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Stresses and strains in colloidal films during lateral drying

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Abstract

Cracking and warping during drying are everyday phenomena of great importance, yet the processes that lead to them are still not fully understood. Existing ideas generally focus on the relaxation of capillary tension in the liquid as the driving force for cracking and predict that cracking should occur as the pores drain of liquid. However cracking is observed to occur before this. Recently this approach has been modified to include viscous flow of water through the particle network. An alternative view, based on observations of the height changes that of a drying film, is that when the water-filled network first forms the particles are not in contact, although the material has residual strength and is bonded to the substrate. The strengths and shortcomings of these two approaches are considered by comparison with experimental observations to outline areas of future work.

Keywords: Drying; Suspensions; Tape casting; Cracking

1. Introduction

Ceramic (and also polymer) films are often made by spreading a colloidal suspension onto a substrate and evaporating the liquid.[1] This simple process is used in inks, paints, adhesives, paper coatings, pharmaceuticals, ceramic films for electronics and, more recently, to make colloidal crystals for photonic band-gap applications. However it is often limited by the stresses and strains that build up during drying, causing distortion and cracking. Because of its importance in many spheres of activity, there are several extensive reviews of drying,[2,3] the most recent being that of Scherer,[4] which focused on the drying of bulk materials. This paper discusses the work on cracking in films made from suspensions cast onto a substrate.

2. Stresses during drying of an unconstrained droplet

Scherer[4] describes the stresses that build up during the drying of an unconstrained droplet of a colloidal dispersion, where the particles are initially freely dispersed in the liquid with repulsive stresses acting between them, ensuring they do not agglomerate. As liquid evaporates, the particle separation must diminish or new particle surface will be exposed increasing the overall surface energy. A force therefore acts on the particles in the liquid, pushing them closer together against the repulsive colloidal forces.

Eventually sufficient liquid has evaporated that the particles are pressed into contact with one another, although liquid remains in the spaces between the particles. It is generally accepted that the stresses in the particles are now compressive as the liquid menisci press the particles at the outer edge of the droplet inwards. This compression is thought to increase until the increase in energy associated with the elastic deformation of the particles is balanced by the decrease in surface energy that this compression enables, both at the outer edges of the droplet and also at each inter-particle contact. Further drying requires that the menisci move into the particle network. That the particle network is under compression is indicated by the measurement of a slight expansion as the pores empty of liquid, normally water.[5] Similar observations have been made in drying gels[6] and cements.[7]

As the liquid drains from the pores, there is an increase in the magnitude of the surface forces between the particles, leading to an increase in contact area, so that further elastic deformation of the particles can occur, as described by Johnson, Kendall and Roberts[8] (JKR). The dried film, even in the unsintered state, can therefore have significant mechanical strength. The magnitude of the stiffness of an unsintered film is consistent with the operation of attractive van der Waals forces,[9] so at some stage during drying, the forces between the particles switch from being repulsive to being attractive.

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There is a difficulty here. The JKR analysis, which is supported by careful experiments, would predict that, on drying, an unconstrained body should shrink rather than expand. Possibly the expansion requires that liquid is still at the necks. However given the central importance of the JKR analysis in drying theories,[10–12] this difficulty needs to be resolved.

3. Drying of a film on a substrate

Consider a colloidal dispersion cast onto a substrate. The film does not usually dry by a water/air front moving downward from the top surface of the film over the entire area of the film, although this can occur under certain circumstances.[13] Rather as liquid evaporates, capillary forces push the particles toward one another until a particle network is formed, which retains liquid in the inter-particle spaces which empties as further evaporation takes place. For a film drying on a substrate, the formation of the network and the emptying of the pores take place at fronts that move from the outer edge to the centre of the film.[14–20] This is known as *lateral drying*.

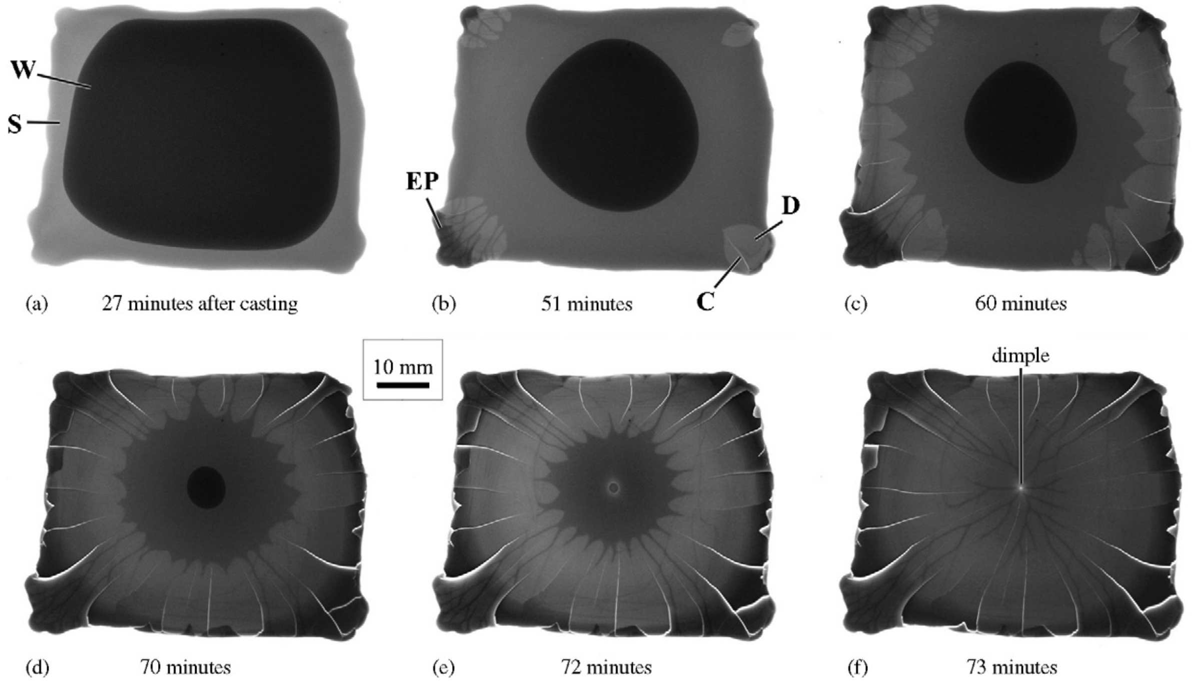
One can therefore observe a central region where the colloid remains fluid (the *wet region*, marked W in Fig. 1(a)[21]) surrounded by the compacted body with the pores filled with liquid (the *saturated region*, marked S in Fig. 1(a)), which in turn is surrounded by a region in which the fluid has drained from the pores (the *empty-pore region*, marked EP in Fig. 1(b)) with the boundaries between the wet and saturated regions (the *packing front*) and between the saturated and empty-pore regions (the *pore-emptying front*) both moving inward.

Evaporated water from the saturated region is replenished by water flowing from the wet region, W, driven by a gradient in capillary pressure through the saturated region, S.[15] It has been suggested that this outward water flow is responsible for particles being swept outwards, so that in dilute suspensions a ring of material is formed.[22] However in certain situations a greater amount of material is found at the centre of the dried film.[16]

The distance between the packing and pore-emptying fronts, l_{sat}, has been estimated.[15] Where samples have a radius, l, less than l_{sat} the wet region disappears before the pore-emptying front moves in from the edge. As soon as the packing front has reached the centre, further evaporation requires that the pore-emptying front moves inward from the sides and the top surface of the sample. As this occurs cracking can be observed, often initiated at the central dimple and growing rapidly across the sample. If l is greater than l_{sat}, cracking occurs in a more stable manner with the cracks generally grow in from the drying edges, as shown in Fig. 1.[21]

4. Stresses in drying films

To form a crack pattern of the type shown in Fig. 1(f), the film must be in tension at some stage during drying. The importance of the substrate in causing cracking was demonstrated convincingly by Chiu and Cima[14] who found that films cast on liquid mercury did not crack whereas those that were cast on a conventional substrate did.



(a) 27 minutes after casting (b) 51 minutes (c) 60 minutes

(d) 70 minutes (e) 72 minutes (f) 73 minutes

Fig. 1. (a–f) The process of lateral drying in a film at different times after casting. In this film $l > l_{\mathrm{sat}}$, so that the empty-pore region (EP) appears before the wet region (W) has disappeared. Initially a packing front moves in from the edge of the film, giving a saturated region (S). By 60 min cracks have started to form in the saturated region. The darker part of the saturated region is uncracked, the lighter part is cracked. The difference in contrast is associated with the film starting to peel away from the substrate.

The evidence that a tensile stress develops in a film as it dries comes from observations of curvature when a film is dried on a thin substrate. Such measurements have been made by casting a suspension on a beam fixed at one end and measuring the deflection of the free end,[23,24] or on a free substrate using Newton's rings, which form as a substrate placed on a optical flat curves.[14,16] In the former technique, the shape of the beam must be assumed, normally the arc of a circle. In the latter, the local curvature may be obtained at any point on the substrate. This is clearly an advantage given the non-uniform nature of a laterally drying film. To obtain the stress in the film, Stoney's equation, or some modification of it, is used,[25] assuming that the film is uniform.

The evolution of curvature with time has been studied in a wide range of materials, including alumina,[14,26–28] silica,[16] calcium carbonate[29] and lead zirconate titanate.[30] Systems with added binders[26–28,30–33] have also been studied as well as latex dispersions.[11,26,27] Where no binder has been added, the stress rises initially, before decaying. Very often a residual stress is measured, but this sometimes falls to zero. The residual strain is a difficulty if the curvature is caused simply by capillary tension, as the substrate should relax entirely once the sample has dried. In fact relaxation is generally observed when the film cracks.[16] The residual strains have been associated with necks forming between particles during drying.[15,34]

Whether cracking is observed or not, the measured values of the stress normally lie close to the value of the maximum capillary stress, $P_{\mathrm{c,max}}$, given by

$$P_{\mathrm{c,max}} = -k\frac{\gamma_{\mathrm{L,V}}}{r} \tag{1}$$

where $\gamma_{\mathrm{L,V}}$ is the liquid/vapour surface tension, r the particle radius and k is some numerical constant with a value of approximately[35] 10. Even more compelling are the correlations of capillary pressure both with the onset of cracking[15] (often expressed as a critical cracking thickness) and with the crack spacing.[36] Furthermore, Chiu and Cima[14] have reported values of the measured peak stress for suspensions containing different sizes of particles and with added surfactants to change the surface energy term. They found that the maximum stress was inversely proportional to the particle size and proportional to the surface energy as expected.

It is not clear why cracking should be so closely associated with the maximum capillary stress, $P_{\mathrm{c,max}}$. Indeed many models consider only the capillary stress and neglect the resistance of the drying film to cracking. Given the many different types of particles and experimental conditions, one might have expected large differences in the resistance, that would give considerable scatter in comparisons between data and predictions.

It is always assumed that the curvature arises because of a misfit strain between the unconstrained film and substrate,[12,37] as has been used to explain cracking in laminates made of layers with different expansivities and also to consider the sintering of a ceramic film on a substrate[38] or in sintering powder compacts containing large inclusions.[38–42]

In sintering, the ceramic film must undergo a change in shape, as well as a volume contraction,[43] so that the deformation is entirely in the through-thickness direction. For this to occur the work required to drive macroscopic shear processes (creep in this case) must be small compared with that required to drive uniform shrinkage.[44] In the case of the drying film, this macroscopic shear can occur by the particles changing their neighbours, so that the number of particles in the plane of the film increases.

In existing analyses of drying, it is assumed that the particle network will deform easily, until the particles are in touching contact, at which point, no further shear, or densification, occurs. As the measurements of curvature in the literature have been made on samples with a dimension smaller than l_{sat}, this should occur when the packing front reaches the centre of the drying film, so that further evaporation requires that the pore-emptying front both at the top surface and at the sides must move inwards. It is at this point that the capillary forces must increase and cracking is generally observed.

In the drying film, the capillary forces act at the edge of the film and compress the network. The situation is analogous to placing a rubber band around some pegs fixed to a flat sheet. This will cause the flat sheet to curve, although the constrained film is in compression rather than tension.

Curvature experiments therefore give the magnitude of the any stress, but they cannot themselves give the direction of the stress. As this compressive stress is equal to the capillary stress, it is expected that the curvature measurements give a stress of the magnitude of the maximum capillary stress. At no stage is the particle network in tension, even though the fluid is. However, as the network is fixed to a relatively stiff substrate, the substrate is carrying the main part of the capillary stress and the average stress in the film must be tensile.

5. The driving force for cracking

So if the network is under compression, and the cracking patterns are tensile in nature, how can capillary stresses give rise to cracking?

Based on observations that the drying front was not uniform,[45] Zarzycki et al.[46] suggested that this might arise as the pressures on regions separating filled and unfilled regions would not be balanced. Scherer[4] has pointed out that such a mechanism would give rise to a general fragmentation of the network, as opposed to the relatively few cracks that are normally seen. Instead Scherer suggested that if the irregularities in the drying front were treated as if they were cracks acted upon by a macroscopic stress with the magnitude of the capillary stress, the stress intensity factor would increase linearly with drying rate, consistent with the observation that cracking occurs more readily at higher drying rates.[4] No other supporting evidence was presented for this view.

It has been suggested that a tensile stress might occur in a particle network, once the pores had substantially emptied of liquid, leaving small amounts of liquid at the inter-particle necks, so-called pendular rings. Analysis showed that such forces might act to pull the particles towards one another and that it was this shrinkage that the caused cracking.[47]

More recently Tirumkudulu and Russel,[12] using an analysis of the fluid flow by Routh and Russel,[10,48–50] estimated the contraction that would occur when two spheres are brought into touching contract and a contact area allowed to form, as described by Johnson et al.[8] This misfit strain would arise when the liquid drained from a pore, in other words at the pore-emptying front. For a colloidal film bonded to a substrate, this strain is a true misfit strain, similar to differential thermal expansion.

Dufresne et al.[51] have studied the drying of a suspension in a glass capillary tube with one end closed after filling. Cracks grew in from the open end and in the saturated region slightly behind the packing front. Cracking did not seem to occur as the cracks drained of fluid as has been required in all the ideas considered so far. Using coherent anti-Stokes Raman scattering microscopy, they showed that there was no gradient in the concentration of water in the saturated region indicating that the observed water flow was driven by capillary stresses as described previously. Furthermore it was shown that when the cracks formed, they contained no water.

Based on these observations, Lee and Routh[35] have considered cracking of a constrained film as a uniform body held in fixed grips. The opening of a crack in the particle network allows relaxation of the capillary tension in the liquid, which occurs not so much by elastic relaxation but by viscous flow of water through the network.

Dufresne et al.[52] have incorporated viscous flow into an existing analysis for the failure of a uniform film and obtain an expression for the growth-rate of a crack, which is reasonably consistent with the observed behaviour. Although encouraging, it is not clear that an analysis for a uniform film is appropriate here. Any reduction in the capillary tension, by opening of the crack, i.e., by separation of both network and liquid, must cause loading of the particle network, increasing the elastic energy. Relaxation of the capillary tension could be obtained by forming a bubble in the liquid, without either breaking or loading the network. A detailed description of this situation is required to enable further experimental work. However the viscous flow of the water acts as the driving force for the cracking. One might have expected viscous flow to act simply as a dissipative mechanism, resisting cracking, similar to plastic flow in metals.

Such a mechanism also requires that other means of relaxing the capillary tension do not operate. For instance, the capillary tension might be reduced by allowing the particles, considered here to be in contact, to change their neighbours, as described earlier, allowing a change in the shape of the network as well as decreasing the free volume. For cracking to occur there should be no further density increase as the saturated material dries. However studies in alumina have shown that the dried material may have a solids volume fraction of 0.62 compared with 0.54 in the saturated region.[21] Similar increases have been found in dried silica layers, where the solids volume fraction increased from 0.61 in the saturated material to 0.68 in the dried bodies.[53] In a touching network, the existence of such strains requires that the increase in volume fraction occurs by particles changing their neighbours, reducing any misfit strain.

One way of overcoming this difficulty is to allow the particles, when they first come together in the saturated region, to form a non-touching network.[21,53,54] A misfit strain can then be obtained if the particles are then allowed to collapse into contact, provided the original network is both bonded to the substrate and has some mechanical strength.[21]

Experiments[21] on slurries of alumina particles, 350 nm in diameter, dispersed in water at pH 3, that is by charge-stabilization, showed that the saturated region was firmly bonded to the (glass) substrate and could not be washed off and required some force to remove it. The particles would also not redisperse if more water was added. This showed that the particles were not simply being pressed together by some external (capillary) stress, but were in some local energy minimum.

Measurements of the changes in height of the drying surface showed an initial reduction in height associated with the passage of the packing front and the initial formation of the saturated region, see Fig. 2. The experiments were conducted on samples where $l < l_{\mathrm{sat}}$ so that the packing front disappeared before the pores had started to drain of liquid. As the packing front disappeared, it is expected that there is a rise in the capillary tension. As this occurred a second reduction in height was observed, as shown in Fig. 2, and coincided with the onset of cracking. From measurements of the height changes and the volume fractions of solid in the two materials, the change in average inter-particle separation was estimated to be approximately 7 nm. After this collapse into touching contact, the film would be in tension, giving the required driving force for cracking.

An estimate for the capillary pressure required to cause the collapse of the particles into contact can be obtained as follows. From Fig. 1(d), the cracks are observed to have grown a distance approximately 1/2 of the way through the saturated region. If the capillary pressure at the pore-emptying front equals $P_{\mathrm{c,max}}$ and that at the packing front it is negligible[14,52] and using the results of the fluid flow analysis the capillary tension at the crack tip should be approximately 1/4 of the maximum capillary pressure. That the pressure to cause this collapse is a significant fraction of the capillary pressure and explains why the tendency for cracking scales with the capillary pressure.

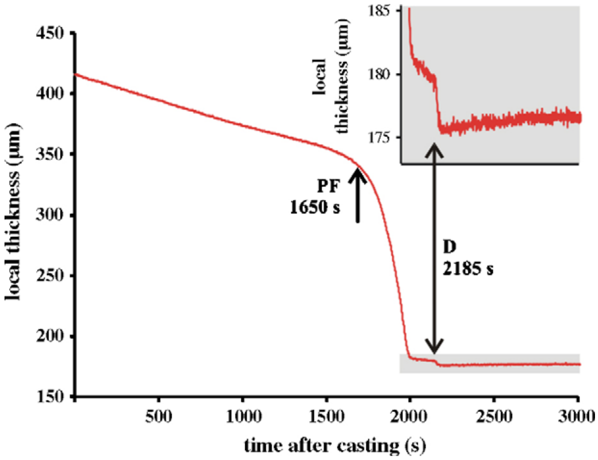


Fig. 2. Variation of local thickness with time after casting for an alumina suspension (350 nm diameter, 0.3 volume fraction of solids). The large drop in thickness, at PF, at approximately1650 s corresponds to the passage of the drying front. Note that there is a subsequent contraction, at 2185 s, which is associated with a change in thickness of the saturated region.

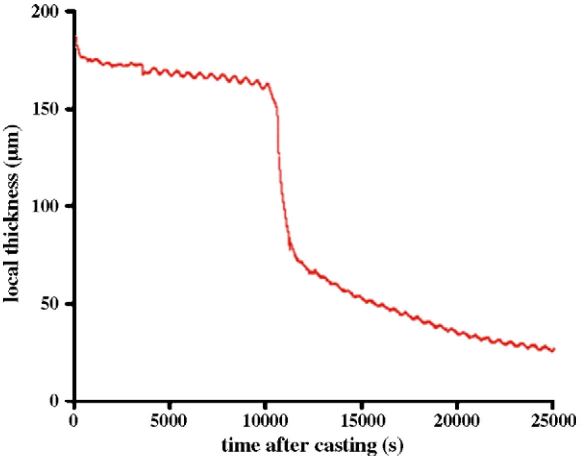


Fig. 3. The variation of the local thickness in a colloidal silica (22 nm diameter, 0.45 weight fraction of solids), Ludox CL-X. The passage of the drying front is clear. A post-packing strain occurs but over a longer period and is much larger than in the alumina in Fig. 2 with a larger particle size.

The similarity of the crack patterns in many systems indicates that a strain after the packing front has passed should be observed in many different systems, although this has only ever been reported in alumina.[14,21] To investigate this, colloidal silica (Ludox CL-X) was dried on a glass substrate. Cracking occurred in a manner very similar to that in the alumina, although the crack patterns were somewhat finer. The change in surface height measured at some fixed position on the drying film is shown in Fig. 3. The passage of the packing front past the measuring front can be clearly seen. However there is no rapid collapse of the type seen in the alumina suspensions. Rather there is a gradual strain occurring over some considerable time interval. If the height change is actually associated with the collapse of some residual repulsive layer, so that particles in the saturated zone come into proper contact it would appear that this is taking place gradually, perhaps as the drying front moves inward from the top surface.

This gradual reduction in height was not associated with the colloid spreading out. Not only was there was no evidence of any height change while the material was fluid, but also the later contraction took place after the passage of the packing front and the saturated region had formed. The height change must therefore be associated with a decrease in the average particle separation. Post-packing front strains are therefore not specific to alumina.

6. Non-touching networks

It seems sensible to ask whether there is evidence for the formation of non-touching networks with some mechanical strength. However inter-particle forces at small separations are still not fully understood see the reviews by Ninham[55] or Lewis[56] for example. Oscillatory force behaviour has been reported at small separations and has been associated with successive layers of electrolyte being squeezed out from between the particles.[57] Furthermore, repulsive forces have been measured at small separation between mica plates[58,59] and attributed to competition between hydronium ions and counterions for surface sites.

These ideas have been developed by Lange and coworkers[54,60–71] on alumina suspensions containing large quantities of salt. Wet bodies with a solid volume fraction less than 0.54 were ductile, but at higher volume fractions (∼0.6) became brittle.[64,67] They suggested that the ductile networks were made up of non-touching particles. Furthermore they found that the pressures required to transform a ductile (non-touching) network into a brittle (touching) one were of the order of the capillary pressure.[72]

A similar, everyday observation is that of paint in the *touch-dry* state, where a light touch has no effect, but continued pressing leaves a print. Such an effect might be more easily explained by a change in inter-particle forces, rather than by a relatively small increase in the volume fraction of solids. The idea is also consistent with the observations of Dufresne at al.,[52] who found that the particles behaved as if they were approximately 5 nm larger than the size of the silica particles used, suggesting that the effect was associated with surface layers of some kind, and similar to the values found in the alumina suspensions described above. The existence of such non-touching networks is therefore quite consistent with existing ideas on inter-particle forces.

7. Cracking in non-touching networks

For a non-touching network to form, the overall potential energy must vary with separation during drying according to the schematic shown in Fig. 4, as described elsewhere.[54,73,74] In the fluid colloid, the separation corresponds to the point marked ‘A’. As drying occurs the particles are pushed toward one another with a first maximum at ‘B’. This gives the separation of the particles forming the saturated region and the magnitude of the peak is presumably associated with some DLVO-type potential. Once the particles enter the saturated region, the potential energy falls so that the particles are trapped and will not redisperse when rewet. However to be pressed into contact requires that the particles are pushed over the barrier at ‘D’. From the estimates

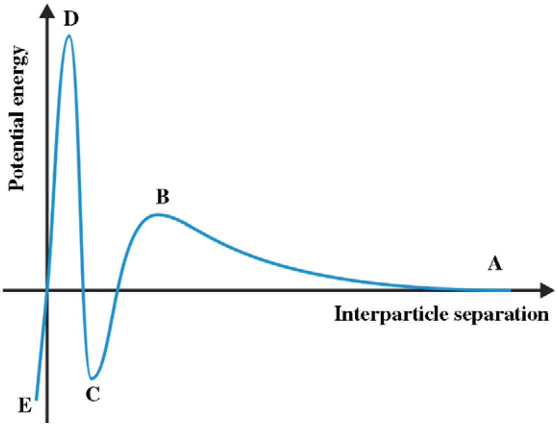


Fig. 4. A schematic of the potential energy change with separation during drying: (A) corresponds to the initial separation of the particles in the colloid; (B) is the first DLVO-type maximum; (C) is the secondary minimum in which the particles in the saturated region lie; (D) is the maximum energy that must be given to a particle before it will spontaneously fall into contact at (E).

above, the magnitude of this energy barrier (into the primary minimum) is about 10^6 times greater than the thermal energy, so that thermal activation is negligible. It is for this reason that the compressive force on the particles is so important. However once the particle's potential energy has been increased to that at the maximum, 'D', the particles will move spontaneously into touching contact, so that the misfit strain is associated with the decrease in particle separation between 'D' and 'E'. In this case the action of the stress has given rise to a spontaneous stress-free strain in the unconstrained free film, as required.

Although this approach is cast in different terms to those based on the relaxation of capillary tension, capillary forces are what push the particles into contact. When the collapse occurs, there will be a reduction of the capillary tension in the liquid. The requirement to have the particles initially non-touching is so that the observed densification can occur, while at the same time giving rise to a genuine tensile misfit strain as the particles are pulled over the large repulsive barrier. Furthermore, it gives an explanation for the residual strain that is often observed, where cracking has not occurred, for instance where the layers are very thin.[14]

The viscous flow of water now acts as a resistive term in the fracture process against which the driving force for cracking must operate, similar to plastic flow in a metal,[75] rather than being a process driving cracking.[35,52] There is still the requirement that the particles do not change their neighbours, as this would relax any driving force. There is as yet no direct evidence that shows how the particles move in the later stages of drying and in particular whether the strains that occur allow all driving forces to be relieved.

8. Concluding remarks

There is clear evidence that cracking of a particulate network during drying is associated with the maximum capillary pressure. Cracking has been described either in terms of relaxation of the capillary tension in the liquid or in terms of the collapse of a particle network where the particles were not initially in contact. It is shown that the latter gives rise to a reduction in capillary tension of the liquid and could, presumably, also be described in this way. However capillary tension may also be relaxed by particles changing their neighbours and allowing a drying film to undergo a macroscopic shear strain. If it is assumed that the particles initially come into touching contact, then the observed densification can only occur by particles changing their neighbours. This reduces the crack driving force and occurs in the region where such relief would have maximum effect. Furthermore the idea of a non-touching network allows the viscous flow of the water to enter any analysis as a resistance term, rather than being essential to allowing cracking to take place. There is work in the literature consistent that would give the required variation of potential energy with particle separation, as well as other experimental evidence that has been interpreted in terms of non-touching networks. However there is no direct evidence for such networks. A central feature of any further work should therefore be the nature of the network in the saturated state and how the particles move with respect to one another as the saturated region disappears and the liquid enters the drying compact.

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