eigenvalue problem

$$\eta'\{\phi(\nu_u^m - k^2 u_x) + \nu'\{\nu_u^m + k^2 u_x}\}' - k^2\{\phi u_x + 2\nu' u_x' + \nu\nu_u^m - k^2 u_x\}' \right)$$

with the spatial derivative $\ldots = d\ldots/dx$, the strength of the gravitational field $g$ and the fluid velocity field in gravity direction $u_x(x)$. For a system confined between two rigid walls we impose $u_x = 0$ along with the no-slip boundary conditions $d u_x/d x = 0 \text{ at } x = 0, L$.

We account for colloid diffusion by the correction term $\eta^{*}(k) = n(k) - D k^2 [17, 18]$, with diffusion constant $D = k_B T/3\pi \eta \sigma$ ( $\sigma$ colloid diameter) and dynamic solvent viscosity $\nu_s$.

In our computer simulation, which includes solvent-mediated momentum transfer between the colloidal particles, we consider a suspension of $N = 15,048$ hard sphere particles of mass $M$ immersed in a bath of typically $N_s = 14,274,843$ solvent particles of mass $m$ and number density $n_s = N_s/V$. The solvent particles are subjected to multi-particle collision dynamics [16, 20], which consist of two steps. In the streaming step, solvent particles move ballistically for time $\delta t$. In the collision step, particles are sorted in cubic cells of size $a$, and their velocities relative to the center-of-mass velocity of each cell are rotated by an angle $\alpha$ around a random axis. We employed the parameters $\delta t = 0.2 \sqrt{m a^2 / k_B T}$, $\alpha = 3\pi/4$, $n_s a^3 = 5$ and $M = 167 m$ in order to achieve the hierarchy of time scales and the same hydrodynamic numbers as in the experiment, see Ref. [8, 21] for details. To enforce no-slip boundary condition on the colloid surface and the confining walls a stochastic-reflection method [22] is applied. Statistical averages for time-dependent quantities are performed over 200 independent configurations.

In our single-particle level confocal microscopy experiments we used polymethylmethacrylate colloids sterically stabilised with polyhydroxy-stearic acid. The colloids were labeled with the fluorescent dye coumarine and had a diameter $\sigma = 2.8 \mu m$ with around 4% polydispersity as determined by static light scattering. To almost match the colloid refractive index we used a solvent mixture of cis-decalin and cyclohexyl bromide (CHB), which we tuned to yield different Peclet numbers, owing to changes in the degree of density mismatch between colloids and solvent. Specifically, $Pe_c = 1.1$ and $Pe_e = 2.4$ correspond to 80% and 87.5% CHB by weight respectively. The characteristic time to diffuse a radius $\tau_D \approx 29$ s. The data were collected on a Leica SP5 confocal microscope, fitted with a resonant scanner, at a typical scan-rate of around
10 s per 3D data set. Prior equilibration was achieved by placing the suspension overnight such that it sedimented across a thin (typically 50 µm) capillary. The capillary was then inverted, and the evolution under sedimentation was followed.

We begin our discussion by presenting snapshots of the system, in Fig. 1d–e from computer simulation, and in Fig. 1f–i from confocal-microscopy. The similarity is remarkable, and we note that, at the very least, our simulation qualitatively reproduces the experiment. For a quantitative comparison, we consider the dispersion relation of wavenumber against growth rate in Fig. 2a. The time evolution in the development of the RT instability with a characteristic wavelength is clear. While snapshots in the gravity plane (Fig. 1b, c, d, f, g, and h) illustrate the overall process of sedimentation, snapshots in the horizontal yz plane show the transient pattern or network-like structure that results from the RT instability (Fig. 1b and i). At later times, the network structure decays and a laterally homogenous density profile develops where the colloids start to form a layer at the bottom of the cell which becomes more compact with time. The time evolution is shown in detail in the Movies 1–4, see EPAPS Document No. [].

The linear stability analysis predicts the existence of the initially fastest growing wavelengths in the RT instability. We plot the results of the linear stability analysis for a range of slit widths L keeping Pe fixed, and for a variety of Péclet numbers keeping L fixed in Fig. 2a, b and c respectively. The dimensionless growth rates, $n\tau_D$, are plotted as a function of wave number $k\sigma = 2\pi \sigma/\lambda$, where $\lambda$ is the wavelength of the fluctuations as indicated in Fig. 1a. Without diffusion, fluctuations at all wave numbers are unstable, as shown by the solid lines in Fig. 2a, b and c. Due to diffusion, we find that growth rates at higher wavevectors are suppressed as expected, i.e., diffusion destroys the Rayleigh-Taylor instability at sufficiently small wavelengths. We find excellent agreement between the theory with diffusion and both simulation and experimental data, up to $k\sigma \approx 1$, which is surprising for a coarse-grained continuum description. With decreasing wall separation $L$, the growth rate $n_{\max}$ decreases and $k_{\max}$ increases, see Fig. 2h. Since the fluid velocity in the gravity direction decreases as $e^{-kx}$, where $x$ is the distance from the interface, only long wavelength undulations feel the presence of the walls [12]. Figure 2b and c show that for fixed L, driving the sedimentation more strongly by increasing the Péclet number leads to an increase in the wave number of the fastest-growing undulation $k_{\max}$ and the corresponding growth rate $n_{\max}$.

So far we have considered only the linear regime of the instability, which is valid at small times, when the amplitude of the fluctuations is smaller than the wavelength. Our experiments and simulations permit detailed access to all relevant time- and length-scales in the non-linear regime, where the colloids form foam-like structures in the (confined) xz plane (Fig. 1e, g) and a network-like structure in the yz plane (Fig. 1i) appears. Apparently, both continue to exhibit the characteristic length scale $\lambda_{\max} = 2\pi/k_{\max}$ of the fastest growing wavelength in the linear regime.

In order to quantify the different regimes of the instability we use the first moment of the density $S(x)$, i.e. the centre of mass of the colloid coordinates and the second moment of the density $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$. Here, $\langle x \rangle$ is a measure of the degree of sedimentation, while $\sigma_x$ quantifies the extent to which the instability spreads out the colloids in the gravity direction. Three regimes are clearly visible in Fig. 2d, f, h, e, g and i. Firstly we

![FIG. 2: a-c Growth rate $n\tau_D$ versus wave number $k\sigma = 2\pi \sigma/\lambda$. a. Simulation results of $n(k)$ for different wall separation distances $L/\sigma = 18, 12, 9$ and fixed $Pe = 1.6$. b. Simulation and experimental results of $n(k)$ for different Péclet numbers $Pe = 4.8, 1.6, 1.1, 0.8, 0.4$ and fixed $L/\sigma = 18$. c. Experimental results of $n(k)$ for different Péclet numbers $Pe = 2.42, 1.21$ and fixed $L/\sigma = 36$. The open symbols are the results obtained from simulation, filled symbols are experimental results, solid lines represent the solutions from the instability analysis and the dashed lines are the same numerical solutions plus the diffusion correction. First moment of the colloid density $\langle x \rangle/L$ (d), (f), (h) and second moment of the colloid density $\sigma_x/L$ (e), (g), (i) versus time $t/\tau_S$. Solid lines indicate simulation data whereas the dashed lines indicate experimental data. d, e, $L/\sigma = 18, 12, 9$ and $Pe = 1.6$. f, g, $Pe = 4.8, 1.6, 1.1, 0.8, 0.4$ and $L/\sigma = 18$. h, i, $Pe = 2.42, 1.21$ and $L/\sigma = 36$.](image-url)
of a hydrodynamic instability in a colloidal system at non-equilibrium conditions. We have presented a quantitative analysis under non-equilibrium conditions. A new insight into this poorly understood phase transition at the single particle level has the potential to provide a microfluidic lengthscale. Our results show excellent agreement between experiment and simulation, showing that the latter accurately describes the fundamentally and practically important phenomena caused by hydrodynamic instabilities. Furthermore, by employing a simple theoretical treatment to the initial linear behaviour, we find considerable predictive power. The theory can flexibly be used to predict conditions for separation and mixing. We also note that the theory reveals even the length scale of the network structure that results from the instability. We finally emphasise that the full access and accuracy to all relevant length scales in this problem allowed for the observation of novel phenomena, not yet explored further, such as the inverse gravity induced crystal melting.

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find the linear regime in which the flat interface develops undulations and hence ⟨x⟩ slowly decreases and σₓ slowly increases, secondly the non-linear regime where ‘droplets’ of colloid-rich material fall to the bottom and therefore ⟨x⟩ sharply decreases and σₓ sharply increases, and thirdly the regime in which the colloids start to form a layer at the bottom of the cell which becomes more compact with time under settling as can be seen from the slow decrease of both ⟨x⟩ and σₓ. Clear agreement between simulation and experimental data can be seen from Fig. 2f and g.

In the case of a rather large slit width L/σ = 36, there is a sufficiently high sediment for a region of colloidal crystal to form, see Fig. 3 and EPAPS Document No. for Movie 5. Since the crystal has a finite (albeit small) yield stress, the only flow we observe initially occurs in a thin fluid layer between the crystal and the lower solvent region via narrow vertical tubes, in marked contrast to Fig. 1b-d. The crystal melts layer by layer until finally it becomes sufficiently thin that it peels off the wall in a second instability, which leads to a change of slope for the Pe = 2.42 line in Fig. 2h and i at t/τS ≈ 20 – 30, see Fig. 3d, until most of the particles have sedimented down (Fig. 3e). This observation of driven surface melting at the single particle level has the potential to provide new insight into this poorly understood phase transition under non-equilibrium conditions.

Using state-of-the-art simulation and experimental techniques, we have presented a quantitative analysis of a hydrodynamic instability in a colloidal system at...