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Michael S. Strano
Carbon P. Dubbs Professor of Chemical Engineering
Department of Chemical Engineering, Strano Research Group
Massachusetts Institute of Technology

Two sides of the same leaf: fluids under extreme confinement and the nanotechnology of living plants

Abstract

Nanotechnology has given us a large number of new materials with which to confine fluid phases, altering their thermodynamic and transport properties considerably. Over the past decade, my laboratory at MIT has been centrally focused on quantitatively understanding these alternations, and ultimately using them to solve longstanding research challenges. In this lecture, I will highlight two distinct but fundamentally linked examples of nanoscale confinement effects that prove to be highly enabling once understood. The first system is a phenomenon of lipid exchange that occurs at certain nanoparticle surfaces upon impingement with the plasma membrane of a living plant cell. My laboratory has shown that a relatively simple thermodynamic model of the exchange that occurs in the confined region between the particle surface and the membrane has surprisingly robust predictive power. We show that for a broad range of positively and negatively charged nanoparticles, lipids can exchange with unsaturated sites on the particle corona to energetically drive its irreversible transport across the membrane. Applying these energetics to a chemical engineering model of how nanoparticles traffic and localize within a living plant yields what we call the Lipid Exchange Envelope Penetration (LEEP) model. This framework can predict with surprising accuracy the localization of a broad array of nanoparticles, including carbon nanotubes, semiconductor nanocrystals, plasmonic nanoparticles and nanoceria in a wide array of plant species. The framework predicts how to design the charge and size of a nanoparticle to traverse lipid bilayer membranes associated with the plant plasma membrane, protoplasts, chloroplast, and even pollen. In this application space, we have shown that LEEP enables many new technologies. We can deliver genetic material to the chloroplasts of a broad range of plant species and realize new gene expression.

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Pollen can also be transformed, using LEEP, into a potent plant engineering tool. We can insert a new generation of nanoparticle based sensors within the living plant, controlling the specific compartments within tissues from which the information is conveyed. A nanosensor for H2O2 is able to intercept the rapid stress signaling wave associated with the plant immune response, allowing us to ‘decode’ for the first time the type and magnitude of this stress: thermal, mechanical, photo or pathogenic. This information can even be projected to a nearby user’s cell phone. In addition to new tools for plant biology, my laboratory at MIT has also been pursuing a longer term goal of what we call Plant Nanobionics, or the transformation of living plants into alternatives to the devices we currently stamp out of plastics and electronic circuit boards. We seek the engineering fundamentals required for such transformations to establish new methodologies as well as plant/machine interfaces for human advancement. Examples include living plants as internet enabled sensors for explosives and other impurities in groundwater. We have also made progress on plant based light emission to reduce the 7 EJ/year and 2 Gt/year of CO2 associated with conventional, grid-connected lighting.

Nanoscale confinement effects also confound our understanding of phase equilibria and transport properties within porous media and membranes of all kinds. Over the past decade, my laboratory has been pioneering the measurement and mathematical modeling of confined fluids within a precision model system consisting of a single walled carbon nanotube. We have developed a theory of single component solid-liquid phase transitions under Gibbs-Thomson confinement that is remarkably accurate. For pore sizes larger than approximately 4 nm in diameter, our theory is surprisingly predictive independent of pore type, including, zeolites, controlled pore glass, and carbon, as well as fluid, from organic to inorganic phases. We show that the metal nucleation work of Turnbull, can be adapted to the confined liquid-solid interface by employing his eponymous dimensionless number and the fact that the ratio of the enthalpy of melting and solid-liquid surface energy are approximately constant. The situation changes completely for pores that exhibit extreme levels of confinement. In single walled carbon nanotubes, we and others have experimentally measured non-Gibbs-Thomson phase boundary distortion. We are actively investigating these effects both experimentally and theoretically as a part of the newly established Center for Nano-Enhanced Transport (CENT) at MIT, a Department of Energy sponsored Engineering Frontier Research Center.