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Multiphase Coexistence and Non-linear Rheology of Colloidal Dispersions as Observed in a Model Capillary Viscosimeter

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Abstract. — Investigations of the flow properties of colloidal substances by viscometry and rheometry are a valuable tool in understanding many transport processes of importance in biology, medicine and industrial treatment of materials. The streaming of cytoplasm, blood, micellar solutions or crude oil emulsions are but some obvious examples. One of the most intriguing properties of colloidal systems is their ability of thinning or thickening under shear. To characterise this non-Newtonian flow behaviour different visco- and rheometric experiments have been devised, the capillary viscometer being one of the classical instruments. The underlying physical mechanisms of non-linear rheometry are the shear-induced formation and destruction of long range positional and orientational order. Since only in rare cases comprehensive structure and velocity information is accessible from inside a viscosimeter, generally, homogeneous samples are assumed. However, there are indications of a geometry dependent evolution of inhomogeneous phase and flow behaviour from recent experiments on colloidal model systems, in particular for denser systems of strongly interacting particles. We here present investigations performed on a well characterised suspension of spherical particles interacting via a screened electrostatic potential. We give a detailed study of the local structures and shear rates in an optical model capillary viscosimeter. As a function of the overall flux several different flow scenarios are observed within the viscosimeter and the most striking feature is the simultaneous existence of up to four concentrically arranged phases under conditions of stationary flow.

For a Newtonian fluid the shear stress $\sigma$ within the fluid is proportional to the shear rate $\gamma = \frac{dv}{dx}$ times the viscosity $\eta$: $\sigma = \eta \gamma$. While this behaviour is observed for most simple fluids, colloidal dispersions often show significant deviations from this simple law, and this property finds a number of interesting applications. Thixotropy or shear-thinning, for example, is a welcome aid in painting without the formation of tears. This is due to the parallel arrangement of the pigment platelets under the shearing forces of the brush. After termination of shear the particles again become orientationally disordered due to their Brownian motion. Such behaviour may be connected to a phase transition under shear [1]. For example, recent investigations in a cone and plate rheometer on wormlike micelles showed a plateau value in the measured shear stress upon increasing the shear rate [2]. It corresponds to a first order transition from the isotropic to the nematic phase, with the phase boundary shifting

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under increasing shear towards lower micellar concentrations. In order to explain the observed non-linear rheology a nucleation and growth mechanism was proposed leading to a two phase coexistence.

Non-Newtonian behaviour is also found in systems of simpler particle shape exhibiting sufficiently strong interaction between the particles. Under these conditions shear may induce several different transitions to states of either lower or higher viscosity. Fluid states may first order under shear to form layered structures; above a critical shear rate, however, extreme dilatancy is observed and attributed to cluster formation [3]. Other experiments report the structural changes observable during the transition from colloidal crystals to isotropic fluid states [1, 4–6]. Measurements with a capillary viscosimeter revealed a many orders of magnitude decrease of the apparent viscosity during this shear melting process [7]. Although shear induced phase transitions thus show pronounced effects on the rheology of colloidal suspensions, only very few papers exist giving detailed connections between the suspension structure and the colloidal flow properties [3, 8, 9]. Most studies on shear melting focused on structural aspects alone or discuss the underlying microscopic mechanisms [5, 8–11]. Some of the experiments [12] have been supported by computer simulations and non-equilibrium phase diagrams have been derived [10, 13].

In most studies homogeneous stationary states had to be assumed. Obviously this will not hold for complicated flow geometries or oscillatory shear. In fact, the formation of coexistent phases has been observed in a Taylor-Couette flow or in oscillatory capillary flow. In both cases instabilities connected to phase coexistence evolve due to the hydrodynamics of the system [13]. First observations of two phase coexistence for simple geometries have only very recently been reported on charge stabilised silica [9] and polystyrene spheres [14]. We here examine a simple colloidal system in a simple flow geometry. Charged latex spheres may be manufactured with well defined shape, radius and charge. Such monodisperse suspensions have already acquired the state of model systems within the heterogeneous class of colloidal dispersions [15]. Due to their long ranged interaction they show an equilibrium phase transition from the fluid to a crystalline ordered state at micromolar concentrations of screening electrolyte even at packing fractions well below one percent. Since then the typical interparticle spacing is on the order of the wavelength of visible light the systems are optically accessible by light scattering or microscopy. The particles under investigation here and the equilibrium suspension properties have been carefully characterized in both the fluid and the solid state (Lot # 2011 M9R, Seradyn, U.S.A., radius \( a = 51 \) nm, bare charge \( Z = 620 \); [16]). The shear modulus of the solid formed at \( \Phi = 0.0035 \) and under completely deionized conditions is on the order of \( G = 0.4 \text{ Nm}^{-2} \) The system therefore may be shear molten simply by shaking the sample. Once shearing is terminated the system instantaneously relaxes to a metastable state of fluid order, from which it crystallises back to the solid state on the time scale of some seconds to minutes.

All these investigations were performed at mechanical equilibrium. We here subject the system to continuous flow through a horizontally mounted model capillary viscosimeter of 4.0 mm inner diameter and a length of 50 cm. It flows under the hydrostatic pressure difference between two reservoirs of fixed height difference. A peristaltic pump refills the upper reservoir through a closed Teflon tubing system containing an ion exchange chamber and a conductivity measurement to maintain and control conditions of complete deionisation at a packing fraction fixed to \( \Phi = 0.0035 \) [17].

In Figure 1a we present the adjusted height difference between the reservoirs \( \Delta h \) in dependence on the overall flux \( V \), as integrated from the spatial velocity distribution \( \nu(r) \). The data points discontinuously approach a linear behaviour, i.e. a limiting Newtonian case. An apparent viscosity \( \eta_{\text{APP}} \) is deduced following the procedures suggested by Laun et al. [3] and
Fig. 1. — Evolution of several quantities measured in the stationary state in dependence on the overall flux \( V \), as measured by integrating the observed velocity profiles \( v(r) \) and varied in equidistant steps by increasing the speed of the refilling pump. The suspension and shear parameters are: \( \Phi = 0.0035 \), \( c = 0 \ \mu \text{mol} \text{l}^{-1} \), \( a = 51 \ \text{nm} \), \( Z = 620 \). The measured quantities are: a) Height difference \( \Delta h \) between the two reservoirs adjusted to provide a constant flux. b) Apparent viscosities \( \eta_{\text{APP}} \) as deduced following the procedures of Laun et al. [3]. Note the strong overall tendency for shear thinning, the saturation behaviour at large fluxes and the three steplike increases. c) Shear rates as deduced from local velocity measurements. Stars: HL\(_1\) showing registered sliding; open circles: HL\(_2\) showing continuous sliding; open squares: fluid phase. d) Radial distribution of the respective phases. Stars denote the boundary of the polycrystalline core to other phases; circles denote the boundary of the HL\(_2\) phase to other phases and triangles the boundary between HL\(_1\) and fluid phase. Note that for each phase the shear rate increases linearly with increasing flux until a further phase is observed and the shear rate saturates. The fluid phase shows an onset of shear thinning at highest fluxes.

assuming the relevant pressure drop to happen along the capillary tube. This viscosity is presented in Figure 1b. Four regions of apparent shear thinning are clearly discernible separated by seemingly discontinuous increases in \( \eta_{\text{APP}} \). For high fluxes (completely shear molten state) a limiting viscosity is approached. Comparison to measurements with pure water at 18 °C give an absolute value of \( \eta_P = 1.05 \ \text{cp} \) for the melt. Thus shear thinning of colloidal suspensions as observed in a capillary rheometer may be a complex multistep process and an interpretation in terms of a single first order phase transition will not suffice for its explanation.

We therefore carefully analysed the structural evolution of the suspension along and across
Fig. 2. — a) Cut through the model capillary viscosimeter along the direction of flow showing sketch of the structural evolution along the cell at \( V = 128 \text{ mm}^3\text{s}^{-1} \). It was drawn after visual observations and was placed upright for layout reasons. The drawing exaggerates the length of the region of nucleation and growth in order to clarify the observable phenomena, a stationary state usually is reached already after some centimeters. Throughout the experiments the model viscosimeter was mounted horizontally. The cross hatched area denotes the polycrystalline core, the striped area denotes the region of hexagonal sliding layers, the remaining part is of fluid order. b) cut through the cell perpendicular to the cell axis. Note the concentric arrangement of the respective phases nicely reflecting the instrumental geometry.

The tube. We first report the observations already possible by eye. If the tube is illuminated with white light from aside and perpendicular to the flow direction, and looked at from a point on the other side of the tube but from above, the different phases are observed as iridescent areas of different intensity, colour and texture. The suspension enters the capillary in the shear molten state and relaxes into a partly crystalline flow pattern. In Figure 2a we sketch a sample at constant flux of \( V = 80 \text{ mm}^3\text{s}^{-1} \). After entering the tube small crystallites nucleate in the centre and grow, until they form a polycrystalline solid core (crosshatched area, henceforth denoted PC). The crystallite size increases with increasing distance to the cell centre. This is consistent with the findings of Palberg et al. [18] who report a strong decrease in nucleation rates with increasing shear rate. Both on the outside of this core and on the quartz wall of the capillary two regions form and grow to roughly one mm thickness. Their long ranged positional order in the plane parallel to the wall is reflected by the restriction of their extremely bright iridescence to a small angular region opposite and above the illuminating lamp. They appear dark from other directions. These regions are drawn as hatched areas and henceforth denoted HL_1 and HL_2. As will be shown below they are of similar structure but significantly different flow properties. The remaining region stays fluid (unmarked area in Fig. 2 and henceforth denoted F).

A stationary state is reached for most overall fluxes well before the end of the capillary.
Only for the highest fluxes the tube length is too short to allow for complete relaxation within the passage time. While the relative volume of each region is a strong function of the overall flux, their radial sequence seems to be fixed. Figure 2b shows a cut through the cell at the stationary state reached in Figure 2a after $l_{\text{stat}} = 30$ cm. This was drawn after Bragg-microscopic measurements (see below) performed at several different orientations of the tube. Note the concentric arrangement of the respective phases nicely reflecting the instrumental geometry.

The structure of the individual phases was confirmed by static light scattering and we will report about details of the scattering arrangement and the observed scattering patterns in a forthcoming paper. A laser beam crosses the cell perpendicular to the flow direction. We corrected for the distortions of the scattering pattern caused by the capillary using a specially designed index matching bath. The scattering pattern is observed on a screen placed behind the bath with 3% angular resolution in latitudinal ($\Theta$) and azimuthal ($\varphi$) direction. We observe three different scattering patterns. The core (PC) shows the typical powder pattern of the body centered cubic (110) reflection of randomly oriented small crystallites. The fluid phase (F) shows the unstructured smeared ring known from observations of Couette shear experiments by neutron or X-ray scattering. Unlike there, the ring observed here does not show significant distortions nor variations in intensity which would indicate the formation of shear enforced orientational or positional ordering. However due to the restricted precision of this set-up, we cannot completely rule out the possibility of a shear-deformed fluid state.

The HL-regions both show a hexagonal scattering pattern at practically identical angle $\Theta$ as the other two phases. The azimuthal angles $\varphi$ between the maxima are consistent with 60 degree within the resolution of our set-up. For similar light scattering pattern from equilibrium b.c.c. crystals [19] and neutron scattering pattern from equilibrium randomly stacked f.c.c. crystals both observed under Couette flow, the corresponding structure was analysed to be of hexagonal sliding layers. To unequivocally identify the structure in our experiment, both higher order diffraction patterns and absolute intensities would be necessary [11]. Since however our observations for both regions are compatible with hexagonal layers, we will continue using the abbreviations HL$_1$ and HL$_2$.

We then performed an analysis of the structural distribution and the local shear rates at the stationary states ($l > l_{\text{stat}}$) under variation of the overall flux. The local velocities are measured by Laser Doppler velocimetry using a fibre optic detection scheme to gain a sufficiently high spatial resolution of 10 $\mu$m. From each velocity profile the local shear rate is precisely determined by differentiating with respect to $r$ and the overall flux by integration. Simultaneously the distribution of individual phases is determined using high resolution Bragg microscopy. A second laser beam crossing the capillary is observed with a video camera equipped with a macro lens. The camera is placed at the position of one of the Bragg spots of the HL phase and oriented under the scattering angle $\Theta$. The image of the laser beam then appears with different brightness, since the static structure factor of the three (four) regions differ significantly at this particular choice of observation angles. HL-regions appear extremely bright, the fluid shows a much smaller intensity and the core appears practically dark, since only rarely an individual crystallite fulfills the orientational Bragg condition.

As a function of the increasing overall flux we observe a very complex behaviour including the formation of coexisting shear stabilised phases. For a flux of $V = 80$ mm$^3$s$^{-1}$ the radial intensity distributions is shown in Figure 3 together with the locally measured velocities. This remarkable case of a four phase coexistence corresponds to the situation in Figure 2. The local shear rate shows a step-like behaviour reflecting the radial phase distribution. The core region remains unsheared and flows as a solid plug. The outer phases each show different shear rates. The boundaries seem to be continuous which, however, is an effect of the long integration time.
for the velocity measurements used to enhance the signal/noise ratio. With short integration times, say of less than 10 s, we observe a sharp (< 50 μm) boundary slowly moving in and outward over a distance of Δr ≈ 250 μm.

The HL phases do not merge completely but stay separated into two regions of different flow behaviour. A remarkable result is the linear decrease of velocity with the radius giving a shear rate independent of the position. The inner HL shows the lower gradient, which only very slightly increases with further increasing flux, while the HL adjacent to the wall shows a strongly flux dependent velocity gradient. At the same time the scattered intensity of the outer region is decreased. This is attributed to a transition from a state of planes registered between single sliding events to a state of continuous gliding as suggested by several authors [5, 7, 11]. As expected for a Hagen-Poiseuille flow, the velocity profile within the fluid phase is parabolic. For small fluid regions it may be approximated by a straight line and a constant shear rate may be assigned. In Figure 3 it has a considerably lower value than the shear rate in the HL-regions. The interesting conclusion is that at V = 80 mm²s⁻¹ the fluid phase is lubricated on both sides by a phase of higher order and lower viscosity.

To compare all the flow data collected in the stationary states in dependence on the overall flux we plot the shear rates measured within the different phases in Figure 1c. The solid core representing the equilibrium stable phase remained unsheared in all experiments and was lubricated by one or two HL phases and/or a fluid phase. Note that for all fluxes at least two phases coexist. While the possibility of a coexistence between two phases has recently been confirmed experimentally [9, 14], this is the first demonstration of a multiphase coexistence. Within all phases the shear rates increase nearly linearly until a new phase is observed. The saturation values are approximately 6 s⁻¹ and 17 s⁻¹ for the two HL phases. As shown in Figure 1c, for our capillary viscosimenter the typical sequence of phases appearing under increasing shear is PC, HL₁, HL₂, F. From intuitive considerations one would expect that smallest shear rates are found in the cell centre and increase towards the cell walls. The concentric arrangement therefore should also reflect the above mentioned succession of non-

![Graph showing velocity and intensity profiles](image-url)
equilibrium phases with increasing perturbation of the mechanical equilibrium. Clearly this is not the case. One may speculate that the unexpected radial arrangement of phases is determined by the kinetics of heterogeneous nucleation and growth of the HL phases on the wall and the polycrystalline core, respectively.

Figure 1d shows the corresponding distributions of phases as observed in the stationary state. With increasing flux the HL$_1$ phase grows at the expense of the solid core, then HL$_2$ grows at the expense of the solid core, while the volume of HL$_1$ stays nearly constant. Between $V \approx 80$ mm$^3$s$^{-1}$ and $V \approx 120$ mm$^3$s$^{-1}$ the fluid phase increases on expense of both the HL and above $V \approx 120$ mm$^3$s$^{-1}$ on expense of the solid core. The observed stepwise melting process therefore seems to be a succession of first order transitions. A detailed explanation of the observed behaviour, however, remains a challenge. In addition to thermodynamic and kinetic considerations it will have to include geometrical influences, too. To stress the latter point, we note that a 150 $\mu$m thick HL$_2$ phase remains rather unchanged in thickness with increasing flux. This stability of the wall based HL$_2$ is not understood. Layering of colloidal particles next to a wall has been observed but under mechanical equilibrium it does not exceed some ten ordered sheets [21]. We further note that a solid-fluid transition without the intermediate formation of HL was recently observed for a colloidal crystal flowing through a parallel plate arrangement [13].

We finally compare Figures 1c and 1d to the non Newtonian behaviour depicted in Figures 1a and 1b in order to explain both the overall shear thinning and the seemingly discontinuous increases observed at fluxes of approximately 40, 80 and 120 mm$^3$s$^{-1}$. The HL$_1$ phase shows a lower viscosity than the HL$_2$ phase. The viscosity of fluid phase is somewhat larger but still much smaller than for the polycrystalline solid. Therefore the regions of monotonously decreasing $\eta_{\text{APP}}$ may be interpreted as the increase in volume of low viscosity phases on expense of the solid core, while each increase in $\eta_{\text{APP}}$ represents the stabilisation of a further, less ordered phase of relatively higher viscosity. In HL$_1$ the long range positional order is still present for three dimensions, since the particles remain registered between sliding events, it is lost in radial direction upon the transition to the continuously sliding state HL$_2$. It is completely lost for the fluid phase.

The system under study was an example of a very simple colloidal suspension. All particles were spherical and the samples may safely be considered monodisperse. Therefore complications due to polydispersity, as they are often observed for technical samples, were not addressed here. Furthermore, the interaction between the particles was sufficiently high to allow for a description in terms of an effective Yukawa potential while the packing fraction was sufficiently low to neglect hydrodynamic interactions between particles in the bulk phases. In addition the chosen geometry was the simplest one of radial symmetry. On the other hand the observed behaviour already was rather complex and we hope to have caught a large number of effects typical for simple colloidal systems. The usefulness of colloidal suspensions as models of condensed matter has already been demonstrated for a number of equilibrium situations. The present experiments under conditions far from mechanical equilibrium, might therefore have an impact also on investigations of solidification of atomic or molecular material under shear.

We have presented an example of the possibilities to quantitatively characterize the flow behaviour of a suspension of well defined colloidal spheres by means of a combination of light scattering and microscopic methods. In an optical model capillary viscosimeter the combined evolution of the sample’s local structure and shear rate was monitored under carefully controlled shear conditions. For the first time it was possible to assign the observed strongly non-linear viscosity behaviour to a succession of non-equilibrium phases, which for themselves seem to obey a Newtonian rheology. Up to four different phases were observed to coexist which strongly differ in their degree of long range order.
The emerging qualitatively consistent picture demonstrates the value of opto-rheometric experiments and should stimulate enhanced experimental and theoretical efforts to quantify existing microscopic models of both phase transitions under shear and their correspondence to the complex flow behaviour observed in colloidal systems.

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