

Liquid Flow in Assembly of Ordered Colloidal Crystals

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Colloidal self-assembly techniques are being actively investigated as routes to monolayer and multilayer crystals. Among the most promising applications for self-assembly processes are membrane separations and photonic crystals. Since early observations of phase behavior in colloidal suspensions, experiments and simulations have showed that face centered-cubic (fcc) packings are favored over random and hexagonally close-packed (hcp) structures. Because the free energy difference between hcp and fcc packings is a miniscule quantity (on the order 0.005 $k_B T$ per particle), hydrodynamic and colloidal interactions must direct crystal assembly in all but the most extraordinary phase-transition processes.

There can be no uncertainty about the role of hydrodynamic and colloidal forces in ordered crystal assembly, for spheres as they take their places at the boundaries of a crystal must displace liquid, and this displacement of liquid constitutes flow. Liquid flow induces or follows in all aspects of the self-assembly process: expulsion of liquid from between latex or silica spheres as they are brought into actual contact by van der Waals forces; the motion of liquid that bears suspended particles towards the sphere pack boundary, or growth front, and continues into and through the packed particles.

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Among the predominant descriptions of fluid flow in both ordered and disordered porous media, the network model has provided insight into the link between microscopic structure and macroscopic transport properties. In this approach, an equivalent electrical network describes fluid motion through a connected graph of nodes. The network approach is particularly useful in elucidating the relationships between pore structure and fluid transport in the pore space. By distilling the constitutive equations for creeping flow through complex geometries, the network model enables one to describe key features of the colloidal assembly: packing selectivity, particle convection and growth rates, boundary facets, and capillary pressure distributions.

In this discussion, we highlight microscopic features of the colloidal assembly process and their relationships with the macroscopic particulate coating. Selectivity for face-centered cubic packing through the $\{111\}$ growth facet is discussed, as is solvent flow through $\{100\}$ and $\{311\}$ planes. Differences amongst these boundary arrangements are shown to dictate the distribution of liquid amongst the available pore throats, while not influencing the total convective flux. Network simulations of the entire wetted domain provide a self-consistent approximation for the capillary pressure and flow rate distributions in the assembling crystal as key processing parameters vary; convective flux and crystal growth rates can also be estimated.