Surface forces between rough and topographically structured interfaces

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ABSTRACT

Within colloidal science, direct or indirect measurements of surface forces represent an important tool for developing a fundamental understanding of colloidal systems, as well as for predictions of the stability of colloidal suspensions. While the general understanding of colloidal interactions has developed significantly since the formulation of the DLVO theory, many problems still remain to be solved. One concrete problem is that the current theory has been developed for interaction between flat and chemically homogenous surfaces, which is in contrast to the surfaces of most natural and manufactured materials, which possess topographical variations. Further, with technological advances in nanotechnology, fabrication of nano- or micro-structured surfaces has become increasingly important for many applications, which calls for a better understanding of the effect of surface topography on the interaction between interfaces. This paper presents a review of the current state of understanding of the effect of surface roughness on DLVO forces, as well as on the interactions between topographically structured hydrophobic surfaces in water. While the first case is a natural choice because it represents the most general description of colloidal interactions, the second case represents examples of how intentionally built-in surface structures can significantly alter the interactions between surfaces.

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1. Introduction

The variation in surface topography, often referred to as surface roughness, is a natural part of all surfaces, with a few exceptions. Together with the media in which a surface is located, the bulk properties of the material and the surface chemistry, the surface topography is a key parameter in understanding surface-related phenomena, such as wetting, adhesion, adsorption, and friction. While the correlation between topography and wetting has been a hot topic in past decades, there is still little understanding of the effect of surface topography on the remaining topics. Surface topography represents a challenge in studies of interactions between interfaces, which is often experimentally avoided by the use of flat, model surfaces such as mica or silicon wafers. However, for the surfaces of natural or fabricated materials such as steel [1], calcium carbonate [2], and silicon oxide [3], or for deposited layers of, for example, gold [4], titanium [5] and polymers [6], surface topography cannot be neglected without significant discrepancies between theory and experimental results. In other cases, such as for nanostructured devices [7] and nanopatterned surfaces [8], surface topography is a feature which is intentionally built-in, in order to produce or enhance certain functional properties, such as specific adhesion [9], controlled reflectivity [10], self-cleaning [11] and directional controlled wettability [12].

A lack of understanding of the effect of surface topography is problematic because it prevents theoretical predictions of the conditions for colloidal stability, and hampers the interpretation of experimentally obtained force-distance data. It can further lead to direct misinterpretations of experimental deviations from theory, which are often explained by the influence of surface roughness without any further proof. On the other hand, a full understanding of the influence of surface topography can potentially offer a new additional tool for "tuning" the interaction between two surfaces by a particular design of the surface topography. This could, for example, be used to enhance or reduce colloidal stability in line with the use of sterically repulsive polymer layers and regulation of electrostatic interactions by variations in salt concentration or pH.

Although the effect of surface topography on surface forces is not substantially implemented in the surface force theories, it is a field of growing interest and development. Thus far, various studies of the effect of surface topography on capillary force [13–15], surface contact mechanics [16,17**,18], Casimir forces [19–21], hydration forces [22], and steric forces [23] have been conducted. This short review is limited to the discussion of the effect of roughness on DLVO forces, i.e., the electrical double layer force and van der Waals forces, and the effect of nanometre-to-micrometre topographical surface variation on the interaction between hydrophobic surfaces in water.

2. DLVO forces

The DLVO theory represents the classical description of interactions between colloids in a liquid medium and consists of the sum of van der Waals forces and electrical double layer forces [24,25]. It is well-known that this theory builds on certain assumptions and has limitations due to, for example, ion-ion correlations and specific ion hydration effects

[26–29]. However, in the context of this review, an important assumption is that the interactions are described to occur between perfectly smooth and chemically homogeneous surfaces. With respect to electrical double layer forces, it implies that the double layer potential is smeared out and that surface potentials and charge densities of two interacting surfaces can be described by a single variable, i.e., the distance between the surfaces [30]. For van der Waals forces, the assumption implies that the interaction potential is characterized by a single adjustable material property, the Hamaker constant, which does not vary with distance as long as retardation effects are neglected. For both cases, these assumptions are obviously challenged when surface roughness is introduced.

Although the effect of roughness is often ignored in the evaluation of experimentally obtained surface force data, several theoretical [17••, 30–33••,34,35] and experimental [17••,33••,35–38] studies have attempted to investigate its effect on DLVO forces in a more or less systematic way. However, before going into the findings and methods of dealing with surface roughness, it is appropriate to address an apparent disagreement in literature about whether DLVO forces are generally enhanced [2–4,8,10,11] or reduced [33••,34–35,39,40•] by surface roughness. This is not a real disagreement but rather a matter of different definitions of the separation distance between two rough interfaces. In the former works, the separation distance, D_{mp}, is defined as the distance between the midplanes of the surface asperities, while in the latter works, the separation distance, D_{min}, is defined as the distance between the first points of mechanical contact (see Fig. 1a). Thus, if using the former definition, the zero-separation distance is hidden behind the point of mechanical contact and the surfaces cannot be brought closer than the peak-to-valley distance before repulsive contact forces kick in. While this definition has some computational advantages, it is, in the authors opinion, a bit misleading because it is in contrast to the experimental observations, in which the effective DLVO forces before mechanical contact and elastic (or hard-wall) repulsion are reduced by surface roughness [41] – e.g., aggregation between rough particles due to attractive van der Waals forces is less likely than between smooth particles of the same material [38,42].

Basically, the effect of roughness on the DLVO forces has been treated in three different ways. In the first type of approach, the surface roughness has either been modelled by a certain geometry and density of surface asperities [31,32,34,36], by a probability distribution [17••,35], by a lattice model [30] or directly measured by AFM imaging [17••,37], and the interaction potentials have subsequently been obtained by appropriate mathematical techniques, such as surface element integration techniques or a mean-field lattice analysis. These studies demonstrate good agreement between theory and experimental results – especially when a repulsive contribution for elastic deformation of the surface asperities is included. It is demonstrated that the effect of roughness becomes pronounced when the separation distance between the surfaces becomes comparable with the magnitude of the amplitude roughness parameters. For typical surfaces with an amplitude roughness on the order of 1–10 nm, it will strongly affect van der Waals forces, which also typically become significant in this interaction range. By defining the zero-separation distance at the midplane of the amplitude roughness, D_{mp}, the surface roughness is shown to amplify the van der Waals forces independently of the surface roughness model and the integration method. However, as the plane of mechanical contact, D_{min}, is shifted outwards as the amplitude roughness increases, the van der Waals forces at the point of first mechanical contact decrease with increasing roughness (see Fig. 1). These models therefore support the general assumption that surface roughness suppresses the impact of van der Waals forces in surface force measurements (see Fig. 1c). Similarly, electrical double layer forces are enhanced or reduced based on the definition of zero-separation. However, because the roughness only plays a significant effect at small surface separations, the effect on electric double layer forces is weak at low salt concentrations, i.e., when the length scale of the amplitude roughness is much smaller
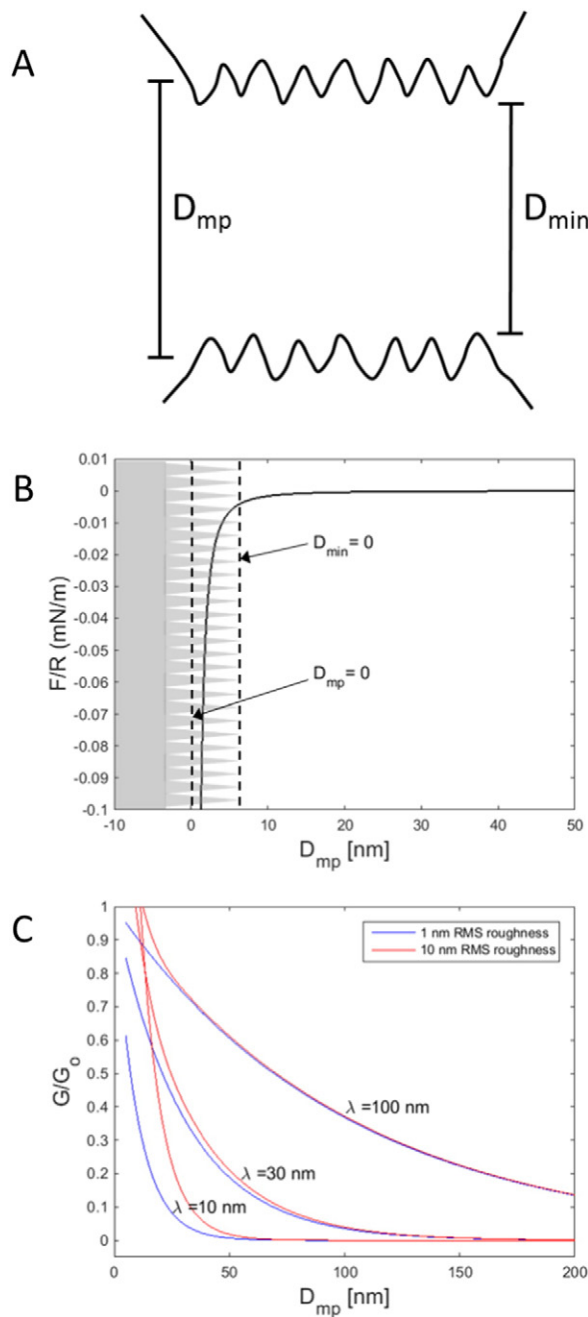

Fig. 1. (A) Because the separation distance between two topographically structured surfaces is not uniquely defined, DLVO forces can be considered to be either enhanced or reduced by the surface structure. The two most common definitions of the separation distance are the distance between the weighted midplanes of the surface asperities, D_{mp}, and the distance between the outer parts of the surface asperities, D_{min}. The latter definition thus sets the point of zero separation as the first point of mechanical contact, while by the former definition, the point of zero separation cannot be reached due to elastic or hard-wall repulsion. (B) Calculated van der Waals forces between a smooth spherical particle and a plane surface with 10 nm asperities. As observed here, the attractive interaction is weak at the point of first mechanical contact, $D_{min} = 0$, explaining the apparent lack of strong attraction observed in force-distance data for interactions between rough surfaces. A non-retarded Hamaker constant of $A = 10^{-21}$ J was used for this calculation. (C) Normalized electrical double layer energies for interactions between two sets of identical surfaces with RMS roughness of 1 and 10 nm, respectively, and for three different Debye lengths (λ). G_0 is the prefactor for the interaction potential, which depends of the surface charge and surface potential. A significant effect of surface roughness is observed for small Debye lengths (high salt concentrations) while the interaction energy is almost unaffected for larger Debye lengths (low salt concentrations). For more details about these calculations, the reader is referred to the supporting information of the work by Parsons et al. [17••].