The Influence of Interphase Characteristics on the Attraction of Particles in Aqueous and Gaseous Media

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Abstract—The dependence of the attraction energy of particles on the formation of thin layers on their surface with characteristics different from those of dispersion medium has been investigated. It is shown that at local reduction of the water density or formation of gaseous interlayer on the surface of hydrophobic particles, their attraction at small distances substantially increases. In contrast, the formation of a thin layer of water on the surface of hydrophilic particles in the air leads to weakening of their attraction. The most pronounced effect is obtained for the energy of interaction of hydrophobic disperse particle and bubble: the interaction value and sign changes depending on the specific ratio of parameters.

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INTRODUCTION

The stability of disperse systems essentially depends on the dispersion medium characteristics and the condition of surface of particles forming this system. Earlier studies that laid the foundation of DLVO (Derjaguin–Landau–Vervey–Overbeek) theory, primarily, were focused on the surface charge and the electrostatic repulsion of particles associated with this charge, and also the dispersion attractive forces (Van der Waals forces) determined by bulk properties of the particle material and dispersion medium [1, 2]. The extended DLVO theory included steric interaction [3, 4]. A separate factor changing the stability of disperse systems is adsorption on the surface of particles of various substances affecting all components of interparticle interaction [3, 5, 6]. Investigations conducted in recent years show that hydrophobicity of disperse particles also plays an important part in their interaction in aqueous medium [7–9]. This hydrophobicity reduces the local density of water [10–13] and contributes to fixing nanobubbles on the surface of particles [14]. As a result of these changes, the attraction of disperse particles substantially increases [15–18] that results in their accelerated coagulation, i.e., destabilization of dispersions.

The specified studies aimed at refining the DLVO theory by virtue of the peculiarities of water behavior near the phase contact area not only feature the pioneer character, but also demonstrate essentially new effects. It should be also noted that the conducted investigations refer, primarily, to the liquid dispersion medium. At the same time the development of the theory of surface forces and its application to solving practical tasks is no less actual for gaseous medium [19, 20], especially in the case of nano- and microparticles [21]. In particular, the formation of thin layers of condensed water on their surface should appreciably reduce the aggregate stability of dispersions, i.e., ensure the opposite effect as compared with gaseous interlayers on particles in liquid medium.

The purpose of this paper is to study the main trends of the impact of the surface condition on particle interaction and their differences in aqueous and gaseous media. Van der Waals attraction energy representing one of the components of DLVO forces will be analyzed and the dependence of this energy on characteristics of near-surface layers will be elucidated. As will be shown below, the presence and properties of these layers can fundamentally change the dispersion stability.

THEORETICAL MODEL OF INTERACTION OF PARTICLES COATED WITH UNIFORM SURFACE LAYERS

Modern investigations of the water state near the interphase performed by using the neutron scattering [10–11] and X-rays [12–13] indicate that the surface hydrophobicity leads to the local reduction of water density covering the distance of about several nanometers. It is also known that in the presence of dissolved gases
in water the hydrophobicity of solid surface results in adhesion of nanoscale air bubbles forming on this surface a sufficiently lengthy layer of variable thickness (5–30 nm) [5, 22–24]. In both cases, the interparticle interaction can be viewed as interaction through inhomogeneous medium changing the local Hamaker constant and thereby changing the Van der Waals energy. Note that larger size bubbles can be recorded on the hydrophobic surface [22, 23]. According to earlier research [16, 22], the interaction between particles should be considered as three-particle (particle–bubble–particle) at the sizes of gas inclusions comparable or exceeding the distance of action of surface forces.

We shall limit our analysis by the case of two-particle interaction. Let us consider several variants of the state of particle/medium system: particles in homogeneous aqueous and gaseous media; particles in aqueous medium with quasi-uniform surface layers of gas or water, local characteristics of which differ from the bulk properties; particles in the air with surface layers of water. We shall also consider the interaction of particles with macroscopic gas bubbles that is of interest in microflotation [8, 22].

A relatively small length of surface layers makes it possible to substantially simplify the calculation of particle interaction energy. If radii of particles \(a_{1,2}\) distinctly exceed the thickness of surface layers \(\delta\), it is possible to apply the locally flat model developed by Deryagin [3], according to which the energy of interaction of spherical particles can be calculated from the interaction energy of flat surfaces by introducing a coefficient related to the particle surface curvature: \(K = \frac{2\pi a_1 a_2}{(a_1 + a_2)}\). With due regard for this approximation, van der Waals energy \(U_{A,spb}(h)\) for interaction of identical particles coated with uniform layers of any substance having equal thickness \(\delta\) can be presented in the simplified form [5, 6]:

\[
U_{A,spb}(h) = -\frac{K}{12\pi} \sum_{n=1}^{4} \frac{A_n}{H_n^4},
\]

where \(H_n\) are the characteristic distances taking into account the thickness of each of layers \(\delta\), and \(h\) is the distance between these layers (distance between particle surfaces is equal to \(h + 2\delta\)); \(A_n\) are the parameters that can be calculated with due regard for the Hamaker constants for particle material \(A_P\) dispersion medium \(A_M\), and surface layers \(A_L\):

\[
A_1 = (\sqrt{A_L} - \sqrt{A_M})^2, H_1 = h; \\
A_{2,3} = (\sqrt{A_P} - \sqrt{A_L})(\sqrt{A_L} - \sqrt{A_M}), H_{2,3} = h + \delta; \\
A_4 = (\sqrt{A_P} - \sqrt{A_L})^2, H_4 = h + 2\delta.
\]

Despite the simplicity of above expressions, they are suitable for describing both the particles coated with identical adsorptive layers [6, 7] and the particles coated with the gas layer or water layer, the local properties of which differ from its bulk properties [11, 13]. These expressions can be also used for describing the interaction of particles coated with a water layer in gaseous medium. However, in each of the above cases constants \(A_P, A_M\) and \(A_L\) will be determined by the properties of material of particles, dispersion medium, and surface layer. For example, in the case of aqueous dispersion, the Hamaker constant for dispersion medium \(A_M\) is equal to the Hamaker constant for water \(A_W = 4.8 \times 10^{-20}\) J, while in the case of particles in gaseous medium, the same constant \(A_M\) under the normal conditions is equal to the Hamaker constant for vacuum \(A_G = 0\). If an air layer is present on the surface of hydrophobic particles, the Hamaker constant for this layer \(A_L = A_G = 0\), while in the presence of a layer of water condensate on the surface of particles in gaseous medium we have \(A_L = A_W = 4.38 \times 10^{-20}\) J.

Since the purpose of this study is the elucidation of main tendencies of the variation of interaction energy, numerical calculations will be carried out for a monodisperse system with particle diameter \(2a_1 = 2a_2 = 1\) μm, but in a wide interval of Hamaker constants \(A_P\) covering both natural and artificial particles. Though not all particles possess hydrophobic surfaces, for some of them, for example, for quartz or quartz glass, the hydrophobization methods have been developed [7, 10–13]. Since the Hamaker constant for organic compounds used in the majority of cases for these purposes does not significantly differ from the Hamaker constant for water, while the thickness of hydrophobic layers is small, their impact on Van der Waals forces can be neglected. However, if necessary, the variation of interaction energy can be taken into account by using the analogues of formulas (1) and (2) for two-layer coatings [5, 6].