Current Opinion in Colloid & Interface Science 25 (2016) 89–97

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Interfacial routes to colloidal gelation

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ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form 6 July 2016
Accepted 8 July 2016
Available online 01 August 2016

Keywords:
Colloidal gel
Gelation
Pickering emulsion
Bijel
Capillary gel

ABSTRACT

Colloidal gelation is a rheological transition from fluid-like to solid-like viscoelasticity in a particulate suspension and is often instigated by causing the net interparticle interaction to be attractive. In this article, three routes to colloidal gelation that have been discovered recently and involve interfacial phenomena at a fluid interface are reviewed. As in conventional systems, gelation is due to a percolating particle network that imparts elasticity to the mixture, but the network formation involves interfacial particle jamming or bridging, or capillary interactions along or across interfaces, in a mixture of immiscible fluids. Gelation imparts mechanical stability to these multiphase mixtures and paves the way for their use as templates for the synthesis of functional, microstructured materials and composites. The gel mechanical properties are mediated by the interfacial forces and the mixture's microstructure, and therefore show different dependencies on particle volume fraction across the three systems.

1. Introduction

Colloidal gelation is conceptually defined as the emergence of a finite elastic modulus in a suspension at particle volume fractions much below the glass transition value ($\phi < \phi_g$). This is a non-equilibrium transition that generally occurs when attractive interactions exceeding a few kT (where k is Boltzmann's constant and T is the absolute temperature) are present between the particles, causing them to aggregate into a sample-spanning network, which is ultimately responsible for the arrest of colloid dynamics and the development of gel-like rheological properties. The net-attractive interactions can be induced by various means, including the displacement of surface charges [1], the screening of repulsive electrostatic interparticle potentials [2], depletion interactions from non-adsorbing dissolved species [3,4•], polymer-induced bridging [5•], or changing the solvent quality [6•]. From a practical standpoint, gelation is often utilized to impart texture or elasticity to a fluid mixture or to create a solid backbone for materials processing; for example, in the formulation of personal care products or pharmaceutical compounds, lightweight construction materials, catalyst supports, and ceramics, and in the direct-write assembly of complex 3D structures [7,8]. Gelation can also be detrimental to the target application of a suspension, for example, in mineral oil emulsions for oil recovery [9]. In the limit of low colloid volume fractions and strong, short-ranged interparticle interactions, gelation results from the growth of low-density fractal clusters that, in principle, can fill up the entire sample volume at arbitrarily small particle loadings, due to their fractal nature [10•]. Within this limit, fractal theories can describe the onset of network formation, the colloid dynamics, and the origins and scaling of the elastic modulus [11–13]. For systems with weaker interparticle interactions, gelation has been attributed to dynamic percolation [14•,15], arrested spinodal decomposition [16–18•,19•,20], or viscoelastic phase separation [21]. Partly because of their industrial relevance, the rheology of gels in this regime has been characterized extensively, showing a power-law dependence of the zero-shear elastic modulus, G_0', and yield stress, σ_y, with the colloid volume fraction ($G_0' \sim \phi^m$, $\sigma_y \sim \phi^n$) [22•,23•,24•,25,26•,27–29]. Colloidal gels remain a principal topic of both fundamental and applied research because of their diverse technological applications and potential as model materials for the fundamental understanding of the physics of non-equilibrium soft matter. Regardless of the gelation pathway and the resultant microstructural details, it is generally agreed that 1) percolation of a particle network is a requirement for gelation, 2) the rheological properties are strong functions of the colloid volume fraction, and 3) the nature and strength of interparticle interactions sharply influence both the morphology and rheology of colloidal gels.

In this article, I review three new classes of colloidal gels in which interfacial phenomena in mixtures of immiscible fluids and colloidal particles are responsible for clustering and network formation. These systems uniquely intersect two well-studied areas: colloidal gels and colloids at fluid interfaces. Therefore, the systems expand the library of colloidal gels into multiphase mixtures that involve two or more immiscible fluid phases. This not only introduces many questions related to the physics of colloidal gels and gelation kinetics but also dramatically expands the potential use of colloidal gels in the personal care, pharmaceutical, petroleum, and materials manufacturing industries, to name a few. For clarity, I will use the term “conventional colloidal gels” to refer to the more familiar particulate systems, discussed at the beginning of this article, in which the attractive interparticle interactions are not of an interfacial or capillary nature. The rest of this article is organized as follows: Section 2 reviews the basics of particle sequestration at

http://dx.doi.org/10.1016/j.cocis.2016.07.005
1359-0294/

fluid–fluid interfaces, Sections 3–5 discuss the three classes of colloidal gels formed by an interfacial route, and Section 6 provides closing remarks and suggests possible directions for future research in this area.

2. Colloids at fluid interfaces

Solid particles with characteristic sizes between a few nanometers and a few microns can strongly adsorb to fluid interfaces if their surface chemistry provides neutral wetting properties with respect to the interface (that is, if the particle surface chemistry is nearly equally compatible with the two fluids that make up the interface) [30••]. Ramsden and Pickering were the first to observe this phenomenon more than a century ago [31,32]. The particle's equilibrium position with respect to the interface (here referred to as an oil–water interface for convenience) is characterized by a three-phase contact angle, θ, which is conventionally measured with respect to the aqueous phase, is governed by the system's interfacial energetics and is calculated from a mechanical stability criterion known as the Young equation: $\cos\theta = (\gamma_{po} - \gamma_{pw})/\gamma_{ow}$. Here, γ_{po}, γ_{pw}, and γ_{ow} are the particle–oil, particle–water, and oil–water interfacial tensions, respectively. The minimum energy to remove a spherical particle of radius r from the interface is then $\Delta G = \pi r^2 \gamma_{ow}(1 - |\cos\theta|)^2$. With $\theta \sim 90°$ and $\gamma_{ow} \sim 20$ mN/m, sequestration of nano- and micro-particles ($r > 30$ nm) at the interface is nearly irreversible, as ΔG then far exceeds the particle's thermal energy ($\Delta G > 10^4 kT$). A monolayer of irreversibly adsorbed solid particles at droplet interfaces can then impart long-term kinetic or even thermodynamic stability against coalescence [33•,34•,35•,36•,37•]; this stability forms the basis of the famous Pickering–Ramsden emulsions, which have diverse technological applications for example in food [38,39], drug delivery [40], and oil recovery [41]. More recently, particle assembly at fluid interfaces has been exploited for the formation of new classes of multiphase mixtures and exotic materials, such as solid-stabilized oil-in-oil or double emulsions [42,43], responsive foams [44], capsules [45], colloidosomes [46], dry water [47•], ionic liquid emulsions [48], and powdered oil [49•], among others. Anisometric particles have also been utilized in both water-in-oil and oil-in-water emulsions, showing enhanced stability against coalescence as the particle aspect ratio is increased [50]. In the above examples, the particles serve to stabilize discrete and independent droplets (or bubbles) of a dispersed phase in another continuous fluid phase, while the mixture primarily retains fluid-like properties (except when the droplet volume fraction approaches the close-packed limit for spheres, frustrating the mixture dynamics due to crowding). In contrast, as I will discuss below, particle sequestration at fluid interfaces leads to the formation of a percolating colloid network, imparting gel-like properties to the system at colloid volume fractions far below the glass transition or random close-packing limits.

2.1. Capillary interactions

The chief governing principles of particle sequestration at fluid interfaces, such as the well-known Young equation, were derived for model systems with smooth colloidal spheres residing at a perfectly flat fluid interface. In reality, this situation is almost never encountered. Several factors can result in the distortion or curvature of the fluid interface in the particle's vicinity. These include particle surface heterogeneities resulting in contact line pinning or local variations in the equilibrium contact angle, overall geometrical constraints such as interfaces with a negative Gaussian curvature or an increasingly low volume fraction of the wetting fluid phase, and gravitational effects. The implications of interfacial curvature on interparticle interactions at fluid interfaces, and the subsequent influence on structuring, have been studied both theoretically and experimentally [51•,52•]. Gravitational effects, though insignificant in most colloidal systems, were discussed in 1981 by Cheng and coworkers [53•]. They considered local depressions in the fluid surface caused by heavy particles and showed that bringing the particles together into a single trough can minimize the interfacial area and the system's free energy, which produces an attractive force between the particles. Van der Waals forces have been considered for systems in which gravitational effects are insignificant, but such forces are unable to explain the observed range of attractive interactions. In 1997, two independent research groups observed the clustering of negatively charged polystyrene colloids at the air–water interface, which was not explicable by van der Waals or gravitational capillary forces [54,55]. Stamou and coworkers subsequently showed that the observed long-range attractive interparticle interactions can be rationalized by undulations of the fluid interface caused by particle surface heterogeneities and non-uniform wetting [56•]. The excess interfacial area created by these distortions can be minimized when particles assume particular configurations, which can result in a long-range attractive interparticle potential. Wurger subsequently showed that the geometry of the interface itself can also cause attractive capillary forces [57•,58•]. For example, the mere presence of smooth spherical particles at a fluid interface with a negative Gaussian curvature results in a deformation field, with the particle's contact line representing a complex curve in 3D space. Using a perturbative expansion, Wurger showed the leading term to result in attractive interactions of quadrupolar symmetry. Finally, in a series of investigations, Stebe and coworkers extended these concepts to anisotropic particles at curved interfaces and derived the resulting capillary forces, torques, and stable states from theory, experiment, and computation [59–61]. Capillary interactions resulting from curved fluid interfaces are responsible for the cracking of colloidal materials upon drying [62]. These interactions have been exploited for the formation of 2D colloidal crystals [63•] and anisometric particle assemblies [64] and play an important role in governing the viscoelastic properties of at least two of the classes of interfacial colloidal gels discussed in this article.

3. Pickering emulsion gels formed by droplet bridging

The first class of interfacial colloidal gels discussed here is formed by particle-induced bridging of dispersed droplets in a solid-stabilized emulsion. For example, consider partially hydrophobic particles with $\theta > 90°$, which tend to stabilize water-in-oil emulsions, with the particles slightly protruding from the droplet surfaces to maintain an obtuse contact angle. This configuration also facilitates efficient packing and can provide a steric barrier against droplet coalescence. However, with a contact angle of $\theta > 90°$, particles can also adsorb to two flat interfaces simultaneously, effectively forming a bridge between two faceted droplets across a thin film of the continuous phase. This preferred configuration allows each particle to reduce twice as much interfacial contact between the immiscible liquid phases, with the same equilibrium contact angle satisfied on opposite sides of the particle. With a large energetic incentive to reside at the interface, bridging particles can impart strong adhesive forces between the two bodies of fluid that they adjoin (aqueous droplets in the example given above). Such forces were first measured by Fuller and coworkers by characterizing the deformation of a fluid interface being pulled by a bridged droplet [65••]. Particle-induced bridging in solid-stabilized emulsions has since been demonstrated in a variety of systems, including ionic liquids [66•], immiscible polymer blends [67•], and index-matching mixtures that enable direct studies of the gel microstructure [68••].

3.1. Gelation mechanism

The suggested pathway to network formation and a gelation transition in these systems is based on the partial coalescence of droplet pairs with a shared colloidal monolayer in between. An obvious requirement is for droplets to be only partially covered at first, as complete coverage would create a barrier to bridging. French and coworkers performed a systematic study of the processing and physicochemical aspects that