

## Irreversible Shear-Activated Aggregation in Non-Brownian Suspensions

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We have studied the effect of shear on the stability of suspensions made of non-Brownian solid particles. We demonstrate the existence of an irreversible transition where the solid particles aggregate at remarkably low volume fractions ( $\varphi \approx 0.1$ ). This shear-induced aggregation is dramatic and exhibits a very sudden change in the viscosity, which increases sharply after a shear-dependent induction time. We show that this induction time is related exponentially to the shear rate, reflecting the importance of the hydrodynamic forces in reducing the repulsive energy barrier that prevents the particles from aggregating.

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Stable dispersions of solid particles in a fluid are particularly important in many technologies. For small particles, in the colloidal regime, stability is determined by a repulsive barrier in the interparticle potential, and is dictated by the effect of thermal energy. This regime is well understood. By contrast, for larger particles, thermal effects are no longer dominant. Instead, stability is usually dictated by the consequences of processing or aging, for which shear or gravitational forces are crucial. When the suspended particles are strongly repulsive at any distance and interact solely by volume exclusion, the concentrated suspensions can exhibit dramatic changes in their rheological properties with increasing shear rates. The corresponding behaviors range from continuous shear thickening [1] to shear-induced jamming [2,3], which can have a significant impact on the processing of these suspensions. For instance, for spherical particles, shear-induced jamming can occur at volume fraction above roughly  $\varphi = 0.4$  [1], whereas for anisotropic particles, this can occur at substantially lower values of  $\varphi$  [2]. However, technologically important dispersions are rarely purely repulsive. The corresponding particles are generally repulsive at long distances and slightly attractive at shorter ones. In this case, shear forces due to processing can induce even more dramatic and irreversible changes in the texture of the material, transforming it from a fluid into a highly elastic paste [4]. This transition can occur at very low volume fractions, for spherical particles [4] as much as for highly anisotropic ones [5], making the processing of these materials extremely delicate. This behavior is well known to anyone who cooks; some cold creams can be gently stirred with a spoon, whereupon they suddenly become very viscous and nearly solidlike. For instance, this happens during the first steps of churning, which consists of stirring a milky cream to make butter [6]. While this behavior is quite generic, its physical origin has never been explored.

In this Letter, we demonstrate the existence of an irreversible aggregation activated exclusively by shear, in

suspensions of non-Brownian solid particles at remarkably low volume fraction. We use slightly repulsive particles that exhibit a good kinetic stability at rest. They consist of oil globules containing water droplets, the oil being partially solidified at room temperature. The observed aggregation under shear is dramatic, exhibiting a very sudden onset where the viscosity increases sharply after a shear-dependent induction time. We show that, unexpectedly, this induction time is exponentially related to the shear rate. This reflects the importance of the hydrodynamic forces in reducing the repulsive energy barrier that prevents the particles from aggregating. This also proves that the pairwise aggregation of particles under shear is controlled by the height of this energy barrier and is the kinetically limiting step for the observed aggregation. These shear-induced effects also have consequences on the appearance of the suspension: even at these low volume fractions, large-scale aggregates develop in the sample.

We make a double emulsion consisting of water droplets dispersed in larger globules of crystallizable oil [7]. The use of a double emulsion enables us to tune the kinetics of aggregation under shear by changing the quantity of internal droplets within the globules. Indeed, this aggregation takes place too rapidly to be studied experimentally when the oil globules contain no water droplet. The oil used is comprised of many components with a wide range of melting temperatures, from 30 °C to -20 °C. As a result, upon solidification, it forms a soft waxy solid. The emulsion is prepared at high temperature (65 °C) where the oil is fully liquid. At this temperature, the emulsion remains stable under shear and is easily processed. We prepare a nearly monodisperse water-in-oil-in-water double emulsion using a two-step procedure [8,9]. The dispersed phase is water with 0.1M NaCl, and the surfactant is a sorbitan monooleate [10]. We use a thermoregulated Couette-type device [11] to make an inverse water-in-oil emulsion with a droplet size of 400 nm with 25% polydispersity [12]. This inverse emulsion is diluted with the crystallizable oil to a

volume fraction  $\varphi_i$  of 40% and is used as the dispersed phase for the second step of the emulsification procedure. Following the same strategy, we prepare a double emulsion of this dispersed phase in an aqueous phase containing a surfactant, which is a diblock poly(ethylene glycol) (PEG) phospholipid at 8 wt %, with glucose at 2.9 wt %, to match the osmotic pressure of the internal water phase [13], and alginate at 1.5 wt % as a thickener for controlling the globule size during emulsification. We end up with a nearly monodisperse double emulsion consisting of globules of diameter  $d_g \approx 4.5 \mu\text{m}$  with less than 20% polydispersity [11,12]. The double emulsion is diluted with 2.9 wt % glucose in water at  $65^\circ\text{C}$  to make samples with final volume fractions  $\varphi_g$  varying from 10% to 20%. These samples are cooled and stored at  $5^\circ\text{C}$  for at least 12 hours to ensure that the oil has reached its final solidified state. Once the emulsion has cooled and the oil has solidified, the emulsion remains kinetically stable. This proves the repulsive nature of the interactions between the globules. However, there is a slight but noticeable change in the texture of the globules. The spherical shape of the warm fluid globules evolves into a slightly rough and rippled surface as shown in Fig. 1, where the same emulsion is imaged with a microscope at both  $65^\circ\text{C}$  (a) and room temperature (b). The rheological behavior of the double emulsion also changes dramatically on cooling. It is no longer stable under shear, but is instead highly susceptible to shear-induced aggregation.

We measure the time evolution of the viscosity  $\eta$  using a controlled-shear rate rheometer with a cone-plate geometry and a gap of  $45 \mu\text{m}$  [14]. In Fig. 2 we show the time evolution of  $\eta$  measured for different applied shear rates,  $\dot{\gamma}$ . It remains essentially constant for an induction time  $t_c$  that depends on  $\dot{\gamma}$ , whereupon it suddenly and sharply increases by a factor of about 3. Although the measured viscosity increases only by a factor 3, the actual change in the state of the material is much more pronounced. Inside the gap of the rheometer, the sample turns from a fluid to a solidlike paste. We have measured the stress as a function of the applied shear rate for a sample that has undergone this irreversible transition (results not shown). A minimum stress value of about 1 Pa is required to achieve even the smallest shear rates, confirming the solidlike structure of

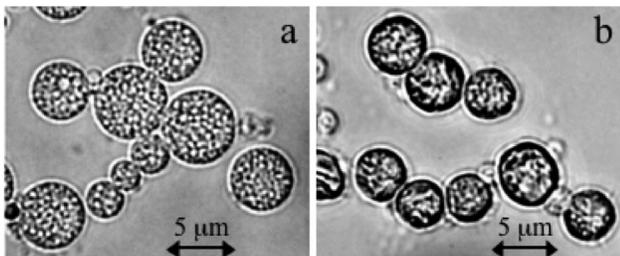


FIG. 1. Double emulsions imaged with an optical microscope ( $\times 100$  objective) at  $65^\circ\text{C}$  (a) and at room temperature (b).

the sample. Above this minimum stress value, the flow properties of the sample seem to be much more complex than those of a classic yield-stress material. These properties have not been further investigated since, in this Letter, we focus on the early stages of the irreversible aggregation.

Considerable insight into the nature of this irreversible transition is obtained by directly imaging the structures formed in the sample while shearing in a controlled-shear rate “rheoscope” with a cone-plate geometry and a gap of  $45 \mu\text{m}$  [15]. A precursor of the onset of the viscosity increase is seen well before it occurs: large voids develop where the globule concentration is significantly reduced, as seen by comparing Figs. 3(a) and 3(b), which correspond to the early time evolution of the sample for a shear rate of  $80 \text{ s}^{-1}$ . As the shear is applied for a longer time, the viscosity increases sharply and these voids (white regions) become more pronounced, as shown in Fig. 3(c). The sharp viscosity increase following the induction time takes place in between Figs. 3(b) and 3(c). Ultimately, the sample reveals the formation of solidlike aggregates or clusters of large length scale, at least that of the  $45 \mu\text{m}$  gap, as shown by the dark regions in Fig. 3(d). Similar behavior is observed for larger applied shear rates. However, the induction time  $t_c$  is reduced with increasing  $\dot{\gamma}$  and the typical length scale of the final solid clusters is also significantly reduced as shown in Figs. 3(e) and 3(f). Despite the fact that this phenomenon is strongly nonequilibrium and irreversible, the structures formed may recall those produced by equilibrium phase transitions such as spinodal decomposition. Large length-scale structures are formed as the transition is initiated, and they coarsen as the transition proceeds. Moreover, the final length scale decreases as  $\dot{\gamma}$  increases, reminiscent of the behavior expected for a deeper temperature quench in a demixing system. Here,

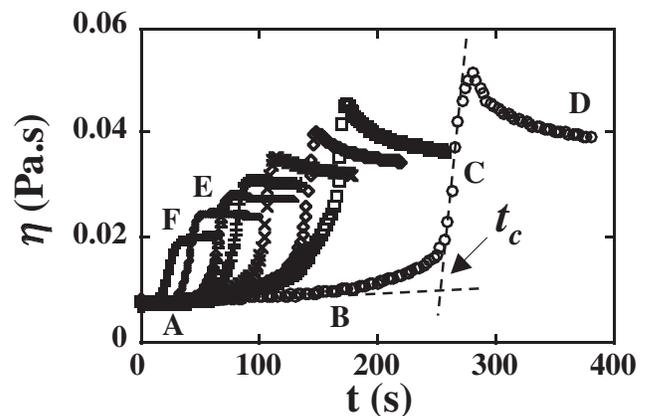


FIG. 2. Evolution of the viscosity of crystallizable double emulsions ( $d_g \approx 4.5 \mu\text{m}$ ,  $\varphi_g = 13\%$ ) sheared at different shear rates:  $80 \text{ s}^{-1}$  ( $\circ$ );  $100 \text{ s}^{-1}$  ( $\square$ );  $120 \text{ s}^{-1}$  ( $\diamond$ );  $140 \text{ s}^{-1}$  ( $\times$ );  $160 \text{ s}^{-1}$  ( $+$ );  $180 \text{ s}^{-1}$  ( $\triangle$ );  $200 \text{ s}^{-1}$  ( $\bullet$ );  $300 \text{ s}^{-1}$  ( $\blacksquare$ ); the dotted lines correspond to the definition of the induction time  $t_c$  (see text for details), in the case of a  $80 \text{ s}^{-1}$  shear rate; the capital letters refer to the photographs of Fig. 3

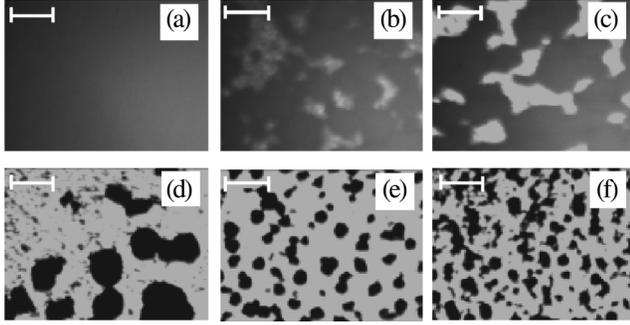


FIG. 3. Time evolution of crystallizable double emulsions imaged with a microscope during shear: (a)–(d) correspond to a shear rate of  $80 \text{ s}^{-1}$ . (e) is the final state after shearing at  $200 \text{ s}^{-1}$ . (f) is the final state after shearing at  $300 \text{ s}^{-1}$ . The scale corresponds to  $200 \text{ }\mu\text{m}$ .

both the appearance and the evolution of these large length-scale clusters must reflect the role of the macroscopic flow behavior. This behavior is very complex and not well understood. However, we believe that the interspersed solid and fluid regions in the dispersion are responsible for this flow behavior.

Quantifying the dependence of the induction time on the applied shear rate is essential to determine the origin of this unusual behavior. We do so by defining a more precise value for the induction time,  $t_c$ : we linearly extrapolate both the initial slow increase in viscosity and the rapid rise, and determine  $t_c$  from the intersection of these two extrapolations, as shown in Fig. 2. To capture the dependence of the transition on the main control parameter, we plot  $t_c$  as a function of  $\dot{\gamma}$  for different volume fractions in Fig. 4. Surprisingly, the induction time depends exponentially on  $\dot{\gamma}$  for all values of  $\varphi_g$  and is well described by the expression  $t_c = t_0 \exp(-\frac{\dot{\gamma}}{\dot{\gamma}_c})$  where  $\dot{\gamma}_c$  is a critical value of the shear rate for a given volume fraction and  $t_0$  is a prefactor (with the dimension of a time). Experimentally,  $t_0$  may depend slightly on  $\dot{\gamma}$ , but this dependence can be

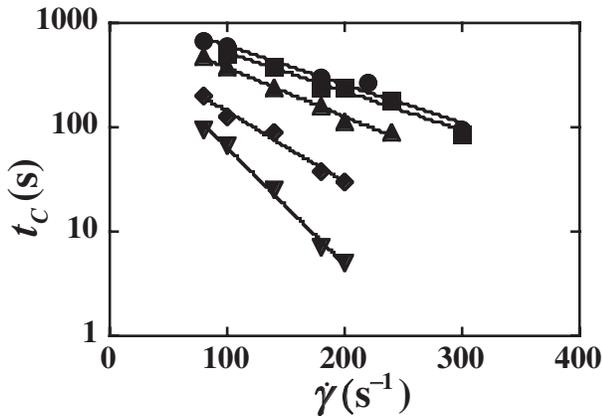


FIG. 4. Evolution of  $t_c$  (in log scale) with  $\dot{\gamma}$  for different  $\varphi_g$ : 10% (●); 11.5% (■); 13% (▲); 15% (◆); 17% (▼); the solid lines are exponential fits.

neglected by comparison with the exponential one. A clear decrease of  $\dot{\gamma}_c$  with increasing  $\varphi_g$  is observed. This precludes any measurement when  $\varphi_g$  becomes too large since the aggregation is almost instantaneous.

This exponential dependence is unexpected and has never been observed previously. An algebraic dependence, with an exponent between  $-1$  and  $-0.75$ , is typically encountered for the aggregation time of two spheres when convection is the dominant transport mechanism [16]. Experimentally, for dispersions under shear, an algebraic dependence on the shear rate is typically measured for the induction time before aggregation, and the exponent is close to  $-1$  [17,18]. However, if we try to fit our experimental data to an algebraic decay, we find an exponent ranging between  $-3.5$  and  $-1.5$ , depending on the volume fraction considered. This precludes any interpretation in terms of a purely convective phenomenon.

The exponential dependence is reminiscent of a thermally activated Arrhenius process, characterized by an attempt frequency and an energy barrier. However, there is no apparent thermal activation here. Instead, the effective thermalization, which generates an attempt frequency for the pairwise aggregation, must arise from the shear itself. The shear flow causes the globules to run into each other at some frequency, which depends on  $\dot{\gamma}$ . Similarly, thermal effects alone are not sufficient to overcome the activation barrier, since the suspension is kinetically stable at rest. Instead, the hydrodynamic forces between the colloidal particles are essential to reduce the activation barrier and enable the observed irreversible aggregation. Therefore, the exponential dependence must reflect the decrease in the energy barrier between the particles caused by the hydrodynamic energy,  $\eta \dot{\gamma} a^2 \delta$ , where  $\delta$  is the microscopic length over which the interparticle repulsive potential is effective and  $a$  is the particle radius. This concept of reduction of an energy barrier by the shear has also been used by Ozon *et al.* [19] to describe a completely different system, the rejuvenation of a colloidal glass. In our experiments, the shear-induced reduction in the repulsive barrier can be easily estimated: the barrier is reduced by amounts ranging from  $1k_B T$  to  $8k_B T$  (where  $k_B T$  is the thermal energy), depending on the set of experiments considered. Following this approach, the average time for two particles to aggregate irreversibly is given by  $\tau = \tau_0 \exp(\frac{E - \eta \dot{\gamma} a^2 \delta}{k_B T})$ , where  $\tau_0$  is the pairwise attempt time generated by the shear and  $E$  the repulsive energy barrier in the absence of shear. As already mentioned, in the absence of an energy barrier, the pairwise attempt time depends algebraically on  $\dot{\gamma}$  with an exponent close to  $-1$  [16], so we take  $\tau_0 \propto \frac{1}{\dot{\gamma}}$ . This leads to  $\tau \propto \frac{1}{\dot{\gamma}} \exp(-\frac{\eta \dot{\gamma} a^2 \delta}{k_B T})$ .

The exact relation between the experimental induction time  $t_c$  and the theoretical time  $\tau$  is uncertain. A hypothesis based on a reaction-limited cluster aggregation (RLCA) is certainly a simplification in view of our observations under

the microscope, which suggest a more cooperative mechanism. However, with this hypothesis,  $1/t_c \propto (1/\tau)^{F(\varphi_g)}$ , where  $F(\varphi_g)$  is the probability of a particle to belong to a final solidlike cluster, at a volume fraction  $\varphi_g$ . The exact analytical form of  $F(\varphi_g)$  is unknown, but  $F$  must be an increasing function of  $\varphi_g$ . This leads to the theoretical expression  $t_c \propto \frac{1}{\dot{\gamma}^{F(\varphi_g)}} \exp\left[\frac{-\eta\dot{\gamma}a^2\delta}{k_B T} F(\varphi_g)\right]$ . This formula is in very good agreement with the experimental exponential dependence of  $t_c$  on  $\dot{\gamma}$ . Indeed, since  $0 \leq F(\varphi_g) \leq 1$ , the preexponential dependence on  $\dot{\gamma}$  is negligible compared with the exponential one. This model may also explain the experimental decrease of  $\dot{\gamma}_c$  with increasing  $\varphi_g$  since  $F$  is an increasing function of  $\varphi_g$ . However, a deeper understanding of the shear hydrodynamics would be required to improve this prediction, particularly the form of the probability  $F(\varphi_g)$ .

In the existing literature on the aggregation of suspensions under shear, the pairwise aggregation is driven only by the hydrodynamic doublet formation rate. This leads to an algebraic scaling of the induction time before aggregation on the shear rate, with an exponent close to  $-1$ . However, in our experiments, there is an energy barrier that must be overcome in order to form irreversible doublets. The hydrodynamic energy induced by the shear provides the extra energy required to overcome this barrier. We emphasize the similarity between our experimental system and that described by Legrand *et al.*, who use an algebraic fitting with an exponent close to  $-1$  [18]. Indeed, they deal with bitumen emulsions that do not aggregate unless shear is applied, and thus there should also be an energy barrier to overcome in their case. However, their published data can be perfectly fitted to an exponential decay. Moreover, the exponential fit is even better, as it describes the slight concavity that appears on their experimental curves in a log-log representation [18]. In contrast, we cannot use an algebraic decay with an exponent  $-1$  to fit our data. Thus, by contrast to the data of Legrand *et al.* [18], our experimental fit with an exponential decay is not merely an improvement of a more commonly used approach but is the only way to describe the behavior of our system.

For the final solidlike aggregates, we speculate that the shear-induced forces, which drive the globules together, also induce plastic deformation of their surfaces, allowing nucleation of liquid bridges between fluid portions of the globules. Indeed, if the final aggregated state is rewarmed, the globules lose their integrity and form a single continuous structure, which nevertheless still contains the small internal water droplets. Finally, our ability to control and characterize this shear-activated aggregation rests in large measure on our use of a crystallizable oil to form double emulsions that are neither too strongly nor too weakly repulsive. However, this type of behavior is ubiquitous and occurs in a wide range of technological materials

from food to emulsified coatings containing solid particles [18]. The most intriguing result of this work is certainly the existence of the exponential relation between the induction time before aggregation and the shear rate. We have shown that this original behavior can be interpreted in terms of the reduction, by the hydrodynamic forces, of the repulsive energy barrier that prevents the particles from aggregating.

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