Demixing, remixing and cellular networks in binary liquids containing colloidal particles - supplementary information

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Abstract

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Part I

Nearly space-filling networks: an explanation involving phase diagrams

In the main text, we have presented the formation of polyhedral cellular networks in two different binary-liquid/particle systems en route to remixing. However, we still need to explain why we were able to fabricate nearly space-filling networks using cyclohexene-nitromethane/PMMA but not using hexane-methanol/silica. This can be accounted for by quantitatively comparing the binary-liquid phase diagrams using the lever rule[1]

$$\phi_{\text{AR}} = \left| \frac{\varphi_{\text{B}}^{\text{SF}} - \varphi_{\text{B}}^{\text{BR}}}{\varphi_{\text{B}}^{\text{BR}} - \varphi_{\text{B}}^{\text{AR}}} \right| \, . \tag{1}$$

Here, ϕ_{AR} is the volume fraction of the A-rich phase, $\varphi_{\text{B}}^{\text{SF}}$ the volume fraction of component B in the single-fluid phase and $\varphi_{\text{B}}^{\text{AR}}$ $\left(\varphi_{\text{B}}^{\text{BR}}\right)$ is the volume fraction of component B in the A-rich (B-rich) phase. Note that Eq. (1) only holds if the global volume fraction of component B $(\varphi_{\text{B}}^{\text{SF}})$ does not change upon crossing the binodal.

The reasons for the formation of nearly space-filling networks in cyclohexene-nitromethane/PMMA are twofold. First of all, the corresponding phase diagram is more symmetric than that of hexane-methanol (Fig. 1).[2–7] Combined with the near-critical composition of the sample (see Sec. 2.1 in main text), this results in a larger volume fraction of the dispersed phase ϕ_{AR} at room temperature (Eq. (1)). In other words, the creamed emulsions fill a larger proportion of the sample cell to start with.

Secondly, creaming takes the cyclohexene-nitromethane system further across the symmetry line than it does in the case of hexane-methanol. Actually, to prevent the droplets from shrinking upon heating, the creamed emulsions must have a liquid-liquid ratio on the left-hand side of the *critical* composition. In the case of cyclohexene-nitromethane, this requires a droplet packing fraction in the cream $\phi_{\text{droplet}}^{\text{cream}}$ of only 57 vol-% at 38 °C (Fig. 1 and Eq. (1)), whereas it must exceed 61 vol-% at 22 °C for hexane-methanol (equal ΔT to T_{crit}). This can easily be achieved in a random packing, which has a maximum filling fraction of 64 vol-% for monodisperse spheres. As the droplets in our emulsions are highly polydisperse (e.g. Fig. 2e in main text), they may even pack more efficiently, up to 78 vol-% for a polydispersity of 40%.[8]

As buoyancy keeps the droplets in the cream closely packed, heating the emulsion toward the single-fluid phase can be considered as a quench at constant ϕ_{AR}. This is different from cooling from the single-fluid phase, which is a quench at constant $\varphi_{\text{B}}^{\text{SF}}$ (Eq. (1)). Using a fixed value of $\phi_{\text{droplet}}^{\text{cream}} = 64$ vol-% as a reasonable assumption, the lever rule predicts the trajectories in Fig. 1 for the compositions of the creamed emulsions upon heating. Note that the trajectory for cyclohexene-nitromethane is further to the left of the critical-composition line than for hexane-methanol. In fact, for a fixed value of $\varphi_{\text{N}}^{\text{cream}} = 0.32$, corresponding to $\phi_{\text{droplet}}^{\text{cream}} = 64$ vol-% at 38 °C, the phase diagram predicts that

the volume fraction of the cyclohexene-rich phase (ϕ_{AR} in Eq. (1)) should rapidly increase close to the binodal. As no new droplets are formed, the existing ones will tend to grow, i.e. the cream will expand.
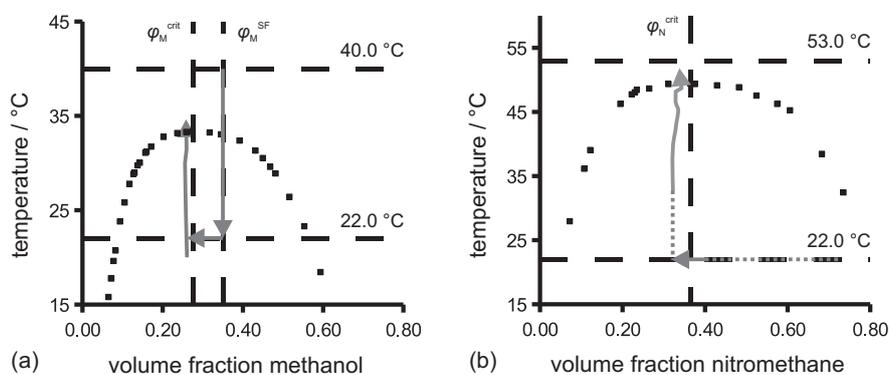

Figure 1: Phase diagrams for the binary mixtures (a) hexane-methanol and (b) cyclohexene-nitromethane,[2–4] in which $\varphi_{\mathrm{M(N)}}^{\mathrm{crit(SF)}}$ is the critical(single-fluid) volume fraction of methanol(nitromethane). The arrow pointing downward represents the quench from the single-fluid phase. The one pointing to the left depicts the system crossing the symmetry line due to creaming. Its dotted tail in panel (b) indicates that we do not know the exact initial sample composition (see Sec. 2.2 in main text). The arrow pointing upward depicts the local volume fraction of methanol(nitromethane) in the cream, calculated from the phase diagram using the lever rule (Eq. (1)), assuming a fixed droplet packing fraction of $\phi_{\mathrm{AR}} = 64$ vol-%.
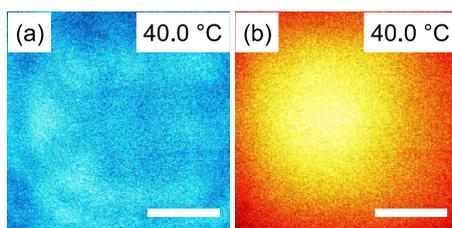
Part II
Movie guide

Figure 2: (*xyt004_f40t22a5_Refl/Fluo_12xrt*): (a) Reflection and (b) fluorescence confocal *xyt*-series of nucleation and growth of droplets in a hexane-methanol mixture (65/35 v/v) containing 2.0 vol-% of R812 silica. The sample was cooled from 40.0 °C to 22.0 °C at 5.0 °C · min^{-1}. Both movies are 12× real-time; they have been resized from 512×512 to 448×448 pixels and subsequently JPEG compressed to reduce file size. Series were taken at approximately 14 μm from the top of the sample; scale bars represent 200 μm.
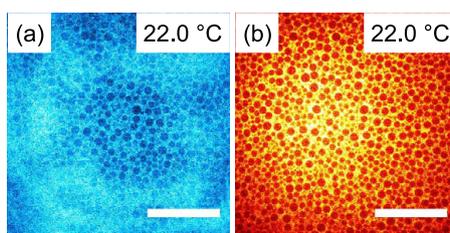
Figure 3: (*xyt006_f22t40a3_Refl/Fluo_16xrt*): (a) Reflection and (b) fluorescence confocal *xyt*-series of network formation from a hexane-in-methanol emulsion (65/35 v/v) containing 2.0 vol-% of R812 silica. The sample was heated from 22.0 °C to 40.0 °C at 3.0 °C $\cdot$ min^{-1}. Both movies are 16× real-time; they have been resized from 512 × 512 to 448 × 448 pixels and subsequently JPEG compressed to reduce file size. Series were taken at approximately 14 μm from the top of the sample; scale bars represent 200 μm.
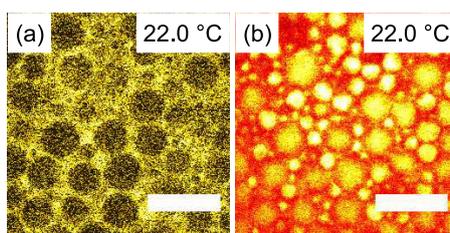
Figure 4: ($a002\_xyt002\_f22t53a20\_NBD/NR\_6\_5xrt$): (a) NBD and (b) Nile Red confocal fluorescence xyt-series of network formation from a cyclohexene-in-nitromethane emulsion (63/37 v/v) containing 2.1 vol-% of PMMA. The sample was heated from 22.0 °C to 53.0 °C at 20.0 °C·min^{-1}. Panel (a/b) corresponds to Figs. 2(i-l)/2(m-p) in the main text. Both movies are 6.5× real-time and they have been JPEG compressed to reduce file size. Series were taken at approximately 30 μm from the top of the sample; scale bars represent 100 μm.
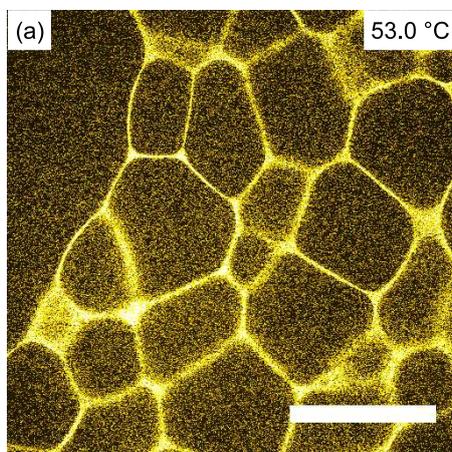
Figure 5: (*xyt008_T53_NBD_100xrt*): Confocal NBD fluorescence *xyt*-series of dynamics in a network formed from a cyclohexene-in-nitromethane emulsion (64/36 v/v) containing 1.9 vol-% of PMMA. The sample was heated from 22.0 °C to 53.0 °C at 20.0 °C·min^{-1}. The movie is 100× real-time and was started after the target temperature of 53.0 °C was reached. It corresponds to Figs. 3e/f in the main text and it has been resized from 512 × 512 to 192 × 192 pixels to reduce file size. Series were taken at approximately 0.44 mm from the top of the sample; scale bar represents 200 μm.

References

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