
**THEORETICAL PRINCIPLES OF WATER
PURIFICATION AND TREATMENT TECHNOLOGY**

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–Verwey–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 δ , 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: $K = 2\pi a_1 a_2 / (a_1 + a_2)$. With due regard for this approximation, van der Waals energy $U_{A, sph}(h)$ for interaction of identical particles coated with uniform layers of any substance having equal thickness δ can be presented in the simplified form [5, 6]:

$$U_{A, sph}(h) = -\frac{K}{12\pi} \sum_{n=1}^4 \frac{A_n}{H_n}, \quad (1)$$

where H_n are the characteristic distances taking into account the thickness of each of layers δ , 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 :

$$\begin{aligned} A_1 &= (\sqrt{A_L} - \sqrt{A_M})^2, H_1 = h; \\ A_{2,3} &= (\sqrt{A_P} - \sqrt{A_L})(\sqrt{A_L} - \sqrt{A_M}), H_{2,3} = h + \delta; \\ A_4 &= (\sqrt{A_P} - \sqrt{A_L})^2, H_4 = h + 2\delta. \end{aligned} \quad (2)$$

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 $2a_1 = 2a_2 = 1 \mu\text{m}$, 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].

CALCULATION RESULTS AND DISCUSSION

In the limiting case of $\delta = 0$, expressions (1) and (2) make it possible to describe the interaction of particles in terms of the uniform dispersion aqueous or gaseous medium without its local changes. For comparing the interaction values of particles having different nature, but equal size, Fig. 1 presents data for particles of quartz glass ($A_p = 6.5 \times 10^{-20}$ J), natural quartz ($A_p = 8.8 \times 10^{-20}$ J) and titanium oxide (anatase, $A_p = 15.8 \times 10^{-20}$ J). Hence, we can see that the attraction of natural particles of quartz (curve 2) and titanium oxide (curve 3) in aqueous medium is about 10 times as weak as their attraction in the air (curves 2' and 3'), while the attraction of artificial particles of quartz glass (curves 1 and 1') is about 40 times weaker. It should be also noted that the value of Hamaker constants [4] and, consequently, the attraction of amorphous quartz glass in both media is visibly less than that of the natural (crystalline) quartz that is determined by both the dependence of dipole-dipole interaction of molecules on the internal structure of particles and the presence of porosity in the first case.

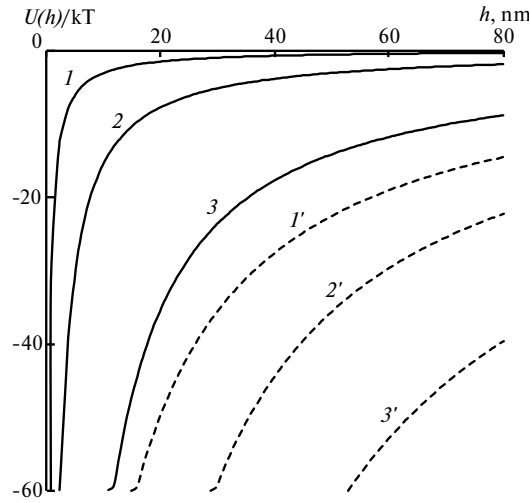


Fig. 1. The interaction energy of particles as a function of the distance between them in aqueous (1–3 and air (1'–3') media: quartz glass (1, 1'), natural quartz (2, 2'), and titanium oxide (3, 3').

The obtained relationship between the values of interaction energy calculated by formulas (1) and (2) for aqueous (see Fig. 1, curves 1–3) and gaseous (curves 1'–3') media fully reflects the ratio of Hamaker constant A_p for vacuum and the Hamaker constant for particles A_p^w calculated by formula for the interaction of particles through the aqueous medium [21]:

$$A_p^w = (\sqrt{A_p} - \sqrt{A_w})^2. \quad (3)$$

The closer are the Hamaker constants for particle and water, the smaller is A_p^w , i.e., the larger is ratio A_p/A_p^w and, consequently, the more distinct is the difference between the attraction energies in air and aqueous media.

It is clear that the presence of gas films on the particle surface in aqueous medium or water films in gaseous medium leads to such values of interaction energy that are found in the interval between the curves for aqueous or gaseous dispersion medium. How strong the water or gas film influences the variation of the energy of particle interaction also depends on the ratio of A_p and A_p^w . Figure 2 illustrates the calculation results of the interaction energy of micron particles in water in the presence of surface gas layers having thickness δ depending on the distance between these layers $H_1 = h$.

As can be seen from Fig. 2a, in the presence of air layer on the particle surface, the attraction energy at small distance between particles increases, while at large distance this energy gets smaller. This pattern can be qualitatively explained as follows. At small distances between the gas layers the interaction of just these layers is more important, moreover, as the thickness of air layer δ increases, the interaction energy (curves 1–4) tends to that of bubbles (curve 1'), i.e., the absolute value of the attraction energy increases. At large distances between particles and, correspondingly, between gas layers, the direct interaction of gas layers decreases. In

this case, the particle with a gas layer behaves like a quasi-particle with the averaged value of the Hamaker constant lower than A_p i.e., the absolute value of attraction energy decreases.

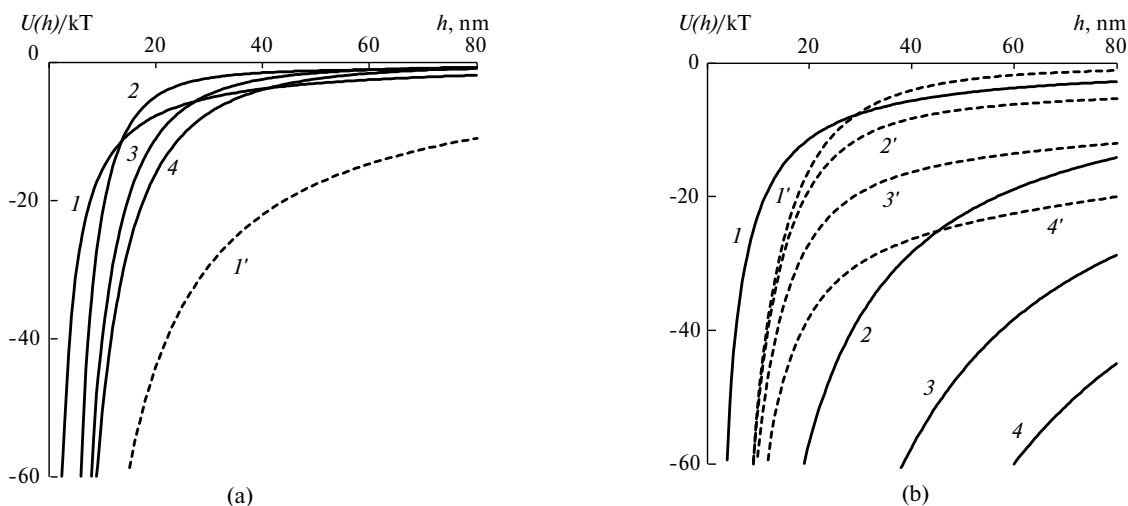


Fig. 2. The interaction energy of particles in aqueous medium as a function of the distance between them: $\delta = 0$ (1), 10 (2), 20 (3), 30 (4) nm for quartz particles at $A_p = 8.86 \times 10^{-20}$ J and air bubbles at $\delta = 0$ and $A_p = 0$ J (1') (a); in the absence (1–4) and presence of gas film (1'–4') of thickness $\delta = 30$ nm. $A_p = 10 \times 10^{-20}$ J (1, 1'), 20×10^{-20} J (2, 2'), 30×10^{-20} J (3, 3'), and 40×10^{-20} J (4, 4') (b).

Figure 2b displays the patterns of the variation of Van der Waals energy for a wide interval of Hamaker constants (in terms of the order of magnitude: $A_p = 10 \times 10^{-20}$ J corresponds to a series of polymers, e.g., polystyrene or polyurethane, $A_p = 20 \times 10^{-20}$ J corresponds to titanium dioxide with structure of rutile or barium titanate, $A_p = 30 \times 10^{-20}$ J corresponds to diamond and $A_p = 40 \times 10^{-20}$ J corresponds to copper and gold) that demonstrate the same qualitative dependence on the distance between particles as those in Fig. 2a. However, the larger is the Hamaker constant for the given substance, the stronger is the impact of gas interlayer on the resultant dependence.

Note that though the calculations were carried out for a homogeneous gas layer, in effect, due to different factors, in particular the roughness of particles or not very large hydrophobicity, the gas layer could consist of segments having various heights or coat the particles with discontinuous layer. In this case, the trend of variation of the interaction energy is maintained, however its calculation method becomes essentially more complicated [16].

Calculations for the opposite situation (air medium and particles with thin uniform surface layer of water) are presented in Fig. 3. In order to form such a layer, particles should be hydrophilic, otherwise the water condensed on the particle surface will form separate droplets rather than the homogeneous layer. An approach proposed in paper [16] is also applicable for separate droplets. The opposite situation is observed during the interaction of particles in gaseous medium: the increasing thickness of water layer results in the Van der Waals energy tending to the energy of interaction through the aqueous medium (see Fig. 3a). Similar to the cases presented in Fig. 2b, the resultant effect is stronger at the larger Hamaker constant for the material of particles (see Fig. 3b).

The calculation of Van der Waals forces is more complex when the density [11] and, correspondingly, the dielectric permittivity [14, 16] of near-surface layers of water for hydrophobic particles are different from their bulk values. In this case, the Hamaker constant of near-surface layer will be determined by using an approximate stepwise variation of the Hamaker constant [16, 22] and assuming that depending on the degree of surface hydrophobicity the constant for near-surface water layer A_L can assume values in the interval from A_W to $A_G = 0$. As could be expected, the reduction of Hamaker constant in the near-surface layer from $A_L = A_W/2$ (Fig. 4, curve 2) to $A_L = A_W/32$ (curve 5) demonstrates gradual transition to curve 6 for the gas interlayer with $A_L = 0$.

Thus, data in Figs. 1–4 testifies that the presence of surface layers with characteristics different from those of dispersion medium results in perceptible energy changes of interaction between the identical particles. However, an even stronger effect can be obtained for the particle–bubble interaction.

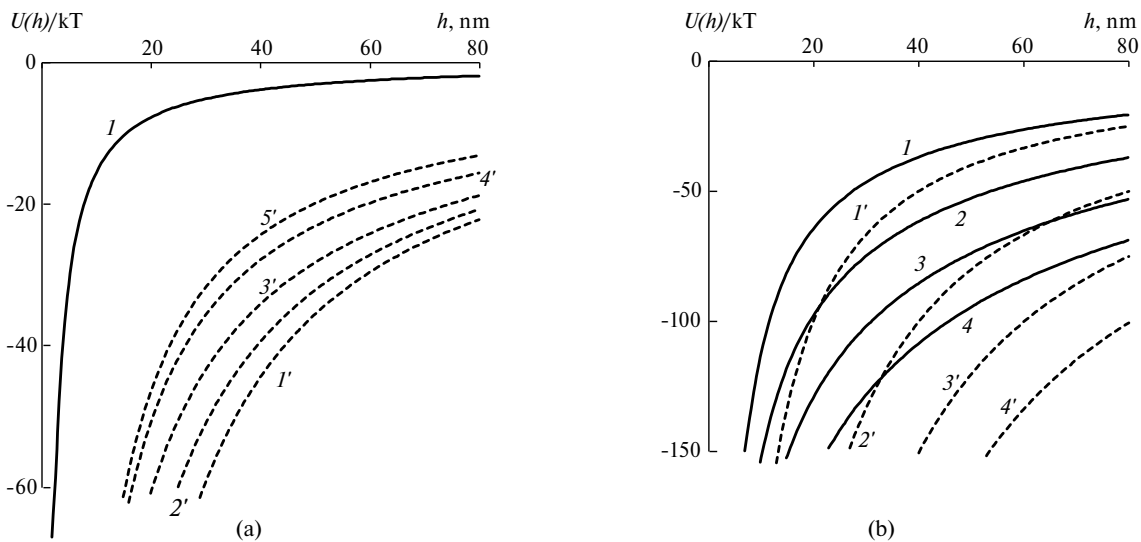


Fig. 3. The interaction energy of particles as a function of the distance between them: $\delta = 0$ (1), 10 (2), 30 (3), 100 nm (4) in gaseous and aqueous media at $A_p = 8.86 \times 10^{-20}$ J (a); in the gaseous medium in the absence (1'–4') and presence of water film (1–4) of thickness $\delta = 30$ nm. $A_p = 10 \times 10^{-20}$ (1, 1'), 20×10^{-20} (2, 2'), 30×10^{-20} (3, 3'), and 40×10^{-20} J (4, 4') (b).

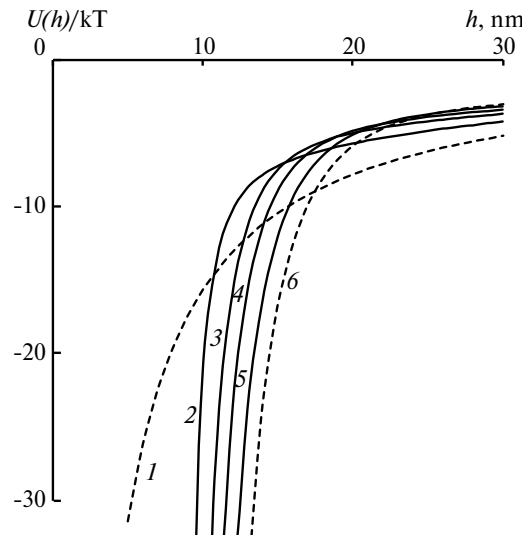


Fig. 4. The interaction energy of particles in aqueous medium as a function of the distance between them in the presence of near-surface layer with modified properties of water for $\delta = 4$ nm and $A_p = 8.86 \times 10^{-20}$ J at $A_L = A_W$ (1), $A_L = A_W/2$ (2), $A_L = A_W/4$ (3), $A_L = A_W/8$ (4), $A_L = A_W/32$ (5), and $A_L = 0$ (6).

According to data presented in Fig. 5, the presence of a gas interlayer on the particle surface results in not only quantitative, but also qualitative change of the energy interaction of particle and bubble. Particularly strong changes occur at small distances, where, primarily, the interaction of gas on the particle surface with bubble gas manifests itself, i.e., the repulsion of particle and bubble is replaced (see Fig. 5a, curve 1 and Fig. 5b, curves 1–4) with their attraction (see Fig. 5a, curves 2–5 and Fig. 5b, curves 1'–4'). At large distances the interaction of a bubble with the particle having a gas layer is similar to interaction with macro-object, which is characterized by certain averaged Hamaker constant decreased at the expense of the gas layer that qualitatively corresponds to the above analysis of the behavior of two particles with surface gas layers.

For convenience of comparison with previous calculations, Fig. 5 presents data for bubbles of the same size as particles. However, under conditions of microflotation the bubbles are larger by a factor of hundreds. With due regard for coefficient K (Eqs. (1) and (2)), it follows that differences between curves in Fig. 5 will also rise by a factor of hundreds. Thus, the presence of gas interlayers on the surface of particles can fundamentally change the kinetics of microflotation processes.

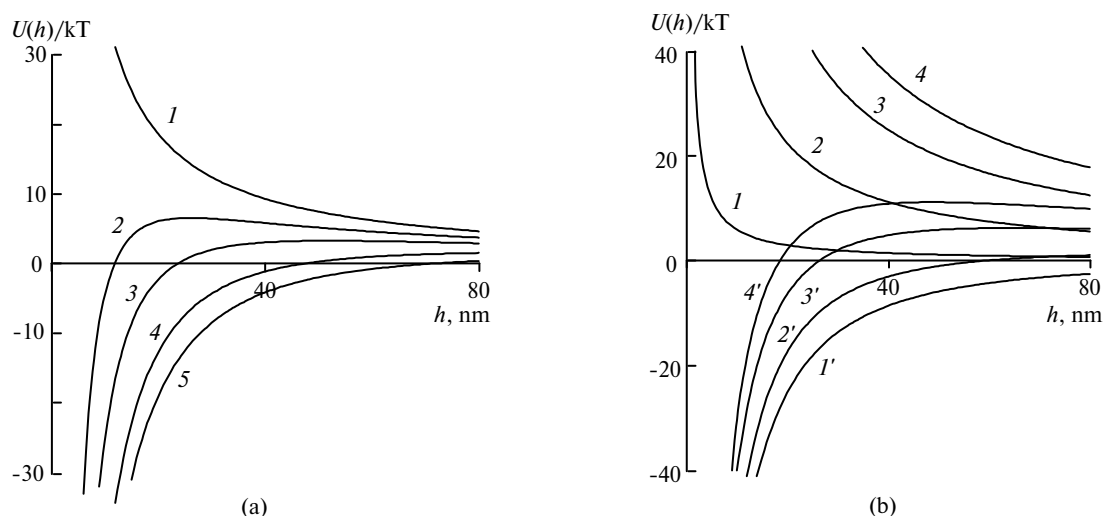


Fig. 5. The interaction energy of particles and bubbles in aqueous medium as a function of the distance between them in the presence of near-surface gas layer: $A_p = 8.86 \times 10^{-20}$ J and $\delta = 0$ (1), 5 (2), 10 (3), 20 (4) and 30 (5) nm (a); $\delta = 0$ (1–4), 30 (1'–4') nm and $A_p = 5 \times 10^{-20}$ (1, 1'), 10×10^{-20} (2, 2'), 20×10^{-20} (3, 3'), and 30×10^{-20} J (4, 4') (b).

CONCLUSIONS

The performed calculations regarding the influence of surface layers on the particle interaction in aqueous and gaseous media have demonstrated a significant variation of the Van der Waals energy. The presence of air or water layer with reduced Hamaker constant on the surface of hydrophobic particles results in a noticeable strengthening of their attraction that corresponds to the reduced stability of disperse system and enhancing the shear stresses in concentrated disperse systems. The interaction of bubbles with particles having the identical surface layers contributes to the variation of both the value and sign of interaction that fundamentally changes the conditions of microflotation.

Vice versa, the presence of water layer on the surface of particles in gaseous medium results in the reduction of their attraction and, consequently, enhanced stability of dispersions and reduction of shear stresses in concentrated systems.

It should be noted that unlike solid (incompressible) adsorption layers, the water interlayer in the case of gaseous medium or gas interlayer in the case of aqueous medium could be pressed out from interparticle gap that leads to additional variation of the interaction energy that should be taken into account in analyzing the specific experimental data.

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