Structure of the nanobubble clusters of dissolved air in liquid media

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Abstract A qualitative model of the nucleation of stable bubbles in water at room temperature is suggested. This model is completely based on the property of the affinity of water at the nanometer scale; it is shown that under certain conditions the extent of disorder in a liquid starts growing, which results in a spontaneous decrease of the local density of the liquid and in the formation of nanometer-sized voids. These voids can serve as nuclei for the following generation of the so-called bubstons (the abbreviation for *bubbles, stabilized by ions*). The model of charging the bubstons by the ions, which are capable of adsorption, and the screening by a cloud of counter-ions, which are incapable of adsorption, is analyzed. It was shown that, subject to the charge of bubston, two regimes of such screening can be realized. At low charge of bubston the screening is described in the framework of the known linearized Debye–Huckel approach, when the sign of the counterion cloud preserves its sign everywhere in the liquid surrounding the bubston, whereas at large charge this sign is changed at some distance from the bubston surface. This effect provides the mechanism of the emergence of two types of compound particles having the opposite polarity, which leads to the aggregation of such compound particles by a ballistic kinetics.

Keywords Nanobubbles · Structure of aqueous media · Breathing of marine organisms

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1 Statement of the problem. Introduction

The present study is devoted to the problem of spontaneous nucleation of quasi-stable phase of dissolved gas nanobubbles in an equilibrium liquid, which is kept under normal conditions, i.e., at room temperature and atmospheric pressure. It will be shown that these nanobubbles are capable of coagulation with one another with the formation of clusters composed of such nanobubbles. The given problem arises, for instance, in the interpretation of the ultrasonic cavitation phenomenon. Actually, if we focus an ultrasonic wave of high enough intensity in a liquid, we can see in the focal volume of an ultrasonic lens a track of vapor-gas bubbles. This phenomenon is termed cavitation and is widely explored by specialists in the field of underwater acoustics, as the cavity effect plays a key roles in the destruction process of ship screw propellers. Furthermore, as follows from the model that we elaborated in this work, the higher the content of ions, the greater the density of bubston clusters. This fact has significance for the biological sciences. Indeed, there exists a problem of how marine organisms, for example, fish breathe. It is possible to imagine that in respiration process the extraction of oxygen molecules, dissolved in water, from the grid of hydrogen bonds is executed. However, this process obviously is slow and also requires considerable expenditures of energy. Let us assume, that fish breathe oxygen, stored in the free state inside nanobubbles and their clusters. We can see, however, that remarkable concentrations of such clusters are achieved only if a salt is present in the water. It is well known that decorative aquarium fish perish in deionized and distilled water; that is why, for aquarium water, a special mineralization is needed. Thus, the bubston clusters can perform the function of the agent supplying oxygen in the free state to the gills of an aquatic organism.

Consider now the physical premises for the existence of long-living bubbles in liquids that are free of solid micro inclusions. The rupture strength of a liquid can be expressed by the known formula $\sigma n_l^{1/3} \sim 10^4$ atmospheres, where σ is the coefficient of the surface tension of a liquid, n_l is the bulk density of molecules of a liquid (all numerical estimates will be hereinafter made for water). At the same time, experimental data on cavitation indicate that it can be induced already at the amplitudes of a sound wave of about 1 atmosphere. It follows from here that long-lived (quasi-stable) centers of cavitation must be present in the liquid for the cavitation effect to occur. The steady gas bubbles at the micron scale are evidently related to such centers. We mean here the micron-sized bubbles, since the bubbles of smaller size are squeezed by the surface tension forces and disappear, whereas larger bubbles (whose size achieves 1 mm) promptly float up.

The mechanical equilibrium condition for the micron-sized bubble is given by the known Young–Laplace equation:

$$P_{in} = P_{atm} + \frac{2\sigma}{R} > P_{atm}, \quad (1)$$

where R is the radius of a bubble, P_{in} is the pressure of gas inside a bubble, P_{atm} is the pressure of atmospheric gas above a surface of a liquid, i.e., the atmospheric pressure. Let us note that in the formula (1) we did not take into account the hydrostatic pressure associated with the weight of the bulk of liquid above the bubble: we can obviously do it, since all experiments on a cavitation are carried out, as a rule, under the laboratory conditions, i.e., when the hydrostatic pressure is much less than the atmospheric pressure. The formula (1) implicates that the pressure of gas inside the micron-sized bubble is always higher, than the

pressure of the same gas above the liquid surface. Thus, the solution of the gas in the liquid, whose content, according to the Henry law, is dictated by the pressure P_{atm} , appears to be unsaturated with respect to the pressure P_{in} of the same gas inside the bubble. It follows from here that such a bubble is diffusively non-stable: the gas escapes from such a bubble by diffusion kinetics, and such a bubble eventually disappears. This fact was analyzed (probably for the first time) in Ref. [1]. As was shown in this study, if we deal with a bubble with the initial radius of 10^{-3} cm, located in water saturated with dissolved air, the lifetime of that bubble does not exceed 10 s. This time drastically falls upon decreasing the radius of the bubble. For example, if the bubble radius is about 100 nm, the lifetime of such a bubble in a wide range of temperatures does not exceed 10 μ s; see, for example, [2]. Hence, to observe regularly the cavitation effect, we should require the forces of the surface tension to be somehow neutralized.

One of the mechanisms of such neutralization can be associated with externally introduced solid impurities, i.e., bubbles arise at solid (possibly hydrophobic) micro-particles suspended in the liquid. The wetting angle changes along the rough and non-planar (in general) surface of a hydrophobic particle, and the formation of a dissolved gas bubble at the solid–liquid interface becomes energetically favorable. This is why for the gas bubbles, attached to a solid interface, the surface tension forces appear to be balanced and such bubbles become stabilized both mechanically and diffusively. The model where the stable heterogeneous centers of a cavitation arise due to the presence of solid impurities, is widely accepted, see, e.g., [3–6]. It is necessary to note, however, that even a fine filtration of a liquid and removing the solid impurities cannot completely suppress the cavitation effect. At the same time, it is well known (see, e.g., [7]) that the cavitation ability in aqueous media increases upon adding various salts, albeit new solid particles are definitely not introduced into the water together with a salt. Thus, it should be recognized that the above-considered mechanism of micro-bubbles stabilization is inconsistent.

The study presented below is devoted to theoretical description of an alternative (not associated with the solid impurities) model of the origin and stabilization of micro-bubbles in water and aqueous solutions of salts. The liquids are considered to be in the equilibrium state under normal conditions and saturated by dissolved gas (for example, atmospheric air). The suggested mechanism of stabilization is stipulated by a selective adsorption of ions of the same sign on a bubble interface. It is necessary at once to note that the adsorbed ions (here we speak about the ions of inorganic salts) can result in a slight growth of the magnitude of the surface tension coefficient (see, e.g., the tables [8] and also the studies on this topic [9, 10]), which should be taken into account at numeric estimations. Such bubble was termed as *bubston* (abbreviation of *bubble, stabilized by ions*). The bubston model was first put forward in the study [11], and then was developed in subsequent works [12, 13].

The following formula gives the condition for the bubston mechanical stability:

$$P_{in} + P_e = P_{atm} + 2\sigma/R. \quad (2)$$

Here $P_e = -\left(\frac{\partial \Phi_e}{\partial V}\right)_T$ is the ponderomotive pressure, caused by the presence of charge Q_0 at the spherical bubston interface, and Φ_e is the energy of electrostatic field of the system in question. This expression follows from the general definition of pressure $P = -(\partial \Phi / \partial V)_T$, where Φ is the free energy of the system. In our case, the system is a region of the medium with a radius $r \geq R$, where the electric field is non-zero (the field inside the bubston is equal to zero because of the spherical symmetry). For this reason, energy

$\Phi_e = \frac{1}{2\varepsilon} \int_R^r [\mathcal{Q}^2(x)/x^2] dx$, and the volume $V = \frac{4\pi}{3} (r^3 - R^3)$. The pressure exerted by a bubble on the system (i.e., for $r = R$) is

$$P_e(R) = -\frac{1}{4\pi R^2} \frac{\partial \Phi_e}{\partial R} = -\frac{1}{8\pi\varepsilon} \frac{\mathcal{Q}^2(R)}{R^4} = -\frac{1}{8\pi\varepsilon} \frac{\mathcal{Q}_0^2}{R^4}, \quad P_e(R) = \frac{2\sigma}{R}. \quad (3)$$

This pressure is due to the attractive forces of ions of the opposite sign localized in the volume of a liquid. It is clear that the pressure P_e stretches the bubble and equilibrates the squeezing surface tension forces at the certain radius R . Formula (3) implies that the pressure exerted on the outer surface of the region of radius r is $P(r) = -(1/4\pi r^2)(\partial \Phi_e/\partial r) = (1/8\pi\varepsilon)\mathcal{Q}^2(r)/r^4$, i.e., the magnitude of the pressure falls at growing r . As was already noted, for calculating the value of R it is necessary to know the real magnitude of the surface tension coefficient σ with making allowance for the presence of adsorbed ions, which results in a slight growth of σ . Additionally, we should know the value of $\mathcal{Q}_0$ at the bubble interface. The approach for calculating the charge $\mathcal{Q}_0$ will be described below. Refs. [14–20] contain a direct experimental proof of the bubston existence in an equilibrium aqueous solution of salts, saturated by dissolved air. However, key evidence supporting this hypothesis was inferred from observations of low-threshold laser-induced breakdown in water and aqueous electrolytic solutions that were transparent to the laser beams employed [21–26]. Laser-induced breakdown results from development of electron avalanches inside separate bubstons followed by cluster coalescence into a large bubble (usually called *cavitation bubble*).

The structure of this work is the following. In the second chapter, we analyze the mechanisms of the bubston nucleation in the equilibrium aqueous solution of an electrolyte, and the third chapter is devoted to the mechanisms of bubston coagulation, leading to the formation of bubston clusters. It is well to say that the bubstons and bubston clusters should play an important role in the living biological processes. In our opinion, the breathing of marine organisms (for instance, fish) is performed with the help of bubston clusters. Indeed, as is widely known, for the breeding of fish under the artificial conditions (as related, for example, to aquarium fish) a certain level of mineralization of the aquarium water is required, since the fish perish in the distilled (ion-free) water. If we assume that at breathing the extraction of molecules of the dissolved oxygen out of the hydrogen bonds network occurs, we should reckon that the additional mineralization is not necessary. At the same time, the process of extraction is energy and time consuming. Assuming that at breathing the fish captures the bubston clusters by gills, the certain problem associated with the extraction of molecules of dissolved oxygen disappears. However, as was shown in our recent experimental work [18], for the bubstons and bubston clusters to exist in water the increased content of ions is necessary. Besides, in the same work it was shown that the bubston clusters play a negative role in living tissues at a sharp decrease of arterial pressure. As follows from our results, the bubston clusters are nucleated at the erythrocyte membranes at a steep reduction of pressure that essentially worsens mechanic and elastic properties of the erythrocytes. The erythrocytes, whose membranes bear the bubston clusters, cannot take part in the gas exchange processes that can be one of reasons of the caisson disease.

Prior to concluding this section, it is worth saying that for a long time the question of the adsorption of ions at the gas–liquid interface was not discussed in literature. It was coupled to the fact that, as was demonstrated in the studies [9, 10], such adsorption should result in growth of the surface tension coefficient σ , which obviously means an increase of a surface energy, i.e., such adsorption is energetically unfavorable. Note that these works have been carried out on the basis of the mean field approach, and the

liquid was considered as a continuum characterized only by its macroscopic parameters (the surface tension coefficient σ , the dielectric permittivity ε etc.), i.e., the specific local properties of the liquid were by no means taken into account; here we speak about the dipole moments and polarizabilities of molecules, and their sizes. The subsequent numerous theoretical works allowed for the geometrical characteristics of water molecule [27], numerical MD simulation in the view of the effect of polarization of water molecules [28–38], and also series of experimental results including vibrational sum frequency generation spectroscopy [39–44], second harmonic generation spectroscopy [45, 46], high-pressure VUV photoelectron spectroscopy [47, 48], and X-ray photoelectron spectroscopy combined with scanning electron microscopy [49, 50] allow us to make a conclusion about an opportunity of adsorption of some anions, for example, Cl^- , I^- and Br^- on the water–gas interface. The fact that basically negative ions are capable of adsorption at this interface is also supported by the data obtained in Ref. [51], where the negative density of the charge on the surface of the gas bubble in pure water was directly measured: at pH = 6.9 its value is $\alpha = -18 \cdot 10^{-6} \text{ C/m}^2$.

2 The mechanism of nucleation of bubstons

This approach is essentially based on the model of nanometer-scaled water as a quasi-crystal ice-like medium, where the hydrogen bonds are present. Such a model was apparently first put forward in literature in the known study [52] and then was developed in the works [53–61]. Within the framework of this approach it is possible to explain many anomalies of liquid water (it is possible to find details on the website [62]). The considered model is based on the assumption that water is generally a disordered crystal. Let us note, however, that the statistical description of the disordered structures still remains poorly developed. Another (probably, more traditional) approach for describing a structure of liquids is based upon the consideration of pair correlation functions in the statistical mechanics, where the zero approximation is the equation of state of an ideal gas, see, e.g., [63]; in this model the solutions obtained are essentially dependent upon the potential of inter-molecular interaction. On the contrary, in the framework of the approach suggested below it is implied that the zero approximation corresponds to an ideal crystal. For the amorphous structures, we cannot indicate any coordination spheres; it is possible only to specify the coordination peaks in the pair distribution function. Thus, it is necessary to develop a new technique for describing a structure, which is crystal-like in a particular case, and is amorphous in others cases. The ordered structure can be preset by the geometry of bonds in an elementary cell; the crystal-like structure formation can be modeled by the series of translations and spatial turns of the elementary cell. In our case, the icosahedral structure of water matrix is generated by the combinations of translations and spatial turns of the elementary tetrahedrons of water molecules [64].

Let us study the transition from the ordered state to the disordered state by considering an example of a one-dimensional chain of atoms, and then generalize the results to a more common case. In case of the disordered lattice it is necessary to set the density of probability for the distance between two nearest lattice points, which will be termed as s -function. According to the definition, the s -function is normalized to unity,

$$\int_{-\infty}^{\infty} s(r) dr = 1, \quad (4)$$

is positively defined, $s(r) \geq 0$, and in extreme case of ideal crystal it should transform into the Dirac delta-function $\delta(r - a)$, where a is the distance between two lattice points in the ordered structure. Besides, the condition $s(r) = 0$ at $r \leq 0$ should be met. Thus the complete density of probability for localization of an atom in the given point is expressed by the sum:

$$p(r) = \sum_n p_n(r),$$

where $p_n(r)$ is the density of probability for the atom, related to n -th coordination peak, to be located in a point with the coordinate r . The density of probability of finding an atom in the first coordination peak is s -function, i.e.,

$$p_1(r) = s(r).$$

The considered structure has the property of affinity: the ratio of the second atom coordinate to the first atom coordinate is the same as for the third and the second atoms and so on. The one-dimensional chain of atoms is constructed by consecutive shifts of an initial cell in the positive direction of r . Therefore, all $p_n(r)$ -functions can be calculated in the recurring way, i.e., by using only s -function

$$p_{n+1}(r) = \int p_n(z)s(r - z)dz.$$

It is straightforward to verify that all functions of $p_n(r)$ are normalized.

Let us illustrate this approach by using an example of s -function of the Gaussian type:

$$s(r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(r - a)^2}{2\sigma^2}\right], \quad (5)$$

where a is the average distance between the nearest neighbouring atoms and has the sense of the lattice constant, σ is the dispersion, characterizing the scatter of distances between the neighbouring atoms. After integrating over the interval $r \in (-\infty, +\infty)$ we arrive at

$$p_n(r) = \frac{1}{\sigma\sqrt{2n\pi}} \exp\left[-\frac{(r - na)^2}{2n\sigma^2}\right].$$

Figure 1 illustrates the functions $p(r)$ calculated for the cases of $\sigma/a = 0.2, 0.3$. At $\sigma \rightarrow 0$ the function $p(r)$ transforms to a set of the Dirac delta-functions in the points $r = na$.

Fig. 1 The function of density of the probability for the distances between two atoms at: (1) $\sigma/a = 0.15$; (2) $\sigma/a = 0.3$

In the case where the degree of disorder is low, it is possible to distinguish the coordination peaks, but at higher degree of disorder we can see only a pronounced but essentially diffuse first peak. As expected, the transition to the disordered state is accompanied by washing out the far coordination peaks, i.e., the long-range ordering disappears.

The described way of using s -function is based on the assumption of affinity of the structure, and can be generalized to the case of three-dimensional spatial disordered structure. Let us introduce three-dimensional s -function, with the help of which the considered above pair distribution function $p(r)$ can be represented as

$$p(\mathbf{r}) = \sum_{\alpha} p_{\alpha}(\mathbf{r}), \quad (6)$$

where $p_{\alpha}(\mathbf{r})$ is the probability density of finding in the point with the radius-vector $\mathbf{r}$ the particle of the lattice node α . By definition, s -function is the probability density for some chosen lattice point of the first coordination peak to be located in the point with the radius-vector $\mathbf{r}$, i.e.

$$p_1(\mathbf{r}) = s(\mathbf{r}).$$

The normalizing condition here is the following:

$$\int s(\mathbf{r}) d\mathbf{r} = 1,$$

where $d\mathbf{r} = dr_x dr_y dr_z$ is an element of volume. It is necessary to note that, as earlier, the spatial s -function is positively defined ($s(\mathbf{r}) \geq 0$), is equal to zero in the point of origin ($s(0) = 0$), and for the ordered structure it should approach the Dirac delta-function of vector argument:

$$s(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{a}),$$

where $\mathbf{a}$ is the radius-vector of the location of the lattice point in the ordered structure.

A simple routine for calculating any function for n -th coordination peak may be formulated from here: it is necessary to choose a node α in the ordered lattice, then to construct a graph with the minimum number of steps $1, 2, \dots, n-1$ that leads to the lattice point α . After that the function $p_{\alpha}(\mathbf{r})$ can be found as the $n-1$ -multiple integral

$$p_{\alpha}(\mathbf{r}) = \int \dots \int s_{0,1}(\mathbf{r}_1) s_{1,2}(\mathbf{r}_2 - \mathbf{r}_1) \dots s_{n-1,n}(\mathbf{r} - \mathbf{r}_{n-1}) d\mathbf{r}_1 \dots d\mathbf{r}_{n-1}. \quad (7)$$

Thus the function $s_{k-1,k}(\mathbf{r})$ describes the density of probability for a k -th lattice point to be located in the point $\mathbf{r}$ at the movement from the $k-1$ -th lattice, and is connected with the function $s(\mathbf{r})$ by the relationship

$$s_{k-1,k}(\mathbf{r}) = s(T\mathbf{r}),$$

where T is the operator of turn, which transforms the bond-vector $(k-1, k)$ (connecting the vector from a node $k-1$ to a node k) to the bond-vector, for which the s -function was introduced. For the spatial structures, the process of calculating the $p_{\alpha}(\mathbf{r})$ function by using the algorithm (7) can be presented in more direct kind (see Fig. 2).

The $p_{\alpha}(\mathbf{r})$ function is calculated through integrating the products of $s_{k-1,k}$ -functions over all intermediate coordinates $\mathbf{r}_1 \dots \mathbf{r}_{n-1}$ for subsequent lattice points $1, 2, \dots, n-1$. According to Fig. 2, the initial s -function is preset for the point A , and therefore, the operator of turn for each $(n-1, n)$ transition transforms the direction of the bond-vector $(n-1, n)$ to the

Fig. 2 The schematic picture explaining the procedure for calculating the $p_r(\mathbf{r})$ function

radius-vector $\mathbf{a}$. The function of radial distribution of the lattice points can be found by integrating the $p(\mathbf{r})$ function in spherical coordinates over all directions:

$$p(r) = \iiint p(\mathbf{r}) r^2 \sin \varphi d\varphi d\theta. \quad (8)$$

This function does not depend any more on a specific direction in space. Thus, the calculation of the probability density for pair distribution function, according to (7) and (8), is reduced to setting some function, whose form should be chosen from the criterion of the best conformity to experimental data.

We can see that the s -function allows us to describe the molecular structure of any liquid at the nanometer scale. Let us now investigate the mechanic and elastic properties of a liquid at increasing the degree of disorder. First of all, we assume that such properties can be completely described by the parameter, related to the degree of disorder of the system. When choosing a concrete form of the disorder parameter, let us use the s -function given by (5). Namely, denoting such dimensionless parameter as $\eta \equiv \sigma/a$, we suppose that $\eta \neq 0$ in the disordered state, while $\eta \equiv 0$ in the ordered state. The phenomenological theory reported below does not allow us to speak generally about the peculiarities of evolution of strongly disordered structures, for which η is not small. The initial symmetry of the ordered structure is broken in the disordered state, and therefore, the corresponding considerations should be based on the statistical description, since we deal with an average statistical cell instead of a crystal cell. As follows from the above analysis, the parameter η is connected with the statistics of distribution of interatomic bonds. Let us note that we consider slow (in comparison with the sound velocity) transformations of isotropic disordered structures. It is thus possible to assume that the evolution of the disordered structures is the quasi-equilibrium process, whose kinetics is defined only by evolution of the parameter η . Let us consider that at small deformations the expansion in series of the bulk density of the free energy of isotropic disordered structure is given by the formula [64, 65]

$$F = A(\eta) - B(\eta) u_{ll} + \frac{1}{2} C(\eta) u_{ll}^2 + D(\eta) \left(u_{jk} - \frac{1}{3} u_{ll} \delta_{jk} \right)^2, \quad (9)$$

where $A(\eta)$, $B(\eta)$, $C(\eta)$, $D(\eta)$ are some coefficients, u_{jk} is the deformation tensor, which is defined by the displacements u_j of the points of structure as

$$u_{jk} = \frac{1}{2} (\nabla_k u_j + \nabla_j u_k), \quad \nabla_k = \partial / \partial x_k,$$

here the summation over the repeating indices is implied.

In the absence of deformations we have $u_{jj} = 0$, and the free energy is expressed as $F = A(\eta)$, i.e., $A(\eta)$ is the bulk density of energy, which is required to form the structure having the degree of disorder η . In the absence of the transitions to the disordered state, i.e., when $\eta = 0$ the (9) should coincide with the known expression for the bulk density of the free energy related to elastically deformed isotropic homogeneous body. It follows from here that $C(\eta) = K(\eta)$ is the compression modulus, and $D(\eta) = \mu(\eta)$ is the shear modulus.

The coefficient $B(\eta)$ in (9) is associated with expansion or compression accompanied the transition to the disordered state:

$$B(\eta) = \alpha \eta K, \quad \alpha(\eta) = \frac{1}{V} \frac{\partial V}{\partial \eta},$$

where α is the amorphous expansion coefficient.

Under the conditions of quasi-static mechanical equilibrium we arrive at

$$\nabla_j \left(\left(K - \frac{2}{3} \mu \right) \nabla_l u_l \right) + \nabla_k \left(\mu \left(\nabla_k u_j + \nabla_j u_k \right) \right) = \beta \nabla_j \eta, \quad (10)$$

where we introduce the function $\beta(\eta) = \frac{dB}{d\eta}$.

Equation 10 should be supplemented with the equation of the evolution of the parameter η . Let us assume that the kinetics of changing the disorder parameter η obeys the Landau–Khalatnikov equation [66]:

$$\frac{\partial \eta}{\partial t} = -\gamma \frac{\partial F}{\partial \eta}, \quad (11)$$

where $\gamma > 0$ is the generalized “viscosity”, controlling the kinetics of the parameter η , while the sign “−” in the right-hand side of this equation means that the system tends to achieve the minimum of the free energy. Substituting (9) in (11) with making allowance for the connection of the coefficients A , B , C , D with the properties of the disordered structure gives the equation for the parameter η evolution:

$$\frac{\partial \eta}{\partial t} = -\gamma \left[\lambda - \beta u_{ll} + \frac{1}{2} K_\eta u_{ll}^2 + \mu_\eta \left(u_{jk} - \frac{1}{3} u_{ll} \delta_{jk} \right)^2 \right], \quad (12)$$

where $\lambda(\eta) = \frac{dA}{d\eta}$, $K_\eta = \frac{dK}{d\eta}$, $\mu_\eta = \frac{d\mu}{d\eta}$. Formulas 10 and 12 together with the initial conditions define the model of evolution of the isotropic disordered structure. In the case where the shear deformations can be ignored (this is the case for liquids, for which $\mu \ll K$), the system of the equations (10) and (12) can be expressed as

$$\begin{cases} \nabla_j (K \nabla_k u_k) = \beta \nabla_j \eta, \\ \frac{\partial \eta}{\partial t} = -\gamma \left(\lambda - \beta \nabla_k u_k + \frac{1}{2} K_\eta (\nabla_k u_k)^2 \right). \end{cases} \quad (13)$$

The first equation of this system has the solution in the form

$$\nabla_k u_k = \frac{1}{K} (B + p(t)), \quad (14)$$

where $p(t)$ is the function of time, which stands for the pressure in a liquid. With regards to (14), the system of the equations (13) can be reduced only to the equation for the parameter η evolution:

$$\frac{\partial \eta}{\partial t} = -\gamma \left[\lambda - \frac{\beta (B + p(t))}{K} + \frac{1}{2} \frac{K_\eta}{K^2} (B + p(t))^2 \right]. \quad (15)$$

To solve this equation, it is necessary to know the explicit dependences of $B(\eta)$, $K(\eta)$, $\lambda(\eta)$. However, in some cases we can establish the form of such dependences from the general assumptions. For instance, close to the ordered state (i.e., at $\eta \ll 1$) the dependences $\lambda(\eta)$, $K(\eta)$, $\alpha(\eta)$ can be expanded in series over the parameter η :

$$\begin{aligned} \lambda(\eta) &= \lambda_0 + \lambda_1 \eta + \lambda_2 \eta^2 + \dots, & K(\eta) &= K_0 + K_1 \eta + K_2 \eta^2 + \dots, \\ \alpha(\eta) &= \alpha_0 + \alpha_1 \eta + \alpha_2 \eta^2 + \dots \end{aligned}$$

Substituting these expansions to the right-hand side of (15) and implying $p(t) \equiv 0$, we arrive at

$$\begin{aligned} \dot{\eta} &= -\gamma (\lambda_0 + a_1 \eta + a_2 \eta^2 + a_3 \eta^3), \\ a_1 &= \lambda_1 - \alpha_0^2 K_0, \quad a_2 = \lambda_2 - 3K_0 \alpha_0 \alpha_1 - \frac{3}{2} \alpha_0^2 K_1 \\ a_3 &= \lambda_3 - 4\alpha_0 \alpha_1 K_1 - 4\alpha_0 \alpha_2 K_0 - 2\alpha_1^2 K_0 - 2\alpha_0^2 K_2 \end{aligned} \quad (16)$$

Let us assume that the ordered state is steady (in this case $\lambda_0 = 0$), and the transition to the disordered state is always accompanied by the expansion of the structure, i.e., $\alpha_0 = 0$. In this situation (16) has the form

$$\dot{\eta} = -\gamma \eta (\lambda_1 + \lambda_2 \eta - (2\alpha_1^2 K_0 - \lambda_3) \eta^2).$$

Factorization of the right-hand side of this formula gives

$$\frac{d\eta}{d\tau} = \eta (\eta - \eta_1) (\eta - \eta_2), \quad (17)$$

where $\tau = \gamma (2\alpha_1^2 K_0 - \lambda_3) t$ is the dimensionless time, and

$$\eta_{1,2} = \frac{\lambda_2 \pm \sqrt{\lambda_2^2 + 4\lambda_1 (2\alpha_1^2 K_0 - \lambda_3)}}{2 (2\alpha_1^2 K_0 - \lambda_3)}.$$

Integrating (17), we obtain an inverse dependence $\tau(\eta)$

$$\tau(\eta) = \frac{1}{\eta_1 - \eta_2} \left[\frac{1}{\eta_2} \ln \left(\frac{\eta (\eta_0 - \eta_2)}{\eta_0 (\eta - \eta_2)} \right) - \frac{1}{\eta_1} \ln \left(\frac{\eta (\eta_0 - \eta_1)}{\eta_0 (\eta - \eta_1)} \right) \right],$$

where η_0 is the value of the disorder parameter in the initial moment of time.

Figure 3 illustrates the curves $\eta(\tau)$ for the case where $\lambda_2 = 0$ (i.e., $\eta_1 = -\eta_2$) at various initial conditions preset by the parameter η_0 . The parameter η_1 in this case is defined as

$$\eta_1 = \sqrt{\frac{\lambda_1}{2\alpha_1^2 K_0 - \lambda_3}}$$

The found solutions enable us to analyze the process of transition from the ordered to the disordered state. First, assuming that $\eta_1 \ll 1$, the limiting equilibrium states, for which $\dot{\eta} = 0$, appear to be possible. The parameters $\eta_{1,2}$ are defined by the ratio between the heat

Fig. 3 Dependences $\eta(\tau)$ at various initial conditions η_0/η_1 : (1) $\eta_0/\eta_1 = 0.4$; (2) $\eta_0/\eta_1 = 0.7$; (3) $\eta_0/\eta_1 = 0.95$; (4) $\eta_0/\eta_1 = 0.99$; (5) $\eta_0/\eta_1 = 1.0005$; (6) $\eta_0/\eta_1 = 1.005$; (7) $\eta_0/\eta_1 = 1.05$

release at the ordering of the disordered structure (the amorphous condensation) and the energy consumptions, which are necessary for the structure deformation. Generally, various scenarios of evolution of the disordered structure become possible, which depends on the initial conditions for the parameter $\eta(t)$ and the pressure $p(t)$.

As is seen in Fig. 3, at $|\eta_0/\eta_1| < 1$ the developing deformations cannot prevent the amorphous condensation (or the ordering). At $\eta = \eta_{1,2}$ the unsteady equilibrium state of the disordered structure becomes possible. However, even the small perturbations can result in either the amorphous condensation, or growing the disorder. The last can be treated as formation of less dense structures, which develop, eventually turning in a cavity. When the spatial gradients of density become significant, the interface between the high and low density media is formed. Let us remark that the condition of the disorder growth does not depend on symmetry of the parameter η , i.e., supposes the existence of cavities of spherical, cylindrical and other forms, which was obtained earlier in the method of molecular dynamics [67].

The mechanism of the local decrease of liquid density (12), (14) must be taken into consideration at explaining the discrepancy between the volume, which should be occupied by densely packed molecules of a liquid, and its real volume. Indeed, the volume of the water gram-molecule under normal conditions is 18 cm^3 . At the same time, it is generally accepted that radius of the water molecule δ_l is equal to $1.38 \text{ \AA}$ (it is just half of the distance between two nearest neighboring molecules in ice under the atmospheric pressure, see, for example, [53, 62]). Thus, with allowing for the packing factor of spheres we can obtain that the volume, occupied by the Avogadro number of spheres having such radius, is approximately 12.6 cm^3 . Additionally, the suggested mechanism, in our opinion, is the basic one for the homogeneous nucleation of the boiling centers in a liquid at high temperatures. As follows from the analysis presented here, this mechanism is involved at any temperature (probably, even in ice, as the temperature was not explicitly included in this analysis), but results in physically observable phenomenon of homogeneous boiling only at the temperature of superheating; this temperature, obviously, is defined by pressure of ambient gas, the surface tension coefficient, and saturated vapor pressure, (the last two items depend on the temperature of liquid). Note that it would be interesting to investigate the spontaneous growth of the disorder parameter near to the critical point of a liquid, i.e., when the correlation radius of the positions of the liquid molecule grows, and some kinetic coefficients in (12)–(15) may diverge.

This mechanism is also responsible for the bubston nucleation at room temperature; we term the process of local decrease of the liquid density as the early stage of nucleation of the bubstons. We assume that this stage is associated with relative shear movements of the liquid molecular layers on the nanometer scale. It is well to note that a specific type of potential of the interaction between the liquid molecules was not taken into account here. This is why the basic results obtained within the framework of this model are of a general nature, and are free of specific properties of a liquid and its molecular structure. They should remain fair in case of polar liquids, i.e., for the water and aqueous electrolyte solutions, which is the subject of the subsequent sections of the present work.

As was noted above, at high enough gradients of the material density the interface of the cavity is formed. It is clear that after the formation of such cavity the surface tension forces start compressing the void. Assuming that the size of the void is about 1 nm (see above), the time of its collapse is of the order of 10 ps, see Ref. [68]. Thus, the lifetime of such density fluctuations is $\tau > 10$ ps. A question arises of whether such density fluctuations can be revealed in some experiment? In this connection we would like to say that the value of half-width at half of maximal intensity of the non-shifted (i.e., centered at zero frequency) Rayleigh wing scattering peak in water is $\Delta\omega \sim 100 \text{ cm}^{-1}$, see, e.g., [69]; remind that the Rayleigh wing scattering is basically due to the anisotropy fluctuations. Thus the minimal relaxation time of the random processes leading to the Rayleigh wing scattering is $1/\Delta\omega \sim 0.3$ ps. This is why we can conclude that the considered density fluctuations should for certain contribute to the whole variety of random processes, which result in the Rayleigh wing scattering of an optical wave.

Let us now imagine that the fluctuations of the bulk density of ions arise simultaneously with the formation of the voids. Thus we can expect that the boundary of the forming void will appear to be charged, and the ponderomotive pressure arising will keep the void from the immediate collapse due to the mechanism described by (3). It is clear that the intensity of such ionic fluctuation can be estimated, implying, for example, that these fluctuations obey the Poisson distribution. Assuming, for the sake of definiteness, that the average bulk density of ions is 10^{17} cm^{-3} (this corresponds to doubly distilled water), it is possible to estimate the probability of getting three or more ions into the volume of liquid of 1 nm^3 , i.e., 10^{-21} cm^{-3} . The sought probability will be found as

$$P = 1 - \sum_{n=0}^2 \frac{e^{-\alpha} \alpha^n}{n!} = 1.66 \cdot 10^{-12},$$

where $\alpha = 10^{17} \cdot 10^{-21} = 10^{-4}$ is the mean number of ions in the volume equal to one cubic nanometer. As is seen, the probability of such ionic fluctuations is extremely small. The following estimations are reasonable only provided that we know the effective frequency of generation of such voids. In that case we would be able to calculate the effective frequency of generation of the voids, which already contain the necessary quantity of ions in their shells for keeping the voids from collapse, i.e., such voids do not disappear within several picoseconds. However, any theoretical predictions about the frequency of generation of the voids are still missing, and this is why the detailed analysis of the nanobubble nucleation at the present moment seems meaningless. The solution of this problem will be the subject of separate work; the corresponding results will be published elsewhere. In the next chapter, we analyze the screening of bubstons by the mixture of basic ions and counter-ions. As will be shown, such screening together with the viscous friction forces applied to the moving charged bubbles provides the mechanism for coagulation of such bubbles with the formation of the bubston clusters.

3 Adsorption of ions and screening of strongly charged gas bubbles in aqueous salt solution and their aggregation

The model of ionic adsorption is essentially based on several assumptions. First of all, we consider ions with different adsorptivity to the liquid interface: ions, capable of adsorption at the void interface will be hereinafter referred to as basic ions, while the ions, not capable of adsorption, will be termed as counter-ions. This subdividing is confirmed by the data on the selective adsorption of ions at the water–gas interface, see Refs. [27–51]; these results are also briefly reviewed in the Introduction. In accordance with those results, a gas bubble in a liquid solution of electrolyte acquires an electric charge Q_0 owing to the selective adsorption of negative ions on its surface, i.e., $Q_0 < 0$.

As was noted in the Introduction, the necessary condition for the stability of the bubston is the mechanical equilibrium condition, when the surface tension pressure $2\sigma/R$ ($\sigma = 73$ erg/cm² is the surface tension for aqueous solutions under normal conditions; here, as earlier, R is radius of a bubble) is balanced by the negative (tensile) ponderomotive pressure P_e associated with the presence of the surface electric charge Q_0 . If the surface tension is equilibrated by the pressure P_e , i.e., $2\sigma/R = P_e$, the condition $P_{in} = P_{atm}$ holds, see (1)–(3); under the laboratory conditions we obviously can neglect the additional hydrostatic pressure caused by weight of a liquid above the bubble. In this case, obviously, the condition of diffusion balance of gas inside the bubble in relation to the gas dissolved in a liquid is fulfilled. So the bubble appears simultaneously in the mechanical and diffusion equilibrium, i.e., in the steady state; such bubble appears in the state of *bubston*. We assume an ionic solution together with equilibrium gas bubbles is in equilibrium with the external gaseous medium under a pressure P_{atm} . Accordingly, the concentration C_g of the gas dissolved in it obeys the Henry law: $C_g = \Gamma(T)P_{atm}$, where $\Gamma(T)$ is the Henry coefficient, T is the temperature. However, the condition of equilibrium between the dissolved gas and the gas in a bubble under pressure P_{in} also implies $C_g = \Gamma(T)P_{atm}$ (with the same value of the Henry coefficient $\Gamma(T)$). It follows that in complete equilibrium the pressure in the bubbles $P_{in} = P_{atm}$ (i.e., it is balanced by the external pressure) and, hence, is not revealed in the stability condition $2\sigma/R = P_e$. It is important that pressure P_e depends only on the surface charge Q_0 , but not on the entire charge distribution for $r \geq R$ and is equal to

$$P_e = \frac{1}{8\pi\epsilon} \frac{Q_0^2}{R^4} = (2\pi\epsilon) e^2 (\gamma_i^{AD})^2, \quad (18)$$

where γ_i^{AD} is the surface density of adsorbed ions; this magnitude is scaled in cm^{−2}. The equality $2\sigma/R = P_e$ leads to

$$R = \sigma\epsilon / \left[\pi e^2 (\gamma_i^{AD})^2 \right]; \quad (19)$$

we would like to emphasize here that the radius of stable bubble grows with increasing the surface tension coefficient σ .

At modeling the adsorption of basic ions we make two assumptions. First, we assume that the water molecules form a regular quasi-crystalline lattice of the Wigner–Seitz hexagonal type at the water–gas interface. Second, we consider that the adsorbed basic ions form the sub-lattice, adjacent to the interfacial water molecules; this sub-lattice settles totally inside the bulk of the liquid (since the surface water molecules are packed very densely). As to the positions of counter-ions, we will analyze this question later. The spatial arrangement of the basic and counter-ions is schematically illustrated in Fig. 4.

Fig. 4 Bubston surface as seen from the side of water. Molecules of water form the regular hexagonal Wigner–Seitz cells at the surface (indicated by the *dashed lines*). Ion adsorption centers (*dark circles*) form a two-dimensional lattice with spacing $d = 2\sqrt{3}\delta_l$ between centers (δ_l is the radius of liquid molecules depicted by large *gray circles*). Each center (adsorbed ion) is at a vertex of its Wigner–Seitz cell, having an area of $S_{WS} = 6\sqrt{3}\delta_l^2$. The density of adsorbed ions is $\gamma_i^{AD} = 1/S_{WS}$. The white circles denote the positions of surface counterions, each of which corresponds to three individual Wigner–Seitz cells. Consequently, the surface density of counter-ions can be found as $\Gamma_i = \gamma_i^{AD}/3$, see below. The distance between each of the three adsorbed basic ions and the counterion is $d_1 = 2\delta_l$

This model differs from the ionic adsorption model described in the review [38], where the spatial mutual arrangements of ions and the molecules of water were supposed to be non-correlated. As follows from our model, the basic ions are located in the centers of the corresponding Wigner–Seitz cells, covering the entire surface of the bubston. We assume that the basic ions are kept at the surface of a liquid due to the existence of attractive forces between an ion and a neutral particle (atom or molecule). The energy of such attraction is known to be equal to $(-\beta q^2/2r^4)$, where β is electronic polarizability of the neutral particle, q is the ion charge, and r is the distance between the ion and the particle. In our case, we must set $q = Ze$ and $r = (\delta_l + \delta_i)$, where δ_l is the ion radius, δ_i is the radius of molecule of a liquid, and Z is the valence of an ion. The adsorption energy U_{AD} in this case is determined by the absolute value of the energy corresponding to simultaneous attraction of the ion to three surface molecules (which form the Wigner–Seitz cell) of the liquid with the formation of a densely packed tetrahedron. In the rigid sphere model, such an arrangement of an ion corresponds to its location in a “crater” of the surface layer of spherical molecules. Thus, we can assume $U_{AD} = (3/2) Z^2 e^2 \beta / \delta_0^4$, where $\delta_0 = \delta_l + \delta_i$, and for aqueous solution we assume $\delta_l \sim 1.4 \text{ \AA}$ and $\beta \sim 10^{-24} \text{ cm}^3$. Naturally, this condition idealizes the surface of the bubble itself, presuming that it has no microscopic structure. According to such concepts, uniform distribution of adsorption centers with the maximal surface density must correspond to their arrangement at sites (craters) of such a lattice with spacing $d = 2\sqrt{3}\delta_l$ between the centers. The value of d is the minimal distance, for which each of three liquid molecules in a tetrahedron can interact only with single ion, thus ensuring maximal energy U_{AD} . Each adsorbed ion is located at the center of its own Wigner–Seitz cell with the minimal possible area $S_{WS} = (\sqrt{3}/2) d^2 = 6\sqrt{3}\delta_l^2$. The assumptions concerning the arrangement of ion adsorption centers make it possible to determine the surface density γ_i^{AD} of steadily

adsorbed basic ions: since Wigner–Seitz cells densely cover the entire surface of a bubble, we have $\gamma_i^{AD} = 1/S_{WS}$. Thus,

$$\gamma_i^{AD} = 1 / (6\sqrt{3}\delta_l^2). \quad (20)$$

For aqueous solutions, (20) gives $\gamma_i^{AD} \approx 5 \cdot 10^{14} \text{ cm}^{-2}$. The substitution of this value into (19) gives $R = 2 \text{ \AA}$, which is a physically meaningless result. The reason is that radius R of a bubston is not a preset quantity, but is determined from the self-consistent mechanical equilibrium condition $2\sigma/R = P_e$ for a certain density of steadily adsorbed ions, which satisfied the general condition $R \gg d$ of our model. As applied to gas bubbles, the physical meaning of the condition $R \gg d$ is that the discrete distribution of adsorbed ions at the lattice sites must be such that the tensile pressure P_e associated with these ions could differ from the spherically symmetric pressure ensuring the bubston stability only slightly. In other words, the ions should be located in the vertices of central-symmetric polyhedron inscribed into a sphere of radius R .

By virtue of condition $R \gg d$, the admissible distances d between adsorption centers in this case must exceed the minimal distance $d = d_{\min} = 2 \cdot \sqrt{3}\delta_l$ (which corresponds to the density $\gamma_i^{AD} = 6 \cdot 10^{14} \text{ cm}^{-2}$). For such a lattice, the complete set of possible distances d is defined by the formula $d = k\delta_l$, where coefficient k can be found from trivial geometric considerations as the following discrete values:

$$k = 2\sqrt{3}, 4, 6, 4\sqrt{3}, 8, 10, 6\sqrt{3}, 12, 8\sqrt{3}, 14, 16, 10\sqrt{3}, 18, 20, \dots \quad (21)$$

In other words, the basic ions can occupy not arbitrary vacancies, but settle down symmetrically, i.e., in the vertices of equilateral triangles with the side $d = k\delta_l$. Remind that molecules of water are approximated by rigid spheres with isotropic potential of the interparticle interaction. More realistic model, which implies the an-isotropic contribution of hydrogen bonds to the interaction potential, should result in change of packing of the water molecules at the bubble surface. It however will not essentially influence the series (21). Indeed, the ions will form regular interfacial structure, which is characterized by average distance d . Thus various values of d , as earlier, can be represented by a discrete sequence, whose neighboring members differ from one another by the value of about δ_l . Following to our model, we should assume $\gamma_i^{AD} = 1/S_{WS}$, where S_{WS} is the area of a Wigner–Seitz cell corresponding to $d = k\delta_l$ with a certain value of k from series (21). For a densely packed hexagonal lattice, we have $S_{WS} = (\sqrt{3}/2)d^2$ and $\gamma_i^{AD} = (2/\sqrt{3})(k^2\delta_l^2)^{-1}$. Substituting this value into (19), we arrive at

$$R = \frac{3}{4\pi} \frac{\sigma \varepsilon}{e^2} \delta_l^4 k^4. \quad (22)$$

The requirement $R \gg d = k\delta_l$ leads to the following condition for admissible values of k : $k^3 \gg (4\pi/3) e^2 / (\sigma \varepsilon \delta_l^3)$; for aqueous solutions this gives $(k/4.4)^3 \gg 1$. From the series of possible values of k , this condition holds for $k \geq 10$. In other words, the increase of the value of k results in a steep growing the bubston radius R . We only should bear in mind that the bubston radii should not be too large, as in that case the bubstons should rapidly float up. For example, let us estimate the bubston parameters at $k = 10$. In this case, $(k/4.4)^3 \approx 12$, the surface density of adsorbed ions is

$$\gamma_i^{AD} = \frac{2/\sqrt{3}}{(10\delta_l)^2} = 6 \cdot 10^{13} \text{ cm}^{-2}, \quad (23)$$

the total number of adsorbed ions is

$$N_i = 4\pi R^2 \gamma_i^{AD} = \frac{3\sqrt{3}}{2\pi} \cdot 10^6 \frac{(\sigma\varepsilon)^2}{e^4} \delta_l^6 = 3.7 \cdot 10^3, \quad (24)$$

and the bubston radius is

$$R = \frac{3}{4\pi} \cdot 10^4 \frac{\sigma\varepsilon}{e^2} \delta_l^4 = 22.0 \text{ nm}; \quad (25)$$

note, for example, that for $k = 20$ we obtain $R = 350 \text{ nm}$. Thus, our model of adsorption permits various values of the bubston radii, which depends neither on the type of dissolved ions, nor on their concentration in a liquid. At the same time, the concentration of ions determines the bulk density of the bubstons themselves. Remind that the natural restriction to the number k in (21) is that the positions of the adsorbed ions should correspond to the vertices of central-symmetric polyhedron inscribed into the sphere of radius R . In accordance with our model, the condition (22) for the bubston radius holds for all (1: 1) aqueous solutions of electrolytes, including pure water. Summarizing, starting from the value of $k = 10$, the bubston radius and the surface density of adsorbed basic ions can be arbitrary; the only requirement is that the number of adsorbed ions should be sufficient for compensating the surface tension forces at a given R .

Of course, we must take into account the repulsive interaction of adsorbed ions, leading to their desorption (escaping) from the surface of a bubble. Such a desorption energy can be expressed as $U_D = U_{AD} - U_L$, where U_L is the adsorption activation energy determined by the energy of lateral Coulomb repulsion of adsorbed ion located at adsorption centers. This energy should be set equal to $U_L = Z_0 (Ze)^2 / [(\varepsilon/2) d]$, where Z_0 is the coordination number of such centers. The value of Z_0 is determined from the condition that the packing of molecules of liquid on the surface of a bubble is close to dense; as earlier, we assume that the molecules form a two-dimensional hexagonal lattice, i.e., $Z_0 = 6$. The fact that U_L is doubled as compared to the conventional energy of Coulomb interaction (the term $(\varepsilon/2)$ appears instead of ε) is due to the location of interacting ions on the liquid surface. Here, we use the well-known result of electrostatics [70], according to which the energy of interaction between two charges q located on the plane surface of half-spaces having permittivities ε and ε_p and separated by distance d is equal to $2(q^2/d)/(\varepsilon + \varepsilon_p)$. The applicability of this result to the case in question is ensured by the general requirement $R \gg d$ and the assumption of $\varepsilon_p \ll \varepsilon$. It is clear that the adsorption is stable provided that the process of desorption has a potential barrier, and the ions should overcome this barrier to escape from the interface. This means that the height of this barrier $U_D = U_{AD} - U_L$ should be positive. For calculating U_L we should assume $d = k\delta_l$. For $Z = 1$, the energy $U_L = 12e^2/\varepsilon d = (12/k)e^2/\varepsilon\delta_l$, $U_{AD} = (3/2)e^2\beta/\delta_0^4$. Thus the desorption energy is

$$U_D = U_{AD} - U_L = \frac{3}{2} \frac{e^2}{\varepsilon\delta_l} \frac{1}{A\alpha_0^4} \left(1 - \frac{8}{k} A\alpha_0^4 \right) > 0, \quad (26)$$

where $A = \delta_l^3/\varepsilon\beta = 0.03$, and $\alpha_0 = (1 + \delta_l/\delta_l)$. Thus, in the case of bubstons (for the sake of definiteness) of radius $R = 22 \text{ nm}$ (see (24)) the condition $U_D > 0$ has the form

$$\delta_l/\delta_l < \left[\left(\frac{k\varepsilon\beta^{1/3}}{8\delta_l} \right)^{1/4} - 1 \right]_{k=10} = 1.92, \quad (27)$$

or $\delta_l < 1.5 \cdot \delta_l = 2 \text{ \AA}$. It holds for a wide class of singly charged ions, including both cations and anions, in particular, for all ions emerging at dissolution of salts of alkaline metals.

This condition holds for Cl^- ($\delta_i = 1.8 \text{ \AA}$) and Br^- ($\delta_i = 1.96 \text{ \AA}$), while for I^- anions ($\delta_i = 2.2 \text{ \AA}$) this condition is still not fulfilled. However, at $k > 10$ (see (21)) the condition (27) is satisfied for I^- as well. Note that the anions Cl^- , Br^- and I^- are known to be capable of adsorption, see Ref. [38]. Note that the condition (27) is obviously met for larger radii of bubstons.

In what follows we will consider the Coulomb screening of charged bubston. Under equilibrium conditions, the charge Q_0 is screened by the ionic shell with electric charge density $\rho(\mathbf{r})$. Henceforth, we will consider only spherical bubston of radius R and, accordingly, we assume that the charge density $\rho(\mathbf{r})$ is spherically symmetric. The screening (quasineutrality) condition can be written in the form

$$Q_0 + 4\pi \int_R^\infty r^2 \rho(r) dr = 0 \quad (28)$$

(r is the distance from the bubston center). Generally speaking, the particles (not necessarily the bubstons) can be divided into weakly charged, when the parameter $B \equiv |ZeQ_0/\varepsilon RkT| = 4\pi l_B R \gamma_i^{AD} \ll 1$, and strongly charged, when $B \gg 1$. Here Z is the valence of dissolved ions; in what follows we will assume that $Z = 1$, e is the elementary charge, T is the temperature, ε is the permittivity of a liquid, and $l_B = e^2/\varepsilon kT$ is the Bjerrum length ($l_B = 7 \text{ \AA}$ for water at room temperature). Bubstons themselves turn out to be strongly charged since, for example, for $R = 22 \text{ nm}$ the parameter B for them is $B = 4\pi l_B R \gamma_i^{AD} = 120$. In the case where $B \ll 1$, using the Poisson–Boltzmann equation in the Debye–Huckel approximation we obtain the well-known result [71] for the charge density distribution $\rho(r)$, satisfying the condition (28):

$$\rho(r) = -\frac{Q_0 \kappa^2}{4\pi(1 + \kappa R)} \frac{e^{-\kappa(r-R)}}{r}, \quad r \geq R, \quad (29)$$

$$\kappa = a_D^{-1} = \sqrt{8\pi Z^2 e^2 n_{i0}/\varepsilon kT} = Z\sqrt{8\pi l_B n_{i0}}. \quad (30)$$

Here, $a_D = \sqrt{\frac{\varepsilon kT}{8\pi Z^2 e^2 n_{i0}}}$ is the so-called Debye length, and n_{i0} is the equilibrium bulk density of ions. A distinguishing feature of weakly charged bubstons is that, in accordance with (29), the sign of density $\rho(r)$ is opposite to the sign of the surface charge Q_0 for all values of $r \geq R$; in other words, counter-ions always prevail in the screening ionic shell. As a result, the ionic screening of charged bubbles is impossible for finite values of radius r , in accordance with (28). For a long time, this circumstance was indisputable for specialists in colloidal systems irrespective of values of parameter B . However, some experimental data obtained in recent years obviously have contradicted the concept of screening ionic shell with absolute prevalence of counter-ions. Above all, this concerns the experimental proof of attraction of likely charged macro-particles in aqueous solutions of salts under certain conditions [72–85], which contradicts the Deryaguin–Landau–Verwey–Overbeek (DLVO) theory [86, 87] based on the model of the Debye screening (29). Such contradictory facts also include recent experimental results on electrophoresis of macro-particles in solutions of various salts, indicating an ambiguous dependence of the electrophoretic mobility of particles on the polarity of their surface charge [88–90].

These contradictions, as well as other facts, stimulated a number of theoretical publications [91–105], in which the so-called inversion (or superscreening) effect of the charge

of macro-particles in aqueous solutions of electrolytes was predicted. The effect is that for strongly charged particles (i.e., when $B \gg 1$) the charge density distribution $\rho(r)$ in the ionic shell can reverse its sign upon an increase in r . In this case, the sign of the total charge within the sphere with a certain finite value of radius $r > R$,

$$Q(r) = Q_0 + 4\pi \int_R^r x^2 \rho(x) dx, \quad (31)$$

can be inverted, i.e., $\text{sgn } Q(r) = -\text{sgn } Q_0$. The existence of this effect opens wide possibilities in interpreting the experimental facts mentioned above. In the cited publications theoretical concepts were developed, according to which the condensation of counter-ions can occur on the surface of a particle with the formation of a two-dimensional strongly correlated liquid for large values of B . Under certain conditions the charge density (per unit area) of such a liquid may exceed (in absolute value) the unscreened (initial) surface charge density $Q_0/4\pi R^2$ that is the main reason for charge inversion. According to the results obtained by these authors, the screening of the inverted charge can be successfully described on the basis of the Poisson–Boltzmann equation.

An important step in explaining the details of the charge inversion effect were the publications [106–108], which described the results of numerical calculating aimed at the study of the structure of the screening ionic shell of a strongly charged macro-particle in an aqueous salt solution. For instance, in the study [106] a strongly charged macro-particle (a macro-ion) with the charge $|Q_0| = 20e$, and the binary (Z : $Z = 2$: 2 or 1: 1) ionic salt solution were analyzed. In this case the parameter $B = 20Z(l_B/R)$; consequently, this parameter for 2: 2 and 1: 1 solutions was equal to $280/R(\text{\AA})$ and $140/R(\text{\AA})$, respectively. In calculations, only the Coulomb interactions between dissolved ions, as well as between ions and the charged macro-particle were taken into account for $T = 300$ K. For various concentrations of both types of solutions only three values of parameter B were allowed for: $B = 14$ (2: 2 solution, $R = 20$ Å, and 1: 1 solution, $R = 10$ Å), $B = 22.4$ (2: 2 solution, $R = 12.5$ Å), and $B = 28$ (2: 2 solution, $R = 10$ Å). The main result obtained in [106] is as follows: inversion misses for $B = 14$, and inversion can occur for $B = 22.4$ and 28. Note that qualitatively similar results are summarized in Refs. [107, 108], but in these works the authors considered the planar negatively charged surface. It is important that the sign reversal of charge $Q(r)$ always occurs not jump-wise, as follows from the concepts of the formation of a two-dimensional liquid formed by the basic ions and counter-ions, but as a result of a smooth approaching $Q(r)$ to zero for $r \rightarrow R + \Delta r$, where Δr is the scale of considerable decrease in the volume density of counter-ions near the particle surface (in the immediate vicinity of the surface their density is maximal, but finite). Thus, the results of [106–108] indicate that, first, the inversion effect is indeed of the threshold type with respect to the parameter B . Second, the charge inversion occurs not at the particle surface proper, but as a result of a gradual mixing of counter-ions with basic ions upon an increase in $(r - R)$. For large values of B such mixing leads to the prevalence of basic ions, i.e., to the sign reversal of the charge density $\rho(r)$ and to the inversion of the charge $Q(r)$. These conclusions make it possible to refute the model of the inversion effect due to surface condensation of counter-ions (formation of two-dimensional liquid), and to consider another model, which is free of such concepts. This model is proposed here as applied to dilute solutions of electrolytes, for which the parameter $\zeta \equiv \kappa R \ll 1$. Hereinafter we will consider the Coulomb screening for spherical nanometer-sized or coarser bubstons, whose characteristics should obey the condition $B \gg 1$.

The quasineutrality condition (28), which should be valid for arbitrary values of B , implies the ionic charge $Q(r)$ within a sphere of radius $r > R$ tends to zero at increasing $(r - R)$. This leads to the situation when the value of $e|Q(r)|/\varepsilon r kT$ becomes smaller than unity for large values of $(r - R)$ and, hence, the density $\rho(r)$ of the screening ionic charge for such values of $(r - R)$ should be described by the Debye–Huckel law, i.e., should be $\sim (1/r) \exp[-\kappa(r - R)]$, where κ is defined by (30). On the other hand, in accordance with numerical simulations [106–108], the decrease in $\rho(r)$ for small values of $(r - R)$ must be much more rapid, but smooth. On the basis of these two features of the behavior of density $\rho(r)$, our model of screening stems from the representation of $\rho(r)$ in the entire range of $(r - R)$ in the form

$$\rho(r) = C_1 \frac{e^{-b(r-R)}}{r} + C_2 \frac{e^{-\kappa(r-R)}}{r}, \quad r \geq R, \quad (32)$$

where C_1 and C_2 are the sought parameters, which are independent of r and having the opposite signs. Here C_1 has the sign opposite to Q_0 , whereas C_2 has the same sign as Q_0 . We will consider only dilute solutions, for which $\xi \equiv \kappa R \ll 1$. As will be clear from the subsequent analysis, parameter $\xi \equiv bR$ is on the order of or greater than unity, where $b \gg \kappa$ is unknown yet factor; consequently, $\xi/\xi \ll 1$ in all cases.

The substitution of (32) into (28) and the inclusion of the boundary condition $C_1 + C_2 = R\rho(R)$ gives the system of two equations for C_1 and C_2 . Its solution, accurate to the terms on the order of $\sim \xi^2$, has the form

$$C_1 = -\frac{Q_0 F}{4\pi R^2} \left(1 + \frac{f}{F} \xi^2\right), \quad C_2 = \frac{Q_0 f}{4\pi R^2} \xi^2, \quad (33)$$

where

$$F = -\frac{4\pi R^3 \rho(R)}{Q_0} > 0, \quad f = F \frac{\xi + 1}{\xi^2} - 1. \quad (34)$$

For strongly charged bubstons the density of charge $\rho(R)$ on the surface of a bubston is completely determined by the density $n_i(R)$ of counter-ions having the positive charge e , i.e., $\text{sgn } \rho(R) = -\text{sgn } Q_0$ (as Q_0 is negative). Consequently, $\rho(R) = en_i(R)$ and parameter $F > 0$ is defined by the formula

$$F = \frac{4\pi R^3 en_i(R)}{|Q_0|}. \quad (35)$$

Equations 34, 35 contain two as yet unknown parameters, viz., the number density $n_i(R)$ of counter-ions at the bubston surface, and $\xi = bR$. To determine $n_i(R)$ we use the Boltzmann equation

$$n_i(R) = n_{i0} \exp \left[\frac{e\phi(R)}{kT} \right]. \quad (36)$$

Here, $\phi(R)$ is the potential of the electric field produced by the charge density distribution $\rho(r)$ in (32). The density $n_i(R)$ of counter-ions defined in such a way increases indefinitely with growing B . It is this circumstance that mainly stimulated other authors to develop the concept of counter-ion condensation at the surface of a particle, leading to the formation of a two-dimensional layer of ionic solution. Remaining in the framework of our model, we proceed from the fact that in accordance with (36) the counter-ion density $n_i(R)$ for $B \gg 1$ attains its maximal but still a finite value $n_i^{\max}(R)$. Thus, the parameter ξ can be defined in terms of $n_i^{\max}(R)$.

First of all, we determine the dependence of $\phi(R)$ on ξ and $n_i^{\max}(R)$. For an arbitrary distribution $\rho(r)$ satisfying the quasineutrality condition (28) the solution of the Poisson equation $\nabla^2 \phi(r) = -(4\pi/\varepsilon) \rho(r)$ with the boundary conditions $\phi(\infty) = 0$, $\phi'(R) = -Q_0/\varepsilon R^2$ can be represented in the form

$$\phi(r) = -\frac{4\pi}{\varepsilon r} \int_r^\infty (x^2 - xr) \rho(x) dx. \quad (37)$$

Substituting expression (32) into this formula, integrating, setting $r = R$, and taking into account (33), we arrive at

$$\phi(R) = \frac{Q_0}{\varepsilon R} \left(1 - \frac{F_0}{\xi} \right), \quad (38)$$

where, in accordance with (35),

$$F_0 = \frac{4\pi R^3 e n_i^{\max}(R)}{|Q_0|} = \frac{R n_i^{\max}(R)}{|\gamma_i^{AD}|}. \quad (39)$$

Substituting now $n_i(R) = n_i^{\max}(R)$ into the left-hand side of (36), and expression (38) into the right-hand side, we derive the following relationship between ξ and $n_i^{\max}(R)$:

$$\xi = \frac{F_0}{1 - \alpha} = \frac{R}{1 - \alpha} \frac{n_i^{\max}(R)}{|\gamma_i^{AD}|}, \quad (40)$$

where $\alpha = L/B$, $L \equiv \ln[n_i^{\max}(R)/n_{i0}]$. In this case, the quantity f (see the second equation of (34)) has the form

$$f = \frac{1 - \alpha}{\xi} - \alpha. \quad (41)$$

It remains for us to determine the value of $n_i^{\max}(R)$. Counter-ions are not capable of adsorption, but being near the surface of a bubble, they are attracted to it by the Coulomb forces exerted by adsorbed basic ions. The maximal surface density $\Gamma_i^{\max}$ of counter-ions obviously corresponds to their arrangement at the same distance $2\delta_l$ from three adsorbed ions (it is just impossible to arrange the counter-ions otherwise); each adsorbed basic ion mainly interacts with only one counter-ion (see Fig. 4). It is this arrangement that corresponds to a stable state. Since each counter-ion in this case corresponds to three individual Wigner-Seitz cells, we have $\Gamma_i^{\max} = 1/3 S_{WS} = (\sqrt{3}/6) (k\delta_l)^2$, where for the sake of definiteness we put $k = 10$, $R = 14$ nm, see (21)–(23). Assuming $\Gamma_i^{\max} = [n_i^{\max}(R)]^{2/3}$, we obtain

$$n_i^{\max}(R) = \left(\frac{\gamma_i^{AD}}{3} \right)^{3/2} = \frac{2(4/3)^{1/4}}{9(10\delta_l)^3} = 0.9 \cdot 10^{20} \text{ cm}^{-3}. \quad (42)$$

It can be seen from (32) that the distribution of $\rho(r)$ must vanish at a certain point $r = r_0$ if the quantities C_1 and C_2 have opposite signs. In accordance with (33) and (34), this is valid for $f > 0$ or, due to (41), for $\xi < (1 - \alpha)/\alpha$. Introducing a new variable,

$$\lambda = \frac{R/\delta_l}{18(12)^{1/4}} \equiv \frac{F_0}{2}, \quad (43)$$

we have

$$\xi = \frac{2\lambda}{1-\alpha}; \quad (44)$$

consequently, condition $f > 0$ assumes the validity of inequality

$$\frac{\alpha}{(1-\alpha)^2} < \frac{1}{2\lambda}. \quad (45)$$

When this inequality holds, we can easily obtain the expression for the position of the point r_0 :

$$r_0 = R \left[1 + \frac{1}{\xi} \ln \frac{F_0}{f\xi^2} \right] = R \left\{ 1 + \frac{1}{\xi} \ln \frac{(\xi/\zeta)^2}{\left[1 - 2\lambda \frac{\alpha}{(1-\alpha)^2} \right]} \right\}. \quad (46)$$

It is the point, where the charge density $\rho(r)$ of the ionic shell changes its sign: $\text{sgn } \rho(r < r_0) = -\text{sgn } \rho(r > r_0)$, see Fig. 5. This leads to the sign inversion of the total charge $Q(r)$, occurring at a certain value of radius $r_1 \neq r_0$. Let us now determine r_1 . On the basis of (28), (30), (35), and (36), we have

$$Q(r) = -4\pi \int_r^\infty x^2 \rho(x) dx = Q_0 \left\{ \frac{F_0}{\xi^2} (1 + br) e^{-b(r-R)} - f(1 + \kappa r) e^{-\kappa(r-R)} \right\}, \quad (47)$$

$$\frac{dQ}{dr} = 4\pi r^2 \rho(r). \quad (48)$$

It follows from (47) that the necessary condition for vanishing $Q(r)$ is $f > 0$, i.e., the inequality (34). In this case, introducing a new variable $y_1 \equiv r_1/R$, we have the equation

$$y_1 = 1 + \frac{1}{\xi} \ln \frac{1 + \xi y_1}{1 - \frac{\alpha\xi}{1-\alpha}} \equiv \frac{r_0}{R} - \frac{1}{\xi} \ln \frac{(\xi/\zeta)^2}{1 + \xi y_1}. \quad (49)$$

Since $(\xi/\zeta)^2 \gg 1$, it follows from (47) that radius $r_1 < r_0$; i.e., the sign inversion of the total charge $Q(r)$ ($\text{sgn } Q(r < r_1) = \text{sgn } Q_0 = -\text{sgn } Q(r > r_1)$) occurs at such distances from the bubston surface, where the sign of the charge density remains unchanged ($\text{sgn } \rho(r_1) = \text{sgn } \rho(R) = -\text{sgn } Q_0$, see Fig. 5). In accordance with (49), charge $Q(r)$ attains its extreme value at point $r = r_0$. On the basis of (46), (47) we obtain the following relation (accurate to the terms on the order of $(\zeta/\xi)^2$) for the value of $Q(r_0)$:

$$Q(r_0) = -Q_0 f(1 + \xi r_0/R). \quad (50)$$

As the value of r increases further, the charge $Q(r)$ tends to zero.

While considering the screening of bubstons by the ionic shell, we tacitly assumed that a bubston is at rest, and its ionic shell is not subjected to hydrodynamic action; such a shell will be referred to as an equilibrium shell. As a matter of fact, bubstons perform thermal Brownian motion; in this case, a compound particle with total charge Q_c , which consists of the initial bubston of radius R and surface charge Q_0 and a certain layer of the liquid with the “frozen-in” ionic shell, distorted by viscous forces, is involved in the motion. If the velocity of the particle is small, we can assume that the distortion of the ionic shell under steady-state conditions boils down to washing out (vanishing) of the equilibrium charge density distribution $\rho(r)$ due to acting the viscous forces on a peripheral layer $r > a_c$, while

Fig. 5 The total charge $Q(r)$ and the charge density $\rho(r)$ in the liquid surrounding the bubston of radius R . The bubston charge Q_0 is negative. The curve for $Q(r)$ was modeled to have the same form as the corresponding graphs for the symmetric 1:1 electrolyte solution in works [106–108]

the remaining part of this distribution ($r < a_c$) is spherically symmetric as before. Such a pattern is widely used in theoretical treatment of electrophoresis, see, e.g., [109]. In this case, the radius a_c of a compound particle will be referred to as the hydrodynamic radius of a bubston and the spherical surface with such a radius will be called the glide surface. Our task is to establish the relation between the parameters Q_c and a_c of a compound particle and the initial parameters Q_0 and R of the bubston and of the solution itself. As before, we assume the solution is dilute ($\zeta \ll 1$).

The physical foundation for solving the formulated problem is that the pressure of viscous forces destroying the ionic shell is always opposed by the electrostriction-induced pressure p_{str} stabilizing the compound particle and associated with its charge Q_c , which coincides with the charge $Q(r)$ for $r = a_c$ (see (31)), i.e.,

$$Q_c = Q_0 + 4\pi \int_R^{a_c} x^2 \rho(x) dx = -4\pi \int_{a_c}^{\infty} x^2 \rho(x) dx, \quad (51)$$

and $\rho(r)$ is the equilibrium charge density distribution defined above. The electric field strength at the surface of a compound particle ($r = a_c$) is $E_c = Q_c / (2\epsilon a_c^2)$, while the pressure is given by

$$p_{\text{str}} = \frac{\epsilon E_c^2}{8\pi} = \frac{Q_c^2}{8\pi \epsilon a_c^4}. \quad (52)$$

The stationary state corresponds to the equality of the spherically symmetric pressure p_{str} to the maximal absolute value of the pressure of viscous forces (i.e., the pressure of detachment from the rear side relative to the motion), which sets in for a certain value of radius a_c of the glide surface. Under the laminar flow conditions for a compound particle with velocity u , the maximal pressure of detachment is given by [110]

$$p_v = \frac{3\eta u}{2a_c} \quad (53)$$

(η is the viscosity of a liquid). Consequently, for the given velocity u , the parameters Q_c and a_c can be defined from the equation

$$\frac{3\eta u}{2a_c} = \frac{Q_c^2}{8\pi\epsilon a_c^4}, \quad (54)$$

and (51). In the study of thermal motion of bubstons, we can use the approach based on the stochastic differential equation of the Langevin type, see Ref. [111]

$$m_c \frac{du}{dt} = -F(u) + f(t), \quad (55)$$

where

$$F = 4\pi\eta a_c u \quad (56)$$

is the regular Stokes frictional force corresponding to the motion of a gas particle of radius a_c in a liquid of viscosity η (see, e.g., [110]), m_c is the mass of a compound particle, and $f(t)$ is a stochastic force standing for instantaneous random hitches onto the gas particles,

$$\langle f(t) \rangle = 0, \quad \langle f(t) f(t + \tau) \rangle = \delta(\tau),$$

where the angular brackets mean the averaging, $\delta(\tau)$ is the Dirac delta-function. It is implied in the framework of this approach that the velocity $u = u(t)$ (here and below, $u(t)$ stands for the velocity component along a certain fixed direction s) is a stationary random process with the average value $\langle u(t) \rangle = 0$, and the stationary autocorrelation function $\langle u(t) u(t + \tau) \rangle \sim \exp\left(-\frac{|\tau|}{\tau_0}\right)$. Here τ_0 is the correlation time of random process $u(t)$. The spectral intensity of this process is expressed by

$$g(\omega) = \frac{2\tau_0}{\pi} \frac{kT/m_c}{1 + (\omega\tau_0)^2}, \quad \int_0^\infty g(\omega) d\omega = \langle u^2 \rangle = \frac{kT}{m_c}, \quad (57)$$

as the Maxwellian distribution for the velocity u should be established in the stationary regime. In this formula the correlation time τ_0 should be close to the relaxation time, standing for appearance of the system on the stationary level; this time depends directly on the dissipative properties of the system. Thus we arrive at the following formula

$$\tau_0 \approx m_c / 4\pi\eta a_c. \quad (58)$$

Obviously, it would be incorrect to substitute the quantity $\langle u^2 \rangle^{1/2} = (kT/m_c)^{1/2}$ for u into (56). In fact, the velocity $u(t)$ can be represented as the sum $u(t) = u_1(t) + u_2(t)$. Indeed, the motion of a compound particle consists of fast “vibrations” with amplitudes smaller than its radius a_c ; we will denote the characteristic velocity of such process as $u_1(t)$. It is easy to show that the relative (normalized to a_c) amplitude of such vibrations is $\langle u_1^2 \rangle^{1/2} (\tau_0/a_c) \sim 10^{-2}/a_c^2 [\text{nm}] \ll 1$. Besides, there exist “smooth” displacements with amplitudes comparable to a_c . The second type is of our interest, since only such movements of a compound particle may lead to viscous washing out of the peripheral layer of the ionic shell. The smooth velocity random process will be denoted as $u_2(t)$; this process corresponds

to the low-frequency part of spectrum $g(\omega)$ in the interval $(0, \tau_2^{-1})$, where $\tau_2 \gg \tau_0$, and can be represented as the random process $u(t)$ averaged over the time interval τ_2 :

$$u_2(t) = \frac{1}{\tau_2} \int_{-\infty}^t e^{-(t-t')/\tau_2} u(t') dt', \quad \tau_2 \gg \tau_0. \quad (59)$$

The spectral intensity $g_2(\omega)$ of this process is given by

$$g_2(\omega) = \frac{g(\omega)}{1 + (\omega\tau_2)^2}, \quad \int_0^\infty g_2(\omega) d\omega = \langle u_2^2 \rangle = \langle u^2 \rangle \frac{\tau_0}{\tau_2}, \quad (60)$$

and the spectral intensity for the complete random process $u(t) = u_1(t) + u_2(t)$ can be written in the form

$$g(\omega) = g_1(\omega) + g_2(\omega), \quad g_1(\omega) = g(\omega) \frac{(\omega\tau_2)^2}{1 + (\omega\tau_2)^2}. \quad (61)$$

Spectrum $g_1(\omega)$ stands for a rapid component $u_1(t)$ of velocity $u(t)$; it vanishes for $\omega = 0$ and has a width $\Delta\omega_1 \cong \tau_0^{-1}$. The rapid component $u_1(t)$ is responsible only for small vibrations of the gas particles, and makes zero contribution to their diffusive movements. Indeed, as is known, for the random Wiener (diffusion) processes the diffusion coefficient is expressed as $D = \pi g(0)$; thus, for the process $u_1(t)$ the diffusion coefficient $D = 0$. Smooth displacements of particles are controlled by spectrum $g_2(\omega)$ having a width of $\Delta\omega_2 \cong \tau_2^{-1}$, since τ_2 is the correlation time of random process $u_2(t)$. Washing out of the peripheral layer is most effective on intervals of unidirectional motion of a particle, i.e., in the intervals between successive extrema of the process $u_2(t)$. It is well known (see, e.g., [112]) that the mean value of such intervals coincides by the order of magnitude with the correlation time of the random process, i.e., with time τ_2 . During this time, the particle is displaced on the average by the distance $\langle \Delta s^2 \rangle^{1/2} = \langle u_2^2 \rangle^{1/2} \tau_2 \approx a_c$. However $\tau_2 = \langle u^2 \rangle \tau_0 / \langle u_2^2 \rangle$ in accordance with the second equation in (60). This leads to the expression $\langle u_2^2 \rangle^{1/2} \approx \langle u^2 \rangle \tau_0 / a_c \approx kT/4\pi\eta a_c^2$, where we used (57), (58). After substituting $\langle u_2^2 \rangle^{1/2}$ instead of u into formula (53), we arrive at

$$\frac{Q_c^2}{2\epsilon a_c} = \frac{3kT}{2}, \quad (62)$$

where $(3/2)kT$ is the average thermal energy of the particle; the left-hand side of this formula defines the energy of the electric field created by the compound particle. It is worth noting that the formula establishing the relation between a_c and Q_c was derived on the basis of (53), (54), (56), and (57), i.e., on the universal results of macroscopic electrodynamics, hydrodynamics, and the theory of Brownian motion. Thus, it is not associated with our model (including the condition $\kappa R < 1$) and, being independent of viscosity η , is of the thermodynamic nature: in the steady state, the energy of the electric field of a compound particle for an arbitrary value of the adsorbed charge Q_0 is a function of the temperature of the medium only, and is exactly equal to its mean kinetic energy. It should also be noted that this result is not associated with the sign inversion effect, and is also valid for weakly

charged macro-particles, for which $B \ll 1$, and the Debye screening (29) takes place. The charge of a compound particle in this case is given by

$$Q_c = Q_0 \frac{1 + \kappa a_c}{1 + \kappa R} e^{-\kappa(a_c - R)}. \quad (63)$$

Here, for all values of a_c , charge Q_c has the same sign as charge Q_0 and tends monotonically to zero with increasing a_c . As a result, the system of (62) and (63) has only one pair of roots (Q_c, a_c) for all possible temperatures, which corresponds to a single type of compound particles. In the case of strongly charged particles, in accordance with (47), see also Fig. 5, the quantity Q_c^2 as a function of a_c has a two-hump shape (Fig. 6), and the system of (47), (62) for $T < T^*$ (the temperature T^* will be defined below) has three pair of roots $(Q_c^{(i)}, a_c^{(i)})$ ($i = 1, 2, 3$), the relation between Q_c and a_c in each pair being

$$(Q_c^{(i)}/e)^2 = 3(a_c^{(i)}/l_B), \quad (i = 1, 2, 3). \quad (64)$$

As can be seen, only two pairs of roots $(Q_c^{(1)}, a_c^{(1)})$ and $(Q_c^{(3)}, a_c^{(3)})$ correspond to stable states of compound particles, i.e., only these two types of such particles can exist, while parameters $(Q_c^{(2)}, a_c^{(2)})$ are found to be impracticable. This follows from the fact that for radii $a_c < a_c^{(2)}$ (but for $a_c > a_c^{(1)}$), pressure $p_{str} < p_v$ (see Fig. 6); consequently, the particle size should continue to decrease in the course of Brownian motion (ionic shell is washed out) down to value $a_c^{(1)}$. For $a_c > a_c^{(2)}$ (but $a_c < a_c^{(3)}$), pressure $p_{str} > p_v$, and the motion does not hamper the growth of the ionic shell of a compound particle up to value $a_c^{(3)}$. At the same time, radii $a_c^{(1)}$ and $a_c^{(3)}$ are stable since the condition $\text{sgn}(a_c - a_c^{(1,3)}) = \text{sgn}(p_{str} - p_v)$ holds for small deviations $(a_c - a_c^{(1,3)})$.

Thus, compound particles can be divided into two types: “small” particles with radii $a_c^{sm} \equiv a_c^{(1)}$ and charges $(Q_c^{sm}/e) = (3a_c^{sm}/l_B)^{1/2}$ ($\text{sgn } Q_c^{sm} = \text{sgn } Q_0$) and “coarse” particles with radii $a_c^{cr} \equiv a_c^{(3)}$ and charges $-Q_c^{cr}/e = 3(a_c^{cr}/l_B)^{1/2}$ ($\text{sgn } Q_c^{cr} = -\text{sgn } Q_0$). Such a division of compound particles into two types with opposite charge polarities is a peculiar

Fig. 6 The graphic solution of the equations (47) and (62)

manifestation of the charge inversion effect; its presence follows from independent data on parameters of compound particles.

Now let us find the temperature T^* limiting the possible temperature range. In accordance with (50), (62), temperature T^* is defined by the formula (see Fig. 6)

$$kT^* = \frac{Q_0^2 f^2 (1 + \zeta r_0/R)^2}{3\epsilon r_0}. \quad (65)$$

Using formulas (40), (41), (47) and taking into account the fact that $\alpha \sim 0.1$ and $\zeta \leq 0.1$, we obtain the approximate formula $(T^*/T) \approx 10^2 (Rl_B |\gamma_i^{AD}|)$. For aqueous solutions this gives $(T^*/T) \geq 10^3$, i.e., for any temperatures T , all three pairs of roots $(Q_c^{(i)}, a_c^{(i)})$, i.e., both types of compound particles should exist. It can be easily verified that $a_c^{(1,2)} = r_1 [1 \mp O(T/T^*)^{1/2}]$. Since $(T/T^*)^{1/2} \ll 1$, for small compound particles we have

$$a_c^{sm} \approx r_1, \quad \frac{|Q_c^m|}{e} \approx 4 \sqrt{\left(\lambda + \frac{1}{2}\right)}, \quad (66)$$

where the parameter λ is given by (43). The roots $(Q_c^{(i)}, a_c^{(i)})$ for coarse compound particles can be deduced from (62), into which we should substitute only the second term of the formula (47) (the first term is exponentially small since $(a_c^{(3)} - R)b \gg 1$). Using (65) and the above approximate formulas for (T^*/T) , we can obtain the following approximate results (we assume $(r_0/R) \sim 3$, $(T^*/T) \geq 10^3$):

$$\frac{a_c^{cr}}{R} = \frac{1}{2\zeta} \ln \left[\frac{Q_0^2 f^2 r_0 (1 + \zeta a_c^{cr}/R)^2}{3\epsilon r_0 kT a_c^{cr}/R} \right] \approx \frac{1}{2\zeta} \ln \left(\frac{3T^*}{T} \right). \quad (67)$$

For $\ln(3T^*/T) \approx 10$ and $\zeta = 0.1$, we obtain

$$a_c^{cr} \approx 50R, \quad \frac{Q_c^{cr}}{e} = - \left(\frac{42}{1 + 2/4\lambda} \right)^{1/2} \left(\frac{Q_c^{sm}}{e} \right). \quad (68)$$

It is clear that the absolute values of the corresponding charges obey the inequality $|Q_c^{cr}| > |Q_c^{sm}|$. It is well to say that parameters a_c^{sm} and Q_c^{sm} do not depend on the adsorbed charge Q_0 to within the terms on the order of $(T/T^*)^{1/2}$, while a_c^{cr} and Q_c^{cr} depend on the charge only logarithmically.

The analysis of the effect of Brownian motion of charged bubbles on their screening shows that the effect of charge inversion manifests itself in the formation of two types of compound particles differing in their radii by an order of magnitude and having opposite charges, see (66)–(68). Thus, the mutual attraction of such compound particles can play essential role in the cluster formation. As the mass of a coarse compound particle and its charge (by the absolute magnitude) exceed drastically the mass and the charge of a small compound particle, it seems possible to consider the particle–cluster aggregation model [113]. In the view of this model, a small, light, and highly mobile compound particle coagulates with heavy, coarse and low mobile compound particle, thus forming charged dimeric particle. As the attraction between the oppositely charged compound particles, which are far from one another, is the dominant factor, we can use the ballistic particle–cluster model of bubstons aggregation [113]. As a result of this process, a cluster composed of the small and the coarse compound particles occurs. The charge of such cluster is obviously defined by a ratio between small and coarse compound particles in the cluster. It is clear however that the cluster, consisting of limited number of compound particles of both signs, cannot be neutral. The sign of the charge of such cluster should be determined in

Fig. 7 Stochastic model of the bubston cluster with the bubston size distribution parameters: the mean radius of the bubston 45 nm, the number of bubstons in the cluster $N = 420$

a direct experiment. In Fig. 7 the sample the bubston cluster, derived form laser polarimetric scatterometer data, is shown.

For the case illustrated in this figure we have the mean bubston radius $R = 45$ nm. In accordance with (22) we obtain for this radius that the corresponding value of k from the series (21) is 12. The surface charge density $\gamma_i^{AD} \approx 4 \cdot 10^{13} \text{ cm}^{-2}$, and the parameter $B = 4\pi l_B R \gamma_i^{AD} = 170 \gg 1$. Thus the bubstons of that size are strongly charged particles and still capable of coagulation. As is seen from this figure, the experimental realizations of radii of the bubstons belong to rather wide range, which is in agreement with our model (see the series (21)). Summarizing, let us note that the offered model of the coagulation of strongly charged macro-particles should be considered as an alternative to the known model of coagulation put forward in the DLVO theory [86, 87].

4 Conclusions

We showed that under certain conditions the nanometer sized disordered structure of a liquid becomes unstable, which results in a spontaneous growth of the disorder parameter and a local decrease of density of a liquid. This model looks promising for describing the process of nucleation of nanobubbles in a liquid under normal conditions. Besides, the model of screening of strongly charged particles indicates that the charge inversion effect can be interpreted in the framework of a modified Poisson–Boltzmann model. The quantitative basis of this model is the assumption that liquid molecules are arranged on the surface of bubbles in the form of densely packed two-dimensional hexagonal lattice. This assumption gives us the opportunity to connect the surface density of the basic ions and the bulk density of the counter-ions on the surface of a bubble. The performed analysis of the effect of the Brownian motion of charged bubbles shows that the charge inversion effect is manifested in the formation of two types of compound particles of the opposite polarities, which strongly differ in their radii and in the absolute values of their charges. In this case, the equipartition law (62) is obtained for the mean energy of the electric field, created by

both types of compound particles. This result transfers our concepts of the interaction of the charged bubbles in aqueous solutions of electrolytes to a new qualitative level. For example, according to these conceptions, coagulation of identical nanobubbles in an ionic solution should be attributed not to the interaction of likely charged particles (as was done in numerous theoretical publications), but to the interaction of oppositely charged compound particles. Naturally, the proposed model requires further refinement, primarily with respect to the requirement that the ionic solution must be dilute ($\zeta = \kappa R \ll 1$). Of course, the charge inversion effect should exist also in the case, where this requirement is not satisfied, i.e., when the solution is not dilute. It can obviously be affirmed that the effect of Brownian motion on the process of screening must also survive, but the quantitative parameters of the compound particles, formed in this case, may change. Thereby, we may figuratively conclude that in all cases “like likes unlike”.

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References

1. Epstein, P.S., Plesset, M.S.: On the stability of gas bubbles in liquid-gas solutions. *J. Chem. Phys.* **18**(11), 1505–1509 (1950)
2. Ljunggren, S., Eriksson, J.C.: The lifetime of a colloid-sized gas bubble in water and the cause of the hydrophobic attraction. *Colloids Surf. A* **129–130**, 151–155 (1997)
3. Crum, L.A.: Tensile strength of water. *Nature (London)* **278**, 148–149 (1979)
4. Crum, L.A.: Acoustic cavitation thresholds in water. In: Lauterborn, W. (ed.) *Cavitation and Inhomogeneities in Underwater Acoustics*, pp. 3–12. Springer-Verlag, New York (1980)
5. Crum, L.A.: Nucleation and stabilization of micro-bubbles in liquids. *Appl. Sci. Res.* **38**, 101–115 (1982)
6. Crum, L.A.: Nucleation and stabilization of microbubbles in liquids. In: van Wijngaarden, L. (ed.) *Mechanics and Physics of Bubbles in Liquids*, pp. 101–115. Martinus Nijhoff Publishers, The Hague (1982)
7. Sirotyuk, M.G.: Experimental investigations of ultrasonic cavitation. In: Rozenberg, L.D. (ed.) *High Intensity Ultrasonic Fields*, pp. 319–337. Plenum Press, New York (1971)
8. Washburn, E.W. (ed.): *International Critical Tables*, vol. 4. McGraw-Hill, New York (1928)
9. Wagner, C.: Die Oberflächenspannung verdünnter elektrolytlösungen. *Phys. Z.* **25**, 474–477 (1924)
10. Onsager, L., Samaras, N.N.T.: The surface tension of Debye-Hückel electrolytes. *J. Chem. Phys.* **2**, 528–536 (1934)
11. Bunkin, N.F., Bunkin, F.V.: Bubbstons: stable microscopic gas bubbles in very dilute electrolytic solutions. *J. Exp. Theor. Phys.* **74**, 271–278 (1992)
12. Bunkin, N.F., Bunkin, F.V.: Screening of strongly charged macroparticles in liquid electrolyte solutions. *J. Exp. Theor. Phys.* **96**, 730–746 (2003)
13. Bunkin, N.F., Bunkin, F.V.: Adsorption and desorption of ions at the surface of liquid. *Z. Phys. Chem.* **215**, 111–132 (2001)
14. Bunkin, N.F., Lobeyev, A.V., Lyakhov, G.A., Ninham, B.W.: Mechanism of low-threshold hypersonic cavitation stimulated by broadband laser pump. *Phys. Rev. E* **60**, 1681–1690 (1999)
15. Bunkin, N.F., Suyazov, N.V., Shkirin, A.V., Ignatiev, P.S., Indukaev, K.V.: Nanoscale structure of dissolved air bubbles in water as studied by measuring the elements of the scattering matrix. *J. Chem. Phys.* **130**, 134308 (2009)
16. Bunkin, N.F., Suyazov, N.V., Shkirin, A.V., Ignatiev, P.S., Indukaev, K.V.: Screening of strongly charged macroparticles in liquid electrolyte solutions. *JETP* **108**, 800–816 (2009)
17. Bunkin, N.F., Shkirin, A.V., Kozlov, V.A., Starosvetskiy, A.V.: Laser scattering in water and aqueous solutions of salts. *Proc. SPIE* **7376**, 73761D (2010)
18. Bunkin, N.F., Ninham, B.W., Shkirin, A.V., Ignatiev, P.S., Kozlov, V.A., Starosvetskiy, A.V.: Long-living nanobubbles of dissolved gas in aqueous solutions of salts and erythrocyte suspensions. *J. Biophotonics* **4**(3), 150–164 (2011)

19. Bunkin, N.F., Bunkin, F.V.: The new concepts in the optical breakdown of transparent liquids. *Laser Phys.* **3**, 63–78 (1993)
20. Bunkin, N.F., Lobeyev, A.V.: Bubbston-cluster structure under conditions of optical breakdown in a liquid. *Quantum Electron.* **24**, 297–301 (1994)
21. Vinogradova, O.I., Bunkin, N.F., Churaev, N.V., Kiseleva, O.A., Lobeyev, A.V., Ninham, B.W.: Sub-microcavity structure of water between hydrophobic and hydrophilic walls as revealed by optical cavitation. *J. Colloid Interface Sci.* **173**, 443–447 (1995)
22. Bunkin, N.F., Lyakhov, G.A.: Microbubbles of dissolved gas in water: physical studies and possible applications in biological technologies and medicine. *Phys. Wave Phenom.* **13**, 61–80 (2005)
23. Bunkin, N.F., Bakum, S.I.: Role of a dissolved gas in the optical breakdown of water. *Quant. Electron.* **36**, 117–124 (2006)
24. Bunkin, N.F., Kochergin, A.V., Lobeyev, A.V., Ninham, B.W., Vinogradova, O.I.: Existence of charged submicrobubble clusters in polar liquids as revealed by correlation between optical cavitation and electrical conductivity. *Colloid Surf. A* **110**, 207–212 (1996)
25. Bunkin, N.F., Kiseleva, O.A., Lobeyev, A.V., Movchan, T.G., Ninham, B.W., Vinogradova, O.I.: Effect of salts and dissolved gas on optical cavitation near hydrophobic and hydrophilic surfaces. *Langmuir* **13**, 3024–3028 (1997)
26. Bunkin, N.F., Ninham, B.W., Babenko, V.A., Suyazov, N.V., Sychev, A.A.: Role of dissolved gas in optical breakdown of water: differences between effects due to helium and other gases. *J. Phys. Chem. B* **114**, 7743–7752 (2010)
27. Chattoraj, D.K., Birdi, K.S.: Adsorption and the Gibbs Surface Excess. Plenum Press, New York (1984)
28. Wilson, M.A., Pohorille, A., Pratt, L.R.: Molecular-dynamics of the water liquid vapor interface. *J. Phys. Chem.* **91**, 4873–4878 (1987)
29. Wilson, M.A., Pohorille, A.: Interaction of monovalent ions with the water liquid vapor interface—a molecular dynamic study. *J. Chem. Phys.* **95**, 6005–6013 (1991)
30. Benjamin, I.: Theoretical-study of ion solvation at the water liquid–vapor interface. *J. Chem. Phys.* **95**, 3698–3709 (1991)
31. Jungwirth, P., Tobias, D.J.: Surface effects on aqueous ionic solvation: a molecular dynamics simulation study of NaCl at the air/water interface from infinite dilution to saturation. *J. Phys. Chem. B* **104**, 7702–7706 (2000)
32. Jungwirth, P., Tobias, D.J.: Molecular structure of salt solutions: a new view of the interface with implications for heterogeneous atmospheric chemistry. *J. Phys. Chem. B* **105**, 10468–10472 (2001)
33. Mucha, M., Frigato, T., Levering, L.M., Allen, H.C., Tobias, D.J., Dang, L.X., Yungwirth, P.: Unified molecular picture of the surfaces of aqueous acid, base, and salt solutions. *J. Phys. Chem. B* **109**, 7617–7623 (2005)
34. Knipping, E.M., Lakin, M.J., Foster, K.L., Yungwirth, P., Tobias, D.J., Dabdub, R.B., Finlayson-Pitts, B.J.: Experiments and simulations of ion-enhanced interfacial chemistry on aqueous NaCl aerosols. *Science* **288**, 301–306 (2000)
35. Stuart, S.J., Berne, B.J.: Surface curvature effects in the aqueous ionic solvation of the chloride ion. *J. Phys. Chem. A* **103**, 10300–10307 (1999)
36. Herce, D.H., Perera, L., Darden, T.A., Sagui, C.: Surface solvation for an ion in a water cluster. *J. Chem. Phys.* **122**, 024513 (2005)
37. Vrbka, L., Mucha, M., Minofar, B., Yungwirth, P., Brown, E.C., Tobias, D.J.: Propensity of soft ions for the air/water interface. *Curr. Opin. Colloid Interface Sci.* **9**, 67–73 (2004)
38. Jungwirth, P., Tobias, D.J.: Specific ion effects at the air/water interface. *Chem. Rev.* **106**, 1259–1281 (2006)
39. Baldelli, S., Schnitzer, C., Shultz, M.J.: The structure of water on HCl solutions studied with sum frequency generation. *Chem. Phys. Lett.* **302**, 157–163 (1999)
40. Schnitzer, C., Baldelli, S., Shultz, M.J.: Sum frequency generation of water on NaCl, NaNO₃, KHSO₄, HCl, HNO₃, and H₂SO₄ aqueous solutions. *J. Phys. Chem. B* **104**, 585–590 (2000)
41. Shultz, M.J., Schnitzer, C., Simonelli, D., Baldelli, S.: Sum frequency generation spectroscopy of the aqueous interface: ionic and soluble molecular solutions. *Int. Rev. Phys. Chem.* **19**, 123–153 (2000)
42. Shultz, M.J., Baldelli, S., Schnitzer, C., Simonelli, D.: Aqueous solution/air interfaces probed with sum frequency generation spectroscopy. *J. Phys. Chem. B* **106**, 5313–5324 (2002)
43. Liu, D.F., Ma, G., Levering, L.M., Allen, H.C.: Vibrational Spectroscopy of aqueous sodium halide solutions and air-liquid interfaces: observation of increased interfacial depth. *J. Phys. Chem. B* **108**, 2252–2260 (2004)
44. Scatena L.F., Richmond, G.L.: Isolated molecular ion solvation at an oil/water interface investigated by vibrational sum-frequency spectroscopy. *J. Phys. Chem. B* **108**, 12518–12528 (2004)

45. Petersen, P.B., Saykally, R.J.: Confirmation of enhanced anion concentration at the liquid water surface. *Chem. Phys. Lett.* **397**, 51–55 (2004)
46. Petersen, P.B., Johnson, J.C., Knutsen, K.P., Saykally, R.J.: Direct experimental validation of the Jones-Ray effect. *Chem. Phys. Lett.* **397**, 46–50 (2004)
47. Weber, R., Winter, B., Schmidt, P.M., Widdra, W., Hertel, I.V., Dittmar, M., Faubel, M.: Photoemission from aqueous alkali-metal-iodide salt solutions using EUV synchrotron radiation. *J. Phys. Chem. B* **108**, 4729–4736 (2004)
48. Winter, B., Weber, R., Schmidt, P.M., Hertel, I.V., Faubel, M., Vrbka, M., Yungwirth, P.: Molecular structure of surface-active salt solutions: photoelectron spectroscopy and molecular dynamics simulations of aqueous tetrabutylammonium iodide. *J. Phys. Chem. B* **108**, 14558–14564 (2004)
49. Ghosal, S., Shbeeb, A., Hemminger, J.C.: Surface segregation of bromine in bromide doped NaCl: implications for the seasonal variations in Arctic ozone. *Geophys. Res. Lett.* **27**, 1879–1882 (2000)
50. Finlayson-Pitts, B.J., Hemminger, J.C.: Physical chemistry of airborne sea salt particles and their components. *J. Phys. Chem. A* **104**, 11463–11477 (2000)
51. Kelsall, G.H., Tang, S., Yurdakul, S., Smith, A.: Electrophoretic behaviour of bubbles in aqueous electrolytes. *J. Chem. Soc. Faraday Trans.* **92**, 3887–3893 (1996)
52. Bernal, J.D., Fowler, R.H.: A theory of water and ionic solutions, with particular reference to hydrogen and hydroxyl ions. *J. Chem. Phys.* **1**, 515–548 (1933)
53. Eisenberg, D., Kauzmann, W.: *The Structure and Properties of Water*. Oxford University Press, London (1969)
54. Pauling, L.: The structure of water. In: Hadzi, D., Thompson, H.W. (eds.) *Hydrogen Bonding*, pp. 1–6. Pergamon Press Ltd, London (1959)
55. Kamb, B.: Ice polymorphism and the structure of water. In: Rich, A., Davidson, N. (eds.) *Structural Chemistry and Molecular Biology*, pp. 507–542. W.H. Freeman, San Francisco (1968)
56. Dore, J.C.: Structural studies of water and other hydrogen-bonded liquids by neutron-diffraction. *J. Mol. Struct.* **250**, 193–211 (1991)
57. Boutron, P., Alben, A.: Structural model for amorphous solid water. *J. Chem. Phys.* **62**, 4848–4853 (1975)
58. Svishchev, I.M., Kusalik, P.G.: Structure in liquid water - a study of spatial-distribution functions. *J. Chem. Phys.* **99**, 3049–3058 (1993)
59. Kusalik, P.G., Svishchev, I.M.: The spatial structure in liquid water. *Science* **265**, 1219–1221 (1994)
60. Narten, A.H., Thiessen W., Blum, L.: Atom pair distribution-functions of liquid water at 25-degrees-c from neutron-diffraction. *Science* **217**, 1033–1034 (1982)
61. Chialvo, A.A., Cummings, P.T., Simonson, J.M., Mesmer, J.M., Cochran, H.D.: Interplay between molecular simulation and neutron scattering in developing new insights into the structure of water. *Ind. Eng. Chem. Res.* **37**, 3021–3025 (1998)
62. <http://www.lsbu.ac.uk/water>
63. Balescu, R.: *Equilibrium and Nonequilibrium Statistical Mechanics*. Wiley, New York, (1975)
64. Landau, L.D., Lifshitz, E.M.: *Theory of Elasticity*. Butterworth-Heinemann, Oxford (1986)
65. Landau, L.D., Lifshitz, E.M.: *Statistical Physics, Part 1*. Butterworth-Heinemann, Oxford (1980)
66. Pitaevskii, L.P., Lifshitz, E.M.: *Physical Kinetics*. Pergamon Press Ltd, London (1981)
67. Archer, A.J., Wilding, N.B.: Phase behavior of a fluid with competing attractive and repulsive interactions. *Phys. Rev. E* **76**, 031501 (2007)
68. Lugli, F., Hofinger, S., Zerbetto, F.: The collapse of nanobubbles in water. *J. Am. Chem. Soc.* **127**, 8020–8021 (2005)
69. Fabelinskii, I.L.: *Molecular Scattering of Light*. Plenum Press, New York (1968)
70. Conway, B.E.: The evaluation and use of properties of individual ions in solutions. *J. Solution Chem.* **7**, 721 (1978)
71. Debye, P.W., Huckel, E.: Zur theorie der elektrolyte II. Das grenzgesetz für die elektrische leitfähigkeit. *Physik Z.* **24**, 305–325 (1923)
72. Ise, N., Okubo, T.: Ordered distribution of electrically charged solutes in dilute solutions. *Accounts Chem. Res.* **13**, 303–309 (1980)
73. Kepler, G.M., Fraden, S.: Attractive potential between confined colloids at low ionic-strength. *Phys. Rev. Lett.* **73**, 356–359 (1994)
74. Dosho, S., Ise, N., Ito, K., Iwai, S., et al.: Recent study of polymer latex dispersions. *Langmuir* **9**, 394–411 (1993)
75. Matsuoka, Y., Harada, T., Yamaoka, H.: An exact evaluation of salt concentration-dependence of interparticle distance in colloidal crystals by ultra-small-angle x-ray-scattering. *Langmuir* **10**, 4423–4425 (1994)

76. Crocker, J.C., Grier, D.G.: Microscopic measurement of the pair interaction potential of charge-stabilized colloid. *Phys. Rev. Lett.* **73**, 352–355 (1994)
77. Crocker, J.C., Grier, D.G.: When like charges attract: the effects of geometrical confinement on long-range colloidal interactions. *Phys. Rev. Lett.* **77**, 1897–1900 (1996)
78. Larsen, A.E., Grier, D.G.: Like-charge attractions in metastable colloidal crystallites. *Nature* **385**, 230–233 (1997)
79. Ise, N.: When does like like like? Microscopic inhomogeneity in homogeneous ionic systems. *Proc. Jpn. Acad. B* **78**, 129–137 (2002)
80. Zheng, J., Pollack, G.H.: Long-range forces extending from polymer-gel surfaces. *Phys. Rev. E* **68**, 031408 (2003)
81. Gomez-Guzman, O., Ruiz-Garcia, J.: Attractive interactions between like-charged colloidal particles at the air/water interface. *J. Colloid Interface Sci.* **291**, 1–6 (2005)
82. Zheng, J., Chin, W., Khijniak, E., Khijniak Jr., E., Pollack, G.H.: Surfaces and interfacial water: evidence that hydrophilic surfaces have long-range impact. *Adv. Colloid Interface Sci.* **127**, 19–27 (2006)
83. Liang, Y., Hilal, N., Langston, P., Starov, V.: Interaction forces between colloidal particles in liquid: theory and experiment. *Adv. Colloid Interface Sci.* **134–135**, 151–166 (2007)
84. Zheng, J., Wexler, A., Pollack, G.H.: Effect of buffers on aqueous solute-exclusion zones around ion-exchange resins. *J. Colloid Interface Sci.* **332**, 511–514 (2009)
85. Nagornyyak, E., Yoo, H., Pollack, G.H.: Mechanism of attraction between like-charged particles in aqueous solution. *Soft Matter* **5**, 3850–3857 (2009)
86. Derjaguin, B.V., Landau, L.D.: Theory of stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochimica (USSR)* **14**, 633–645 (1941)
87. Verwey, E.J., Overbeek, J.T.G.: *Theory of the Stabilization of Lyophobic Colloids*. Elsevier, Amsterdam (1948)
88. Yoon, R., Jordan, J.L.: Zeta-potential measurements on microbubbles generated using various surfactants. *J. Colloid Interface Sci.* **113**, 430–438 (1986)
89. Li, C., Somasundaran, P.: Reversal of bubble charge in multivalent inorganic salt-solutions—effect of magnesium. *J. Colloid Interface Sci.* **146**, 215–218 (1991)
90. Li, C., Somasundaran, P.: Reversal of bubble charge in multivalent inorganic salt-solutions—effect of lanthanum. *Colloid Surf. A* **81**, 13–15 (1993)
91. Mateescu, E.M., Jeppesen, C., Pincus, P.: Overcharging of a spherical macroion by an oppositely charged polyelectrolyte. *Europhys. Lett.* **46**, 493–498 (1999)
92. Park, S.Y., Bruinsma, R.F., Gelbart, W.M.: Spontaneous overcharging of macro-ion complexes. *Europhys. Lett.* **46**, 454–460 (1999)
93. Joanny, J.F.: Polyelectrolyte adsorption and charge inversion. *Eur. J. Phys. B* **9**, 117–122 (1999)
94. Perel, V.I., Shklovskii, B.I.: Screening of a macroion by multivalent ions: a new boundary condition for the Poisson-Boltzmann equation and charge inversion. *Physica A (Amsterdam)* **274**, 446–453 (1999)
95. Shklovskii, B.I.: Screening of a macroion by multivalent ions: correlation-induced inversion of charge. *Phys. Rev. E* **60**, 5802–5811 (1999)
96. Nguyen, T.T., Grosberg, F.Yu., Shklovskii, B.I.: Screening of a charged particle by multivalent counterions in salty water: strong charge inversion. *J. Chem. Phys.* **113**, 1110–1125 (2000)
97. Nguyen, T.T., Grosberg, F.Yu., Shklovskii, B.I.: Macroions in salty water with multivalent ions: giant inversion of charge. *Phys. Rev. Lett.* **85**, 1568–1571 (2000)
98. Levin, Y.: Electrostatic correlations: from plasma to biology. *Rep. Prog. Phys.* **65**, 1577–1632 (2002)
99. Quesada-Perez, M., Gonzalez-Tovar, E., Martin-Molina, A., Lozada-Cassou, M., Hidalgo-Alvarez, R.: Overcharging in colloids: beyond the Poisson-Boltzmann approach. *ChemPhysChem* **4**, 235–248 (2003)
100. Grosberg, F.Yu., Nguyen, T.T., Shklovskii, B.I.: Colloquium: the physics of charge inversion in chemical and biological systems. *Rev. Mod. Phys.* **74**, 329–345 (2002)
101. Zhang, R.; Shklovskii, B.I.: Long-range polarization attraction between two different like-charged macroions. *Phys. Rev. E* **72**, 021405 (2005)
102. Pittler, J., Bu, W., Vakhnin, D., Travesset, A., McGillivray, D.J., Losche, M.: Charge inversion at minute electrolyte concentrations. *Phys. Rev. Lett.* **97**, 046102 (2006)
103. Gracheva, M.E., Leburton, J.P.: Electrolytic charge inversion at the liquid-solid interface in a nanopore in a doped semiconductor membrane. *Nanotechnology* **18**, 145704 (2007)
104. Faraudo, J., Travesset, A.: The many origins of charge inversion in electrolyte solutions: effects of discrete interfacial charges. *J. Phys. Chem. C* **111**, 987–994 (2007)

105. Calero, C., Faraudo, J.: Enhancement of charge inversion by multivalent interfacial groups. *Phys. Rev. E* **80**, 042601 (2009)
106. Terao, T., Nakayama, T.: Charge inversion of colloidal particles in an aqueous solution: screening by multivalent ions. *Phys. Rev. E* **63**, 041401 (2001)
107. Wang, Z.Y., Ma, Y.Q.: Monte Carlo determination of mixed electrolytes next to a planar dielectric interface with different surface charge distributions. *J. Chem. Phys.* **131**, 244715 (2009)
108. Wang, Z.Y., Ma, Y.Q.: Insights from Monte Carlo simulations on charge inversion of planar electric double layers in mixtures of asymmetric electrolytes. *J. Chem. Phys.* **133**, 064704 (2010)
109. Dukhin, S.S., Deryaguin, B.V.: *Electrophoresis*. Nauka, Moscow (1976, in Russian)
110. Landau, L.D., Lifshitz, E.M.: *Fluid Mechanics*. Pergamon Press, Oxford (1987)
111. Langevin, P.: Sur la théorie du mouvement brownien. *Coptes Rendus (Paris)* **146**, 530–533 (1908)
112. Tikhonov, V.I.: *Outliers in Random Processes*. Nauka, Moscow (1970, in Russian)
113. Jullien, R.: Aggregation phenomena and fractal aggregates. *Cont. Phys.* **28**, 477–493 (1987)