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Review

Craquelures and pictorial matter

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ABSTRACT

Craquelures in pictorial layers are the most visible aspect of the "life" of a painting. The large variety of morphologies is caused by the different mechanical behaviours of the layers such as support, preparation layer and paint layer exhibiting specific physicochemical properties. In general, cracking affects the aesthetics of a paint layer: thus, from a strictly aesthetic point of view, craquelures are undesirable. However, the presence of craquelures can be of great interest in judging authenticity of a painting, for conservation and restoration of paintings, and to follow the evolution of a network of craquelures as a function of the environmental conditions. Moreover, the morphology of craquelures reveals the mechanical behaviours of the pictorial layer that change due to the ageing of the painting and give information about the methods used by the artist or the conditions of conservation. In this way these processes are highlighted using model systems to propose a potentially non-invasive method to deduce quantitative information about mechanical properties of a pictorial mater that are of great interest for cultural heritage.

Introduction

The large variety of crack patterns as depicted in Fig. 1 reflects the complexity of paint layers. The main components of a paint layer are the pigments, e.g., stiff particles, and the binding medium that is a compliant matrix. The function of the binding medium is to ensure cohesion of the pigments together. Binding could be drying oil (linseed, poppy or safflower oil for the most common), animal glues (of skin, fish, rabbit, deer antlers . . .), wax, eggs. . . In the 20th century, synthetic binders appear and are emulsions of water and acrylic resins [1]. The oils are generally siccative (linseed oil, walnut oil, flaxseed oil . . .) which means that they solidify through oxidation and polymerization processes. This chemical drying process concerns oils whereas glues solidify through physical drying process with solvent evaporation. The oils are composed of unsaturated triglycerides. The polymerization finally results in a three-dimensional network that constitutes a solid paint layer. This whole process depends on the temperature, exposure to light and oxygen. For acrylic paints, the binder is an aqueous emulsion of acrylic polymers. Pigments provide the colour of the paint layer and are made up of solid particles obtained mainly from natural origin (mineral elements, plants . . .). Depending on the material used and the preparation method, pigments exhibit various mechanical properties, size, polydispersity and surface roughness [2]. These characteristics affect the mechanical properties of the solid paint layer. Pigments can interact with the binding medium; they can be acidic, basic or siccative; the so-called siccative pigments increase the speed of chemical drying which means that the oxidation is faster and the cross-linking network denser. Basic pigments combine with the fatty acids of the binder and strengthen the cohesion of the film by covalent bonds with a higher elastic modulus [3]. In general, cohesion and mechanical properties of paint are related to interactions between pigments and binder. Two parameters are key factors to characterize the interactions: the concentration of pigment particles and their shapes. Experiments in the domain of conservation-restoration of art paintings have shown that, from pigment to another (with the same binder), the elastic modulus of paint can vary by three orders of magnitude.

Some additives are possibly incorporated into the paint to change its viscosity, its stability or its mechanical properties. They can be surfactants, solvents, plasticizers, additional binder or other painting medium, to change the viscosity or cohesion or appearance (opacity, brightness . . .), or even antioxidants whose effects are opposite to siccatives and delay the drying process. Over time, each colour maker has added specific components whose number currently exceeds more than 30 components in a colour tube. It turns out that because of the varying chemical composition, paints after drying, exhibit a wide range of mechanical properties from elasto-visco-plastic to brittle.

To make a painting, the artist coats a superposition of various layers, each exhibiting specific composition and thickness (impasto, glazes, washes. . .). The most common supports are

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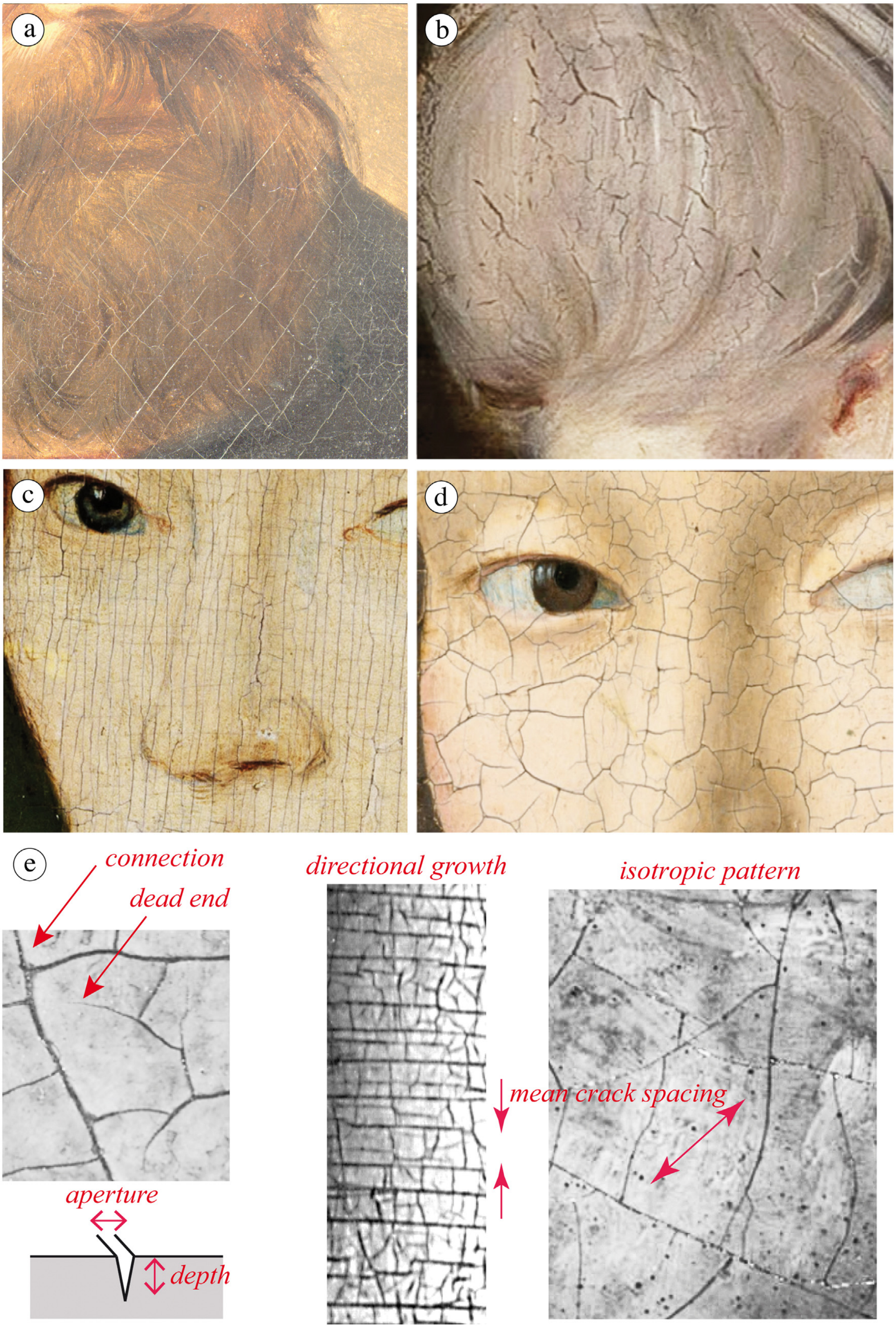

Fig. 1. A few examples of the large variety of craquelures in easel paintings. (a) A network of cracks along with the diagonal stripes due to the deformation of the canvas (Saint Jacques le Majeur, Georges de La Tour (1593–1652) - Toulouse- Lautrec d'Albi - Copyright C2RMF - P. Cotte, R. Pillay). (b) Junctions or terminations of cracks (The Ladies Waldegrave Joshua Reynolds - National Gal- leries of Scotland - Google Art Project). (c) Cracks along the vertical axis on a panel painting (Portrait of Mary of Guise, Queen of James V of Scotland and mother of Mary, Queen of Scots Corneille de Lyon - National Galleries 730 of Scotland - (Google Art Project). (d) Broken network of cracks ("Portrait of a Young Girl", Petrus Christus (between 1465 and 1470), oil-on-oak panel, Gemaldegalerie, Berlin (Google Art Project, http://www.prestel.com, Prestel Verlag / Rainald Grosshans // Photo: http://www.bpk-images.de, b p k - Photo Agency / Gemaldegalerie, Berlin / Jorg P. Anders)). (e) Some characteristics of a network of cracks.

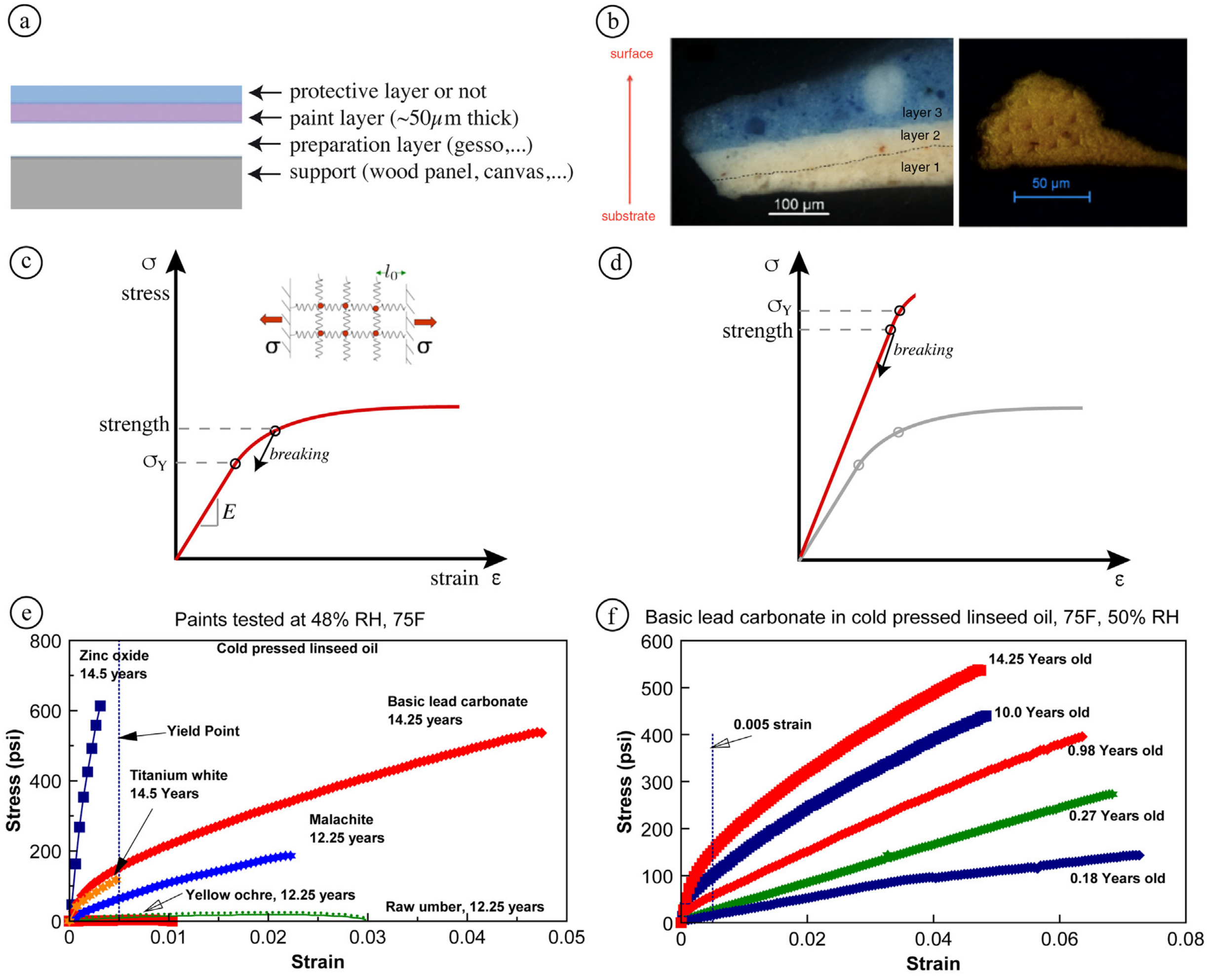

Fig. 2. (a) Cross-section showing a typical stratification of a paint layer. (b) Optical microscope image showing the white ground layers (layer 1 and layer 2, applied on top of the canvas) and the blue painting layer (layer 3, applied on top of the ground layers); optical microscope image after nanoindentation measurements. Reprinted by permission from [19] (e.g. Nature/Springer/Palgrave). (c,d) Typical stress/strain curve for a ductile material (c) and for a brittle material (d). The main physical properties are highlighted: elastic modulus, E, strength and yield stress, σY. (e) Stress strain tests conducted of paints made with different pigments: the different pigments have a dramatic effect on the mechanical properties of oil paints. (f) Stress versus strain plots of basic lead carbonate (lead white) paint made with cold pressed linseed oil at different ages. Even after 14.25 years, the paint is still gaining in stiffness and strength. These plots indicate that the processes that cause the increase in stiffness and strength show little indication of slowing down. (e,f) Reprinted from [20] (https://repository.si.edu/handle/10088/7055).

wooden panels (for the oldest paintings) or canvas, most of the time covered with a primer (glues...), to reduce the porosity of the support and improve the adhesion of the following layers. The glues can be of animal origin (rabbit, fish...) or synthetic (vinyl and acrylic adhesives in emulsions). They can be a mixture, as happens in the case of the" ajicola", which is a mixture made with garlic and animal glue. In all cases, they consist of polymers in an aqueous medium which, after drying, generally form a solid white layer. Sometimes, these glues can even be applied in a solid state in the case of the natural glues. For example, it was common that the glue ("cola de guantes") was applied in a solid gel with a spatula along the canvas during the Spanish Barroque period. The preparation layer allows the artist to obtain a favourable surface for the paint layer, interfering in its texture, colour and absorption. This layer isolates the pictorial layer from the support, to both protect the support, and erase its irregularities. This preparation layer can be water-based (if using glues), oil-based (if using oil) or a mixture (if using eggs, half water-based, half oil-based).

It is made of basically three components which are: (i) binder (glue, oil, eggs...) (ii) inert filler-charge (calcium carbonate, calcium sulfate in the case of the first layers of preparation for panel paintings) which affects the texture of the paint layer (iii) other additives: siccatives, pigments (to obtain a colour-based or a coloured background -which affects the appearance of the paint layer) [4].

Then comes the successive paint layers (usually 50 μm thick). Finally, to protect the pictorial layer, most of the paintings are covered with varnish (varnish being a binder without pigment, Fig. 2a). Obviously, the thicknesses of the different layers are very variable according to ages or artists and according to the characteristics of the painting medium. The preparation layer exhibits a thickness between 30 and 200 μm, while the pictorial layer is between 100 and 500 μm. Besides, the layer of varnish is around 100 μm. Each layer exhibits specific formulation and mechanical properties; therefore, each layer evolves specifically over time and has its own drying time. In addition, the interfacial conditions (adhesion between layers, relative elastic modulus) will play an important role too. Thus, the multi-layered structure of the pictorial layer adds complexity to the study over time of a paint [5]. This system is subjected to various sources of stress with ageing. The stress build-up in the pictorial layer is caused by various factors: chemical drying (cross-linking mechanisms for oil or physical drying, e.g. evaporation of solvent) [3,6], environmental changes (hygrometry and temperature variations) [7,8], chapter by S. Michalski in [9], physicochemical modifications due to ageing (oxidation, polymerization), possible impacts, or vibrations due to transportation [9].

Table 1
Non-comprehensive list of characteristics of cracks and mechanical instabilities; some references are given on an indicative basis.

Craquelures	Pattern of cracks visible at the surface of a paint layer [11].
Channeling crack	Crack that may arise in a solid layer subjected to in-plane tensile stress. The layer is supported by a substrate/sub-layer of finite thickness. The term channeling highlights the fact that the crack extends on the layer thickness [13].
Drying or premature crack	A crack that forms at early stages of the paint layer solidification. The process results from internal stresses induced by evaporation of solvent, either water or organic liquid, or chemical process. Such a crack usually confines to the layer and does not penetrate the entire layered-structure from the surface to the support [12].
Age crack	A crack that develops during the lifetime of the paint layer. Such a crack results most of the time from mechanical stresses originating when the painting is subjected to environmental changes (temperature, humidity rate, light,,. . .). Age crack has sharp edges and usually penetrates deeper in the layered-structure; its aperture is generally smaller than for a premature crack [12].
Delamination	Interfacial cracking leading to the separation of a layer from a support. Such a process occurs along a plane parallel to a surface [13,14].
Blistering	Disruption leading to a separation of the paint layer from the ground, or both layers from a support [13].
Blanching	Alteration resulting in a blurring effect or partial whitening of the varnish or the paint layer; this alteration is generally known to appear on paintings kept in a humid environment [15].

The consequences of this stress built-up will be the appearance of degradations on the painting. The mechanisms of degradation are numerous and complex, they differ over time. Some process happens very quickly after the creation of the painting, others are very slow and can appear years, even centuries later. Curators have identified the various alterations observed on a painting and the main ones are yellowing, formation of metal soap [10], discoloration, cracks, blistering or loss of adhesion (detachments, flaking). The alteration processes are of various origins: chemical, physicochemical, mechanical or even biological. Chemical alterations correspond to the chemical ageing of materials mainly due to oxidation, hydrolysis or photo-oxidation reactions (UV irradiation which initiates an oxidation reaction). These mechanisms are respectively due to the action of oxygen, water and light and they act on optical (yellowing, discoloration), and mechanical properties of materials (loss of cohesion). However, the great majority of damages on a painting are caused by mechanical instabilities in the material [11–13].

Research aims

In this paper we present results obtained on model systems such as colloidal suspensions in the aim of proposing potentially non-invasive method to deduce quantitative information about mechanical properties of the pictorial matter in paintings. By studying the morphologies of crack patterns observed in paintings, one can deduce some physical parameters characteristics of the pictorial matter. This can help to authenticate paintings and to improve our knowledges on the techniques used by the artists.

Alterations leading to mechanical instabilities in pictorial layers

Among the mechanical instabilities occuring in pictorial layers are: “channeling cracks” (or cracks in the film thickness), “delamination” process governed by a loss of adhesion between layers, or “blistering” (Table 1). These alterations arise in a material which can no more withstand high stresses. Cracks are doubtless the most apparent sign of ageing of painting. Cracks are organized in a network and form specific patterns whose morphology can be related to the mechanical properties of the matter. In this way crack patterns can be considered as the fingerprint of the painting and they are a testimony of the history of the work of art. Thus, the perception of a painting depends on the preexisting cracks. The visual perception of painting with cracks is a subjective appreciation as it depends on the watcher, the moment and the conditions of contemplation. Cracks may appear undesirable as it is a network of lines more or less contrasted which divide the subject into small fragments. This network superposes to the image and can affect the effect of depth of field. However, it could be perceived as pleasant through these lines more or less short and wide that makes the visual result less smooth. Crack networks give clearly a sense of authenticity provided that they are limited in number [14]. Whatever the perception is, the presence of “craquelures” (Table 1) increases the market value of the painting since related to the time elapsed. Thus, the way the crack pattern affects the perception of a painting and the aesthetics of the image is a multidisciplinary work which requires a joint analysis between specialists such as historians, curators, semiologists and physicists. Besides, a large variety of craquelures affects easel paintings throughout their lifetimes and results from a multitude of effects. As a consequence, a crack network can be characteristic of a period or of a country. A classification by de Willigen [13] proposed to take into account a reduced number of criteria among which the shape of the cracks (sinuous or straight), the type of connections between cracks, the distance between cracks, the aperture of a crack, the mean orientation (anisotropy or not) or the organization of crack. Few examples of the variety of crack patterns encountered in the carnation (face of a portrait) for paintings of XVI and XVIII centuries are reported in Fig. 1a–d. These include physical damage such as shock and vibration due to possible transportation [9]), biological agents (insects) or contaminants, radiation including light and ultraviolet, variation in relative humidity rate [7,8], and temperature, or paintings flood [15], etc. . . Besides craquelures are related to the type of materials used as well as the techniques used by the artist, or the conditions for drying or conservation. In particular, some craquelures are a characteristic feature of the period of the country of the artwork. Hence, Bucklow proposed a classification of the crack pattern morphologies based on the geographic location: it is Italian, Flemish, Dutch or French typical styles leading to distinct crack patterns with specific features (straight cracks in Flemish or curved ones in French style) [16]. In light of the multiplicity of craquelures encountered, the analysis of painting cracks is guided by various motivations. Craquelures are particularly relevant to authenticate paintings as they represent the fingerprints of the painting and the mark of time left on painting throughout its life. In this way, work was investigated on an incomplete series of ten Apostles and a blessing Christ, of Georges de La Tour (1593–1652) [17]. It was known that most of the originals in this series have given way to copies on a date which remains unknown. Among the ten paintings, only two were identified as autograph work. It was then essential to distinguish between original or variants in the other paintings. By comparing relevant characteristics of crack patterns, it has been shown that some paintings of the series were possibly associated with original paintings as autograph works, while others were suspected to be copies. Thus, such a study is a way to compare different paintings and possibly highlight or not the association of a painting to a particular artist.

Fig. 3. Example of premature cracks. "Cherubini and the Muse of Lyric Poetry" Ingres (1842); Louvre Museum (Wikimedia Commons). A network of opened cracks formed in the face of the Muse.

Therefore, the stability of a crack network with time in relation to the surrounding is of great importance in the domain of conservation. Moreover, the study of the crack morphologies is a non-invasive method to reveal local and global physical properties of the matter. This method could be complementary to other techniques of investigation to obtain information on the materials and methods used by the artist as well as the conservation and restoration methods executed on the artwork. Quantitative information on the painting can then be revealed thanks to the strong link between crack pattern and physical properties of the matter. To understand this link, it is essential to consider the mechanical properties of the matter that is subjected to drying and then ageing. Finally, one of the main aims of conservation of artworks is to avoid mechanical instabilities or to limit their time evolution.

Mechanical and physical properties of the paint layer

Paint layers combine different rheological and physical properties that provide visco-elasto-plastic to brittle behaviour from the solidification process to the ageing. Depending on the composition of the paint layer, the time evolution of the mechanical behaviour may take tens of years or even centuries. The main physical parameters that determine the mechanical properties of a paint layer are the elastic modulus, E, that captures the stiffness of the material, the strength at which the material breaks, and the yield stress, σY, at which irreversible plastic deformation becomes noticeable (Fig. 2c). A typical stress/strain curve displays two regions: the elastic one for low strain and the plastic one for higher strain values. A material behaves elastically up to the yield stress σY; then the material enters a plastic regime characterized when unrecoverable plastic deformation takes place. Hence, the solid material is called elastic when it recovers its original shape after stresses applied to it are removed. The magnitude of the elastic modulus E is governed by the intensity of bonds between particles (see insert in Fig. 2c) if the material is considered as a particulate system. Thus, a high value of E means that a high level of stress is required to produce a small strain; such materials are referred to be stiff. If a fracture appears in this elastic regime, the material is called brittle (Fig. 2d) and both broken pieces can perfectly fit together. It is not the case in the plastic regime as a result of the ductile behaviour of the material (Fig. 2b). These physical properties are linked to the structure of system. In particular, in the case of dry powder compacts, even if the exact applications of this model, in simple systems, is still under discussion in the community, the mechanical behaviour of a single particle, the particle size, the arrangement and the interaction energy between the particles are responsible for the stiffness of the material as highlighted through the following equation [18]:

$$E \sim \varphi^4 \left(\frac{E_0^2 \gamma}{a} \right)^{1/3} \tag{1}$$

$$\sigma_Y \sim \frac{\varphi \gamma}{a} \tag{2}$$

where φ is the volume fraction of the spheres, a their size, $E0$ the elastic modulus of a single particle, and γ the interaction energy between the sphere assembly. In particular Eq. 1 shows a strong dependence of the stiffness of the material with the packing of solid particles, φ. A paint layer is a more complex system made of particles, e.g. pigments, and a binding medium. A model of packing of spheres could be considered to model the paint layer provided modifications in the interactions between particles are considered due to the binding component. Thus, the nature of the solvent in a drying colloidal dispersion impacts the mechanical properties of the final consolidated gel [19] and consequently the crack patterns. Another degree of complexity involved in artworks lies in the time evolution of these mechanical parameters. The difficulty to predict the evolution of these parameters with ageing lies in the time evolution of each component under their mutual interactions. In the field of conservation, direct measurements on paint samples have been performed to estimate the mechanical properties. The main techniques used are unidirectional stretching [20] and indentation testing was performed as a local method of mechanical investigation on cross-sectional paint layers [21,22] (Fig. 2b). Experiments are performed at constant humidity rate with a model paint made of various pigments in a cold-pressed linseed oil. Measurements reveal a high variability of mechanical behaviours as a function of the pigment used (Fig. 2e). The binding medium affects the mechanical properties of the paint, given that, over time the nature of the binding medium has changed from water or egg (tempera paint) to oil leading to softer paintings and finally to acrylic systems by now. For oil binding medium, generally, the paint layers may get stiffer during ageing (Fig. 2e). Crack patterns display various and complex morphologies and arise at different moments of the painting life. Some cracks appear a few hours or days after the creation of the painting (drying cracks) and many years after, new crack patterns can occur (ageing cracks). These two main types of cracks emerge in a material with different mechanical properties as young and age paint layers exhibit different response from mechanical stress.

Young paint layers generally exhibit ductile behaviour as sketched in the stress-strain curve in Fig. 2c. In the first hours of the painting life, the drying process induces large internal stresses due to the solvent evaporation (physical drying) [23], or chemical alterations (chemical drying). As a consequence of these stresses associated with defects in the paint, cracks can occur in the plastic regime. These cracks are named “drying or premature cracks” (Table 1) as they appear in the first days of the life of the painting. Such a crack network propagates at short timescale. A pattern typical of drying cracks can be observed in the face of the “Muse of the Lyric Poetry” in the painting in Fig. 3. An important feature of this pattern is the large aperture of the cracks. In the case of this painting, the artist has left his disciple finishing the face of the Muse. The disciple possibly proceeded differently by using other components to make the colour or using a different method or both. This results in a pattern of drying cracks only in this part of the paint layer which exhibits very specific with large aperture [24]. The matter undergoes large strain as it presents a ductile behaviour which implies this large aperture between 2 cracks revealing the underlayer in black colour. The properties of the paint layer evolve during its lifetime. In particular the mechanical properties change from a ductile to a brittle material (Fig. 2f). They result from a modification of the structure with time, ageing, due to oxidation, light, or many other processes. Thus “age cracks” (Table 1) are specific of a brittle material with having a thin aperture as the medium exhibits a higher resistance to shrinkage than a ductile material. These cracks penetrate deep in the stratigraphy of the pictorial layer and the resulting crack patterns are similar to what is observed in ancient ceramics (Fig. 6f).

Laboratory models

In the light of the complexity of a pictorial matter that evolves, laboratory models with tunable physicochemical properties are considered to recover typical patterns such as age or drying cracks. Recovering typical crack networks observed in real paintings using laboratory models allows us to relate crack patterns and properties of the matter as well as crack patterns and their causes. The use of laboratory models does not pretend to mimic the number of processes that occur throughout the life of a paint layer, that is still not well known. However, the model aims to relate one specific morphology to the properties of the matter and the involved mechanical stress. Good candidates are aqueous dispersions of well calibrate stiff or soft nanoparticles that are charged in surface.

The adaptability of the systems, such as particle volume fraction, interparticle forces, size, allows us to deal with a wide range of mechanical instabilities. If the well-calibrated size of the particles does not reflect the pigment size used in real paint layers, the nanoparticle size corresponds to the lengthscale associated with the surface roughness of pigments such as Carbon [2].

During the solidification of such a dispersion, the physical properties vary from a classical Newtonian behaviour to an elastic-viscous-plastic, then to brittle behaviour. More precisely, there are two main routes to solidify a particulate dispersion. A first way is to tune the interparticle interaction by adding ionic species to the dispersion: hence, by screening the charges borne by the particles, the viscosity increases with kinetics strongly dependent on the concentration of the ionic species content [25]. The so-called gelation process is then governed by a “chemical drying”. For dispersion of nanoparticles, the chemical drying consists of an aggregation process which ends to the formation of a gel then to a solid. A second route to solidify a layer is to evaporate the solvent: therefore, the structuration is governed by a “physical drying”. In the following section, we only report laboratory models related to paint layers using this second process to solidify. The drying process is classically divided into successive stages of [25]. During the first stage, the particle volume fraction increases as the solvent evaporates at a constant rate. Then the resulting close-packed network of particles shrinks due to the solvent removal. Due to the adhesion on a sublayer, a non-uniform shrinkage can arise, that causes differential stress over the layer thickness. The resulting stresses are the driving process for crack formation in the system layer/sublayer.

Informations extracted on the pictorial layers from the crack patterns

A descriptive framework of crack patterns was proposed at the end of the 1990s [13,18,26]. Adapted from this classification, a list of parameters characterizing a network of crack lies in:

- the predominant direction and orientation of crack network: in particular, cracks along the diagonal stripes can be caused by an over stretching in the corner of the frames (Fig. 1a).
- the connection between cracks (Fig. 1e).
- the mean crack spacing in an isotropic or anisotropic patterns (Fig. 1e).

As well, the main features characterizing an individual crack lie in:

- the crack aperture (Fig. 1e).
- the crack depth (Fig. 1e).
- the local change of direction of a crack path (jagged or smooth depending particularly on the heterogeneous materials). It has to be noted that the heterogeneity of the pictorial layer plays an important role in the formation of cracks. In particular, the more heterogeneous a material is, the most defects the material is supposed to contain. Historical paints are more heterogeneous than models, resulting in easier nucleation processes.

The challenge is then to quantitatively relate the main parameters of craquelures and the mechanical behaviour of the material. In the following three parameters will be particularly considered to link crack pattern and the mechanical properties of the paint layer: i) the connection between cracks, ii) the mean crack spacing, and iii) the crack aperture.

i) Connection between cracks. The terminations of cracks reveal the mechanical properties of layered material. In this way, a craquelure often results from a broken or connected network determining the difficulty or the capacity for a crack to propagate in a solid. The following considerations aim to relate the connection between cracks and the mechanical properties of layered material. For a linear elastic material, the critical condition for cracking is governed by Griffith fracture theory. This theory states that the elastic energy available for crack growth requires the energy needed to create new crack surfaces in the layer. In the case of a layer of thickness h and elastic modulus Ef on a sublayer of elastic modulus Es, it comes [27]:

$$\frac{\sigma(h)^2 h}{2E_f} g(\alpha, \beta) = h\,\Gamma_f E \sim \varphi^4 \left(\frac{E_0^2 \gamma}{a}\right)^{1/3} \tag{3}$$

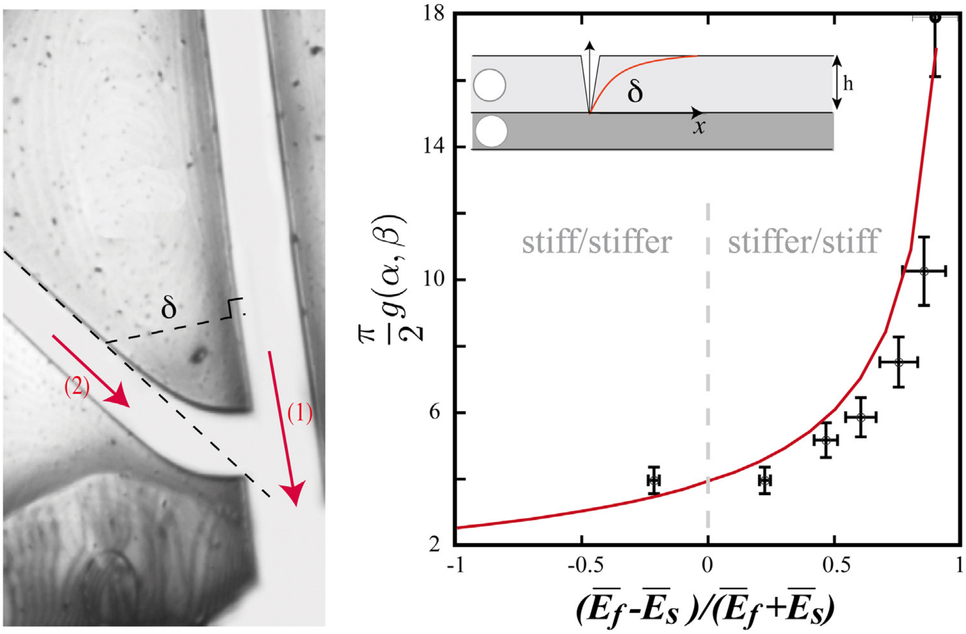

Fig. 4. The interaction between two connecting cracks is quantified by the function g(α, β) as a function of the elastic modulus mismatch between the layer and the sublayer. Reprinted from [24], with the permission of AIP Publishing.

Where *σ(h)* is the mechanical stress that possibly depends on the layer thickness, Ef = Ef /(1 − *ν*f) is the effective elastic modulus of the layer (Poisson ratio *νf* of the layer), and Γf is the fracture energy of the newly created interfaces. *g(α,β)* is a dimensionless function of the Dundurs parameters α and β that depend on the plane-strain elastic moduli, and the Poisson ratios of both the layer and the sublayer. Since the ranges of variation of the dundurs parameters are −1 < α < 1 and 0 < β < α/4, the function g(α,β) accounts for stiff layers on stiffer sublayer or the opposite as reported in Fig. 4. In particular, when the elastic modulus of the layer is negligible with respect to the substrate: g(α, β) = 1. Through this function, the crack pattern in a layered material depends on the mechanical properties of both the layer and the sublayer. This is depicted in the connection between two cracks (see Fig. 4). When a crack of second-order (2) approaches a pre-existing one (1), the path of (2) starts to be affected by (1) at a distance of δ. This parameter increases with the thickness of the layer, and this evolution is well fitted by a scaling law which takes into account the role of the substrate. The value of δ depends on the thicknesses and the stiffnesses of the layer and sublayer that exerts a retiring force on the layer at the interface. For small strains, δ is found to be equal [27] to: $\delta/h = \pi/2\, g(\alpha,\ \beta)$. This behaviour was highlighted experimentally using a laboratory model made of two superposed layers; the properties of each layer were independently tuned from soft (deformable) to stiff [24]. For each experiment, we report the measured values of δ/h as a function of the elastic mismatch between the layer and the sublayer, e.g., α. The theoretical predictions related to the Dundurs model, well fit the experimental data [27]. For very soft sublayer, δ diverges and varies from *2 h* for two layers with the same elastic moduli to 1.2 h for a sublayer very hard. We have tested the validity of this model with two layers made of a binary mixture of stiff and soft particles. This method could easily be applied to provide quantitative mechanical behaviour such as the elastic modulus of the *2Ef* where *σ(h)* is the mechanical stress that possibly depends on the layer thick-sublayer or the thickness of a paint layer.

ii) The mean crack spacing particularly reveals the layer thickness and the mechanical properties of the layer. Indeed, one of the key parameter affecting the craquelures is the layer thickness. This geometrical parameter governs the elastic energy available in the system. The dependence of the layer thickness on the crack network, more quantitatively the crack spacing, has been investigated in several works. This is highlighted in paint layers as well as in laboratory models with different layer thicknesses as shown in Fig. 5. The fragment size has been extensively described as a function of the thickness in directional crack growth [28–30], in layered materials [31], and in isotropic materials [32–34]. Below a critical thickness, hc, the layers are generally crack-free as the elastic energy stored in the material is too low to extend any precursor of cracks (Fig. 5a). h_c is given by $h_c = \frac{2}{(1-\upsilon_f)Z}\frac{\Gamma_f E_f}{\sigma^2}$, where *Z* is a parameter depending on the crack geometry [28]. A typical value of hc is a few tens microns for our laboratory models.

Above this critical thickness, nucleation is energetically more favourable than below hc leading to various crack patterns. For thin layers, but close to the hc, the crack growth stops shortly after their initiation leading to crack junctions (Fig. 5b). Propagation is predominant in thicker layers: the network connectivity of a crack pattern usually changes with the layer thickness leading to a broken or close network of cracks (Fig. 5c,d). In the last case, the craquelures invade the plane of a layer following well-defined rules of Mechanics and Physics (Fig. 6). A crack path is governed by tension in the layer and as one is propagated, the component of the stress normal to the crack surface is released in the surroundings of the crack. Indeed, a first crack that propagates along the x-axis, relaxes the stress components along the y-axis, σyy, in its vicinity (see sketch in Fig. 6e); hence, the stress components parallel to the crack lips, σxx, are only weakly affected. The presence of a crack then affects the trajectory of a future one by modifying the stress field in its vicinity; the new crack connects to its neighbour perpendicularly (circled in red in Fig. 6b). Overall the network of cracks is formed by successive generations and is governed by a minimization of the energy. The plane of the layer is progressively divided into adjacent fragments with more or less regular sizes (Fig. 6a–d). One feature of this space division by the cracks is the number of neighbours of a fragment in accordance with the Euler theorem based on optimization of a network taking into account the number of edges and vertices [35] (insert of Fig. 7a). At the final stage of the process, it is possible to reconstruct approximately the temporal order of the cracking: the longer cracks are the first to appear, the cracks of second-order connect to the first one, and so on . . .

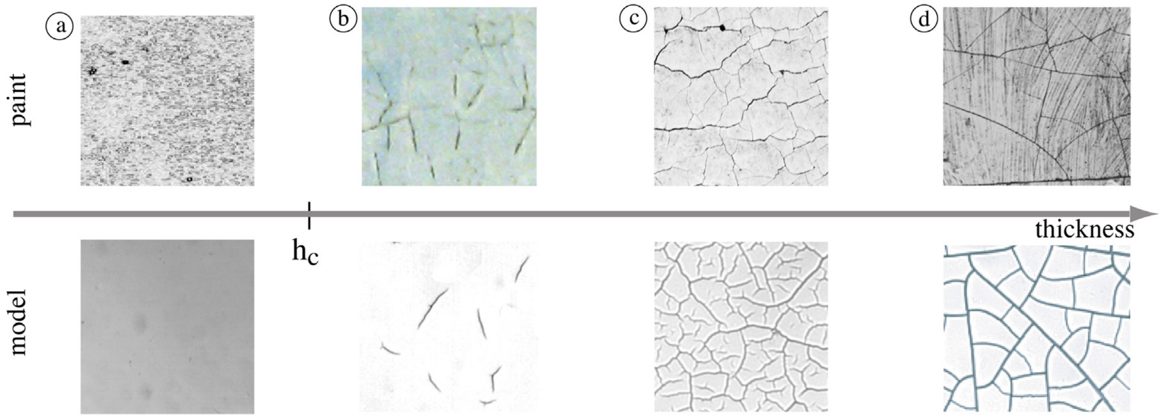

Fig. 5. Classical crack patterns as a function of the layer thickness. Similar crack patterns can be observed in real paint layers and laboratory models. For increasing layer thicknesses: (a) the layer is free of cracks below a critical thickness hc, (b) junction cracks are distributed over the surface, (c) a broken network of cracks or (d) a close network of cracks is formed.

[36]. It may be noted that the hierarchical organization of cracks is a generic process governed by tensile stresses in brittle materials. Thus, that kind of patterns can be recovered in materials such as Chinese ceramics subjected to temperature variations [37] as reported in Fig. 6f. Indeed, the resulting stresses satisfy the same constitutive laws. In the case of poroelastic media, tensile forces can be induced by variation in pressure of liquid pore whereas in the case of ceramics, cracks formed due to cooling: the shrinkage of the material is a response to cooling in this case. Considering a solid layer under given external stresses: the crack spacing depends on the mechanical properties of the layer, the sublayer properties and the layer thickness. Thus, the mean fragment size increases with the layer thickness in agreement with the following scaling law [38] (Fig. 7a):

$$\bar{l} = \left(\frac{2N\Gamma_f E_f}{P^2}\right)^{1/3} h^{2/3} \qquad (4)$$

where P is a typical local tensile stress in the structure, possibly related to the capillary pressure (difference in pressure across the interface between a liquid phase and the air, P being closed to the tensile strength of the material). Eq. 4 comes from a balance between surface and elastic energy in the same way than Eq. 3. Here, one starts from a fragment with an average number of edges, N, on an infinitely stiff substrate. Here the significant point is that the increase of the fragment size with the layer thickness strongly depends on the properties of the layer, through the elastic modulus Ef and the surface energy Γf.

However, Eq. 4 neglects the fact that the crack spacing will eventually saturate, rather than continuing to get narrower and narrower indefinitely. In this way, the saturation of the crack spacing can be explained by the existence, when the spacing is small enough, of a compressive stress in the center of one cracked segment, prohibiting the creation of a new crack [33].

Besides the mean crack spacing is a relevant indicator of the mechanical properties of the layer. In particular, in aged paint layers, craquelures are typical of brittle materials that behave mainly elastically. In this way systematic measurements of crack patterns were performed in a corpus of paintings selected in specific pictorial layers: the carnations (face of portraits) in paintings from the sixteenth century to the nineteenth century [22]. The results have shown a variation of the crack spacing over centuries as reported in Fig. 7b. In particular, the increase of the number of cracks over the years reveals the evolution of the material over time.

On the contrary, young paint layers exhibit viscoelastic behaviour and the resulting crack patterns mainly exhibit large crack spacing and large crack aperture [12,13]. Craquelures induced by drying process was reproduced in different modelled layers exhibiting tunable mechanical properties. These last were performed using a binary mixture of suspensions of both stiff and soft (deformable) solid particles, e.g. latex particles, in controlled proportions. The deformability of particles depends on the glass transition temperature of the latex particles in comparison with the ambient temperature. If the glass transition temperature of the latex particles is higher than the ambient temperature, particles are stiff. Contrarily, when the glass transition temperature is lower than the ambient temperature, particles are more deformable. As the drying proceeds, the colloidal dispersion turns into either a close-packed array of particles (stiff particles) or a continuous polymer layer (for only soft particles), with both having mechanical integrity [39]. The mechanical properties of dried layers were characterized using indentation testing. The method that consists in measuring the penetration depth, p, of an indenter tip of radius R in the material. In particular, we proceed to creep measurements where an applied force, $F0$, is maintained constant and the mechanical response is recorded as a function of time (Fig. 8). The resulting viscoelastic response of various layers was well described by a two-parameters law following the Kelvin-Voigt model [22]:

$$p^{3/2} \sim \frac{3}{4\sqrt{R}}\frac{F_0}{E_f}\left(1-e^{-t/\tau}\right) \qquad (5)$$

τ is the viscoelastic timescale that is characteristic of the material. This timescale varies from a few seconds to a few tens minutes when the viscoelastic properties of the material are modified. The behaviour of a layer during drying is driven by the mismatch between the viscoelastic timescale and the drying timescale, tD, that governs the mechanical stress buildup in the layer. This last depends on the layer thickness as well as the evaporation rate that is controlled by the environmental conditions. If the viscoelastic timescale is larger than the drying timescale, $\tau \gg$ tD, the stress is released in the material through viscous dissipation. As a result, the deformation of soft particles is energetically favourable and the layer is crack-free at the final stage. Inversely, if $\tau \ll$ tD, the stress is released by the formation of craquelures (Fig. 8). For soft material, the fragment size is larger than for brittle material [39]. Thus, modifying the mechanical properties of the model systems, it is possible to recover the different kind of patterns observed in paintings from crack-free to open or close networks of cracks.

To illustrate the strong link between craquelures and the mechanical properties of layers or the layer thickness, some particular patterns can be highlighted in Mona Lisa (Fig. 9). Indeed, particular craquelures can be hypothetically associated with the materials and methods used by Leonardo Da Vinci. Some craque-

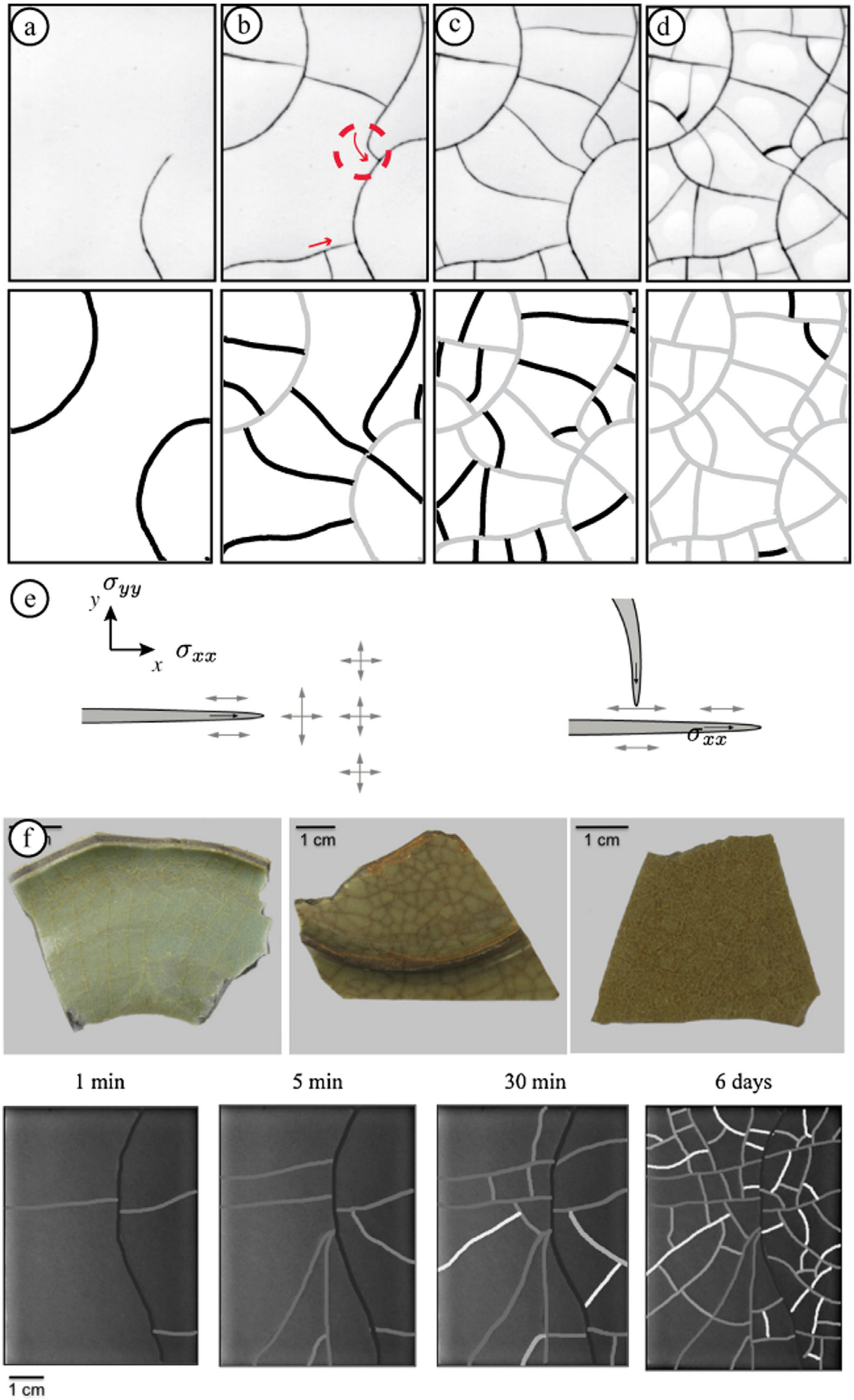

Fig. 6. Hierarchical formation of a crack network (laboratory model). In snapshot (a) a first crack propagated in the layer; then cracks of the second generation propagate and connect perpendicularly to the existing one. Cracks divide the plane of the layer into adjacent cells leading to the final pattern in (b,c,d). Reprinted figure with permission from [28]. Copyright 2019 by the American Physical Society. Below: The geometrical orders of the cracks. From left to right: first, second, third and fourth order. The cracks of lower orders are drawn in grey. (e) Sketch of the growth of cracks in an initially homogeneously stretched plane. (f) Photographs of three crackle wares from the Song Dynasty (960–1279 AD). Photograph series taken at different time intervals showing the propagation of successive cracks in a synthesized Song-like glaze during the cooling. From left to right: first generation in red, second in blue, higher orders (green, yellow, pink, light-pink). Reproduced from [29]. Copyright 2019 Elsevier Masson SAS. All rights reserved.

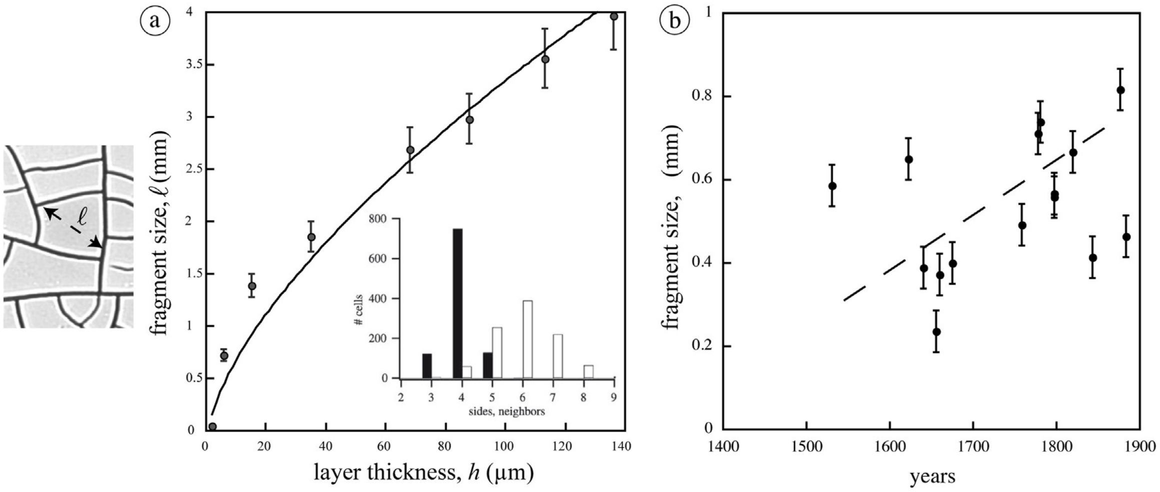

Fig. 7. (a) Measurements of fragment size as a function of the layer thickness in modelled layers. Each dot is an average value obtained on approximately 20 fragments of a layer made of silica nanoparticles (Ludox HS). The line is the scaling law. Insert: topological characteristics of a crack pattern: histograms of the number of sides (filled bars) and of the number of neighbours (empty bars); measurements investigated in ceramic plates. The average number of sides is 4.007 and the average number of neighbours is 5.98; Reprinted from [28], Copyright (2019), with permission from Elsevier. (b) Mean crack spacing, l, over years in real pictorial layers. Measurements have been performed on isotropic crack patterns, typical of ageing cracks, specifically in carnations (face of portrait), on high spatial resolution images provided by Cultural Institute of Google, The Art Project. It has to be noted that an important parameter, that is the layer thickness, is unknown. The dashed line is a guide for the eyes. Reprinted from [24], with the permission of AIP Publishing.

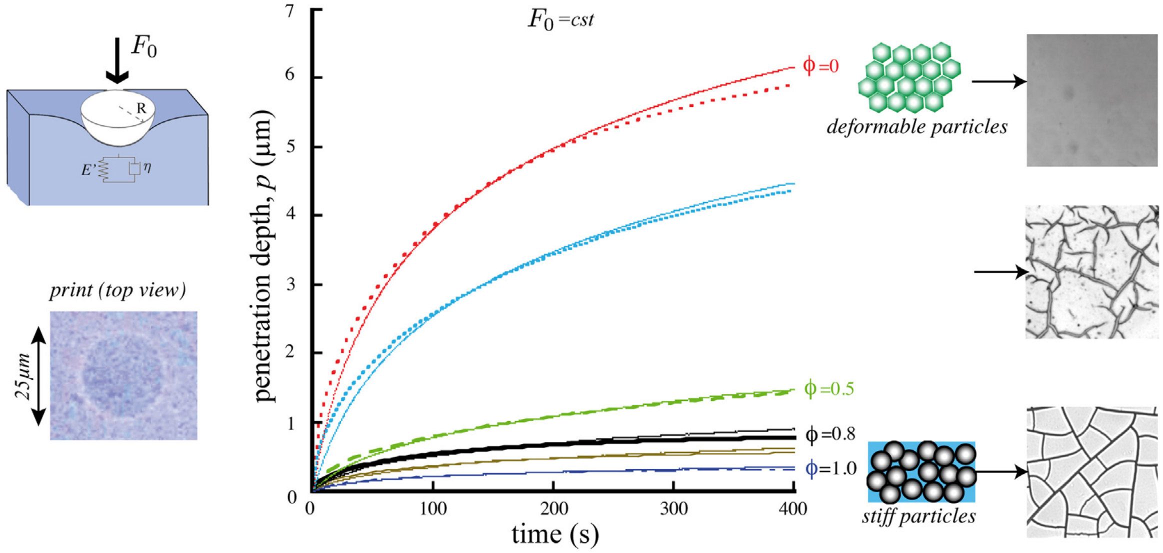

Fig. 8. Mechanical characterization of laboratory models using indentation testing on dried layers made of dispersed hard and soft spheres in controlled proportions (particle size ~ 30 nm). Left: schematic representation of the spherical tip-layer interaction; optical micrograph of the print at the layer surface after the spherical tip has been removed. Plot: Time variation of the penetration depth under a constant applied force F0; dried layers are 100 μm thick on a glass microscope slide. φ denotes the proportion of stiff particles: '$\varphi = 0$ corresponds to a layer fully made of soft particles resulting in an important viscous dissipation; $\varphi = 1$ corresponds to a layer fully made of stiff particles leading to brittle material. Dots are experimental measurements and lines correspond to theoretical predictions following the Kelvin-Voigt model [41]. Right: some typical crack patterns.

lures exhibit an isotropic organization as revealed in some in the sky and the landscape as shown. Another typical pattern of cracks can be observed in the carnation (pinkish colour of skin) exhibiting an array of parallel and deep cracks in the main direction of the ground of the poplar panel. The deformations of the panel with the variations of the humidity rate and temperature are possibly responsible for the formation of such pattern. Besides, a specific region of the paint layer in crack-free: the veil of Mona Lisa. In this region, Leonardo da Vinci applied his famous technique of Sfumato which consists in a layer-by-layer deposition of very thin paint layers made of a dilute solution of pigments; this technique permitted to tune the shades of colour and to smooth the facial outlines. The very low thicknesses of the layers, of the order of few microns, explain this crack free region.

iii) Crack aperture. The propagation of a crack path is irretrievably accompanied by the crack aperture in the perpendicular direction of propagation. The crack aperture depends mainly on the ability of the material to mechanically resist to shrinkage. Indeed, the aperture of one crack is a consequence of the rate of shrinkage possibly during the drying. This was highlighted by a model based on a balance between the drying stress in the layer and the shear friction force with the sublayer [24]. The main parameters in this model are the mechanical properties of the material such as the elastic modulus and the yield stress. This leads to a linear relationship between the final crack aperture and the thickness of the layer. Hence, the direct measurement of this parameter lies in quantifying information on the mechanical properties of the material. Statistics on the crack aperture were measured as a function of the layer

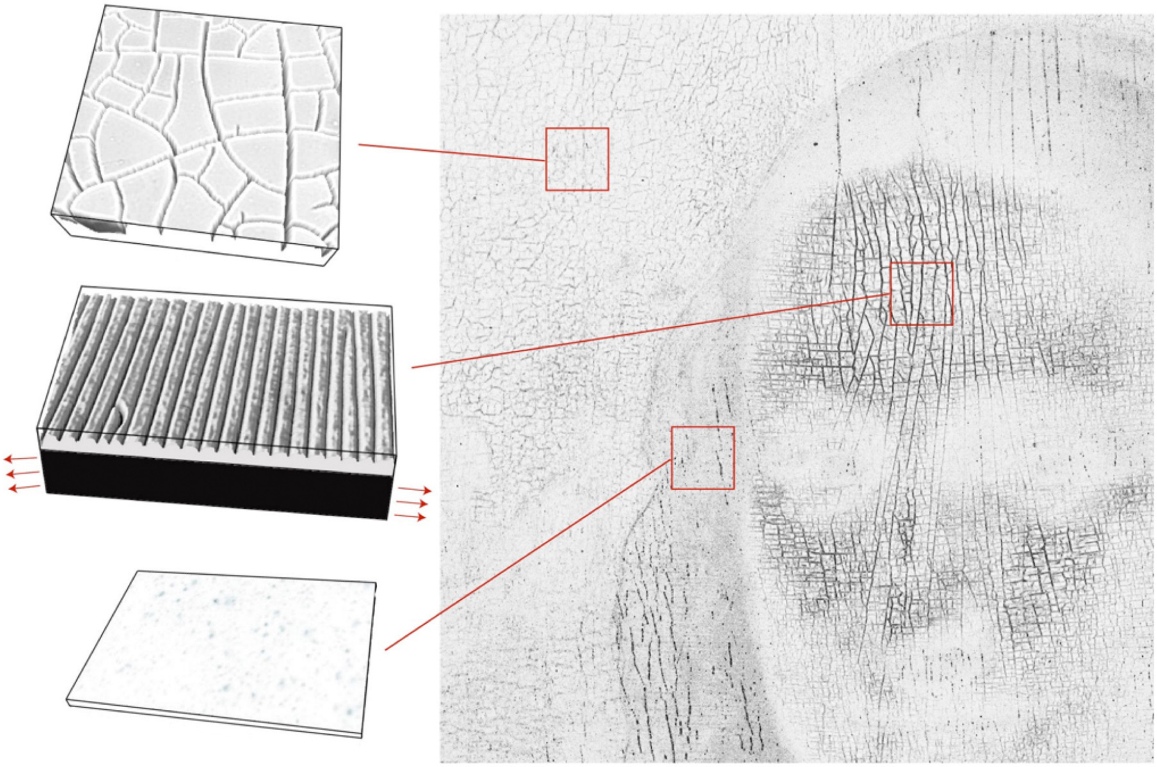

Fig. 9. Multispectral imaging showing some visible crack patterns in the painting "Mona Lisa". Reprinted from [24], with the permission of AIP Publishing. On the right of the face in the sky, in the forehead, and in the veil. At right: similar crack patterns were reproduced in laboratory models in the case of isotropic crack pattern; cracks due to the deformation of a substrate under a uni-axial load; thin layer free of cracks.

thickness in a particular painting: "Jeanne d'Arc en prison" by Louis Crignier. Measurements on modelled systems or on the real painting appear to be well fitted by the model [24]. In particular, these results validate the use of the modelled system to reproduce and explain the crack patterns in paintings.

Craquelures: restoration and conservation

The time evolution of the mechanical properties of a paint layer is a crucial subject for the life of a painting, but due to the number of components of a paint layer, and the complexity of their physico-chemical properties, its prediction is a complex task. Nevertheless, during ageing paint layer becomes generally more and more brittle. This implies that a painting is increasingly sensitive to the ambient conditions, such as humidity rate, temperature variations or deformations of the support, for example [40]. The role of the conservator/restorer is then to stabilize the artwork and integrate any repairs in order to preserve the visual appearance of artworks. This involves the general care and cleaning of artworks. The motivations of Conservation and Restoration are also to deal with the stability of an existing crack pattern so that to prevent its possible evolution. Besides, the presence of cracks, whatever their cause and nature, adds complexity to the restoration process as crack patterns can affect the curator operations. Precisely, one specific restoration treatment consists of removing aged and discoloured varnish or dirt particles laid on the top surface of the painting. For this operation, curator uses organic solvents to remove old varnish through solubilization. During this operation, the presence of cracks can favour the solvent penetration since each crack acts as a potential water tank that imbibes the paint layer. Such a process possibly results in further damages such as swelling, deflation, or formation of new craquelures, as well as dissolution or extraction of any components of the paint layer. In addition, the effect of water on a paint layer is the so-called "blanching" (Table 1) as a result of excessive humidity or possible flood. This process involves a partial whitish haze or whitening of the varnish or the paint layers [15]. This alteration strongly alters the visual appearance of the painting and can be located around crack patterns. Indeed, a crack acts as a water tank that favours imbibition process. Such a water volume does not usually stand between the crack surfaces or evaporate in the surroundings but imbibes the porous layer depending on both the permeability of this last and the wetting properties of the paint layer. The pictorial layer is more or less permeable to the solvent, depending on the void size and the pigments wetting properties. Moreover, a crack surface is more porous due to its intrinsic roughness than an uncracked paint layer usually covered by a thin varnish layer with low permeability. Thus, there is an obvious link between this blanching effect and the presence of cracks which can influence the water penetration and promote the blanching. For all these reasons, the presence as well as the stability of craquelures is a challenging problem.

To study this stability, the first step is to understand the different modes of propagation of a crack. Among cracks, the ones having the most dramatic impact for the painting, are interfacial cracks which separate layers from each other or paint layer from the support (delamination). This can result in the lacuna, or small area where the paint is missing (image 2 in Fig. 10). This loss of material is irreversible and should be avoided. We consider then the two main modes of propagation of cracks: the channeling cracks and the interfacial cracks. The first ones propagate through the thickness of the paint layer. They can propagate deep within the multi-layered structure and/or possibly kink into a plane parallel to the substrate [28,41]. This usually results in a curled region (image (2) in Fig. 10) and the appearance of an interfacial crack. The curvature and the surface area of the adhering region are characteristics of the mechanical properties of the material, also the adhesion of the layer on the sublayer [13]. Thus, the different modes of propagation of a crack depend on the elastic energy associated with

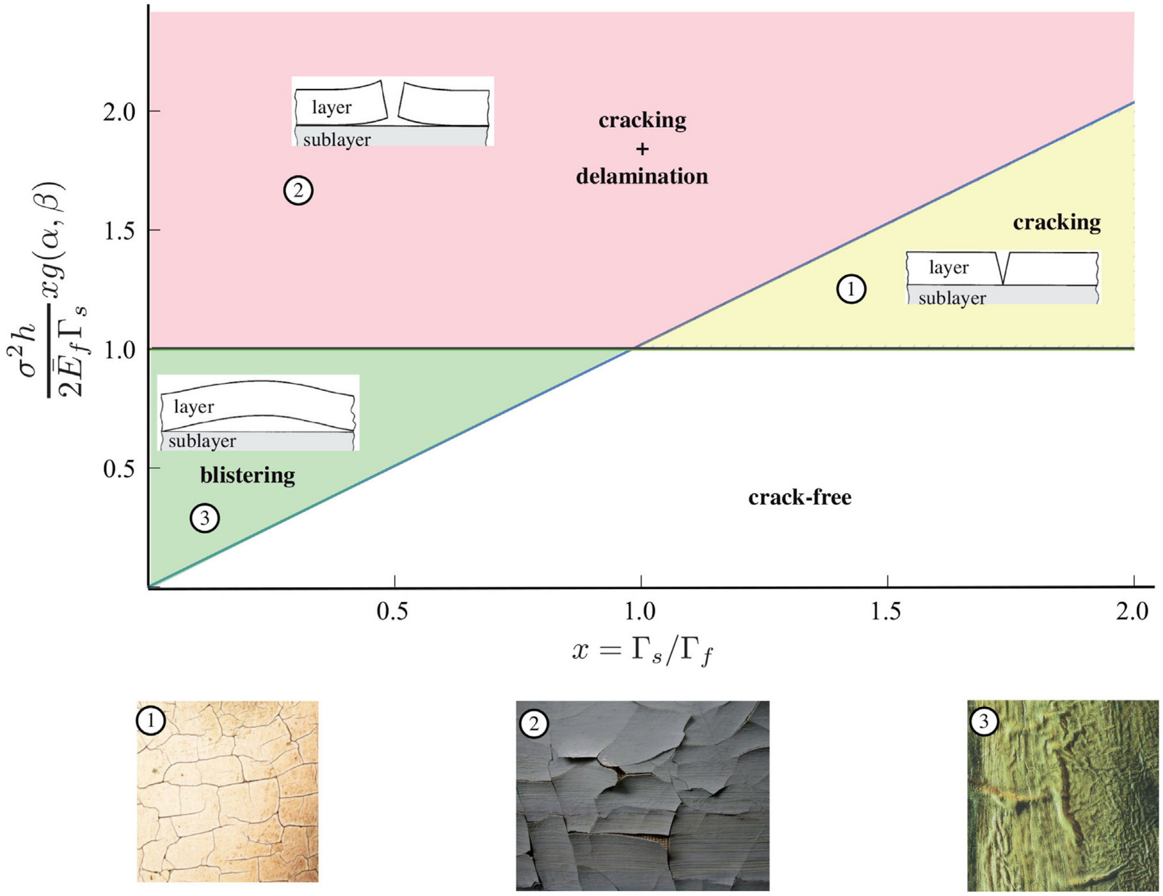

Fig. 10. Diagram showing the main behaviours of a system layer/sublayer in the plane of dimensionless parameters (energy vs. surface energy). The most energetically favourable states results in the formation of channeling cracks (1), possibly followed by a delamination process (2). Also, interface delamination can result in a blistering process (3). Corresponding images: (1) pattern of channeling cracks (image width: 2 cm); (2) partial delamination of a paint layer resulting in the layer lift upward (image width: 5 cm); image courtesy of Carole Clairon-Labarthe; (3) blisters in a paint layer (image width: 2 cm).

the mechanical stress and the surface energies involved. In this way, the complexity to predict the evolution of a crack pattern particularly lies in the state of the mechanical stress imposed by the pre-existing crack pattern. The case of a broken network of cracks with some dead-end cracks (Fig. 5c) can evolve as a result of the stress concentration at the crack tips. Moreover, depending on the stiffness and plasticity of the paint layer, further stress generation can lead to the widening of the existing cracks as a result of the shrinkage of the paint layer. To discriminate between the two kind of cracks, channeling and interfacial cracks, one has to consider the ratio between the elastic energy available for a crack growth and the fracture energy of the layer, Γf, in agreement with Eq. 3 as a function of the ratio, $x = \Gamma s/\Gamma f$, between the fracture energy of the layer and the surface energy at the layer/sublayer interface, Γs. Hence the different configurations of the paint layer can be depicted with the two following conditions: (i) the elastic energy is sufficient to create new surfaces at the interface between two layers or the paint layer and the support; (ii) the elastic energy is sufficient to create new surfaces within the layer. The diagram in Fig. 10 divides the plane into regions with specific cracking modes such as layer cracking (image (1) in Fig. 10), interface delamination (image (2) in Fig. 10) or blistering (image (3) in Fig. 10). The borders between regions are defined by the following equations:

$$\text{(i)}\ \frac{\sigma^2 h}{2\Gamma s \bar{E}_f} x g\left(\alpha,\beta\right) = x,\ \text{and (ii)}\ \frac{\sigma^2 h}{2\Gamma s \bar{E}_f} x g\left(\alpha,\beta\right) = 1$$

When the elastic energy is larger than both the fracture energy of the layer and the surface energy at the layer/sublayer interface, a channeling crack and delamination process occurs. This is the case when large stress is applied, when the layers are thick or when the surface energies are comparatively low.

Conclusion

The large variety of crack patterns observed in paintings reflects a large number of processes causing damages, and the wide complexity of the pictorial layer itself in chemical, mechanical, physical and geometrical points of view. Investigations conducted on various laboratory models reveal the crack patterns as the signature of the mechanical properties of the solid matter. The laboratory models are based on the drying of layers of nanoparticles. Such models do not pretend to mimic the overall processes occurring during the lifetime of a painting but aim to isolate the effect that results in specific mechanical in-stabilities. The wide adaptability of the colloidal dispersions takes into account the changes in rheological properties and mechanical behaviour during its solidification. Thus, the resulting crack patterns depend on the tunable parameters governing the structuration of the layer as well as the macroscopic characteristics of the layered structure. In this way, generic crack morphologies are related to a given microstructure and layered structure. These morphologies are quantified by measuring appropriate lengthscales related to the crack network such as the crack spacing, the crack aperture and depth, as well as the interaction lengthscale between cracks. The model used are only 2D models and give good agreement with data measured on real paintings. The analysis of craquelures appears to be a non-invasive method to obtain information on the mechanical and physical properties of paintings. These data on the material can provide information on the methods used by the artist as well as the methods of Conservation. There are many perspectives on this subject; among them, one can cite the quantification of the shape of cracks in-depth of a layer in order to analyze the spatial variations of the mechanical properties of the layer in depth. Another important question is to determine the nucleation center of a crack in the layer and to study the stability of a network of cracks that is of great interest in the domain of conservation/restoration of paintings. In particular, this can help to answer the following questions: what is the crack extent in the layer thickness? What is the stability of a network of crack and how, for example, preexisting cracks patterns can play a role when imbibition of water or solvents arise because of restoration operations or accidents such as flood? To achieve such works, tomographic and scattering techniques (SAXS, SANS) should be needed to study the structure in the bulk at the scale of the pigment size.

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