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Abstract – A scientific hurdle in manufacturing solid films by drying colloidal layers is preventing them from fracturing. This paper examines how the drying rate of colloidal liquids influences the particle packing at the nanoscale in correlation with the crack patterns observed at the macroscale. Increasing the drying rate results in more ordered, denser solid structures, and the dried samples have more cracks. Yet, introducing a holding period (at a prescribed point) during the drying protocol results in a more disordered solid structure with significantly less cracks. To interpret these observations, this paper conjectures that a longer drying protocol favors the formation of aggregates. It is further argued that the number and size of the aggregates increase as the drying rate decreases. This results in the formation of a more disordered, porous film from the viewpoint of the particle packing, and a more resistant film, i.e. less cracks, from the macroscale viewpoint.

Obtaining solid layers via drying of colloidal suspensions is central to many technological fields [1]: Printing and painting [2], manufacturing protective or decorative coatings [3], designing materials at the nanoscale by low-cost processes [4, 5]… From a fundamental viewpoint, colloidal systems provide model systems to mimic the atomic behavior at a larger, more accessible length-scale [6, 7]. Understanding, predicting and controlling the mechanisms driving their self-assembly represents a major challenge. Obtaining this control will aid in ensuring the resistance to failure while staying eco-friendly [3], especially for applications requiring thick and/or hard coatings. Amongst several other parameters (thickness [8], ionic strength [9], substrate adhesion [10]…), the drying rate significantly impacts the cracking patterns [11–13]. This observation remains poorly understood for several reasons. During drying, mass loss plays simultaneously [12] on the evolution of both the loading applying externally to the layer [14, 15] and the intrinsic material properties of the forming solid [16]. From a macroscopic point of view, these two effects can hardly be deconvoluted. An important question to clarify is whether the drying rate plays only on the formation kinetics yielding the same material or if it changes the way the material self-structures during evaporation leading to variation in the final state.

This Letter experimentally investigates how the evaporation kinetics influences the material properties at the particle (nano)scale and the fracture patterns at the continuum scale. For this purpose, a colloidal suspension of hard monodisperse nanospheres was dried in a controlled atmosphere of tunable humidity. An atomic force microscope (AFM) captures the particle arrangement of the final layer topography. Bulk measurements of the packing density complement these surface analyses. Counter-intuitively [4], these systems exhibit a progressive transition from disorder to order when increasing the drying rate. This transition goes along with an increase of density and more cracks. The balance between particle convection and diffusion alone cannot explain this transition, and particle agglomeration should be considered. Longer drying protocols enhance fracture resistance and favors particle agglomeration, and consequently disordered packing structure and porosity.

Setup– Drying experiments herein invoke model col-
loidal suspensions of monodisperse silica nanospheres (Ludox HS-40: $D_{m, \text{SiO}_2} = 40 \pm 1\%$ in mass of SiO$_2$ colloids with a spec nominal diameter of 12 nm; $D_{m, \text{Na}_2\text{O}} = 0.42 \pm 0.04\%$ in mass of free alkalinity as Na$_2$O; and spec density $\rho_{\text{Ludox}} = 1.30 \pm 0.01$ g/cm$^3$). Experiments herein use the same bottle of suspension [17] and occur over a restricted time period ($\sim 9$ months). This ensures a minimal variation and aging of the initial suspension. A glass Petri dish (inner radius $R = 3.5$ cm) initially contains 25 g ($m_0$) of Ludox. To capture the in-situ mass loss, the Petri dish rests on a precision scale (Sartorius Cubis series, accuracy $10^{-5}$ g). The layer dries uniformly and forms a flat surface, except in the vicinity of the dish edges where an upwards meniscus prevents the drop singularity (hence the coffee-quality putty to minimize leaks.

Labview records the suspension’s mass ($m$), the temperature ($T$), and the relative humidity (RH) during the whole drying process. For all the experiments, the temperature was $T = 25 \pm 2^\circ$C. Hence, RH controls the drying rate. Initially, the mass decreases linearly with time (i.e. $dm/dt \sim \text{constant}$) for a prescribed RH, as reported in the literature [20]. Transforming the mass loss into the evaporation rate, $E_0$ ($E_0 \equiv (dm/dt)/(\rho_{\text{water}} \pi R^2)$), one finds that $E_0$ decreases linearly with the applied RH. Experiments verified that $E_0$ for pure water and Ludox are equal barring the same drying conditions. Modulating RH from 10% to 95% makes $E_0$ vary over a decade from $E_0 = 36.1 \pm 0.7$ nm/s to $E_0 = 3.4 \pm 0.2$ nm/s.

After the constant evaporation rate regime, a falling-rate regime occurs where the evaporation slows down and eventually stops. Once $dm/dt$ is negligible (after $\sim 50$ h for RH = 10% and after $\sim 700$ h for RH = 95%), the sample is brought back to ambient humidity. Postmortem observations reported hereafter are independent of the returning protocol: An abrupt return (obtained by opening the housing) or progressive one (obtained by bringing the RH inside the box back to ambient humidity in a stepwise process as slow as 10% humidity steps every 12 h) does not alter the solid porosity nor the particles surface arrangement. It has also been checked that increasing the Petri dish radius from 2.5 to 6.8 cm, keeping the same initial thickness, does not alter experimental observations reported henceforth.

![Image](321x525 to 419x624)

![Image](452x525 to 551x624)

A camera (USB2 uEye from IDS imaging), located above the scale’s enclosure, images the evolution of the sample. As the solvent evaporates, the particles move closer to one another forming a solid network which progressively retreats. The rigid substrate (i.e. the Petri dish) hampers the retraction leading to tensile stresses which cause the layer to fracture (Fig. 1). These cracks begin to appear just as the evaporation rate enters the falling-rate regime. This point also coincides with the time at which the meniscus forms at the top of the particles layer, yielding a decreasing capillary pressure in the pores [8, 15, 21]. A Bruker Dimension Icon Atomic Force Microscope (AFM) images the particle arrangement on the evaporation surface of the fragmented morsels. The AFM records topographical images in Tapping mode using a Bruker RTESP A tip (radius of curvature $\sim 8$ nm). The scan sizes are 500 $\times$ 500 nm$^2$ with a resolution of 512 $\times$ 512 pixels$^2$.

Determining the packing fraction, $\phi = m_{\text{dry}}/(\rho_{\text{silica}} V_T)$, sheds light on the bulk ordering of the solids. The mass of a dried sample ($m_{\text{dry}}$), its total volume ($V_T$) and the silica density ($\rho_{\text{silica}}$) are estimated as follows. To obtain $m_{\text{dry}}$, the sample are heated at 200$^\circ$C for more than 3 hours to remove remaining water [22]. To obtain $V_T$, imbibition and Archimedes’ principle are used: After immersion, the pores soak up water and the sample’s total volume is obtained via hydrostatic weighing [23]. This process was repeated using ethanol rather than water; the two values of $V_T$ agree within less than 2%. To obtain an accurate estimation of $\rho_{\text{silica}}$, the dilution method is invoked [24, 25]: Several diluted suspensions of Ludox, of densities $\rho_{\text{diluted}}$, are prepared at prescribed mass fractions ($\phi_{\text{dilute}}^m$). The initial mass fraction $\phi_0^m$ is estimated by weighing dry residues at 200$^\circ$C and $\rho_{\text{silica}}$ is inferred by linear regression using the rela-
Evaporation rate effects during colloidal drying

**Results**—Figures 1A and B show snapshots of the cracking pattern observed in the Petri dish after drying (i.e. when the mass loss is negligible) for the two extremes. Drying quickly (RH = 10%) leads to a large quantity of small fragments (∼50 visible fragments in the center of the Petri dish, within a disk of radius ∼1.75 cm). On the contrary, the slowest drying rate (RH = 95%) leads to a small quantity of large fragments (5 fragments visible over the same area). Generally, the typical fragment size decreases as $E_0$ increases (or equivalently as RH decreases).

The drying rate also alters the nanoscale arrangement of the colloids at the layer surface as observed via the AFM. An almost 2D crystalline structure forms for the fastest rate (RH = 10%; Fig. 1A'), and an amorphous one for the lowest rate (RH = 95%; Fig. 1B').

Two-dimensional Fourier spectrum conducted on the AFM topographical images shown in Figs. 2A (RH = 10%) and B (RH = 95%) access the differences in particle arrangements on the drying surface. For the fastest evaporation rate, the pattern exhibits a sixfold symmetry characteristic of a hexagonal 2D lattice. On the contrary, no discrete wavenumber can be identified for RH = 95% and only a central circular halo occurs. This is characteristic of an amorphous structure.

The pair correlation function, $g(r)$, represents the probability of finding the center of a particle at a distance $r$ away from a given reference particle. Moreover, it aids in characterizing the long range order of the images. As in standard practice, $g(r)$ is normalized by that of an ideal gas (i.e. non-correlated particle positions) [29]. Fig. 2C depicts the two extreme cases: RH = 10% (top curve with circular points) and RH = 95% (bottom curve with triangular points). For RH = 10%, $g(r)$ presents a well defined sequence of peaks extending more than 12 $d$ where $d \approx 15$ nm is the particle diameter acquired from Fig. 1A' and 1B' (note that this value is slightly higher than the spec one). The first several $g(r)$ peaks coincide well with the theoretical values for a perfect hexagonal lattice (indicated by dash vertical lines), even if they widen as $r$ increases.

This is the signature of a quasi-long range translational order. Conversely, the RH = 95% peaks become barely visible for $r \geq 2d$ indicating a loss of translational order, as expected for amorphous structure.

The orientational order evolution can be investigated via the bond angle order parameter $\psi_n$ defined by

$$\psi_n = \left| \frac{1}{M} \sum_{k=1}^{M} \frac{1}{N_k} \sum_{l=1}^{N_k} \exp \left( i n \theta_{kl} \right) \right|, \quad (1)$$

where $n$ is the number of nearest neighbors, $M$ is the number of particles in the AFM image, $N_k$ corresponds to the number of nearest neighbors of particle $k$, and $\theta_{kl}$ is the angle between a fixed direction and the line linking the centers of particles $k$ and $l$ [30]. For the six-fold symmetry visualized in Fig 2A, $n$ should be set to 6. For a perfect hexagonal arrangement $\psi_6 = 1$ while for an amorphous phase $\psi_6 = 0$. The evolution of $\psi_6$ with $E_0$ (shown in Fig. 3A) exhibits two regimes with a crossover at $E_0 \sim 10 \text{ nm/s}$. For $E_0 \leq E_c$, $\psi_6 \approx 0.05 \ll 1$. This reflects a disordered surface for low evaporation rates. On the other hand when $E_0 > E_c$, $\psi_6$ increases linearly with $E_0$. This is consistent with the observations of the translational order (fig. 2C): Increasing the drying rate yields increasing hexagonal order at the surface. The fact that $\psi_6$ remains significantly lower than one reveals that even for the fastest drying rate the surfaces are not perfect 2D hexagonal lattices.

The above AFM analysis is restricted to surface characterizations of the particle arrangement. In a complementary way, the particle volume fraction $\phi$ provides in-
formation on the bulk particle arrangement. Fig. 3B displays the evolution of $\phi$ as a function of $E_0$. Two regimes occur with a crossover $E_c \approx 10\, \text{nm/s}$. This crossover coincides with that observed in Fig. 3A which is related to the surface orientational order. In the first regime $E_0 \leq E_c$, $\phi$ increases linearly with $E_0$. In the second regime $E_0 > E_c$, $\phi$ increase rapidly slows down and even saturates to $\phi \approx 0.65 \pm 0.02$, which is just above the random close packing value ($\phi_{\text{RCP}} = 0.64$ for monodisperse packing) but below the value of a compact structure ($\phi_{\text{HCC/FCC}} = 0.74$). This shows that the bulk is, to a large extent, disordered and raises the question to what extend does the order extend into the bulk.

Discussion – The packing structure results from the way the particles bundle. Its dependency on the drying rate is usually rationalized [31,32] via the dimensionless Péclet number: $Pe \equiv h_0 E_0 / D_0$ where $D_0$ is the diffusion coefficient for silica particles. Using Stokes-Einstein relation, one gets $D_0 \approx 2.04 \times 10^{-11}\, \text{m}^2/\text{s}$ at $T = 25^\circ\text{C}$. $Pe$ represents the ratio between the convection time for the particles toward the suspension surface and their Brownian diffusion time. A high $Pe$ indicates directional packing implying the solid forms layer by layer. A low $Pe$ means uniform and isotropic bulk compaction.

Checking whether or not $Pe$ controls the packing structure requires two additional experimental runs. The experiments invoke two parameter sets $\{h_0, RH\}$ at a similar Péclet number well above $Pe = 1.5$ (i.e. $E_0 > E_c = 10\, \text{nm/s}$) which should result in a similar surface crystalline arrangement. The first experimental run uses $h_0 = 5\, \text{nm}$ and $E_0 = 36.1\,\text{nm/s (RH=10 %)}$ and yields $Pe = 4.4$. The second run uses $h_0 = 10\, \text{nm}$ and $E_0 = 26\,\text{nm/s (RH = 50 %)}$ and yields $Pe = 6.4$ (slightly larger). The first run exhibits an ordered surface arrangement, while a disordered arrangement occurs for the second one. This demonstrates that $Pe$ is not the relevant parameter driving the particle packing.

Beyond the competition between convection and diffusion, the formation of aggregates within the suspension could be an important mechanism driving the crystalline-to-amorphous arrangement in the solid. If this is the scenario, then slower drying favors the formation of aggregates and subsequently the formation of an amorphous solid. Testing this hypothesis calls for two new experimental runs. Both runs invoke $RH = 10\%$ and $h_0 = 5\, \text{mm}$ (Fig. 4). The first experimental run uses, as previously, a continuous drying scheme and gives a crystalline surface arrangement. The second experimental run invokes an 180 hours holding period (i.e. $E_0 \sim 0\, \text{g/h}$ for 180 hours) launched when $m = 18.2\, \text{g}$. During this holding period, the sample resumes drying with RH = 10% until $E_0 \sim 0$. The solid layer exhibits an amorphous arrangement on the drying surface. Thus, it is conjectured that long drying protocols (including holding periods) favor the agglomerate formation which subsequently alters the nanostructure packing (amorphous instead of crystalline as imaged with
the AFM). At the macroscale, the crack patterns of the second run are larger than the ones obtained, without a holding period, although they appear under the same external drying conditions. This implies that slowing down the drying enhances the macroscopic resistance to fracture by changing the way the particles bundle.

Conjecturing agglomerate formation sheds new light on the $\psi_0$ vs. $E_0$ and $\phi$ vs. $\dot{E}_0$ curves displayed in fig. 3. At first glance, one expects a correlated increase of $\psi_0$ and $\phi$ with $E_0$ as they both increase with the packing order, yet this does not occur. Still, the curves can be understood assuming that $\dot{E}_0$ is a critical value below which every particle of the suspension is part of an aggregate before solification. Subsequently:

- For $\dot{E}_0 < \dot{E}_c$, the packing has to be amorphous and $\psi_0 \sim 0$. Increasing $E_0$ causes the mean size of the aggregates to decrease, hence the mean size of the pores decreases, thus increasing the packing fraction (i.e. $\phi$ increases).

- For $\dot{E}_0 > \dot{E}_c$, the number of isolated particles increases with $E_0$, making it more likely to have crystalline zones, at least at the surface, where surface tension possibly drives the ordering [33].

As a result, $\psi_0$ increases with $E_0$. Additionally, isolated particles fill the space between the remaining aggregates. This explains the slower increase, and even the saturation of $\phi$.

In conclusion, this paper demonstrates that the evaporation rate, during drying of a colloidal layer, modifies not only the drying kinetics but also the final dried material: Increasing the rate favors more ordered arrangements and denser packing. Explaining this scenario requires more than the Pelet number and its simple balance between advection and diffusion. Studies herein suggest that aggregation as a result of the drying protocol plays a significant role in the formation of the solid. This may be of practical interest in the design of colloidal drying processes to obtain tunable and well-controlled 3D nanoparticle self-assemblies (e.g. crystals, modulated porosity solids...) over large dimensions, with innovative photonics and biotechnology applications [34]. This rate dependent solid formation has a consequence on the fracture behavior: The resistance to fracture increases by decreasing the drying rate or by introducing a holding period at a wisely chosen time. Work in progress aims at quantifying how the material properties at the macroscale, notably its elastic modulus and toughness, emerge from the nanostructure and its history of formation.

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