Shearing or Compressing a Soft Glass in 2D: Time-concentration superposition

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We report surface shear rheological measurements on dense insoluble monolayers of micron sized colloidal spheres at the oil/water interface and of the protein β-lactoglobulin at the air/water surface. As expected, the elastic modulus shows a changing character in the response, from a viscous liquid towards an elastic solid as the concentration is increased, and a change from elastic to viscous as the shear frequency is increased. Surprisingly, above a critical packing fraction, the complex elastic modulus curves measured at different concentrations can be superposed to form a master curve, by rescaling the frequency and the magnitude of the modulus. This provides a powerful tool for the extrapolation of the material response function outside the experimentally accessible frequency range. The results are discussed in relation to recent experiments on bulk systems, and indicate that these two dimensional monolayers should be regarded as being close to a soft glass state.

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The rheology of systems with very large surface to volume ratios, such as foams or emulsions, depends on the flow behavior of material that is added to provide stability and remains constrained to the surfaces. This has been particularly investigated in the case of foams [1, 2], highlighting the need for experiments on model systems. Insoluble surface films (Langmuir monolayers) represent the most basic model system, and quantitative measurements of their viscous and elastic response when subject to a shear deformation are possible with modern instruments [3, 4]. Understanding flow and dynamical transitions in this simple geometry promises to aid in the design of cosmetics and food products with desirable textures, and to be of value in polymer processing and oil recovery, the industries that have traditionally driven the interest in this field.

In this Letter, viscoelasticity is investigated quantitatively on two very different systems that are confined to fluid interfaces, where flow is effectively two dimensional. Latex colloids have a non-deformable hard core, and we show how a soft solid is formed and the system progressively jams as the close packing concentration is approached. The β-lactoglobulin proteins, which partially unfold at surfaces, can (like polymer chains) be described as soft spheres. A surprising scaling behavior, similar to recent results on three dimensional systems [5], is reported for both monolayers. We believe that the generality of behavior between two (2d) and three (3d) dimensions should be of value and interest for both the theoretical understanding and the numerical simulations in this field, and also sheds light onto the origin of monolayer viscoelasticity and other related glassy behavior such as long time scale stress relaxation or aging.

In contrast to surface techniques, instrumentation to perform bulk rheology is well established and widespread, and the flow behavior of soft matter bulk systems has been extensively studied [6]. There has recently been much interest in the dynamics of soft matter systems, from foams [7] to concentrated emulsions and colloidal suspensions [8, 9] that become jammed at high density. These are materials that respond like elastic solids to small stresses but they have a yield modulus and, like pastes, flow above a threshold stress. They are known phenomenologically as Bingham bodies [6]. In viscoelasticity measurements on these systems the complex shear modulus $G^* = G' + iG''$ is measured, and an elastic plateau $G'(\omega) > G''(\omega)$ is typically observed at low frequency, crossing over to a viscous response $G''(\omega) > G'(\omega)$ at high frequency. In this context quantitative rheological measurements exist only on three dimensional, bulk systems. In two dimensions it has only recently been possible to perform a relative measurement of the divergence of viscosity upon close packing of solid lipid domains [4].

Well established methods exist to perform experiments on macromolecules that are irreversibly confined at the air/water or oil/water interfaces in a Langmuir trough: the surface concentration Φ is varied by a sweeping barrier, the osmotic pressure Π is determined by measuring the interfacial tension γ and using $\Pi = \gamma_0 - \gamma$ where γ_0 is the surface tension of a clean interface, the temperature is fixed by thermostating the subphase liquid and finally the surface can be easily imaged with optical microscopy. Nima (Coventry, U.K.) and KSV (Helsinki, Finland) troughs are used, with either platinum or filter paper Wilhelmy plates. The colloid monolayers are made of 3.1μm diameter Polystyrene spheres (Interfacial Dynamics Corporation), with a surface charge density of 9.1μC/cm^2. The colloids are dispersed onto the interface between an aqueous solution (0.01M NaCl) and decane (Fischer). The same methods are followed as in [10], and monolayers of similar particles have been investigated in [11]. The milk protein β-lactoglobulin is obtained from Sigma (mixture of A and B types, bovine milk, 90% pure) and used without further purification[20]. Monolayers of this protein have been studied extensively because of

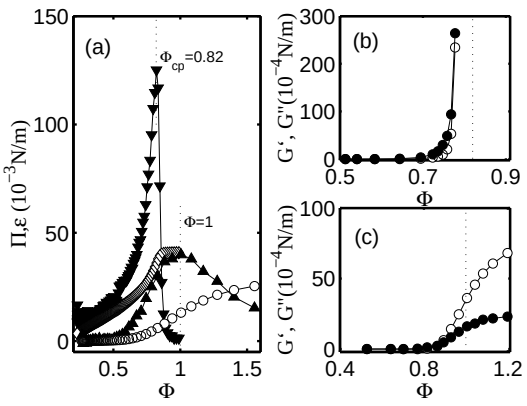

FIG. 1: (a) Two dimensional osmotic pressure Π as a function of the surface concentration Φ, for ($\diamond$) 3μm colloids and ($\circ$) β-lactoglobulin. The dotted lines correspond to the maxima in the dilational compression modulus ε, which occur at close packing ($\Phi = 0.82$) for the colloid monolayer ($\blacktriangledown$) and at $\Phi = 1$ for β-lactoglobulin ($\blacktriangle$). The elastic ($\circ$) G' and viscous ($\bullet$) G'' components of the shear modulus at $\omega \simeq 1$Hz are plotted as a function of the concentration for (b) the colloid and (c) the β-lactoglobulin monolayers.

their importance in the food industry [12]. Data is collected for about 15 minutes at each concentration, and over the timescale of 2 hours no aging effect has been noticed. Full details of our experiments, comprising creep and stress relaxation measurements, will be published elsewhere.

The osmotic pressure dependence on the surface concentration is related to the intermolecular interactions. $\Pi - \Phi$ isotherms for the two systems studied are shown in Figure 1(a) and are well known in the literature [11, 12]. Determining Π is the simplest measurement on a monolayer, and the isotherms serve as a reference to establish the concentration of the monolayer in separate experiments. The packing fraction Φ for the colloids is determined by optical microscopy, and the osmotic pressure of the colloidal layer is mainly due to electrostatic repulsion [11]. The maximum in the dilational modulus $\varepsilon(\Phi) = 1/\Phi\, d\Pi/d\Phi$, see Figure 1(a), occurs at $\Phi = 0.82$, which is the two dimensional random close packing value for disks. For $\Phi \gtrsim 0.82$ the colloids are forced out of the monolayer plane. It is well known that proteins can unfold at an interface, and that the initial upturn region of their isotherms is well described by a polymer-like semi-dilute regime scaling law which starts at the overlap concentration of coils [12]. Within this regime, in 2d the polymer coils are expected to be segregated and to be progressively compressed. The protein surface concentration in Figure 1 has been normalized so that the scaling regime terminates at $\Phi = 1$ (assuming no loss to the subphase on spreading, at $\Phi = 1$ the surface concentration of β-lactoglobulin is 1.45mg/m^2). This concentration corresponds to the peak in the compression elastic modulus $\varepsilon(\Phi)$. For polymer systems the maximum signals the transition to a concentrated regime, in which there is still space for additional monomers on the surface. The proteins act like soft disks and the monolayers can be compressed above $\Phi = 1$.

Rheological measurements on monolayers are performed with an interfacial stress rheometer (ISR), which has been described in detail elsewhere [3]. It consists of a 5cm long and 0.5mm diameter magnetized rod confined to the plane of the interface, set into oscillation by applying a sinusoidally time-dependent magnetic field gradient and tracked by projecting the rod image through an inverted microscope onto a linear photodiode array. A half-cylinder glass channel of length 10cm and radius 3.2mm was kept submerged in the water phase and its position was adjusted so that the interface meniscus was pinned to the inside of the glass wall, ensuring well defined and reproducible open channel flow boundary conditions. After calibration of the instrumental parameters by performing reference runs on clean water/air or water/oil interfaces, the amplitude and phase of the rod motion can be analyzed to give the dynamic surface shear modulus $G^*(\omega)$:

$$G^*(\omega) \;=\; \frac{\sigma_s}{\gamma_0} \exp\left(i\delta(\omega)\right), \qquad (1)$$

where σ_s is the amplitude of the applied sinusoidal stress with frequency ω, γ_0 is the amplitude of the resulting strain, having the same frequency ω and a phase difference $\delta(\omega)$. Measurements are performed for fixed strain amplitude of 3%, at a range of frequencies. Strain sweep experiments, not shown, are used to check that the response is in the linear regime.

The shear modulus $G^*(\omega)$ shown in Figure 1(b) and (c) is determined as the average of measurements at frequencies between 0.7 and 1Hz, at successive concentrations. For colloidal spheres, Figure 1(b), the complex modulus G^* shows an initial upturn at $\Phi \simeq 0.64$ and, at the frequency of this experiment, a predominantly viscous response $G''(\omega) > G'(\omega)$ is observed across the measured concentration range. The modulus G^* of the β-lactoglobulin monolayer, see Figure 1(c), shows an upturn at $\Phi = 0.77$ and $G''(\omega) > G'(\omega)$ only for $0.77 < \Phi < 0.87$. There is a wide range of concentrations where the elastic modulus dominates the loss modulus. In contrast to the colloidal layer, there is a change in the concavity of G' and G'', occurring at the same concentration ($\Phi \simeq 1$) where the elastic compression modulus is maximum.

Trappe and Weitz [5] recently showed for a 3d system of very dilute weakly attractive colloidal particles that the viscoelastic moduli obtained as a function of frequency at different volume fractions (and even for different interaction potentials) could be scaled on a single master curve. The overlap for different volume fractions occurs because of a self-similar response at different concentrations, and implies the same change in behavior

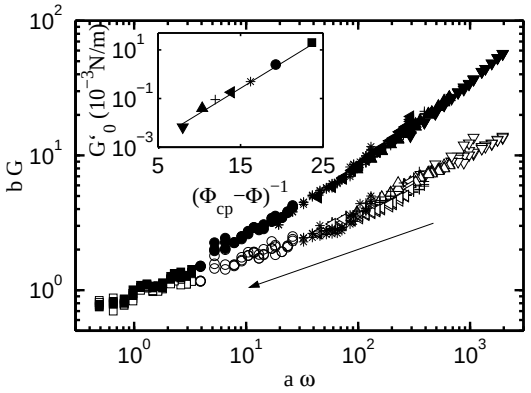

FIG. 2: Master curve showing log plots of the scaled values of (open symbols) G' and (solid symbols) G'' against the scaled frequency for the monolayer of colloidal particles. The arrow indicates the direction of increasing surface concentration, which coincides with increasing magnitude of moduli. As described in the text, the time-concentration superposition enables the extrapolation of data outside the experimental frequency window. The inset shows an exponential divergence of the elastic modulus as the concentration approaches the close-packing fraction Φ_{cp}.

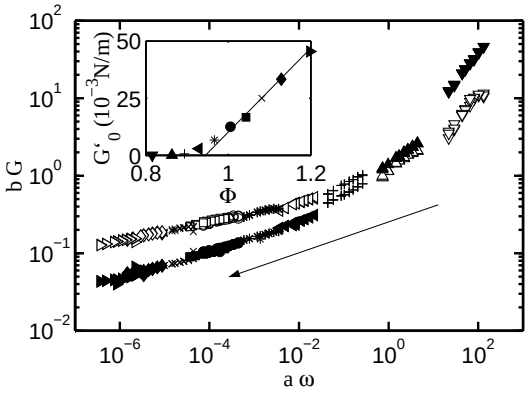

FIG. 3: Master curve showing log plots of the scaled values of (open symbols) G' and (solid symbols) G'' against the scaled frequency for β-lactoglobulin. The arrow indicates increasing concentration. As in Figure 2 the inset presents extrapolated data, which shows a linear dependence of the elastic modulus on concentration for $\Phi \geq 1$.

if the concentration is reduced or the shear rate is increased. With the ISR it is possible to measure the shear elastic moduli of Figure 1(b) and (c) over almost two decades in frequency, between 0.015 and 1.1Hz, enabling a study of the response behavior as a function of frequency (as well as concentration) and an analysis similar to [5]. In contrast to the system studied by Trappe and Weitz, in this work flow is in two dimensions, the packing is dense, the interactions are repulsive and the structure does not appear fractal. We find that above a threshold concentration $\Phi_c = 0.7$ for the colloids and 0.8 for β-lactoglobulin, the frequency dependent measurements of $G^*(\omega)$ taken at different concentrations can be overlayed on a master curve by rescaling the frequency ω by a factor a and G^* by b. The concentration Φ_c can be understood to be the cross-over point at which the system develops a stress-bearing network [13] and it is expected to depend on both the temperature and the details of the interaction potential. In principle, the concavity of $G^*(\omega)$ is such that the conditions of continuity and smoothness determine a and b, however in practice the overlap between consecutive datasets is small and the choice of a and b is made by hand. The main results of this Letter are Figures 2 and 3, which show the master curves for the two systems.

The colloidal monolayer response, Figure 2, is most elastic at low frequencies and predominantly viscous at high frequency. The rheological behavior of the colloid particles can be expected to be close to that of hard disks, and the value of Φ_c for the colloids coincides with the entropically induced freezing transition density for monodisperse hard disks in 2d [14]. This suggests that the master curve of Figure 2, which is at present an empirical observation, is the material response function of a soft 2d solid, in which the motion of each particle is hindered by the cage-like structure of its neighbors. There is a remarkable similarity with the rheological curve for dense three dimensional colloidal suspensions [9], including the high frequency shear-thinning $G'' \sim \omega^{0.5}$ limiting behavior [15]. The existence of a master curve allows the extrapolation of data to experimentally inaccessible timescales and moduli, in the same way as allowed by time-temperature superposition in polymer systems [6]. By this approach it is possible to measure, at extremely low concentrations, the value of the modulus where the viscous and elastic components are equal, G'_0. The inset in Figure 2 shows that the modulus diverges exponentially as the concentration approaches close packing, which is the concentration of the glass transition of hard disks [16]. The same divergence has been recently reported for the viscosity of 3d colloidal hard-sphere dispersions approaching the glass transition [17], and the exponential dependance was explained in terms of cooperatively rearranging groups of particles. It should be possible to test this hypothesis directly by 2d particle tracking in future monolayer experiments.

The master curve for β-lactoglobulin, Figure 3, has the same qualitative shape as for the colloidal monolayer, but the rescaling of data is most evident at lower frequencies. The cross-over to a solid-like response dominated by the elastic component of the modulus, which is at the experimental limit of the measurements on colloids, can be clearly seen here. The protein layer can be thought of as a system of compressed and deformed disks. In the limit of high concentration (or low frequencies), the elastic moduli follow power law frequency dependencies $G' \sim \omega^{0.1}$ and $G'' \sim \omega^{0.2}$. These very small exponents are

consistent with the soft glassy rheology model [18] proposed for materials close to the glass transition, which does not however account for the time-concentration superposition reported here. The master curve enables the measurement of G_0' at high density and the study of its concentration dependence, shown in the inset of Figure 3. Above $\Phi \simeq 1$ the modulus scales linearly with the concentration. This is the same behavior observed in 3d compressed emulsions [19] above the random close packing concentration, and supports the analogy between the β-lactoglobulin monolayer and a system of soft disks.

The relationship between the scaling factors for the frequency and the modulus contains information on the underlying physics. Trappe and Weitz [5] found a linear relationship in their attractive particle system, and proposed a simple explanation in which the particle network elasticity increases as a function of Φ in agreement with results for elastic percolation, and the viscosity is due to coupling with the solvent. A consequence of their model is that at large frequencies $G''(\omega)$ tends asymptotically to $\omega\eta_0$, where η_0 is the solvent viscosity. This does not happen in our data, and we believe that in the dense systems studied in this work the time-concentration superposition has a different origin. For the colloidal monolayer a and b are approximately linearly dependent, as shown in Figure 4. This means that if the shear modulus grows as a function of the concentration, the dynamics slows down with the same concentration dependance. This can be understood trivially for the viscous component G'': The viscosity of the 2d suspension grows as the concentration increases (and G'' is proportional to the viscosity), and the dynamical timescales are inversely proportional to the viscosity. The scaling factors for β-lactoglobulin do not hold the same relationship throughout the concentration range, meaning that there are likely to be complex sources of elasticity and viscosity for the system of highly compressed soft particles.

The measurements reported above have explored the similarity in viscoelastic response between surface monolayers and bulk systems, and between systems with very different interaction potentials. They indicate that models should be general to both dimensions and might stimulate further experiments to probe specific issues in soft glassy materials, such as the spatial and temporal extent of dynamical events, that could most easily be realized in surface monolayers.

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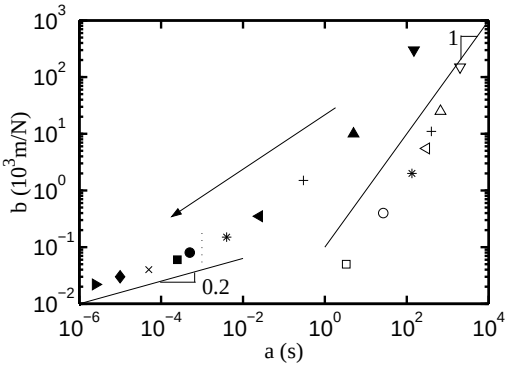

FIG. 4: Log plot of the scaling factor b *vs.* a, for colloids (open symbols) and β-lactoglobulin (solid symbols). The symbols correspond to different concentrations and are consistent with Figures 2 and 3, enabling the experimental data to be reconstructed. The arrow indicates increasing concentration, and the dotted line delimits the region $\Phi \geq 1$ in the β-lactoglobulin monolayer. For both systems the scaling factors have been chosen so that the crossover from elastic to viscous response occurs when the reduced frequency and modulus are equal to 1.

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[20] In the present study a water (MilliQ) solution subphase, 0.01M phosphate buffer and 0.1M NaCl having pH6.1 is used, and the proteins are spread by successively touching the air/liquid surface with $\sim 2\mu$l drops of a concentrated protein solution (1mg/ml in water).