Theory of Microemulsion Glasses

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We show that the tendency towards microphase separation in microemulsions leads to the formation of a glassy state after sufficiently strong correlations between polar and hydrophobic regions have been established. Glassiness is predicted to occur above a critical volume fraction of surfactant, which is determined by the length of the amphiphilic molecules. Our results are obtained by solving the dynamical equations for the correlation functions of the system and by using a replica approach.

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Oil and water phase separate at low temperatures, an effect which can be altered by adding amphiphilic surfactant molecules like soap or lipids. Depending on the nature of the surfactant and its volume fraction, complex inhomogeneous structures occur \(^1\). These are caused by the competition between short-ranged forces between oil and water, favoring the separation of uniformly condensed phases, and long-range forces due to the surfactant which energetically frustrate this separation. Examples of such structures are emulsions, which are nonequilibrium colloidal suspensions, and microemulsions in which oil and water are intertwined in complex structures but at equilibrium. The former consist of macroscopically large droplets or bicontinuous networks of oil and water separated by monolayer interfaces of amphiphiles. Microemulsions, on the other hand, are composed of self-organized mesoscopic structures in form of micelles, vesicles or lamellae. These strongly correlated fluids are of great scientific and technological interest: they present extreme materials properties, like ultrasmall surface tensions; they are essential for the stability of cell membranes, formed by phospholipid molecules; their applications range from medicine to biomolecular assemblies such as the Golgi apparatus, to food science in the preparation of sauces, and to petroleum industry, just to name a few prominent examples.

Many of the mesoscale structures found in these amphiphilic systems are extremely long lived i.e., the dynamics is glassy. Sometimes, the macroscopic mechanical properties are like those of a soft solid, as in “stiff mayonnaise”. Light and neutron scattering reveal the hallmarks of glassy motions also on the mesoscopic scale \(^2\) of amphiphilic assemblies. While this glassy behavior is in many ways analogous to that of vitrifying molecular liquids, it goes on at a larger length scale which provides both new opportunities for probing glass physics, and as we shall see for tuning it.

In this paper we develop a theory for glassiness in oil-water-surfactant mixtures for the case of equal water and oil volume fractions, using an electrostatic analogy \(^3\) to describe the competition between entropic effects and stoichiometric constraints of amphiphiles. Although the equal volume fraction case is easier to analyze, our study suggests that little is changed for unbalanced compositions. Glassy behavior in those cases has been attributed to the dynamics of random packed pre-formed micelles or inverse micelles.

**FIG. 1.** Phase diagram of the water-oil-surfactant mixture for \(r_s = 10a\), with \(t\) as the reduced temperature and \(f\) the surfactant volume fraction. The dashed line represents a crossover between the mixed (A) and the microemulsion (B) phases, while the full line separating the emulsion phase (C) from the other phases represents a phase transition. The microemulsion glass transition appears on the region where the correlations between the micellar structures are strong.

The main result of this paper is summarized in the phase diagram, Fig.1. We find that a self generated microemulsion glass forms above a critical volume fraction of the surfactant, \(f\), provided that the mean square root length, \(r_s\), between the head and the tail parts of the surfactant molecule exceeds a minimum value (at least 6 times the typical correlation length of the water and oil molecules, \(a\)). The emergence of glassiness is determined by solving the dynamical equations for the density-density correlation and response functions of the system \(^4\) as well as by using a replica approach for systems without quenched randomness \(^5\). In the dynamical approach, glassiness is manifested in the form of anom-
lous long time dynamics and aging effects. In the replica approach, it is reflected in the emergence of an exponentially large number of metastable states $N_{\text{mas}}$ which renders the system unable to behave as a fluid, resulting in the divergence of the configurational entropy, accompanied by a loss of the configurational entropy $S_c = -k_B \log N_{\text{mas}}$. Both approaches yield identical criteria for the emergence of glassiness. In addition to the glassy state, we also find, in agreement with earlier studies, a region of volume fractions and temperatures where the system forms emulsions and a region where a fluid of microemulsions, built of small micelles or lamellar structures, forms. Finally, for large temperatures there is a region where the mixing entropy favors a homogeneous state.

Self assembled lamellar or micellar structures form in water-oil mixtures due to the competition between entropic effects and constraints caused by the stoichiometry of the amphiphilic surfactants, which are hydrophobic at one end and hydrophilic (polar) at the other end. An elegant description of this complex competition is achieved by using an electrostatic analogy. Stoichiometry enforces that the averaged densities of polar and hydrophobic surfactant groups have to be the same over regions of the size of the mean square root length of the surfactant molecule, $r_s$. This is achieved if one introduces a fictitious Coulomb potential, see Eq. below, where the effective charges are positive (negative) for hydrophobic (polar) molecules. $r_s$ acts as the screening length of this potential since it is the scale on which charge neutrality must be enforced. In Ref. the relevant parameters of the electrostatic model have been expressed in terms of macroscopically well motivated physical quantities like the oil-water surface tension, $\sigma$, the correlation length of the water and oil molecules, $a$, the volume fraction of the surfactant, $f$, as well as $r_s$. In what follows we use a version of the theory, obtained by (approximately) integrating out the surfactant degrees of freedom, which leads to an effective interaction between all hydrophilic and all polar molecules of the system.

A system without surfactants which consists in equal parts of oil-like and water-like molecules is described by the energy

$$E_0 = \frac{1}{2} \int d^4x \left( -\frac{6}{a^2} \rho^2 + (\nabla \rho)^2 + \frac{u}{2} \rho^4 \right),$$

where $\rho(x) > 0$ in a region with hydrophobic molecules and $\rho(x) < 0$ for polar molecules and $\langle \rho(x) \rangle = 0$ on the average. Macroscopic phase separation occurs at a temperature $T_c^0 = 3\sigma a^2$ where the regions with opposite sign of $\rho$ are separated by an interface with surface tension $\sigma$, determined by $a$ as well as the quartic interaction, $u$. If water and oil occur in unequal parts, additional odd powers of $\rho$ occur. For simplicity, here we neglect these effects, although the generalization of our approach is straightforward.

Adding surfactant molecules with volume fraction, $f$, frustrates this macroscopic phase separation and results in an effective interaction between the hydrophobic and polar species

$$V = \frac{9ft}{2\pi r_s^2 a} \int d^d x \int d^d x' \frac{\rho(x)\rho(x')}{|x-x'|}.$$  

(2)

Here $t = T/T_c^0$ is the reduced temperature of the system and, as expected, $q_0 = 6^{1/2}/r_s^{-1}$ plays the role of a Debye wave vector with screening length $\propto r_s$.

A Hartree-Fock analysis of a model with energy $E = E_0 + V$ yields at high temperatures, $T \gtrsim T_c^0$, a homogeneous mixed phase (region A in Fig.1). For lower temperatures $T \lesssim T_c^0$ (i.e. $t < 1$) the competition between $E_0$ and $V$ leads to essentially two distinct regimes: either to a macroscopic phase separation in form of an emulsion (region B in Fig.1) or to a fluid with micro-phase separation (region C in Fig.1). For the latter to be stable within Hartree-Fock theory one needs large surfactant molecules with not too small volume fractions at not too low temperatures (at least $t \gtrsim \frac{q_0}{l_m}$). Consequently, micro-phase separation into a microemulsion occurs only for intermediate temperatures $\frac{q_0}{l_m} \lesssim t \lesssim 1$, a behavior caused by the fact that the frustrating interaction, Eq. is entropy-driven and vanishes as $T \to 0$. The typical size of an oil or water micro-phase is $l_m$; these regions of given size are then correlated over a distance $\xi$. For a sufficiently strong correlated fluid, $\xi > l_m$, the density-density correlation function $G(q) = T^{-1} \langle \rho(q)\rho(-q) \rangle$ is given by

$$G(q) = \frac{q^2 + q_0^2}{(q^2 - a^2/) \langle \rho(q)\rho(-q) \rangle^2},$$

(3)

with $q_m = \frac{2\pi}{l_m}$. In the limit of large $\xi$, the Fourier transformation gives $G(x) = \frac{2\pi q_0 x}{2\pi q_0 x} \cos(q_0 x) (\xi \propto \sqrt{\frac{q_0}{l_m}})$, which clearly demonstrates our physical interpretation of $\xi$ and $l_m$. Within Hartree-Fock theory $\xi$ and $l_m$ are determined by the equation $G(q = 0)^{-1} = \frac{d}{dt} (fa/r_s - 1) +$
An illustrative visualization of the various regimes can be obtained by using the clipped random wave analysis of Ref. [3]. In Fig. 2 we show two typical configurations, for the regions B and C of Fig.1, obtained through this analysis.

Based on these results for the equilibrium’s behavior we will now study glass formation in amphiphilic systems. A glass transition was recently identified in a model for modulated charge inhomogeneities (“stripes”) in doped Mott insulators, which is very similar to Eq. [14] however with infinite screening length. [11,12] It was shown that self generated vitrification occurs if the charge correlation length, ξ, exceeds a critical value. These results were obtained for an infinite range potential. In what follows we will apply the theoretical framework of Ref. [11,12] to investigate vitrification for the model, Eq.[13] with finite range interactions. We start from a Cahn-Hilliard equation

\[\gamma \frac{\partial \rho (x,t)}{\partial t} = \nabla^2 \left( \frac{\delta E[\rho]}{\delta \rho (x,t)} \right) + \eta (x,t)\]

with damping coefficient, \(\gamma\), and random \(\eta (x,t)\), with white-noise correlation \(\langle \eta (x,t) \eta (x',t') \rangle = -2\gamma T \nabla^2 \delta (x - x') \delta (t - t')\) which simulates the effects of a thermal bath at temperature \(T\). We then determine the dynamical equations for the retarded response function, as well as the correlation function of the system within the self consistent screening approximation [2,4]. The onset of glassiness is signaled by a finite Edwards-Anderson order parameter

\[F(q) = T^{-1} \lim_{t' \to \infty} \lim_{t \to \infty} \langle \rho(q,t + t') \rho(-q,t') \rangle.\] (5)

Note that the correlation function, Eq.[2], vanishes in the equilibrium fluid state. The solution of Eq.[1] using the weak ergodicity breaking approach of Ref. [7] (neglecting time derivatives in the long time limit [7]) yields a non-linear self consistent equation for \(F(q)\). The same result is obtained by determining the configurational entropy via the replica approach of Refs. [4,5], where the glass transition is signaled by a proliferation of metastable states, which become exponentially many with the system size. We then find the region in the parameter space with finite Edwards Anderson order parameter, \(F(q)\). We obtain that glassiness occurs if the system undergoes micro-phase separation into a microemulsion (i.e. is located in the region C of Fig.1) and if it forms a strongly correlated fluid of micro-phases with \(\xi > 2l_m\). This rather simple criterion for glassiness, obtained by analyzing the dynamical correlations and the spectrum of metastable states, along the lines of Refs. [1,2], is the central result of this paper.

The boundary of the glassy state can then be obtained by determining the dependence of \(\xi\) and \(l_m\) on \(t, f\), and \(r_s/a\). Since the glass occurs for a fairly moderate correlation length, we can ignore effects due to critical fluctuations (relevant as \(\xi \to \infty\)) and use our results for \(\xi\) and \(l_m\) of the Hartree Fock analysis to determine the boundary of the microemulsion glass state. This leads to the following implicit equation for the onset temperature of glassiness \(T_A = t_A T_0\).

\[f = \frac{(1 + B (t_A, \frac{r_s}{a}) f)^2}{\frac{r_s}{a}^2 T_A}\]

(6)

where \(B(t, x) = \frac{4^{1/3} x^{1/3}}{x(t-1)^{1/2}}\). The solution of this equation for \(r_s = 10a\) gives the boundary of the microemulsion glass shown in Fig.1; a more detailed analysis for various ratios \(r_s/a\) is shown in Fig.3, where we also present the dependence of the point \(f^*\) for the onset of glassiness as function of \(r_s\). Since the frustrating potential, Eq.[3] is of finite range, a finite critical strength of the frustration, \(\sim f^*\), must be reached to form a microemulsion glass. Only as \(r_s \to \infty\) there is a glass for arbitrarily small frustration [1,2]. The larger the amphiphilic molecule and the larger its volume fraction, the more pronounced is the glass state. In these limits, it has also been shown [10] that the bending rigidity of amphiphilic membranes grows considerably, supporting our results for a mechanically stable (high viscosity) glass.

![Glass transition boundaries for different sizes, r_s of amphiphilic molecules (r_s = 20, 15, 10, 7, 6 from left to right). Inset: Temperature dependence of the critical volume fraction, f*, for glassiness as a function of the size of the amphiphilic molecule](image)

The glassy state of our theory is self generated, i.e., it is due to the frustrated nature of the interactions of the system. One way to test our theory is to deliberately “lift” this frustration. For example, we expect that if some disorder is imposed in the surfactant chain length, the glass formation might be reduced. In fact, glassiness will disappear if we add a certain amount of short chain amphiphiles to a system with long chain surfactants. Since the effective mean square root length of the surfactant molecule is then given by \(r_s = (\sum_i x_i s_{i,s}^2)^{1/2}\), with \(x_i\)
being the mole fraction of a surfactant with length $r_s$, $r_s$ can easily become smaller than the critical value $r^\ast$. Another way of testing our theory is to compare the transitions on the high-$T$ and low-$T$ side of the glass state for given $f$. The low-$T$ transition has a larger modulation length. Thus, it has a smaller configurational entropy ($S_i \propto l_{m}^{-3}$) compared to the high-$T$ side of the transition, an effect which can be observed by measuring the specific heat anomaly at the vitrification. At the same time, along the glass transition curve $\xi/l_{m} \simeq 2$. Thus, the position of a small angle neutron scattering (SANS) peak should be shifted along the transition curve, whereas the peak-width ratio should stay essentially unchanged.

In a recent experiment [15] the rheological and structural (as probed by SANS) properties of an aqueous solution of a four branched copolymer were studied and a phase diagram similar to our Fig.1, with a “stiff gel” at the position of our microemulsion glass was found. It was shown that above a critical volume fraction of the polymer ($f \geq 0.3$), the viscosity of the emulsion diverges at a finite temperature which is a monotonically decreasing function of $f$. Furthermore, the divergence of the viscosity is associated with an enhancement of the liquid correlations in a form consistent with the criteria for glassiness proposed in this paper ($\xi \approx 2l_{m}$). All these experimental findings seem to be in agreement with the theory proposed here, even though this system is actually a mixture of block copolymers and water only, without the oil. We argue that the “quasi-solid” or “stiff-gel” [15] found in Ref. [17] is in fact a self generated glass formed by correlated structures of the microemulsion.

In conclusion, we have shown that the competition between entropic effects and stoichiometric constraints responsible for the formation of micelles in microemulsions can lead also to the emergence of a self generated glassy behavior in these systems. This effect is prominent when the effective size of the amphiphile molecules, $r_s$, exceeds a critical value of $6a$, where $a$ is the typical correlation length of water and oil. Furthermore, we show that there is a critical volume fraction to achieve the glassy behavior which depends solely on $\frac{r_{s}}{a}$. Owing to the smaller energy densities at the larger length scales relevant to them, nonlinearity is easier to achieve in the laboratory for microemulsion glasses than the usual structural glasses. In fact, the mechanical properties of the microemulsion glass proposed here are likely much closer to soft materials [19,21] such as gels and pastes than to a rigid window glass. Nevertheless, the universality class of the microemulsion glasses is identical to the one which is believed to apply to structural glasses [22], a conclusion which is also supported by the results of Refs. [19,21]. The fact that the parameters governing the emergence of glassiness in these systems are easily tunable, makes them perfect probes for the entropy crisis scenario attributed to glasses.

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