

Soft Matter

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Watching paint dry; more exciting than it seems.

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With an ever-increasing demand for sustainable alternatives to solvent-borne coatings and paints, the pressure to develop aqueous alternatives that match or exceed the performance of their traditional counterparts rises. A crucial step in this sustainability challenge for the years to come is to arrive at a deep, and complete, understanding of how aqueous paints dry and form their final protective films. As it turns out, this is no minor challenge. Yet, understanding drying and film formation is a prototypical soft matter problem at heart, displaying a rich variety of complex non-equilibrium phenomena that are waiting to be understood. Watching paint dry is far from the boring activity the saying suggests.

Traditional paints are composed of a polymeric binder, dissolved in a organic solvent, in which additional paint ingredients, such as pigments or fillers, are suspended. Upon drying, the polymer forms a solid layer which shields the material underneath from environmental conditions while simultaneously trapping the pigments to generate an aesthetically appealing surface. During drying the solvent evaporates into the air and atmosphere. These volatile organic compounds (VOCs) emitted from paints and adhesives are among the main contributors to greenhouse gases in the earth's atmosphere, and simultaneously endanger the health of consumers or professionals applying the paints. Prolonged exposure to VOCs emitted from paint can lead to severe brain damage, impairing sensory, motoric and behavioural function, in a syndrome that has become known as "painters disease".¹ Not surprisingly, this has motivated paint manufacturers and policy makers to embark on a road to phase out the use of solvent-borne paints.

Effectively eradicating solvent-based paints across the wide variety of applications where they find use, requires the availability of sustainable and non-toxic alternatives that offer the same quality of performance and appearance. One of the key technologies to replace solvent-based paints are water-based coatings in which the organic solvent has been replaced, partially or completely, by water. For most applications however, the final film must be resistant to water irrespective of the carrier medium in which the paint was formulated. The water-insoluble binder polymer, which was traditionally dissolved

in the organic solvent, is now added to the waterborne paint as a dispersion of colloidal polymer particles, known as a latex.

Film formation in solvent-based paints, in which the binder is molecularly dissolved, involves the continuous thickening of the paint as the solvent evaporates, until it leaves behind a homogeneous polymer layer in which pigments and opacifiers are embedded. By contrast, in water-based systems, in which the binder is dispersed rather than dissolved, film formation proceeds completely differently; as the aqueous continuous phase dries, the particles become close packed, until at some point phase inversion takes place, in which the binder phase forms a continuous film through coalescence. This process of film formation is at the core of determining the resilience and aesthetics of the final coating.

While it has been the subject of intense study for decades, much remains to be understood before waterborne and VOC-free paints can be rationally designed to offer the high-quality performance we have come to know and expect from traditional solvent-borne paints. Our deep understanding of the film formation process is obscured by its inherent complexity which arises from the multitude of phenomena which come into play as soon as a paint starts drying. It requires us to connect knowledge on colloidal interactions in multicomponent mixtures, the thermodynamic and kinetic stability of thin liquid films, fluid flows through porous media induced by evaporative fluxes, the yielding and flows of highly viscoelastic matter which simultaneously undergoes chemical curing, the mechanics of thin paint layers that gradually transition from particulate to continuous, and much more. It is this fascinating complexity, emerging in an everyday situation, that makes understanding film formation a prototypical soft matter challenge.

One of the central paradigms in soft matter science is to connect phenomena acting on the relevant microscopic length scales, be it molecular or colloidal, to those phenomena observable in the macroscopic realm. Applying this approach to film formation requires detailed experimental investigation into structure and dynamics on the smallest length scales across a wide range of time scales: from the moment a paint is applied, throughout its drying and ageing, until the moment it becomes so brittle that it may delaminate from the surface onto which it was applied. While indirect methods based on scattering, resonance or spectroscopy are invaluable, direct visualisation at the colloidal scale in real space and time is ideally suited for this task. With the wide range of imaging methods

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available this is now excellently feasible.

Below, we will highlight several of the key challenges we face in understanding film formation and sketch how a combination of smart chemistry, quantitative imaging and emerging techniques such as microfluidics, may allow us to watch paint dry with fresh eyes. Please note that the scientific foray into drying dispersions and film formation extends far beyond what is discussed here; for a comprehensive overview we refer to the excellent reviews of Keddie,² Winnik,³ Steward *et al.*,⁴ and Routh.⁵

Thin film stability: A crucial part of the transformation of a dispersion of liquid-like latex colloids into a homogeneous coating film is the coalescence of the individual particles or droplets to form a macroscopic polymer phase. We can divide coalescence into two characteristic processes; (i) the rupture of the liquid film that initially separates the colloids and (ii) the subsequent mixing of the contents of the two colloids.

The stability of thin liquid films has been intensively studied for many years, using a variety of experimental techniques such as the surface force apparatus, atomic force microscopy and the thin film balance.^{6–9} These methods allow careful measurement of the interactions between two fluid phases separated by a thin, nanometre-thick, film of a liquid. Upon decreasing the film thickness, and consequently, increasing the disjoining pressure, the thin film becomes unstable when a critical disjoining pressure is exceeded.⁶ While there are strong links between well-established knowledge of colloidal interactions and the stability and rupture of thin liquid films separating emulsion droplets, a predictive understanding of what sets the exact magnitude of the critical disjoining pressure remains lacking. For example, it is well established that surfactant adsorption reaches a plateau around the critical micelle concentration (CMC) of the surfactant in solution.¹⁰ If the critical disjoining pressure of a thin film of surfactants depends only on the amount of adsorbed surfactants, which is thought to provide the film stability by means of electrostatic and/or steric repulsion, we may expect a plateau in the critical disjoining pressure as well. However, we recently showed that the critical disjoining pressure continues to rise with increasing surfactant concentration, and reaches a plateau at a concentration several decades above the CMC.¹¹ While the origins of this surprising finding are unclear, we speculate that diffusion-limited surfactant exchange at the interface plays a role. Moreover, while the critical disjoining pressure describes film stability in the thermodynamic limit, in practice kinetic effects may also be important. The rupture of a thin film involves temporary expansion of the interface, thus creating an energy barrier, and drainage of the thin film such that hydrodynamic and lubrication forces also come into play.^{12–14}

In drying paints, film rupture is caused by the increasing osmotic and/or capillary pressure developing as water evaporates. However, in this scenario, also solute concentrations in-

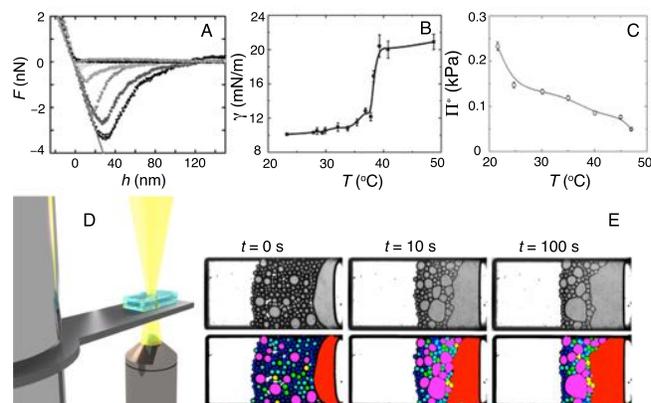


Fig. 1 Measuring and manipulating thin film stability: With a thermoresponsive surfactant, exhibiting a lower critical solution temperature, droplets can be made adhesive upon increasing the temperature, as demonstrated in colloidal probe atomic force microscopy experiments,¹⁵ (A) while simultaneously increasing the interfacial tension¹⁶ (B) and decreasing the critical disjoining pressure.¹⁷ (C) In combination with microfluidic centrifugation and synchronised high-speed imaging, as illustrated in (D),¹⁷ this allows the direct observation and quantitative analysis of triggered coalescence in emulsions as shown in raw (top) and processed (bottom) images in (E).¹⁷ Reproduced from Refs.^{15–17} with permission from The Royal Society of Chemistry.

crease and may lead to spatial heterogeneities throughout the coating. Experimentally disentangling the interplay between various thermodynamic and kinetic parameters is difficult.

One approach involves the use of responsive surfactants, so that the stability of the liquid films separating droplets can be tuned during an experiment. For example, thermoresponsive surfactants, composed of a hydrophobic tail and a thermoresponsive polymeric head group, can be switched between soluble and insoluble during an experiment by means of a small temperature trigger. Triggering the surfactant renders the emulsion droplets adhesive, which can be measured with atomic force microscopy (Fig. 1A),¹⁵ and simultaneously increases the interfacial tension¹⁶ and decreases the critical disjoining pressure (Fig. 1B–C).¹⁷ This allows creating emulsions which are highly stable at room temperature, even when densely packed, which can be made to coalesce within seconds.¹⁶

This tuneable system can be combined with new tools to study the stability of emulsion layers, for example the microfluidic centrifuge combined with high-speed synchronised imaging, as illustrated in Fig. 1D. For a given system, the pressure applied to the emulsion can be easily varied by changing the rotation speed. By means of image processing algorithms, detailed information down to the single particle or droplet level can be quantitatively extracted (Fig. 1E).¹⁷ This

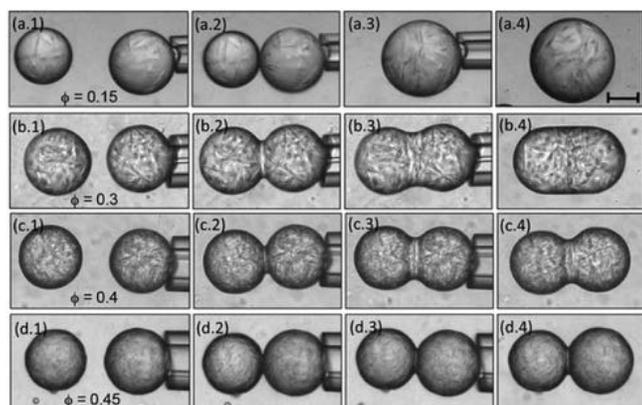


Fig. 2 Transition from complete (a) to partial (b–d) coalescence of droplets of a yield stress fluid with increasing yield stress from top to bottom. Reproduced from Ref. ³² with permission from The Royal Society of Chemistry.

makes it possible to begin to unravel the effects of thermodynamic stability, emulsion properties and osmotic pressure (or packing density) on film rupture and coalescence in a clean and reproducible manner.

Content mixing: After the rupture of the liquid film that separates two latex particles, the inner phases begin to mix. For simple viscous liquids this process occurs on very short time scales, accessible only with high-speed imaging¹⁸ or high-frequency conductometry¹⁹ and can be described by hydrodynamics alone. However, for aqueous paints, the latex particles are composed of a highly visco-elastic entangled polymer melt with a glass transition temperature T_g at or around the relevant application temperature of the coating. As a result, the mixing process following film rupture occurs over much longer time scales, and may continue well after the coating has dried. Routh and Russel have described several regimes of film formation depending on the relative rates of particle deformation – which precedes content mixing – and water evaporation.^{20–23} These regimes have also been identified experimentally,²⁴ for example by Magnetic Resonance Imaging (MRI) which allows measuring local water concentrations in a drying paint layer.^{25–28} With a typical resolution of approximately 10 micrometre, MRI profilometry does not give direct insight into particle deformation and coalescence at the single-particle scale. By contrast, polymer intermixing upon coalescence can be studied at the molecular scale using Förster Resonance Energy Transfer (FRET)^{29–31} in which lateral and depth information are usually lost.

Highly entangled polymer phases, such as those forming typical latex particles, may show not only a very high viscosity but in some cases, depending on the ratio between processing temperature and T_g , will also exhibit an effective yield stress. As a result, coalescence may never reach completion if

the yield stress outweighs the interfacial pressure which drives coalescence. This was demonstrated elegantly for the coalescence of two isolated droplets of yield stress fluids (Fig. 2);³² yet how these effects manifest in dense systems in which each particle is surrounded by many others and how this influences the ultimate fate of a drying paint layer, remains unclear. Our knowledge is particularly incomplete when it comes to aqueous dispersions which do not only dry and coalesce, but also undergo chemical curing when applied, as is the case for alkyd dispersions or two-component latices. In these systems, an additional time variable which describes the gradual increase in particle viscoelasticity due to the chemical reactions occurring, needs to be considered. We may expect that the relative rates of drying, polymer intermixing and chemical crosslinking give rise to new regimes of film formation, analogous to those described by the Routh–Russel model.^{20,21,23}

Complex suspensions: The phenomena of film rupture and content mixing described above are already significantly complex when studied in the simplest limit, of two interacting droplets or particles. However, additional complexity emerges, even in simple systems, when the particle concentration is increased. During paint drying, as solvent evaporates, the initially liquid-like suspension reaches particle volume fractions where glassy dynamics prevail, and ultimately reaches a close-packed state, which can be ordered or disordered dependent on the particle interactions, polydispersity and drying rate.

Under these conditions, film rupture is no longer a problem merely depending on the thermodynamic stability of a single film, but collective effects must be taken into account. The first film to rupture in a homogeneously compressed packing of equally sized droplets is a problem of symmetry breaking governed by thermal or external fluctuations. However, once coalescence has nucleated, geometrical effects come into play in deciding which film will rupture next. This can lead to propagating coalescence fronts,^{11,33} governed by local curvature effects and recoil of the fluid interfaces.³⁴ On a global scale, these effects can be ideally studied by for example water profilometry using MRI,^{26,28} while insight into the phenomena on smaller scales requires the use of higher-resolution methods such as optical microscopy, including confocal microscopy,³⁵ and electron microscopy.^{36–39} Also here, the use of microfluidic tools to manipulate and *in situ* visualise the fate of droplets on their way to instability, has proven invaluable.^{33,40}

Direct imaging gives us access to details of the film formation process which are not accessible in other techniques. For example, using confocal fluorescence imaging we have shown how coalescence in emulsion films, subjected to a unidirectional drying stress, can manifest in two distinct modes. Coalescence either occurs by the propagation of a coherent coalescence front from the dry end of the dispersion towards the wet region, or as a sequence of random nucleation-and-

growth steps throughout the bulk of the dispersion. Using the same images, not only can the sequence of nucleation events be traced, but also local capillary pressures can be measured by analysing the curvature of the Plateau borders. In this way, we have related these two distinct modes of coalescence in a drying emulsion to the temporal development of a pressure gradient across the drying emulsion.¹¹ This illustrates how direct imaging can provide new insights and reveal new phenomena that remain hidden with methods in which all data is spatially averaged.

In a typical aqueous paint formulation, the dispersed phase comprises a mixture of polymeric particles which coalesce, known as the binder as it provides the final film with its mechanical integrity, and solid colloids, typically inorganic, which do not coalesce, such as pigments, opacifiers and fillers. This gives rise to new phenomena as is beautifully illustrated in experiments by Xu *et al.*⁴¹ These authors studied the drying of a mixture of small, hard, particles, and larger liquid emulsion droplets using three-dimensional confocal fluorescence microscopy (Fig. 3A). As drying progressed, and a densely packed state was reached, air invaded the structure. When the Laplace pressure within the droplets exceeded the osmotic pressure of the bath of small particles, air invasion caused the spontaneous break-up of emulsion droplets and their dispersal into the porous surroundings (Fig. 3B); showing a distinct departure from the classical picture of droplet coalescence upon drying. Moreover, in drying dispersions containing particles of very different sizes, a distinct layering, or stratification, can occur resulting in an inhomogeneous distribution of the different particle species across the final film.^{42,43}

Waterborne paints typically also contain large amounts of dissolved components, such as surfactants and/or polymeric stabilisers, and thickeners such as network-forming associative polymers. Upon drying, the concentration of these solutes increases; as a result, the interactions between each of these species evolve in time, as well as the interactions between the solid or liquid particles mediated by the presence of polymers and surfactants, which in turn affects the phase behaviour and dynamics of the system. No clear understanding exists so far to what extent this will affect the structure and properties of the final film; for example, in some cases films are known to exhibit a heterogeneous distribution of inorganic pigment particles. It is not clear whether this structure is already present in the liquid state or if it emerges during drying, for example due to increasing depletion attractions between the particles as the polymer concentration increases. Water flow during drying can also transport dissolved species to the dry end of the paint layer, potentially leading to accumulation of solutes at the paint–air boundary, depending on the relative rates of water flux and thermal diffusion of the solutes. Modelling of the water and solute flows through the porous particle network may provide insight into this matter.¹¹

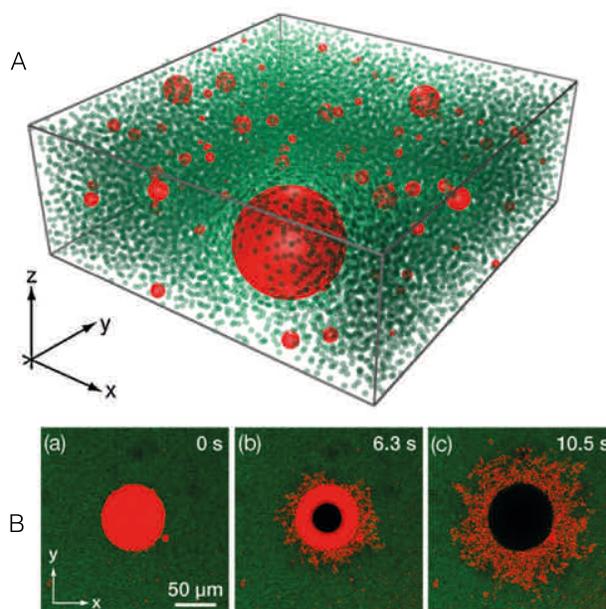


Fig. 3 Confocal fluorescence microscopy of a drying mixture of hard particles (green) and emulsion droplets (red); three-dimensional reconstruction of the particle mixture (A) and time sequence showing break-up and invasion of a single emulsion drop into the surrounding matrix during drying (B). Data reprinted from⁴¹ with permission from the American Physical Society.

Instabilities: The design of a new generation of sustainable water-based coatings requires not only control over the deformation and coalescence of individual particles during drying, but equally vitally requires the effective mitigation of large-scale instabilities which occur during the application, drying and ageing of these coatings. Typical instabilities include cracking and delamination,⁴⁴ wrinkling⁴⁵ and the formation of exposed areas of the substrate, either in small spots, known as pinholes,⁴⁶ or in larger domains, for example by dewetting or by Marangoni-stress induced delevelling.⁴⁷ These instabilities, which significantly deteriorate the performance and appearance of the coating, occur on length scales much larger than the scale of the individual particles. They must arise from collective effects within the paint, and the paint–substrate interactions. Identifying the origins of such instabilities is therefore a major challenge, especially for formulations containing a variety of components. This challenge is exacerbated by the fact that some of instabilities may not manifest directly but appear gradually during ageing of the coating. For example, the cracking and delamination of paint films composed of air-curing polymers such as in artist oil paints poses a significant threat to the preservation of many seminal artworks, yet these cracks only become visible decades or even centuries after the paintings were first created.

The complete suppression of cracking requires an understanding spanning multiple length and time scales. Crack nucleation is a highly localised event, but once it leads to a propagating crack, this strongly influences the nucleation and growth of subsequent cracks⁴⁸ as well as the internal stresses throughout the coating.^{49–52} Because of the directional release of stresses around the growing cracks, fracture networks typically display distinct statistical features, such as polygonal cracks in dried silica suspensions and mud^{53,54} or regularly spaced radial cracks in dried colloidal droplets.^{45,55}

The majority of literature on cracking in colloidal coatings is centred around two topics: the propagation mechanism of individual cracks, and the correlation between dispersion parameters and the final fracture pattern. Imaging of propagating cracks has provided a wealth of information about the stress distribution and particle arrangement around the cracks,^{37,39,56,57} the reversibility and trajectory of crack opening,^{56–60} and the characteristic crack spacing.^{39,51,61,62} Furthermore, a variety of strategies have been proposed to prevent cracking, such as reducing the interparticle adhesion,^{45,57} increasing the elastic modulus of the particle network,^{53,63} and mitigating stress build-up by adding soft colloids.^{55,64,65} Despite the great fundamental and practical value of these insights, it remains difficult to predict *a priori* if and how a coating will fracture. Typical unanswered questions concern the extent of brittle vs. plastic fracture and the moment of crack nucleation, either following the drying front or throughout the coating after consolidation. In-depth knowledge of the collective phenomena occurring at all scales is therefore desired.

As mentioned above, instabilities may develop well after drying of a coating, suggesting the need for long-term measurements. A simple yet effective technique for this purpose is brightfield microscopy. Recently, we measured the transmitted light intensity through latex droplets over extended periods to visualise and quantify the local changes in droplet homogeneity. Using this method, we uncovered that in many cases, pronounced cracks show self-healing over longer periods of time (Fig. 6). Scanning electron microscopy revealed how crack healing occurs; first particles deform and form facets (Fig. 6B1), then they coalesce (B2) upon which the cracks heal by creep of the now homogeneous polymer film (B3). Surprisingly, this gradual self-healing persisted up to relatively high $T_g - T$ values of 13 °C, where by common definition the polymer is in a glassy state. Due to the universality of the self-healing mechanism, independent of particle softness, we could fit the accompanying rise in the transmitted intensity by a single function from which we obtained a typical time scale of crack healing (τ_{heal}). Increasing the T_g of the polymer phase allowed us to tune τ_{heal} from zero (no cracks) to several hours (self-healing cracks) to more than ten days (presumed permanent cracks) (Fig. 6C).⁶⁶ Although the practical applicability of long ageing times is questionable and preventing cracking

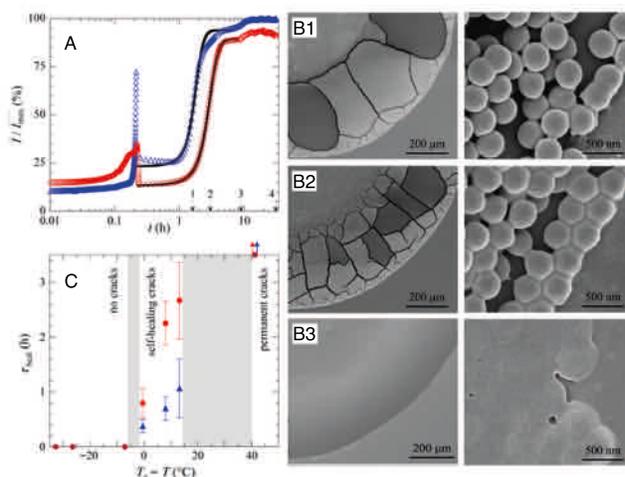


Fig. 4 Cracking and crack healing: (A) Transmitted light intensity through a drying droplet of poly(styrene-*co*-butyl acrylate) colloids with a T_g at room temperature, measured using brightfield microscopy, showing distinct phases of drying, cracking and crack healing. (B) Scanning electron microscopy time series showing particle deformation, coalescence and crack healing at the edge of a dried droplet of particles with $T_g - T = 13$ °C at $t = 24$ h (1), 48 h (2) and 10 days (3) after deposition. (C) Typical time scale of crack healing as a function of the difference between the glass transition and room temperature, showing three regimes. Adapted with permission from⁶⁶. Copyright 2015 American Chemical Society

may be preferred over curing them slowly, these results suggest that in polymeric films cracking may be a transient phenomenon when the film is relatively soft.

Outlook

Much of the effort in improving and innovating sustainable waterborne coatings is dedicated to the development of new types of particles and stabilisers, fine-tuning formulations, and improving or redesigning application procedures. However, with so many unknowns regarding the mechanisms with which complex colloidal suspensions dry and form films, these efforts remain largely empirically driven. Extending our fundamental insight into the governing mechanisms of film formation will pave the way for a more rational approach towards improving water-based paints and replacing environmentally unfriendly solvent-based systems. With the advent of a plethora of novel imaging techniques and enabling technologies such as microfluidics, and the rise of new types of soft responsive materials to control and tune film formation, this challenge, though complex, can now be effectively addressed.

Future challenges lie primarily in connecting the interactions among the components of multicomponent aqueous paints to the complexity that emerges when particle and solute concentrations rise and couple to non-equilibrium phenomena such

as fluid flows, thin film rupture and particle coalescence. Quantitative imaging, combined with complementary methods, may provide a crucial tool to span the length scales from individual particles to the properties of entire systems. This leaves the challenge of capturing dynamics on a wide range of time scales for which not one single technique may be suitable; for example while 3D confocal microscopy may resolve processes in unprecedented detail, the acquisition time of a single three-dimensional image stack may be too slow to capture fast processes such as coalescence. Another pressing challenge is to develop methods which allow imaging of inherently turbid dispersions, especially their internal structure and dynamics. Although designing systems for microscopy, through refractive index matching, most certainly has its merits, ideally, similar studies could be performed on realistic formulations which are typically highly scattering and coloured. Speckle-based imaging tools, such as that proposed by Zakharov and Scheffold⁶⁷, or methods based on optical coherence, may provide the solution.

In addition, film formation is in part so complex, and ill-controlled in certain circumstances, because drying and the associated flows of solvent and solute occur simultaneously with coalescence of the particles. The use of responsive, or triggerable, surfactants or particles, could in principle enable the formulation of systems which are extremely stable against coalescence, allowing the system to dry without particle destabilisation, after which coalescence can be triggered by means of an external impulse, such as temperature^{16,17} or light. At least for the study of film formation such an approach may have merit, but even for certain industrial applications decoupling of various stages in the coating process may prove to be useful.

Finally, all of the issues discussed here originate from the fact that conventional solvent-based paints, in which the binder is molecularly dissolved, have been reformulated in a colloidal dispersion for their application in water-based systems. Clever polymer chemistry may allow circumventing the issues associated with the formation of a film from a dispersed system by rethinking this strategy in its entirety, for example by using dissolved polymers which become hydrophobic upon drying, or through the use of solvent-free systems.

With these challenges ahead, many of which lie at the heart of the soft matter field, much needs to be done before a full replacement of toxic and harmful solvent-based coatings can take place. Nevertheless, studying these problems offers an opportunity to reveal and unravel fascinating phenomena that remain to be explained, with a clear societal relevance. In short: watching paint dry is hardly a boring or idle endeavour.

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Fig. 5 H. van der Kooij

Hanne van der Kooij obtained her MSc degree at Wageningen University in 2013, after a research project in the group of Prof. Martien Cohen Stuart and an internship at the University of Cambridge in the group of Prof. Ulrich Steiner. She is currently a PhD candidate at Wageningen University, where she works on understanding film formation using a variety of imaging techniques, under the supervision of Dr. Joris Sprakel.



Fig. 6 dr. J. Sprakel

Author biography

Dr. Joris Sprakel obtained his PhD under Prof. Martien Cohen Stuart at Wageningen University, for which he received the Polymer Award of the Royal Netherlands Chemical Society. After a postdoctoral fellowship with Prof. David Weitz at Harvard University, he started a research group in the Laboratory of Physical Chemistry and Soft Matter at Wageningen University. Work in his group focusses on both fundamental and applied aspects of colloidal systems, ranging from the physics of film formation, the microscopic origins of mechanical stability in soft solids, to the development of conjugated polymer building blocks for self-assembled soft optoelectronics.

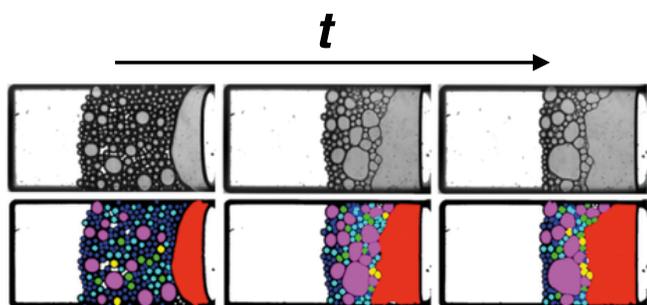


Fig. 7 dr. J. Sprakel

TOC

We highlight the challenges that lie ahead in understanding film formation of coatings and show some of the exciting soft matter phenomena which can be observed beneath surface of drying paints.