Controls of Interfacial Structure on Nanorod Assembly at Liquid-Crystal Interfaces

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Interfaces play a critical role in solution-based crystallization and self-assembly. The interface alters the distribution of water and ions from that of the bulk, introduces an interfacial free energy that largely determines the barrier to nucleation, and creates an entropic repulsion that drives colloidal assembly. The origins and length scales of these phenomena are inherently atomic-to-molecular but are manifest in ensemble dynamics and outcomes. Using protein nanorods designed *de novo* to present arrays of carboxylic groups that match the K^+ sublattice of mica (001), here we investigate the development of order and the resulting 2D liquid crystal phases (LCPs) that emerge in aqueous electrolyte solutions as the nanorods interact with the surface. We do so by combining high speed *in situ* AFM, molecular simulations, 3D fast force mapping (3D FFM), machine learning (ML), and Monte Carlo (MC) simulations.

We compare the behavior on fluorophlogopite (f-) mica with that on muscovite (m-) mica. Both present the same three-fold symmetric K^+ sublattice, but while the hexagonal f-mica lattice is strictly three-fold symmetric in the (001) plane, that hexagonal symmetry is broken in m-mica due to the geometry of subsurface OH molecules, which makes m-mica monoclinic and results in a slight corrugation of the aluminosilicate network that forms the framework of the (001) lattice. Molecular simulations and 3D FFM show that the resulting solution structure above these two types of mica is fundamentally different. Above f-mica, the symmetry of water, like that of the mica surface lattice, is three-fold symmetric in both the first and second hydration layers. However, above m-mica, the first layer exhibits three-fold positional symmetry, but, due to the corrugation, the water dipoles all orient along the unique axis, which corresponds to one of the K^+ sublattice vectors. The second water layer then forms stripes along this axis.

The AFM and MC results reveal the importance of both nanorod mobility and the orientational symmetry of the interfacial solution structure in determining the LCP. At 100mM KCl, small domains of coaligned nanorods pointing along the three K^+ sublattice vectors — i.e, a high-density disordered phase (HDDP) — is observed on both f- and m-mica. In contrast, at KCl levels of 3M, the behavior on these two surfaces dramatically diverges. On f-mica, the HDDP is maintained, while on m-mica a highly ordered 2D smectic phase forms in which all nanorods are coaligned in parallel rows. MC simulations show that non-interacting nanorods in a 3-fold potential at high coverage only have two potential states: the HDDP, which is kinetically trapped, and a nematic phase, with the latter forming as long as the nanorods have adequate mobility. However, in a two-fold potential, the simulations predict the emergence of a phase exhibiting a high degree of smectic order, as is seen on m-mica at 3M KCl. Given that KCl is expected to effect the electrostatic potential, we hypothesize that the distance at which the proteins reside varies with KCl concentration with the nanorods residing in the 1st hydration layer at 100 mM and the 2nd hydration layer at 3M, thus enabling the selection of a 3-fold or 2-fold interaction potential on m-mica and therefore the choice of an HDDP or a smectic LCP.