Translated from *Uspekhi Khimii*, 51 92-118 (1982) U.D.C. 541.183.5

Kinetic Theory of the Flotation of Small Particles

B.V.Deryagin, S.S.Dukhin, and N.N.Rulëv

The present state of the theory of the elementary step in flotation as a multistage process is surveyed. The characteristics of the flotation of small particles both in the stage where they approach the bubble and in the stage involving their fixation to the surface of the bubble are described. It is shown that the deposition of small particles (in contrast to large particles) on the surface of the bubble takes place without inertia and is not accompanied by a significant deformation of the surface. The usefulness of the application of ionogenic surfactants in order to overcome or modify the sign of the disjoining pressure of electrical double layers, which is the commonest factor hindering the flotation of small particles, is demonstrated. The possible ways of intensifying the flotation of submicron particles by their aggregation are analysed.
The bibliography includes 96 references.

CONTENTS

I. Introduction 51
II. Characteristics of the mechanism of the fixation of small particles on the surface of the bubble 51
III. Characteristics of the mechanism of the transfer of small particles to the surface of the bubble 54
IV. A quantitative theory of the flotation of spherical particles of small and moderate sizes 55
V. Quantitative experimental studies of the flotation of small particles 59
VI. The breaking away of small particles in contact-free flotation and the dynamic adsorption layer of the bubble 60
VII. Non-equilibrium surface forces in flotation 62
VIII. The efficiency of the collision and flotation kinetics 64
IX. The influence of the aggregation of particles on the elementary step in non-inertial flotation 64
X. The flotation of submicron particles 65

I. INTRODUCTION

Until recently the theory of flotation was limited to the thermodynamic consideration of the adhesion of particles to the surface of a bubble, which permitted the analysis of the most important question, from the point of view of enrichment, namely that of the selectivity of the flotation of large particles (with dimensions of ~100 μm and more). The flotation of small particles constitutes an independent scientific problem, because, on transition from coarse to fine grinding, there is a possibility of qualitative changes in the mechanism of the elementary step in flotation (this is understood as the interaction of a single particle with a single bubble).

In the general case one must distinguish in the elementary flotation step the stage involving the approach of the surfaces of the particle and the bubble and the stage in which the particle is fixed on the bubble. In a more detailed treatment it is found that the number of these stages is greater and that the subdivision into stages is itself arbitrary. On passing from large to small particles, the mechanism of the elementary step in flotation is altered both in the approach stage and in the fixation stage. This was first pointed out almost two decades ago[1-10]. At the present time the theory of the elementary step in the flotation of small particles has been developed in a number of investigations[11-22].

II. CHARACTERISTICS OF THE MECHANISM OF THE FIXATION OF SMALL PARTICLES ON THE SURFACE OF THE BUBBLE

The probability of the fixation of a particle is determined by the probabilities of the adhesion of the particle and its retention on the bubble, since in the general case there is a possibility that the initially adhering particle will break away either under the influence of the gravitational force or under the influence of inertial forces. These forces are proportional to the volume of the particles, i.e. are large for large particles and small for fine particles. This trivial fact leads to cardinal consequences in the analysis of the role of particle size in the mechanism of the elementary step in flotation. The forces tending to break away a 100 μm particle are 10^6 times greater than for a 1 μm particle. Therefore for large particles only one form of fixation is possible—via the formation of a three-phase wetting perimeter able to counteract the large forces tending to break it away; we shall henceforth refer to such flotation as contact flotation. For fine particles, there is a possibility, together with contact flotation, also of non-contact flotation, which is not accompanied by the formation of a three-phase wetting perimeter, because for small particles the stripping forces can be balanced by London–van der Waals molecular attraction forces.

Sheludko[23] points to the difficulty of fixing small particles on the surface of a bubble due to the need to overcome the energy barrier to the formation of a three-phase wetting perimeter. One should note that, owing to the Sheludko effect, only contact flotation of small particles may become impossible. The formation of the wetting perimeter is not obligatory for the flotation of small particles; long-range surface forces, in particular the London–van der Waals molecular attraction forces or, what amounts to the same thing, the molecular component of the wedging pressure of the liquid layer separating them are of primary importance. This is the first fundamental difference between the flotation of small particles and the flotation of large particles.

Furthermore, one must take into account the fact that surface forces comprise also the electrostatic interaction forces arising as a result of the overlap of the electrical double layers (DL) of the particle and the bubble, which usually have charges of the same sign[24,25]. The ionic-electrostatic component of the disjoining pressure, due to the interaction of the DL of the bubble and the particle, is an important factor, which can hinder the adhesion of

small particles to the surface of the bubble. This is the second significant characteristic feature of the flotation of small particles. For large particles, the disjoining pressure is overcome by the inertial impact against the bubble surface; for small particles, there is no such impact and the bubble and the particle approach one another without inertia.

The general characteristics of the influence of both components of the disjoining pressure on the fixation of small particles can be established by considering the familiar relation between the interaction energy and the shortest distance between the surfaces of the particle and the bubble which are not in general charged to the same potential[26]. In the case where the bubble and the particle are charged to the same potential and the molecular component of the disjoining pressure is negative, the general theory of the stability and coagulation of lyophobic colloids is applicable[27-30].

In view of the different natures of the bubble and the particle, the condition of the equality of their potentials is attained extremely rarely. It can be observed mainly when the potentials of both the particle and the bubble are so large that the electrostatic component of the disjoining pressure reaches its maximum value. This case is rarely realised; it is possible only in the presence of ionic surfactants, which are capable of imparting a large charge not only to the particle but also to the bubble. Fig.1*a* illustrates the free energy of the total interaction W of the identically charged particle and the bubble as a function of the distance H between them. This energy is defined by the expression

$$W = a\int_{H}^{\infty} F(H')\,dH' \qquad (1)$$

where F is the force of the interaction described by the familiar formula

$$F(H) = 2\pi a\int_{H}^{\infty} \Pi_e\,dh\ , \qquad (2)$$

where a is the radius of the particle, h the thickness of the plane-parallel layer between the particle and air, $H = h/a$, and Π_e is the electrostatic component of the disjoining pressure.

Eqns.(1) and (2) were derived on the assumption that the particle is a sphere with a radius a, which is much smaller than the radius of the bubble R. Over long and short distances, molecular attraction forces play the main role, while over moderate distances, electrostatic repulsion can predominate. This leads to the formation of an energy barrier separating the near and far potential wells (Fig.1*a* and 1*b*).

In reality the bubble and the particles differ not only in the surface potentials but also in their behaviour, which can alter qualitatively the interaction arising under these conditions. Thus the case where the potential of the surface of

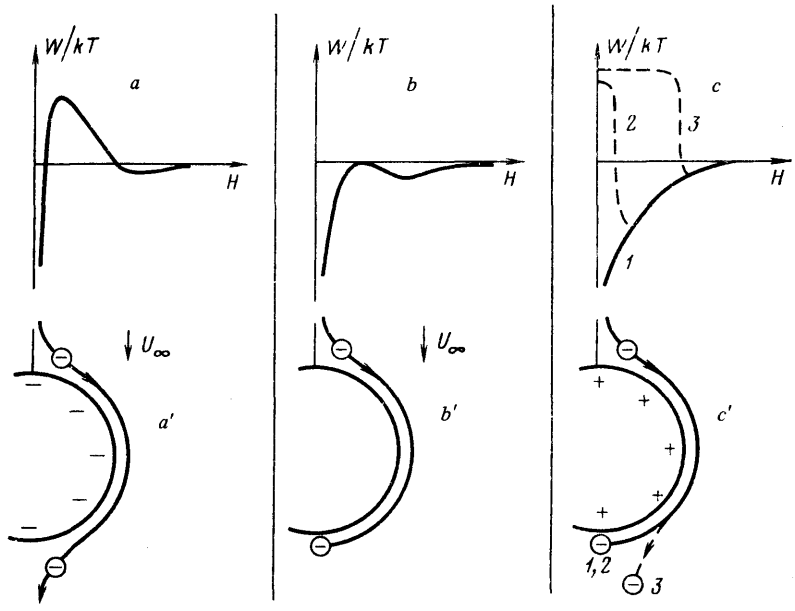


Figure 1. The resultant curves characterising the contribution of molecular attraction forces and electrostatic forces, due to the overlap of the diffuse double layers, to the energy of the interaction W of the bubble and particle at different distances for like surface charges (*a*), on neutralisation of the bubble charge (*b*), and when the bubble charge is altered (*c*, curve *1*). The dashed lines in Fig.1*c* characterise the contribution of the structural component to the interaction energy over distances shorter (curve *2*) and longer (curve *3*) than the thickness of the double layer. Schemes demonstrating the possibility of flotation for sufficiently large like charges of the particle and bubble (1*a'*), on neutralisation of the bubble charge (*b'*), or on its alteration (*c'*, curve *1*) are shown. Curves *2* and *3* in Fig.1*c'* illustrate the possibility of flotation for a radius of action of non-electrostatic repulsion forces shorter than the thickness of the double layer (curve *2*) and its impossibility in the opposite case (curve *3*).

the particle and the charge density of the air bubble remain unchanged as h is altered is close to reality. Frumkin[31] and Langmuir[32] showed that, in the special case where the charge of the bubble is zero, a repulsion force arises, which is exactly equal to the repulsion force between two identical particles with a double thickness of the intervening layer. In the light of the theory of heterocoagulation, one should expect that non-inertial flotation is not possible when the bubble and the particles have charges of the same sign, the absolute values of their surface potentials are not small, and the electrolyte concentrations are low (Fig.1*a*). The general theory of heterocoagulation then makes it possible to calculate the potentials (or charges) of the interacting objects for which the electrostatic repulsion force falls so much that the force barrier disappears.

Although the electrostatic repulsion forces persist also when the charge of the bubble is neutralised by the adsorption of surfactants, nevertheless here too the van der Waals attraction forces can predominate and flotation is possible (Fig.1*b*).

Flotation can be ensured by influences of two kinds. When electrolytes are introduced into the system, the thickness of the diffuse component of the double layer diminishes, which leads to a decrease of the electrostatic repulsion forces. The negative surface potential can be reduced by the adsorption of surface-active cations, which also results in coagulation.

The possibility of intensifying the flotation of small particles by lowering the electrostatic repulsion forces was first demonstrated experimentally by Deryagin and Shukakidze[33]. The treatment of the adhesion process in the flotation of small particles on the basis of the heterocoagulation theory, proposed by Deryagin and Dukhin[2], has been described in a series of reviews of the theory of heterocoagulation[34-36]. The importance of reducing the electrostatic repulsion forces for the occurrence of flotation has been proved in recent years in many investigations[37-40]. On varying the electrokinetic potential of silver iodide particles by the adsorption of a cationic surfactant, Jaycock and Ottewill[37] observed a floatability maximum at the isoelectric point. It has been established[37-39] that the rate of flotation is high over a narrow range of pH values and very low outside this range. The above range coincides with the region of very low ζ-potentials of the particle in the vicinity of its isoelectric point. The addition of aluminium hydroxide extends the pH range favouring flotation.

The authors of the above studies interpreted their data as evidence for the decisive influence of the electrostatic component of the disjoining pressure on the adhesion of particles to the bubble. Collins and Jameson[40] assumed in addition the possibility of another interpretation of the results. The disappearance of the electrostatic repulsion force barrier can cause intense coagulation of particles at the isoelectric point. The aggregates thus arising can be more rapidly precipitated on the surface of the bubble than single particles. In order to rule out this possibility, the authors[40] measured the change in the distribution of spherical polystyrene particles 4–20 μm in size, in the flotation process at different electrolyte concentrations and correspondingly for different electrophoretic mobilities of the particles, i.e. for different values of the electrokinetic potential. For each of the eight fractions investigated separately, the rate of flotation increased monotonically with decrease of the ζ-potential of the particles and bubbles. Since these experiments made it possible to follow the influence of both the size and the charge of the particles separately on flotation, the necessity for eliminating the disjoining pressure of the double layers as an essential condition for flotation was demonstrated unambiguously by the above investigators†.

The special introduction of electrolytes in order to ensure floatability is naturally not technologically viable. A more economical method of controlling the electrostatic component of the disjoining pressure and hence the floatability consists in the use of ionogenic surfactants at specific concentrations whose adsorption on the bubble causes a change in its charge. However, very low surfactant concentrations do not ensure floatability if the latter is hindered not only by the electrostatic barrier but also by non-electrostatic factors preventing the mutual approach of the surfaces of the particle and the bubble. One of such factors may be the presence on the surface of the particle of a polymolecular hydrate layer. The possibility of the existence of a polymolecular hydrate layer, preventing a decrease in the thickness of the wetting films as a result of the structural component of the disjoining pressure, on lyophilic surfaces has been established by a number of investigators[41-43].

The barrier due to the structural component of the disjoining pressure is illustrated schematically in Fig.1*b* for those cases where its radius of action is smaller (curve *2*) or greater (curve *3*) than the thickness of the double layer. One of the ways of ensuring or improving floatability in the presence of the structural component consists in employing surfactants whose adsorption renders the surface of the particle hydrophobic, or destroys the structural component of the disjoining pressure, or alters its sign.

Another way of overcoming the difficulty associated with ensuring the flotation of dispersions in the presence of a non-electrostatic factor stabilising colloids has been indicated by Deryagin and Dukhin[2]; it consists in stimulating electrostatic attraction. For this purpose, it is necessary to generate, by means of a high degree of adsorption of surfactants, a high charge on the surface of the bubble opposite in sign to that of the particle; the interaction between the double layers then ensures the operation of attraction forces. If the thickness of the double layer exceeds that of the hydration layer, then, outside the limits of the radius of action of non-electrostatic repulsion forces, attraction forces will operate between the opposite charges of the particle and the bubble. Thus an aggregate comprising the bubble and the particle, between the surfaces of which there is a gap of the order of magnitude of the thickness of the non-electrostatic repulsion force barrier, is produced. If the radius of action of the repulsion forces is increased for the same double layer thickness, then the potential well becomes smaller. It is desirable to select surfactants in such a way that not only the electrostatic attraction is increased but also the repulsion due to the structural factor is reduced. Thus, if the radius of action of electrostatic attraction forces exceeds that of the non-electrostatic repulsion forces (of structural origin), floatability is possible (Fig.1*c*, curves *2*). If the radii of action of these forces are comparable, then in the presence of the non-electrostatic barrier flotation proves to be impossible (Fig.1*c*, curves *3*).

Thus the third characteristic of the flotation of small particles consists in the fact that it can be controlled with the aid of ionogenic surfactants and it is possible to ensure floatability even when non-electrostatic stability factors operate. This conclusion is confirmed by the available experimental literature data. Thus it has been shown[44] that the surface not only of pure but also of methylated

---

† The possibility of the aggregation of particles was ruled out by sufficiently high values of their ζ-potentials.

quartz has hydrophilic sections which ensure the stability of suspensions and hinder flotation. The floatability of quartz has been ensured[45] in the range of dodecylammonium chloride concentrations in which the surface charges of the bubble and the particle have opposite signs.

Systematic studies by Schulze[46,47] have shown that the water–air and water–quartz interfacial films become unstable under the influence of the adsorption of tervalent cations or cationic surfactants if their thickness is smaller than a critical value h_{cr}. The critical thicknesses are 300–450 Å under conditions where the surface of quartz is altered by tervalent cations. The change in the charge of the bubble surface by the adsorption of cationic surfactants leads to the rupture of the film for thicknesses of 150 Å if the electrolyte concentration is high and for thicknesses of 1500 Å if it is low, which agrees with the electrical nature of the attraction arising under these conditions. Schulze also suggests that floatability be increased by altering the surface charge of the bubble as a result of the adsorption of surfactants at the lowest possible electrolyte concentration, which should increase the thickness of the double layer and hence h_{cr}.

The above conclusions by Schulze agree with the data of Goddard and coworkers[48], who ensured the flotation of quartz particles by the adsorption modification of the surface charge of the bubble using amines. A sharp increase in floatability corresponds to a sharp increase in the degree of adsorption of amines. Whereas floatability is usually controlled by rendering the surface of the particle hydrophobic, in the present instance we are dealing with a completely new trend in flotation, where the surface charge of the bubble is modified by introducing a surfactant. The insignificant changes in the surface of quartz are indicated by the fact that in Goddard's experiments the ζ-potential of quartz changed very little after the introduction of the surfactant.

The depth of the potential well arising outside the limits of the non-electrostatic barrier when the surface of the bubble is altered is insufficient for the contact-free flotation of large particles. The contact-free flotation of particles in the presence of the non-electrostatic component of the disjoining pressure can therefore be ensured by altering the charge of only fairly small particles.

III. CHARACTERISTICS OF THE MECHANISM OF THE TRANSFER OF SMALL PARTICLES TO THE SURFACE OF THE BUBBLE

The approach of the particle to the surface of the bubble undergoes qualitative changes on passing from long (compared with the particle size) distances between their surfaces to short distances. Over long distances, the above process is determined by the operation of only two factors—inertial forces and hydrodynamic interaction. Under the influence of inertial forces, a fairly large particle moves almost linearly until its collision with the surface of the bubble, which occurs if $b < R + a$ (Fig.2). The stream of liquid flows around the surface of the bubble, the flow lines of the liquid are curved, and the particle is involved in this movement in one way or another. The smaller the particle size and the smaller the difference between its density and that of the medium, the smaller the inertial forces acting on it and the closer the agreement between its trajectory and the flow lines of the liquid. Thus, for the same target distance, large particles move along virtually straight lines (Fig.2, line *1*), whereas the trajectories of small particles virtually coincide with the corresponding flow lines of the liquid (line *2*). The trajectories of particles of intermediate size are distributed in the region bounded by lines *1* and *2* and, with decrease of particle size, they shift from line *1* to line *2* and the possibility of collision diminishes.

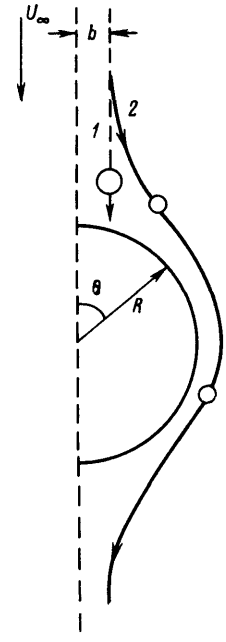


Figure 2. The influence of the inertia of the particles on their trajectories in the vicinity of a rising bubble. The trajectories of large (inertial, line *1*) and small (non-inertial, line *2*) particles for the same target distance *b* are shown.

The deviation of the trajectories of small particles from the linear path towards the surface of the bubble over distances of the order of magnitude of the size of the bubble is caused by a hydrodynamic effect, which can be naturally referred to as a long-range effect. The bubble curves the flow lines of the liquid and thereby curves the trajectories of small particles, i.e. acts on them via the velocity field of the liquid. For large particles, inertial forces greatly exceed the long-range hydrodynamic interaction (LHI) forces and such interaction therefore has only weak effects. On the other hand, for small particles, the inertial forces are small compared with LHI forces[1]. Thus the approach of large particles to the bubble is ensured by inertial forces, whereas in the case of small particles the process is non-inertial and is greatly hindered by the long-range hydrodynamic interaction. This constitutes the first difference in the transport of small particles to the surface of the bubble.

Together with the long-range hydrodynamic interaction, in which the trajectory of the non-inertial movement of the particle coincides with the flow line of the liquid, there exists a hydrodynamic interaction over distances of the order of magnitude of the radius of the particle. The latter leads to the deviation of the particle trajectories from the corresponding flow lines of the liquid. It is natural to refer to such interaction as the short-range hydrodynamic

interaction (SHI). On the basis of Taylor's solution of the hydrodynamic problem of the displacement of liquid from the gap as a spherical particle approaches a planar surface, it has been shown[2] that the SHI can prevent contact between the particle and the bubble. According to Taylor, for a gap thickness $h \ll a$, the hydrodynamic resistance of the film to a decrease of its thickness is given by

$$f = va/h \ , \qquad (3)$$

where v is the rate of approach of the particles to a section of the bubble surface which can be regarded by convention as planar. If the particle is acted upon by a constant adhesional force F, then according to Eqn.(3), we have

$$v \propto Fh/a \ . \qquad (4)$$

Hence it follows that, for the complete removal of the liquid from the gap, an infinitely long time is required:

$$T = \int_h^0 \frac{dh}{Fh} = \frac{1}{F} \ln h \Big|_h^0 \to \infty \ . \qquad (5)$$

The problem therefore arises of the nature of the forces adhering the particle to the surface of the bubble. This paradox is removed if account is taken of the action of the surface attraction forces arising with decrease of the distance faster than the viscous resistance of the film. The decrease of the thickness of the latter for thicknesses of the order of magnitude of the effective radius of action of the surface forces occurs under the influence of the adhesional hydrodynamic force. Above the equatorial plane, the flow lines of the liquid approach the surface of the bubble. This implies that the radial component of the velocity of the liquid is directed to the surface of the bubble. Since in the SHI zone the movement of the particles to the surface is hindered, the radial component of the velocity of the liquid is greater than the radial component of the velocity of the particle and for small gaps and correspondingly for a high viscous resistance it is much greater. As a result the radial flow of the liquid around the particle, which retards its approach to the bubble, clamps it to the bubble. To a first approximation, this hydrodynamic force can be estimated from the Stokes formula by substituting in the latter the radius of the particle and the difference between the local velocities of the liquid and the particle.

Thus the decrease of the thickness of the interfacial film in the case of large particles takes place as a result of inertial impact, while in the case of small particles it is caused by the adhesional hydrodynamic force, which constitutes yet another significant difference characteristic of the flotation of small particles.

The decrease of the thickness of the interfacial film is complicated for large particles by the presence of a dent arising on the surface of the bubble following the inertial impact by the particle. It has been shown[22] that, in the non-inertial deposition of small particles on the surface of the bubble, the deformation of the latter under the influence of the adhesional hydrodynamic force is insignificant. This third considerable difference facilitates the derivation of a quantitative kinetic theory of the flotation of small particles.

IV. A QUANTITATIVE THEORY OF THE FLOTATION OF SPHERICAL PARTICLES OF SMALL AND MODERATE SIZES

The approach of the particles to the surface of the bubble can be described quantitatively by taking into account both the long-range and the short-range hydrodynamic interactions. In order to estimate the efficiency of flotation, we introduce the dimensionless parameter E, given by

$$E = b_{cr}^2/R^2 \ , \qquad (6)$$

where R is the radius of the bubble and b_{cr} the maximum radius of the tube of streaming liquid incident on the bubble, in which all the particles are deposited on the surface of the bubble (Fig.3). The particles moving along a flow line with a target distance $b < b_{cr}$ are deposited on the surface of the bubble (Fig.3, curve *2*); otherwise the particle is carried away by the stream. Fig.3 shows that the calculation reduces to the evaluation of the so-called "limiting trajectory" (Fig.3, curve *1*) and hence of the target distance b_{cr}.#

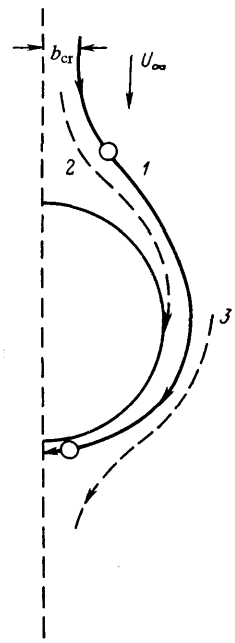


Figure 3. Illustration explaining the concept of the limiting particle trajectory (curve *1*). The trajectories of particles for $b < b_{cr}$ (curve *2*) and $b > b_{cr}$ (curve *3*) are shown by dashed lines.

The flow of liquid around a rising bubble is of the potential type if the movement of its surface is not retarded by the influence of a surfactant and the Reynolds number

$$\mathrm{Re} = \frac{2RU_\infty}{\nu} \qquad (7)$$

greatly exceeds unity (U_∞ is the rate at which the bubble rises and ν is the kinetic viscosity of the medium). If account is taken of the quadratic relation between the velocity of the bubble and its radius, it is easily seen that the Reynolds number varies very rapidly with the radius.

#An analogous approach is used in the theory of aerosols[49].

This number is unity for $R \cong 80$ μm. The concept of the length of the inertial path of the particle l, i.e. the distance which the particle can traverse, despite the viscous resistance of the liquid, as a result of its initial velocity

$$l = \frac{2}{9}\frac{U_\infty a^2 \rho'}{\eta} , \qquad (8)$$

where ρ' is the difference between the densities of the particles and the medium and η is the viscosity of the medium, is important for the understanding of the mechanism of the inertial deposition of particles on a rising bubble.

The normal component of the velocity of the liquid on the surface is zero; the thickness of the layer of liquid in which this component decreases as the surface is approached is of the order of magnitude of the radius of the bubble. The particles traverse this layer of liquid because it falls within the limits of their inertial path. Hence it is clear that the possibility of the inertial deposition of the particle depends on a dimensionless parameter of the type

$$\lambda = l/R . \qquad (9)$$

For $\lambda > 1$, deposition is evidently possible. However, calculations showed that it is possible also for $\lambda < 1$ provided that λ is not too small. This can be understood if account is taken of the fact that a particle in a layer with a thickness R moves to the surface not only as a result of inertia but also together with the liquid. Inertial deposition is impossible if λ is smaller than a critical value λ_{cr}. Under the condition of a potential regime in the flow of liquid around the bubble and when the particle size is neglected, calculation yields the following result[50]:

$$\lambda_{cr} = {}^1/_{2\lambda} . \qquad (10)$$

Using Eqns.(8) and (9), it is easy to obtain a formula for the critical radius of the particle, below which inertial forces do not ensure the approach of the particle to the bubble:

$$a_{cr} = \frac{9}{\sqrt{48}}\sqrt{\frac{\nu\eta}{9\rho' g R}} \simeq 4 \cdot 10^{-1} R^{-1/2} \qquad (11)$$

where g is the acceleration due to gravity.

For $a > a_{cr}$, the inertial deposition of the particles on the surface of the bubble takes place, but its intensity diminishes with decrease of a. This is reflected in the formula for the efficiency of the collision, obtained initially in relation to the coagulation of aerosols[49] and then extended[2] to the elementary step in flotation:

$$E = \frac{\lambda^2}{(\lambda + 0.5)^2} . \qquad (12)$$

This formula has been recently confirmed[52] in the range $\lambda = 0.07-3.5$.

In the light of the studies described above, it is convenient to introduce the subdivision of particles into large, medium, and small. Particles for which E, calculated by Eqn.(12), is close to unity can be regarded as "large". Particles with $a < a_{cr}$ can be naturally referred to as "small", while "medium" particles are those for which inertial deposition is possible but the collision efficiency is less than unity.

As will be seen from what is to follow, in the non-inertial approach of particles to the surface of the bubble, the intrinsic size of the latter plays an important role. The closest approach of the flow lines of the liquid to the surface of the bubble is attained in the equatorial plane. Fig.4 illustrates schematically by a dashed line the flow line of the liquid (curve *1*) whose distance from the surface of the bubble in the equatorial plane is equal to the radius of the particle. Some workers believe erroneously that this is the limiting flow line for particles of this radius, the error consisting in the fact that one does not then take into account the SHI. Under the influence of the SHI the particle is displaced from this flow line of the liquid, since its trajectory (curve *2*) in the equatorial plane is separated from the surface by a distance exceeding the radius. There is therefore no contact with the surface and hence b is not the critical target distance. Bearing in mind that, owing to the SHI, the distance of the particle from the surface in the equatorial plane is greater than the distance along the flow line, with which the particle trajectory coincides over longer distances from the bubble, one may conclude that $b_{cr} < b(a)$. A characteristic feature of the limiting flow line (curve *3*) is that the particle trajectory branching away from it under the influence of the SHI (curve *4*) passes at a distance a from the surface of the bubble in the equatorial plane.

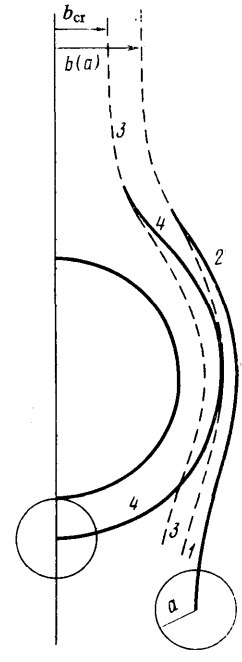


Figure 4. The influence of particle size in non-inertial flotation on their trajectories in the vicinity of the rising bubble. The flow lines in the liquid, corresponding to the target distances b (a) and b_{cr}, are shown dashed. The continuous lines characterise the deviation of the particle trajectories from the flow lines of the liquid under the influence of SHI.

Thus b_{cr} diminishes, firstly, as a result of the deviation of the flow lines of the liquid and the influence of the LHI and, secondly, as a result of the deviation of the particle trajectory from the flow line under the influence of the SHI. The efficiency of the collision is therefore expressed by the product of two factors, E_0 and f, each of which is less than unity; the former expresses the influence of the LHI and the latter that of the SHI.

In the potential flow regime the following expression holds[53]:

$$E_{0p}=3a/R_p \qquad (13)$$

where the subscript p corresponds to the potential regime in the flow around the bubble. For Re < 1, the flow of liquid becomes viscous. The movement of the surface of the bubble is then usually fully retarded by the absorption layer of surfactant, so that the distribution of velocities is then described by the Stokes formula. Furthermore, according to Okazaki[54], for Re < 20 the bubble rises like a solid sphere also in the absence of surfactants. An analogous formula for Stokes regime, which we shall denote by subscript s, is§

$$E_{0s}=\frac{3}{2}\left(\frac{a}{R_s}\right)^2 , \qquad (14)$$

The problem of the adhesional hydrodynamic force, favouring a decrease of the thickness of the interfacial film in the SHI, has been solved for the Stokes regime[56] and for the potential regime[19]. It was established that the adhesional force is 2–3 times greater than the value calculated from the Stokes formula. The adhesional hydrodynamic force cannot ensure contact between the particle and the bubble, since it has a finite value and the resistance increases infinitely as the thickness of the interfacial film diminishes.

It has been shown[2] that non-inertial flotation is possible by virtue of the operation of surface forces. Here there is a possibility of two cases. It is known[57,58] that interfacial films can lose their stability and can be disrupted spontaneously when a critical thickness h_{cr} is reached as the thickness diminishes. On replacing zero by h_{cr} in the integration limits in Eqn.(5), we obtain as a result of integration $\ln(h_0/h_{cr})$ instead of infinity. Thus non-inertial flotation is possible in the presence of flotation agents ensuring the validity of the condition $h_{cr} \neq 0$.

The molecular force of the interaction between a spherical particle and a planar surface is given by the following formula[59] for a sufficiently small value of h:

$$F=Aa/6h^2 , \qquad (15)$$

where A is the Hamaker constant. Since the attractive force defined by Eqn.(15) increases with decrease of h faster than the resistance force of the viscous layer, contact leads to the rupture of the layer. The influence of the SHI on the efficiency of the capture of the particle has been calculated[11,12] for $h_{cr} \neq 0$ neglecting the long-range molecular forces. The formulae obtained using the Stokes and potential distributions of velocities are

$$E_s=E_{0s}f_s , \qquad (16)$$

$$E_p=E_{0p}f_p , \qquad (17)$$

where f_S and f_p are functions reflecting the influence of the SHI on the elementary step in flotation. For any value of the dimensionless parameter $H_{cr} = h_{cr}/a$, these functions are less than unity, decrease with decrease of H_{cr}, and become zero when $H_{cr} = 0$, which agrees with the hypothesis concerning the mechanism of the influence of the SHI on the deposition of the particles described above. With decrease of H_{cr} from 10^{-1} to 10^{-3}, the function f_S diminishes from 0.5 to 0.15, i.e. the dependence of E_S on the absolute value of h_{cr} is very weak. Thus SHI can be taken into account only when one considers the question of the possibility of flotation; this effect diminishes severalfold the number of steps in which the particles come into contact with the bubble.

The SHI theory has been developed[13] without using the phenomenological parameter h_{cr} by allowing directly for the dependence of the molecular forces on h. The following expressions were then obtained:

$$E_s = E_{0s}f_s(w_s);\ w_s=\frac{2AR_s^4}{27U_s\pi\eta a^4} ; \qquad (18)$$

$$E_p = E_{0p}f_p(w_p);\ w_p=\frac{4AR_p}{27U_p\pi\eta a^3} , \qquad (19)$$

where U_S and U_p are the rates at which the bubble rises in the Stokes and potential regimes. Numerical analysis of the universal functions f_S and f_p made it possible to approximate Eqns.(18) and (19) (in the CGS system) as follows:

$$E_s \simeq 0.11\frac{a^{1.4}}{R_s^2}A^{1/4} , \qquad (20)$$

$$E_p \simeq 1.1\frac{a^{0.8}}{R_p}A^{1/8} . \qquad (21)$$

Although the absolute value of E depends very slightly on the Hamaker constant, whose value is in the range from 10^{-14} to 10^{-12} erg, nevertheless flotation is impossible for $A < 0$, i.e. when the dispersion force is directed away from this surface of the bubble. Thus molecular forces act almost in accordance with the "yes or no" principle depending on the sign of A.

The adhesional hydrodynamic force can exceed the force barrier due to the disjoining pressure and hence can ensure the possibility of reagent-free flotation. This question can be investigated by considering the movement of the particle along the symmetry axis of the bubble from the side of the advancing stream of liquid[60]. Since the adhesional force is a maximum under this condition, it is possible to obtain the necessary and sufficient condition for the deposition of particles on the surface of the rising bubble.

Along the bubble axis, the tangential flow rate of the liquid is zero, so that the deposition process can take place over an infinitely long period. However, this implies that the viscous resistance of the interfacial film can then be infinitely small and can be neglected in the balance of the acting forces[60]:

$$F(h, a)=F_V+F_E+F_H+F_G , \qquad (22)$$

where F_V is the adhesional hydrodynamic force, F_H the molecular force of attraction, F_E the electrostatic force, and F_G the gravitational force. Condition (22) implies that a force directed towards the surface (to the upper pole) of the bubble should act on the particle for any h, since otherwise deposition is impossible. Condition (22) sets limits to the parameters in the formulae for the four forces at which the "disjoining" pressure can be overcome. These limits are illustrated graphically in Figs.5 and 6 by curves characterising the dependence of the particle radius on the electrolyte concentration and covering the region close to the original of coordinates, where flotation is impossible. The regions of floatability due to the adhesional hydrodynamic force have been calculated for the Stokes (Fig.5) and potential (Fig.6) regimes in the rise of the bubble. As was to be expected, flotation is possible also appreciably below the heterocoagulation theshold when the particle size is not unduly small. In the potential regime, the adhesional

§Eqn.(14) was apparently first obtained[1] by analogy with the mechanics of aerosols. Eqn.(14), revised by taking into account the gravitational component, has been derived by Reay and Ratcliff[55].

hydrodynamic force is much greater than in the Stokes regime, as a result of which flotation becomes possible for larger electrostatic attraction forces or smaller particles sizes.

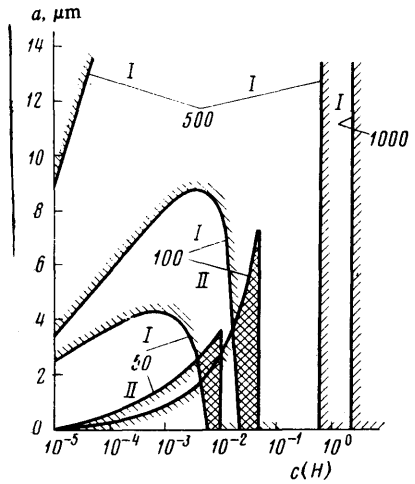


Figure 5. The a – c regions illustrating the floatability in the Stokes regime (shown dashed): I) the lower limit of flotation at the primary minimum; II) the upper limit of flotation at the secondary minimum; 50, 100, 500, and 1000—numerical values of the product $\psi_a\psi_R$ expressed in mV^2. The following quantities are expressed in CGS units: $A = 5 \times 10^{-14}$, $\varepsilon = 80$, $g = 10^3$, and $\rho_{particle} = \rho_{water} = 1$.[60]

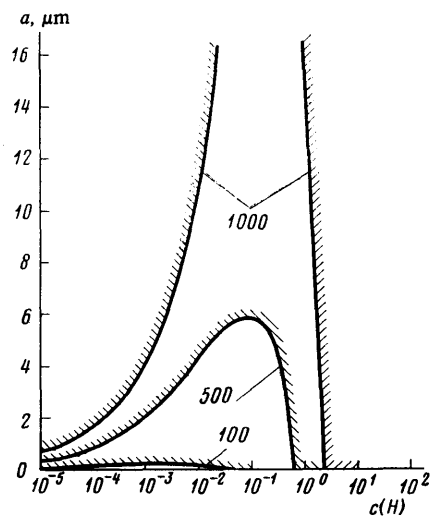


Figure 6. The a–c regions of floatability in the potential regime (shown dashed); 100, 500, and 1000—numerical values of the product $\psi_a\psi_R$ expressed in mV^2. The following quantities are expressed in CGS units: $A = 5 \times 10^{-14}$, $\varepsilon = 80$, $R = 2.5$, $\eta = 10^{-2}$, and $U_r = 15$.[60]

Flotation without overcoming the barrier is difficult owing to the breaking away of the particles at the lower pole of the bubble. The component of the flow rate of the liquid at the upper pole, at right angles to the bubble surface, is responsible for the force adhering the particle to the surface, while that at the lower pole is responsible for the force tending to break it away. Consequently the stripping force differs from the adhesional force only in sign. Therefore the possibility of the fixation of the particles at the secondary energy minimum[30] can be analysed also with the aid of condition (22). Since the stripping force diminishes with particle size, flotation via the fixation of the particles at the secondary minimum proves to be possible for sufficiently small particles. Therefore curve II in Fig.5 sets the upper limit to the size of the particles undergoing flotation. In view of the increasing stripping force, in the potential regime the fixation at the secondary minimum is possible only for very small particles, for which the effect is complicated by thermal movement.

Thus a quantitative description of non-inertial flotation has been given at the present time only in two limiting cases—for sufficiently small and sufficiently large values of the product of the Stern potentials of the particle (ψ_a) and the bubble (ψ_R). In the former case electrostatic interaction does not complicate flotation and Eqns.(20) and (21) can be used; in the latter case flotation is impossible¶.

Since the electrical double layer is compressed with increasing electrolyte concentration and the parameter $\psi_a\psi_R$ decreases, in the light of the data presented in Fig.6 one should expect the possibility of the reagent-free flotation of small particles below the heterocoagulation threshold but at a fairly high concentration of the electrolyte (naturally provided that there are no non-electrostatic stability factors). The significant differences in the Stokes and potential regimes both in the LHI and in the process involving the overcoming of the disjoining pressure already discussed demonstrate the importance of an adequate description of the hydrodynamic field surrounding the bubble in the elementary flotation step. It is useful to employ the hydrodynamic field calculated[62,63] for intermediate values of Re. A formula has been obtained[61] for E [analogous to Eqn.(14)] for conditions under which the hydrodynamic field described by Hamielec and coworkers[62,63] is applicable and the surface of the bubble is stationary.

Within the framework of the general consideration of the equation for particle trajectories, it has been shown[1] that the sedimentation of particles has very little influence on their capture by the bubble, provided that its probability is sufficiently high, so that condition (7) does not hold. For this reason, Deryagin and Dukhin[2] disregarded the sedimentation term in the equation for the particle trajectories. Flint and Howarth[64] regard the force of gravity as the most important factor influencing the capture of small particles by bubbles of any size and object to the neglect of sedimentation, as was done by Deryagin and Dukhin[2,5]. According to Flint and Howarth[64], the quantity E_0 is proportional to the difference between the densities of the particle and the medium ρ' or more precisely to the dimensionless parameter $G = 2\rho' a^2 g/9\eta U_\infty$. However, this implies that, when the densities of the particle and the

¶In the course of the preparation of this review for the press, the paper by Rulev et al.[97] was published in which the kinetic theory of the flotation of small particles was extended to the case of arbitrary values of ψ_a and ψ_R and a quantitative interpretation of the experimental data of Rulev et al.[15] was given.

medium are equal, i.e. when $\rho' = 0$, non-inertial flotation is impossible. This conflicts particularly with Sutherland's equation (13) in which the difference ρ' is not included at all. This conflict arose because Flint and Howarth did not take into account the most important factor in the non-inertial flotation of small particles, namely their finite size.

Anfruns and Kitchener[61] disregarded the finite particle size and Sutherland[53] disregarded the force of gravity. It is easy to take these factors into account simultaneously and to compare their influences on this basis. The functions characterising the particle trajectories in the studies of the above investigators[53,61] differ only by the fact that Anfruns and Kitchener took into account the influence of sedimentation. We shall therefore use the more general formula [Eqn.(6)] of Anfruns and Kitchener[61] describing the family of particle trajectories:

$$\Psi_p^* = \frac{1}{2}\sin^2\theta\left[r^2\left(1 + G - \frac{1}{r^3}\right)\right].$$

Anfruns and Kitchener[61] isolate the limiting trajectory from the entire family of trajectories by taking into account the following condition: $r = 1$ when $\theta = \pi/2$. If this condition is refined by allowing for the finite particle radius ($r = 1 + a/R$ when $\theta = \pi/2$), then the following more general and more accurate formula is obtained:

$$E_0 = \frac{(1+G)\,E_p + G}{1+G} \quad . \qquad (23)$$

If the force of gravity is neglected (we than have $G = 0$), Sutherland's formula is obtained from Eqn.(23). If the finite particle size is neglected, i.e. if we put $E_p = 3a/R = 0$, the equation of Flint and Howarth[64] is obtained.

In the hydrodynamic theory of flotation no account is taken at the present time of the influence of the particle on the hydrodynamic field of the bubble, i.e. the ratio a/R plays the role of a small parameter. The factor G, proportional to $(a/R)^2$, is therefore a small second-order quantity, while the factor E_p, proportional to (a/R) [Eqn.(13)], is a small first-order quantity. The quantity G in Eqn.(23) can therefore be neglected and the equation is transformed into Sutherland's formula also when the force of gravity is neglected. Thus, under the conditions of potential flow, the force of gravity does not influence the kinetics of non-inertial flotation and the conclusions of Flint and Howarth[64] are incorrect.

At the same time one must introduce the correction that, with decrease of the size of the bubble and particularly with increase of the retardation of the movement of its surface, the influence of the sedimentation of particles on the flotation kinetics increases. For example, the allowance for the force of gravity on the kinetics of the flotation by bubbles rising in the Stokes regime, carried out by Reay and Ratcliff[55], is quite appropriate. This is consistent with the finding that in this instance E_{0S} and G are of comparable order of magnitude, as can be seen from Eqn.(14).

V. QUANTITATIVE EXPERIMENTAL STUDIES OF THE FLOTATION OF SMALL PARTICLES

In recent years considerable advances have been made in the experimental study of the influence of the sizes of the bubble and spherical particles on the collision efficiency in the Stokes regime[40,65]. A study has also been made of the flotation[15] of a petroleum emulsion by bubbles whose size ensures a close approach to the potential regime. In satisfactory agreement with Eqn.(21), it was then established that $E_p \propto a$. Studies by Deryagin and coworkers[9,10] confirmed the marked influence of the LHI in non-inertial flotation. Its most important manifestations, observed experimentally, are a rapid decrease of E with decreasing particle size and increasing bubble size and also a sharp alteration of the nature of the dependence of E on R and a on passing from the viscous to the potential flow regime. It must be emphasised that Eqn.(20) is in quantitative agreement with the data of Collins and Jameson[40] and Reay and Ratcliff[65] in relation to the dependence both on the particle size and on the radius of the bubble. The experimental finding that $E \propto a^{1.5}$ implies a better agreement with Eqn.(20) than with Eqn.(14). This can be regarded as experimental confirmation of the influence of the SHI on the elementary step in flotation. However, one must recognise that there have been no systematic experimental studies of the SHI at the present time.

Studies of the efficiency of capture by single bubbles 0.5–1.1 mm in diameter of several fractions of quartz which has been rendered hydrophobic (methylated), confirmed[61] the formula taking into account only the long-range hydrodynamic interaction. The authors[61] therefore concluded that the disjoining pressure of the double layers does not complicate the flotation step at least under the conditions of their experiment. An analogous conclusion could be formulated in relation to the SHI.

However, these conclusions cannot be regarded as firmly justified, since it is possible to propose a different interpretation of these interesting experimental data. This other possibility is associated with the fact that the theory of the SHI and of the influence of the double layer on flotation has been developed for spherical particles, while Anfruns and Kitchener[61] investigated non-spherical particles—fragmented Brazilian quartz. One must therefore postulate the existence of edges separating the faces on the surface of such particles. The resistance to the decrease of the thickness of the interfacial film can be much more readily overcome if the angles between the faces (or between the edges) are sufficiently small, so that the interfacial film can be "pierced" by the sharpened section of the particle surface. Similar geometrical conditions in the elementary step in flotation sharply facilitates also the overcoming of the disjoining pressure. The surface microrelief cannot have a strong influence on the LHI, since Eqns.(13) and (14) and the formula of Anfruns and Kitchener[61], which have been derived for spherical particles, remain in force also as an approximation for non-spherical particles.

In the light of the foregoing and the results of Anfruns and Kitchener, the formulation of the theory of the flotation of small particles has been significantly revised: the characteristics of the influence of the SHI and of surface forces on the elementary step in flotation can differ sharply in relation to spherical and non-spherical particles and must therefore be investigated separately. The deviation of the shape of the particle from the spherical can not only reduce but can also greatly increase the role of the SHI and of the double layer in flotation. The decrease of the thickness of the plane-parallel interfacial film between the bubble and a lamellar particle is even slower than for a spherical particle, so that the role of the SHI sharply increases in this instance. This is to be expected for a thin lamellar particle. On the other hand, if the particle is not thin, one may expect that its migration along the surface of the bubble is accompanied by rocking. In the course of rocking, orientations of the particle relative to the bubble surface arise in which the viscous resistance of the interfacial film and the disjoining pressure of the double layer are overcome so rapidly that the

SHI has only slight influence on E.†

VI. THE BREAKING AWAY OF SMALL PARTICLES IN CONTACT-FREE FLOTATION AND THE DYNAMIC ADSORPTION LAYER OF THE BUBBLE

If flotation is uncomplicated by energy barriers and $h_{cr} \neq 0$, then the approach of the particles terminates with the rupture of the film and the establishment of a wetting angle so that the possibility of breaking away is ruled out under these conditions.

If the double layer does not complicate flotation but there is a non-electrostatic barrier with a thickness h_0, then the possibility of the particle breaking away can be estimated as in the study of Deryagin et al.[60], where the possibility of coagulation at the secondary minimum in flotation was examined (Fig.5). For this purpose, it is sufficient to consider the condition of the equality of the sum of the hydrodynamic and gravitational stripping forces to the molecular attraction force at $h = h_0$ at the lower pole of the bubble. This leads to the following estimate of the particle radius a_{max} below which contact-free flotation is possible in the Stokes regime (in the CGS system):

$$a_{max} = 3 \cdot 10^{-3} \frac{\sqrt{A}}{h_0} \quad . \qquad (23')$$

If it is assumed that A varies in the range 10^{-14}–10^{-13} erg and h_0 varies in the range 10–100 Å, then a_{max} is in the range 3–100 μm. Thus difficulties for contact-free flotation arise when the Hamaker constant A is small or the thickness of the barrier h_0 is large. In this situation the opposite charges of the particle and the bubble must be achieved by introducing an ionogenic surfactant in order to ensure contact-free flotation. This is possible for a greater thickness of the barrier the lower the electrolyte concentration.

By overcoming the disjoining pressure of the double layer via the adhesional hydrodynamic force (Figs.5 and 6), one guarantees that the particle, which has migrated to the lower pole of the bubble, cannot break away only when the depth of the primary (near) potential energy minimum is sufficiently great. It has been shown[65,67,68] that after coagulation subsequent breakdown of the resulting aggregate is possible, since the depth of the primary minimum may be small. Coagulation at the primary minimum does not occur or is reversible with increase of concentration in the range characteristic of the coagulation of lyophobic colloids if the Stern potential is fairly high and the depth of the well is small. The question of the depth of the primary minimum is very complex. In the case of flotation it is complicated still further in view of the lack of information about the charge of the bubble.

Since the question raised in connection with the study described in Refs.65–68 is far from solved, we shall confine ourselves to a single general remark. The depth of the primary potential well decreases with increasing charge of the interacting surfaces. Therefore the smaller the product $\psi_a\psi_R$, involved in the theory of heterocoagulation (Figs.5 and 6), the smaller is the probability that the particles which had previously overcome the disjoining pressure of the double layer via the adhesional hydrodynamic force will break away. The greater the value of this product, the smaller the depth of the primary potential well, and the greater the probability that the particles will break away (particularly if the Hamaker constant is small). In other words, the condition for overcoming the disjoining pressure via the adhesional hydrodynamic force for sufficiently low values of the product $\psi_a\psi_R$ is necessary and sufficient for flotation. For higher values of this product, the above condition becomes only necessary.

The possibility of breaking away increases with increasing size and the rising velocity of the bubble. The mechanism of the stripping process can then be complicated by the deformation of the double layer on the mobile bubble surface, which can lead to an increase of the surface charge and hence of the electrostatic repulsion forces at the lower pole of the bubble. When the size of the bubble is not unduly small, its surface is mobile. Its upper part becomes extended as the bubble floats upwards while the lower part is compressed[3,4]. The new surface regions produced are filled with the adsorbable substance, while the contraction of the surface results in its desorption. On the upper half of the rising bubble, the degree of adsorption is lower than on a stationary surface (Γ_0), which ensures a continuous supply of the surfactant (or of adsorbable inorganic ions) from the bulk phase to the expanded surface. On the lower half of the rising bubble, the degree of adsorption is higher than Γ_0, which gives rise to the desorption of the surfactant. Thus the degree of adsorption $\Gamma(\theta)$ increases in the direction of the migration of the surface of the bubble, i.e. from the upper pole ($\theta = 0$) to the lower pole ($\theta = \pi$).

The supply of the surfactant to the upper half of the bubble and the removal to the bulk phase of the surfactant desorbed from the lower half take place owing to the existence near the surface of the so-called diffusion boundary layer. Its thickness is much smaller than the radius of the bubble R and is defined by the formula

$$\delta = R/\mathrm{Pe}^{1/3} \quad , \qquad (24)$$

where Pe is the Peclet number defined by the expression

$$\mathrm{Pe} = \frac{RU}{D} = \mathrm{Re}\,\frac{\nu}{D} \quad . \qquad (25)$$

Since the diffusion coefficient $D \cong 10^{-5}$ cm^2 s^{-1} and $\nu/D \cong 10^3$, in the relevant range of Reynolds numbers the quantity Pe should be large (~10^4–10^6); the surfactant concentration in the diffusion boundary layer on the upper half of the bubble is smaller than in the bulk phase and increases from the upper to the lower pole, as in the dynamic adsorption layer. For any specified angle θ, which is reckoned from the upper pole, equilibrium between the degrees of adsorption $\Gamma(\theta)$ and the volume concentration in the bulk of the diffusion layer directly at the surface $c(R, \theta)$ persists:

$$\frac{\Gamma(\theta)}{c(R, \theta)} = \frac{\Gamma_0}{c_0} \qquad (26)$$

where Γ_0 is the equilibrium degree of adsorption on the surface of a stationary bubble at a surfactant concentration in the bulk of the solution c_0.

Not only the movement of the bubble surface influences the formation of a dynamic adsorption layer; the opposite influence of the dynamic adsorption layer on the movement of the surface also obtains. The degree of adsorption increases in the direction of motion of the liquid, while the surface tension σ falls. This leads to the generation of forces directed in opposition to the stream of liquid and retarding the movement of the surface. Thus the theory of the dynamic layer must be based on the simultaneous

†During the preparation of this article for the press, we learnt of the communication by Anfruns and Kitchener[98], in which they described an experimental confirmation of the above considerations.

solution of the equation for diffusion, complicated by allowance for the influence of the movement of the surface on adsorption–desorption processes, and the hydrodynamic equations complicated by the influence of the adsorption layer on the movement of the interface between the liquid phases[68–71].

The simultaneous allowance for the influence of the hydrodynamic field on the distribution of adsorption and volume concentration and for the influence of dynamic adsorption on the velocity field for Pe $\gg$ 1 has been achieved in the limiting cases of weak (Re $\gg$ 1) and strong retardation of the surface (Re $\ll$ 1).

For weak retardation of the main section of the surface and for a moderate surface activity, i.e. when

$$\Gamma_0/c_0 \ll \delta \quad , \tag{27}$$

the change in the degree of adsorption is slight: $\Gamma_0 - \Gamma|_{\theta=0} \ll \Gamma_0$. The angular relation $\Gamma(\theta)$, obtained by Deryagin et al.[3], can be roughly approximated by a cosine, as assumed by Frumkin[69], only on the upper half of the bubble. A virtually uniform and weak retardation of the surface can be characterised by the retardation coefficient

$$\gamma = \frac{2}{3}\frac{\partial\sigma}{\partial c}\Gamma_0 \mathrm{Pe}^{-1/3} D^{-1} \tag{28}$$

and $\gamma \ll \eta$.

For weak retardation and a high surface activity, i.e. when

$$\Gamma_0/c_0 \gg \delta \quad , \tag{29}$$

the degree of adsorption on the main section of the bubble surface is much smaller than the equilibrium value and a very rapid growth of adsorption and a strong inhibition of the surface should be observed only for $\theta \to \pi$.[4]

In connection with the influence of the surface on the adsorption layer discussed above, the problem arises of the change in the structure of the electrical double layer along the mobile bubble surface. A characteristic feature of the structure of the equilibrium double layer at the air–water interface is that it is caused by the negative and not positive adsorption of ions. Numerous experimental studies, which have been reviewed[73,74], have established that the surface tension in solutions of inorganic electrolytes increases. According to the Gibbs formula, this indicates negative adsorption. The magnitude of the effect is frequently characterised by the thickness of the ion-free layer (h). This thickness is of the order of magnitude of the size of water molecules. The expulsion of ions from the surface layer is caused by their electrostatic interaction with the interface, which can be characterised in terms of electrostatic image forces.

In order to test the validity of condition (27), one can use the following estimate:

$$(\Gamma_0/c_0) \simeq h \simeq 10^{-7}\ \mathrm{cm} \ll \delta \quad . \tag{30}$$

Thus condition (27) is valid, which means that, under the conditions of negative adsorption, the double layer is hardly deformed on the mobile bubble surface.

On passing from the Stokes field of the bubble to the potential field, the stripping hydrodynamic force increases by a factor R/a, since the radial flow rate of the liquid at the distance of closest approach of the centre of the particle to the surface of the bubble (a) increases by the same factor. This difference between the Stokes and potential regimes in the treatment of the possibility of the breaking away of particles diminishes somewhat if account is taken of the retardation of the bubble surface. On the fully retarded section of the bubble surface, the radial component of the velocity of the liquid at a distance y from the surface of the bubble diminishes according to a quadratic law for $y \ll R$, as in the Stokes regime. On a partly retarded section of the surface, the charge proceeds in accordance with a linear law but with a coefficient which is comparable to the ratio of the local retardation coefficient to the viscosity of water. The higher the degree of retardation of the bubble surface, the smaller the possibility that the particles will break away in contact-free flotation. For this reason, the question of the degree of retardation of the surface is of great interest.

The literature data[54,75] presented in Fig.7 show that, for Re > 40, the velocity of the bubble is greater the lower the concentration of the surfactant introduced and that, for Re < 40, bubbles rise as solid spheres even when the water has been very carefully freed from impurities. The agreement of the rate at which the bubble rises with the value calculated for a solid sphere is regarded by many investigators as the criterion of the retardation of the entire surface of the bubble. In the light of theoretical studies of the retardation of the movement of the bubble surface, this condition is believed to be necessary but not sufficient. When a considerable proportion of the bubble surface is retarded, some of it, near the upper pole, can retain mobility[70]. There is also a possibility of a uniform, strong, but incomplete retardation of the entire surface[71,72]. In both cases the rate at which the bubble rises can be the same, within the limits of the error of the measurement, as that for a solid sphere. However, the degree of adsorption of the surfactant at the upper pole can then be much less than Γ_0.[71,72]

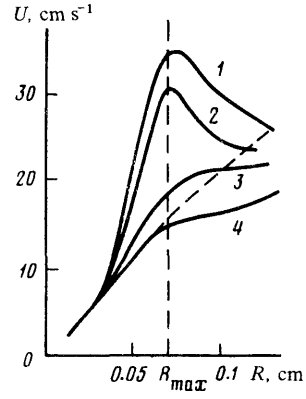


Figure 7. The rate of the rise of bubbles in aqueous solutions of sodium dodecyl sulphate: *1*) distilled water; *2*) 10^{-6} M; *3*) 1.2×10^{-5} M; *4*) 10^{-3}–10^{-4} M. The dashed curve corresponds to bubbles with a fully retarded surface in distilled water or a millimolar solution[54].

The hydrodynamic resistance, which determines the rate of the upward rise of the bubble, consists of the shape resistance, which depends on the position of the line at which the particle breaks away, and the viscous resistance, which depends on the degree of retardation of the entire surface. Since the contribution of the viscous resistance is not small, one must assume that, for Re < 40, the entire lower half of the bubble is retarded, since otherwise the velocity of the bubble would have differed significantly from

the velocity of the solid sphere owing to the contribution of the viscous resistance. Hence follows the important conclusion that, at Re < 40, the stripping force increases insignificantly compared with the Stokes regime.

The transitional regime (1 < Re < 40) can be optimal for reagent-free flotation. Its advantage over the Stokes regime consists in the fact that, when it obtains, the possibility of fixation at the primary energy minimum increases. A necessary condition for reagent-free flotation is sufficient depth of the primary energy minimum. If this condition does not hold, then ionogenic surfactants must be introduced to prevent the breaking away of the particles.

The agreement of experimental data for the rates at which bubbles rise with the calculated values[54], obtained on the assumption that the surface is unretarded implies that, at Re > 40, a considerable proportion of the lower half of the bubble is mobile, to which corresponds a sharp increase of the normal component of the velocity responsible for the breaking away of the particles. Therefore, on passing to the condition where Re > 40, contact-free flotation becomes hindered. Hence the introduction of an ionogenic surfactant is necessary even when the adhesional hydrodynamic force ensures the overcoming of the disjoining pressure, except in the case where the depth of the primary well is large or contact flotation obtains.

The introduction of a cationic surfactant (for a negative particle charge) leads to three effects ensuring flotation, namely the difficulty associated with the overcoming of the disjoining pressure in the deposition of particles on the bubble is eliminated, attraction forces (stronger under certain conditions than the van der Waals forces) preventing the breaking away of the particles are ensured and, as a result of the retardation of the movement of the lower half of the bubble surface, the stripping hydrodynamic force diminishes.

The consumption of the ionogenic surfactant should ensure the neutralisation of the bubble charge, which can be roughly estimated by specifying the surface potential ψ, as was done by Ekserova and Zakharieva[76]. It follows from the Gouy–Chapman theory that

$$\sigma = F\Gamma' = Fc_e\varkappa^{-1}\sinh(\Psi/2) \qquad (31)$$

where Γ' is the degree of adsorption of the cationic surfactant necessary for the neutralisation of the bubble charge at an electrolyte concentration c_e and $\varkappa^{-1}$ is the thickness of the diffuse component of the double layer. The consumption of the surfactant should ensure a fairly high degree of adsorption, i.e. the following relation should hold:

$$\Gamma > \Gamma' \simeq c_e\varkappa^{-1} . \qquad (32)$$

In the most important case where

$$\varkappa^{-1} \ll \delta \qquad (33)$$

conditon (32) can be ensured both for low and high surface activities. The use of surfactants with a very high surface activity, corresponding to condition (29), is undesirable since the adsorption layer is then displaced to the lower pole of the bubble. The introduction of such a surfactant does not facilitate the deposition of particles on the upper half of the bubble and does not prevent their breaking away from the lower half, since the surfactant is concentrated in the small region near the lower pole of the bubble and the particles can break away from any section of the surface near which the normal component of the velocity is directed into the bulk of the liquid. By increasing the concentration c_0, it is possible to expand the retarded zone. This question has been considered by Dukhin and Buikov[71,72], but these investigations do not answer the question whether the retardation of the entire lower half of the bubble is possible at a sufficiently high c_0.

The use of surfactants with a very low surface activity is inconvenient, since it is associated with an excess consumption of the reagent. The same necessary degree of adsorption Γ' can be ensured at a lower concentration c_0 the higher the ratio Γ_0/c_0 within the limits of the validity of condition (27). With increase of Γ_0/c_0, the retardation coefficient also increases [see Eqn.(28)] even for an equivalent decrease of c_0, which is also important for the prevention of the breaking away of the particle. One may therefore conclude that it is useful to employ surfactants with a surface activity such that $\Gamma_0/c_0 \cong \delta$. A surfactant concentration equal to

$$c_0 = \frac{c_e\varkappa^{-1}}{\delta} \qquad (34)$$

is then necessary to ensure condition (32). At this retardation concentration γ may be comparable to the viscosity, which shows that a certain section of the bubble surface is retarded, because the following relation holds:

$$\frac{\gamma}{\eta} = \frac{2}{3}\frac{\partial\sigma}{\partial c}\Gamma_0 \mathrm{Pe}^{-1/4}D^{-1}\eta^{-1} \simeq \frac{RT}{\eta U}\varkappa^{-1}c_e . \qquad (35)$$

VII. NON-EQUILIBRIUM SURFACE FORCES IN FLOTATION

A characteristic feature of the mechanism of the deformation of the thin double layer by various kinds of external influences is that equilibrium conditions, particularly the electroneutrality condition, hold for each section of the surface[3,77]. The degrees of adsorption (surface charge) and the concentration in the diffusion layer vary along the mobile surface of the bubble. Thus the thickness of the double layer varies along the surface of the bubble in accordance with the variation of the surface charge and the electrolyte concentration but on each section of the surface its three-dimensional double layer structure is described by the equilibrium theory. This justifies the consideration of the elementary step in flotation on the basis of the theory of heterocoagulation. However, qualitatively new effects also arise on formation of the double layer. Diffusion in an electrolyte is known to be usually coupled with the generation of an electric field. The vector lines of the electric field E_D coincide with the vector lines of the concentration gradient grad c. In a binary electrolyte solution the electric field strength is expressed in terms of the local concentration gradient by the familiar formula[3,78]

$$E_D = \frac{D^+ - D^-}{z^+D^+ + z^-D^-}\frac{RT}{F}\frac{\mathrm{grad}\, c}{c} , \qquad (36)$$

where D^+, D^-, z^+, and z^- are the diffusion coefficients and the electrovalences of the anions and cations and F is the Faraday. An electric field should therefore arise within the limits of the diffusion boundary layer coupled with the dynamic adsorption layer of the ionogenic surfactant. This is caused by the slight deviation from the electroneutrality condition. Like the grad c vector lines, the E_D vector lines begin at the upper boundary of the quasi-equilibrium double layer, are oriented approximately at right angles to the surface, and terminate at a point within the diffusion layer. However, the sources of electric field lines are known to be positive charges, while negative charges diminish the field. Hence it follows that charges of opposite sign, approximately cancelling out, are localised within the limits of the quasi-equilibrium double layer and

in the diffusion layer (Fig.8). These two layers of charges constitute a single system in the sense that the change in the distribution of charges of one layer is necessarily accompanied by redistribution of charges in the other layer.

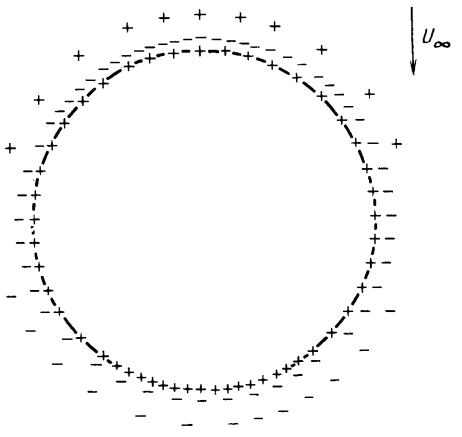


Figure 8. Distribution of the charge signs in the primary and secondary double layers for a substance with moderate surface activity[5].

This system of charges, arising on deformation of the equilibrium double layer, can be naturally called the secondary double layer[78-80]. Since the thickness of the secondary double layer exceeds that of the equilibrium double layer by several orders of magnitude (except at low electrolyte concentrations), the deposition of particles on the surface of the bubble can be controlled under certain conditions primarily by the stage in which the particles pass through the diffusion layer[81]. The consideration of this question simplifies if the particle size is less than δ, so that a particle passing through the diffusion layer can be regarded as subject to homogeneous electric and diffusion fields. Consequently a particle crossing the diffusion layer is subjected to electrophoresis and diffusiophoresis[82,83].

In a study of the deposition under gravitational forces of galenite particles of different size on the mobile surface of a fixed bubble from a vertical stream of liquid[9], it was observed that particles whose size is below a critical value a_{cr} do not reach the surface of the bubble. On the basis of the measured values of ζ, it was established that, for $a < a_{cr}$, the joint action of electrophoresis and diffusiophoresis is responsible for the force repelling the particles from the bubble, which exceeds the gravitational force. With increasing electrolyte concentration, the repulsion force weakens, which is revealed experimentally by a decrease of a_{cr}.

The thickness of the diffusion layer of a freely rising bubble is much smaller, in view of its high velocity, than in the experiments described. The effect can therefore appear only for particles which are so small that their thermal motion is significant. Electrophoresis and diffusiophoresis must be taken into account in the description of the Brownian diffusion of submicron particles to the mobile surface of a bubble and at a fairly low electrolyte concentration. It has been shown[84] that the concentration drop in the diffusion layer δc is very small when the surface of the bubble is fully mobile:

$$\frac{\delta c}{c} \simeq \frac{\mathrm{Pe}^{1/3}}{(\varkappa a)^2} \quad . \tag{37}$$

The mechanism of the action of non-equilibrium surface forces for particles whose size exceeds δc can be established fairly simply only when the same ionogenic surfactant is sorbed on the surfaces of the bubble and the particle. This mechanism is associated with the desorption of the reagent from the surface of the particle, diffusion through the film, and adsorption on the surface of the bubble. The diffusional transport of the adsorbate is caused by the decrease of the concentration of the reagent in the diffusion layer of the bubble, which extends over the upper half of the bubble and, when condition (29) holds, also over a considerable proportion of the lower half. The section of the bubble surface where adsorption takes place acquires an excess charge, whose sign is the same as that of the rapidly diffusing ion. An equal charge of the opposite sign arises on the section of the surface of the particle from which the reagent is desorbed. An estimate showed that an electric field of $\sim 10^3$ V cm arises under these conditions. The excess charges of the bubble are attracted to the excess charges of the particle, so that the interfacial film is as it were clamped between the plates of a condenser, as a result of which its thickness diminishes. The non-equilibrium surface forces decrease in the presence of an indifferent electrolyte if its concentration is much greater than that of the ions in the adsorption layer. For a quantitative estimate of this important factor, which reduces the non-equilibrium surface forces, it is necessary to extend the theory[8] developed in relation to a binary electrolyte to the case of three kinds of ions.

High electrolyte concentrations have only a weak influence on the non-equilibrium surface forces due to the dynamic adsorption layer of the non-ionogenic surfactant[85,86]. In the course of migration along the mobile surface of the bubble the surfactant concentration in the diffusion boundary layer in the vicinity of the particle increases continuously. Therefore in the centre of the interfacial film the concentration of the surfactant and the degree of adsorption are lower than on the periphery of the film, where the concentration increases continuously as a result of the migration of the particle along the diffusion layer. Since the degree of adsorption at the centre of the interfacial film is smaller than on its periphery, the surface tension at the centre of the film is higher. The increase of the surface tension towards the centre of the film from its periphery should be accompanied by surface flow from the periphery to the centre, involving the entire liquid of the film. The flow of liquid into the gap between the particle and the bubble prevents a decrease of the thickness of the film and rules out the possibility of flotation. This analogue of the Marangoni–Gibbs effect does not arise if the surface of the bubble is stationary and the degree of adsorption does not change along it.

The decrease of the collision efficiency due to this effect has been calculated[99] for spherical and disc-shaped particles under the conditions of a weak retardation of the surface and a moderate adsorbability of the surfactant, satisfying condition (27). For a disc-shaped particle, the collision efficiency can diminish by several orders of magnitude. For spherical particles, the diffusional exchange in the interfacial film between the centre of the latter and its periphery is more intense, which leads to a decrease of the drop in adsorption and surface tension, i.e. a weakening of the effect. However, the deposition of even a spherical

particle is possible only in the small region near the upper pole of the bubble.

The effect involving the stabilisation of the interfacial film discussed above can weaken if the surfactant is adsorbed not only by the bubble but also by the particle. There is then a possibility of the diffusional transfer of the surfactant from the surface of the particle to the surface of the bubble, which should lower the surface tension at the centre of the interfacial film, compensating to some extent its increase as a result of the tangentian movement of the particle.

Diffusional non-equilibrium surface forces have been observed experimentally[87,88]. A thin layer of soluble ionogenic surfactant was first deposited on a small section of an inclined surface of the solid. When water had flowed off the surface, the thickness of the inclined surface layer under stationary conditions was always constant except for the section coated by the surfactant. Over the surfactant-coated section, the film became appreciably thinner under the influence of the surfactant. Since the surface of the film in the attenuated region was significantly curved, the authors[87,88] reached the completely correct conclusion that appreciable forces, which must compensate for the capillary pressure due to the curvature of the surface of the film, act at right-angles to the water–air interface. A theory of this effect has been proposed[89], taking into account the electrocapillary effects, which were significant in both the experiments of Evans and Ewers[87,88] and in the application of ionogenic surfactants in the flotation of small particles.

By introducing ionogenic surfactants, it is possible to eliminate the hindrance of the flotation of small particles associated with the operation of equilibrium surface forces (neutralisation of the charge of the bubble and decrease of the electrostatic component of the disjoining pressure), but the effect of the stabilisation of the interfacial film can then be considerable, as a result of which flotation is impaired. The introduction of ionogenic surfactants in flotation by small bubbles therefore appears to be more reliable, since in the Stokes regime one may expect the complete retardation of the surface of the bubble and a sharp weakening of the non-equilibrium surface forces. This can also be achieved in the transitional regime by increasing the consumption of the reagent, ensuring thereby the retardation of the surface.

VIII. THE EFFICIENCY OF THE COLLISION AND FLOTATION KINETICS

Flotation is usually carried out with large volume fractions of bubbles, which leads to an appreciable deviation of the distribution of the velocities of the liquid in the vicinity of the bubbles compared with the case of a single bubble discussed above. As a result of allowance for the velocity distribution engendered by the system of bubbles[17], a formula was obtained for the capture efficiency. The efficiency depends not only on the bubble size but also on the fraction of dispersed gas[18]. The study of the flotation of monodisperse particles by a system of bubbles led to the formula

$$n(t)=n_0e^{-kt} \quad , \tag{38}$$

which had been obtained earlier in another study[90]. Here $n(t)$ and n_0 is the concentration of particles at time t and the initial concentration. Under these conditions, the following expression was obtained for k (in the case of monodisperse systems):

$$k=\frac{3qE}{4R} \tag{39}$$

where q is the rate of bubbling, equal to the volume of gas blown across a unit cross-sectional area of the flotation chamber per unit time. This formula was extended[17] to the case of polydisperse systems and it was found that under conditions of a nearly normal distribution of particles to the bubbles, one may use Eqn.(39) in which the statistical mean particle and bubble sizes are employed.

Thus the kinetic theory of the flotation of small particles described above makes it possible to relate the technologically most important parameter k to the measured characteristics of the flotation system. The parameter k can be related to E also when particles with sizes greater than a_{max} can break away after deposition. In the summation with respect to fractions of deposited particles [in the integration of $E(a)$] it is sufficient to use a_{max} as the upper integration limit.

IX. THE INFLUENCE OF THE AGGREGATION OF PARTICLES ON THE ELEMENTARY STEP IN NON-INERTIAL FLOTATION

The introduction of surfactants in order to reduce the electrokinetic potential [of the bubble?] can lead simultaneously to a decrease of the electrokinetic potential of the particles and hence to their aggregation. The influence of aggregation on the elementary step in flotation has been considered[20] on the assumption that the aggregate is rigid and spherical in shape and that its radius a^* is small compared with R. With these simplifying assumptions, the efficiency of the collision of the aggregate with the bubble E^* can be described by Eqns.(13) and (14) having replaced the particle radius a by the radius of the aggregate a^*. Then the following estimates can be obtained from Eqns.(13) and (14) for the intensity of the deposition of particles on the bubble as a result of aggregation in relation to the Stokes and potential regimes:

$$E_s^*/E_s \simeq (A/a)^2;\ (E_p^*/E_p) \simeq a^*/a \ . \tag{40}$$

Since under the conditions of the short-range hydrodynamic interaction, there is a possibility of the outflow of the liquid from the film separating the bubble and the aggregate into the pores within the aggregate, the attenuation of the film is faster and the ratio E^*/E may prove to be greater than that found by Eqns.(40).

The increase in the size of the aggregate plays a positive role in flotation only at the stage involving the formation of the aggregate–bubble system, since the probability that the aggregate will break away from the bubble increases simultaneously. Indeed, the greater the size of the aggregate or particle, the greater the radial component of the velocity at the centre of the aggregate, which is oriented outwards at right angles on the lower half of the surface of the bubble. Formulae have been obtained[20] for the stripping hydrodynamic force and the maximum radius of the bubble capable of flotation without the breaking away of aggregates of given radius. The derivation of the formulae was based on the solution[91,92] of the hydrodynamic problem of two spheres rising upwards along a common axis in the Stokes regime.

For a given bubble size, there is an optimum size of the aggregate ensuring the most intense flotation, since larger aggregates break away from the surface of the bubble and smaller aggregates are deposited on its surface at a lower frequency. It is inconvenient to increase appreciably the size of the bubble, since, under the conditions of a simultaneous decrease of the size of the aggregate, this leads to a sharp diminution of the ratio of the volumes of the aggregates undergoing flotation and of the gas bubbled

through the system. An appreciable decrease in the size of the bubble is also inconvenient, because the rate of transport of the aggregates by the bubbles decreases sharply at the same time. This means that there is an optimum bubble size for the flotation of aggregates of given dimensions. Unfortunately, it is difficult to estimate this optimum reliably. Firstly, it is difficult to estimate the number of aggregate particles in contact with the bubble, in proportion to which the force acting against the stripping force increases. This number depends on the deformation of the aggregate under the influence of the adhesional hydrodynamic force and the tangential stream of liquid. Secondly, the aggregate may break away owing to the rupture of the coagulation linkage between the particle adhering to the bubble and the neighbouring particles of the aggregate.

X. THE FLOTATION OF SUBMICRON PARTICLES

With decrease of the radius of the non-inertial particles and when the latter attain the region of submicron dimensions, they acquire the capacity for intense Brownian diffusion. In this case the electrostatic barrier impenetrable to comparatively large but non-inertial particles can be overcome by small "Brownian" particles owing to the energy of their thermal movement.

The efficiency of the capture of Brownian particles by the bubble can be determined by solving the equation for the convective diffusion of particles to a spherical obstacle in the field of the forces of interaction between the particles and the bubble. It is then possible to isolate two limiting cases. If the interaction force promotes rapid adhesion of the particles to the surface of the bubble, then the rate of deposition and hence the capture efficiency will be limited by the rate of diffusion of the particles to the surface of the bubble. It follows from the work of Ruckenstein and Prieve[93] and Spielman and Friedlander[94] that the efficiency of the capture of particles by a bubble rising under the conditions of small Reynolds numbers and having a fully retarded surface is then expressed by the formula

$$E_s = \frac{3}{2\Gamma(4/3)}\left(\frac{D_a^2\pi^2}{3R_s^2U_s^2}\right)^{1/3}, \qquad (41)$$

where Γ is the gamma-function and D_a the diffusion coefficient of the particles. On the other hand, if the bubble rises in the potential regime ($Re \gg 1$) and its surface is fully mobile then, as shown by Rulev[95], the capture efficiency is defined by the expression

$$E_p = \left(\frac{32D_a}{\pi U_p R_p}\right)^{1/2}. \qquad (42)$$

If the deposition of the particles on the surface of the bubble is hindered by their interaction (for example, electrostatic), then the capture efficiency will be limited solely by the rate of diffusion in the field of surface forces. In this case

$$E = \frac{4K}{U}, \qquad (43)$$

where K is the deposition rate constant which is determined by the energy of the interaction of the particle with the bubble. If we denote this energy by ϕ, then it follows from the work of Ruckenstein and Prieve[93] that the following expression is valid:

$$K = \frac{1}{D}\int_0^\infty \left\{\exp\frac{[\varphi(h)/kT]}{f(h/a)} - 1\right\} dh, \qquad (44)$$

$$f(H) = \begin{cases} \dfrac{H}{1+H} & \text{when } H = \dfrac{h}{a} \leqslant 1 \\ \dfrac{H-1/6}{H+1} & \text{when } H \to \infty . \end{cases} \qquad (45)$$

Eqns.(41) and (42) show that, in contrast to the second case, in the first case the capture efficiency is determined exclusively by the diffusion coefficient, which is inversely proportional to the particle radius. Hence it follows that

$$E_s \propto a^{-2/3},\ E_p \propto a^{-1/2}, \qquad (46)$$

i.e. the capture efficiency increases with decreasing particle radius in the submicron region, which has in fact been observed experimentally[55].

Thus, with decrease of the particle radius and on transition from the non-inertial deposition regime to the diffusional regime, a minimum in capture efficiency is observed in the region of $a \cong 0.1$ μm. The intensification of the flotation of particles of this size is particularly important and can be achieved by means of their aggregation.

If one excludes from consideration effects complicating the elementary step in flotation at a fairly low electrolyte concentration and for a fairly large bubble size, then the theory developed here, whose fundamental postulates have already been confirmed experimentally, indicates ways of optimising the purification of water by flotation. In the absence of non-electrostatic stability factors and at an electrolyte concentration above the threshold value, one must test the possibility of reagent-free flotation. On the other hand, if the level of the electrolyte concentration in the water to be purified is low or when a non-electrostatic stability factor is characteristic of the particles, then their fixation on the surface of the bubble must be ensured by introducing ionogenic surfactants.

The intensity of extraction in water purification by flotation and the possibility of increasing the productivity of flotation water purification plants without increasing their size can be achieved by employing bubbles of optimum dimensions and at the optimum concentration. In this connection one should note that the experience gained in water purification by flotation, although the latter has so far been developing solely on an empirical basis, is consistent with the hydrodynamic theory described. Indeed, in order to ensure an acceptable rate of extraction of disperse contaminations by flotation, one resorts to small bubbles, which corresponds to an increase in the efficiency of particle capture by the bubble as its size diminishes. Instead of flotation by large bubbles, formed on mechanical dispersion of air, in water purification one employs electroflotation, microflotation, flotation by bubbles evolved from supersaturated solutions of air in water, i.e. methods ensuring bubbles of small size. The observed intensification of flotation on passing to small bubbles (electroflotation, microflotation) can be associated with the weakening of the forces tending to strip the particles off the bubble. However, for maximum rates of extraction of disperse contaminations, one must use bubbles which are not simply small but have the optimum size.

Full control of the flotation of small particles can be achieved only by studying the entire set of problems associated with the hydrodynamics and stability of thin films which are and are not in equilibrium with surface forces.

REFERENCES

1. B.V.Deryagin and S.S.Dukhin, Izv.Akad.Nauk SSSR, Otd.Tekh.Nauk, Metallurgiya i Toplivo, 1959(1), 82.
2. B.V.Derjaguin and S.S.Dukhin, Trans.Inst.Min. and Metall., 1960, 70, Part 5, 221.

3. B.V.Deryagin, S.S.Dukhin, and V.A.Lisichenko, Zhur.Fiz.Khim., 1959, **33**, 2280 [Russ.J.Phys.Chem., 1959(10)].
4. B.V.Deryagin, S.S.Dukhin, and V.A.Lisichenko, Zhur.Fiz.Khim., 1960, **34**, 524 [Russ.J.Phys.Chem., 1960(3)].
5. S.S.Dukhin, Zhur.Fiz.Khim., 1960, **34**, 1053 [Russ. J.Phys.Chem., 1960(5)].
6. B.V.Deryagin and S.S.Dukhin, Zhur.Fiz.Khim., 1961, **35**, 1247 [Russ.J.Phys.Chem., 1961(6)].
7. B.V.Deryagin and S.S.Dukhin. Zhur.Fiz.Khim., 1961, **35**, 1453 [Russ.J.Phys.Chem., 1961(7)].
8. S.S.Dukhin, Dokl.Akad.Nauk SSSR, 1960, **130**, 1298.
9. B.V.Deryagin and V.D.Samygin, "Sbornik Trudov Gintsvetmeta" (Collected Reports from the State Institute of Non-Ferrous Metals), Metallurgizdat, Moscow, 1962, No.9, p.240.
10. B.V.Derjaguin and S.S.Dukhin, "III Intern.Congr. für grenzflächenaktiv Stoffe im Köln", Mainz, 1960, Vol.2, Sect.B, p.324.
11. B.V.Deryagin, S.S.Dukhin, and N.N.Rulev, Kolloid. Zhur., 1976, **38**, 251.
12. B.V.Deryagin, S.S.Dukhin, N.N.Rulev, and V.P.Semenov, Kolloid.Zhur., 1976, **38**, 258.
13. N.N.Rulev, Kolloid.Zhur., 1978, **40**, 898.
14. N.N.Rulev, Kolloid.Zhur., 1978, **40**, 1202.
15. N.N.Rulev, V.K.Ososkov, and L.D.Skrylev, Kolloid. Zhur., 1977, **39**, 580.
16. N.N.Rulev, V.K.Ososkov, A.N.Purich, and L.D.Skrylev, Kolloid.Zhur., 1978, **40**, 1132.
17. N.N.Rulev, Kolloid.Zhur., 1977, **39**, 80.
18. N.N.Rulev, B.V.Deryagin, and S.S.Dukhin, Kolloid. Zhur., 1977, **39**, 314.
19. S.S.Dukhin and N.N.Rulev, Kolloid.Zhur., 1977, **39**, 270.
20. S.S.Dukhin, N.N.Rulev, and V.P.Semenov, Kolloid. Zhur., 1969, **41**, 263.
21. S.S.Dukhin, Abh.Wiss.DDR, 1976(1), 561.
22. B.V.Deryagin, S.S.Dukhin, and N.N.Rulev, Kolloid. Zhur., 1977, **39**, 1051.
23. A.Sheludko, B.V.Tochev, and D.T.Bojadjiev, J.Chem.Soc., Faraday Trans.I, 1976, **72**, 2845.
24. R.W.Huddleston and A.L.Smith, Intern.Conf. Organized by the Society of Chemical Industry, Brunel University Preprint, 1975, p.147.
25. B.V.Derjaguin, Kolloid.Zhur., 1934, **69**, 155.
26. B.V.Deryagin, Kolloid.Zhur., 1954, **16**, 425.
27. B.V.Deryagin, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 1153.
28. B.V.Deryagin and N.I.Kusakov, Izv.Akad.Nauk SSSR, Ser.Khim., 1937, 1119.
29. B.V.Deryagin and L.D.Landau, Zhur.Eksper. Teor.Fiz., 1945, **15**, 663.
30. E.L.Verwey and J.T.Overbeek, "Theory of Stability of Lyophobic Colloids", Amsterdam, 1948.
31. A.N.Frumkin and A.V.Gorodetskaji, Acta Phys.-Chem., URSS, 1938, **9**, 327.
32. I.Langmuir, Science, 1938, **88**, 430.
33. B.V.Deryagin and N.D.Shukakidze, Dokl.Akad.Nauk SSSR, 1960, **134**, 376.
34. A.S.Joy and A.I.Robinson, Recent Progress in Surface Science, 1964, **2**, 169.
35. S.Usui, Progress in Surface and Membrane Science, 1972, **5**, 233.
36. S.R.Rao, Minerals Sci.Engng, 1974, **6**, 45.
37. M.J.Jaycock and R.H.Ottewill, Trans.Inst.Min. Metall., 1963, **72**, 497.
38. A.J.Rubin and S.C.Lackey, J.Amer.Water Works Assoc., 1968, **10**, 1156.
39. D.G.Devivo and B.L.Kargen, Sep.Sci., 1970, **5**, 145.
40. C.L.Collins and G.L.Jameson, Chem.Eng.Sci., 1977, **32**, 239.
41. B.V.Derjaguin and N.V.Churaev, Croat.Chem.Acta, 1977, **50**, 187.
42. B.V.Derjaguin and N.V.Churaev, J.Colloid Interface Sci., 1974, **49**, 249.
43. B.V.Derjaguin, Chem.Scripta, 1976, **9**, 97.
44. J.Laskowski and J.Kitchener, J.Colloid Interface Sci., 1969, **29**, 670.
45. N.F.Dibbs, L.L.Sireis, and R.Bredin, Research Rep., Department of Energy, Mine and Resources, Ottawa, 1972, R.248, 145.
46. H.J.Schulze and C.Cichos, Z.phys.Chem., 1972, **251**, 252.
47. H.J.Schulze and C.Cichos, "Miteilung aus Forschungsinstitut für Aufberetung", Freiberg, 1972, p.7.
48. A.Bleier, E.D.Goddard, and R.D.Kulkarni, J.Colloid Interface Sci., 1977, **599**, 490.
49. I.Langmuir and K.Blodgett, "Investigation of Water Droplet Trajectories", Gen.El.Comp.Rep., July, 1945.
50. L.I.Levin, "Issledovaniya po Fizike Grubodispersnykh Aerozolei" (Studies of the Physics of Coarsely Disperse Aerosols), Izd.Akad.Nauk SSSR, Moscow, 1961, p.267.
51. H.Herne, in "Aerodynamic Capture of Particles" (Edited by E.I.Richardson), Pergamon Press, London, 1960, p.26.
52. V.D.Samygin, B.S.Chertilin, and V.P.Nebera, Kolloid.Zhur., 1977, **39**, 1101.
53. K.L.Sutherland, J.Phys.Chem., 1948, **52**, 394.
54. S.Okazaki, Bull.Chem.Soc.Japan, 1964, **37**, 144.
55. D.Reay and G.A.Ratcliff, Canad.J.Chem.Eng., 1973, **51**, 178.
56. S.L.Goren and M.E.O'Neill, Chem.Eng.Sci., 1971, **25**, 325.
57. B.V.Deryagin and E.M.Zorin, Zhur.Fiz.Khim., 1955, **29**, 1755.
58. I.V.Churaev, Symposium, "Issledovaniya v Oblasti Poverkhnostnykh Sil i Tonkikh Plenok" (Studies on Surface Forces and Thin Films) (Edited by B.V.Deryagin), Izd.Nauka, Moscow, 1974, p.81.
59. J.Mahanty and B.V.Ninham, "Dispersion Forces", Acad.Press, London–New York–San-Francisco, 1976.
60. B.V.Deryagin, N.N.Rulev, and S.S.Dukhin, Kolloid.Zhur., 1977, **39**, 680.
61. J.F.Anfruns and J.A.A.M.Kitchener, Gaudin Memorial Volume 2 (Edited by M.G.Furstenau), Amer.Inst.Chem.Eng., New York, 1976.
62. A.E.Hamielec and A.I.Jonson, Canad.J.Chem.Eng., 1962, **40**, 41.
63. A.E.Hamielec, S.H.Storey, and J.M.Whitenead, Canad.J.Chem.Eng., 1963, **41**, 246.
64. L.R.Flint and V.T.Howarth, Chem.Eng.Sci., 1971, **26**, 1155.
65. D.Reay and G.A.Ratcliff, Canad.J.Chem.Eng., 1975, **53**, 481.
66. B.V.Deryagin and N.M.Kudryavtseva, Kolloid.Zhur., 1964, **26**, 61.
67. J.T.G.Overbeek, J.Colloid Interface Sci., 1977, **58**, 408.
68. G.A.Martynov and V.M.Muller, Symposium, "Poverkhnostnye Sily v Tonkikh Plenkakh i Dispersnykh Sistemakh" (Surface Forces in Thin Films and Disperse Systems) (Edited by B.V.Deryagin), Izd.Nauka, Moscow, 1972, p.7.

69. A.N.Frumkin and V.G.Levich, Zhur.Fiz.Khim., 1947, **21**, 1183.
70. R.M.Grifith, Chem.Eng.Sci., 1962, **17**, 1057.
71. S.S.Dukhin, Doctoral Thesis in Chemical Sciences, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow, 1965.
72. S.S.Dukhin and M.V.Buikov, Zhur.Fiz.Khim., 1965, **39**, 913 [Russ.J.Phys.Chem., 1965(4)].
73. J.E.B.Randles, Phys.Chem.Liquids, 2(1–2), 107.
74. J.Lopis, in "Modern Aspects of Electrochemistry" (Edited by J.O'M.Bockris and B.E.Conway), Plenum Press, New York, 1971, Vol.6, p.91.
75. S.Okazaki, Kolloid Z.–Z.Polymere, 1962, **185**, 154.
76. D.Ekserova and M.Zakharieva, Symposium, "Poverkhnostnye Sily v Tonkikh Plenkakh i Dispersnykh Sistemakh" (Surface Forces in Thin Films and Disperse Systems) (Edited by B.V.Deryagin), Izd.Nauka, Moscow, 1972, p.234.
77. S.S.Dukhin, Symposium, "Issledovaniya v Oblasti Poverkhnostnykh Sil" (Studies on Surface Forces) (Edited by B.V.Deryagin), Izd.Nauka, Moscow, 1964, p.47.
78. S.S.Dukhin and B.V.Deryagin, "Elektroforez" (Electrophoresis), Izd.Nauka, Moscow, 1976.
79. S.S.Dukhin and B.V.Deryagin, Kolloid.Zhur., 1958, **20**, 705.
80. S.S.Dukhin, Zhur.Fiz.Khim., 1960, **34**, 1053 [Russ.J. Phys.Chem., 1960(5)].
81. S.S.Dukhin, Symposium, "Issledovaniya v Oblasti Poverkhnostnykh Sil" (Studies on Surface Forces) (Edited by B.V.Deryagin), Izd.Akad.Nauk SSSR, Moscow, 1961, p.738.
82. B.V.Deryagin, S.S.Dukhin, Z.R.Ul'berg, and T.V.Kuznetsova, Kolloid.Zhur., 1980, **42**, 464.
83. B.V.Deryagin, S.S.Dukhin, and A.A.Korotkova, Kolloid.Zhur., 1961, **23**, 409.
84. S.S.Dukhin and M.V.Buikov, Zhur.Fiz.Khim., 1964, **38**, 3011 [Russ.J.Phys.Chem., 1964(12)].
85. S.S.Dukhin, "Materialy II Vsesoyuznoi Konferentsii po Poverkhnostnym Yavleniyam v Zhidkosti" (Proceedings of the IInd All-Union Conference on Surface Phenomena in Liquids), Leningrad, 1978, p.56.
86. S.S.Dukhin, "Trudy VII Mezhdunarodnogo Kongressa po PAV" (Proceedings of the VIIth International Congress on Surfactants), Moscow, 1978, No.2, p.1144.
87. L.E.Ewans and W.E.Ewers, in "Recent Developments in Mineral Dressing", Inst.Min.and Metal., London, 1953, p.457.
88. L.F.Evans, Ind.Eng.Chem., 1954, **46**, 420.
89. S.S.Dukhin, Kolloid.Zhur., 1961, **33**, 408.
90. K.F.Beloglazov, "Osnovnye Zakonomernosti Flotatsionnogo Protsessa. Zapiski Leningradskogo Gornogo Instituta" (Fundamentals of the Flotation Process. Bulletin of the Leningrad Mining Institute), Metallurgizdat, Moscow, 1956.
91. H.Brenner, Chem.Eng.Sci., 1961, **16**, 242.
92. M.Stimson and G.B.Jeffery, Proc.Roy.Soc., 1926, **A110**, 1117 [sic].
93. E.Ruckenstein and D.C.Prieve, J.Chem.Soc., Faraday Trans.II, 1973, **69**, 1522.
94. L.A.Spielman and S.K.Friedlander, J.Colloid Interface Sci., 1974, **46**, 22.
95. N.N.Rulev, Kolloid.Zhur., 1979, **41**, 527.
96. B.V.Deryagin, M.A.Pavlikhina, and L.P.Smirnov, Kolloid.Zhur., 1972, **34**, 782.
97. N.N.Rulev, E.S.Leshchov, and V.D.Nazarov, Khim. i Tekhnol.Vody, 1980, **2**, 395.
98. J.F.Anfruns and J.A.Kitchener, Trans.Inst.Mining Metal., 1977, **86**(3), 9.
99. S.S.Dukhin, in "Sovremennaya Teoriya Kapillyarnosti" (The Modern Theory of Capillarity) (Edited by A.I.Rusanov), Izd.Khimiya, Leningrad, 1980.

Institute of Physical Chemistry,
USSR Academy of Sciences, Moscow

Institute of Colloid Chemistry and the Chemistry of Water,
Academy of Sciences of Ukrainian SSR,
Kiev