

**REARRANGEMENT OF 2D CLUSTERS OF DROPLETS UNDER
COMPRESSION: FROM CRYSTAL TO GLASS**

REARRANGEMENT OF 2D CLUSTERS OF DROPLETS UNDER COMPRESSION: FROM CRYSTAL TO GLASS

By

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A Thesis

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Abstract

Emulsions and colloidal suspensions have various industrial applications but are also used in laboratories as model systems for studying the different phases of matter. They are versatile as their nature, size and inter-particle interactions are easily tunable. These systems are perfect for studying questions such as the phase transition. In this thesis, we investigate the transition from an ordered crystal to a disordered glass. Perfectly ordered crystals are modeled by clusters of highly monodisperse droplets. We study the transition toward a glassy system by mixing two monodisperse populations of droplets in different proportions. The clusters are compressed between two thin glass rods, one of which is a force transducer. The forces within the clusters are directly measured and used as an indicator of the composition of the cluster. Upon introduction of disorder, the number of peaks in the force measurement increases drastically. We find that the way the energy is dissipated in the cluster is valuable information to characterize the crystal-to-glass transition.

In addition to the experimental study of the crystal-to-glass transition, we have developed an analytical model that is in full agreement with the experimental observations. A crystal is modeled as an assembly of Hookean springs that will store elastic energy until it reaches a fracture point. We are able to predict the number of peaks in the force measurements when defects are introduced using simple geometric arguments. From this prediction, the way the work is dissipated in a given transition can be predicted.

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Moving to Canada two years ago has been one of the most important decisions in my life. Looking back at these two years, I can now say that it has been one of the best. Of course, it would have been easier to stay in my home country but I could always count on everyone around me to “teach” me how things work here and always support me.

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Contents

Abstract	iii
Acknowledgements	iv
1 Introduction	1
1.1 Suspensions	2
1.1.1 Colloids	4
1.1.2 Emulsions	5
1.2 Interactions	6
1.2.1 Hard spheres	6
1.2.2 Van der Waals	7
1.2.3 Electrostatic repulsion	7
1.2.4 Depletion forces	9
1.3 Mechanical properties	10
1.3.1 Assembly of springs	10
1.3.2 Young's modulus	12
1.3.3 Yield stress and rupture	13
2 Suspensions as model systems	15
2.1 Glass transition and jamming	16
2.2 Forces between particles	17
2.3 The crystal-to-glass transition	18
3 Experimental Details	21
3.1 Sample cell	21

CONTENTS

3.1.1	Solution	21
3.1.2	Addition of a surrounding wall	23
3.2	Micropipettes	24
3.2.1	Droplet pipette	25
3.2.2	Pushing pipette	26
3.2.3	Force sensing pipette	27
3.3	Image Analysis	30
3.3.1	Force measurement and cross correlation	30
3.3.2	Droplet and bond detection	32
4	Crystal-to-glass transition	35
5	Conclusions	51

List of Figures

- 1.1 Illustration of the steric stabilization. (a) two colloids with polymers grafted on their surface. (b) As the particles come closer to each other, the polymer chains start interacting which leads to a repulsive force between the particles 4
- 1.2 (a) Illustration of the screening effect. A negatively charged particle in water is surrounded by counter-ions and co-ions. In the direct surrounding of the particle, there is an excess of positively charged ions. The ions are only shown on the right side of the particle for clarity. (b) Schematic curves of the concentration of the different ions as a function of the distance d away from the charged particle. The concentrations of both ions converge to the average concentration c_∞ away from the particle. The decay is characterized by the Debye screening length κ^{-1} . 8
- 1.3 (a) Two large droplets are surrounded by small depletant (black disks). When the particles are far away, the depletant particles cannot enter depletion zone around both particles (shown by the dashed circles) (b) When the particles come closer to each other, the forbidden regions overlap leading to more space available to the depletant. This configuration is more favorable because of the increase in the entropy of the depletant. The large particles feel an attractive force and they stick together. 9

LIST OF FIGURES

- 1.4 Schematics of two springs assembled in series. The force F is applied at point B . Once the system is stretched, point A is at equilibrium. To ensure that no net force is applied on A , the force from spring ①, F_1 , must be the same as the force from spring ②, F_2 10

- 1.5 Schematics of two springs assembled in parallel. The elongation of both springs must be the same. The force F is the sum of the forces resulting from the elongation of spring ①, F_1 , and spring ②, F_2 . . . 11

- 1.6 Illustration of the stress-strain curves for two different materials. Material ① (red) has a smaller Young's modulus and a smaller yield stress σ_y . Its elongation at failure is much larger than material ② (blue) and deforms plastically over a large range of strain: it is a ductile material. The elongation at failure is much smaller for material ② which deforms plastically over a short range of strain: material ② is brittle. 14

- 3.1 Schematics of the sample cell. (a) Top view - the area shaded in blue corresponds to the part that is filled with the aqueous solution. (i) "the droplet pipette"; (ii) "the pushing pipette"; and (iii) "the force sensing pipette". The chamber is closed on the sides by 3D-printed walls to prevent evaporation. Small slits are designed for the pipettes to be inserted. (b) Side view - the droplets are buoyant and rise to the top of the chamber forming a 2D aggregate under the top coverslip. The chamber is imaged using an inverted optical microscope. 22

- 3.2 3D render of the experimental setup. The chamber wall is glued onto the bottom glass slide. In order for the pipettes to be inserted, small slits are designed on three side of the chamber. The top glass slide is simply placed atop of the wall. The holders on the side prevent the top glass slide from moving with respect to the bottom one. 23

- 3.3 (a) The wall is glued onto the bottom glass slide and the bottom glass slide is inserted into holders (gray pieces). (b) Pipettes are inserted in the chamber (c) A glass slide is placed atop of the wall. 24

LIST OF FIGURES

3.4	(a) Picture of the pushing pipette. The perpendicular short end is the part used to compress the cluster. (b) Schematics of top view of the pipette. (c) Schematics of the side view of the pipette. This view corresponds to the eye shown in frame (b)	26
3.5	(a) Picture of the force sensing pipette. The part in contact with the droplets is the flat end of the pipette. (b) schematics of top view of the pipette. (c) schematics of the side view of the pipette. The view corresponds to the eye shown on (b)	27
3.6	Calibration of the reference pipette with the droplet of water. The applied force corresponds to the weight of the droplet. The deflection is measured using cross correlation (see 3.3.1). The spring constant of the pipette is obtained by fitting a straight line to the experimental data.	28
3.7	(a) displacement of the reference pipette as a function of time. When contact is made, the reference pipette deflects and the slope decreases. The deflection corresponds to the difference between the actual (in blue) and the extrapolated (in black) displacement. (b) Force calculated from Δx_1 as a function of the deflection of the accordion pipette. Δx_1 and Δx_2 are in opposite direction. Δx_2 is counted as positive which leads to a negative force.	29
3.8	(a) Microscopy picture of the force sensing pipette in its original position when no force is applied. (b) The force sensing pipette deflects under the force applied by the cluster. (c) The blue line corresponds to the auto-covariance performed on (a). The position of the maximum gives the initial position of the pipette. The red line corresponds to the cross-covariance between images (a) and (b). Measuring the distance between the maxima of the blue and the red line gives the deflection of the pipette. Inset - Zoom on the peaks. A Gaussian profile is fitted to the data points to measure the position of the maximum with sub-pixel resolution.	31

LIST OF FIGURES

3.9	(a) Microscopy picture of a droplet surrounded by its 6 neighbours. (b) Example of the lines along which the profiles are studied for the bond detection. (c) Five different profiles drawn for the bond with droplet 2. We see only one extremum: there is a bond with droplet 2. (d) Five different profiles drawn for the bond with droplet 3. The profiles show three extrema so there is no bond with droplet 3	32
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Chapter 1

Introduction

Material in contact with another material is typically driven to minimize the interfacial area. For example, when making dressing for a salad, one mixes an aqueous phase (vinegar) and oil. The interface between oil and water is characterized by an interfacial energy γ_{wo} . By reducing the interfacial area, the mixture minimizes its total energy. The lowest energy state corresponds to two distinct phases. The vinegar does not spontaneously form small droplets dispersed in oil and one has to provide mechanical energy through mixing to reach a suspension. This suspension is not even stable as it quickly reduces its interfacial energy by coalescing into larger domains. In contrast, stable suspensions are fairly common in nature. For instance, milk is a suspension of fat globules in water and blood is a suspension of red blood cells in a liquid phase. In fact, many commercial products used in our everyday life are stable suspensions: wall paint, toothpaste, shaving foam or mayonnaise. At first glance, all of these products have little in common but they all correspond to the definition of a suspension: microscopic particles of a substance suspended into a continuous phase [1].

In addition of being ubiquitous in nature and commonly used in industry, suspensions are also widely used in laboratories. They have been shown to be accurate models for the different phases of matter such as crystals or glasses [2–4]. The particles can assemble and form structures analogous to atomic systems such as crystals or glasses. In crystals, the atoms (or particles) are ordered on a lattice whereas glasses do not show long range order. An interesting question arises from these definitions:

how does a material, or a suspension, transition from a crystal to a glass?

In this thesis, we address this specific question by using oil droplets dispersed in water as a model system. We directly characterize the mechanical behaviour of the suspension under compression. We study the impact of disorder on the response of the assembly of droplets to external forces. Chapter 1 addresses the physics required to understand the results presented in this work. In particular, the most common suspensions used in laboratories are reviewed and the interactions between particles are presented in detail. Finally, important mechanical properties such as elasticity and yield are presented. In chapter 2, examples of studies where suspensions have been used to model phenomena such as glass transition or jamming are discussed. An in-depth discussion about the crystal-to-glass transition is also presented. The experimental details required to reproduce our measurements are outlined in chapter 3. Finally, in chapter 4, a manuscript of the research is included, which describes the main conclusions we reached on the crystal-to-glass transition. The supplemental information, which will accompany the manuscript, is also presented.

1.1 Suspensions

The most basic definition of a suspension is a mixture of small particles of a substance a dispersed in a continuous phase b [1]. The typical size of the suspended particles ranges from couple nanometers up to tens of microns. If a suspension is made of particles that all have the same size, it is called monodisperse. Otherwise the dispersion is said to be polydisperse. One way to quantify the polydispersity is to use the coefficient of variance CV, defined as the ratio between the standard deviation in the particle radii and the mean value of the radius [5]. Even though all the examples listed previously fall into the category of suspensions, it is clear to everyone that paint is not the same product as shaving foam. This is due to the nature of the dispersed phase. Paint is a suspension of solid pigments particle in a liquid whereas shaving foam is a dispersion of air in a liquid. Specific names are given to each different kind of suspension. This classification is summarized in Table 1.1. Here we focus on suspensions in a liquid, in which one can disperse three types of substances. If the particles are solid it is called a colloid. The word emulsion refers to a suspension

of droplets in a liquid. Finally, if the dispersed substance is a gas, they are named foams.

Table 1.1: Classification of the different suspensions in a liquid continuous phase [1,6].

Continuous phase	Liquid		
Particles	Solid	Liquid	Gas
Name	Colloid	Emulsion	Foam
Example	Paint, Toothpaste	Milk, Mayonnaise	Shaving foam, whipping cream

A common issue with suspension is their stability. For example a mixture of oil droplets in water is unstable [7] and stabilizers must be added to the mix. This phenomenon is due to their high interfacial surface area. Maintaining the interface between the particle and the continuous phase has an energetic cost characterized by the surface tension γ . The total energy cost is directly proportional to the surface A : $E_{\text{surf}} = \gamma A$. For example, the surface tension between water and air is 72 mN/m [7] and the surface tension between water and oil (hydrocarbonated liquids) is $\gamma_{wo} \sim 50$ mN/m [8]. The total energy ends up being large because of the total interfacial area. Let us consider a simple emulsion that everyone has already encountered: mayonnaise. This emulsion is usually made of $\sim 20\%$ of water in oil and the size of the water droplets is ~ 500 nm [9]. If we consider 1 kg of mayonnaise, there are $\sim 4 \times 10^{14}$ droplets of water in oil. The total surface of all the droplets is approximately 1000 m² which leads to an energy cost of approximately 50 J to maintain the interface between oil and water. In comparison, if the water was forming a single droplet, its radius would be 36 mm which leads to an interfacial surface area of $\sim 2.10^{-2}$ m² and an energetic cost of the order of 1 mJ. From this estimate, it is clear that the water would rather be in the single droplet configuration. Of course, mayonnaise is not only made of water and oil, otherwise it would be unstable. Suspensions stabilizers are discussed in the following sections for the two suspensions relevant to this work: emulsions and colloids.

1.1.1 Colloids

Colloids are solid particles dispersed in a liquid. The solids can be made of organic materials such as polymers. Common polymers used in colloidal suspensions are poly(methylmethacrylate) - PMMA or polystyrene. Another class of colloidal particles is inorganic materials such as silica or carbon black. Many colloidal particles are available commercially in different sizes and polydispersity indexes.

When two colloids come into contact they tend to stick irreversibly. By sticking to another particle, a colloid reduces its surface of contact with the liquid which is energetically favorable. This phenomenon is called aggregation [10]. Two strategies can be used to prevent aggregation: steric stabilization and charge stabilization [10]. The steric stabilization consists in grafting long polymer chains onto the surface of the particles to prevent them from coming too close to one another as shown in Fig. 1.1. As the particles approach, the polymer chains interact which leads to a repulsive force between them (see Fig. 1.1 (b)). For example, PMMA particles are commonly stabilized using poly-(12 hydroxystearic acid) in many experiments that study phase transitions [3, 4, 11].

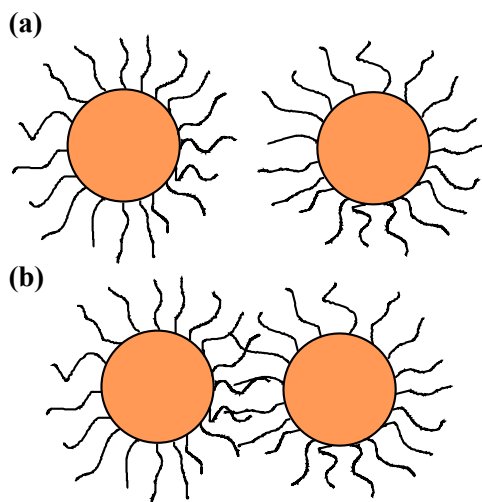


Figure 1.1: Illustration of the steric stabilization. (a) two colloids with polymers grafted on their surface. (b) As the particles come closer to each other, the polymer chains start interacting which leads to a repulsive force between the particles

The second strategy relies on electrostatic forces between the particles if their surface is charged. This stabilization will be discussed in more details in section 1.2.3, when the electrostatic interaction between particles is described.

1.1.2 Emulsions

Emulsions are made by dispersing liquid droplets into another continuous liquid phase. The two liquids must be immiscible to form an emulsion otherwise they would simply mix and form a single homogeneous liquid phase. Examples of milk and mayonnaise were already mentioned but emulsions are not only used in the food industry. In fact, emulsions in high-tech applications is a growing field. The demand for energy is constantly growing but shrinking oil reserves mean extraction is becoming more difficult. Emulsions are used for enhanced oil recovery (EOR) to improve the extraction of oil [12,13]. Another active field of research is the use of emulsions for drug delivery. If the drug is not soluble in water but in oil (lipophilic) then droplets of oil can be used to carry the drug in the human body [14]. Finally, individual droplets can be used as micro-reactor or growing media for applications like DNA sequencing [15] or growing organisms [16].

The commonly used liquids to produce emulsions are oil and water. If the dispersed phase (the droplets) are made of oil (O/W) it is a direct emulsion. The emulsion is inverse if the droplets are made of water (W/O). Emulsions can be made by mechanically shearing a mix of oil and water [7]. A more sophisticated technique is the use of microfluidic devices, which allows for better control on the size of the droplets [17–20]. These devices usually require flow in the continuous phase. In this work, we use the snap-off instability [5]. There is no flow in the continuous phase with this technique and it leads to highly monodisperse droplets with $CV < 0.7\%$.

As discussed with the example of the mayonnaise, emulsions are not always stable. Oil and water will phase separate to minimize the interfacial area. Stabilizing agents must be added to lower the surface tension between oil and water γ_{wo} . Mayonnaise is stabilized by the proteins contained in egg yolk [9]. In laboratories, molecules called surfactants are used which absorb at the oil-water interface to lower the surface tension. These molecules have a polar head that is hydrophilic (interacts preferably with water) and a carbonated tail that is lipophilic (interacts preferably with oil). For

the emulsion to be stable the surface tension must be lower than 5 mN/m compared to its initial value of $\gamma_{wo} \sim 50$ mN/m [7]. This can be achieved in laboratories by using surfactants such as sodium dodecyl sulfate (SDS) [8].

1.2 Interactions

Interactions between particles are critical to the stability of the suspensions. If the sum of the interactions is attractive, then particles will aggregate and the suspension is not stable. If the sum of the interactions is repulsive then the suspension is stable. Stability is not the only reason why interactions between particles are important. Indeed, suspensions are used in laboratories as model systems and one may want the particles to be attractive or repulsive. Suspensions are also often studied using computer simulations. A particle is modeled by a sphere that evolves in time by interacting with other particles. In these simulations, the potential energy between two particles is set using a mathematical model. It is important for this potential to be realistic and that the formula is coherent with what is observed experimentally. In the following section, we describe four potentials encountered in suspensions.

1.2.1 Hard spheres

The particles can be considered as hard sphere that interact only upon contact: the repulsion is infinite, *ie.* the spheres cannot interpenetrate. The potential between the two droplets can be written as a function of the distance between two particles, r , and the sum of the droplets radii, σ :

$$V(r) = \begin{cases} \infty, & \text{if } r \leq \sigma \\ 0, & \text{otherwise.} \end{cases}$$

This interaction is a good approximation for sterically stabilized colloids such as PMMA [6]. The hard sphere model is also widely used in simulations to study the glass transition [21, 22].

1.2.2 Van der Waals

Van der Waals forces are attractive forces between any pair of atoms that originates from quantum mechanics. Atoms do not need to have a permanent dipole to experience van der Waals forces [10]. The interaction depends on the distance between the two atoms: $U(r) \propto 1/r^6$. Knowing the interaction between each atom pair, one can calculate the interaction between two macroscopic bodies. The exact calculation for the force between two spheres was carried out by Hamaker [23]. The potential can be simplified if the spheres are close to one another and leads to an attractive force F :

$$F = -\frac{AR_1R_2}{6r^2(R_1 + R_2)}, \quad (1.1)$$

where A is the Hamaker constant which depends on the material. The order of magnitude for A is $\sim 10^{-19}$ J [10]. If the spheres have the same radius $R_1 = R_2 = R$, Eq. 1.1 further simplifies to:

$$F = -\frac{AR}{12r^2}. \quad (1.2)$$

If we consider two spheres with radius $R \sim 10 \mu\text{m}$ in contact $r \sim 0.2 \text{ nm}$, the force required to separate them is $F \sim 2 \mu\text{N}$. A force of the order of a micro-Newton is small at the macroscopic scale but it is large in comparison to nano-Newton forces usually measured in suspensions [24].

1.2.3 Electrostatic repulsion

Up to this point, we have only considered particles without charges. If the particles have charges on their surface, the interaction between particles are modified [10]. In vacuum or in air, two charged particles experience a net Coulomb repulsion. The interaction is more complicated if the particles are suspended in water. The ions dissolved in water interact with the charged particles and modify the electrostatic repulsion [10]. If the surface of a particle is negatively charged, then the positive counter-ions are attracted and the negative ions are repelled. Positive ions accumulate close to the particles forming an electrostatic double layer, as shown on Fig. 1.2(a). These positive charges are screening the negatives charges on the particle [10].

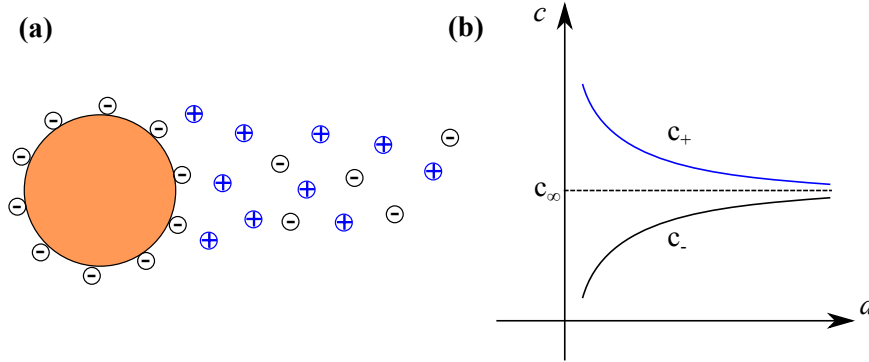


Figure 1.2: (a) Illustration of the screening effect. A negatively charged particle in water is surrounded by counter-ions and co-ions. In the direct surrounding of the particle, there is an excess of positively charged ions. The ions are only shown on the right side of the particle for clarity. (b) Schematic curves of the concentration of the different ions as a function of the distance d away from the charged particle. The concentrations of both ions converge to the average concentration c_∞ away from the particle. The decay is characterized by the Debye screening length κ^{-1} .

The distribution of charge and the potential ψ at a distance d of the particle can be calculated [1]. In the limit of a small potential ψ , the Debye-Hückel approximation, the potential decreases exponentially: $\psi(d) = \psi_0 \exp(-\kappa d)$ (see schematics Fig. 1.2(b)). κ^{-1} is called the Debye screening length and characterizes the extent of the double layer. If two particles approach one another, the two double layers start overlapping. The positive ions are confined in a small region which is not favorable entropically. The particles experience an entropic repulsive force that originates from the interaction of their double layer [10]. The direct consequence of screening is that the repulsive forces between particles depends on the concentration of counter-ions in the solution. Screening effect gives a direct control on the strength and range of the electrostatic repulsion.

Colloids can be stabilized using electrostatic double layer repulsive forces. For this kind of stabilization, the screening length must be taken into account. If the charges are screened over a short Debye length (high concentration in ions) then the colloids can still aggregate and the suspension is not stable [10].

1.2.4 Depletion forces

Depletion is an attractive interaction which occurs when smaller particles, called depletants, are co-dispersed in the solution. These small particles cannot overlap with the large particles. they are effectively excluded from the volume surrounding the large particles. they are effectively excluded from the volume surrounding the large particles [10]. When two large particles approach each other, their depletion zones overlap, reducing the forbidden volume for the depletants (see Fig. 1.3 (b)). The number of available configurations for the small particles increases as large particles approach one another, which results in an increase in entropy. The large particles are attracted to one another by the depletion forces. This potential has a purely entropic origin.

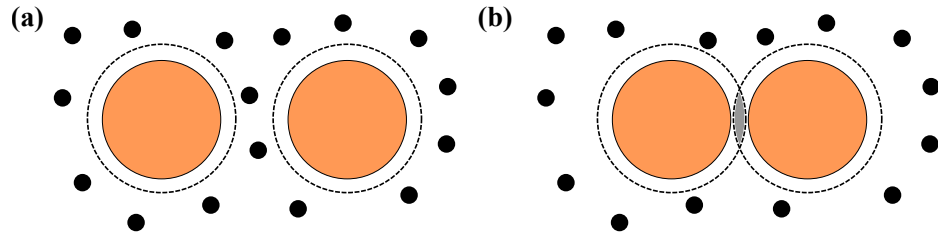


Figure 1.3: (a) Two large droplets are surrounded by small depletant (black disks). When the particles are far away, the depletant particles cannot enter depletion zone around both particles (shown by the dashed circles) (b) When the particles come closer to each other, the forbidden regions overlap leading to more space available to the depletant. This configuration is more favorable because of the increase in the entropy of the depletant. The large particles feel an attractive force and they stick together.

Typical depletant particles used in laboratories are glycerol or surfactant micelles. When the concentration in surfactant exceeds a certain value called critical micelle concentration (CMC) the surfactant particles aggregate into spheres called micelles [7]. Depletion forces are particularly important in our work as we use them in chapter 4 to ensure that the droplets are sticking together to form clusters.

1.3 Mechanical properties

In order to study the crystal-to-glass transition, we probe the mechanical properties of the clusters of droplets. A theoretical model is developed to model the response of a crystal (assembly of monodisperse droplets) to compression. A single droplet is modeled by an Hookean spring and the cluster is considered as an equivalent spring. In this section, we derive the relationship between the equivalent spring constant and the spring constants of the individual springs. The derivation for the assembly of two springs in series is also used in section 3.2.3 when dealing with the calibration of the force sensing pipettes. Finally, important quantities such as the Young's modulus and the yield stress of a material are defined.

1.3.1 Assembly of springs

When dealing with elasticity, the first intuitive example is that of a Hookean spring. The applied force, F , is directly proportional to the elongation, x , of the spring via the spring constant, k : $F = kx$.

Series

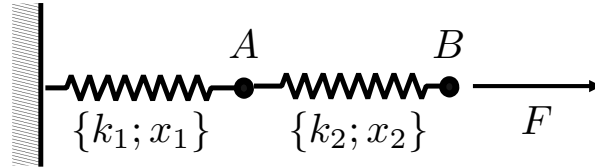


Figure 1.4: Schematics of two springs assembled in series. The force F is applied at point B . Once the system is stretched, point A is at equilibrium. To ensure that no net force is applied on A , the force from spring ①, F_1 , must be the same as the force from spring ②, F_2 .

Springs can be assembled in series as shown in Fig. 1.4. The springs are lined up and the force is exerted at the end of the second spring (point B). Let us consider two springs of constant k_1 and k_2 . We call the elongation of the springs x_1 and x_2 respectively, which leads to: $F_1 = -k_1x_1$ and $F_2 = -k_2x_2$. For point A to be at equilibrium, the force exerted by spring ① must be the same as the force from

spring ②: $F_1 = F_2 = F$. The consequence is that the elongation of spring ②, x_2 , is proportional to x_1 .

$$x_2 = x_1 \frac{k_1}{k_2}. \quad (1.3)$$

The force F can also be written in terms of the equivalent spring constant, k_{eq} , from the assembly: $F = k_{eq}(x_1 + x_2)$.

$$F = k_{eq}\left(x_1 + x_1 \frac{k_1}{k_2}\right) = k_1 x_1, \quad (1.4)$$

$$k_{eq}\left(\frac{k_1 + k_2}{k_2}\right) = k_1, \quad (1.5)$$

$$\frac{1}{k_{eq}} = \frac{1}{k_1} + \frac{1}{k_2}. \quad (1.6)$$

Eq. 1.6 can be generalized to n springs in series:

$$\frac{1}{k_{eq}} = \sum_{j=1}^n \frac{1}{k_j}. \quad (1.7)$$

If every spring has the same spring constant $k_j = k$, the equivalent spring constant is $k_{eq} = k/n$.

Parallel

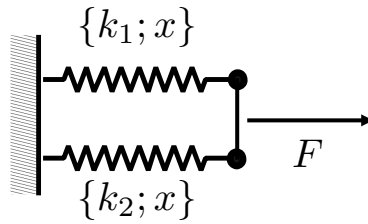


Figure 1.5: Schematics of two springs assembled in parallel. The elongation of both springs must be the same. The force F is the sum of the forces resulting from the elongation of spring ①, F_1 , and spring ②, F_2 .

Two springs can also be assembled in parallel (Fig. 1.5). The resulting force F applied on both springs is the sum of the force from spring ① and spring ②. The

elongation x of both spring is the same in this case.

$$F = F_1 + F_2 = -(k_1 + k_2)x \quad (1.8)$$

By comparing the force from the equivalent spring $F = -k_{eq}x$ to Eq. 1.8, the equivalent spring constant is found to be $k_{eq} = k_1 + k_2$. This relation can also be generalized to n springs:

$$k_{eq} = \sum_{j=1}^n k_j \quad (1.9)$$

If every spring has the same spring constant, the equivalent spring constant is $k_{eq} = nk$

1.3.2 Young's modulus

For many materials, the stress (force divided by the cross section S : $\sigma = F/S$) is proportional to the strain ($\epsilon = \Delta l/l$) in the elastic regime: $\sigma = E\epsilon$. This constant is called the Young's modulus, E and characterizes the stiffness of a material. For example, metals have a Young's modulus of ~ 100 GPa when the Young's modulus of polystyrene is ~ 1 GPa. To deform a piece of metal and a piece of plastic with the same length l and cross section S , the applied force must be one hundred time larger. This relationship is analogous to Hooke's law, $F = -kx$, for a 3D continuous material. The strain-stress relationship can be explained using the assembly of springs discussed above.

Let us consider a piece of material of cross section S and length l . We can model it by springs of length l_0 and constant k assembled together. If we assume that a spring has a section s_0 then we can assemble $n_p = S/s_0$ in parallel to model the cross section of the piece. The number of springs in series is $n_s = l/l_0$. According to Eq. 1.7 and 1.9, the equivalent spring constant is:

$$k_{eq} = \frac{kn_p}{n_s} = \frac{kSl_0}{s_0l}. \quad (1.10)$$

The force required to deform the piece by x is:

$$F = k_{eq}x = \frac{kl_0}{s_0} \frac{x}{l} S. \quad (1.11)$$

Eq. 1.11 can be rearranged in order to express the stress $\sigma = F/S$ as a function of the strain $\epsilon = x/l$:

$$\sigma = \frac{kl_0}{s_0}\epsilon = E\epsilon. \quad (1.12)$$

Identifying both sides of the equation, we find that the Young's modulus is equal to $E = kl_0/s_0$. If l_0 is small, many small springs are assembled in series. We know that the more springs in series the smaller the equivalent constant is so the less stiff the material should be. If s_0 is small, many springs are assembled in parallel leading to a stiff material. This derivation shows that the simple model of assembling springs in different ways can explain macroscopic properties of a material.

Experimentally, the Young's modulus is measured by measuring the stress-strain relationship. A force is applied on a piece of known cross section S and length l and the deformation is measured. Stress is plotted as a function of strain as shown in the schematic Fig.1.6. The elastic regime corresponds to the linear part of the curve. The stress is directly proportional to the strain and the slope corresponds to the young's modulus. The Young's modulus of material ① is smaller than material ②.

1.3.3 Yield stress and rupture

The following discussion mainly follows the textbook from F. P. Beer *et al.*: *Mechanics of materials* [25]. Deformation is reversible in the elastic regime: if the external load is removed, the material comes back to its original shape. A material will remain elastic up to a certain amount of deformation. Once the material is deformed beyond that threshold, the material cannot fully recover its shape. The non-reversible deformation is called plastic deformation. This regime is characterized by internal rearrangements between atoms and the creations of defects. The relationship between stress and strain becomes non linear. The transition between elastic and plastic behaviours is called yielding and it is defined by the yield stress σ_y . The transition from the elastic to plastic regimes depends strongly on the nature of the material. Elastomers, for example, can be deformed by $\sim 200\%$ and still be in the elastic regime, where metals quickly transition to the plastic regime.

During plastic deformation, internal rearrangements occur and defects are created. If the material is further deformed, cracks propagate and the material fails. This

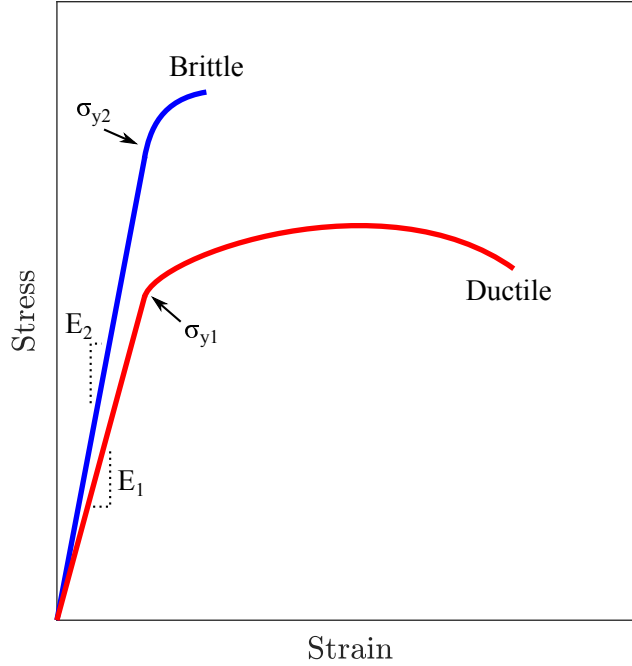


Figure 1.6: Illustration of the stress-strain curves for two different materials. Material ① (red) has a smaller Young's modulus and a smaller yield stress σ_y . Its elongation at failure is much larger than material ② (blue) and deforms plastically over a large range of strain: it is a ductile material. The elongation at failure is much smaller for material ② which deforms plastically over a short range of strain: material ② is brittle.

event is called rupture. Again, each material behaves differently with regard to crack propagation. Some materials resist the propagation of cracks over a large range of deformation. This category of materials, called ductile materials, is characterized by an extended plastic regime as drawn in Fig. 1.6 for material ① (red curve). Resistance to crack propagation is called ductility. For other materials the stress at which they break is almost the same as the yield stress: they are brittle materials. The stress-strain curve for such a material is shown in Fig. 1.6 with material ②. The yield stress and the stress at rupture characterizes the plastic behaviour of a material where the Young's modulus describes its elastic behaviour.

Chapter 2

Suspensions as model systems

Suspensions are used as model systems to study the different phases of matter [6]. The main advantage of emulsions or colloids compared to atomic matter is the size of the particles which typically ranges from tens of nanometers to tens of microns. Due to their larger size, the particles can be directly imaged using techniques such as confocal microscopy [11]. One can directly access information at the single particle scale. As particle size is comparable to the wavelength of light, particles can be studied using light. Light scattering experiments give access to average properties of the particles rather than the individual particle information. Some examples include size and dynamical properties such as mean square displacement [26]. Another benefit of the larger size is that quantum effects can be neglected [6]. Depending on the focus of the study, thermal motion can be tuned by changing the size of the particles, and temperature.

The richness of suspensions explains why they have been widely used to investigate fundamental physics such as phase transitions. In this chapter, we review recent studies of colloidal systems and emulsions. We particularly focus on questions that are linked to the work presented in chapter 4 dealing with the transition from ordered to disordered aggregates.

2.1 Glass transition and jamming

The glass transition is a phenomenon where a viscous liquid becomes an amorphous solid due to a decrease in temperature [27]. When temperature decreases towards the glass transition temperature, T_g , the viscosity increases dramatically. This transition is observed in many materials, including metals or polymers, but is not yet fully understood. Interestingly, a similar phenomenon happens with colloidal systems. When the density of colloidal particles is increased, the viscosity diverges. The control parameter is no longer the temperature but the density of particles ϕ . This transition is called the colloidal glass transition or jamming [6]. The similarity is not just qualitative but also quantitative. When studying the glass transition, despite the lack of a consistent theory to explain the transition, an empirical law has been shown to capture the divergence of the viscosity for molecular glasses [27]:

$$\eta(T) = \eta_0 \exp \left(\frac{T_A}{T - T_V} \right), \quad (2.1)$$

where η_0 , T_A and T_V are constants which depends on the material under consideration. Eq. (2.1) is known as the Vogel-Fulcher law. The way the viscosity increases for colloidal systems as a function of ϕ can be written as [28]:

$$\frac{\eta(\phi)}{\eta_0} = C \exp \left(\frac{D\phi}{\phi_m - \phi} \right), \quad (2.2)$$

where η_0 , C and D and ϕ_m are fitting parameters. Eq. (2.1) and (2.2) are clearly equivalent, the only difference being the parameter that triggers the transition. Foams and droplets can also experience a transition from liquid to amorphous solid when sheared [29]. The change in viscosity can be fit by a Vogel-Fulcher type behaviour replacing temperature by shear rate [29]. Increase in viscosity is not the only feature of the glass transition. For example, dynamical heterogeneities have been observed in simulations for supercooled liquids [30,31], also referred to as cooperative motion. Dynamical heterogeneities have also been observed in colloids [32–34]. Force networks (more details in section 2.2) between particles have also been observed in molecular glasses (simulation), emulsions and granular materials. These similarities between colloids, emulsions, foams and granular materials have motivated the development of

an unified description of the glass transition. Lui *et al.* [35] proposed a phase diagram with three axes: temperature, density and shear rate to describe the “jamming” of the suspensions mentioned above. This phase diagram was further generalized by Trappe *et al.* [36] who added the impact of attraction between particles. In their work, they also give experimental proof for the phase diagram.

The implications of this unified phase diagram are far reaching. Findings on a specific system, for example colloidal suspension, could be generalized to others such as molecular glasses. Finally, this generalized phase diagram further supports the use of colloids and emulsions as model systems as they are easier to study.

2.2 Forces between particles

A typical example of experiments made possible by the use of model systems is the study of force networks. When an external load is applied on a suspension, the forces between particles are not homogeneously distributed. Some particle pairs experience no force while others experience large forces. These large forces tend to line up into “chains”; this phenomenon is called force chains or force networks.

While the inter-particle forces can be studied experimentally with larger particles, it is more challenging with molecules. Force chains in molecular glasses have been studied using molecular dynamics [37] but to the best of our knowledge have not been directly measured experimentally. Emulsions or bubbles are good candidates for the study of force chains as the particles are deformable. Forces acting on the individual particles can be inferred from the shape of the droplets [24, 38]. When two soft droplets are pushed against one another, they deform resulting in a change in their surface area which leads to inter-particle forces. The force depends on the change in radius of curvature and the contact patch that forms due to compression.

Another closely linked system is a granular material [35]. They are made of solid beads of ~ 1 mm diameter packed together; the typical example being a sand pile. Interestingly, disordered granular material also show properties similar to colloidal suspensions or emulsions. For example, they develop force chains when they are compressed. A way to study the inter-particle forces between grains is the use of photo-elastic disks. These disks are made of a material that is birefringent upon

application of a force. The light going through the material experiences two different refractive indices along the two principal stress directions. Placing these particles between two crossed polarizers, one can see dark and light bands on the particles. The stress distribution among the grains can be deduced from the fringe pattern [39].

Finally, it has recently been shown in an computational study that disordered porous materials also develop force chains [40]. A porous material can be thought of as the “negative” of a granular material. It is a continuous solid material with multiple holes while a granular material is made of grains packed in a gas. Laubie *et al.* [40] have shown that the response to external loading for an ordered porous material (holes forming a square lattice) is homogenous. As disorder is increased, the holes are randomly moved from their original position and force networks are formed.

2.3 The crystal-to-glass transition

Many studies have investigated the transition from a liquid to a solid state as described in section 2.1. The solid state can be either a crystal, characterized by long range order, or a disordered glass. Polydispersity has been shown to prevent crystallization and aggregates form glasses instead [41]. The crystal-to-glass transition has been far less studied and many questions remain unanswered. A recent study by Goodrich *et al.* [42] addressed one of these questions using simulation. They compared three model packings: a crystal, a disordered glass and a packing with a small number of defects. They used both microscopic properties (average number of contacts between particles) and macroscopic properties (ratio between bulk and shear modulus) to differentiate glassy and crystalline behavior. Surprisingly, the intermediate state behaved like the glassy system even though its structure was closer to the crystal. The main conclusion from this study is that a lightly disturbed crystal is best described by the physics of a jammed system. Glassy behavior in highly ordered (but not perfectly crystalline) structures has also been observed in other numerical studies [43, 44].

On the experimental side, few studies have looked at the crystal-to-glass transition. One strategy is to look at the microscopic arrangement of particles [45, 46]. Different mathematical functions can be used to quantify the order in the arrangement of particles. For example, the bond orientational order parameter ψ_6 describes the

arrangement of the six closest neighbours to a given particle [45]. If the packing is hexagonal (crystalline packing) then $|\psi_6| \sim 1$. Another function that is especially important to differentiate crystals and glasses, is the correlation function $g_6(r = |r_j - r_i|) = \langle \psi_6(r_i) \psi_6^*(r_j) \rangle$ where r is the distance between two particles. Crystals are characterized by long ranged order; the correlation function peaks at regular spacings showing correlation between two particles that are far away from each other. For a glass, the peaks disappear quickly as correlation is lost. The study of these functions as disorder is systematically added in the systems gives insight into the transition from a crystal to a glass. The conclusion of these studies is consistent with a rapid transition toward glassy material as disorder is added.

Another strategy involves studying the response of a material under external loading. Blair *et al.* [47] experimentally measured the normal forces between millimeter-sized particles. They compressed both amorphous and crystalline packings and characterized the distribution of forces on individual particles at the boundaries of the packings. They showed that there was little change between the amorphous and crystalline packings. The distribution of forces on particles away from the edges of the packing was investigated by Hanifpour *et al.* [48] combining 3D x-ray tomography and numerical simulations. The force is not directly measured but inferred from the position of the particles and their neighbours. They reported changes in the force distribution as crystalline order grows. Despite this finding, the work shows that even a packing of lightly polydisperse particles has a random mechanical response. Finally, a study by Keim and coworkers [49] probed the rheological behavior of soft jammed solids. They compared the response to a known shear stress for monodisperse (model for crystal) and bidisperse aggregates (model for a glass). Once again, even though the model aggregates for a crystal and a glass are different in their structure, their response to shear is similar.

The real challenge when studying the transition from order to disordered structure experimentally is to generate “perfect crystals”. To differentiate the transition from glassy to crystalline, one has to first characterize both limiting cases behaviours. As discussed above, even weakly polydisperse packing leads to glass-like properties. Defining the crystalline behaviour requires the use of monodisperse particles. The direct mechanical characterization of the packing is also a difficult task as typical

forces for micron size particles are of the order of nN [24]. This explains why the forces are usually inferred from other information and not directly measured (see section 2.2)

In chapter 4, we take advantage of our ability to produce highly monodisperse droplets [5] using the snap-off instability to model perfectly ordered crystals. We study the crystal-to-glass transition by mixing two monodisperse populations of droplets in different proportions. We couple the mechanical characterization of the clusters under compression to the internal microscopic rearrangements of the droplets. The forces acting on the cluster of droplets are directly measured with a resolution of ~ 100 pN. The force measured during compression is used as a signature of crystalline or amorphous behavior.

Chapter 3

Experimental Details

The experimental details needed to understand the results presented in the manuscript are clearly outlined in Chapter 4. Here we give additional details that would be useful to someone attempting similar experiments. We particularly focus on what is not discussed in the paper.

In this experiment, quasi-2D emulsions of oil in water are compressed between two parallel boundaries. The sample cell is made of two glass slides separated by a gap of 3 mm. The chamber is filled with an aqueous solution with sodium dodecyl sulfate (SDS), a surfactant, and NaCl. Droplets of oil are produced *in situ* and gather at the top of the chamber because of buoyancy. The droplets are sticky and are assembled into 2D clusters that are compressed between two thin glass pipettes, of which one is a force sensor. The system is imaged, from below, using optical microscopy. From these images, we extracted two types of information: the internal rearrangement of the droplets under compression and the forces applied on the cluster as it rearranges. The following chapter details the chamber, the pipettes and their different roles, and the image analysis.

3.1 Sample cell

3.1.1 Solution

The aqueous solution is made of SDS at 3% and NaCl at 1.5% in mass. SDS is added to stabilize the emulsion. As discussed in 1.1.2, the oil droplets would coalesce and

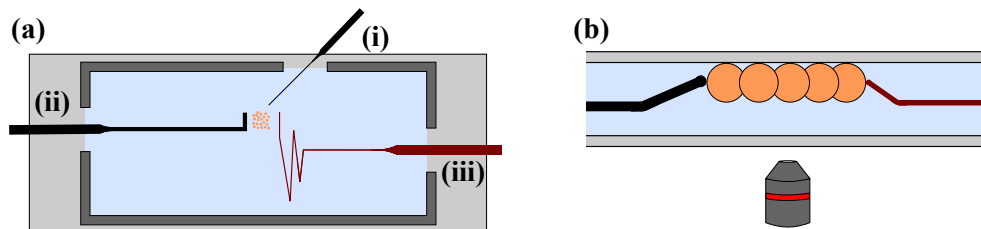


Figure 3.1: Schematics of the sample cell. (a) Top view - the area shaded in blue corresponds to the part that is filled with the aqueous solution. (i) “the droplet pipette”; (ii) “the pushing pipette”; and (iii) “the force sensing pipette”. The chamber is closed on the sides by 3D-printed walls to prevent evaporation. Small slits are designed for the pipettes to be inserted. (b) Side view - the droplets are buoyant and rise to the top of the chamber forming a 2D aggregate under the top coverslip. The chamber is imaged using an inverted optical microscope.

the solution would eventually phase separate without the addition of a surfactant. SDS is added in large quantity to ensure that there is enough to stabilize the droplets and generate micelles in the solution. The concentration in SDS corresponds to 0.1 mol/L which is two orders of magnitude higher than the critical micelle concentration (CMC) of SDS: 8 mmol/L [50]. As explained in 1.2.4, these micelles are responsible for depletion forces between the droplets. Because of these forces, we expected the droplets to stick to one another. With SDS only, the interaction turned out to be weak and the clusters were almost impossible to assemble. SDS is an anionic surfactant which means that its polar head is negatively charged. When it adsorbs onto the surface of the droplets, the tail goes into the oil phase and the charged head stays in the continuous phase (water). The droplets can be seen as a sphere covered in negative charges leading to electrostatic repulsion between them. It results in a competition between attractive depletion forces and repulsive electrostatic forces. We introduced NaCl in the solution to screen the repulsive interaction. Upon addition of 0.5% in mass of NaCl, the strength of the attractive interaction was significantly improved. The screening hypothesis is supported by the fact that the strength of the interaction is not increased by adding more NaCl (within the tested range: 0.5% to 2%). When enough salt is added then the repulsive forces are screened and adding more salt does not improve the interaction between the droplets. We chose to use 1.5% for the concentration of salt.

3.1.2 Addition of a surrounding wall

The chamber was originally designed without the surrounding wall. Two glass slides were separated by a small spacer made of rubber. This design was convenient for the introduction of the pipettes as well as filling the chamber. The main drawback was the evaporation of water from the sides. Because of evaporation, the concentrations of both SDS and NaCl were changing and the depletion forces were becoming larger. A typical experiment is conducted over 30 minutes and evaporation was not negligible over the course of a single experiment.

To reduce the impact of evaporation we first increased the total volume of the chamber. For the same evaporated volume, the change in concentration is smaller. We also added 3D-printed walls to minimize the surface between air and water and thus reduce the evaporation. As we still needed to introduce the pipettes in the chamber, small slits of ~ 1 cm were designed on three sides of the chamber. The wall was glued onto the bottom glass slide to prevent any leakage. Evaporation still occurred through the slits but is significantly reduced. The strength of the interaction was found to be constant within experimental error for at least 3 hours. A 3D render of the setup is shown in Fig. 3.2.

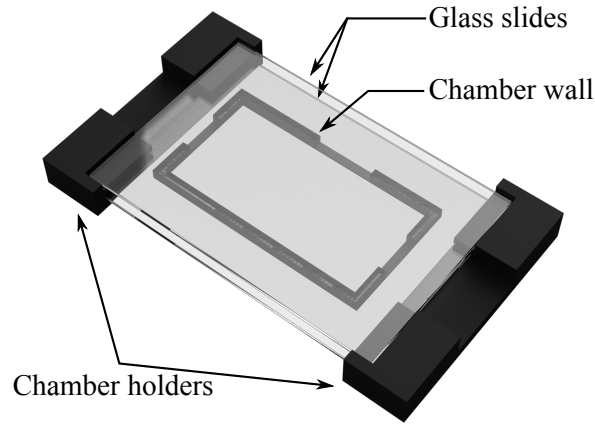


Figure 3.2: 3D render of the experimental setup. The chamber wall is glued onto the bottom glass slide. In order for the pipettes to be inserted, small slits are designed on three side of the chamber. The top glass slide is simply placed atop of the wall. The holders on the side prevent the top glass slide from moving with respect to the bottom one.

The standard process for preparing the chamber is the following: (i) the pipettes are inserted in the chamber when empty and not covered (Fig. 3.3(b)); (ii) the top glass slide is placed on top of the wall, making sure the pipette are not touching the top (Fig. 3.3(c)); (iii) the chamber is filled with the solution through one of the pipette slit using a 10 mL syringe; (iv) the droplets are produced and finally the droplet pipette is removed.

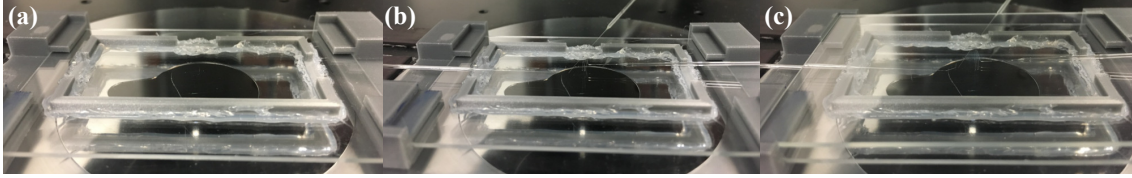


Figure 3.3: (a) The wall is glued onto the bottom glass slide and the bottom glass slide is inserted into holders (gray pieces). (b) Pipettes are inserted in the chamber (c) A glass slide is placed atop of the wall.

3.2 Micropipettes

As shown in Fig. 3.1, three micropipettes are used in this experiment. They were made by pulling glass capillary tubes (outer diameter: 1 mm; inner diameter: 0.58 mm - World Precision Instruments, USA) using a PN-31 pipette puller (Narishige, Japan). The pipette is passed through a thin platinum ribbon bent into an annulus shape and both ends of the pipette are attached to electromagnets. The filament is heated by passing current through it. Provided that the pipette and the annulus are well aligned, the pipette is homogeneously melted over a small region (~ 1 mm). Both ends are then pulled apart by a fixed amount using the electromagnets. The pipette is usually pulled over ~ 3 cm with a constant diameter of $\sim 10 \mu\text{m}$. The force applied on the magnets and the temperature of the filament can be tuned in order to change the characteristics of the pipette. For the purpose of this experiment, the settings were adjusted to give the thinnest diameter. These settings strongly depend on the platinum filament used and need to be adjusted every time the filament is changed or moved.

Once the pipettes are pulled, we shape them differently depending their application. To shape them, we use a 0.5 mm platinum-iridium filament (Alfa Aesar, USA). Current is passed through until it turns faint red. The wire must be hot enough to melt the glass locally, but if it is too hot the micropipette tends to stick to the filament and break. The micropipette is brought into contact with the wire and we apply a force to bend it. Any angle between 0° and 180° can be achieved. This procedure can be repeated several times to give the pipette a complex shape.

We used micropipettes for three purposes. One is to produce the oil droplets with the droplet pipette (described in 3.2.1). The other use for the pipette was to manipulate the droplet clusters and to compress them (see details in 3.2.2). Micropipettes are also used as cantilevers springs that deflect under an external force [51–54]. The deflection is proportional to the applied force: $F = k_p \Delta d$, where k_p is the spring constant of the pipette and Δd its deflection. The spring constant depends on two main parameters: 1) the length of the pipette perpendicular to the force; the longer this part is, the smaller the spring constant. 2) the diameter of the pipette; the smaller the diameter, the smaller the spring constant.

3.2.1 Droplet pipette

The droplet pipette is used to produce oil droplets in an aqueous solution using the snap-off instability [5, 55]. No bending is required to make this pipette. The pipette is pulled and the tip is broken off using tweezers. This makes the end of the pipette irregular which facilitates the production of the droplets. This irregularity allows the continuous phase to enter the pipette more easily and thus for the snap-off instability to occur. The tip of the pipette is pre-wetted with the continuous aqueous phase and then mineral oil is pushed through with a syringe. The pre-wetting step is critical as the continuous phase must enter the pipette in order for the instability to occur. This way of producing droplets leads to remarkably monodisperse droplets ($CV < 0.7\%$). As the radius of the droplets depend on the radius of the pipette, the droplet size can be changed by using a different droplet pipette. This is especially important for the experiments presented in chapter 4 where bidisperse clusters are studied. The droplets were produced with two different pipettes leading to two highly monodisperse populations with different sizes mixed together.

3.2.2 Pushing pipette

The pushing pipette is used to compress the cluster against the third pipette. It is important that the pushing pipette does not deflect doing so. If it did deflect, the two pipette would no longer be parallel and the different parts of the cluster would be compressed in different ways. The parallelism of the pipettes is already challenging as the force sensing pipettes must deflect in order to measure internal forces. Making the pushing pipette stiff in comparison to the force sensing pipette minimizes the angles between the two pipettes during compression.

The pushing pipette is made from two bends (see Fig. 3.4). First, a 90° in plane bend to form the part in contact with the cluster (where the force is applied). This part must be short to make the pipette stiffer. The typical length is ~ 3 mm. The second bend is $\sim 45^\circ$ out of plane so the pushing part is not in the same plane as most of the pipette. The end of the pipette must be in a different plane for practical reasons. The droplets gather at the top of the chamber under the top glass slide. The pushing pipette comes in contact with the droplets in their equatorial plane as shown in Fig. 3.1. The distance between the top glass slide and the pipette is a few tens of microns. For the experiment to be accurate, the glass pipette cannot touch the glass slide. If the out of plane bend was not there, it would mean perfectly aligning the whole pipette with the glass slide within $\sim 20 \mu\text{m}$ which is not realistic. Because of the 45° bend, the alignment only needs to be performed over three millimeters only.

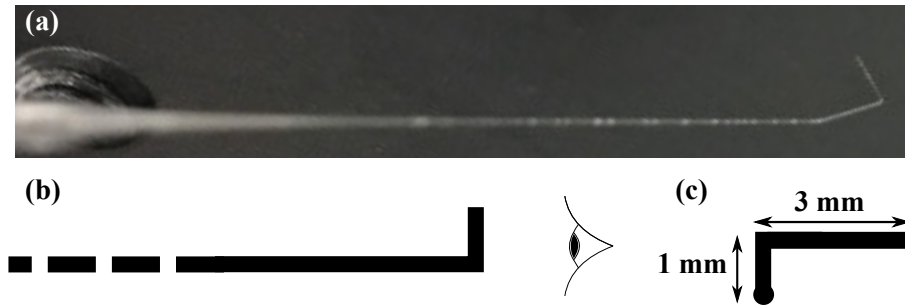


Figure 3.4: (a) Picture of the pushing pipette. The perpendicular short end is the part used to compress the cluster. (b) Schematics of top view of the pipette. (c) Schematics of the side view of the pipette. This view corresponds to the eye shown in frame (b)

3.2.3 Force sensing pipette

The force sensing pipette is used to simultaneously compress the clusters and act as a force sensor. The order of magnitude of the force measurements ranges from 1 to 15 nN. To measure such small forces, the spring constant must be of the order of 1 nN/ μm . To make compliant pipettes, the total length perpendicular to the force must be on the order of a few centimeters and the radius should be $\sim 10\ \mu\text{m}$. Pipettes that have this kind of spring constant have been previously used to study living-cells [53] or micro-swimmers [54]. This centimeter-long pipette cannot fit inside the chamber. It must be bent into a zig-zag shape so that the total length perpendicular to the force stays the same but the pipette is more compact. The bent force sensing pipette is equivalent to a straight pipette which has the same size in terms of force sensing.

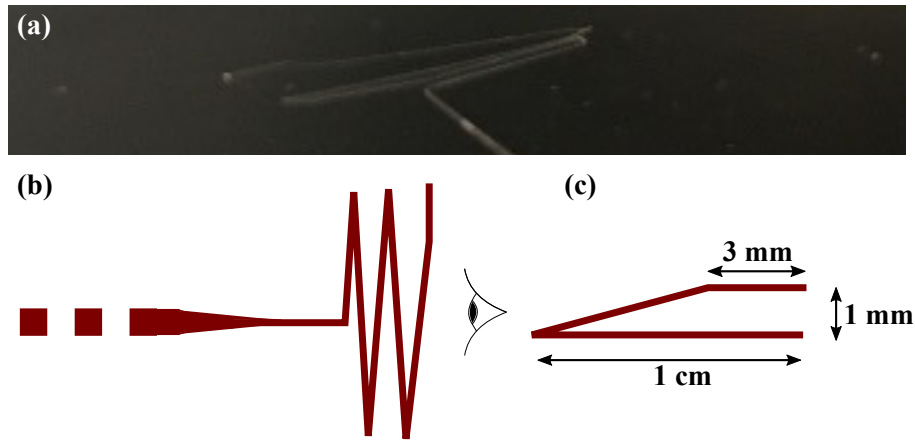


Figure 3.5: (a) Picture of the force sensing pipette. The part in contact with the droplets is the flat end of the pipette. (b) schematics of top view of the pipette. (c) schematics of the side view of the pipette. The view corresponds to the eye shown on (b)

The force sensing pipette is bent with the same technique as the pushing pipettes but is made of many bends. The first step is to make several in plane 180° bends of approximately one centimeter. The pipette is bent all the way to the conical part where the diameter increases, as shown on Fig. 3.5(b). This typically corresponds to four bends at 180° . The closest bend to the end of the pulled part of the pipette (furthest left on Fig. 3.5(b)) is only 90° , so that all of the bends previously made are now at 90° with respect to the main part of the pipette. Finally, the first bend

(furthest right on Fig. 3.5(b)) is bent out of plane at $\sim 45^\circ$ and the tip flattened out (see Fig. 3.5(c)). The out of plane bend is made for the same reason as for the pushing pipette. The total length is $\sim 3 - 4$ cm, and the diameter is constant over at least 3 cm. The pipette becomes thicker closer the conical part. With these pipettes, we can measure forces as small as hundreds of pico-Newton.

Calibration

The quantity measured is the deflection of the force sensing pipette during the compression of the cluster. The deflection can be linked to the force applied on the pipette via the spring constant of the pipette, k_p . The calibration of a pipette is usually done by measuring the deflection of the pipette resulting from the weight of a water droplet [54]. Water is injected in the pipette until a droplet forms at the end. As more water is injected the droplets grows, and the deflection of the pipette due to gravity as a function of the volume of the droplet is measured. Because of the complex shape of the force sensing pipette, this method cannot directly be applied. We first calibrate an intermediate pipette, called reference pipette, using the droplet technique. An example of such a calibration is shown on Fig. 3.6. We calibrated three different reference pipettes.

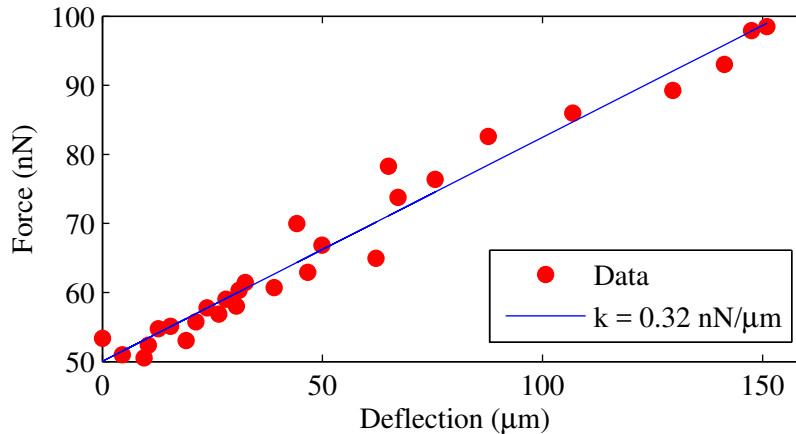


Figure 3.6: Calibration of the reference pipette with the droplet of water. The applied force corresponds to the weight of the droplet. The deflection is measured using cross correlation (see 3.3.1). The spring constant of the pipette is obtained by fitting a straight line to the experimental data.

We then push the reference pipette of known spring constant, k_{ref} , against the force sensing pipette. This experiment is equivalent to pushing two springs against each other in series. In section 1.3.1, we have shown that the force in both springs has to be the same, leading to:

$$k_{\text{ref}}\Delta x_1 = k_p\Delta x_2, \quad (3.1)$$

with Δx_1 and Δx_2 the deflection of the reference pipette and the force sensing pipette respectively. The spring constant k_p is obtained by measuring the deflection of both pipettes when pushed against each other.

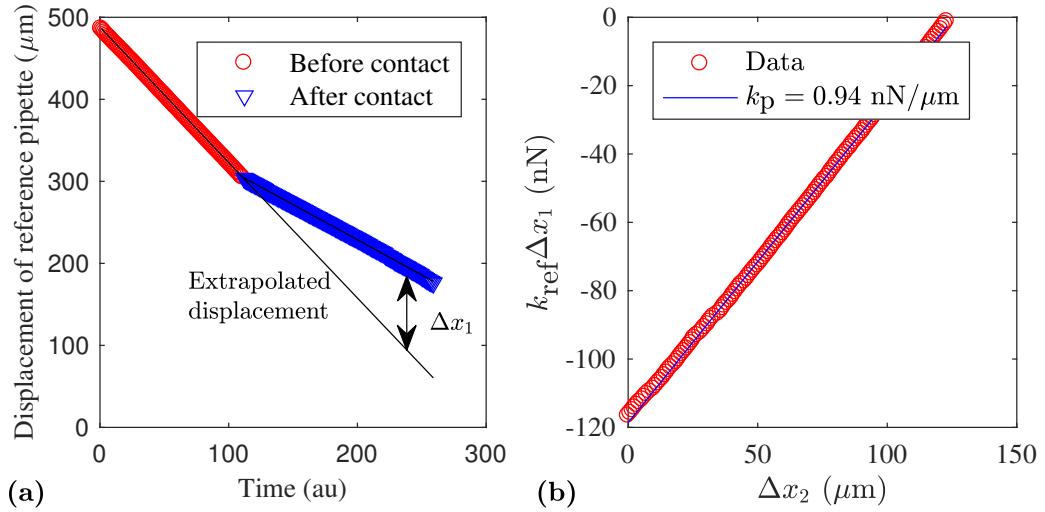


Figure 3.7: (a) displacement of the reference pipette as a function of time. When contact is made, the reference pipette deflects and the slope decreases. The deflection corresponds to the difference between the actual (in blue) and the extrapolated (in black) displacement. (b) Force calculated from Δx_1 as a function of the deflection of the accordion pipette. Δx_1 and Δx_2 are in opposite direction. Δx_2 is counted as positive which leads to a negative force.

Experimentally, both pipettes start away from each other so they are not in contact. The reference pipette is affixed to a translation stage moving at a constant speed. We record microscopy pictures of the pipette moving toward the force sensing pipette. When contact happens, both pipettes start deflecting. The deflection of the force sensing pipette Δx_2 can be directly measured with cross correlation between the current picture and the reference (initial position). For the reference pipette,

we see a change in the speed of the pipette (slope on Fig. 3.7(a)) when contact happens. Taking the difference between the extrapolated and the measured displacement, we calculate the deflection of the reference pipette Δx_1 . Finally, we plot the force $F = k_{\text{ref}}\Delta x_1$ versus the deflection of the force sensing pipette (Fig. 3.7(b)). The slope corresponds to the spring constant of the force sensing pipette according to Eq. 3.1. We repeated that measurement several times for each of the three reference pipettes. All the data presented in Chapter 4 have been obtained using the same force sensing pipette with spring constant equal to $k_p = 1.3 \pm 0.1 \text{ nN}/\mu\text{m}$.

3.3 Image Analysis

The droplet cluster is imaged using optical microscopy as it is compressed. We use the images of the cluster to study both the rearrangement of the individual droplets in the cluster and measure the forces applied on the cluster. In this section, we discuss how the images are analyzed to access this information.

3.3.1 Force measurement and cross correlation

Cross correlation is used to measure both the pushing and the force sensing pipette displacements during compression. The difference in their position is the spacing between the pipette, δ . The displacement of the force sensing pipette is also converted into a force. The deflections observed during our experiments range from less than 1 to ~ 10 pixels. The measurement of such a small displacement requires a high-resolution technique. Cross-correlation is used here as it offers sub-pixel resolution [56].

The cross-correlation measures how similar a vector, its lagged copies, and a reference vector are. Let us consider a simple example with a vector $X = [1 \ 2 \ 3]$ and we want to measure how similar it is to itself. The lagged copies are $X_i \{[3 \ 2 \ 1]; [2 \ 3 \ 1]; [1 \ 2 \ 3]; [3 \ 1 \ 2]; [2 \ 3 \ 1]\}$. For each of these vectors we calculate $C(i)$ the elements of the correlation vector:

$$C(i) = \sum_{j=1}^3 X(j) * X_i(j). \quad (3.2)$$

For the analysis of the experimental data, we use the MATLAB function `xcov` which calculate the cross-covariance. Using the previous example, the covariance vector is

given by:

$$C'(i) = \sum_{j=1}^3 (X(j) - \bar{X}) * (X_i(j) - \bar{X}). \quad (3.3)$$

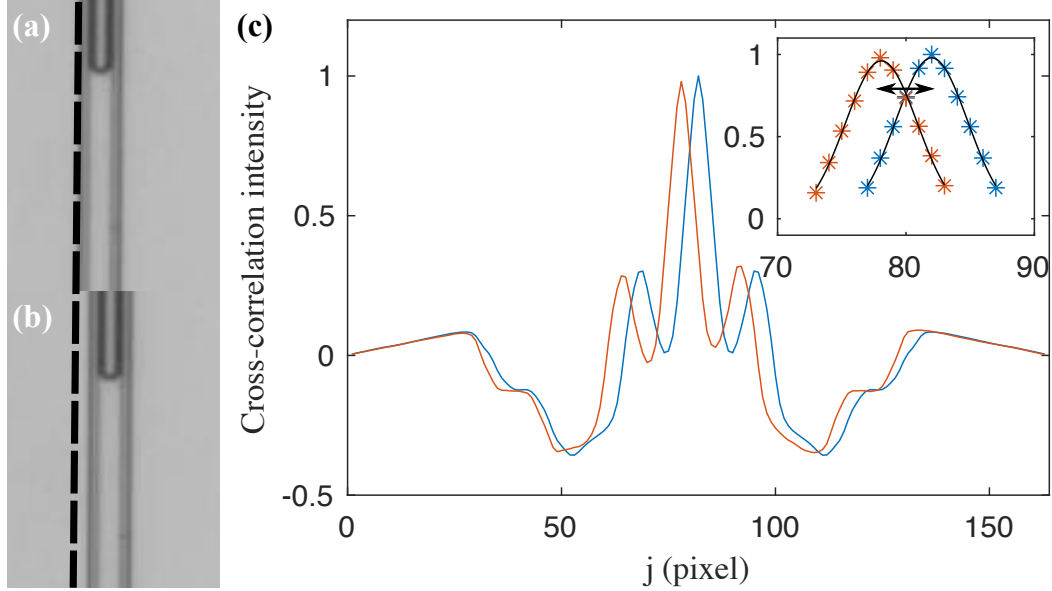


Figure 3.8: (a) Microscopy picture of the force sensing pipette in its original position when no force is applied. (b) The force sensing pipette deflects under the force applied by the cluster. (c) The blue line corresponds to the auto-covariance performed on (a). The position of the maximum gives the initial position of the pipette. The red line corresponds to the cross-covariance between images (a) and (b). Measuring the distance between the maxima of the blue and the red line gives the deflection of the pipette. Inset - Zoom on the peaks. A Gaussian profile is fitted to the data points to measure the position of the maximum with sub-pixel resolution.

The same idea is used to measure the pipette deflection. We measure the intensity profile along the same line throughout the compression. The line must be perpendicular to the pipette of which we study the displacement. It is important that the line never crosses another pipette or a droplet on any images. We first measure the auto-correlation of the first image (red curve in Fig. 3.8(c)) to find the initial position of the pipette (when no force is applied). The vectors from the other images are then tested against the intensity profile from the first image (blue curve in Fig. 3.8(c), for example). We measure the lag required so the profiles match (maximum in the cross-correlation function). The position of the peak is measured by fitting a Gaus-

sian curve to the data points (black curve in the inset Fig. 3.8(c)), which enables a resolution of ~ 0.2 pixel. The difference in the position of the peaks corresponds to the displacement of the pipette.

3.3.2 Droplet and bond detection

The images analyzed for the force measurement also contain information about the rearrangement of the cluster. We use the built-in Matlab function `imfindcircles` to detect the droplets and track their positions during the experiment. To reorganize the bond must break and form bonds. As will be described in chapter 4, the fracture events in the cluster are correlated to peaks in the force measurement. Therefore it is important to know if two droplets are linked by a bond or not to detect fracture events. The first idea is to measure the distance between the centers of the droplets and compare it to the sum of the two droplet radii. This method is sensitive to the detection of the droplets, however it is not accurate enough in many cases. We simply use it as a prerequisite for the next step of the detection described below. If the distance between two droplets is larger than twice the sum of their radii, we do not proceed to step two.

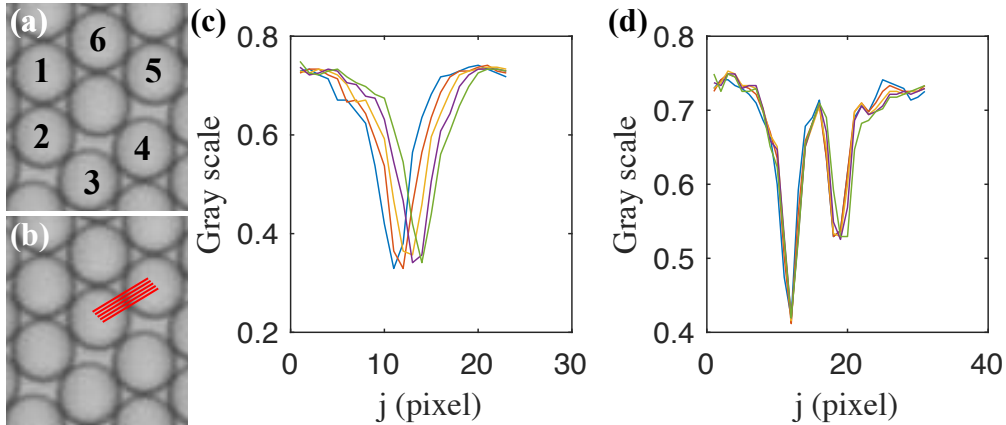


Figure 3.9: (a) Microscopy picture of a droplet surrounded by its 6 neighbours. (b) Example of the lines along which the profiles are studied for the bond detection. (c) Five different profiles drawn for the bond with droplet 2. We see only one extremum: there is a bond with droplet 2. (d) Five different profiles drawn for the bond with droplet 3. The profiles show three extrema so there is no bond with droplet 3

The second step of the bond detection is closer to the way our eyes tell if there is a bond or not (see Fig. 3.9(a)). If the droplets are not touching then we can see a lighter patch between the black edges of the droplets. We study the intensity profile along the center-to-center line (Fig. 3.9(b)) and count the number of extrema. Such profiles are shown on Fig. 3.9(c) for two droplets touching and (d) for two droplets not touching. We study the profile along five lines and if any of them only shows one extremum then there is a bond. This has been implemented after seeing disagreements between what we could say by eye and what the software decided when only one line was studied. We found a better agreement by scanning the profile along several lines.

Chapter 4

Crystal-to-glass transition

Jean-Christophe Ono-dit-Biot, Pierre Soulard, Solomon Barkley, Eric R. Weeks, Thomas Salez, Elie Raphaël, Kari Dalnoki-Veress.

This chapter presents a manuscript, along with its supplemental material, intended for a peer-reviewed publication. In this work, we study the mechanical response of 2D clusters of droplets under compression as a function of its composition. The force required to break the clusters is directly measured using a micropipette. The force curves are a signature of the composition of the cluster. By gradually introducing disorder, we study the transition from a perfectly ordered crystal to a disordered glass. A model which fully support experimental results has also been developed.

Initial versions of this experiment were designed by Solomon Barkley and Kari Dalnoki-Veress. Solomon wrote the first Matlab analysis scripts as well as performed preliminary experiments. My contribution was to improve the experimental set-up and write additional scripts for data analysis. I conducted all experiments presented in this manuscript in consultation with Kari Dalnoki-Veress. The theoretical model was developed by Pierre Soulard, Thomas Salez and Elie Raphaël in collaboration with Kari Dalnoki-Veress and myself. I prepared the figures and wrote the first draft of the manuscript. This first draft of the manuscript has benefitted tremendously from discussions with Eric R. Weeks and all authors.

Rearrangement of 2D clusters of droplets under compression: from crystal to glass

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Oil droplets of two distinct sizes are used to prepare model 2D aggregates in an aqueous environment. We investigate the transition from perfectly ordered monodisperse crystals to disordered bidisperse glasses. These aggregates rearrange under compression between two parallel boundaries, one of which acts as a force sensor. The internal forces measured during the compression are a signature of the composition of the cluster and provide insight into the crystal-to-glass transition. We find that the mechanical properties of the 2D aggregates are strongly impacted by even a small amount of disorder: crystals dissipate all the energy into a single fracture event whereas the glassy aggregates break step-by-step.

Glassy materials are amorphous solids and cannot simply be described as crystals with defects [1]. The intrinsic disorder – for example resulting from molecules that do not neatly pack, or polydisperse colloidal spheres – prevents glassy systems from crystallizing [2, 3]. An interesting question arises: how much disorder is needed before a crystal transitions to a glass? Numerical studies [4–7] have shown that adding a small amount of disorder to crystalline packing results in microscopic and macroscopic properties that are much closer to amorphous structures. Experimental evidence of such a rapid transition has also been demonstrated [8, 9] for systems of thousands of particles.

Several strategies can be used to study the differences between crystals and glasses. The long ranged order of a crystal is distinct from the disorder of a glass. Thus, microscopic properties can provide information about the packing configurations [10–12]. Alternatively, bulk properties also differentiate between glassy and crystalline solids, for example, the bulk and shear modulus [4, 13].

Colloids and emulsions have proven to be model systems for the study of glassy systems and jamming [14–18], force chains [19, 20], and phase transition in crystals [21]. The advantage of these systems is that individual particles can be imaged thus obtaining both structural and dynamical information [14, 22, 23]. Here we use an emulsion of oil in water (soft spheres, no friction, with an attractive potential) confined to form a 2D aggregate. This system is used to model the transition from perfectly ordered monodisperse crystals [24] to disordered bidisperse glasses [25–27]. The amount of disorder is tuned by changing the ratio between large and small droplets in small clusters, which consist of tens of droplets ($N_{\text{tot}} = 3$ to 50 droplets). We investigate the transition from a monodisperse crystal to a bidisperse

glass by measuring the force required to deform and fracture the 2D aggregates. By systematically adding defects in the crystalline structure, we see a rapid increase in the number of fracture events in the cluster. Surprisingly, the total work required to break a cluster is approximately the same for a crystal and a glass, however, the main difference lies in the way the total work is dissipated. An analytical model has been developed which fully supports the experimental observations.

The experimental setup, shown in Fig.1(a), is a chamber (55 x 30 mm) made of two glass slides separated by a gap of 2.5 mm. The chamber is filled with an aqueous solution of sodium dodecyl sulfate (SDS) at 3% and NaCl at 1.5%. This concentration in SDS leads to the formation of micelles acting as a depletant and results in weak adhesion between the droplets [28]. The concentration of SDS and salt is kept constant by adding walls around the chamber to prevent evaporation. Small slits in the walls enable the insertion of three micro-pipettes. The pipettes were made by pulling glass capillaries (World Precision Instruments, USA) with a pipette puller (Narishige, Japan). The micro-pipettes have a diameter of $\approx 10 \mu\text{m}$ over several centimeters. The “droplet pipette” produces nearly monodisperse droplets using the snap-off instability [29]. The droplets are buoyant and form a quasi-2D aggregate under the top glass slide (Fig. 1(b)). Clusters are assembled droplet-by-droplet and thus can be prepared into any arbitrary shape (see movie M1 in SI). We use p to refer to the number of rows of droplets in the cluster and q to the number of droplets per row. Changing the tip radius of the droplet pipette changes the size of the droplets to prepare bi-disperse aggregates [29]. To increase the disorder in a cluster the large droplets were substituted by small droplets. As each droplet is placed individually, the position of the

defects is also controlled. The “pushing pipette” is short and stiff and is used to compress the cluster. The pushing pipette was affixed to a translational stage and its speed set to $0.3 \mu\text{m/s}$ for all experiments. The “force sensing pipette” is a long compliant pipette and the deflection of the pipette is used to measure forces applied to the cluster [30]. To be sensitive to forces as small as $\approx 100 \text{ pN}$, the pipette needs to be long ($\approx 3 \text{ cm}$) and thin ($\approx 10 \mu\text{m}$). The straight pipette is locally heated to soften the glass such that it can be shaped to fit within the chamber. The chamber is placed atop an inverted optical microscope for imaging while the clusters are compressed.

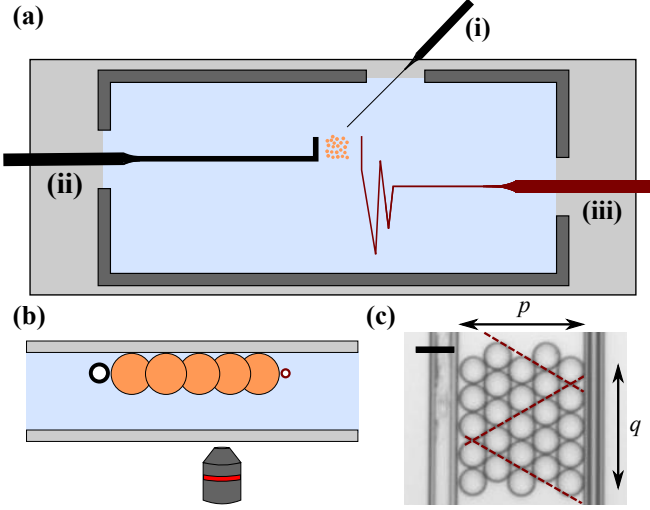


FIG. 1. (a) Schematics of the top view of the experimental chamber. The typical dimensions of the wall are $55 \times 30 \times 2.5 \text{ mm}$. (i) the “droplet pipette”; (ii) the “pushing pipette”; and (iii) “force sensing pipette” (b) Schematics of the side view. The droplets form a quasi 2D aggregate. The pushing pipette and the force sensing pipette must be in the equatorial plane of the droplets so forces are only applied horizontally. (c) - Optical microscopy picture of a typical crystal - scale bar = $50 \mu\text{m}$. Red dashed lines show how a crystal breaks when compressed.

The clusters are compressed between the pushing pipette and the force sensing pipette. The distance between both pipettes, δ , is measured using cross-correlation analysis between consecutive images. Additionally, correlation analysis provides the deflection of the force sensing pipette which is converted to a force using the spring constant of the pipette ($k_p = 1.3 \pm 0.1 \text{ nN}/\mu\text{m}$) obtained by calibration [30]. The cluster rearranges under compression by breaking bonds between the droplets. These events can be directly observed on the optical microscopy images and coupled to the force measurement. Each fracture event corresponds to a local maximum in the force curve.

In Fig. 2(a) is shown the force measurements as a function of the compression for seven different clusters. The

geometry of the cluster is fixed and defined by the number of rows $p = 4$ and the number of droplets per row $q = 5$. Each site can be occupied by either a large or a small droplet, the ratio between the number of large and small droplets is varied from cluster to cluster. The top trace corresponds to a crystal (monodisperse cluster) made of large droplets with radius $R = 25.1 \mu\text{m}$ and the bottom curve to a crystal of small droplets with radius $r = 20.3 \mu\text{m}$ (see Fig. 2(b)). These two force measurements show three peaks corresponding to three fracture events: the transition from $p = 4$ to $p = 3$, which we designate as $4 \rightarrow 3$, $3 \rightarrow 2$, and finally $2 \rightarrow 1$ (see movie M2 in SI). For a crystal, all the bonds are broken in a coordinated manner, consistent with other studies of crystals under compression [31, 32]. We find that the fracture forms equilateral triangles with $(p-1)$ droplets on the triangle’s side, which corresponds to the geometry requiring the smallest number of broken bonds between droplets. After fracture, the triangles slide past each other and re-assemble into a new crystal with $(p-1)$ rows of droplets. By design, the force sensor does not register a friction force during sliding, nor are we sensitive to viscous drag during compression, because slow compression ensures that dissipative forces are negligible.

The position of the peaks in Fig. 2(a) correspond to fracture transitions. Indeed, for a transition $p \rightarrow (p-1)$, a crystal made of large droplets will fracture at a larger spacing between the pipettes $\delta = \delta_{max}^p$, compared to a crystal of smaller droplets $\delta = \delta_{min}^p$. Introducing defects in the structure prevents coordinated fracture from occurring as the cluster is not compressed homogeneously. Thus, additional fracture events occur and extra peaks appear in the force data [see force traces intermediate to the two crystal examples in Fig. 2(a), and typical images Fig. 2(c)-(d)]. When a single defect is introduced (second and sixth traces), extra peaks are observed but peaks corresponding to the fracture of the crystalline portion of the cluster can still be identified (large peaks at the same values of δ). Defects are systematically introduced up to the fourth curve, which corresponds to the most disordered system that we use to model a glass (equal fraction of large and small droplets). The force curves are strongly impacted by increasing disorder: 1) the number of fracture peaks increases; 2) the peaks corresponding to the crystalline structure diminish; and 3) the magnitude of the force peaks decreases with increasing defects. A consequence of having several peaks instead of one is that the transition p to $(p-1)$ can no longer be easily defined. To know which transition a peak belongs to we use the boundaries defined previously: δ_{min}^p and δ_{max}^p . If a peak is found for $\delta \in [\delta_{min}^p : \delta_{max}^p]$ then it is part of the transition p to $(p-1)$.

Fig. 2 shows that the fracture properties are strongly dependent on the cluster composition. In order to investigate this dependence we first turn to understanding the compression of monodisperse clusters prior to fracture.

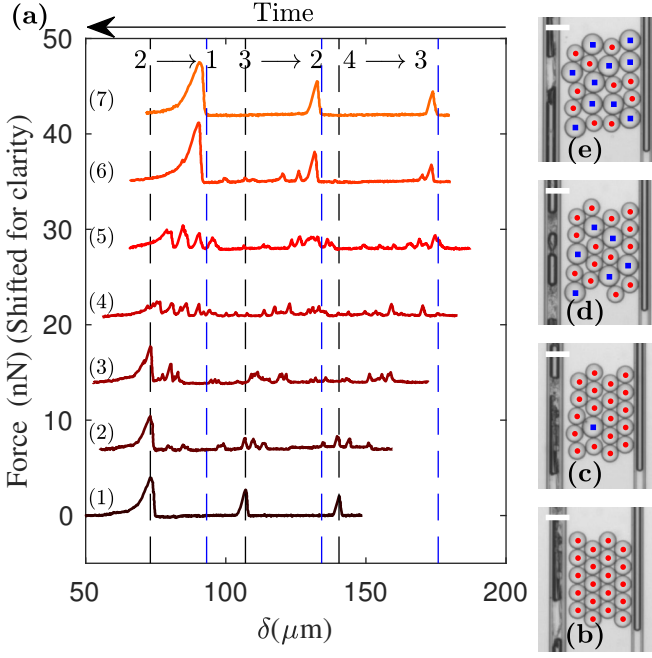


FIG. 2. (a) Force measurements for seven clusters sharing the same lattice but with different compositions. Curves (1) to (7) corresponds respectively to $\{0; 1; 6; 10; 14; 19; 20\}$ large droplets in 20 droplets. The blue dashed lines correspond to the position of the peaks for the crystal made of large droplets δ_{max}^p and the black dashed line to the peaks for the crystal made of small droplets δ_{min}^p . (b) - (e) Microscopy pictures of the clusters, before compression, corresponding to traces (1) to (4). Blue squares correspond to large droplets and red circles to small ones - scale bar = 50 μm

Previous studies have investigated the deformation of a droplet under external forces [19, 33]. A single oil droplet can be modelled as a spring [34] with a spring constant, k_1 , which is directly proportional to the interfacial tension between the liquids (see derivation in SI). Along a row of droplets, q springs are assembled in parallel, while the p rows can be modelled as equivalent springs in series. A cluster can then be represented by an equivalent spring with an effective spring constant $k_{eq}(p) = k_1 q/p$.

To test the equivalent spring model, we compressed an initial crystal with $p = q = 7$. Upon compression, there are six $p \rightarrow (p - 1)$ transition peaks in the force curve. We define the compression as $\Delta x = \delta - \delta_{ini}^p$ with δ_{ini}^p the spacing between the pipettes when the cluster is first compressed. Fig. 3(a) shows the force as a function of the compression for the six peaks. The force is linear with the compression and the slope $k_{eq}(p)$ can be extracted for each curve and plotted as a function of the ratio q/p as shown on Fig. 3(b). The equivalent spring constant k_{eq} scales linearly with q/p as predicted by the equivalent spring model for the monodisperse crystals.

Having validated the equivalent spring model, the elastic energy stored in the cluster during the compression is given by $E_s = 1/2 F \Delta x$. The stored elastic energy builds

during compression and the cluster fractures when this stored energy overcomes the adhesion energy. The total adhesion energy can be expressed as $E_1 b$, where E_1 is the energy per bond and b is the number of broken bonds. Using simple geometrical arguments, the number of bond to break for a crystal to rearrange is found to be $b = 2q$. When the cluster breaks, the adhesion energy and the stored energy are equal and $F_c \Delta x_c / 2 = 2q E_1$, where F_c and Δx_c correspond to the critical force and compression at failure. This expression can be rewritten as $\sigma_c = F_c / q = \sqrt{4k_1 E_1 / p}$ (see SI), and represents the 2D equivalent of a yield stress for a crystal. The yield stress can be accessed experimentally by recording F_c for different values of p . This experiment has been performed with clusters of different geometries and different sizes of droplets. For each size, at least five different clusters were studied to obtain an average value of the critical force for the same p . In Fig. 3(c) we plot a normalized yield stress $\sigma_c / (4k_1 E_1)$ as a function of p . The data points fall on the master curve $\sigma_c = p^{-1/2}$ validating the fracture model for crystals.

Having established a simple model which captures the fracture of monodisperse systems we turn to the bidis-

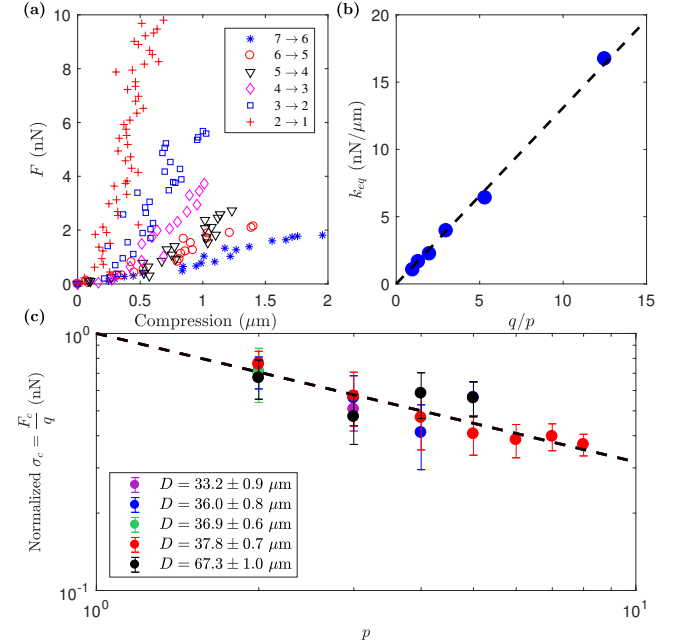


FIG. 3. (a) Increasing portion of the six force peaks measured during the compression of a 7×7 crystal. Compression is defined as the distance between the pipettes relative to the distance at the beginning of the peak. The slope of these straight lines corresponds to k_{eq} . (b) Evolution of k_{eq} as a function of the transitions. The linear relationship between k_{eq} and the ratio q/p validates the spring model. (c) Normalized yield stress as a function of p for five different droplet sizes. Several experiments are performed for each size. Data points are the average for a given size and cluster geometry, error bars correspond to the standard deviation

perse case. The most striking feature when defects are introduced is the rapid increase in the number of peaks in the force measurement as shown in Fig. 2. The number of fracture events can be studied systematically by adding defects in a cluster with a well defined geometry. We have performed such an experiment for two different cluster geometries with $p_{\text{ini}} = 4$, and $q_{\text{ini}} = 5$ as well as $p_{\text{ini}} = 3$, with rows made of 8 - 7 - 8 droplets respectively. The number of defects, N_{defect} , in the system is defined as the number of droplets in the minority phase of the bidisperse droplet system. Thus, the defects can be large or small droplets and the number fraction of defects is given by $\phi = N_{\text{defect}}/N_{\text{tot}}$, where N_{tot} is the total number of droplets. The impact of the position of the defects was not investigated in this study. The defects are distributed throughout the structure to avoid clumps of defects. In Fig. 4(a) we plot the number of peaks, which corresponds to the number of fractures in the system, as a function of the defect fraction.

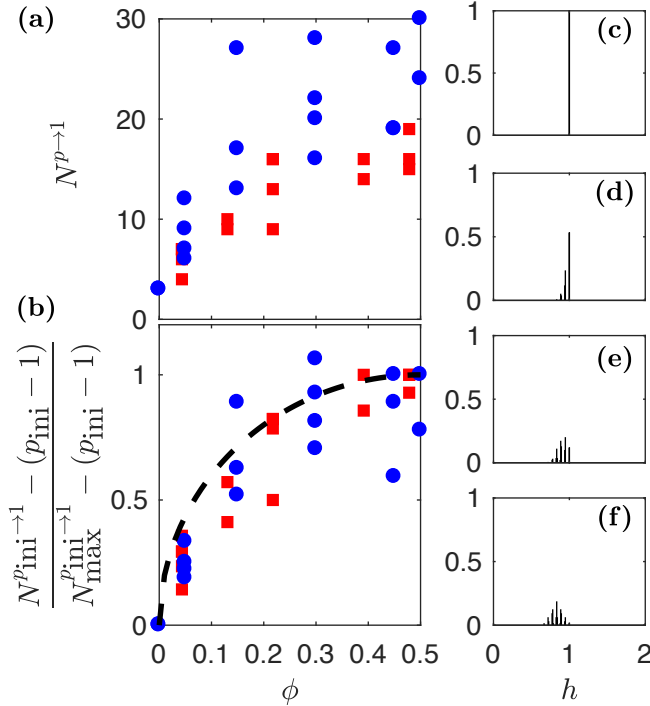


FIG. 4. (a) Total number of peaks for a compression from p to a single row of droplets. (●) initial number of rows $p_{\text{ini}} = 4$; (■) initial number of rows $p_{\text{ini}} = 3$. (b) Normalized total number of peaks for a compression from p_{ini} to a single row of droplets. The black dashed line corresponds to Eq. 4. (c) - (f) Probability of finding a column of reduced height, h , in an infinitely large cluster with $p = 4$ for the numbers fractions of defect $\phi = \{0; 0.1; 0.3; 0.5\}$ respectively. $h = 1$ correspond to a crystal made of large droplets. The smallest value of h correspond to a crystal made of small droplets.

We now turn to a model which captures the number of fracture events as a function of the defect concentra-

tion. One can think of the cluster as being q columns of droplets stacked next to each other (where the number of columns q is the same as the number of droplets per row). The cluster is assembled from these building blocks and each column needs to be the smallest unit that can be compressed. A minimal unit representing a compressible column is that of alternating triads of droplets. This can be modeled by stacking alternating rectangles (made of two droplets side by side) and circles (single droplet). The circles can have two different heights $\{2R, 2r\}$ with probability $\{\phi, (1 - \phi)\}$. The rectangles can have three sizes $\{\tilde{R}, \tilde{r}, (\tilde{R} + \tilde{r})/2\}$ with probability $\{\phi^2, (1 - \phi)^2, 2\phi(1 - \phi)\}$. The heights $\tilde{r}$ and $\tilde{R}$ are linked to r and R via a geometrical factor α .

For a given number of rows p , the columns can be built as a random walk with $p/2$ circles and $p/2$ rectangles. Using the random walk statistics for a finite value of p , one can calculate the resulting heights of the column along with the probability, P_i . This is shown in Fig. 4 (c) - (f) for $\phi \in [0, 0.1, 0.3, 0.5]$, the black bars show the different reduced height h that can be found and their probability P_i . The height h is defined to be equal to one for a column made of large droplets. From these distributions, the number of peaks observed in the cluster can be predicted (see SI). As the number fraction of defects is increased, the number of different heights, and thus the number of peaks, is increased.

The shape of the distributions shown in Fig. 4 for large values of ϕ suggests a gaussian distribution. Indeed, in the limit of a large number of rows p , the probability distribution becomes gaussian for any $\phi \neq 0$. The average value of the height, μ , and the variance, σ , can be calculated analytically with this approach. For the continuous case, all the heights are possible but only the ones included in $[\mu - \sigma, \mu + \sigma]$ are likely. This approach, even for a number of steps as small as $p = 2$, leads to a prediction for the number of peaks as a function of ϕ close to the discrete calculation (see SI). Thus, the number of peaks is proportional to the width of the gaussian distribution. To first order, the theoretical average number of peaks $\langle N^p(\phi) \rangle$ for the transition from p to $(p - 1)$ rows of droplets is

$$\langle N^p(\phi) \rangle = [\langle N^p(\phi = 0.5) \rangle - 1] \frac{\sigma(\phi)}{\sigma(\phi = 0.5)} + 1. \quad (1)$$

The standard deviation σ is linked to the number fraction of defects ϕ by

$$\sigma(\phi) \propto \sqrt{\phi(1 - \phi)}(R - r)^2, \quad (2)$$

which leads to

$$\langle N^p(\phi) \rangle = [\langle N^p(\phi = 0.5) \rangle - 1] 2\sqrt{\phi(1 - \phi)} + 1. \quad (3)$$

In order to compare the experimental data, Eq 3 must be summed over all the transitions because the measured

quantity is the total number of peaks from p_{ini} to $p = 1$:

$$\frac{N^{p_{\text{ini}} \rightarrow 1}_{\text{max}} - (p_{\text{ini}} - 1)}{N^{p_{\text{ini}} \rightarrow 1}_{\text{max}} - (p_{\text{ini}} - 1)} = 2\sqrt{(1 - \phi)\phi}. \quad (4)$$

$N^{p_{\text{ini}} \rightarrow 1}_{\text{max}}$ corresponds to the maximum number of peaks observed at $\phi = 0.5$. All the statistics above are done for an infinite number of columns q which is not realistic experimentally. For example, the number of peaks for a given transition cannot be greater than the number of column q in the cluster. The other assumption is that the columns are independent. To compare experimental and theoretical results, we use the maximum number of peaks observed for the largest ϕ studied experimentally as $N^{p_{\text{ini}} \rightarrow 1}_{\text{max}}$. Fig. 4(b) shows that the model captures the rapid increase of the number of peaks when defects are added.

The compression experiments can also be used to characterize the yield behavior of the material as a function of fraction of defects. The work done on the cluster in order to break bonds between the droplets can be obtained by integrating the force curve, such as the one shown in Fig. 2, for a given transition from p to $(p-1)$. The result of the integration is shown in Fig. 5. As explained previously, a transition is defined by δ_{min}^p and δ_{max}^p , so the integration is performed over this interval. We only consider the increasing part of the peak (elastic deformation of the cluster) as the decay of the force corresponds to the relaxation of the pipette and drag forces. Within resolution of the experiment, the total work is constant for the different experiments $W_{\text{tot}}^{\text{exp}} = 2.2 \pm 0.7 \text{ nN}\cdot\mu\text{m}$ and is not correlated to the composition of the cluster (See SI)

An important distinction between the glass-like and crystal systems is how the work is dissipated during failure of the cluster and how this depends on ϕ . With this analysis, we characterize the energy landscape for the failure of the structure. We directly measure the energy barrier to overcome in order to have the material flowing. For the crystals, all the bonds are broken at the same time which is equivalent to all the energy dissipated at once. The crystal made of large droplets breaks at $\delta = \delta_{\text{max}}^{p=4}$ as shown in Fig. 5 with the normalized work going from zero to one in a single step. The crystal made of small droplets behaves the same way except that the fracture event happens at $\delta = \delta_{\text{min}}^{p=4}$. As soon as defects are introduced, several steps are observed and the average height of the steps decreases. For a single defect, a major step (corresponding to the crystalline structure) is still observed but rapidly fades away as more defects are added. The curves with six defects and the glass both show many small energy barriers making the disordered systems easier to break. The compression experiment elucidates the difference between glasses and crystals. The transition from order to disordered impacts the

way that energy is dissipated as a function of the amount of disorder.

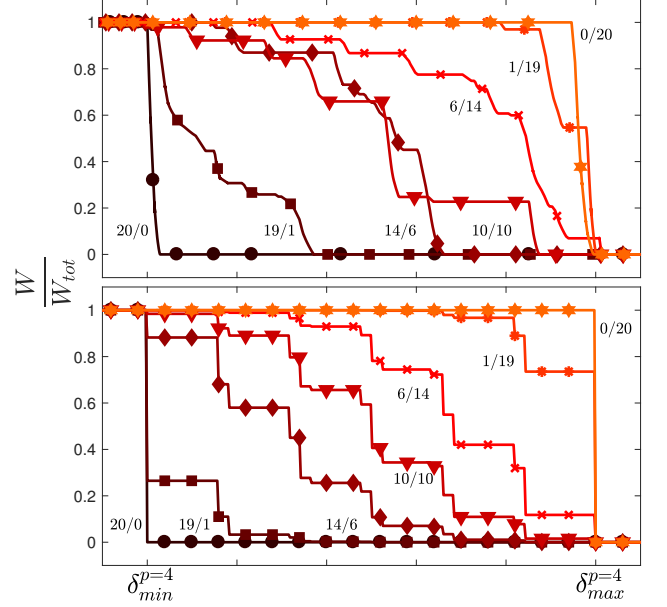


FIG. 5. Breakdown of the total work performed on clusters of different compositions for the transition $p = 4$ to $p = 3$. Top - Experimental results corresponding to the force curves shown in Fig. 2(a). The integral runs from the blue dashed line ($\delta_{\text{max}}^{p=4}$) to the black dashed line ($\delta_{\text{min}}^{p=4}$). Bottom - Corresponding breakdown of the energy according to the theoretical model. The peaks are modeled by Dirac functions which leads to Heaviside steps for the work.

The same work analysis can be performed using the theoretical model developed to predict the number of peaks. Assuming the peaks to be Dirac functions, the work is an Heaviside step of height E_i , the energy required to break the column. We make the assumption that the energy E_i does not depend on the composition of the column as $W_{\text{tot}}^{\text{exp}}$ is approximately constant. The work required at a given δ can be expressed as $W(\delta) = \sum_i E_i \theta[\delta - (1 - h_i)]$. We can finally express the average value of the ratio between the work done at δ and the total work:

$$\left\langle \frac{W(\delta)}{W_{\text{tot}}} \right\rangle = \sum_i P_i \theta[\delta - (1 - h_i)]. \quad (5)$$

The breakdown of the work calculated according to this model is shown in the bottom panel of Fig. 5. It shows a behavior very consistent with the experimental data. Once again, the theoretical framework that has been developed fully supports the experimental data.

In this study we have shown that the model 2D crystals and glasses are markedly different under compression. Crystals deform elastically until a catastrophic fracture event occurs, whereas glasses rearrange locally with many

small fracture events. The deviation from the well established elasticity of a crystal has also been observed in a recent analytical study [35]. Another recent numerical study has shown that materials go from brittle to ductile when transitioning from crystal to glass [7]. These theoretical results are consistent with what has been seen in the model 2D system explored here.

In summary, by systematically adding disorder in crystals we have studied the crystal-to-glass transition. The mechanical properties of the aggregates rapidly transition from crystalline to glassy in both a qualitative and a quantitative way. The number of peaks, corresponding to fracture events, increases rapidly even for small fraction of defects. The energy required to break the system as a function of the disorder has been mapped out. For the 2D crystal, a high energy barrier must be overcome while glasses fracture through failure in many small steps. Lastly, an analytical model has been developed which predicts the number of peaks in the force-compression curve, or the energy landscape, which is consistent with the experimental observations.

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Supplemental Information for: “Rearrangement of 2D clusters of droplets under compression: from crystal to glass”

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LARGE CRYSTAL COMPRESSION

Geometry

In the main text, we describe the compression of a large crystal made of $p = 7$ rows of droplets and $q = 7$ droplets per row. The total number of droplets is $N_{tot} = pq$. Upon compression, the crystal will rearrange in order to accommodate the available space between the pipettes. When the crystal fractures, equilateral triangles with $(p - 1)$ droplets on their side are formed. This is shown in the sequence of images in Fig. S1 for the transitions $p = 7$ to 6 and $p = 6$ to 5.

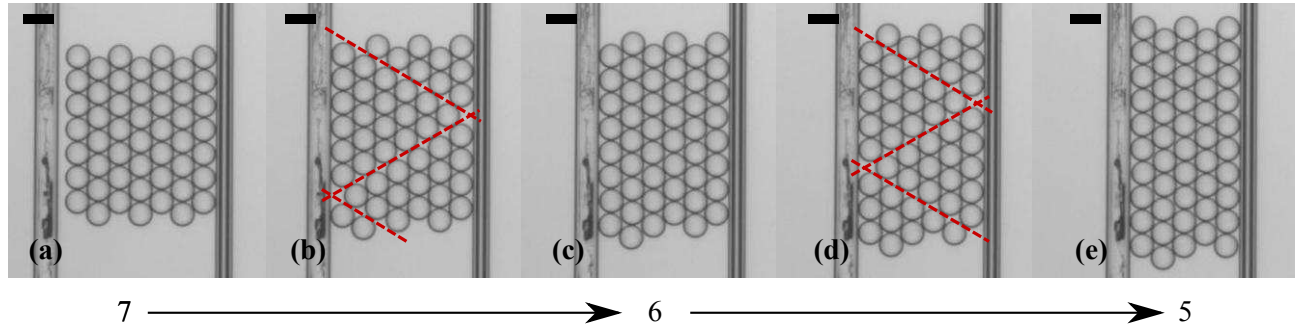


FIG. S1. Microscopy pictures of a crystal as it is being compressed from $p = 7$ rows to $p = 6$ [(a)-(c)] and from $p = 6$ to $p = 5$ [(c)-(e)]. The bonds break simultaneously forming equilateral triangles - scale bar corresponds to $50 \mu\text{m}$

To find the critical yield stress for which the crystal breaks, we claimed that the number of bond broken per transition is $b = 2q$. This equation is based on simple geometrical arguments. Three quantities are defined to describe the breaking events: the number of droplets per triangle d , the number of triangles per transition t and the number of bonds broken b .

$$d = \sum_{i=1}^{p-1} i = \frac{p(p-1)}{2}. \quad (\text{S1})$$

Therefore, the number of triangles t for a transition (excluding edge effects) is:

$$t = \frac{N_{tot}}{d} = \frac{2q}{p-1}. \quad (\text{S2})$$

The bonds are broken along the edge of the triangles only, leading to $(p - 1)$ bonds broken per triangle. Only one side of the triangle is considered to avoid double counting. The total number of bonds b broken during a transition is:

$$b = t(p - 1) = 2q = \frac{2N_{tot}}{p}. \quad (\text{S3})$$

Eq. S3 justifies the use of $b = 2q$ as the number of bonds broken during a transition for a crystal.

EQUIVALENT SPRING MODEL

The force measurement corresponding to the compression of the 7×7 crystal is shown in Fig. S2. As the cluster goes through six transitions, six peaks are observed. Only the increasing part of the peaks, corresponding to the compression of the cluster (black part of the peaks in Fig. S2), is considered. The decaying part of the peak is due to the relaxation of the sensing pipette and drag on the droplets themselves (red). The start point of the peak is taken as the first point for which the slope becomes positive. The end point of the peak is found using the microscopy pictures; we disregard the data points after the first bond is broken in the system. Indeed, if a bond is broken, the droplet is no longer part of the equivalent spring so the model does not apply anymore. For the first peaks, the end point usually corresponds to the maximum of the peak. As the crystal becomes thinner, smaller number of rows p , the number of droplets per row q becomes larger. Because the cluster is now wider, the cluster becomes more sensitive to parallelism between the pipettes and parts of the cluster break slightly before others. Thus, the peak value does not correspond to the theoretical maximum of the force.

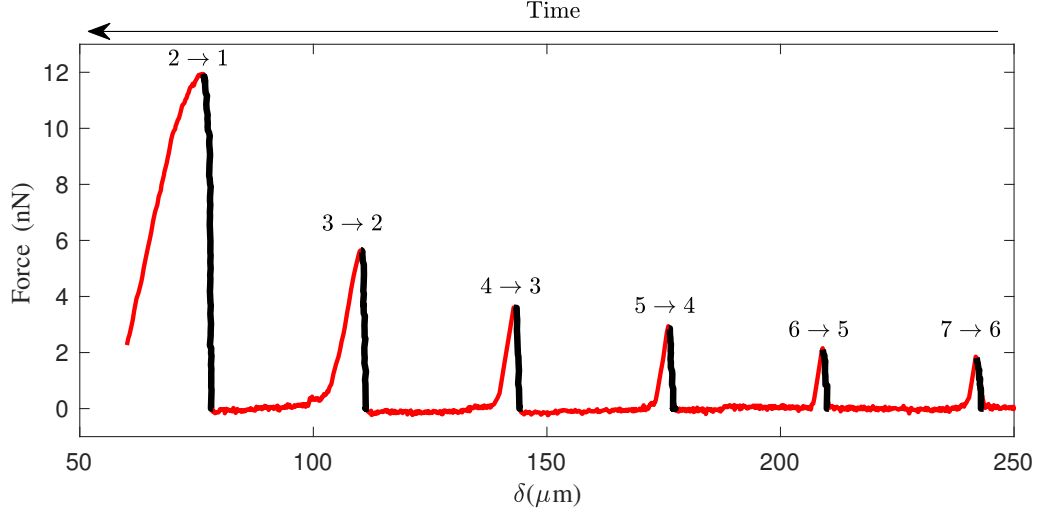


FIG. S2. Force curve for the compression of a 7×7 crystal. The six peaks correspond to the six transitions observed during the compression. As time goes on the pipettes are brought closer to each other and delta decreases. The increasing part that corresponds to elastic compression of the peak is the right side.

Deformation of a droplet

The energy cost of deforming a droplet has been calculated by Pontani *et al.* [1] to be $E_d = 1/2\gamma\pi R_0^2\theta^4$, where R_0 is the undeformed radius of the droplet and θ is defined in Fig. S3. In the main text, we use the analogy between a droplet and a spring. The elastic energy stored in a spring of constant k_1 is $E_s = 1/2k_1x^2$. Comparing E_d to E_s , the relationship between the spring constant and the surface tension between oil and the SDS solution can be found. The deformation energy E_d must be expressed as a function of the compression of the droplet x . Let us first express x as a function of the patch radius R_p and the radius R :

$$R^2 = R_p^2 + (R - x)^2, \quad (\text{S4})$$

which is equivalent to

$$R_p^2 - 2xR + x^2 = 0. \quad (\text{S5})$$

We solve for x ,

$$x_{\pm} = R_0 \pm \sqrt{R^2 - R_p^2}. \quad (\text{S6})$$

Eq. S6 can be written as:

$$x_{\pm} = R \pm R\sqrt{1 - \frac{R_p^2}{R^2}}. \quad (\text{S7})$$

The deformation x must be positive so the only physical solution is x_- . The size of the patch is small compared to the radius of the droplet so Eq. S7 is Taylor expanded :

$$x_- \approx R - R(1 - \frac{R_p^2}{2R^2}) \approx R_p^2/R. \quad (\text{S8})$$

The angle θ defined in Fig. S3 can also be expressed as a function of R_p and R : $\theta = R_p/R$. Finally, to first order, $R \approx R_0$. Using these intermediate steps, the deformation energy E_d becomes:

$$E_d = \frac{1}{2}\gamma\pi\frac{R_p^4}{R_0^2} = \frac{1}{2}\gamma\pi x^2. \quad (\text{S9})$$

This analysis justifies the spring model for a single droplet and also shows that k_1 only depends on the surface tension between oil and the SDS solution, $k_1 = \pi\gamma$, and is independent of droplet size.

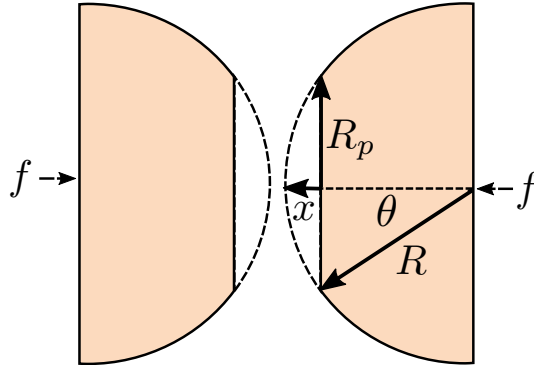


FIG. S3. Schematics of two droplets being compressed against each other with a force f . The compression of the droplet is characterized by x . A patch of radius R_p is formed between the droplets.

Yield stress

As explain in the main text, the cluster stores elastic energy when it is compressed. When the stored energy exceeds the adhesion energy $E_a = bE_1$, the crystal breaks. The breaking criteria can be found by balancing these two energies as explained in Eq. 1. Multiplying both sides of the equation by k_{eq} leads to

$$\frac{F_c k_{eq} \Delta x_c}{2} = 2q k_{eq} E_1. \quad (\text{S10})$$

The force F_c is simply equal to $k_{eq} \Delta x_c$ and using $k_{eq} = k_1 q/p$ we find

$$\frac{F_c^2}{q^2} = \frac{4k_1 E_1}{p}. \quad (\text{S11})$$

We define the 2D yield stress by the force F divided by the number of droplets in a row q : $\sigma_c = F_c/q$,

$$\sigma_c = \sqrt{\frac{4k_1 E_1}{p}}. \quad (\text{S12})$$

HEIGHT OF A COLUMN AND PROBABILITY

In this section, the theoretical model used to predict the number of peaks in the force measurement as a function of ϕ is derived. In this calculation, each transition from p rows of droplets to $(p-1)$ rows is studied individually. In the following, p and q are constant values.

Discrete model

The theoretical model developed for this study is based on geometrical arguments. An assembly of droplet is compressed if its lateral unstrained extent is larger than the spacing between the pipettes. The cluster is modeled by independent columns of height H_i stacked next to each other. The total height of a column only depends on its composition. For a crystal, all the columns are the same so they break at the same time resulting in a single peak in the force measurement. When defects are introduced, large droplets are substituted by small ones (or *vice versa*) which changes the height of the column. Columns constituting the cluster now have different sizes and break for different values of δ : several peaks are observed in the force measurement. A column is made of alternating layers of two droplets (modeled by a rectangle) and a single droplet (a circle) as shown on Fig. S4.

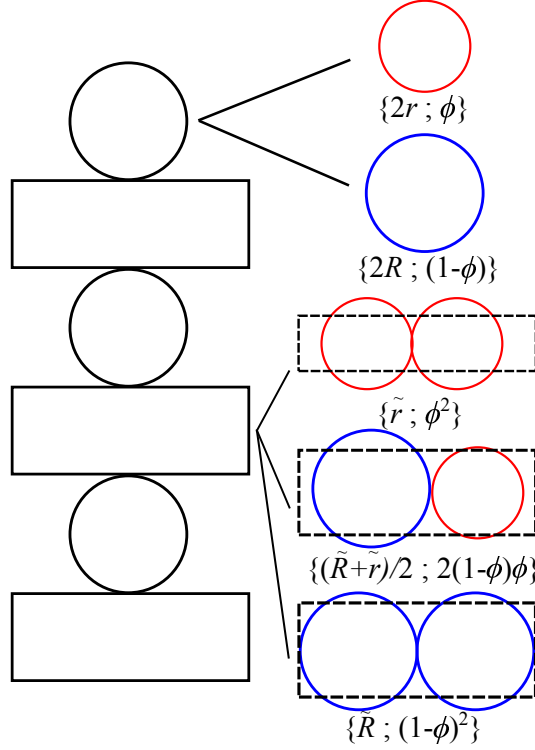


FIG. S4. Schematics of the columns considered in the theoretical model. The left part shows how rectangles and circles are assembled to build a column. The right part shows the different choices for circles and rectangles along with their probability to appear

The random walk statistic can be applied in this model. In fact, building such a column is equivalent to two random walks of $p/2$ steps: one with the circles and one with the rectangles. To simplify, we only consider p being even. The results for p being odd would be similar. The relationship between R and $\tilde{R}$ is a geometrical factor α that cancels later in the calculation. Simply using the random walk statistical background [2], we can express the probabilities $P_{\text{circ}}(H_1, p, \phi)$ of finding a height H_1 by stacking $p/2$ circles of two different sizes for a given ϕ , and $P_{\text{rect}}(H_2, p, \phi)$, the probability of finding a height H_2 by stacking $p/2$ rectangles of three different heights:

$$\begin{cases} P_{\text{circ}}(H_1, p, \phi) = \frac{1}{2\pi} \int_{-\pi}^{\pi} (\phi e^{i\theta r} + (1-\phi) e^{i\theta R})^{\frac{p}{2}} e^{-i\theta H_1} d\theta \\ P_{\text{rect}}(H_2, p, \phi) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \underbrace{(\phi^2 e^{i\theta \tilde{r}} + (1-\phi)^2 e^{i\theta \tilde{R}} + 2\phi(1-\phi) e^{i\theta \frac{\tilde{R}+\tilde{r}}{2}})}_{(\phi e^{i\theta \frac{\tilde{r}}{2}} + 1 - \phi) e^{i\theta \frac{\tilde{R}}{2}}}^{\frac{p}{2}} e^{-i\theta H_2} d\theta \end{cases} \quad (\text{S13})$$

$$\begin{cases} P_{\text{circ}}(H_1, p, \phi) = \sum_{k=0}^{\frac{p}{2}} \binom{\frac{p}{2}}{k} \phi^k (1-\phi)^{\frac{p}{2}-k} \delta(kr + (\frac{p}{2}-k)R - H_1) \\ P_{\text{rect}}(H_2, p, \phi) = \sum_{l=0}^p \binom{p}{l} \phi^l (1-\phi)^{p-l} \delta(l\frac{\tilde{r}}{2} + (p-l)\frac{\tilde{R}}{2} - H_2). \end{cases} \quad (\text{S14})$$

It turns out that the random walk of $p/2$ steps with three different step sizes is equivalent to p steps of two different sizes. The Dirac δ function is a geometrical constraint on the total height. Only the combinations of droplets that leads to the right total heights H_1 or H_2 are considered. The distribution of probability of the total height H is the convolution product of $P_{circ}(H_1, p, \phi)$ and $P_{rect}(H_2, p, \phi)$.

$$P(H, p, \phi) = \int_0^\infty P_{circ}(H - H_2, p, \phi) P_{rect}(H_2, p, \phi) dH_2, \quad (S15)$$

Using S14 :

$$P(H, p, \phi) = \sum_{k=0}^{\frac{p}{2}} \sum_{l=0}^p \binom{\frac{p}{2}}{k} \binom{p}{l} \phi^{k+l} (1-\phi)^{\frac{3p}{2}-k-l} \delta\left(l\frac{\tilde{r}}{2} + (p-l)\frac{\tilde{R}}{2} + kr + (\frac{p}{2}-k)R - H\right). \quad (S16)$$

Eq. S16 is used to calculate the discrete distribution presented in the main text (Fig. 4(c)-(e)). The height H is renormalized in order for the height of a cluster made of large droplets to be one. Eq. S16 is the most rigorous calculation of the distribution of probability but it is a numerical calculation and not analytical.

Continuous model

The other option is to consider large values of p so the distribution can be described by a Gaussian curve with μ , the average value, and σ , the standard deviation:

$$P(H, p, \phi) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(H - \mu(\phi, p))^2}{2\sigma^2(\phi, p)}\right], \quad (S17)$$

with $\mu = p\frac{\alpha+2}{2}[(1-\phi)R + r\phi]$ and $\sigma^2 = p(2+\alpha^2)\phi(1-\phi)(R-r)^2$. The advantage of this approach is that the variance and the average value can be calculated analytically.

NUMBER OF PEAKS

The column model gives access to the probability p_i of finding the height H_i in a cluster for any fraction of defects ϕ . Correlation between two adjacent columns are neglected. Experimentally, a small fraction of the peaks in the force measurement is due to the correlation between columns but most of the peaks are indeed due to compression of independent columns. The number of peaks in the force measurement is calculated from the height distribution. Observing a single peak in the force measurement means that all the columns share the same height. Measuring two peaks means that there are two and only two different $< N^p(\phi) >$ the average number of force peaks during a compression of a cluster of p rows to a cluster of $(p-1)$ rows.

Discrete model

The cluster is built by choosing q columns from a pool of m types of columns with probability p_i , where m is the number of different possible heights found in the height distribution. To predict the number of peaks we calculates the probability A_n of finding strictly n columns in a cluster made of q columns.

$$A_n = \frac{1}{n!} \sum_{\{ijk...\}_n} (P_{\{ijk...\}_n})^q - \frac{1}{n!} \sum_{\alpha=1}^{n-1} \binom{n}{\alpha} \alpha! \prod_{\beta=\alpha}^{n-1} (m-\beta) A_\alpha, \quad (S18)$$

where $\{i, j, k, \dots\}_n$ is the n -tuple with each number between one and m and $P_{\{ijk...\}_n} = \sum_{\alpha \in \{i, j, k, \dots\}_n} p_\alpha$ is the sum of the probability of finding each number in the n -tuple. The average number of peaks $< N^p(\phi) >$ is calculated from this distribution:

$$< N^p(\phi) > = \sum_{n=1}^m n A_n. \quad (S19)$$

The meaning of this distribution A_n can be easily understood for both extreme values of ϕ . If $\phi = 0$, there is only one possible height for the column meaning that $A_n = \delta_{1n}$. On the other hand, if $\phi = 0.5$, it is unlikely to find only one height so $A_1 \approx 0$. It is more likely to find all the different heights in the cluster leading to $A_m \approx 1$. This is illustrated in Fig. S5(a) which shows the probability, A_n , as a function of ϕ . Fig. S5(b) shows the number of peaks as a function of ϕ for $p = 2$. The maximum number of peaks m is six for the transition $2 \rightarrow 1$.

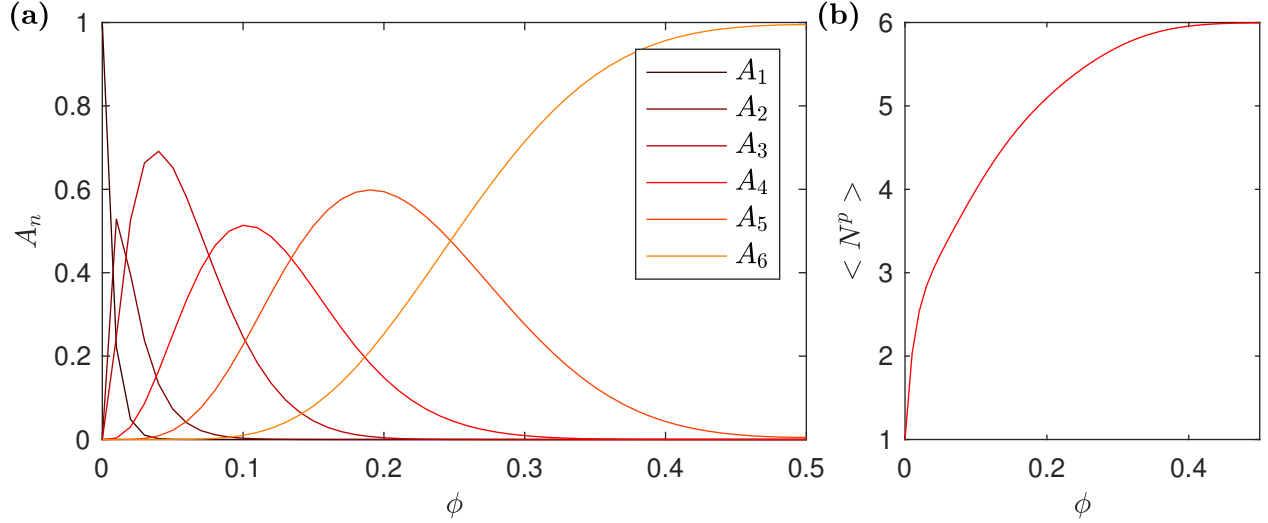


FIG. S5. (a) Probability distribution A_n as a function of ϕ for a cluster made of $p = 2$ rows and $q = 50$ droplets per row. (b) Prediction of the average number of peaks in the force measurement as a function of ϕ based on the distribution A_n

Finite size effect

For the theoretical model, we always considered the system to have a large number of column q (in Fig. S5, $q = 50$) but for the experimental clusters, q varies from 3 to 15. Especially for $p = 3$ or $p = 4$, the number of column is usually ~ 5 . Even if the number of different possible heights m is large, we cannot find more different heights than the number of column q . Fig. S6 shows the impact of the number of columns on the number of peaks for $p = 2$.

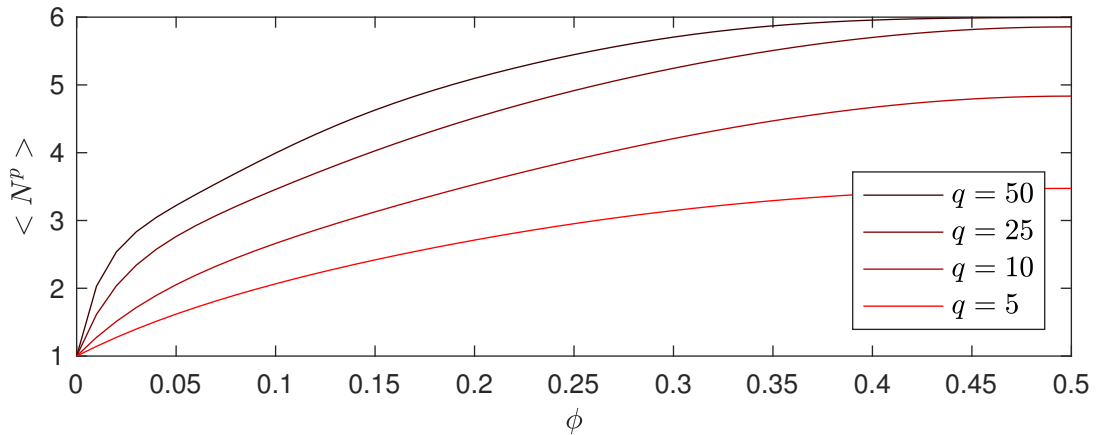


FIG. S6. Impact of the size of the cluster on the number of peaks in the force measurement for $p = 2$ and different values of q

Continuous model

The continuous approach consists in approximating the discrete distribution by a gaussian distribution. With this approximation, all heights are possible but only some of them are likely to be found. This likelihood is given by the variance of the gaussian: if the width of the gaussian is large, then many different heights can be found. We know the maximum number of peaks is found for $\phi = 0.5$ and we only see a single peak if $\phi = 0$. To first order, we can express the number of peaks:

$$\langle N^p(\phi) \rangle = (\langle N^p(\phi = 0.5) \rangle - 1) \frac{\sigma(\phi)}{\sigma(\phi = 0.5)} + 1, \quad (\text{S20})$$

which can be written as

$$\langle N^p(\phi) \rangle = (\langle N^p(\phi = 0.5) \rangle - 1) 2\sqrt{\phi(1-\phi)} + 1. \quad (\text{S21})$$

These two equations satisfy the constraints mentioned above.

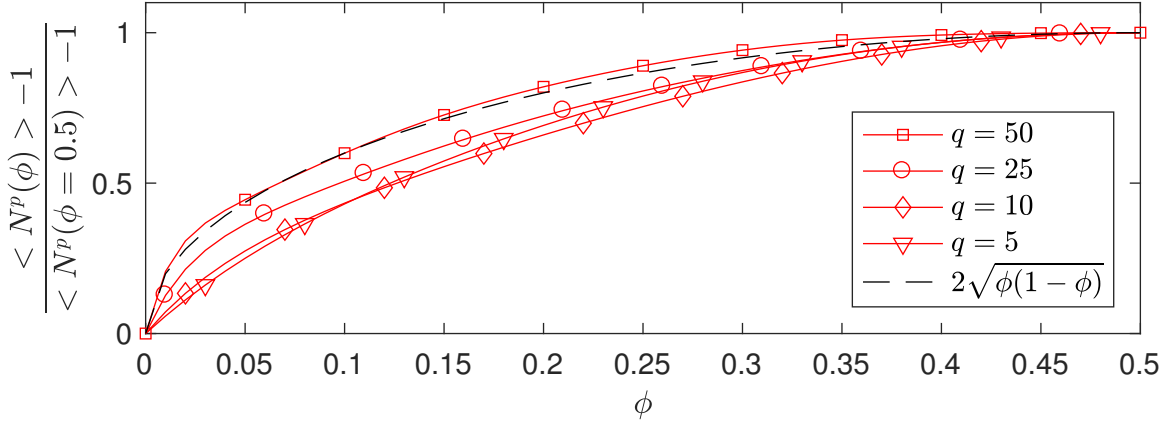


FIG. S7. Comparison between the number of peaks predicted by the discrete calculation (for different values of q) and the continuous approximation for $p = 2$. The continuous model does not take into account the number of droplets per row q in the cluster.

The continuous approach can be tested against the discrete one by comparing the number of peaks predicted by each model with $p = 2$. Eq. S21 can be rewritten as

$$\frac{\langle N^p(\phi) \rangle - 1}{\langle N^p(\phi = 0.5) \rangle - 1} = 2\sqrt{\phi(1-\phi)}. \quad (\text{S22})$$

The left term can be calculated for the discrete model and compared to the analytical expression $2\sqrt{\phi(1-\phi)}$ as shown in Fig. S7. The continuous and the discrete model are in good agreement for the prediction of the number of peaks. The continuous approximation is more accurate for infinite size systems (large value of q). Fig. S7 justifies the use of the continuous approximation in the main text even for small values of p .

FROM A SINGLE TRANSITION TO THE TOTAL NUMBER OF PEAKS

In the main text, we compare the experimental results and the total number of peaks from p_{ini} to $p = 1$. Eq. 3 is obtained by summing Eq. S22 over the different transitions:

$$N^{p_{ini} \rightarrow 1} = \sum_{p=2}^{p_{ini}} N^{p_{ini} \rightarrow p-1} = 2\sqrt{(1-\phi)\phi} \sum_{p=2}^{p_{ini}} (N_{max}^{p_{ini} \rightarrow p-1} - 1) + \sum_{p=2}^{p_{ini}} 1, \quad (\text{S23})$$

$$N^{p_{ini} \rightarrow 1} = 2\sqrt{(1-\phi)\phi}(N_{max}^{p_{ini} \rightarrow 1} - (p_{ini} - 1)) + (p_{ini} - 1), \quad (\text{S24})$$

$$\frac{N^{p_{ini} \rightarrow 1} - (p_{ini} - 1)}{N_{max}^{p_{ini} \rightarrow 1} - (p_{ini} - 1)} = 2\sqrt{(1-\phi)\phi}. \quad (\text{S25})$$

The maximum number of peaks depends on the system size as it has been shown in the previous section. Experimentally, we simply use the maximum number of peaks observed for $\phi \approx 0.5$.

WORK ANALYSIS

In the main text, we study how the work is dissipated as a function of the composition of the cluster. This analysis relies on the assumption that the total work for a given transition does not depend on ϕ . We found that within the uncertainty of the experiment, the total work for the transition from p to $(p-1)$ is constant and is not correlated to the fraction of defects ϕ . Table S1 summarizes the total work, W_{tot} , exerted to go from four to three rows W_{tot} for the different clusters.

Composition	ϕ	W_{tot} (nN. μ m)
20/0	0	1.2
19/1	0.05	2.8
14/6	0.3	2.8
10/10	0.5	2.1
6/14	0.3	3.1
1/19	0.05	1.5
0/20	0	2.0

TABLE S1. Total work needed to transition from $p = 4$ to $p = 3$ for different compositions

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Chapter 5

Conclusions

In the work presented in this thesis, we have investigated the crystal-to-glass transition. Perfectly ordered crystals are modeled by clusters of highly monodisperse droplets. The transition to glasses is studied by mixing two monodisperse populations of droplets in different proportions. As the clusters are compressed, we characterize the internal microscopic rearrangements of and the mechanical response of the aggregates. Forces within the 2D clusters of droplets are directly measured and the force curves are characteristic of the composition of the cluster. In particular the number of peaks rapidly increases with the number of defects. Introducing disorder in the structure also changed the way the energy is dissipated during the compression. The experimental results are supported by a geometrical model based on the random-walk statistics. Our work shows that a small amount of disorder considerably changes the mechanical behaviour of the cluster. This observation is consistent with the work published by Goodrich and co-workers [42].

The experimental setup used in this work can be used in many ways to investigate other questions. For example, here we did not investigate the correlation between two defects in the cluster. As we have full control over the position of the defects, the relative position of two defects can be changed. The size ratio between large and small droplets can also be tuned. It would be interesting to know how much a droplet needs to be different from the other before acting as a defect. Another direction is to investigate the transition from a system with few droplets toward a larger cluster (~ 100 droplets). These questions will form the basis of further studies.

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