DYNAMICS OF SURFACE STRUCTURE EVOLUTION IN COLLOIDAL ADSORPTION: CHARGE-PATTERNING AND POLYDISPERSITY

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ABSTRACT

Colloidal adsorption onto solid surfaces plays a role in applications such as medical implants or transplants, filtration and separation of particulate-laden process streams, and crystalline thin film fabrication. One of the simplest processes that might be considered a nanoscale colloidal fabrication tool, colloidal adsorption is an inexpensive and scalable route to open two-dimensional structures. Additional applications in anti-reflecting coatings, self-cleaning surfaces, optical filters, and photonics can be envisaged if the simple adsorption process is selectively doctored on a patterned (lithographically masked) substrate.

Previous studies on uniform glass, mica, and polyelectrolyte surfaces demonstrate that dynamic computer simulations provide physical insight as well as quantitative models of colloidal adsorption.[1,2] The random sequential adsorption (RSA) model has been most widely used to predict equilibrium surface structures by considering particles only at the surface. The RSA model has been successful in many situations where adsorption is irreversible, such that particles as they approach and attach at the surface have no mobility. In RSA, positions are randomly chosen for particle deposition. If the location chosen is not occupied by another particle, an adsorption event occurs. Successive trials are carried out until particles can no longer adsorb on the surface due to the presence of a critical coverage limit, called the jamming coverage, at which effectively all open surface is obstructed by previously adsorbed particles. In

hard-sphere systems the jamming coverage θ_∞ is 0.547. Additional information about kinetics and structure evolution is gained when the simulation encompasses a small reservoir of colloidal suspension near the adsorption surface. The Brownian Dynamics (BD) simulation methodology has been widely employed to simulate colloidal adsorption processes, particularly where particle-particle and particle-surface interactions influence the adsorption dynamics.

Relatively little attention has been paid to random and lithographically charge-heterogeneous substrates,[3] nor has much emphasis been placed on the possibility of flow. Particle adsorption is common in coating processes designed for paper manufacturing, protective surface finishes, stents or other biologically-sensitive materials, and many others. Flow is invariably an integral part of coating processes as well, models for which must rely on finite, free-surface domains to properly account for momentum and mass transport. For this reason, the study of adsorption from finite coating films is of practical importance. We emphasize here the dynamics of colloidal adsorption from confined liquid films on the order of 200 particle radii. Physically, these correspond to liquid films on the order of several microns, which is the thinnest film accessible by pre-metered coating processes.

Kinetics, surface structures, and extent of surface coverage in adsorption of spherical colloids onto uniform and charge-patterned surfaces are studied using dynamic simulations. A BD simulation methodology is developed to account for double-layer and van der Waals interactions between particles and the adsorption surface, in addition to Brownian motion of the individual particles. Pairwise particle-particle interactions and particle-wall interactions are based on asymptotic solutions of the nonlinear Poisson-Boltzmann equation. The limiting cases of colloidal adsorption under conditions of negligible surface mobility (random sequential adsorption) and finite surface mobility are compared, and the relative extent of surface coverage

is found to be dependent on the strength of double-layer interactions. Adsorption onto charge-patterned stripe, square, and circle patterns is also examined, and it is found that stripe and square patterns induce a greater degree of order than do the circular patterns. The importance of polydispersity in colloidal adsorption is illustrated via simulation of adsorption from a bidisperse mixture of colloidal particles. These dynamic simulations indicate in all cases the importance of kinetics to the surface structures formed by the inherently non-equilibrium colloidal adsorption process.

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