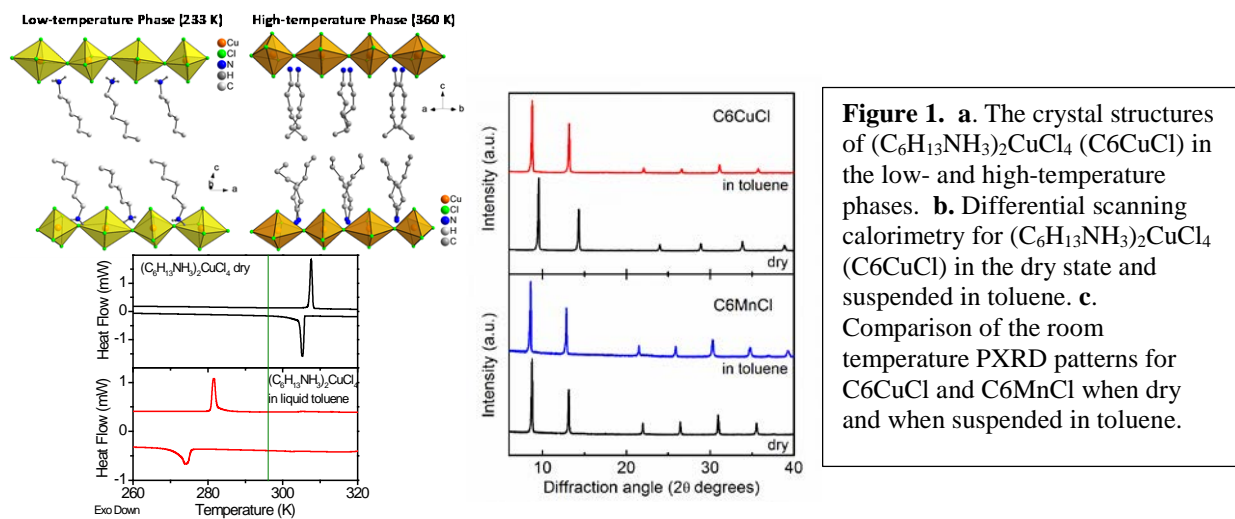


Sheet silicates and related synthetic layered solids are used by the petroleum industry or combined with petroleum products for a number of applications, including use as drilling fluids, rheological control agents, composites, and sorptive materials. They are also found in the targeting rocks of oil and gas exploration. Primary intercalation of organic surfactants through natural or purposeful cation exchange generates particles composed of alternating organic and inorganic networks, and their physical-chemical properties such as hydrophobicity, sorptivity, strength, compressibility, and thermal stability are controlled by the microstructure of the interlayer surfactants. A recent discovery in our lab shows that the solid-state structure of hybrid organic/inorganic layered solids can change upon exposing the surface of mesoscale particles to hydrocarbon media. The effect is different from intercalation and arises when changes in surface environment alter the surface energy (more specifically the surface stress) resulting in an effective pressure change on the particles. If the solids are sufficiently thin and sufficiently compressible, as many layered hybrid solids are, the changing effective pressure alters interlayer spacing. In some cases, the effect can even trigger a solid-solid structural phase transition.

The phenomenon is seen in the hybrid layered solid, $(C_6H_{13}NH_3)_2CuCl_4$ (C6CuCl), Figure 1. This family of alkyammonium metal halides is sometimes referred to as layered perovskites or 2D hybrid perovskites. Differential scanning calorimetry, DSC, shows a phase change at 308 K, which is associated with reorganization of the organic chains as revealed by the crystal structure for the copper halide above and below the transition. If the platelet particles are suspended in toluene, the phase transition moves to lower temperature. Since the transition temperatures for the dry powder and suspended powder are on either side of room temperature, simply suspending the material in toluene induces the phase change, giving rise to a dramatic change in interlayer separation. As for the copper chloride example, the analogous phase transition in the isostructural manganese analogue, $(C_6H_{13}NH_3)_2MnCl_4$ (C6MnCl), shifts when suspended, but the transition temperatures are both below room temperature. Therefore, suspension in toluene results in a less dramatic change at room temperature because the solid is in the same high-temperature phase in both solvents. Nevertheless, the interlayer separation still expands. Similar effects are observed with other organic solvents.



As stated above, the effects are due to changing surface stress when the particles are suspended. Surface stress is the energy required to stretch or compress a surface and is related to surface energy according to

$$f = \gamma \frac{\partial \gamma}{\partial \varepsilon}$$

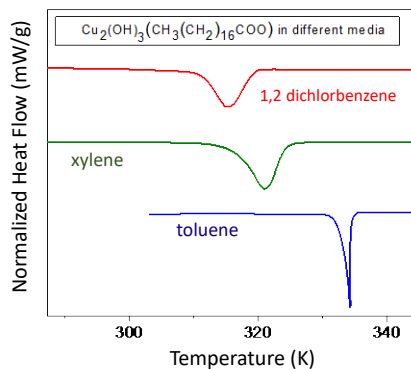
where ε is the strain on the particle. The surface stress leads to a capillary pressure

$$P_{eff} = \frac{2Af}{3V}$$

which causes a volume dilation in small particles if they are sufficiently compressible. For the hydrophobic hybrid layered solids f is positive in air, but its magnitude decreases when suspended in hydrocarbon media. The change has the effect of a tensile force on the particles leading to interlayer expansion. In the case of $(C_6H_{13}NH_3)_2CuCl_4$, the tensile force induces the solid-solid phase transition at room temperature. Ongoing studies are quantifying the magnitude of the changes in surface stress and effective pressure when these and other examples of layered perovskites are suspended in hydrocarbon media.

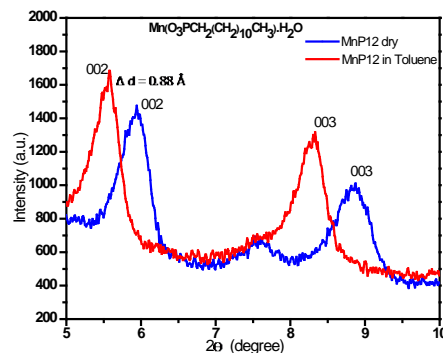
The influence of changing surface stress has now been observed in other families of layered solids. Several examples of layered metal hydroxycarboxylates, based on the general formula $M_2(OH)_3(RCO_2) \cdot H_2O$ ($M = Co, Cu$) have been studied for which R ranges from methyl to octadecyl. These solids also undergo solid-solid transformations, the transition temperatures of which have now been shown to be dependent on the surrounding media. An example is $Cu_2(OH)_3(CH_3(CH_2)_{16}CO_2) \cdot H_2O$. The transition centered around 370K in air shifts to $\sim 325K$ when suspended in dichlorobenzene (Figure 2). The transition temperature can be tuned by changing the suspending solvent.

Figure 2. DSC for $Cu_2(OH)_3(CH_3(CH_2)_{16}CO_2) \cdot H_2O$ suspended in different media, showing the change in transition temperature associated with order-disorder in the organic chains as platelet particles are suspended in different organic media. The exothermic peaks are shown.



The influences of changes in surface stress are also observed in a third family of layered solids, the layered transition metal phosphonates of general formula $M(O_3PR) \cdot H_2O$ characterized by metal phosphonate layers separated by the organic R groups. An example is manganese dodecylphosphonate, $Mn(O_3PC_{12}H_{25}) \cdot H_2O$. In this case, suspension in toluene expands the interlayer spacing by 0.88 \AA , Figure 3. Interestingly, this expansion does not appear to be correlated with a structural phase transition and is simply a result in change in effective pressure on the mesoscale particles.

Figure 3. Powder X-ray diffraction of $Mn(O_3PC_{12}H_{25}) \cdot H_2O$ as a dry powder and when suspended in toluene. The shifts in 001 diffraction peaks correspond to an expansion of the interlayer spacing of 0.88 \AA when the particles are suspended in toluene.



The PRF-ND award has allowed the PI to turn the observation of an apparently new phenomenon into a concerted study aimed at demonstrating the extent to which these effects are general and at quantifying the energetics associated with these supporting media influences. The PI plans to use the outcomes of the award to explore processes potentially impacted by changes in surface stress of mesoscale particles, such as intercalation chemistry and other ion exchange processes. Furthermore, the award has advanced the graduate training of two Ph.D. candidates, providing stipend support and laboratory expense to enable their studies. The materials chemistry topic assures these students receive training in important instrumental techniques and laboratory methods to make them competitive in our high technology economy.