The impact of nanoscale chemical features on micron-scale adhesion: Crossover from heterogeneity-dominated to mean-field behavior

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ABSTRACT

This work explores the impact of nanoscale surface heterogeneity, small relative to the effective contact area between two surfaces, on pairwise colloid-scale interactions. Polycation-based positive patches, of order 10 nm in diameter, arranged randomly and lying flat on otherwise negative substrates, were used to create surfaces whose competing attractive and repulsive features determined the net interactions with opposing surfaces. Lab experiments and simulations of the adhesion of gently flowing dilute negative microparticles varied particle size (0.5–2 μm), ionic strength (κ^{-1} = 1–12 nm) and the density of heterogeneity on the collectors. Limiting behaviors from heterogeneity-controlled at high ionic strength to mean-field-like interactions at low ionic strength are reported. When heterogeneities are important, pairwise interactions are more attractive than predicted by average surface properties (e.g. per DLVO), and an adhesion threshold, describing the minimum average density of cationic features needed for single particle capture (adhesion), depends strongly on Debye length. In the opposite limit, the threshold becomes insensitive to the Debye length, and the average surface character approximates the interactions. An analytical treatment, reduced to a simple scaling argument predicts a −1/2 power-law dependence of the adhesion threshold on Debye length and particle size. A slightly stronger particle size dependence in experiments and simulations results from hydrodynamic contributions along with slight scaling differences in electrostatic, van der Waals, and hydrodynamic forces. An analogy to biological ligands is made for the heterogeneity-dominated limit: it is discovered, for this particular system, that engagement of as few as 20–100 cationic patches dictates particle adhesion (with details depending on flow, particle size, and ionic strength), similar to reports for selectin-mediated rolling of white blood cells during the inflammatory pathway. Also discovered is a heterogeneity-dependent crossover in the effect of ionic strength on particle capture, where added salt promotes particle adhesion in most cases but stabilizes the particles when the heterogeneity becomes relatively dense.

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1. Introduction

All naturally-occurring surfaces are heterogeneous, with great chemical and topographical diversity. Synthetic interfaces (emulsions, foams, suspensions of micron- and sub-micron organic, inorganic, and polymeric particles) are sometimes geometrically and chemically simpler; however, heterogeneity usually exists in all but the most model of systems. Heterogeneity is an especially important feature of biological cells: for instance the clustering of receptors in phospholipid rafts potentially increases binding avidity. Of the two types of heterogeneity, chemical variations or roughness, works targeting the impact of the latter on force, friction, and adhesion are too numerous to review. For chemically homogeneous surfaces, roughness usually shifts the distance of closest approach between two surfaces and convolutes the interaction potential between smooth surfaces [1,2]. Pure roughness may also enhance the adhesion of small particles through an increase in the contact area (for particles of appropriate size), or shielding from hydrodynamic forces [3].

Long before the advent of chemical force spectroscopy to quantify chemical heterogeneities in systems including minerals [4–7], polymers [8–10], and biological cells [11–14], chemical heterogeneity was known to influence and even dominate colloidal forces and adhesion. For instance impurities on mineral surfaces often dictate aggregation [15–18], while small chemical features on polymer surfaces control contact angle and wetting [19–21], produce membrane fouling [22,23], enhance engineering adhesion [8,24,25], and determine biomaterial effectiveness [26–30]. Intracellular surface heterogeneities even govern biological processes such as the initial phases of leukocyte adhesion [31,32].

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Electrostatic heterogeneity is understood to enhance bacterial adhesion [33] if not control it altogether (for some strains) [34,35]; it has been implicated in otherwise unexplained flocculation in colloidal systems [36–38], it is associated with defects in colloidal assemblies and crystals [39], and it has been used to flocculate particles in papermaking and waste-water treatment: patch-wise flocculation is accomplished with low molecular weight polymers of high cationic charge density, added in small amounts to negatively charged dispersions [40–45]. When the chains adsorb to individual negative particles in small amounts, they locally overcompensate the underlying negative charge, creating cationic nanoscale "patches" which are attracted to bare regions on other particles, producing aggregation. (The mechanism differs from bridging which requires higher molecular weight chains to reach between two particles.) The point-wise interactions between antigen- and peptide-presenting biomaterials and living cells are in some ways similar in physical principle to this example.

It is frequently reported, based on quantitative studies, that interaction forces or adhesion are "not additive," as they are dominated by heterogeneities or "hot spots" rather than reflecting the average surface character [46,47]. Attractions are often observed to be stronger, by orders of magnitude, than one would estimate from classical DLVO treatments where an area-averaged surface charge or potential (for instance approximated by zeta potentials) is employed [2,48–52]. Connecting to the current work, we note that the "additive" or "classical" DLVO is a "mean-field" approach, where one electrostatic potential and one Hamaker constant describe the surface.

A comprehensive understanding of how small-scale heterogeneity impacts colloidal forces is still forthcoming, as systematic experimental variations in heterogeneity are difficult. Only a few experimental systems have been developed to controllably vary heterogeneity, most of them with the heterogeneity lengthscales that approach those of the interacting objects or particles, or which utilize surfaces that are not entirely flat (thereby including some topography) [46,47,53–57]: in one exception, half-micron-scale latex deposition was employed to characterize unsaturated adsorbed layers of cationic polyelectrolyte at limited conditions where 2–3 polymer chains captured each latex particle [58,59]. In another, simulations reveal how hydrodynamics alter particle capture and release on surfaces with small heterogeneities [60]. Better experimental headway has been made through the variation of ionic strength, with the heterogeneous surface itself a fixed entity: ionic strength alters the structure of colloidal layers deposited on heterogeneous substrates [61], allowing larger numbers of particles to be deposited on submicron adhesive elements [57]. Increases in ionic strength also increase the particle capture rate on some surfaces with fixed heterogeneity [49].

Modeling of heterogeneity showed that it can impact the ultimate structure of deposited colloidal layers; however, early models assumed that single heterogeneity "elements" were each capable of adhering micron-scale particles, by virtue of their size [49,62] or binding strength [63]. While this assumption can sometimes hold [53,64], is not always the case and becomes less realistic for smaller surface asperities. Renormalization of mean-field expressions by integrating over the distribution of heterogeneity captures some features of experiment, but requires assignment of ionic-strength-dependent heterogeneity parameters [49].

The current work systematically examines of the impact of random chemical heterogeneity on pairwise interactions and dynamic adhesion, as exemplified by the capture of individual flowing particles on heterogeneous planar surfaces. We define "heterogeneity" as variations in surface chemistry at lengthscales at least an order of magnitude smaller than the area of interaction between two surfaces, so that many "features" may engage as surfaces approach. This definition excludes topographically complex surfaces or those with regular patterns or larger features, for instance micron or near-submicron elements or chemical stripes on a planar surface that interact with a microparticle. Indeed, in the current work, the primary action of the heterogeneous features is to provide tiny regions of high attractive energy. In principle, the feature size need not be proportional to its adhesion energy, though this is frequently the case and it is an issue we are examining separately.

Electrostatic heterogeneity is considered in this paper, using a model system consisting of a negative surface randomly decorated with flat cationic patches that are about 10-nm in size. The subsequent adhesion rates of flowing micron-scale particles, in the limit of low particle coverages, are dictated exclusively by collector-particle interactions, avoiding multi-particle interactions. Also presented are simulations incorporating hydrodynamic and colloidal interactions that match the experimental parameters, along with analytical and scaling treatments.

Within the electrostatic paradigm of a repulsive surface containing small random attractive elements, the current paper examines the effects of particle size, ionic strength, and the degree of heterogeneity over a much broader range than prior work, and combines simulation and experiment to reveal aspects of adhesion that are difficult to access by experiment alone. Two limiting regimes are explored. At high ionic strength, particle adhesion is dominated by the heterogeneity of the collector: microparticles adhere onto surfaces even though the net interactions (for instance, anticipated by DLVO based on the average surface charge/potential) would be repulsive. The adhesion is characterized by a particle-sensitive threshold that sets a minimum average density of attractive elements needed to capture particles, with the threshold sensitive to ionic strength. Simulations further reveal the number of cationic patches engaged in particle capture. Since, in this limit, the nanoscale cationic patches act as individual adhesive elements, an analogy to bioadhesion is made: depending on particle size and ionic strength, $O(10)$–$O(100)$ patches are required to capture each microparticle; although the number of patches per unit area of effective particle-collector contact is essentially constant. In the opposite limit, at low ionic strengths mean-field-like behavior is observed and the adhesion rate becomes insensitive to ionic strength.

The study reports an additional interesting observation, as the ionic strength is increased, crossing over from heterogeneity-dominated behavior to mean-field-like action: for surfaces with low densities of heterogeneity, ionic strength increases the rate of particle adhesion, analogous to flocculation, as is frequently found in the literature. Conversely, for surfaces that are slightly more attractive, due to a greater density of cationic patches, ionic strength detracts from the particle capture rate. This effective particle stabilization at increased ionic strength is seen both experimentally and in simulations and is a consequence of the randomness of the distribution of attractive heterogeneities, as added salt also screens the locally attractive regions of the surface.

In this paper, analytical and scaling arguments are also presented for the effect of ionic strength and particle size on the critical surface density of patches required for particle capture. The scaling exponent of $-1/2$ reflects the random distribution of adhesive elements and the effective contact area in a system whose interactions are predominantly electrostatic.

2. Description of the system

These studies utilize a system, shown in Fig. 1, in which microparticles of radius a and relatively uniform negative surface charge are gently flowed in simple shear over electrostatically heterogeneous collecting surfaces and their adhesion monitored. The heterogeneous nanofeatures on the collector are electrostatically attractive while the main portion of the collecting surface is electrostatically repulsive towards approaching particles.