

Dynamics of DPPC-based foam-like 2D structures stabilized by silica nanoparticles

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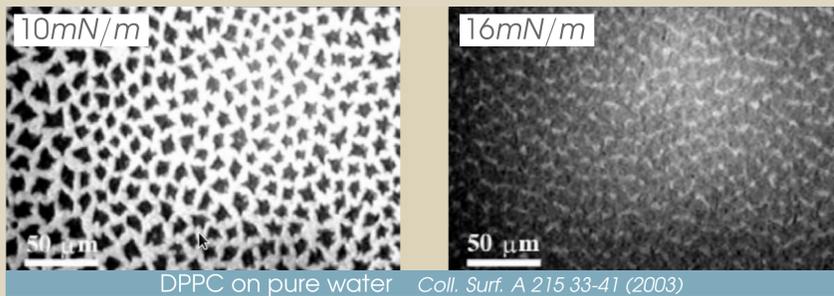
DPPC Langmuir monolayer on a suspension of silica NP

We study mixed surface layers composed by DPPC and silica nanoparticles (NP; size 18 - 120 nm) obtained by spreading a DPPC Langmuir monolayer on a colloidal silica suspension. The incorporation of NP in the monolayer alters the molecular organization and the mechanisms of domain formation.

Previous mechanical measurements of the dilational viscoelasticity of the mixed monolayer have shown an additional relaxation process at $\nu = 0.01 - 0.1$ Hz (not observed in absence of NPs) of unknown origin. (E. Guzmán, L. Liggieri, E. Santini, M. Ferrari, and F. Ravera, *Soft Matter* 8, 3938 - 2012)

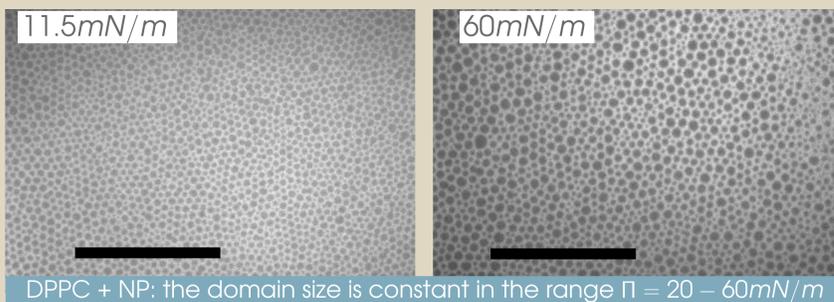
The present XPCS study investigates the origin of this relaxation.

NPs suppress domain coalescence and growth

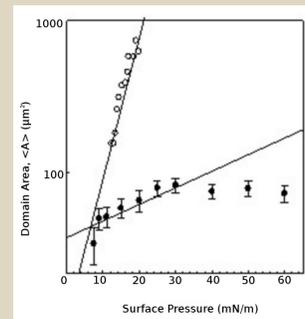


Epifluorescence microscopy at the air/water interface, 20x objective (bars = 200 μm)

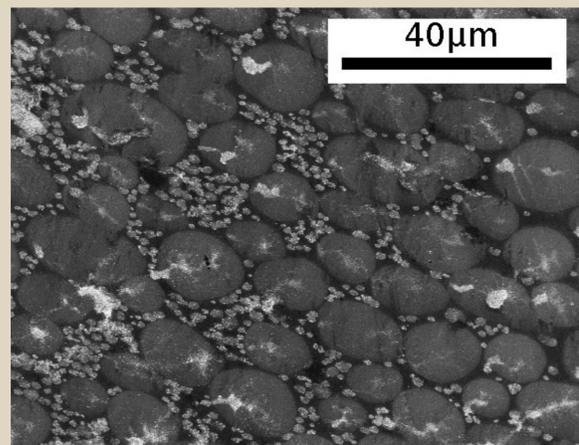
Silica NP hinder the transition to a totally condensed phase that is observed in pure DPPC monolayers. Domains maintain a circular shape and survive up to very high surface pressures.



DPPC + NP: the domain size is constant in the range $\Pi = 20 - 60$ mN/m

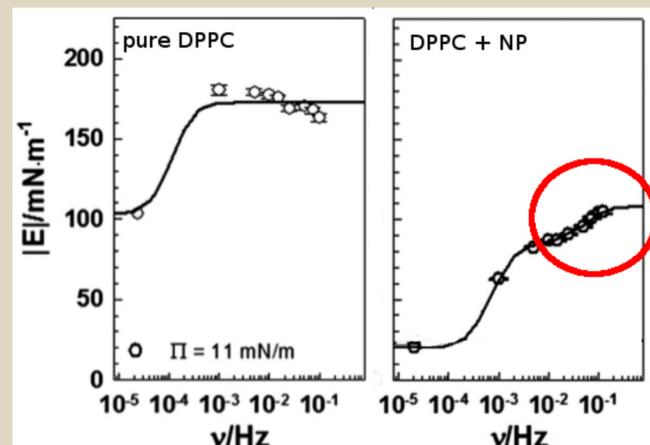


NPs are localized in the LE phase



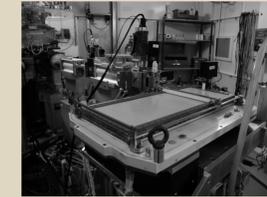
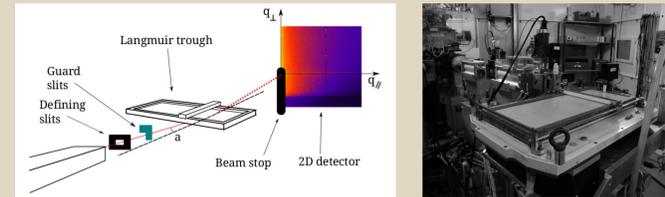
SEM imaging on samples transferred on solid substrate suggests that the nanoparticles mainly localize in the interdomain liquid-expanded (LE) regions, where they hinder the domain coalescence and growth.

NP-induced relaxation process



The measurement of the dilational viscosity shows the onset of an additional relaxation process in the DPPC-NPs system, on the timescale of a few seconds (30 nm NPs).

Dynamics measured by Grazing Incidence XPCS



EXPERIMENT: X-ray Photon Correlation Spectroscopy (XPCS) experiment performed at ID10 (ESRF) in grazing incidence geometry.

We calculate the autocorrelation function of the scattered intensity at given $q_{||}$ at different values of the surface pressure Π .

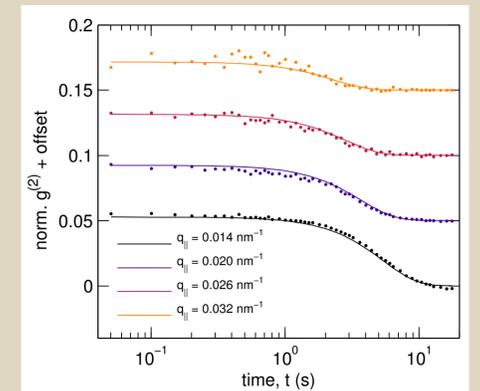
RESULTS: The dynamics is confined at the air/water interface (correlation functions depend only on $q_{||}$).

We fit the correlation functions with:

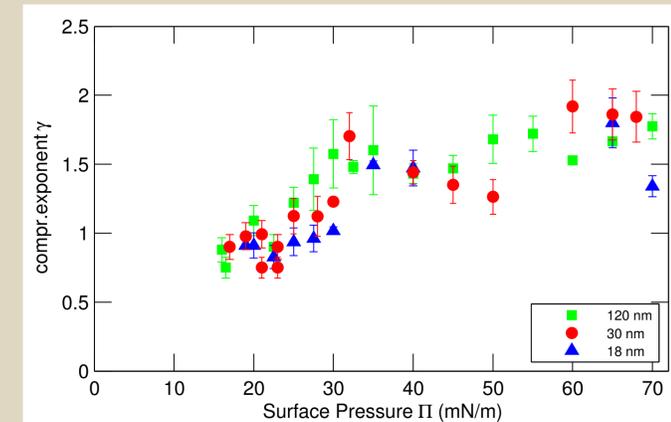
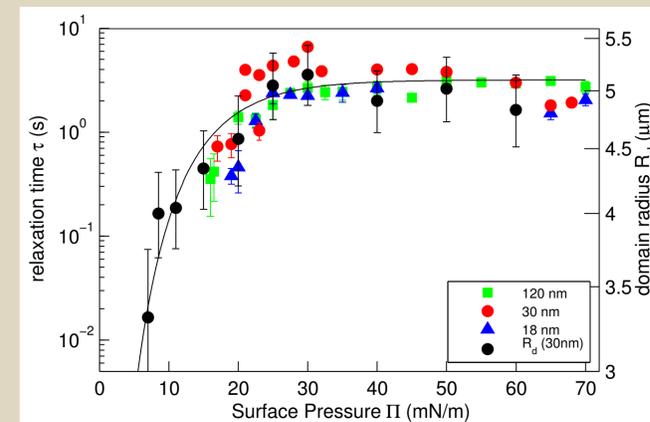
$$g^{(2)}(q_{||}, t) = A + \beta_0 \exp\left(-\frac{u^2 q_{||}^2}{3}\right) \cdot \exp\left[-2\left(\frac{t}{\tau}\right)^\gamma\right]$$

which combines a Kohlrausch-William-Watts exponential decay with a Debye-Waller dependence of the contrast. We also found $\tau \propto q_{||}^{-1}$ at every value of the surface pressure.

(In the figure, DPPC + 120 nm NP at surface pressure $\Pi = 60$ mN/m)



Surface pressure dependence of the dynamics



The dynamics seems to be independent from the size of the silica NP. The relaxation time increases and then saturates in the same fashion as the size of the domains, suggesting that we are indeed probing their diffusional dynamics. The compression exponent γ increases from 1 to 1.5 as the surface pressure is raised: this indicates a transition from a diffusional (Brownian-like) to an arrested dynamics. The localization length u obtained from the Debye-Waller dependence of the contrast is constant over Π and roughly equal to the size of the silica NP.

Our investigation performed by XPCS on the micron-scale allows us to identify the 2nd relaxation time present in the mechanical measurements with the diffusion of microscopic domains

The diffusion coefficient for domains in a DPPC monolayer is

$$D_d = \frac{k_B T}{8\eta_{sub} R_d}$$

(η_{sub} = subphase visc. = 1.5 mPa·s; $T = 293$ K)
Klingler, McConnell, *J. Phys. Chem.* 97, 6096-6100 (1993)

Since $\tau \propto q_{||}^{-1}$, it is not possible to define $D = \frac{1}{\tau q^2}$ as in Brownian Motion. We define

$$D_{XPCS} = \frac{R_d}{\tau q_{||}}$$

For $\Pi = 20$ mN/m (where $\gamma = 1$) we have $\tau \approx 1$ s for $q_{||} = 0.03$ nm⁻¹.

Equating $D = D_{XPCS}$ we get

$$R_d \approx 4 \mu\text{m}$$

as the size of the diffusing object, which is the same as the typical domain size in these conditions