

Coupled Brownian motion at liquid-air surfaces

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This research is a collaboration between the PI at Kansas State University and Professor H. K. Pak's group at UNIST (Ulsan National Institute of Standards and Technology) in Ulsan, South Korea. As mentioned in the previous annual report, due to a number of setbacks in the first year of this award, the original emphasis of the research has had to be altered. The current research emphasis is to study soft matter phenomena at liquids surfaces with Professor Pak's group at UNIST and also with Professor Matsubara's group at Kyushu University in Japan.

In Spring 2019 the PI spent one week visiting Professor Matsubara's group at Kyushu University and 3 weeks visiting Professor Pak's group at UNIST, paid for by Kyushu University and UNIST.

The collaboration with Professor Matsubara's group revolves around understand phenomena associated with charged particles at liquid surfaces. The critical binary liquid mixture 2,6-lutidine (L) + water (W) exhibits a lower critical point at a critical temperature of $T_c \approx 34^\circ\text{C}$ (Fig. 1a, coexistence curve (solid line)). The heavier water-rich phase wets (bulk) silica, in preference to the lighter lutidine-rich phase, at a wetting temperature of $T_w \approx 48^\circ\text{C}$ (Fig. 1a, black dashed line). Experiments by Mr Chiguchi (Matsubara group) found that if 0.5% weight of silica particles are added to a lutidine-water mixture then, upon vigorous shaking, a Pickering emulsion is formed. This Pickering emulsion consists of lutidine-rich droplets surrounded by a water-rich phase where the silica particles reside at the LW interface (Fig. 1b). The Pickering emulsion only forms at temperatures sufficiently far from T_c in the two-phase region. If the temperature is reduced towards T_c the Pickering emulsion is found to de-emulsify, or, equivalently the silica particles undergo a wetting transition from residing at the LW interface to residing in the W phase. The temperature of the wetting transition is found to depend upon the silica particle size (Fig. 1a, colored dashed lines).

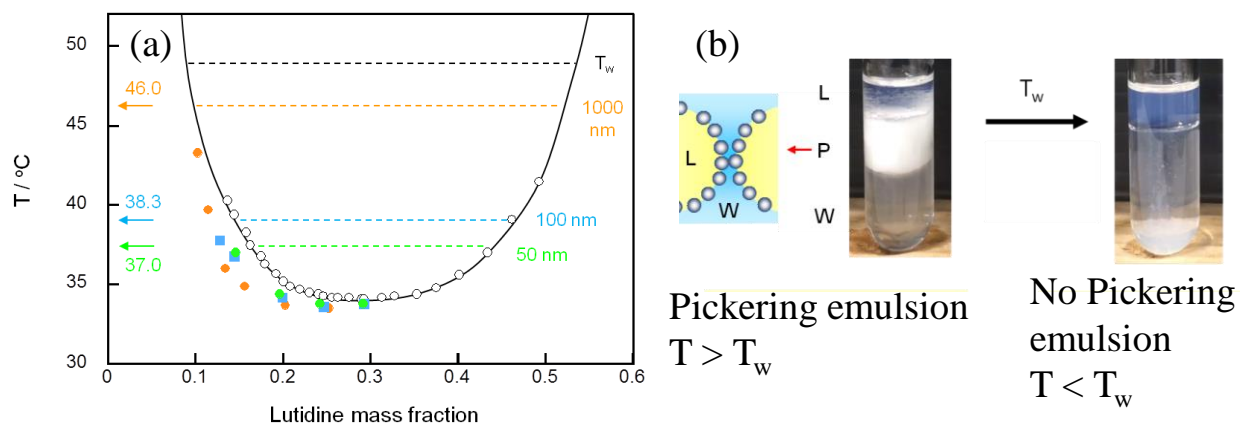


Fig. 1. (a) 2,6-lutidine + water coexistence curve (solid line). Wetting/Pickering emulsion transitions as a function of silica particle size (colored dashed lines). Bulk silica wetting transition (black dashed line). (b) Above (left) and below (right) Pickering transition.

In order to understand this Pickering emulsion behavior we need to understand charged particles at liquid surfaces. Prior work by the PI studied mechanical and thermodynamic equilibrium of *uncharged* particles at liquid/air surfaces where line tension effects play an important role. Mr Rijal, from the PI's research group, is extending this work to the study of *charged* particles at liquid/fluid interfaces. Specifically he is examining how the aqueous-air surface tension changes due to the presence of 20 nm diameter silica particles + salt (KCl) where the concentration of particles and salt is varied. The salt serves to screen the charge on the silica particles. Theoretical models are being developed to explain the mechanical and thermodynamic equilibrium of charge particles at aqueous/fluid interfaces in order to explain the surface tension and Pickering emulsion experiments.

The collaborative work with Professor Pak's group (Mr Park (PhD graduate student) and Dr Paneru (postdoc)) consists of studying an unusual surface nucleation phenomenon in a nano-emulsion of 6CB (4-cyano-4'-pentylbiphenyl) liquid crystal droplets suspended in a water droplet. This phenomenon is studied using the pendant droplet technique to measure the air/liquid surface tension as a function of time (Fig. 2a). 6CB and water possess low miscibility and almost identical densities where the surface tension of 6CB is lower than that of water. The initial surface tension, at time $t = 0$, is approximately the value for pure water. After a surface nucleation time of hundreds of seconds the surface tension starts to decrease where this decrease in surface tension can be fitted by an exponential with a decay time of hundreds of seconds. The nucleation time is found to be a strong function of the 6CB concentration x in water (Fig. 2b) where similar nucleation behavior is found both above (Fig. 2b, red circles) and below (blue circles) the isotropic/nematic transition i.e. this nucleation phenomenon is not influenced by the 6CB liquid crystal properties. The 3 week visit to Ulsan was spent refining the experiments and drafting a manuscript¹. We will be submitting this manuscript for publication shortly.

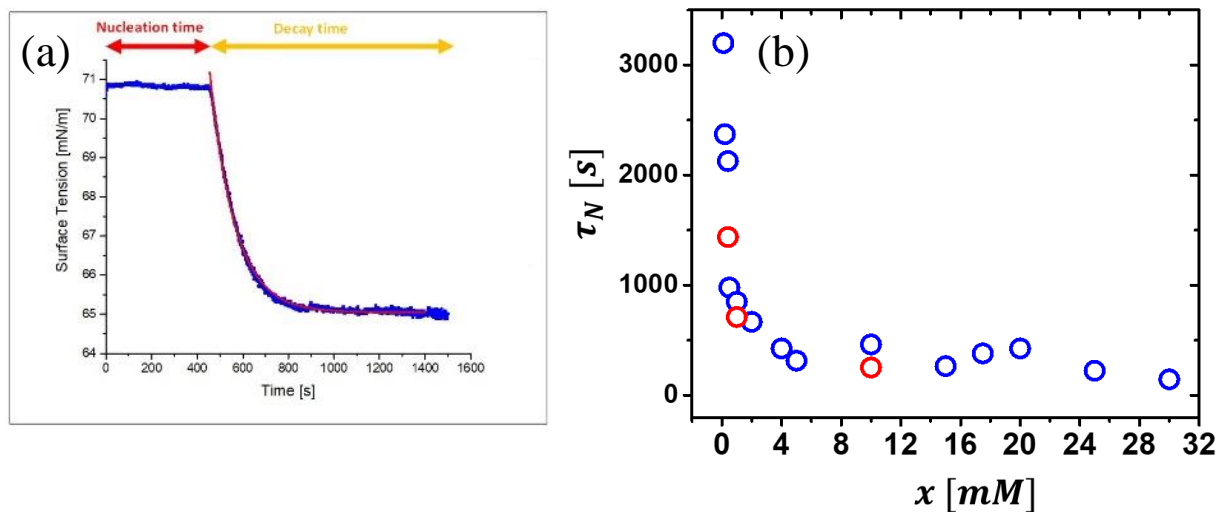


Fig. 2. (a) Surface tension variation with time for a nano-emulsion of 6CB in water. (b) Variation of surface nucleation time τ_N with 6CB concentration x . Red (blue) circles = above (below) 6CB isotropic/nematic transition temperature.

Research Impact:

This research has assisted in developing stronger ties between the PI's research group at Kansas State University and Professor Pak's research group at UNIST and Professor Matsubara's research group at Kyushu University. The work done by Mr Park (UNIST) is part of his PhD research while the work done by Mr Chiguchi (Kyushu University) is part of his BS research. Mr Rijal (Kansas State University) is funded by this ACS PRF grant; his research forms part of his PhD.

1. Park, J.; Paneru, G.; Law, B. M.; Iwamatsu, M.; Pak, H. K., Surface nucleation of 6CB at an air-water interface as a function of bulk composition. *Unpublished 2019*.