Colloidal behavior of nanoemulsions: interactions, structure and rheology

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Abstract. Nanoemulsions exhibit unique behavior due to their nanoscopic dimensions, including remarkable droplet stability, interactions and rheology. These properties are significantly enhanced by nanoscopic droplet size, as well as selection of surfactant and other molecular species in solution. Electrostatic and polymer-induced interdroplet interactions are particularly powerful tools for fine-tuning the interdroplet interactions, and have led to stimuli-responsive nanoemulsion systems that provide deep insight into their unique properties. As such, nanoemulsions have emerged as powerful model systems for studying a number of colloidal phenomena including suspension rheology, repulsive and attractive colloidal glasses, aggregation processes, colloidal gelation and phase instability, and associative network formation in polymer-colloid mixtures. This review summarizes recent advances in understanding the colloidal behavior of nanoemulsions, and provides a unifying framework for understanding the various complex states that emerge, as well as perspective on emerging challenges and opportunities that will advance the use of nanoemulsions in both fundamental colloid science and technological applications.

1. Introduction

Nanoemulsions (also known as miniemulsions)[1,2] are kinetically stable emulsions with droplet dimensions below 100 nm. It is important to distinguish nanoemulsions from microemulsions,[3] the latter being equilibrium structures belonging to the larger class of self-assembled phases of molecular amphiphiles.[4] Compared to microemulsions, the morphology and size of nanoemulsions are insensitive to changes in physicochemical conditions.[3] This allows the formulation of nanoemulsions from a larger cross-section of fluids, including aqueous solutions and hydrocarbons,[5] fluorocarbon oils,[6,7] precursors for polymeric[1,2,8] and inorganic materials,[9,10] and more exotic materials including ionic liquids[11] and liquid metals.[12] As such, nanoemulsions have become important to a wide range of applications including pharmaceuticals[13] and nanomedicine,[6,7,14] foods[15-17] and consumer products,[18] nanotechnology,[19] energy conversion and efficiency,[20,21] sensors[22-24] and sustainable chemistry.[25]

This diverse set of applications has driven significant efforts to understand the colloidal behavior of nanoemulsions including their interactions, stability, microstructure and rheology. In this regard, nanoemulsion droplets are complicated with respect to their larger counterparts in multiple ways. First, their small size results in extreme resistance to deformation that is partly responsible for their kinetic stability.[26,27] Furthermore, their size approaches the characteristic length scales of typical colloidal

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interactions,[28] giving rise to long-range forces between that can lead to remarkable and counter-intuitive behavior. This includes the formation of viscoelastic[29-31] and solid-like[30,32,33] phases with complex rheology,[34] as well as the formation of ordered structures despite the inherent polydisperse nature of nanoemulsion droplets.[26]

Although these unique aspects of nanoemulsions have been acknowledged for some time, a better understanding of how they control and give rise to fluids with complex dispersion structure and rheology, and how this behavior might be used to engineer new applications, has only recently emerged. This review is devoted to recent developments in understanding and controlling the complex colloidal behavior of nanoemulsions, and the interesting and important structures and properties they give rise to. We first briefly review processes by which nanoemulsions form and are (de)stabilized. We then turn to our primary focus – the colloidal interactions that dominate the colloidal behavior of nanoemulsions, which can be used to form and control colloidal states with complex rheology, whose rich behavior has served as the driver for a number of emerging technological applications. We conclude with an outlook on outstanding challenges and new opportunities in controlling the colloidal behavior of nanoemulsions.

2. Nanodroplet formation and stability

There have been a number of recent reviews on both the formation of nanodroplets, and their stability once formed.[3,5,15,26,35-37] As such, the intent here is merely to give a brief overview to inform those unfamiliar with nanoemulsions, and to highlight aspects that are relevant to their colloidal behavior.

2.1 Nanoemulsification

The formation of nanoscale droplets is made difficult by the requirement of forming an immense amount of interface compared to larger droplets, which in turn requires immense energy input.[38] Specifically, the minimum required energy density input, ε_{min}, to produce droplets of size a scales as $\varepsilon_{min} \sim 3\gamma\phi_d^3/a$, where γ is the interfacial tension between the dispersed and continuous phases, and ϕ_d is the volume fraction of the dispersed phase. It is important to note that this minimum energy requirement is the same regardless of the emulsification method. It can be supplied either by applying work to the fluid (usually through flow or mixing), or by a large change in its equilibrium state (e.g. through a composition or temperature change). These two methods of nanoemulsification are typically referred to as "high-energy"[26,39] and "low-energy"[35] emulsification, respectively (with the latter sometimes referred to as the "Ouzo effect").[40] This nomenclature is quite unfortunate for the reason just stated – the minimum energy requirement for forming nanodroplets is the same regardless of whether that energy is supplied mechanically or thermodynamically. It is therefore not surprising that large amounts of surfactants are required to produce nanoemulsions, in order to both lower γ in order to form nanoscale droplets, and to stabilize the large amount of interfacial area that is formed.

Work-based methods to produce nanoemulsions typically involve large amounts of viscous energy dissipation that are achieved in high-power fluidic devices including static mixers (e.g. high-pressure homogenizers, "microfluidizers", etc.)[39,41] and ultrasonicators.[42,43] In such high-energy processes, one can define a mechanically-limiting droplet size, set by the efficiency with which the energy input is converted to mechanical flow, and subsequently with which stresses in the flow are transmitted to deforming and rupturing the fluid-fluid interface of the emulsion into progressively smaller droplets.[38] Based on this concept, flow models for larger-scale emulsions accurately predict the

mechanically-limiting droplet size by either assuming the flow that ultimately deforms the droplets is entirely viscous (i.e. vanishingly small Reynolds number)[44] or entirely turbulent (i.e. large Reynolds number).[45] It was originally anticipated, therefore, that predicting droplet sizes for high-energy processes to create nanoemulsions would require turbulent flow models.[46] However, recent work showed that, due to their small size, the formation of nanoemulsions requires a significant viscous boundary layer, and this concept was used to formulate a new model for the mechanically-limiting droplet size, which compared favorably to droplet sizes observed for oil-in-water (O/W) nanoemulsions.[47]

Thermodynamic methods to produce nanoemulsions typically involve traversing the equilibrium phase diagram of the fluid-fluid-surfactant system from a single, homogeneous phase into a metastable two-phase region in such a way that droplets nucleate, grow and eventually saturate when the newly created interface is limited by the amount of surfactant available in solution.[35,48] Such methods are typically named "phase inversion" methods for the reason just described, and can be accomplished either through dilution with one fluid or another (phase inversion composition or PIC methods)[49,50] or through a well-controlled change in temperature (phase inversion temperature or PIT methods).[51,52] Although PIC and PIT methods require a significant degree of control, both in terms of the surfactant choice and the thermodynamic path to phase inversion, they are advantageous in that the ultimate droplet size is influenced by the thermodynamics of the stabilizing surfactant at the fluid-fluid interface. Specifically, models for a thermodynamically-limiting droplet size or interfacial curvature, set by balances of the equilibrium interfacial activity (or area) occupied by the surfactant and the volume of the dispersed phase, accurately capture droplet sizes obtained by both the PIC and PIT methods.[50,51]

From this overview, one can surmise various advantages and disadvantages of the two primary methods of nanoemulsification. Thermodynamic methods can in principle produce more monodisperse droplets with finer size control than work-based methods.[51] However, they require significant control and understanding of equilibrium phase behavior, and are thus highly sensitive to the material to be emulsified.[53] By contrast, work-based methods are advantageous in that they have been shown to produce nanoemulsions from a versatile cross-section of materials, and are relatively simple to scale to industrial quantities. However, they suffer from a very large external energy input requirement, and as such are more costly to operate. Finally, we see that the mechanically-limiting and thermodynamically-limiting droplet sizes are important concepts for controlling nanoemulsification and resulting droplet size distributions. It should be noted that these limiting sizes are not mutually exclusive, especially in the case of work-based emulsification methods where the mechanically-limiting droplet size may not be achieved due to insufficient surfactant to stabilize the newly created interface. In this way, neither the mechanically-limiting size nor the thermodynamically-limiting size must preclude the other.

2.3. Droplet stability and coarsening

Nanoemulsions are subject to the same mechanisms of droplet instability as ordinary emulsions, that cause coarsening (i.e. increases in average size and polydispersity) and, ultimately, phase separation.[38] However, the rates of instability are significantly altered by the small dimensions of nanodroplets, leading to significantly enhanced kinetic stability of nanoemulsions compared to their larger counterparts.

One mechanism of instability is coalescence, i.e. the mechanical fusion of two droplets due to collision. In coalescence, droplets must first approach (either due to Brownian motion or applied flow), and the film of continuous phase between them must drain before the droplets can eventually come into contact where their interfaces fuse.[54,55] Film drainage produces a significant hydrodynamic lubrication

force on the droplet surfaces, which tends to deform them before they come into contact, resulting in an increase in the interfacial area of the near-contacting surfaces.[56,57] This increased area can either promote or suppress surface contact depending on the relative magnitudes and ranges of attractive and repulsive forces between droplets. Nevertheless, it is the energetics of this surface deformation that leads to qualitatively different rates of coalescence for nanodroplets as compared to larger droplets, since the Laplace pressure, which scales as $\Pi \sim 2\gamma/a$, resisting deformation is orders of magnitude larger for nanodroplets than for micron-scale droplets.[26]

Because of this, most nanodroplets can be considered as nearly nondeformable spheres, since the forces required to do so are not typically encountered in their study except during nanoemulsification, under extreme deformation rates, or at very high concentrations (as will be discussed later).[26] This has considerable effects on droplet stability. For example, certain oil-in-water nanoemulsions exhibit no observable coalescence over extremely long periods, whereas nanoemulsions possessing identical composition and as little as four-fold increase in size coarsen very quickly due to coalescence.[32] It should be noted that this behavior is somewhat counter-intuitive, since one might expect that the fluid film in between nanodroplets might drain faster due to their negligible deformation, thus enhancing coalescence. However, as will be discussed below, this may be balanced by long-range surface forces between droplets.[58] For this reason, the source of nanoemulsions' remarkable stability to coalescence remains an open question, and is a ripe area for further study.

The second primary mechanism of droplet instability is Ostwald ripening (OR), where sparing solubility of the dispersed phase in the continuous phase results in molecular transfer between droplets. In an emulsion with non-zero polydispersity, there is a mismatch in energy between droplets of differing size due to differences in interfacial energy, resulting in a driving force that produces a net flux of dispersed phase into larger droplets at the expense of smaller ones.[59] The rate of droplet growth due to OR was first modeled by Lifshitz and Slyozov[60], and has come to be known as the Lifshitz-Slyozov-Wagner (LSW) theory.[59] The original LSW theory assumed infinitely separated droplets, and predicted a growth rate that is independent of the size of the droplets. However, later refinements of LSW theory to account for non-dilute transport effects predict an initial growth rate that to leading order is proportional to the initial droplet volume.[59] Thus, nanoscale droplets are predicted to have OR growth rates that are reduced by orders of magnitude relative to their larger counterparts. This effect has been well-studied by experiment in a number of nanoemulsion systems,[27,36] and measurements largely agree with results from classical theories for OR, suggesting that their enhanced stability is largely influenced by their size, and not necessarily details of their colloidal interactions.

A third, and perhaps more controversial, mechanism of droplet instability that was recently proposed is so-called "contact ripening" (CR), in which spontaneous fluctuations of the fluid-fluid interface enhance the rate of molecular transfer between nearby but non-contacting interfaces.[61] A phenomenological model for CR is hypothesized to retain the signature qualitative macroscopic feature of Ostwald ripening, i.e. a growth rate that is zero order in the average droplet volume, but with an enhanced effective ripening rate. CR was first proposed to explain abnormally large measured rates of ripening in nearly monodisperse nanoemulsions produced by thermodynamic methods.[61] A similar process has also been implicated in molecular exchange processes in bilayer-forming systems,[62] including ripening in vesicle suspensions.[63] However, much work remains to be done to better test the proposed CR mechanism, including experiments that more directly probe molecular exchange between nearby interfaces as well as first-principles theories to confirm the predictions of phenomenological models.

3. Colloidal interactions between nanodroplets

We turn our attention to the interactions between droplets that control colloidal behavior, and the various ways in which they have been experimentally measured and manipulated.

3.1. Measuring interdroplet interactions

Measurements of colloidal interactions in emulsions have been made using a number of methods, including small angle neutron scattering (SANS),[30,32-34,64,65] atomic force microscopy (AFM)[66,67] and optical methods.[68] For example, SANS can measure the structure factor, $S(q)$, of dispersed droplets, providing an indirect measure of the interaction potential, $U(r)$, where r is the center-to-center separation distance of droplets. Although AFM and the surface forces apparatus (SFA)[69] provide more direct measurements of colloidal forces between nanodroplets, they have yet to be applied to nanoemulsions due to challenges in isolating and attaching nanodroplets to measurement surfaces.

Optomagnetic methods to measure colloidal interactions[70] have also been applied to magnetic nanoemulsions to measure interactions between nanodroplets.[71] In these methods, the application of a magnetic field to ferrofluidic droplets produces dipolar interactions that lead to droplet chaining. By observing the resulting Bragg diffraction spectrum to precisely measurement of interdroplet distances, and calibrating the applied magnetic field to calculate the applied force on the droplets, apparent force-distance curves between droplets can be estimated. The method has mostly been applied to sub-micron droplets with sizes greater than 100 nm, and it is unclear whether these methods can be applied to smaller droplets due to optical limitations. Furthermore, since the method measures interactions in a one-dimensional arrangement of droplets, it is unclear whether one-to-one comparisons can be made to the interactions measured using the optomagnetic method and other methods (such as small angle scattering) that measure interactions in a three-dimensional suspension.

3.2. Surface forces

The most fundamental forces between nanodroplets are those between their interfaces. These include dipolar interactions, i.e. the van der Waals forces, which are attractive and short-ranged (typically several nm or less),[28] and ultimately cause droplet contact during coalescence. In principle, van der Waals forces can be eliminated by matching the dielectric properties of the dispersed and continuous phases. In practice, this can be nearly achieved by matching the refractive index of the two fluids, and has been employed to great effect in studies of interactions in suspensions of hard particles.[72]

The other obvious, and important, surface forces between nanodroplets are those imparted by the surfactant, which are repulsive and help stabilize the droplets against aggregation and coalescence. In the case of non-ionic surfactants, surfactants with bulkier head groups are typically chosen. Examples include ethoxylated alkanes such as Tween, Span and Brij surfactants and polyoxyethylene block co-polymers for the production of both oil-in-water[73-75] and water-in-oil nanoemulsions.[73,76] Not surprisingly, for such surfactants both the size and colloidal dispersion stability of nanoemulsions track qualitatively with the hydrophile-lipophile balance (HLB),[73,77] a heuristic that is commonly used for selection of surfactants to stabilize larger emulsions.[78]

3.3. Electrostatic interactions

Many oil-in-water nanoemulsions are produced using ionic surfactants with large HLB values, e.g. sodium dodecyl sulfate (SDS)[27,29,39,79] and various trimethylammonium surfactants such as didodecyldimethylammonium bromide (DDAB)[80] and cetyltrimethylammonium bromide (CTAB).[79] The large interfacial pressure of nanodroplets leads to large surface activities of these surfactants, and zeta potentials as large as ±100 mV are not uncommon.[81] Although standard electrostatic models such as Gouy-Chapman theory are adequate for modeling the resulting electrostatic repulsions,[22,58] the strength of the electrostatic potential can lead to ranges of electrostatic repulsion that are unusually large – in some cases on the order of the droplet radius or larger.[24] This results in fairly drastic changes in colloidal stability and behavior upon changes in ionic strength (again, as compared to larger droplets).[30,82] As will be explained later, both of these effects have significant consequences for the suspension dynamics, structure and rheology of nanoemulsions.

3.4. Polymer-induced interactions

The colloidal interactions of nanoemulsions can be significantly tailored through the introduction of polymers in solution. For example, polymeric surfactants can lead to polymer brush formation to impart long-range steric repulsions between droplets,[75] just as in other polymer-grafted colloids. A number of studies have also examined routes by which polymer bridging can be used to modify the interactions between nanodroplets. Early studies involved measurements of interactions between nonionic surfactant-stabilized oil-in-water nanodroplets introduced by poly(acrylic acid) (PAA).[83] At low PAA concentration, long-range interdroplet repulsions were induced, and were hypothesized to result from a flat polymer configuration at the oil-water interface and resulting increased electrostatic repulsion. At larger PAA concentration strong, short-range interdroplet attractions were observed, which were hypothesized to be due to loop-and-tail polymer configurations that bridge the droplets.

Other work has explored the addition of telechelic poly(ethylene glycol) PEG possessing hydrophobic end groups to the continuous phase of oil-in-water nanoemulsions.[29,32,33,84,85] In these systems, entropically-driven hydrophobic interactions produce temperature-sensitive polymer bridging at elevated temperatures,[33] similar to what has been observed in oil-in-water microemulsions in the presence of hydrophobically-modified telechelic polymers.[86-88] Unlike the telechelic microemulsions, however, the bridging interactions induced by the modified PEGs are apparent even for extremely small hydrophobes (including methylene groups),[33] such that the resulting attractions can be tuned with temperature.[29,33] The resulting interaction potentials have been measured by SANS and modeled by a temperature-dependent square well attraction,[33,84] from which a qualitative colloidal phase diagram for the system was recently developed.[84] It should be noted that the surfactant, which in this case is ionic, imparts electrostatic interactions to the system that are screened by surfactant in the bulk, and so the relative concentration of surfactant and polymer in the system is an important parameter that can lead to quantitative differences under different conditions.[29,89]

Polymers can impart more complex interactions due to interactions with surfactant – both at the droplet interface, and in bulk solution. Many hydrophilic polymers including PEG and poly(vinyl alcohol) (PVA) exhibit associative interactions with ionic surfactants in solution [90] and at interfaces.[91] These polymer-surfactant complexes can significantly alter the forces between oil-in-water nanoemulsion droplets.[92,93] Separate studies of interdroplet forces by Philip *et al.* [83,93] and combined scattering and rheology studies by Kim *et al.* [29] have demonstrated a consistent framework for understanding

these interactions. Specifically, the interactions observed depend on the concentrations of surfactant and polymer relative to the critical aggregation concentration (CAC) of the polymer-surfactant complexes and micelle concentration (CMC) of the surfactant. Due to kinetic effects of adsorption at the oil-water interface, the resulting interactions can be complicated by the order in which the various components are introduced in solution.[93] For polymer concentrations below the CAC and surfactant concentrations below the CMC, polymer and surfactant co-adsorb at the oil-water interface, resulting in a polymer brush that can increase steric stabilization of the nanoemulsion.[83] However, once the surfactant and polymer concentration rise above the CAC, the polymer can form complexes with surfactant in the bulk solution that can bridge droplets and lead to interdroplet attractions.[29,83,93] From this point, an increase in bulk surfactant concentration to levels above the CMC lead to the formation of micelles, which serve as a sink for polymer and, as a result, a reduction in the number of bridging interactions. Alternatively, addition of polymer above the CAC at constant surfactant concentration results in a reduction in the number of surfactant-polymer interactions, again leading to reduced bridging interactions.

3.5. Field-induced and anisotropic interactions

Nanoemulsions formulated from magnetically-responsive ferrofluids have interactions that can be easily manipulated by electrical and magnetic fields.[70,71] Such field-induced interactions can give rise to anisotropic or directional interactions that are mostly unavailable through most molecular means due to the spherical morphology of the droplets and their fluid interfaces. Indeed, these interactions are the basis for the optomagnetic droplet chaining methods described previously to measure interdroplet interactions.[71] However, recent reports of multi-compartment oil-in-water nanodroplets[94] also leave open the possibility for producing so-called "Janus" droplets with directional interactions. Such interactions might eventually be employed to produce controlled anisotropic droplet structures in nanoemulsions. However, reports on such structuring have yet to appear, presumably do to the difficulty in observing short-range anisotropic structures of droplets at the nanoscale.

3.6. Unique aspects of nanodroplet interactions

An interesting, if perhaps unexplored, feature of nanodroplets is the mobility of molecules at the fluid-fluid interface. One consequence is that droplets at or near contact can rotate with relatively little mechanical resistance. This is significantly different from hard colloids, where rotation of a particle in contact with a neighbor is significantly hindered, either due to the immobilization of surface species or friction induced by small but finite particle roughness.[95,96] This feature of nanoemulsions has motivated a series of theoretical and computational explorations of the effects of "slippery" attractions on colloidal dynamics and aggregation processes.[65,97] Additionally, the mobility of the nanodroplet interface also allows for reconfiguration of surface-adsorbed molecules including surfactants and polymers.[29] Although interfacial fluidity might pose important complications to colloidal interactions between nanodroplets, it has been relatively unexplored both due to a lack of experimental techniques to characterize the motion of molecules at nanodroplet surfaces, as well as theories to predict the effects of surface diffusion and advection on colloidal interactions. Nevertheless, these effects may ultimately play a considerable role in any number of interactions including the electrostatic and polymer-induced interactions described previously, and even surfactant stabilization of nanodroplets more generally.

4. Complex structure and rheology: suspensions, gels and glasses

In this section, we summarize the wide range of interesting and sometimes complex equilibrium and non-equilibrium fluid states that can arise in nanoemulsions due to the various types of interactions just described, and how their structure, dynamics and rheology can be measured and controlled. The range of complex states observed is quite broad in scope, and is summarized in Figure 1.

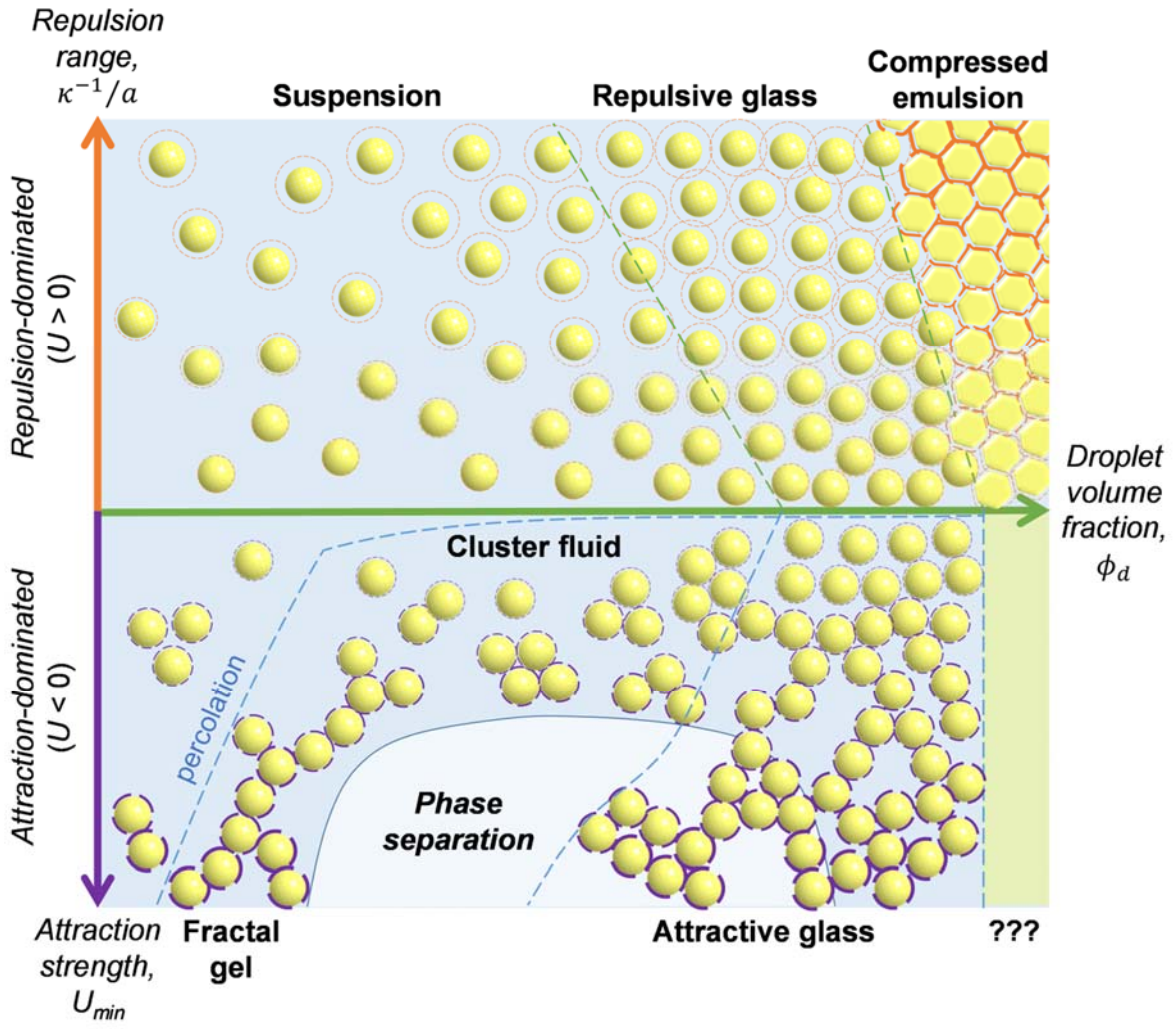

Figure 1. A conceptual "state diagram" for the colloidal behavior of nanoemulsions developed from the literature reviewed here, indicating the structure of various complex rheological states.

4.1. Repulsion-driven systems

Here, we focus on systems and situations in which repulsive interactions (including excluded volume of droplets and electrostatic interactions) dominate the colloidal behavior of nanoemulsions. In this case, the nanoemulsions can be thought of as near hard-sphere fluids, although with effective volume that can be significantly enhanced by long-range repulsions relative to larger colloids.

4.1.1 Dilute and semi-dilute systems. In dilute and semi-dilute nanoemulsion suspensions, characterized by well-dispersed droplets with a volume fraction, ϕ_d, well below any jamming or crystallization transition, nanoemulsions typically exhibit nearly Newtonian rheology, as expected for dispersed colloidal systems. However, colloidally-stable dilute and semidilute nanoemulsions stabilized by ionic surfactants exhibit ϕ_d -dependent viscosities that are much larger and increase with volume fraction much more rapidly than larger emulsions.[98-100] Van der Waarden reported that, in ionic surfactant-stabilized oil-in-water nanoemulsions of identical composition with $\phi_d < 0.33$, the zero shear rate viscosity of the fluid at fixed ϕ_d increased by as much as 50-fold when the droplet radius was reduced from 100 nm to 14 nm.[99] It was recently recognized that this effect is primarily due to the increasing range of electrostatic interactions relative to the droplet size as nanodroplets are driven to smaller and smaller sizes (Figure 1, top axis). To illustrate, one can consider an effective nanodroplet volume that includes the droplet volume with an additional effective excluded volume for electrostatic interactions at a distance from the droplet surface equal to the Debye screening length, κ^{-1}. This results in an effective droplet volume that is larger than the true droplet volume that, to leading order, scales as $(\kappa^{-1}/a)^3$, and thus the effective volume fraction of the suspension is determined by

$$\phi_{d,eff} \sim \phi_d (1 + \kappa^{-1}/a)^3. \quad (1)$$

Recognizing this, Pal recently showed that the intrinsic viscosity for electrostatically-stabilized nanoemulsions could be as large as 4.9 (compared to 2.5 for hard spheres), and constructed a rheological model for nanoemulsion suspensions by extending the Oldroyd model for colloidal suspensions to account for a generic solvation layer (in the case of electrostatic repulsions of width κ^{-1}), the viscosity of the droplet interior, as well as an empirical parameter to account for aggregation between droplets.[100] The model was in quite good agreement with the data of van der Waarden up to droplet volume fractions of $\phi_{d,eff} \sim 0.40$, where the model tends to under-predict the viscosity significantly.

4.1.2 Colloidal glasses and compressed emulsions. The implications of relatively long-range interdroplet repulsions on the behavior of nanoemulsions is perhaps best illustrated by their rheology under relatively concentrated conditions. In the case of hard sphere particles and near-hard sphere emulsions that experience only excluded volume repulsions, repulsively-driven particles at relatively high volume fraction can undergo a non-equilibrium rheological transition to a dynamically arrested state known as a colloidal glass.[101] The dynamical signature of the colloidal glass transition is marked by a significant slowing of the long-time self-diffusivity of the suspended colloids, which is often phenomenologically depicted as the kinetic trapping of particles within a "cage" of nearest neighbors (Figure 1).[102] This behavior results in the development of macroscopic elasticity in the fluid, and non-ergodic dynamical behavior including rheological aging.[103,104]

For monodisperse hard spheres, suspensions begin to exhibit significantly slowed dynamics near a volume fraction of $\phi \sim 0.50$, and a transition to glassy behavior at $\phi \sim 0.56$. However, due to the same enhanced effective volume effects described previously, electrostatically-stabilized nanoemulsions exhibit a glass transition at significantly reduced volume fraction. This phenomenon has been well-studied by Mason and co-workers.[31,34,58,64,105-107] Early evidence included structure factor measurements by SANS on oil-in-water nanoemulsions stabilized by SDS, in which the nearest-neighbor structure peak

was significantly enhanced relative to that of hard spheres at droplet volume fractions up to $\phi_d \sim 0.20$, after which it is suppressed due to droplet deformations as will be described later.[34] Later modeling of these experiments found that renormalizing the droplet volume fraction according to eq. (1) resulted in quantitative prediction of the scattering data using a structure factor for hard spheres.[58] Later refinements showed that polydispersity effects can have subtle, but important, influence on the modeling and interpretation of the resulting structural transition.[64] However, the qualitative picture remains the same: with increasing ϕ_d, the relatively long-range electrostatic repulsions lead to significant enhancements in structural correlations, which eventually leads to a glass transition at concentrations, $\phi_{d,glass}$, in the range of $\phi_{d,glass} \sim 0.27$ to 0.49 with decreasing $\kappa^{-1}/a \sim 0.09$ to 0.05, respectively.[34,108] It is notable that this range of ϕ_d is precisely where the experimental viscosity data of van der Waarden[99] begins to deviate from the model of Pal,[100] which does not account for strong structural correlations. Measurements of dynamics for systems above $\phi_{d,glass}$ using x-ray photocorrelation spectroscopy confirm the glassy behavior of the system.[108] Specifically, the system develops a short-time plateau in the intensity autocorrelation function characteristic of non-ergodic "caged" behavior, whose magnitude increases with effective volume fraction. Furthermore, the longer-time decay of the autocorrelation function exhibits anomalous, so-called "superdiffusive" (i.e. compressed exponential) behavior.

Due to the emergence of non-ergodic behavior and quenched dynamics, the glass transition is accompanied by the emergence of macroscopic elasticity,[101] with a corresponding plateau in the elastic modulus, *G'*, over a large dynamic range in small amplitude oscillatory shear measurements. Studies of electrostatically-stabilized nanoemulsions [31] showed this by performing rheological measurements on a series of nanoemulsions of progressively smaller size for $\phi_d \sim 0.40$, which exhibited a corresponding increase in G' of four orders of magnitude, again illustrating the concept of significantly enhanced structural correlations of nanodroplets due to long-range repulsions. Similar to the previously mentioned SANS measurements, it was found that the elastic modulus of the nanoemulsions over a range of droplet sizes was collapsed by scaling with $\phi_{d,eff}$ as predicted by eq. (1). Here, G' was found to be proportional to the osmotic compressional modulus for close-packed spheres. I.e., to leading order, the glassy emulsions can be approximated as jammed, near hard spheres. Later refinements of the model accounted for the softness of the electrostatic interaction potential, resulting in improved predictions of both the elastic modulus and the yield strain of the nanoemulsions. [106,107]

For ϕ_d sufficiently above $\phi_{d,glass}$, the nanoemulsion droplets can begin to deform due to osmotic compression, resulting in increased elastic energy stored in the deformed droplet interface (Figure 1). Although this occurs for droplets with short-range interactions only near or above the random close-packed limit for near hard spheres, $\phi_{rcp} \sim 0.64$, electrostatically-stabilized (or other long-range repulsive) nanoemulsions can become compressed well below this value. This is evident in various structural signatures, including an increase in the specific surface area of the droplets due to local flattening of the oil-water interface,[34] as well as an increase in the intensity and length scale corresponding to the low-q (large-scale) correlation peak in the structure factor corresponding to a greater degree of long-range order resembling that found in faceted foams.[58,64] Compressed states below ϕ_{rcp} were also evident in a nonlinear dependence of G' on $\phi_{d,eff}$, which was quantitatively captured by balancing the electrostatic osmotic stress with the Laplace pressure of the droplets.[107] In these experiments, volume fractions corresponding to the compressed state as low as $\phi_d \sim 0.52$ were observed.[105] What is remarkable about this behavior is that the electrostatic repulsions alone are sufficient to deform the surfaces of interacting droplets, even though their interfaces may be separated by large distances relative to their size.

Many of the aforementioned studies included variations in the critical effective volume parameter κ^{-1}/a by adding salt to screen electrostatics, showing a remarkable generality to the framework just described. However, the behavior of glassy and compressed nanoemulsions is further complicated when there is excess surfactant in the system, i.e. when the total surfactant in the system exceeds that required to saturate the surface of the droplets. This was demonstrated in a recent study on SDS-stabilized oil-in-water nanoemulsions at a $\phi_d \sim 0.38$ with increasing total SDS concentration.[109] The addition of SDS has two effects – a reduction of κ^{-1}/a, and the formation of micelles in the continuous phase above a concentration corresponding to the CMC of the free surfactant in solution. With increasing SDS concentration, the viscoelastic moduli and yield stress first increase with increasing SDS concentration above a value corresponding to the CMC – opposite to what is predicted from eq. (1) and the resulting theories of Mason and co-workers. It was proposed that the stiffening of the nanoemulsions was due to a transition from a repulsive glass to an attractive gel induced by depletion attractions imparted by the resulting micelles. However, with further increases in the concentration of bulk micelles a re-entrant behavior was observed, where the moduli and yield stress decreased toward their original values. This was proposed to be due to the formation of liquid-like structure of the micelles, resulting in weakened depletion attractions due to the development of oscillatory forces.[28] However, we note that this behavior is also similar to the re-entrant glass-gel-glass transition observed in binary star polymer and star-linear polymer mixtures,[110] where more subtle effects due to the softness of the interactions between species are believed to be responsible. Interestingly, this same re-entrant behavior was not observed in otherwise identical nonionic surfactant-stabilized nanoemulsions, which supports a possible similarity to the star polymer systems, in that re-entrant behavior requires some degree of soft, long-range repulsion in addition to the depletion attractions. Not surprisingly, more recent studies have found that κ^{-1}/a, controlled independently of the surfactant concentration by changing the droplet size, significantly influences the qualitative and quantitative nature of the re-entrant transition.[111] Further studies of this phenomenon are therefore warranted, especially those involving careful measurement of the resulting repulsive and attractive interdroplet interactions.

4.2. Attraction-driven systems

By comparison to repulsion-dominated systems, nanoemulsions with attraction-dominated behavior have received relatively less study. Nevertheless, colloidal attractions can lead to a similarly rich and complex set of structures and phenomena not observed in purely repulsive systems (Figure 1).

4.2.1. Weak attractions: fluid-like clusters and transient networks. Recent work has exploited the interactions induced by the influence of polymer-surfactant complexation described previously[29,83,93] in order to create weak associative interactions between oil-in-water nanodroplets without sacrificing their colloidal stability. In ionic surfactant-stabilized oil-in-water nanoemulsions containing PEG, this leads to the formation of dynamic, transient networks with surfactant and polymer concentrations corresponding to the bridging regime.[29] Due to the relatively weak strength of polymer-surfactant association relative to interdroplet repulsions, the entropically-dominated bridging interactions are highly thermoresponsive, resulting in changes in the viscoelastic moduli up to 5 orders of magnitude over a relatively narrow temperature range that encompasses ambient conditions. The structure of these nanoemulsions measured by SANS was temperature-independent, and could be modeled as a liquid-like dispersion of droplets with mild attractive interactions, consistent with weak bridging by polymer-surfactant complexes.[92,93]

The viscoelasticity was found to follow time-temperature superposition (TTS), suggesting that the temperature-responsive rheology is dictated entirely by the dynamic equilibrium breakage and reformation of the transient network formed by polymer-surfactant-droplet complexes. This was confirmed by dynamic light scattering measurements, where a direct proportionality between the temperature-dependent lifetime of polymer-surfactant complexes and the diffusion time of nanoemulsion droplets was observed. As a result, a simple model was developed for the modulus and viscoelastic relaxation time of the transient networks, in which it was assumed that the network consisted of temporary force chains comprised of polymer-surfactant complexes, with droplets serving as physical crosslinks. The model was validated through systematic changes in the energy scale for complexation, resulting in a remarkable ability to tune the relaxation time of the networks by ten orders of magnitude. This wide tunability of viscoelastic dynamics has led to the use of thermoresponsive transient nanoemulsion networks as a model system to study the nonlinear structure and rheology of Brownian polymer-colloid mixtures under shear flow.[112]

4.2.2. Strong attractions, low ϕ_d: Fractal gels. Stronger attraction strengths are sufficient to drive colloidal instability of droplets due to aggregation. For sufficiently strong attractions and concentrated systems, this can lead to the formation of colloidal gels, i.e. mechanically rigid networks of droplets. Detailed studies of nanoemulsion colloidal gelation were first made in the SDS-stabilized oil-in-water nanoemulsions originally developed by Mason and co-workers.[30,82,113] In these systems, the electrostatic interactions are screened by the addition of salt, which results in aggregation of droplets dominated by van der Waals attractions. Initial studies demonstrated the change from repulsion-dominated to attraction-dominated structure using SANS measurements.[30] Salt concentrations corresponding to relatively mild attractions allowed for time-resolved structural measurements of gel formation. The salient features included suppression of the nearest-neighbor structure factor peak and the emergence of significant low-q scattering suggestive of the formation of large clusters. Although the structure of these clusters could not be directly ascertained due to the limited q-range of the measurements, it was hypothesized that the clusters were fractal in nature due to the asymptotic power law scaling of the scattering intensity, similar to what is found in hard particle systems.

This motivated computational studies that explored the diffusion-reaction processes of colloidal aggregation in these attractive systems with so-called "slippery" bonds.[65,97] In dilute systems (typically $\phi < 0.01$), one can distinguish between diffusion-limited aggregation (DLA),[114] in which gelation is dominated by a single cluster that grows quickly due to fast formation of interparticle bonds, and reaction-limited aggregation (RLA), in which gelation is dominated by a cluster that grows slowly due to constant rearrangement of interparticle bonds.[115] Both processes lead to fractal-like gels characterized by a fractal dimension, d_f, which characterizes the structure of the percolating cluster.[116,117] DLA leads to relatively open structures with $d_f \sim 1.7$, whereas RLA leads to dense structures with $d_f \sim 2.5$.[117] For larger volume fractions, the gelation process proceeds through the growth of multiple clusters in the fluid, with corresponding kinetic limits of diffusion-limited and reaction-limited cluster aggregation (DLCA and RLCA, respectively), with similar definitions to DLA and RLA, but distinguished by the percolation process arising from cluster-cluster interactions.[118] The previously mentioned simulations found that the "slippery" attractive systems were in better agreement with the SANS measurements than for frictional systems,[65,97] and suggested a large-scale structure that resembled predictions for DLCA gelation with an associated fractal dimension $D_f \sim 1.8$-1.9. However, the "slipperiness" of the bonds produces local densification of the network, with a local fractal

dimension $d_f \sim 2.5$, more consistent with an RLA process. By contrast, later experiments tracking the aggregation process over time using light scattering found that the structure and growth of alcohol-containing oil-in-water nanoemulsions stabilized by SDS exhibited a uniform fractal dimension of $d_f = D_f = 2.4\text{-}2.5$ over the range of length scales studied, suggesting that the dominant kinetics of gelation may depend on the relative strengths of the van der Waals attractions and screened electrostatic repulsions.[82]

One disadvantage of the electrostatically-stabilized systems for studies of gelation is that the need for mixing of salt with the nanoemulsion provides relatively poor control over the gelation process. The thermoresponsive polymer bridging system developed by Helgeson and co-workers[29,32,33,84,85] overcomes this limitation, since the strength of the polymer bridging attractions, and therefore the kinetic and thermodynamic path to the gelled state, can be carefully and dynamically controlled. The thermoresponsive bridging nanoemulsions exhibit a highly temperature-sensitive gelation transition, which occurs over as little as a 0.5 °C change in temperature.[32] SANS and USANS measurements (which extend the range of probing length scales beyond what was measured in previous studies) characterized the structure of the resulting gels during careful, quasi-equilibrium quenches into the gelled state to different final temperatures (strengths of attraction).[32] These measurements revealed that gels with $\phi_d < 0.2$ form fractal-like structures, with remarkably homogeneous fractal scattering to the largest length scales of measurement (~10 μm). The features of the gels were quantified using a modified mass-surface fractal model, finding that both the fractal dimension and length scales of droplet clusters changed mildly, but noticeably with the strength of attraction, and took values consistent with the DLCA mechanism.

Interestingly, the thermoreversibility of the gelation in the thermoreversible polymer bridging nanoemulsions and the gels' ultimate elasticity depends qualitatively on the droplet size, with reversible gels only forming for droplet radii below 100 nm.[33] Specifically, it was found that the ratio R_g/a (where R_g is the radius of the bridging polymer), which sets the range for the bridging attractions,[119] produced a clear separatrix in the rheological behavior. For $R_g/a > 0.01$ (small droplets), the gels exhibit solid-like behavior reminiscent of highly elastic gels, with elastic moduli that increase with increasing droplet size, presumably due to a larger number of bridging polymers per droplet, and therefore stronger interdroplet bridging. By contrast, for $R_g/a < 0.01$ (large droplets), paste-like viscoelasticity was observed, with significantly frequency-dependent moduli, and an elastic modulus that decreases with increasing droplet size. This again highlights the critical role that the size of nanoemulsions, in this case through the relative range of bridging attractions, plays in qualitatively determining their colloidal behavior.

Otherwise, the rheology of these gels was mostly consistent with what is observed in fractal hard-sphere gels. Specifically, the elastic modulus scales with droplet volume fraction according to $G' \sim \phi_d^x$, where x is a power law exponent related to the various local and large-scale fractal dimensions.[120] Furthermore, large amplitude oscillatory shear (LAOS) measurements indicated a relatively simple yielding process with increasing strain amplitude,[32] in which G' softens and G'' exhibits a local maximum at the crossover of G' and G'', giving way to a transition to flow characterized by power law behavior at sufficiently large strain amplitude. This process is again consistent to what is observed in dilute, fractal gels.[121] Taken together, the literature in this area show that nanoemulsion colloidal gels with volume fractions up to $\phi_d \sim 0.20$ formed through slow quenching exhibit remarkably similar behavior to dilute hard particle colloidal gels. This suggests that the effects of "slippery" bonds do not dramatically alter the types of gel structures formed under these conditions. However, the various features of the gels, including DCLA and RLA-type structures, appear to vary widely depending on the details of the interaction potential. Further work is needed to more systematically map the possibilities.

As a final note, one may wonder whether the colloidal gelation process results in partial or complete droplet coalescence due to the surface contact that attractive interactions might promote. Some evidence of this has been reported in the electrostatically-screened nanoemulsions studied by Mason and co-workers.[30] By contrast, the thermoresponsive polymer bridging nanoemulsions studied by Helgeson and co-workers exhibit no observable change in the size distribution or specific interfacial area of droplets upon gelation.[32,33] This is presumably because polymer bridging results in a secondary attractive minimum in the interaction potential away from contact,[119] followed by a sharp repulsion at shorter distances due to compression of the polymer that prevents nanodroplets from coming into direct contact.

4.2.3. Strong attractions, moderate ϕ_d: arrested phase separation and attractive glasses. Colloidal gelation processes are not limited to percolation by the formation of fractal structures, and much more complex and rich behavior can be observed at relatively higher ϕ_d.[122] Specifically, an additional mechanism of gelation can occur through an attractively-driven dynamical arrest transition at sufficient volume fraction (Figure 1). This "attractive glass" transition is phenomenologically similar to the glass transition in repulsive systems, in which the self-diffusion of particles, whether part of a percolating structure or not, is critically slowed by a "cage" of nearest neighbor bonds, which must be escaped through thermal excitations in order to relax.[123] Such gels are of considerable fundamental interest, as their structure exhibits qualitative features that are distinct from both more dilute fractal gels and repulsive glasses, with unique structure and dynamics. However, the attractive glass transition is often convoluted with colloidal phase instability. Specifically, the ϕ-dependence of the attractive glass line, often defined by a critical slowing of the long-time collective diffusion coefficient,[124] can intersect the fluid-fluid coexistence region for attractive systems, resulting in gelation by so-called "arrested phase separation" (Figure 1).[125] In this mode of gelation, the fluid is first quenched into the region of phase coexistence, which then proceeds to undergo unstable phase separation (i.e. spinodal decomposition). However, the composition in the dense phase eventually intersects the attractive glass line, at which point the dynamics of phase separation become sufficiently quenched as to arrest the system.

The arrested phase separation mechanism has been widely observed experimentally in hard particle gels formed by polymer depletion attractions,[126] in which the gel exhibits a structure that resembles bicontinuous networks formed by spinodal decomposition.[127] Despite numerous works on the depletion gel systems to study gelation by arrested phase separation,[125,126,128-132] the system suffers from the same limitations as the electrostatically-screened nanoemulsion gels; i.e., the attractive interactions are "switched on" through mixing (in this case with a non-adsorbing polymer). As such, the thermodynamic and kinetic paths through the colloidal phase diagram cannot be readily controlled, and researchers typically must resort to so-called "shear rejuvenation" processes that might corrupt the gel structure in order to obtain an experimentally reproducible state of the material.[120] This has limited the study of gels formed by arrested phase separation mostly to their characterization in the arrested state, with very few studies made during their formation.[133]

The thermoresponsive bridging nanoemulsion system of Helgeson and co-workers has thus emerged as a model system for studying the juxtaposition of phase separation and attractive glass formation as a route to colloidal gelation, again owing to the ability to carefully control the path through the colloidal phase diagram to the gelled state.[29,32,84,89] To illustrate the behavior, the qualitative features of a phase diagram obtained by modeling the bridging interactions as a temperature-responsive square well attraction[84] is reproduced in Figure 1. In this phase diagram, the equilibrium metastable and unstable fluid-fluid phase coexistence boundaries are known,[134,135] as is the percolation

threshold.[136] Here, we have added a sketched attractive glass line to aid the discussion. The first realization from inspecting this diagram is that the system can form a gel either by percolation or arrested phase separation depending on ϕ_d as well as the thermodynamic path to the gelled state, a feature that was demonstrated by combined SANS and USANS measurements of gel structure. Specifically, dilute gels (ϕ_d < 0.20) exhibited uniform fractal-like scattering to extremely large length scales, whereas more concentrated gels (ϕ_d > 0.20) exhibited a clear low-q peak in the structure factor that is characteristic of spinodal decomposition.[32] As such, the thermoreversible bridging nanoemulsions are, to the author's knowledge, the first experimental colloidal system shown to form colloidal gels by both percolation or arrested phase separation has been shown.

The unique features of the thermoresponsive nanoemulsion systems were recently exploited to perform some of the first detailed kinetic and dynamic measurements of the arrested phase separation process, with the goal of elucidating the microscopic mechanisms by which phase separation proceeds and then becomes arrested *en route* to the formation of dense colloidal gels.[84] Specifically, recently developed microscopy and image analysis algorithms[137,138] and accompanying rheological measurements showed that phase separation significantly precedes mechanical gelation, and that the kinetic evolution of the phase separating structure (observable at the micron-scale) proceeds according to classical theories for off-critical spinodal decomposition. Furthermore, it was found that coarsening of the phase separated structure was found to proceed through a slow, intermittent superdiffusive process,[84] with similar signatures to those observed in the repulsive, electrostatically-driven colloidal glasses discussed previously.[108] It was proposed this superdiffusive process from the ballistic-like motion of dense, phase separated domains which undergo interfacial fusion.

In these measurements, it was shown that eventually phase separation slows and arrests after macroscopic mechanical gelation is achieved.[84] However, other experiments, involving reactive "freezing" of the nanoemulsion structure by crosslinking the bridging polymer and subsequent imaging were used to formulate a different hypothesis, in which phase separation was proposed to be preceded by percolation.[89] However, in the latter measurements, it is unclear how the temperature quench and time of "freezing" relative to the extent of phase separation was controlled across the conditions studied, as well as how the gel microstructure is potentially impacted by the crosslinking process. The contradictory nature of these experiments could possibly be explained by the sensitivity of the system to the thermal quench taken to the gelled state. For example, Gao *et al.* showed that the arrested structure was strongly sensitive to the depth of the temperature quench, with the characteristic length scale of phase separation upon arrest varying by nearly an order of magnitude over a relatively small temperature window.[84] These studies suggest that extreme care must be taken in controlling the thermal history to the gelled state in order to make unambiguous interpretations of rheological and microscopy experiments.

These studies have begun to highlight the important role that arrested phase separation (and associated thermal processing) plays in determining the rheology of nanoemulsion gels, and colloidal gels more generally. Specifically Gao *et al.* showed that G' of the phase separated gels could be modulated by an order of magnitude at fixed composition by controlling the depth of quenching into the spinodal,[84] despite the fact that the differentially-quenched gels have nearly indistinguishable local-scale structure measured by SANS.[32] The large-scale heterogeneous structure induced by phase separation also leads to nonlinear rheological properties that are remarkably different than more dilute, fractal gels. Specifically, it was found that the phase separated gels exhibited so-called "two-step yielding" behavior during LAOS stress amplitude sweeps,[32] in which the yielding transition is significantly broadened and delayed, similar to what has been observed in a number of other colloidal gels.[139-142] Later studies

involving rheo-SANS measurements to probe the mechanical deformation of the phase separated structure as well as the nonlinear mechanical signatures during the two-step yielding process.[85] It was ultimately discovered that two-step yielding is a direct consequence of large-scale heterogeneity induced by phase separation. Specifically, poroelastic drainage of fluid through the droplet-lean phase of the gel produces a significant viscous contribution to the stress during nonlinear straining, and it is this viscous contribution that leads to delayed yielding. This was confirmed by frequency-dependent measurements, which showed that the two-step yielding behavior subsided when the rate of straining was decreased below the characteristic time scale for drainage from the phase separated structure.

5. Summary, challenges and opportunities

Nanoemulsions exhibit a number of unique colloidal phenomena that are distinct from what is observed in their larger counterparts. A growing body of work on a diverse set of experimental systems, with accompanying theories and phenomenological models, indicates that the unique features of nanoemulsions stem primarily from the large effective range of colloidal interactions that emerges when droplet sizes are driven to the nanoscale. A number of strategies have emerged to control these various interactions, including electrostatic repulsions, polymer-induced interactions including steric repulsion and bridging attractions, as well as more sophisticated interactions based on surfactant-polymer self-assembly. Systematic studies in the presence of these interactions have revealed complex colloidal states in which droplets remain individually stable, but complex structure, dynamics and rheology emerge. These include enhanced viscosity as well as the formation of colloidal glasses and compressed foams at relatively low volume fraction in repulsion-dominated systems, as well as a range of colloidal gel states in attraction-dominated systems including transient networks, fractal gels, and phase separated gels/attractive glasses. Systematic studies on these systems have led to new theories and conceptual frameworks to explain the rheology of not only nanoemulsions, but colloidal dispersions more generally.

Despite the excellent progress to date in understanding the colloidal behavior of nanoemulsions, a number of challenges and opportunities remain. First of all, despite the numerous studies devoted to the formation and instability of nanodroplets, their unique colloidal behavior has yet to be incorporated into models of these processes. For example, the ability of long-range repulsions to interfacially deform nanodroplets despite relatively large surface separations should significantly modify the coalescence process, and may help explain the remarkable (and still unexplained) stability of nanoemulsions to coalescence.[27] Furthermore, the non-Newtonian rheology of many nanoemulsions has significant implications for the viscous boundary layer encountered in nanoemulsification, and incorporating it could lead to better models to control droplet size and polydispersity. As with most colloidal fluids, the structure and interactions of nanoemulsions is difficult to experimentally observe due to their nanoscopic dimensions.[53] More advanced methods to more directly measure and visualize the interactions, structure and dynamics of nanoemulsions may lead to significant advances in our fundamental understanding of their colloidal behavior. Examples might include recently developed environmental electron microscopy methods[143] and surface force measurements.[69]

Due to their facile preparation, easily controllable size and concentration, extreme kinetic stability, and various methods for controlling their colloidal interactions, it is anticipated that nanoemulsions will become versatile model systems for studying a wide range of colloidal phenomena. Indeed, the work described on electrostatic repulsion-driven nanoemulsions has already contributed to understanding the effects of soft, deformable interactions on the colloidal glass transition,[34,58,64] and

may provide opportunities to study other widely observed, but mechanistically unresolved phenomena in colloid glasses, including aging and rejuvenation,[103,144,145] re-entrant gelation and glass formation,[110,132,146] as well as the role of residual stresses developed during the glass transition.[147] Likewise, thermoreversible bridging nanoemulsions have enabled unprecedented studies to address longstanding questions regarding colloidal gelation, as well as raise some new questions (e.g., what is the role of interfacial mobility and "slipperiness" on aggregation processes and gel rheology?). More detailed characterization of the interaction potentials, phase behaviors and kinetic arrest transitions in these thermoresponsive attractively-driven systems will allow for more thorough exploration of the dependence of colloidal gelation, gel structure and rheology on the thermodynamic and kinetic path to the gelled state, and ultimately provide powerful new strategies for sculpting the structure and rheological properties of colloidal gels and soft matter. In this regard, the inherent polydispersity of nanoemulsions obtained using most conventional methods prevents the formation of ordered equilibrium colloidal phases (e.g. colloidal crystals). Advanced methods to prepare nearly monodisperse nanodroplets (or size-separate them) like those in larger emulsions[148] might lead to unique opportunities to form and study colloidal crystals from colloids with soft, deformable interactions.

Finally, to date, the literature devoted to understanding the colloidal interactions and dispersion behavior of nanoemulsions has focused almost exclusively on oil-in-water systems. More extensive measurements on water-in-oil nanoemulsions would help to develop principles to similarly guide and rationally control their interactions, dispersion stability, microstructure and rheology. Studies on model water-in-oil nanoemulsions may also provide important evidence for and tests of theories to describe colloidal interactions in non-polar media, a longstanding challenge in colloid science.[149] More broadly, studies have recently demonstrated the formation of nanoemulsions from more complex liquids including liquid crystals,[150,151] ionic liquids[11] and liquid metals.[12] These fluids all possess a number of unique and exotic properties compared to more traditional molecular solvents, and may reveal fascinating colloidal behavior based on the modification of these properties under nanoscopic confinement.

Ultimately, it is anticipated that the large emerging framework for understanding the colloidal behavior of nanoemulsions will inspire new engineered approaches to and applications of nanoemulsions. For example, long-range interactions have already inspired the use of magnetically-driven assemblies of nanodroplets as optical sensors for various trace species in solution.[22-24] Alternatively, the ability to control the colloidal behavior of nanoemulsions has long been important to pharmaceutical, food and consumer product formulations, and some of the concepts here may eventually allow for more facile and controlled tailoring of rheology in various formulations. Finally, nanoemulsions have long been used individually to template various organic and inorganic nanoparticles,[19] and so the ability to manipulate interdroplet interactions to control the colloidal assembly of nanoemulsions into larger-scale structures may provide new routes for templating hierarchically-structured soft materials.

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References and recommended reading[*,**]

* of special interest.

** of outstanding interest.

[1] J. M. Asua, *Miniemulsion polymerization*, Progress in polymer science **27**, 1283 (2002).

[2] K. Landfester, *Polyreactions in miniemulsions*, Macromolecular Rapid Communications **22**, 896 (2001).

[3]** D. J. McClements, *Nanoemulsions versus microemulsions: terminology, differences, and similarities*, Soft Matter **8**, 1719 (2012). A detailed discussion comparing nanoemulsions and microemulsions.

[4] L. Prince, *Microemulsions theory and practice* (Elsevier, 2012).

[5] C. Solans, P. Izquierdo, J. Nolla, N. Azemar, and M. Garcia-Celma, *Nano-emulsions*, Current Opinion in Colloid & Interface Science **10**, 102 (2005).

[6] J. M. Janjic and E. T. Ahrens, *Fluorine-containing nanoemulsions for MRI cell tracking*, Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology **1**, 492 (2009).

[7] J. M. Janjic, M. Srinivas, D. K. Kadayakkara, and E. T. Ahrens, *Self-delivering nanoemulsions for dual fluorine-19 MRI and fluorescence detection*, Journal of the American Chemical Society **130**, 2832 (2008).

[8] J. M. O'Donnell, *Reversible addition-fragmentation chain transfer polymerization in microemulsion*, Chemical Society Reviews **41**, 3061 (2012).

[9] M. Porras, A. Martínez, C. Solans, C. González, and J. M. Gutiérrez, *Ceramic particles obtained using W/O nano-emulsions as reaction media*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **270**, 189 (2005).

[10] H. Yoon, J. H. Wu, J. H. Min, J. S. Lee, J.-S. Ju, and Y. K. Kim, *Magnetic and optical properties of monosized Eu-doped ZnO nanocrystals from nanoemulsion*, Journal of Applied Physics **111**, 07B523 (2012).

[11] J. Li, J. Zhang, B. Han, L. Peng, and G. Yang, *Ionic liquid-in-ionic liquid nanoemulsions*, Chemical Communications **48**, 10562 (2012).

[12] Z. Han, B. Yang, Y. Qi, and J. Cumings, *Synthesis of low-melting-point metallic nanoparticles with an ultrasonic nanoemulsion method*, Ultrasonics **51**, 485 (2011).

[13] D. K. Sarker, *Engineering of nanoemulsions for drug delivery*, Current Drug Delivery **2**, 297 (2005).

[14] A. C. Anselmo, M. Zhang, S. Kumar, D. R. Vogus, S. Menegatti, M. E. Helgeson, and S. Mitragotri, *Elasticity of nanoparticles influences their blood circulation, phagocytosis, endocytosis, and targeting*, ACS nano **9**, 3169 (2015).

[15] D. J. McClements, *Edible nanoemulsions: fabrication, properties, and functional performance*, Soft Matter **7**, 2297 (2011).

[16] D. J. McClements and J. Rao, *Food-grade nanoemulsions: formulation, fabrication, properties, performance, biological fate, and potential toxicity*, Critical reviews in food science and nutrition **51**, 285 (2011).

[17] H. D. Silva, M. Â. Cerqueira, and A. A. Vicente, *Nanoemulsions for food applications: development and characterization*, Food and Bioprocess Technology **5**, 854 (2012).

[18] O. Sonneville-Aubrun, J.-T. Simonnet, and F. L'alloret, *Nanoemulsions: a new vehicle for skincare products*, Advances in colloid and interface science **108**, 145 (2004).

[19] N. Anton, J.-P. Benoit, and P. Saulnier, *Design and production of nanoparticles formulated from nano-emulsion templates—a review*, Journal of Controlled Release **128**, 185 (2008).

[20] B. Yang and Z. Han, *Thermal conductivity enhancement in water-in-FC72 nanoemulsion fluids*, Applied Physics Letters **88**, 261914 (2006).

[21] A. Spagnul, C. Bouvier-Capely, G. Phan, F. Rebière, and E. Fattal, *Calixarene-entrapped nanoemulsion for uranium extraction from contaminated solutions*, Journal of pharmaceutical sciences **99**, 1375 (2010).

[22] V. Mahendran and J. Philip, *Influence of Ag+ Interaction on 1D Droplet Array Spacing and the Repulsive Forces between Stimuli-Responsive Nanoemulsion Droplets*, Langmuir **30**, 10213 (2014).

[23] V. Mahendran and J. Philip, in *Underwater Technology (UT), 2015 IEEE* (IEEE, 2015), pp. 1.

[24] V. Mahendran and J. Philip, *Sensing of biologically important cations such as Na+, K+, Ca2+, Cu2+, and Fe3+ using magnetic nanoemulsions*, Langmuir **29**, 4252 (2013).

[25] B. A. Frontana-Uribe, R. D. Little, J. G. Ibanez, A. Palma, and R. Vasquez-Medrano, *Organic electrosynthesis: a promising green methodology in organic chemistry*, Green Chemistry **12**, 2099 (2010).

[26]* T. G. Mason, J. Wilking, K. Meleson, C. Chang, and S. Graves, *Nanoemulsions: formation, structure, and physical properties*, Journal of Physics: Condensed Matter **18**, R635 (2006). A more thorough review of methods to control the formation and composition of nanoemulsions.

[27] T. J. Wooster, M. Golding, and P. Sanguansri, *Impact of oil type on nanoemulsion formation and Ostwald ripening stability*, Langmuir **24**, 12758 (2008).

[28] J. N. Israelachvili, *Intermolecular and surface forces: revised third edition* (Academic press, 2011).

[29]** J. Kim, Y. Gao, C. Hebebrand, E. Peirtsegaele, and M. E. Helgeson, *Polymer–surfactant complexation as a generic route to responsive viscoelastic nanoemulsions*, Soft Matter **9**, 6897 (2013). Demonstrates how polymer-surfactant interactions can be exploited to develop viscoelasticity in nanoemulsions without sacrificing colloidal stability.

[30]* J. Wilking, S. Graves, C. Chang, K. Meleson, M. Lin, and T. Mason, *Dense cluster formation during aggregation and gelation of attractive slippery nanoemulsion droplets*, Physical review letters **96**, 015501 (2006). The time-dependent structure of nanoemulsions with "slippery" attractions is measured, with corresponding similarities and differences to traditional diffusion- and rate-limited cluster models for colloidal aggregation.

[31]** J. N. Wilking and T. G. Mason, *Irreversible shear-induced vitrification of droplets into elastic nanoemulsions by extreme rupturing*, Physical Review E **75**, 041407 (2007). Repulsion-dominated nanoemulsions were found to undergo a transition from a weakly structured liquid to a locally-structured solid with decreasing droplet size, due to changes in the effective range of repulsion.

[32]** M. E. Helgeson, Y. Gao, S. E. Moran, J. Lee, M. Godfrin, A. Tripathi, A. Bose, and P. S. Doyle, *Homogeneous percolation versus arrested phase separation in attractively-driven nanoemulsion colloidal gels*, Soft Matter **10**, 3122 (2014). Attraction-dominated nanoemulsions can form colloidal gels either by percolation in a well-dispersed colloidal phase or by arrested phase separation in a region of phase instability, depending on the concentration of the nanoemulsion.

[33]* M. E. Helgeson, S. E. Moran, H. Z. An, and P. S. Doyle, *Mesoporous organohydrogels from thermogelling photocrosslinkable nanoemulsions*, Nature materials **11**, 344 (2012). Discovery of thermoreversible aggregation and gelation in attraction-dominated nanoemulsions with interdroplet interactions mediated by end-functionalized polymer linkers.

[34]* S. Graves, K. Meleson, J. Wilking, M. Lin, and T. Mason, *Structure of concentrated nanoemulsions*, The Journal of chemical physics **122**, 134703 (2005). Droplet deformability and elasticity are found to qualitatively alter the dispersion microstructure of repulsion-dominated nanoemulsions compared to hard spheres at modest volume fractions.

[35]* C. Solans and I. Solé, *Nano-emulsions: formation by low-energy methods*, Current Opinion in Colloid & Interface Science **17**, 246 (2012). A thorough review of nanoemulsion formation through thermodynamic (or so-called "low energy") routes.

[36] T. Tadros, P. Izquierdo, J. Esquena, and C. Solans, *Formation and stability of nano-emulsions*, Advances in colloid and interface science **108**, 303 (2004).

[37]* A. Gupta, H. B. Eral, T. A. Hatton, and P. S. Doyle, *Nanoemulsions: formation, properties and applications*, Soft Matter **12**, 2826 (2016). A recent, more detailed review of the formation and applications of nanoemulsions.

[38] F. Leal-Calderon, V. Schmitt, and J. Bibette, *Emulsion science: basic principles* (Springer Science & Business Media, 2007).

[39] K. Meleson, S. Graves, and T. G. Mason, *Formation of concentrated nanoemulsions by extreme shear*, Soft Materials **2**, 109 (2004).

[40] S. A. Vitale and J. L. Katz, *Liquid droplet dispersions formed by homogeneous liquid-liquid nucleation:"The ouzo effect"*, Langmuir **19**, 4105 (2003).

[41] C. Qian and D. J. McClements, *Formation of nanoemulsions stabilized by model food-grade emulsifiers using high-pressure homogenization: factors affecting particle size*, Food Hydrocolloids **25**, 1000 (2011).

[42] P.-H. Li and B.-H. Chiang, *Process optimization and stability of D-limonene-in-water nanoemulsions prepared by ultrasonic emulsification using response surface methodology*, Ultrasonics sonochemistry **19**, 192 (2012).

[43] V. Ghosh, A. Mukherjee, and N. Chandrasekaran, *Ultrasonic emulsification of food-grade nanoemulsion formulation and evaluation of its bactericidal activity*, Ultrasonics sonochemistry **20**, 338 (2013).

[44] G. I. Taylor, *The viscosity of a fluid containing small drops of another fluid*, Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character **138**, 41 (1932).

[45] J. Hinze, *Fundamentals of the hydrodynamic mechanism of splitting in dispersion processes*, AIChE Journal **1**, 289 (1955).

[46] I. N. Seekkuarachchi, K. Tanaka, and H. Kumazawa, *Formation and charaterization of submicrometer oil-in-water (O/W) emulsions, using high-energy emulsification*, Industrial & engineering chemistry research **45**, 372 (2006).

[47]* A. Gupta, H. B. Eral, T. A. Hatton, and P. S. Doyle, *Controlling and predicting droplet size of nanoemulsions: scaling relations with experimental validation*, Soft Matter (2016). A dimensional analysis is developed for predicting droplet sizes produced by nanoemulsification, which models the flow around a deforming droplet as a viscous boundary layer within an otherwise turbulent flow.

[48] P. Fernandez, V. André, J. Rieger, and A. Kühnle, *Nano-emulsion formation by emulsion phase inversion*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **251**, 53 (2004).

[49] P. Heunemann, S. Prévost, I. Grillo, C. M. Marino, J. Meyer, and M. Gradzielski, *Formation and structure of slightly anionically charged nanoemulsions obtained by the phase inversion concentration (PIC) method*, Soft Matter **7**, 5697 (2011).

[50] K. Roger, B. Cabane, and U. Olsson, *Emulsification through surfactant hydration: the PIC process revisited*, Langmuir **27**, 604 (2010).

[51] K. Roger, B. Cabane, and U. Olsson, *Formation of 10− 100 nm size-controlled emulsions through a sub-PIT cycle*, Langmuir **26**, 3860 (2009).

[52] P. Izquierdo, J. Feng, J. Esquena, T. F. Tadros, J. C. Dederen, M. J. Garcia, N. Azemar, and C. Solans, *The influence of surfactant mixing ratio on nano-emulsion formation by the pit method*, Journal of colloid and interface science **285**, 388 (2005).

[53] H. S. Lee, E. D. Morrison, C. D. Frethem, J. A. Zasadzinski, and A. V. McCormick, *Cryogenic electron microscopy study of nanoemulsion formation from microemulsions*, Langmuir **30**, 10826 (2014).

[54] J. Qian and C. Law, *Regimes of coalescence and separation in droplet collision*, Journal of Fluid Mechanics **331**, 59 (1997).

[55] L. G. Leal, *Flow induced coalescence of drops in a viscous fluid*, Physics of Fluids (1994-present) **16**, 1833 (2004).

[56] M. A. Rother and R. H. Davis, *The effect of slight deformation on droplet coalescence in linear flows*, Physics of Fluids (1994-present) **13**, 1178 (2001).

[57] F. Baldessari and L. G. Leal, *Effect of overall drop deformation on flow-induced coalescence at low capillary numbers*, Physics of Fluids (1994-present) **18**, 013602 (2006).

[58]* T. Mason, S. Graves, J. Wilking, and M. Lin, *Effective structure factor of osmotically deformed nanoemulsions*, The Journal of Physical Chemistry B **110**, 22097 (2006). The structure of repulsion-dominated nanoemulsions measured in [34] can be adequately predicted using a model for hard spheres by renormalizing the volume fraction according to eq. (1).

[59] P. Taylor, *Ostwald ripening in emulsions*, Advances in colloid and interface science **75**, 107 (1998).

[60] I. M. Lifshitz and V. V. Slyozov, *The kinetics of precipitation from supersaturated solid solutions*, Journal of physics and chemistry of solids **19**, 35 (1961).

[61]* K. Roger, U. Olsson, R. Schweins, and B. Cabane, *Emulsion ripening through molecular exchange at droplet contacts*, Angewandte Chemie **127**, 1472 (2015). A new mechanism, called "contact ripening", is proposed for the coarsening and growth of nanoemulsion droplets, in which molecular exchange between droplets is facilitated by interfacial fluctuations.

[62] A. C. Woodka, P. D. Butler, L. Porcar, B. Farago, and M. Nagao, *Lipid bilayers and membrane dynamics: insight into thickness fluctuations*, Physical review letters **109**, 058102 (2012).

[63] F. J. Martin and R. C. MacDonald, *Phospholipid exchange between bilayer membrane vesicles*, Biochemistry **15**, 321 (1976).

[64]* F. Scheffold and T. Mason, *Scattering from highly packed disordered colloids*, Journal of Physics: Condensed Matter **21**, 332102 (2009). The model of [58] is extended by accounting for droplet polydispersity, with reasonable improvements in accuracy.

[65] C. R. Seager and T. G. Mason, *Slippery diffusion-limited aggregation*, Physical Review E **75**, 011406 (2007).

[66] R. R. Dagastine, G. W. Stevens, D. Chan, and F. Grieser, *Forces between two oil drops in aqueous solution measured by AFM*, Journal of colloid and interface science **273**, 339 (2004).

[67] A. Gunning, A. Mackie, P. Wilde, and V. Morris, *Atomic force microscopy of emulsion droplets: Probing droplet-droplet interactions*, Langmuir **20**, 116 (2004).

[68] J. Nilsen-Nygaard, M. Sletmoen, and K. I. Draget, *Stability and interaction forces of oil-in-water emulsions as observed by optical tweezers–a proof-of-concept study*, RSC Advances **4**, 52220 (2014).

[69] J. Israelachvili *et al.*, *Recent advances in the surface forces apparatus (SFA) technique*, Reports on Progress in Physics **73**, 036601 (2010).

[70] F. L. Calderon, T. Stora, O. M. Monval, P. Poulin, and J. Bibette, *Direct measurement of colloidal forces*, Physical review letters **72**, 2959 (1994).

[71]** R. Dreyfus, D. Lacoste, J. Bibette, and J. Baudry, *Measuring colloidal forces with the magnetic chaining technique*, The European Physical Journal E **28**, 113 (2009). The measurement of colloidal interactions between sub-micron, magneto-responsive droplets is demonstrated.

[72] L. C. Hsiao, M. J. Solomon, K. A. Whitaker, and E. M. Furst, *A model colloidal gel for coordinated measurements of force, structure, and rheology*, Journal of Rheology (1978-present) **58**, 1485 (2014).

[73] L.-C. Peng, C.-H. Liu, C.-C. Kwan, and K.-F. Huang, *Optimization of water-in-oil nanoemulsions by mixed surfactants*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **370**, 136 (2010).

[74] S. Kentish, T. Wooster, M. Ashokkumar, S. Balachandran, R. Mawson, and L. Simons, *The use of ultrasonics for nanoemulsion preparation*, Innovative Food Science & Emerging Technologies **9**, 170 (2008).

[75] M. Wulff-Pérez, A. Martín-Rodríguez, M. J. Gálvez-Ruiz, and J. de Vicente, *The effect of polymeric surfactants on the rheological properties of nanoemulsions*, Colloid and Polymer Science **291**, 709 (2013).

[76] M. Porras, C. Solans, C. Gonzalez, and J. Gutiérrez, *Properties of water-in-oil (W/O) nano-emulsions prepared by a low-energy emulsification method*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **324**, 181 (2008).

[77] K. Bouchemal, S. Briançon, E. Perrier, and H. Fessi, *Nano-emulsion formulation using spontaneous emulsification: solvent, oil and surfactant optimisation*, International journal of pharmaceutics **280**, 241 (2004).

[78] H. Davis, *Factors determining emulsion type: Hydrophile—lipophile balance and beyond*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **91**, 9 (1994).

[79] X. Xin, H. Zhang, G. Xu, Y. Tan, J. Zhang, and X. Lv, *Influence of CTAB and SDS on the properties of oil-in-water nano-emulsion with paraffin and span 20/Tween 20*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **418**, 60 (2013).

[80] L. Wang, R. Tabor, J. Eastoe, X. Li, R. K. Heenan, and J. Dong, *Formation and stability of nanoemulsions with mixed ionic–nonionic surfactants*, Physical Chemistry Chemical Physics **11**, 9772 (2009).

[81] C. Zhang, C. B. O'Donovan, E. I. Corwin, F. Cardinaux, T. G. Mason, M. E. Möbius, and F. Scheffold, *Structure of marginally jammed polydisperse packings of frictionless spheres*, Physical Review E **91**, 032302 (2015).

[82]* A. Lozsan, *Salt-induced fast aggregation of nano-emulsions: structural and kinetic scaling*, Colloid and Polymer Science **290**, 1561 (2012). It is argued that the differences in structure between aggregated nanoemulsions formed by "slippery" attractions and more traditional colloidal systems can be explained by polydispersity effects.

[83] J. Philip, O. M. Monval, F. Leal-Calderon, and J. Bibette, *Forces between colloidal droplets in the presence of a weak polyelectrolyte*, Bulletin of Materials Science **22**, 313 (1999).

[84]** Y. Gao, J. Kim, and M. E. Helgeson, *Microdynamics and arrest of coarsening during spinodal decomposition in thermoreversible colloidal gels*, Soft Matter **11**, 6360 (2015). The thermoresponsive system of [32,33] is used as a model system to investigate the microdynamics and structural kinetics of colloidal phase separation *en route* to colloidal gelation.

[85]* J. Kim, D. Merger, M. Wilhelm, and M. E. Helgeson, *Microstructure and nonlinear signatures of yielding in a heterogeneous colloidal gel under large amplitude oscillatory shear*, Journal of Rheology (1978-present) **58**, 1359 (2014).The thermoresponsive system of [32,33] is used to probe the impact of phase separation and structural heterogeneity on yielding in colloidal gels.

[86] M. Filali, M. J. Ouazzani, E. Michel, R. Aznar, G. Porte, and J. Appell, *Robust phase behavior of model transient networks*, The Journal of Physical Chemistry B **105**, 10528 (2001).

[87] F. Molino, J. Appell, M. Filali, E. Michel, G. Porte, S. Mora, and E. Sunyer, *A transient network of telechelic polymers and microspheres: structure and rheology*, Journal of Physics: Condensed Matter **12**, A491 (2000).

[88] G. Porte, C. Ligoure, J. Appell, and R. Aznar, *Bridging interactions due to telechelic linkers balanced by screened Coulombic repulsions*, Journal of Statistical Mechanics: Theory and Experiment **2006**, P05005 (2006).

[89] L. C. Hsiao and P. S. Doyle, *Celebrating Soft Matter's 10th Anniversary: Sequential phase transitions in thermoresponsive nanoemulsions*, Soft Matter **11**, 8426 (2015).

[90] K. C. Tam and E. Wyn-Jones, *Insights on polymer surfactant complex structures during the binding of surfactants to polymers as measured by equilibrium and structural techniques*, Chemical Society Reviews **35**, 693 (2006).

[91] I. M. Tucker, J. T. Petkov, C. Jones, J. Penfold, R. K. Thomas, S. E. Rogers, A. E. Terry, R. K. Heenan, and I. Grillo, *Adsorption of polymer–surfactant mixtures at the oil–water interface*, Langmuir **28**, 14974 (2012).

[92] J. Philip, T. Jaykumar, P. Kalyanasundaram, B. Raj, and O. Mondain-Monval, *Effect of polymer-surfactant association on colloidal force*, Physical Review E **66**, 011406 (2002).

[93] J. Philip, G. G. Prakash, T. Jaykumar, P. Kalyanasundaram, O. Mondain-Monval, and B. Raj, *Interaction between emulsion droplets in the presence of polymer-surfactant complexes*, Langmuir **18**, 4625 (2002).

[94] M. M. Fryd and T. G. Mason, *Advanced nanoemulsions*, Annual review of physical chemistry **63**, 493 (2012).

[95] J. P. Pantina and E. M. Furst, *Elasticity and critical bending moment of model colloidal aggregates*, Physical review letters **94**, 138301 (2005).

[96] R. Seto, R. Mari, J. F. Morris, and M. M. Denn, *Discontinuous shear thickening of frictional hard-sphere suspensions*, Physical review letters **111**, 218301 (2013).

[97] S. Babu, J.-C. Gimel, and T. Nicolai, *Diffusion limited cluster aggregation with irreversible slippery bonds*, The European Physical Journal E **27**, 297 (2008).

[98] M. Chiesa, J. Garg, Y. T. Kang, and G. Chen, *Thermal conductivity and viscosity of water-in-oil nanoemulsions*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **326**, 67 (2008).

[99] M. Van der Waarden, *Viscosity and electroviscous effect of emulsions*, Journal of Colloid Science **9**, 215 (1954).

[100]** R. Pal, *Modeling the Viscosity of Concentrated Nanoemulsions and Nanosuspensions*, Fluids **1**, 11 (2016). A new model for the suspension viscosity of nanoemulsions is presented, which is able to explain the anomalously large viscosities measured in previous experiments at relatively low volume fractions.

[101] G. L. Hunter and E. R. Weeks, *The physics of the colloidal glass transition*, Reports on Progress in Physics **75**, 066501 (2012).

[102] E. R. Weeks and D. Weitz, *Properties of cage rearrangements observed near the colloidal glass transition*, Physical review letters **89**, 095704 (2002).

[103] D. Bonn, S. Tanase, B. Abou, H. Tanaka, and J. Meunier, *Laponite: Aging and shear rejuvenation of a colloidal glass*, Physical review letters **89**, 015701 (2002).

[104] M. E. Helgeson, N. J. Wagner, and D. Vlassopoulos, *Viscoelasticity and shear melting of colloidal star polymer glasses*, Journal of Rheology (1978-present) **51**, 297 (2007).

[105]** T. G. Mason and F. Scheffold, *Crossover between entropic and interfacial elasticity and osmotic pressure in uniform disordered emulsions*, Soft Matter **10**, 7109 (2014). A near-equilibrium thermodynamic model is developed to predict the transition from jammed glassy states to compressed states in repulsion-dominated nanoemulsions, displaying reasonable agreement with experiment.

[106]* F. Scheffold, F. Cardinaux, and T. G. Mason, *Linear and nonlinear rheology of dense emulsions across the glass and the jamming regimes*, Journal of Physics: Condensed Matter **25**, 502101 (2013). The modulus and yield stress of nanoemulsions in both the glassy and compressed regimes are found to scale as expected by theories for emulsions when the volume fraction is re-normalized according to eq. (1).

[107]* F. Scheffold, J. N. Wilking, J. Haberko, F. Cardinaux, and T. G. Mason, *The jamming elasticity of emulsions stabilized by ionic surfactants*, Soft Matter **10**, 5040 (2014). The model of [106] is extended to account for interfacial deformation of droplets.

[108]* H. Guo, J. Wilking, D. Liang, T. Mason, J. Harden, and R. Leheny, *Slow, nondiffusive dynamics in concentrated nanoemulsions*, Physical Review E **75**, 041401 (2007). The microdynamics of glassy nanoemulsion suspensions is measured, and compared and contrasted to expectations for hard-sphere suspensions.

[109]** V. V. Erramreddy and S. Ghosh, *Influence of Emulsifier Concentration on Nanoemulsion Gelation*, Langmuir **30**, 11062 (2014). With increasing surfactant concentration, nanoemulsions can revert between repulsion-dominated and attraction-dominated regimes due to micelle-induced depletion interactions.

[110] C. Mayer *et al.*, *Asymmetric caging in soft colloidal mixtures*, Nature materials **7**, 780 (2008).

[111]** V. V. Erramreddy and S. Ghosh, *Influence of droplet size on repulsive and attractive nanoemulsion gelation*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **484**,

144 (2015). The changes in dominant behavior found in [109] between repulsion-dominated and attraction-dominated states are found to be senisitive to nanodroplet size.

[112] J. Kim and M. E. Helgeson, *Shear-induced clustering of Brownian colloids in transient polymer networks at moderate Peclet number*, Physical Review Fluids **Submitted** (2016).

[113]* J. N. Wilking, C. B. Chang, M. M. Fryd, L. Porcar, and T. G. Mason, *Shear-induced disruption of dense nanoemulsion gels*, Langmuir **27**, 5204 (2011). Scattering measurements are used to probe structural breakdown in concentrated nanoemulsion colloidal gels at large shear strains and rates.

[114] T. A. Witten and L. M. Sander, *Diffusion-limited aggregation*, Physical Review B **27**, 5686 (1983).

[115] R. Ball, D. Weitz, T. Witten, and F. Leyvraz, *Universal kinetics in reaction-limited aggregation*, Physical review letters **58**, 274 (1987).

[116] J. Teixeira, *Small-angle scattering by fractal systems*, Journal of Applied Crystallography **21**, 781 (1988).

[117] T. Vicsek, *Fractal growth phenomena* (World Scientific, 1992), Vol. 2.

[118] P. Meakin and R. Jullien, *The effects of restructuring on the geometry of clusters formed by diffusion-limited, ballistic, and reaction-limited cluster–cluster aggregation*, The Journal of chemical physics **89**, 246 (1988).

[119] M. E. Helgeson and N. J. Wagner, *Colloidal interactions mediated by end-adsorbing polymer-like micelles*, The Journal of chemical physics **135**, 084901 (2011).

[120] B. Chung, S. Ramakrishnan, R. Bandyopadhyay, D. Liang, C. Zukoski, J. Harden, and R. Leheny, *Microscopic dynamics of recovery in sheared depletion gels*, Physical review letters **96**, 228301 (2006).

[121] H. J. Walls, S. B. Caines, A. M. Sanchez, and S. A. Khan, *Yield stress and wall slip phenomena in colloidal silica gels*, Journal of Rheology (1978-present) **47**, 847 (2003).

[122] E. Zaccarelli, *Colloidal gels: equilibrium and non-equilibrium routes*, Journal of Physics: Condensed Matter **19**, 323101 (2007).

[123] K. A. Dawson, *The glass paradigm for colloidal glasses, gels, and other arrested states driven by attractive interactions*, Current Opinion in Colloid & Interface Science **7**, 218 (2002).

[124] J. Bergenholtz and M. Fuchs, *Nonergodicity transitions in colloidal suspensions with attractive interactions*, Physical Review E **59**, 5706 (1999).

[125] E. Zaccarelli, P. J. Lu, F. Ciulla, D. A. Weitz, and F. Sciortino, *Gelation as arrested phase separation in short-ranged attractive colloid–polymer mixtures*, Journal of Physics: Condensed Matter **20**, 494242 (2008).

[126] P. J. Lu, E. Zaccarelli, F. Ciulla, A. B. Schofield, F. Sciortino, and D. A. Weitz, *Gelation of particles with short-range attraction*, Nature **453**, 499 (2008).

[127] D. Aarts, R. Dullens, and H. Lekkerkerker, *Interfacial dynamics in demixing systems with ultralow interfacial tension*, New Journal of Physics **7**, 40 (2005).

[128] J. Conrad, H. Wyss, V. Trappe, S. Manley, K. Miyazaki, L. Kaufman, A. Schofield, D. Reichman, and D. Weitz, *Arrested fluid-fluid phase separation in depletion systems: Implications of the characteristic length on gel formation and rheology*, Journal of Rheology (1978-present) **54**, 421 (2010).

[129] A. Krall and D. Weitz, *Internal dynamics and elasticity of fractal colloidal gels*, Physical review letters **80**, 778 (1998).

[130] P. J. Lu *et al.*, *Characterizing concentrated, multiply scattering, and actively driven fluorescent systems with confocal differential dynamic microscopy*, Physical review letters **108**, 218103 (2012).

[131] S. Manley, H. Wyss, K. Miyazaki, J. Conrad, V. Trappe, L. Kaufman, D. Reichman, and D. Weitz, *Glasslike arrest in spinodal decomposition as a route to colloidal gelation*, Physical review letters **95**, 238302 (2005).

[132] W. Poon, K. Pham, S. U. Egelhaaf, and P. Pusey, *'Unsticking'a colloidal glass, and sticking it again*, Journal of Physics: Condensed Matter **15**, S269 (2002).

[133] I. Zhang, C. P. Royall, M. A. Faers, and P. Bartlett, *Phase separation dynamics in colloid–polymer mixtures: the effect of interaction range*, Soft Matter **9**, 2076 (2013).

[134] F. Del Rio, E. Avalos, R. Espindola, L. F. Rull, G. Jackson, and S. Lago, *Vapour—liquid equilibrium of the square-well fluid of variable range via a hybrid simulation approach*, Molecular Physics **100**, 2531 (2002).

[135] E. El Mendoub, J.-F. Wax, I. Charpentier, and N. Jakse, *Integral equation study of the square-well fluid for varying attraction range*, Molecular Physics **106**, 2667 (2008).

[136] S. Netemeyer and E. D. Glandt, *Percolation behavior of the square-well fluid*, The Journal of chemical physics **85**, 6054 (1986).

[137] Y. Gao and M. E. Helgeson, *Texture analysis microscopy: quantifying structure in low-fidelity images of dense fluids*, Optics express **22**, 10046 (2014).

[138] A. V. Bayles, T. Squires, and M. E. Helgeson, *Dark-field differential dynamic microscopy*, Soft Matter (2016).

[139] N. Koumakis and G. Petekidis, *Two step yielding in attractive colloids: transition from gels to attractive glasses*, Soft Matter **7**, 2456 (2011).

[140] Z. Shao, A. S. Negi, and C. O. Osuji, *Role of interparticle attraction in the yielding response of microgel suspensions*, Soft Matter **9**, 5492 (2013).

[141] H. K. Chan and A. Mohraz, *Two-step yielding and directional strain-induced strengthening in dilute colloidal gels*, Physical Review E **85**, 041403 (2012).

[142] L. C. Hsiao, R. S. Newman, S. C. Glotzer, and M. J. Solomon, *Role of isostaticity and load-bearing microstructure in the elasticity of yielded colloidal gels*, Proceedings of the National Academy of Sciences **109**, 16029 (2012).

[143] N. de Jonge and F. M. Ross, *Electron microscopy of specimens in liquid*, Nature nanotechnology **6**, 695 (2011).

[144] S. Rogers, D. Vlassopoulos, and P. Callaghan, *Aging, yielding, and shear banding in soft colloidal glasses*, Physical review letters **100**, 128304 (2008).

[145] V. Viasnoff and F. Lequeux, *Rejuvenation and overaging in a colloidal glass under shear*, Physical review letters **89**, 065701 (2002).

[146] T. Eckert and E. Bartsch, *Re-entrant glass transition in a colloid-polymer mixture with depletion attractions*, Physical review letters **89**, 125701 (2002).

[147] M. Ballauff *et al.*, *Residual stresses in glasses*, Physical review letters **110**, 215701 (2013).

[148] J. Bibette, *Depletion interactions and fractionated crystallization for polydisperse emulsion purification*, Journal of colloid and interface science **147**, 474 (1991).

[149] M. F. Hsu, E. R. Dufresne, and D. A. Weitz, *Charge stabilization in nonpolar solvents*, Langmuir **21**, 4881 (2005).

[150] O. Tongcher, R. Sigel, and K. Landfester, *Liquid crystal nanoparticles prepared as miniemulsions*, Langmuir **22**, 4504 (2006).

[151] V. Tomar, S. Hernández, N. Abbott, J. Hernández-Ortiz, and J. de Pablo, *Morphological transitions in liquid crystal nanodroplets*, Soft Matter **8**, 8679 (2012).

Graphical Abstract