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Phase Separation and Equilibrium gels in a colloidal clay

B. Ruzicka,[1,*] E. Zaccarelli,[2] L. Zulian,[3] R. Angelini,[1]
M. Sztucki,[4] A. Moussaid,[4] T. Narayanan,[4] and F. Sciortino[2]

[1] *CNR-IPCF and Dipartimento di Fisica, Università di Roma "La Sapienza", Piazzale A. Moro 2, I-00185, Rome, Italy*
[2] *CNR-ISC and Dipartimento di Fisica, Università di Roma "La Sapienza", Piazzale A. Moro 2, I-00185, Rome, Italy*
[3] *CNR-ISMAC via Bassini 15, 20133 Milan, Italy*
[4] *European Synchrotron Radiation Facility, B.P. 220 F-38043 Grenoble, Cedex France*

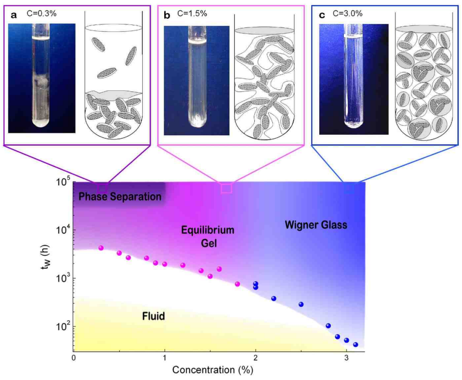

FIG. 1. Phase diagram of diluted Laponite suspensions, in the waiting time vs. concentration plane, resulting from the combined experimental and numerical results. Symbols correspond to experimental waiting time values requested to observe non ergodic behavior according to Dynamic Light Scattering [2]; boundaries inside colored regions are guides to the eye. For long waiting times, three different regions are identified, whose representative macroscopic behavior and a pictorial microscopic view are reported in **a-c**, . **a**, Phase-separated sample with colloid-poor (upper part) and colloid-rich (lower part) regions for $C_w \leq 1.0\%$. **b**, Equilibrium gel for $1.0 < C_w < 2.0\%$, characterized by a spanning network of T-bonded discs. **c**, Wigner glass, expected for $2.0 \leq C_w \leq 3.0\%$ [4], where disconnected platelets are stabilized in a glass structure by the electrostatic repulsion, progressively hampering the formation of T-bonds.

The relevance of anisotropic interactions in colloidal systems has recently emerged in the context of the rational design of novel soft materials. Patchy colloids of different shapes, patterns and functionalities are considered the novel building blocks of a bottom-up approach toward the realization of self-assembled bulk materials with pre-defined properties. New concepts such as empty liquids and equilibrium gels have been formulated[1]. Yet no experimental evidence of these predictions has been provided. Here we report the first observation of empty liquids and equilibrium gels in a complex colloidal clay, and support the experimental findings with numerical simulations.

We investigate dilute suspensions of Laponite, an industrial synthetic clay made of nanometer-sized discotic platelets with inhomogeneous charge distribution and directional interactions. The anisotropy of the face-rim charge interactions combined with the discotic shape of Laponite produce a very rich phase diagram including aging dynamics towards disordered gels and glasses states reached respectively at low and high clay concentrations [2–4]. In this work we extend the observation time for low concentration samples to time-scales significantly longer than those previously studied and discover that, despite samples appear to be arrested on the second timescale, a significant evolution takes place on the year timescale[5]. Samples undergo an extremely slow, but clear phase separation process into clay-rich and clay-poor phases that are the colloidal analog of gas-liquid phase separation. Spectacularly the phase separation terminates at a finite *but very low* clay concentration, above which the samples remain in a homogeneous arrested state. Moreover, the slow aging dynamics peculiar of Laponite suspensions drive an arrest transition through a very slow rearrangement, so that equilibrium gels are formed. The observed features are instead strikingly similar to those predicted in simple models of patchy particles, suggesting that Laponite forms an (arrested) empty liquid at very low concentrations. Furthermore, differently from gels generated by depletion interactions or from molecular glass-formers, where arrest occurs after the phase separation process has generated high-density fluctuation regions, here phase separation takes place in a sample which is already a gel. These new phenomenologies have been observed by direct visual inspection and by Small Angle X-ray measurements performed for very long time (up to more then one year). Furthermore the experimental results for the phase separation and for the structural properties in the various region of the phase diagram have been confirmed by extensive numerical simulations with a primitive model of patchy Laponite discs.

* Corresponding author: barbara.ruzicka@roma1.infn.it

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