Lindemann unjamming of emulsions

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We study the bulk and shear elastic properties of barely-compressed, “athermal” emulsions and find that the rigidity of the jammed solid fails at remarkably large critical osmotic pressures. The minuscule yield strain and similarly small Brownian particle displacement of solid emulsions close to this transition suggests that this catastrophic failure corresponds to a plastic-entropic instability: the solid becomes too soft and weak to resist the thermal agitation of the droplets that compose it and fails. We propose a modified Lindemann stability criterion to describe this transition and derive a scaling law for the critical osmotic pressure that agrees quantitatively with experimental observations.

The mechanical properties of emulsions are controlled by two seemingly irreconcilable energy scales: Dilute emulsions like cream and vinaigrette are fluids with osmotic moduli proportional to the ratio of thermal energy, \( k_B T \), to droplet volume, \( 4\pi R^3/3 \), while compressed emulsions like mayonnaise are jammed solids composed of droplets that are pressed together into amorphous, elastic packings with elastic moduli proportional to the ratio of interfacial tension, \( \sigma \), to droplet size, \( R \) \cite{1, 2}. However, when the applied strain exceeds a critical threshold, \( \gamma_y \), droplets slide past each other and the solid yields. The magnitudes of the shear modulus, \( G \), and \( \gamma_y \) are determined by the strength of the contacts between abutting droplets, which decrease with decreasing osmotic pressure, \( \Pi \): Reducing \( \Pi \) thus makes the solid softer and more fragile, and this direct link between \( \Pi \) and \( \gamma_y \) is possible to vary the shear modulus of a compressed emulsion over several orders of magnitude \cite{1, 2}. A smooth cross-over between this jammed elasticity and an entropic, glass-like rigidity has been observed for pastes and emulsions composed of sub-micron particles, whose thermal energy density, \( \frac{3k_B T}{4\pi R} \), is large enough to easily match the modulus of the jammed solid \cite{1, 2, 3, 4}, however, the gap between thermal and interfacial energy scales grows rapidly with increasing droplet size. For emulsions composed of micrometer-scale droplets—which include food emulsions like mayonnaise and most emulsions produced by mechanical agitation—\( \sigma/R \) can be 10\(^6\) to 10\(^{10}\) times larger than \( \frac{3k_B T}{4\pi R} \), and it is not clear how this enormous energy gap is bridged.

Here, we study the pressure dependent shear and osmotic elasticity of barely-compressed, “athermal” emulsions using Diffusing Wave Spectroscopy (DWS) micro rheology and high-resolution magnetic resonance imaging. We show that the shear rigidity of the jammed solid fails catastrophically and that its osmotic modulus declines rapidly below surprisingly large critical osmotic pressures, \( \Pi^* \sim 10^4 \cdot \frac{3k_B T}{4\pi R} \), but minuscule droplet displacement amplitudes, \( \sqrt{\langle \Delta r^2 \rangle}/2R \sim 0.001 \). We further find that this normalized droplet displacement amplitude coincides with the yield strain, \( \gamma_y \), of an emulsion prepared close to its transition. We propose a modified Lindemann stability criterion \cite{10} \cite{11} that bridges these disparate energy scales and derive a critical scaling law for \( \Pi^* \) that agrees quantitatively with the point where shear moduli determined micro rheologically vanish and where osmotic moduli determined from magnetic resonance densitometry rapidly decline. This instability is unlike anything seen or previously expected for three-dimensional solids, but should be common to a wide variety of soft materials that become softer and weaker at smaller osmotic pressures \cite{2} \cite{7} \cite{12}.

To obtain samples with well-known values of \( \Pi \) we prepare a tall column of sedimented emulsion where the buoyant weight of the droplets themselves establishes a well-defined osmotic pressure gradient. We prepare an emulsion composed of nearly-monodisperse, 7.2 \( \mu \)m diameter droplets of anisole and polystyrene dispersed in a 2 mM solution of sodium dodecylbenzenesulfonate in water. The droplets are slightly denser than the surrounding water and we load enough of them into a rectangular glass tube to form a 20 cm tall sediment. The sample is maintained at a constant temperature, \( T = 31.5 \degree C \), and the sediment slowly consolidates and reaches mechanical equilibrium when the weight of every droplet is supported by the material beneath it \cite{13} \cite{14}. Because the interface energy density of this emulsion, \( \sigma/R = 1400 \) Pa, is \( \sim 10^8 \) times larger than its thermal energy density, \( \frac{3k_B T}{4\pi R} = 16 \) \( \mu \)Pa, emulsions like this are commonly referred to as “athermal”.

Even for these emulsions, thermal motion drives fluctuations in droplet positions that can be measured using dynamic light scattering and Diffusing Wave Spectroscopy (DWS), which discern very small droplet motions interferometrically \cite{15} \cite{22}. We illuminate the sediment at a prescribed vertical distance from the top, \( d \), with a 1 cm diameter, linearly-polarized laser beam, and collect cross-polarized, backscattered light using a camera and a split single-mode fiber connected to avalanche photodiodes (Fig. 1A). We then autocorrelate the light intensities recorded by the camera and by the photodiodes, \( I(t) \), and combine them to compute \( g_2(\tau) = \frac{\langle I(t+\tau)I(t)\rangle}{\langle I(t)\rangle^2} \) for lag-times, \( \tau \), spanning a combined twelve orders of magnitude \cite{24}. The value of \( g_2(\tau \rightarrow 0) - 1 \) is nor-
FIG. 1. Diffusive light scattering from sedimented emulsion. (A) 7.2 µm diameter droplets are sealed in a thermostatted glass tube, where they settle and consolidate for several months. The vertical position of the tube is adjusted so that the laser illuminates the sediment at a specific vertical distance below the top, d. A camera and optical fiber collect cross-polarized, backscattered light. (B) Scattered light intensity autocorrelations, g2(τ)-1, measured at distances d = 0.5 cm (○), 1.3 cm (○), 4.0 cm (○), 4.9 cm (○), and 8.5 cm (⊗) below the top of a sedimented emulsion held at 31.5°C show clear separation between solid-like and fluid-like behaviors. (Inset) Droplets closer to the bottom of the sediment reach a stable plateau MSD, while droplets closer to the top are slowed by the crowding of their neighbors but continue to move.

normalized to one, and its decay for increasing τ is directly related to fluctuations in droplet position and shape.

We measure g2(τ) at distances of 0.5 cm, 1.3 cm, 4.0 cm, 4.9 cm, and 8.5 cm below the top of the sediment equilibrated at 31.5°C. The three correlation functions measured closest to the bottom of the sediment reach constant plateaus, consistent with solid-like elasticity, as shown in Fig. 1B. Using DWS to relate g2(τ) to the average mean squared displacement (MSD) of the illuminated droplet positions, ⟨Δr^2(τ)⟩, we estimate that the magnitude of √(Δr^2(τ → ∞)) is less than 12 nm for all three [19] [20] [22] [24]. By contrast, the two correlation functions measured closer to the top of the sediment continue to decay, falling well below the noise floor of our instrument, and are clearly separate from the others. Because of the limitations of DWS, we cannot determine how far the drops continue to move, but can conclude that the magnitudes of their long lag-time displacements are at least 4 times greater than the samples measured immediately below them. The clear difference between these two behaviors is consistent with a sharp transition between a jammed solid and an entropic fluid or glass approximately 3 cm below the top of the sediment.

To explore the effect of this transition on the shear modulus we use the plateau value of the MSD determined from the DWS measurement to calculate the shear modulus using microrheology, G = k_B T / (π R^2 ∆r^2 (τ → ∞)) [20], and measure G as a function of sample depth. Near the top of the sample, where the emulsion is least compressed, G = 0. There is a sharp rise in modulus at the transition, and then G increases linearly with depth, as shown in Fig. 2A. To expand the range of the data, we also make measurements of the sample after equilibrating it at 27.0°C and 34.9°C. Changing temperature changes the buoyancy mismatch between the water and the oil, leading to a different height dependence of the osmotic pressure. The resultant data show the same trend, with G = 0 near the top, where the emulsion is least compressed, a sharp increase at the transition, followed by a linear increase in G with height, as shown in Fig. 2B. To compare the three sets of measurements we estimate Π(d) for each temperature and d by measuring the density difference between the oil and water, δρ, and assuming that the volume fraction near the bottom of the pile is not much larger than that near the top: Π(d) ≈ g δρ(T) φ_c d, where g is the gravitational acceleration and φ_c is the jamming or random close packing volume fraction (see Supplementary Information). Replacing measurement depth with estimated pressure causes all the data collapse onto a single curve. The data show that G ≈ Π for emulsions in the jammed state, but exhibit a sharp transition to a fluid state at Π* ≈ 2.5 Pa, as shown in Fig. 2C. The strict proportionality between G and Π is fundamentally incompatible with results from simulation [20] but consistent with previous experimental data [1-4].

Surprisingly, though the value of Π* is much smaller than the interfacial energy density of the emulsion (σ / R ≈ 1400 Pa), it is also several orders of magnitude larger than its thermal energy density (3/2 k_B T / π R^2 ≈ 16 µPa), while the RMSD of droplets just above Π* is minuscule: barely above 10 nm (Fig. 1B inset). We thus postulate that this transition corresponds to a mechanical instability, and propose a heuristic, Lindemann-type stability criterion in which the critical confining pressure corresponds to the point where the normalized RMSD is equal to γ_y:

\[ \sqrt{\langle \Delta r^2(\Pi^*) \rangle}/2R = \gamma_y(\Pi^*) \]  

(1)

In its simplest form, the Lindemann melting criterion [10] [11] asserts that crystalline solids melt when the ratio
of atomic RMSD to interatomic separation, $r$, exceeds a universal value, $\sqrt{<(\Delta r^2)>}/r = \rho$. And, though this assertion is not a thermodynamically accurate description of first-order melting transitions in equilibrium, a value of $\rho \approx 0.1$ provides surprisingly good agreement with experimental measurements of this ratio for many crystalline solids. However, this value of $\rho$ is two orders of magnitude larger than that inferred for our emulsion using DWS, and our proposed replacement of $\rho$ by $\gamma_y$ is rooted in the direct relationship between microscopic particle displacements and local strains [27] [28], as described in more detail in § 4 of the Supplementary Information.

To convert our modified criterion into an explicit equation for $\Pi^*$ we combine scaling relations for $\gamma_y$, $G$, and $\Pi$ determined by previous experimental studies far from the transition [1][4]:

$$\gamma_y(\phi) = \frac{\phi - \phi_c}{2}$$

$$G(\phi) = \frac{\sigma}{R} \phi (\phi - \phi_c)$$

$$\Pi = G$$

(2)

with the equipartition relation to solve eq. [1] for $\Pi^*$, and find:

$$\Pi^* = \left( \frac{k_B T \phi_c^2 \sigma^2}{\pi R^5} \right)^{1/2} = \frac{\sigma}{R} T^{1/2} \left( 4 \phi_c^2 \right)^{1/2} \sim \frac{\sigma}{R} T^{1/2}$$

(3)

where $T = \frac{k_B T}{\frac{4 \pi}{3} \rho}$ is a reduced temperature. We can similarly arrive at eq. [3] by equating, $E_y$, the work required to yield a microscopic volume, $V_0$, and $k_B T$:

$$E_y = \frac{1}{2} V_0 G \gamma_y^2 = k_B T$$

(4)

assuming a microscopic activation volume, $V_0 = 6 \cdot \frac{4\pi R^3}{3}$, that coincides with the activation volume of shear transformation zones in metallic and colloidal glasses [29][30]. For this emulsion $\sigma/R = 1400 Pa$ and $T \approx 5 \cdot 10^{-5}$, and eq. [3] evaluates to $\Pi^* \approx 2.8 Pa$: in remarkably close agreement with our measurements.

The value of $\gamma_y(\Pi^*)$ predicted from the empirical scaling relations in eq. [2] $\gamma_y(\Pi^*) \approx \frac{\Pi^*}{\sqrt{2 \pi \phi_c}} \approx 0.0015$, agrees remarkably well with $\sqrt{<(\Delta r^2)(\Pi^*)>}/2R \approx 0.0017$, but is nevertheless strikingly small. To test whether such a small value is valid for these emulsions, we prepare a reference sample that is close to the transition but is strong enough to measure with a conventional rheometer, and measure its yield strain. We adjust the concentration of this emulsion by gentle centrifugation to obtain a linear shear modulus of 10 Pa and use a double-Couette cell oscillating at 0.005 Hz to measure the in phase and out of phase components of the shear modulus, $G'$ and $G''$ respectively, as a function of maximum strain, $\gamma$. The elastic modulus, $G'$, is independent of strain at low $\gamma$, but begins to decay at $\gamma_y \approx 0.001$, ultimately decreasing below $G''$ at larger $\gamma$, as shown in Fig. [3] Thus, these very low values of yield strain are indeed observed for these barely-compressed samples.

Finally, to investigate how this mechanical instability affects the bulk modulus of “athermal” emulsions we program a high-field nuclear magnetic resonance (NMR) spectrometer to serve as a magnetic resonance imaging spectrometer, and prepare an emulsion formulated to provide precise, absolute measurements of $\phi(d)$. We prepare monodisperse, 13.2 µm diameter droplets of a mixture of silicone oil and tetrachloroethylene dispersed in a 2 mM solution of sodium dodecylbenzenesulfonate in...
FIG. 3. Oscillatory rheology of weakly jammed emulsion. Strain amplitude dependence of the elastic \(G'\), • and viscous \(G''\), ○ shear moduli of a homogeneous emulsion measured in a mechanical rheometer at 0.005 Hz. The yield strain, \(\gamma_y\), of this soft and fragile solid can be estimated as \(\approx 0.1\%\) by the intersection of the dashed lines fit to the linear elastic and shear thinning regimes.

\[ \phi(\Pi) = \phi_0 + \frac{\Pi R}{\sigma \phi_0} - \delta \phi \exp \left( -\frac{\Pi}{\Pi^*} \right) \]  

with best-fit parameters \(\phi_0 = 0.716\), \(\sigma / R = 311\) Pa, \(\delta \phi = 0.039\), and \(\Pi^*_\phi = 0.56\) Pa (Fig. 4B). We use this value of \(\sigma / R\) and \(\bar{T} \approx 3.4 \times 10^{-9}\) to compute the value of \(\Pi^*\) predicted by eq. 3 and obtain \(\Pi^* \approx 0.6\) Pa: again \(\sim 10^5\) times larger than \(\frac{3k_B T}{4\pi R^3}\), but effectively identical to \(\Pi^*_\phi\).

These results demonstrate the critical importance of thermal fluctuations and plasticity to the transition between jammed and entropic behaviors of soft solids. The growing softness of the emulsion near this transition amplifies the displacements of thermally agitated droplets, and its fragility lets these displacements continually yield and restructure the emulsion. Based on this intuitive picture we propose a simple stability criterion that accurately identifies the entropic-jammed boundary found from light scattering measurements, and points to a region of the equation of state where the bulk modulus of the emulsion rapidly decreases. The combination of an abrupt drop in shear rigidity with a smoothly decreasing density sets this unjamming transition apart from conventional first-order melting or glass transitions. However, given that a vanishing rigidity at low pressures is

D\(_2\)O, load these droplets into an NMR tube, and wait several weeks for the sediment to consolidate. A simplified version of our combined spin- and gradient-echo sequence [31, 32] is shown in Fig. 4A. We use a similar sequence to simultaneously measure the concentration of D\(_2\)O, which provides an absolute volume fraction reference. Further details and calibrations are available in the Supplementary Information.

The volume fraction measured closer to the bottom of the sediment increases slowly and linearly, but its slope increases rapidly near the top (Fig. 4B, inset). We compute \(\phi(\Pi)\) by combining \(\phi(d)\) with the integrated gravitational stress, \(\Pi(d) = g \delta \rho \int_0^d \phi(z) \, dz\), where \(\delta \rho = 150\) kg/m\(^3\) is the is the buoyant density of the droplets, and extract the interfacial energy density, \(\sigma / R = 330\) Pa, by fitting \(\phi(\Pi)\) to \(\phi(\Pi) = \phi_c + \frac{\Pi R}{\sigma \phi_0} \phi_0\) [1]. A similar, though much steeper straight line also fits the data near the top of the sediment, and the extrapolated lines cross at \(\Pi \approx 0.78\) Pa. A tilted exponential interpolates both regimes, providing a good fit to all the data:

\[ \phi(\Pi) = \phi_0 + \frac{\Pi R}{\sigma \phi_0} - \delta \phi \exp \left( -\frac{\Pi}{\Pi^*} \right) \]  

(5)

The vertical depth dependence of droplet volume fraction, \(\phi(d)\), of a sediment composed of oil droplets in D\(_2\)O measured with a NMR spectrometer programmed to act as a high-resolution densitometer. (A) Simplified form of the spin- and gradient-echo pulse sequence used for proton imaging. (B) Osmotic pressure dependence of oil volume fraction, \(\phi(\Pi)\), computed from \(\phi(d)\) (see text). The dashed red line is proportional to \(\frac{\Pi R}{\sigma \phi_0}\). The dashed blue line is a linear fit to \(\phi(\Pi)\) for small pressures. The dashed black curve is a fit to eq. 5 (Inset) Direct measurement of \(\phi(d)\).
a common property of jammed materials, such an elastic instability may be an inescapable consequence and a universal property of such soft solids. We would like to thank F. Spaepen, T. E. Kodger, and P. M. Chaikin for helpful conversations. Magnetic resonance densitometry was performed at the Harvard Magnetic Resonance Facility. We would like to thank Dr. Shaw Huang for his assistance with the implementation of this measurement. This work was partially supported by the Harvard MRSEC (DMR-1420570).

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