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Electroacoustic theory for concentrated colloids with overlapped DLs at arbitrary κa
I. Application to nanocolloids and nonaqueous colloids

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Abstract

Existing theories of electroacoustic phenomena in concentrated colloids neglect the possibility of double layer overlap and are valid mostly for the "thin double layer," when the double layer thickness is much less than the particle size. In this paper we present a new electroacoustic theory which removes this restriction. This would make this new theory applicable to characterizing a variety of aqueous nanocolloids and of nonaqueous dispersions. There are two versions of the theory leading to the analytical solutions. The first version corresponds to strongly overlapped diffuse layers (so-called quasi-homogeneous model). It yields a simple analytical formula for colloid vibration current (CVI), which is valid for arbitrary ultrasound frequency, but for restricted κa range. This version of the theory, as well the Smoluchowski theory for microelectrophoresis, is independent of particle shape and polydispersity. This makes it very attractive for practical use, with the hope that it might be as useful as classical Smoluchowski theory. In order to determine the κa range of the quasi-homogeneous model validity we develop the second version that limits ultrasound frequency, but applies no restriction on κa. The ultrasound frequency should substantially exceed the Maxwell–Wagner relaxation frequency. This limitation makes active conductivity related current negligible compared to the passive dielectric displacement current. It is possible to derive an expression for CVI in the concentrated dispersion as formulae inhering definite integrals with integrands depending on equilibrium potential distribution. This second version allowed us to estimate the ranges of the applicability of the first, quasi-homogeneous version. It turns out that the quasi-homogeneous model works for κa values up to almost 1. For instance, at volume fraction 30%, the highest κa limit of the quasi-homogeneous model is 0.65. Therefore, this version of the electroacoustic theory is valid for almost all nonaqueous dispersions and a wide variety of nanocolloids, especially with sizes under 100 nm.
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1. Introduction

Electroacoustics is gradually gaining appreciation as a powerful technique for characterizing electric surface properties. It is a potential replacement for microelectrophoresis in many scientific and industrial applications. Many obstacles in this development have been overcome, yet some still remained unresolved.

The main problem that limits applications of this technique to the small nanoscale particles and low-conducting liquids is the lack of the appropriate theory. There are already several versions of the electroacoustic theory for concentrates [1–6], overviewed in the book [7]. They cover concentrated dispersions due to incorporating particle hydrodynamic and electrodynamic interaction. They are valid in the wide frequency range that is essential for electroacoustic measurements.

However, these theories employ one important assumption that restricts the range of their validity. They do not take into account overlap of double layers that might occur in concentrated dispersions. In addition most of them employ a so-called "thin double layer" assumption. The following analysis would demonstrate that these two assumptions are not acceptable for a variety of nanocolloids and nonaqueous dispersions.

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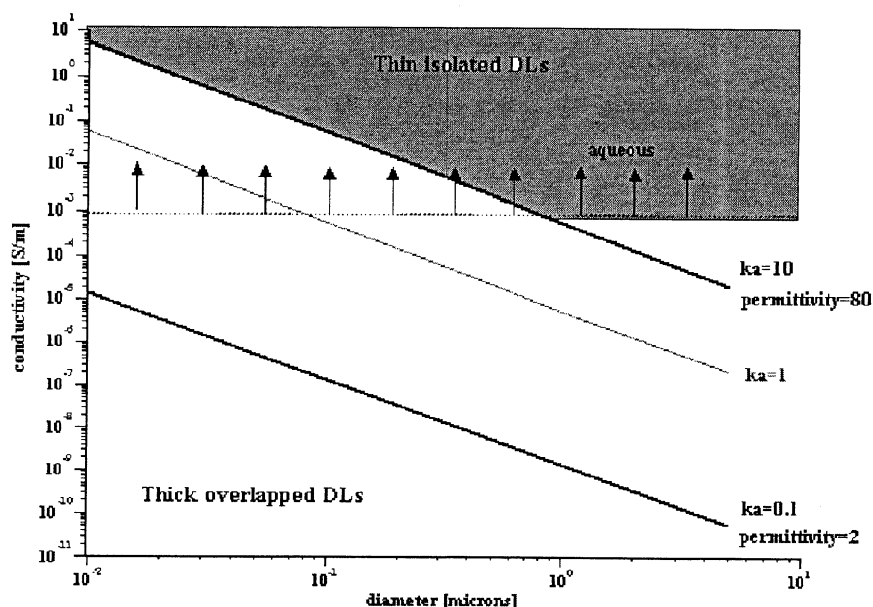 *E-mail address:* adukhin@dispersion.com (A.S. Dukhin).

Fig. 1. Various ranges of κa depending on the conductivity of dispersion and particle diameter.

The "thin DL assumption" implies that the thickness of the double layer (DL), the so-called Debye screening length κ^{-1}, is much smaller than the particle radius a. The "thin DL" assumption restricts particle size. In addition it limits ionic strength, or alternatively conductivity of the solution, due to the Debye length dependence on these parameters. There is a simple approximate expression that allows us to scope a range of the particle size and conductivity values for valid "thin DL" assumption:

$$\kappa a \approx \sqrt{\frac{K_m a^2}{\varepsilon_0 \varepsilon_m D_{\text{eff}}}} \gg 1, \tag{1}$$

where K_m is the conductivity of the medium, ε_0 is the dielectric permittivity of vacuum, ε_m is the dielectric permittivity of the medium, and D_{eff} is the effective diffusion coefficient.

The classical electrokinetic theory [8,9] introduces 3 approximate separate ranges of κa values: $\kappa a > 10$; $\kappa a < 0.1$; $10 > \kappa a > 0.1$ (Fig. 1). The numbers 10 and 0.1 are approximate borders of these ranges. There are much more sophisticated ways to determine these borders using modern electrophoretic theories [10,11]. However, these approximate numbers allow us to explain the main ideas of this paper.

The range of K_m and a where $\kappa a > 10$ can be considered as a range of the "thin DL" theory validity. In regard to the theory of electrophoresis, it is the range where the Smoluchowski theory [12] works.

The range of K_m and a where $\kappa a < 0.1$ can be considered as a range of the "thick DL." This is the range of the Huckel theory [13] for electrophoresis.

The range of K_m and a where $10 > \kappa a > 0.1$ can be considered as a transition range between the "thin DL" and the "thick DL." In the classical electrophoresis theory this transition is described by Henry–Ohshima function [14,15] if surface conductivity is negligible.

The same conventional ranges of κa values, and consequently K_m and a values, can be used for the electroacoustic theory development. The main efforts, as we stated before, have been concentrated on the range of $\kappa a > 10$, the range of "thin DL." The one exception, the theory developed by Babchin with co-authors [37], unfortunately is not valid for concentrates, as we will show below.

As one can see, the "thin DL" range covers aqueous dispersions with sizes above 1 µm. However, the large portion of aqueous dispersions with sub-micrometer belongs to the transition range of moderate κa values. Practically all nanocolloids with sizes under 100 nm belong to this range. This means that "thin DL" electroacoustic theories would have problems dealing with nanocolloids.

This situation becomes even more pronounced for nonaqueous systems. Usually conductivity of the nonaqueous systems is orders of magnitude lower than that of aqueous ones. This leads to the much smaller κa values. Practically all nonaqueous dispersions belong to the range of either moderate or low κa.

Nanocolloids and nonaqueous dispersions are very important classes of heterogeneous systems. The lack of the appropriate electroacoustic theory certainly justifies efforts for creating one. This is not an easy task, compared to the case of the "thin DL." The last one offers several simplifications that cannot be used for other two κa ranges.

One of the main advantages of the "thin DL" range for theoretical development is the possibility to consider double layers as isolated, not overlapped. This assumption brings enormous simplification for mathematical modeling.

Expansion of the electroacoustic theory to the other κa ranges would force us to drop this simplification. It is clear

that thick DLs would overlap at much lower volume fractions compared to the case of the thin DLs. It is possible to introduce a critical volume fraction φ_{over} above which DLs overlap. This parameter can be determined following [7] as a volume fraction for which the Debye length is equal to the shortest distance between the particles. Thus

$$\varphi_{over} \approx \frac{0.52}{\left(1 + \frac{1}{\kappa a}\right)^3}. \tag{2}$$

This expression indicates that a strong nonlinear κa dependence leads to the DL overlap even for practically dilute systems if $\kappa a < 1$. For instance, DLs start to overlap at the volume fraction 0.04% if $\kappa a = 0.1$.

Existing Babchin's [37] electroacoustic theory for small κa neglects DL overlap. This makes it of little use for electroacoustics, which targets concentrated dispersions and emulsions. Creation of a new theory that would take DL overlap into consideration is imperative for further successful development of this characterization technique.

As far as we know, only one attempt has been made to develop electroacoustic theory for concentrates at the low and moderate κa values with overlapping DLs. It is Ohshima's electroacoustic theory for "salt free media" [16–18]. This is an imaginary case where there are only counterions present in the bulk between particles. This could correspond to the real systems with completely overlapped DLs and extremely high surface charge. Unfortunately this model is hardly applicable to the real dispersions, but it revealed several peculiar features of the "not thin DL" theory.

For instance it predicts a completely different nature of the "surface charge–surface potential" relationship. It predicts a so-called "condensation effect" that restricts uncontrolled growth of the surface potential. Stern layer follows directly from the mathematical theory, in contrast to the classical DL theory, where it must be introduced as an additional entity.

We will follow this line and will show that surface charge and surface potential (or ζ-potential) played very different roles in the surface characterization, compared to the "thin DL" case.

Ohshima's theory tells us also that appropriate modeling of the ion distribution in the interparticles space might lead to a significant simplification of the mathematical theory. The question is to find a more suitable distribution.

In this paper we use two different models. The first one, following Ohshima, considers strongly overlapped DLs, when Debye screening length exceeds substantially the characteristic distance between the surfaces of neighboring particles in the dispersion. In this so-called "quasi-homogeneous" case, the relative variation of the concentration of every ionic component in the equilibrium double layer is negligible. This allows us to model ion concentrations as space independent, which leads also to the space independent constant conductivity. This "quasi-homogeneous model" allows us to take into account all ion species, not only counterions as in Ohshima's theory. Consequently,

"quasi-homogeneous model" is much closer to the real colloids.

The quasi-homogeneous model does not apply any restrictions on the frequency. However, it is clear that the "quasi-homogeneous model" is valid for the restricted range of low and, perhaps, moderate κa values. It is impossible to determine the κa validity range being within this model framework. It turns out that there is a possibility for one more model, which would allow us to determine the validity range of the "quasi-homogeneous model."

This possibility corresponds to the case where the double layer is thick enough compared to ion diffusion drift during the period of reciprocal cyclic frequency of ultrasound. It occurs when the DL relaxation time (Maxwell–Wagner relaxation time [18–20]) exceeds substantially the reciprocal cyclic frequency of the ultrasound. In other words, this is the case where frequency of measurement is much higher than Maxwell–Wagner frequency.

It is known that active conductivity current equals the passive dielectric displacement current at the Maxwell–Wagner frequency. For frequencies much higher than Maxwell–Wagner frequency, active conductivity current becomes negligible compared to the dielectric displacement current.

The dielectric displacement current is independent of the concentration of ions, whereas conductivity current completely depends on it. If the measurement frequency exceeds significantly the Maxwell–Wagner frequency, we could neglect conductivity current and consequently eliminate dependence on the ion concentration in the complex structure of the overlapped DLs from the mathematical electrodynamic equations. This simplification is sufficient for creating an analytical electroacoustic theory. We will call this model a "high frequency model."

Summarizing, we could say that we develop in this paper two approximate analytical electroacoustic theories for concentrates. The first one, the "quasi-homogeneous model," is valid for any frequency, but restricts the κa from above. The second one, the "high frequency model," restricts frequency, but is valid for any κa.

The second model is much more complicated mathematically. However, it allows us to determine range of κa where the first model is valid.

We develop these theories for the colloid vibration current mode of electroacoustics predicted 70 years ago by Debye [21]. Expressions for dynamic electrophoretic mobility should be valid for the ESA mode of electroacoustic mode as well.

2. General electroacoustic theory

Colloid vibration current (CVI) is an alternating electric current generated in the dispersion under the influence of ultrasound. There is a detailed description of this phenomenon given in Chap. 5 of Ref. [7].

The general mathematical formulation of the problem includes equations of conservation for electric charge:

$$\operatorname{div} \vec{i} = -\frac{\partial \rho}{\partial t} \tag{3}$$

and Poisson equation:

$$\operatorname{div} \vec{D} = \rho, \tag{4}$$

where $\vec{i}$ and $\vec{D}$ are the vectors of ionic electric current density and sound-induced electrostatic displacement, correspondingly, ρ is the sound-induced component of bulk density of ionic charge, and t is time.

In electrolyte solution vector $\vec{i}$ includes two components:

- electromigration current $\vec{i}_e = K_m \vec{E}$, caused by the action of sound-induced electric field strength $\vec{E}$ on the medium with conductivity K_m;
- convective current $\vec{i}_v = \rho_0 \vec{v}$, caused by sound-induced movement of liquid with velocity $\vec{v}$ and equilibrium[1] bulk charge ρ_0:

$$\vec{i} = \vec{i}_e + \vec{i}_v = K_m \vec{E} + \rho_0 \vec{v}. \tag{5}$$

Vector $\vec{D}$ is proportional to the vector of the electric field strength in electrolyte solution and in the volume of nonconducting disperse particles:

$$\vec{D} = \varepsilon \vec{E}. \tag{6}$$

For the volume of nonconducting particles,

$$K \equiv K_p \equiv 0, \qquad \varepsilon \equiv \varepsilon_p.$$

For the electrolyte solution,

$$K \equiv K_m, \qquad \varepsilon \equiv \varepsilon_m.$$

The system of Eqs. (3) and (4) may be transformed to the one complex equation of continuity of the complex current. This well-known procedure represents the time dependence of all field-induced values X_i with the factor $e^{j\omega t}$:

$$X_i(r, t) = X_i(r) e^{j\omega t}, \tag{7}$$

where j is a complex unit number, and ω is ultrasound frequency.

Applying transformation (7) to the $\vec{i}$, $\vec{D}$, and ρ, and taking into account that $\partial \rho / \partial t = j\omega \rho$, it is easy to derive from Eqs. (3) and (4) the following equation for the complex current:

$$\operatorname{div} \vec{i}^* = 0, \tag{8}$$

where

$$\vec{i}^* = \vec{i}_e^* + \vec{i}_v \equiv K^* \vec{E}_1 + \rho_0 \vec{v} \equiv (K + i\omega\varepsilon) \vec{E}_1 + \rho_0 \vec{v} \tag{9}$$

---

[1] Sound-induced charge density ρ_1 is neglected here because the product of the two (ρ_1 and v) sound-induced multipliers occurs out of the linear approximation with respect to the ultrasonic amplitude.

is a complex electric current density, which besides the contribution of both electromigration $K E_1$ and convective $\rho_0 v$ components includes the contribution of the sound-induced displacement current, $i\omega\varepsilon E_1$, which is connected with the dielectric re-polarization.

Introducing the sound-induced electric potential φ_1

$$E_1 = -\operatorname{grad} \varphi_1 \tag{10}$$

and substituting (10) into (9) and (8) we obtain the equation that describes the space distribution of the sound-induced electric potential φ_1:

$$\operatorname{div}\big\{(K_m + i\omega\varepsilon_m) \operatorname{grad} \varphi_1\big\} = \operatorname{grad} \rho_0 \cdot \vec{v}. \tag{11}$$

This equation can be simplified by taking into account the linear approximation with respect to the applied field. We should consider coefficients ρ_0 and K_m as independent of the driving force that is a gradient of ultrasound pressure for the CVI mode of electroacoustics.

The distribution of the sound-induced potential φ_1 within the dielectric particles should satisfy the Laplace equation:

$$\nabla^2 \varphi_1' = 0. \tag{12}$$

The boundary conditions on the particle–solution interface S for this potential are continuity of the potential,

$$\big(\varphi_1 - \varphi_1'\big)\big|_S = 0, \tag{13}$$

together with continuity of the normal components of the electrostatic induction:

$$\left(\varepsilon_m \frac{\partial \varphi_1}{\partial n} - \varepsilon_p \frac{\partial \varphi_1'}{\partial n}\right)\bigg|_S = 0. \tag{14}$$

The relation between CVI and local complex current i^* is given with the usual (see, for example, [23,24]) definition of CVI as macroscopic electric current, which is induced by ultrasound under the condition of shortly closed effective external circle, providing zero-value of the gradient of macroscopic electric potential:

$$\langle E \rangle = 0, \tag{15}$$

$$\mathrm{CVI} \equiv \langle i^* \rangle = \frac{1}{V} \int_V i^* \, dV \big|_{\langle \vec{E}_1 \rangle = 0} \equiv \varphi \frac{\rho_p - \rho_m}{\rho_m} \mu_d \cdot \langle \operatorname{grad} P \rangle, \tag{16}$$

$$\langle \vec{E}_1 \rangle = \frac{1}{V} \int_V \vec{E}_1 \, dV \equiv -\frac{1}{V} \int_V \operatorname{grad} \varphi_1 \, dV. \tag{17}$$

The macroscopic current and potential gradient defined by Eqs. (16) and (17) represent the average of corresponding local values over the volume element V of a suspension containing a large amount of particles. At the same time this element must be small with respect to ultrasound wavelength. We also use the notion of the dynamic electrophoretic mobility μ_d introduced by O'Brien [22–24]. Parameters φ, ρ_m, and ρ_p are, correspondingly, volume fraction, density of media, and density of disperse particles in the dispersion, $\langle \operatorname{grad} P \rangle$—macroscopic pressure gradient in the ultrasonic wave.

In accordance with the definitions (16) and (6), the value of CVI may be expressed as the averaged sum of the convective current i_v and complex conductivity current i_e^*. Among the distributions ρ_0, $\vec{v}$, K_m, and $\vec{E}_1^*$, only the last one has an entirely electroacoustic nature. Electric charge density ρ_0 and conductivity K_m may be derived from the theory of equilibrium DL.

The space distribution of $\vec{v}$ includes, generally speaking, a weak contribution of the electroacoustic effect. The main part of $\vec{v}$ has a pure acoustic nature. It is induced by inertial forces acting in the vibrating system with space nonhomogeneous density.

Analytical solution of the general mathematical problem formulated by Eqs. (11)–(16) requires further simplifications and modeling, in particular with regard to the conductivity and electric charge space distributions. We use two simplifying models: the "quasi-homogeneous model" and the "high frequency model." These models and corresponding solutions are given in the following sections.

3. Quasi-homogeneous model

In Section 1 we gave a short overview of the role of the parameter κa in the electrokinetic and electroacoustic phenomena. This traditional presentation is based on the comparison of the DL thickness with the characteristic dimension of the dispersion. In the case of the traditional dilute systems there is only one special parameter to compare the Debye length with; it is particle size a. That is why parameter κa is chosen for characterizing many DL related effects.

In concentrated dispersions the other special parameter appears; it is an average distance between particles d. In the case of the "thick DL" this parameter is of greater importance because it determines the degree of DL overlap. In this section we consider the situation where DLs overlap strongly, which corresponds to the following relationship between Debye length and interparticle distance:

$$\kappa d \ll 1. \tag{18}$$

In this case the characteristic space that is accessible for ions is much narrower than the Debye screening length κ^{-1}. There is no noticeable deviation from the homogeneous distribution of ions that may arise in disperse medium. We could neglect these deviations completely, considering ion concentrations $C_0^\pm$ constant, space independent. This is the essence of the quasi-homogeneous model.

In the frame of this model, there is one well-known [25–27] feature of the equilibrium electric potential Φ_0 in the dispersion medium: in the depth of suspension with strongly overlapped double layers the value of Φ_0 occurs to be space-homogeneous and equal to the potential of the surface (ζ-potential)

$$\Phi_0 = \zeta. \tag{19}$$

The theory of a diffuse screening layer connects directly the distribution of screening charge density ρ_0 with equilibrium electric potential Φ_0 and, hence, ρ_0 also occurs to be spatially homogeneous in the dispersion medium:

$$\rho_0 = \frac{RT}{F}\varepsilon_m\kappa^2 \sinh\frac{F\Phi_0}{RT} \approx \frac{RT}{F}\varepsilon_m\kappa^2 \sinh\frac{F\zeta}{RT}. \tag{20}$$

In the frame of the same theoretical approach the local concentrations of cations and anions (upper index "+" and "−") may be expressed as

$$C_0^\pm = \frac{1}{2}\frac{RT}{F^2}\varepsilon_m\kappa^2 \exp\left(\mu\frac{F\zeta}{RT}\right). \tag{21}$$

The space independence of ion concentrations $C_0^\pm$ means space independence of the local conductivity K_m:

$$K_m = \frac{F^2}{RT}\left(D^+ C_0^+ + D^- C_0^-\right). \tag{22}$$

In the frame of the quasi-homogeneous model we can derive a simple relationship between the surface charge density σ and the ζ-potential, even without using the cell model (i.e., for arbitrary geometry of disperse phase). The condition of the dispersion electroneutrality can be written as the following simple equation:

$$\sigma\varphi s = (1 - \varphi)\rho_0, \tag{23}$$

where s is the specific (for unit volume of disperse phase) surface of the disperse phase and ρ_0 local bulk charge density given with Eq. (20).

It follows from Eqs. (23) and (20) that

$$\sigma = \frac{1}{s}\frac{RT}{F}\frac{1-\varphi}{\varphi}\varepsilon_m\kappa^2 \sinh\tilde{\zeta}. \tag{24}$$

For monodisperse dispersion of spherical particles, when $s = 3/a$ Eq. (24) becomes

$$\sigma = \frac{1}{3}\frac{RT}{F}\frac{1-\varphi}{\varphi}\varepsilon_m a\kappa^2 \sinh\tilde{\zeta}. \tag{25}$$

This equation reflects a very important distinction between "thin DL" and "thick, overlapped DL." In the case of the traditional "thin DL" theory, both surface charge and ζ-potential are surface properties, independent of the volume fraction.

In the case of "thick DL," surface charge is a true parameter of the surface properties. The electrokinetic ζ-potential might lead to erroneous conclusions because it depends on the volume fraction, not only on surface charge. For instance, if we have surface charge caused by adsorption of ions, the value of the surface charge characterizes this adsorption. It remains constant and volume fraction independent for the same adsorption. At the same time ζ might be different due to the volume fraction dependence. This means that the ζ-potential value might lead to the wrong conclusions about adsorption. This all indicates that both ζ and surface charge must be reported when dealing with concentrated dispersions with thick DL.

Due to the space independence of the local conductivity K_m and equilibrium screening charge density ρ_0 within the interparticle electrolyte medium, Eq. (11) reduces to the Laplace equation:

$$\nabla^2 \varphi_1 = 0. \tag{26}$$

The problem of the distribution of field-induced electric potential φ_1 in the limiting case of a strongly overlapped electric double layer is completely equivalent to the problem of the potential distribution in the system of dielectric particles in the dielectric medium. It is clear that the condition (15) of the zero macroscopic potential gradient (characteristic of CVI mode) means automatically zero values of the local electric fields $\vec{E}_1$ everywhere in the dispersion.

This leads to the zero values of the local electromigration currents everywhere in the dispersion. As a result, in accordance with Eqs. (9) and (20), formula (16) for CVI reduces to the simple form

$$\text{CVI} = \rho_0 \cdot \langle \vec{v} \rangle = \frac{RT}{F} \varepsilon_m \kappa^2 \sinh \frac{F\zeta}{RT} \langle \vec{v} \rangle, \tag{27}$$

where $\langle \vec{v} \rangle \equiv (1/V) \int_V \vec{v}\, dV$ is the macroscopic velocity of dispersion medium with respect to the dispersed particles. We also take into account that in the case of strongly overlapped double layers the density of screening charge ρ_0 is space-independent everywhere in the liquid that flows with respect to particles with the velocity $\vec{v}$.

The value $\langle \vec{v} \rangle$ represents the drag of the liquid through the system of the particles, under the action of inertial forces caused by sound-induced vibration movement of the considered infinitesimal element V. This drag of the liquid may be expressed through the pressure gradient in the sound wave $\langle \nabla P_\infty \rangle$ by means of the well-known "coupled phase model" (see, for example, [7,28,29])

$$\langle \vec{v} \rangle = \frac{\varphi}{\gamma} \frac{\rho_p - \rho_s}{\rho_s + i\omega(1 - \varphi)\frac{\varphi}{\gamma}\rho_p\rho_m} \langle \nabla P_\infty \rangle, \tag{28}$$

where $\rho_s = \rho_p + (1 - \varphi)\rho_m$ is an average density of the dispersion; $\gamma = (9\eta\varphi\Omega)/2a^2$, η is a dynamic viscosity of the dispersion media; and Ω is a drug coefficient introduced as following in the Stokes law; $F = 6\pi\eta a\Omega v$.

Eqs. (22) and (23) lead to the new equation for the CVI of the strongly overlapped diffuse double layers between the particles (for quasi-homogeneous approximation):

$$\text{CVI} = \frac{2RT\varepsilon_m}{9F\eta\Omega} (\kappa a)^2 \sinh\left(\frac{F\zeta}{RT}\right)$$
$$\times \frac{\rho_p - \rho_s}{\rho_s + i\omega(1 - \varphi)\frac{\varphi}{\gamma}\rho_p\rho_m} \langle \nabla P_\infty \rangle. \tag{29}$$

One of the most interesting peculiar features of this expression is the absence of the linear dependence on the volume fraction. This unusual result becomes clearer if we take into account the volume fraction dependent coefficient between surface charge and ζ-potential (Eq. (24)). We can use this equation to express CVI through the surface charge

$$\text{CVI} = \frac{2\sigma s a^2}{9\eta\Omega} \frac{\varphi}{1 - \varphi} \frac{\rho_p - \rho_s}{\rho_s + i\omega(1 - \varphi)\frac{\varphi}{\gamma}\rho_p\rho_m} \langle \nabla P_\infty \rangle \tag{30}$$

or for monodisperse dispersion

$$\text{CVI} = \frac{2\sigma a}{3\eta\Omega} \frac{\varphi}{1 - \varphi} \frac{\rho_p - \rho_s}{\rho_s + i\omega(1 - \varphi)\frac{\varphi}{\gamma}\rho_p\rho_m} \langle \nabla P_\infty \rangle. \tag{31}$$

These expressions for CVI clarify that the quasi-homogeneous model is consistent with the general notion about electroacoustics as a tool for characterizing surface properties. It shows that CVI is proportional to the degree of the surface ionization indeed.

Following the usual electroacoustic theory path, we introduce dynamic electrophoretic mobility, as was done by O'Brien [23,24]:

$$\mu_d = \frac{\text{CVI}}{\varphi\langle \nabla P_\infty \rangle} \frac{\rho_m}{\rho_p - \rho_m}. \tag{32}$$

According to Eq. (31) for CVI, dynamic electrophoretic mobility in the case of strongly overlapped DLs equals

$$\mu_d = \frac{2\sigma a}{3\eta\Omega} \frac{\rho_m}{\rho_s + i\omega(1 - \varphi)\frac{\varphi}{\gamma}\rho_p\rho_m}. \tag{33}$$

The applicability of Eqs. (29)–(33) is restricted only by the condition (18) of the strongly overlapped diffuse layers. There is no restriction on the frequency of ultrasound and characteristic frequency of the screening charge relaxation (Maxwell–Wagner relaxation).

The second model presented below does just the opposite; it restricts ultrasound frequency keeping κa free.

4. High-frequency model

In this version of the electroacoustic theory we restrict frequency instead of κa. If the measurement frequency is much higher than the frequency of Maxwell–Wagner relaxation ω_{MW},

$$\omega \gg \frac{K_m}{\varepsilon_m} \equiv \omega_{MW}, \tag{34}$$

the contribution of the ionic conductivity current to the total complex current is negligible. In this case Eq. (11) reduces to the Poisson equation

$$\nabla^2 \varphi = -\frac{i}{\omega\varepsilon_m} \vec{v} \cdot \text{grad}\, \rho_0. \tag{35}$$

In addition we could neglect the contribution of the ionic current to total current density. As a result the total current density transforms to

$$\vec{i}* = j\omega\varepsilon \vec{E}_1 + \rho_0 \vec{v}. \tag{36}$$

Unfortunately, these simplifications are still not sufficient for analytical solution of the general electroacoustic problem for the complicated geometry of the concentrated dispersed

phase. To solve the problem for a concentrated suspension with arbitrary thickness of DL we use the electrokinetic cell model that is developed in [30].

This cell model replaces the consideration of the dispersion as a multitude of dispersed particles with the consideration of a single cell. This cell represents a single spherical particle with the fraction of dispersion medium that belongs to it. The outer boundary of the cell is modeled as concentric to the particle spherical shell with the outer radius b. The value of b adjusts the solid content in the cell to be equal to the volume fraction φ of particles in dispersion:

$$\frac{a^3}{b^3} = \varphi. \tag{37}$$

Before its application to electrokinetic theory, the cell model was successfully used:

- for pure electrodynamics problems (first of all it is Maxwell–Wagner theory of dielectric permittivity of concentrated mixtures [18–20];
- for pure hydrodynamic problems (an example is the Kuwabara cell model of hydrodynamic permeability of concentrated array of spheres [31], which we use here for describing the motion of particles in the liquid under influence of ultrasound);
- in the theory of equilibrium double layer of the particles in concentrated suspension (for example, [32–34]).

The basic principles of the cell model that are common for all above-mentioned applications are:

(i) equations describing fields in the dispersed phase and dispersion medium and the conditions at the particle surface have the same less-coordinated form for corresponding parts of the cell (central particle, representing the disperse phase, spherical shell, representing the dispersion medium and the surface between them);

(ii) the surface conditions at the outer boundary of the cell should reflect macroscopic fields that are acting in the dispersion and other features of the system as a whole.

In the frame of a spherically symmetrical cell model, the equilibrium distributions of the electric potential and space charge depend on the distance r from the center of the cell only. However, the action of ultrasound introduces a certain direction in the dispersion, which coincides with the wave vector. Therefore, the space dependence of cell sound-induced distributions should include the angle θ between the wave vector and the radius vector of the given point, in addition to the spherical coordinate r.

Under the conditions of the long-wave approximation (wavelength is much larger than particle size) the distribution of acceleration of macroscopic elements of the suspension volume, vibrating in the sound wave, may be considered a homogeneous vector distribution. Consequently, the components of local sound-induced vector fields, for example,

electric current density $\vec{j}$ and liquid velocity $\vec{v}$, may be represented as

$$
\begin{aligned}
\vec{j}(r, \theta, t) &= e^{j\omega t} \vec{j}(r, \theta, \omega) \\
&= e^{j\omega t} \{ \vec{i}_r j_r(r, \omega) \cos\theta + \vec{i}_r j_\theta(r, \omega) \sin\theta \}, \quad (38)
\end{aligned}
$$

$$
\begin{aligned}
\vec{v}(r, \theta, t) &= e^{i\omega t} \vec{v}(r, \theta, \omega) \\
&= e^{i\omega t} \{ \vec{i}_r v_r(r, \omega) \cos\theta + \vec{i}_\theta v_\theta(r, \omega) \sin\theta \}, \quad (39)
\end{aligned}
$$

while the distributions of sound-induced scalar fields, for example, electric potential φ_1 and pressure P, have the following form:

$$\varphi_1(r, \theta, t) = e^{i\omega t} \varphi_1(r, \theta, \omega) \cos\theta = e^{i\omega t} \varphi_1(r, \omega) \cos\theta, \tag{40}$$

$$P(r, \theta, t) = e^{i\omega t} P(r, \theta, \omega) \cos\theta = e^{i\omega t} P(r, \omega) \cos\theta. \tag{41}$$

In order to find the sound-induced electric potential and current which are in accordance with the above-mentioned basic principles, we have to consider Laplace equation (12) for the inner space of the particle $(0 \leqslant r \leqslant a)$ and Eq. (35) for the space of spherical shell $(a < r \leqslant b)$ that represents the dispersion medium.

For the surface $r = a$ between the particle and dispersion medium, Eqs. (14) and (15) specify the surface conditions.

The surface condition at the outer boundary of the cell $(r = b)$ in the case of CVI should reflect the condition (15) of the absence of sound-induced macroscopic electric field in the dispersion. This requires the definition of the cell analogue of macroscopic electric field strength that must be expressed in terms of electric potential distribution at the outer surface of the cell. We use here a definition that yields according to the work [30] the correct form for entropy production through cell:

$$\langle E \rangle = \varphi_1(r)|_{r=b}, \tag{42}$$

$$\langle i \rangle = i_r(r)|_{r=b}. \tag{43}$$

The electrokinetic cell model formulated by Levine [35,36] does not satisfy the Onsager symmetry requirements between kinetic coefficients for electrophoresis and streaming potential (see Ref. [20]). This leads to incorrect qualitative results (see Ref. [21]). It is interesting to note that definition (42), which is embedded specially for the Onsager symmetry relations, coincides with the definition of the macroscopic electric field given in the Maxwell–Wagner theory of the dielectric permittivity.

It follows from the Eq. (42) that the condition (15) of zero macroscopic field in the dispersion in the frame of cell model transforms to

$$\varphi_1(r)|_{r=b} = 0. \tag{44}$$

Using the CVI definition in accordance with Eq. (16) and comparing it with Eqs. (43) and (36) we obtain the following expression for CVI that is a high frequency asymptotic:

$$\mathrm{CVI} = -j\omega\varepsilon_m \frac{d\varphi(r)}{dr}\bigg|_{r=b} + \rho_0(b) v_r(b). \tag{45}$$

The solution of Eq. (35) corresponding to the form (40) with surface conditions (13)–(15) (surface S is determined by $r = a$) may be represented as

$$\varphi_1(r) = \frac{j}{3r^2\omega\varepsilon_m}\left\{ M\left[b^3 I_1(a,b) - I_2(a,b)\right]\right.$$
$$\left. - r^3 I_1(a,r) + I_2(a,r)\right\},$$

$$M = \frac{a^3(\varepsilon_p - \varepsilon_m) - r^3(\varepsilon_p + 2\varepsilon_m)}{a^3(\varepsilon_p - \varepsilon_m) - b^3(\varepsilon_p + 2\varepsilon_m)},$$

$$I_1(a,r) = \int_a^r v_r(r_1)\frac{d\rho_0}{dr_1}\,dr_1,$$

$$I_1(a,r) = \int_a^r v_r(r_1)\frac{d\rho_0}{dr_1}r_i^3\,dr'. \tag{46}$$

Substitution of the $\varphi_1(r)$ into Eq. (45) leads to the next integral form, expressing the CVI for our limiting case, when the ratio of ultrasound frequency to Maxwell–Wagner frequency is large:

$$\text{CVI} = -\frac{\varphi I_1(a,b)(\varepsilon_m - \varepsilon_p) + (1/b^3)I_2(a,b)(2\varepsilon_m + \varepsilon_p)}{(1-\varphi)\varepsilon_p + (2+\varphi)\varepsilon_m}$$
$$+ v_r(b)\rho_0(b). \tag{47}$$

Further development of the CVI cell theory requires a definite expression for the distribution of electric charge density $\rho_0(r)$ in the equilibrium double layer, as well liquid velocity $\vec{v}(r,\theta)$ with respect to the particle within the cell. The mathematical formulation and solution of the problem of equilibrium double layer for the case of Debye approximation are given in Appendix A. The hydrodynamic problem of the mutual motion of the components of concentrated suspension, induced by its vibration in ultrasonic field, derived by Dukhin and Goetz (see Ref. [7]) for the Kuwabara cell model is given in Appendix B.

5. Results and discussion

In this section we analyze dependences derived in the previous sections for CVI and dynamic mobility for the two approximate versions of the electroacoustic theory. Comparing these versions between themselves would allow us to determine the ranges of their validity.

The first version, the so-called "quasi-homogeneous model," corresponds to the case where the space density of screening charge is almost constant in the liquid medium between the particles. One of the most peculiar features of this approximate theory is CVI dependence on the volume fraction. It is very different for the case of the constant, volume fraction independent, surface charge σ or ζ-potential.

In the case of strongly overlapped DLs the vector field of the density of sound-induced electric current is similar to the vector field of the local liquid velocity with the factor of

similarity

$$\rho_0 = \frac{RT}{F}\varepsilon_m\kappa^2\sinh\frac{F\zeta}{RT}.$$

As a result, a quasi-homogeneous model with constant ζ-potential predicts that dependence of CVI on the volume fraction and geometric parameters of the particles (see Eq. (30)) is completely presented by the factor

$$\frac{\rho_p - \rho_s}{\rho_s + i\omega(1-\varphi)\frac{\varphi}{\gamma}\rho_p\rho_m}.$$

This factor includes, besides the densities of the dispersion medium and dispersed phase, only one characteristic of dispersion, namely hydrodynamic friction coefficient γ. It does not include any electric characteristics. At the same time, the similarity factor, ρ_0, being expressed through the ζ-potential, includes no geometrical parameters. This is illustrated in Fig. 2, which demonstrates that the magnitude of CVI decreases monotonically with increasing volume fraction. This corresponds to increasing hydrodynamic friction coefficient $\gamma(\varphi,\omega)$ while bulk charge density ρ_0 remains constant under the condition of φ-independent ζ-potential. It is important to emphasize, however, that quasi-homogeneous approximation is not valid for small volume fractions φ.

The volume fraction and frequency dependence of CVI for the case of the constant surface charge density in the frame of quasi-homogeneous approximation is presented in Fig. 3. Here, contrary to Fig. 2, CVI increases almost proportionally to volume fraction at the range of small φ. It occurs because the total charge of the particles dispersed in the unit volume is almost proportional to the particle volume fraction. According to the electroneutrality of dispersion, the space-independent density of equilibrium bulk charge is proportional to ($\rho_0 \propto \varphi$). It is also evident that for small enough volume fractions the movement of every particle would be independent of the movement of its neighbors and, correspondingly, the macroscopic velocity $\langle\vec{v}\rangle$ will be independent of the volume fraction φ. Hence, under the above-mentioned conditions and in accordance with Eq. (31), CVI $= \langle\vec{v}\rangle\rho_0$. This means that the magnitude of CVI becomes proportional to the volume fraction. Further increasing of φ induces the hydrodynamic particle–particle interactions and the friction coefficient will increase with φ very fast. Correspondingly, the magnitude of macroscopic velocity $\langle\vec{v}\rangle$ would decrease fast. The linear increase of CVI at small φ will be replaced by a decrease of CVI with φ when it reaches values that are large enough.

There is only one frequency-dependent coefficient in the expression for CVI in the case of quasi-homogeneous approximation:

$$\frac{\varphi}{\gamma(\varphi,\omega)}\frac{\rho_p - \rho_s}{\rho_s + i\omega(1-\varphi)\frac{\varphi}{\gamma(\varphi,\omega)}\rho_p\rho_m}.$$

It reflects the finite time of the establishing of the stationary profile of the local velocity in the liquid between disperse
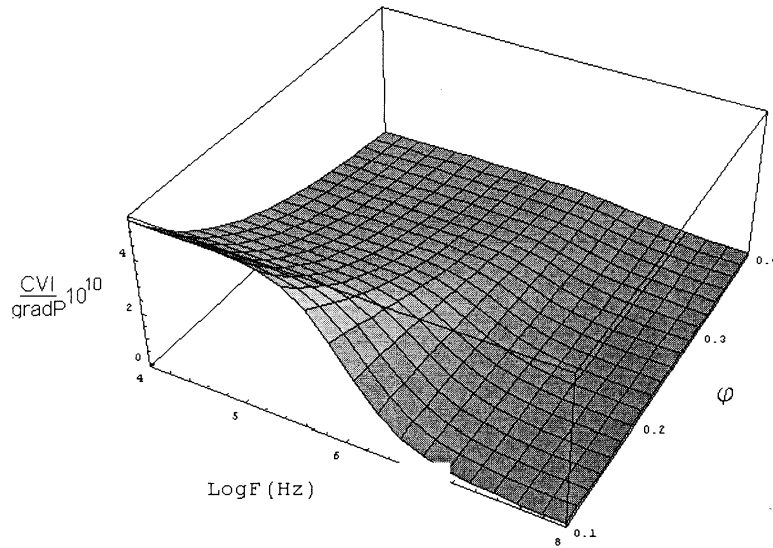
Fig. 2. The dependence of $\mathrm{CVI}/\langle\nabla P\rangle$ on the frequency and on the volume fraction, calculated with the quasi-homogeneous model for constant $\zeta = 25$ mV and the concentration $C = 10^{-4}$ mol/L of 1-1 electrolyte being in thermodynamic equilibrium with suspension. Parameters used: $a = 1$ μm; $\rho_{\mathrm{m}} = 1$ g/cm^3, $\rho_{\mathrm{p}} = 2$ g/cm^3, $\eta = 10^{-3}$ kg/m s; $\varepsilon_{\mathrm{m}} = 30\varepsilon_0$.
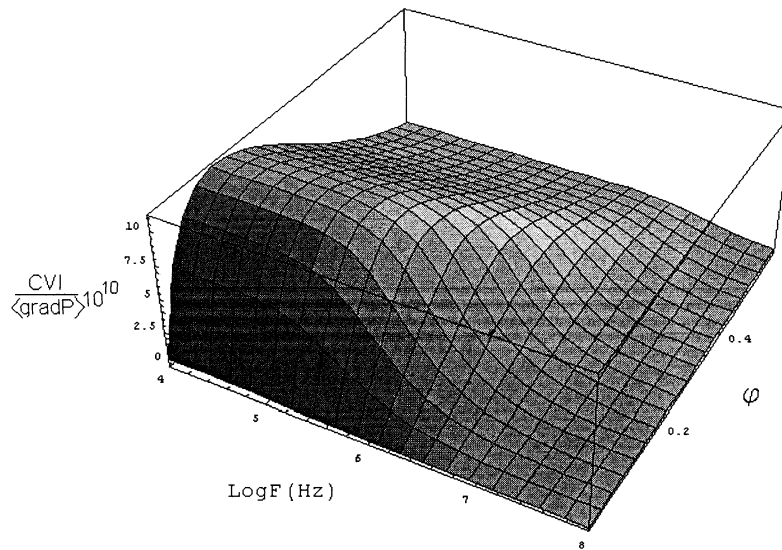
Fig. 3. The dependence of $\mathrm{CVI}/\langle\nabla P\rangle$ on the frequency and on the volume fraction, calculated with the quasi-homogeneous model for constant surface charge density $\sigma = 6.64 \times 10^{-5}$ C/m^2. Other parameters are the same as in Fig. 2 with the exception of the ζ-potential.

particles. As it was pointed in [7] this time τ_{h} decreases with increasing of the volume fraction of the solid phase in suspension and corresponding decreasing of the effective hydrodynamic radius d_{h} of pores in suspension ($\tau_{\mathrm{h}} \propto \rho_{\mathrm{m}}d_{\mathrm{h}}^2/\eta$). This fact manifests itself in Figs. 2 and 3 by the extension of the area with relatively weak frequency dependence of CVI with increasing volume fraction. Such a shift of the CVI relaxation frequency with increasing volume fraction is characteristic for both constant surface charge and constant ζ-potential.

Figs. 4 and 5 correspond to the second version of the theory, the "high frequency model." These figures show the dependencies of CVI on κa at the constant ζ-potential (Fig. 4) and constant surface charge density (Fig. 5). The

low-frequency limit (Eq. (47)) corresponds to the frequencies that satisfy nonequality (34), and simultaneously exceed substantially the characteristic frequency of hydrodynamic relaxation

$$\frac{K_{\mathrm{m}}}{\varepsilon_{\mathrm{m}}} \ll \omega \ll \frac{\eta}{\rho_{\mathrm{m}}d_{\mathrm{h}}^2}. \tag{48}$$

The CVI(κa) curves in Fig. 4 are close to the parabolic dependencies in the vicinity of the coordinates origin. The slope is steeper for the smaller volume fraction. These features are characteristic of the quasi-homogeneous model of overlapped double layers under the condition of φ-independent ζ-potential.
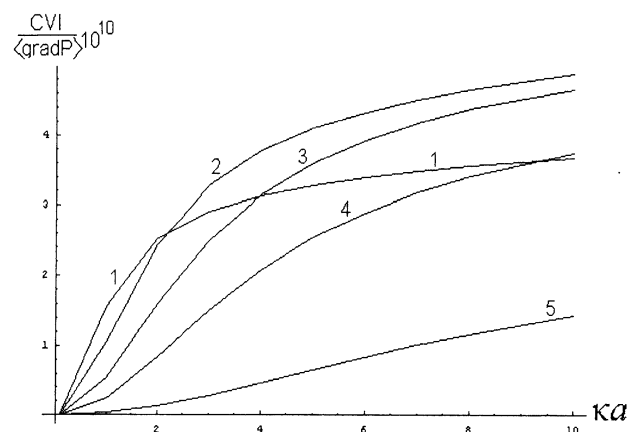
Fig. 4. The dependence of high-frequency $CVI/\langle \nabla P \rangle$ on parameter κa for constant $\zeta = 25$ mV, and for different values of the volume fractions: curve 1, $\varphi = 0.1$; curve 2, $\varphi = 0.2$; curve 3, $\varphi = 0.3$; curve 4, $\varphi = 0.4$; curve 5, $\varphi = 0.6$. Other parameters are the same as in Fig. 2, and $\varepsilon_p = 3\varepsilon_0$.
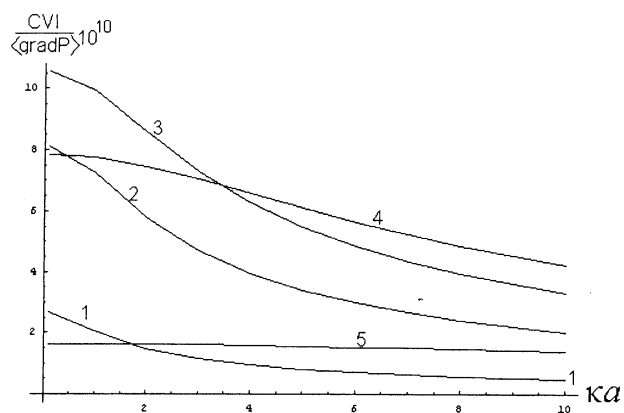

Fig. 5. The dependence of high-frequency $CVI/\langle \nabla P \rangle$ on parameter κa for constant surface charge density $\sigma = 6.64 \times 10^{-5}$ C/m^2, for different values of the volume fractions: curve 1, $\varphi = 0.01$; curve 2, $\varphi = 0.05$; curve 3, $\varphi = 0.1$; curve 4, $\varphi = 0.3$; curve 5, $\varphi = 0.6$. Other parameters are the same as in Fig. 4 with the exception of the ζ-potential.

The $CVI(\kappa a)$ dependence slows down at the range of larger κa, with the rate reciprocal to the volume fraction. As a result, if κa is large enough, the partial inversion of the $CVI(\kappa a)$ dependence takes place (for example, the curve 1 lies below curves 2 and 3). Such an inversion reflects the breakdown of the DL overlap for smaller κa if the volume fraction is small enough. Under these conditions the central zone of the space between the particles becomes filled with electroneutral solution. The expansion of this zone leads to the slowing down of the $CVI(\kappa a)$ dependence.

For the case of constant surface charge density, the dependencies $CVI(\kappa a)$ are shown in Fig. 5. They are decreasing functions, in contrast to the case of constant ζ-potential. This occurs because the total charge of the diffuse layer does not increase (in contrast to the case of constant ζ-potential) with the increasing of ionic strength. Increasing κa or increasing ionic strength causes just one effect in this case— approaching of the moving electric charge to the particle surface due to the decreasing DL thickness. Velocity of the
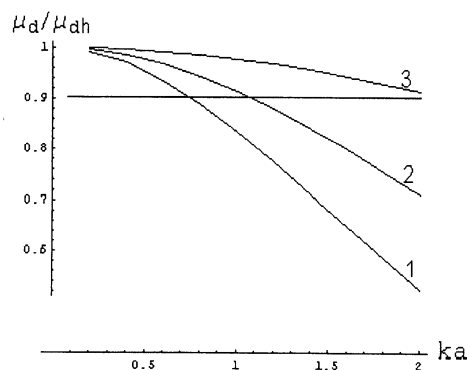

Fig. 6. Dependence of the μ_d/μ_{dh} ratio on κa; μ_{dh} is the dynamic electrophoretic mobility, corresponding to quasi-homogeneous approximation, μ_d corresponding to high-frequency approximation, for different values of the volume fractions: curve 1, $\varphi = 0.3$; curve 2, $\varphi = 0.4$; curve 3, $\varphi = 0.6$. Other parameters are the same as on Fig. 4.

liquid–particle motion is smaller close to the surface. This would lead to the reduction of CVI, which is proportional to the product of the moving electric charge by the velocity of this motion. Such decay of CVI is faster for the smaller volume fraction because of the above-mentioned breaking of the double layer overlap.

It is important to mention that if information about both parameters κ and a is available, interpretation of the CVI measurement would yield data on both ζ-potential and surface charge σ. Volume fraction dependence of CVI would reveal whether the constant ζ-potential model or constant surface charge model is valid for a particular system. However, it seems to us that the surface charge model could be more adequate. It could be justified by the fact that adsorption forces, which could be responsible for the surface charge formation, exceed substantially electrostatic forces induced with volume fraction variation.

The validity of Eq. (47) is not restricted with respect to the parameter κa. This makes it possible to use this equation to find the ranges of applicability of the "quasi-homogeneous model." It is convenient to do this analysis using dynamic mobility instead of CVI. Equation (32) describes the transformation from CVI to the dynamic mobility.

Fig. 6 shows the ratio of the dynamic electrophoretic mobilities calculated using the quasi-homogeneous model μ_{dh} and the high-frequency model for several volume fractions. As one could expect, quasi-homogeneous approximation works better for larger volume fractions.

As a quantitative measure we can use 10% deviation between the quasi-homogeneous model value and the exact number calculated using the high-frequency model. This degree of deviation occurs at

- $\kappa a < 0.65$ for $\varphi = 0.3$;
- $\kappa a < 1$ for $\varphi = 0.4$;
- $\kappa a < 2$ for $\varphi = 0.6$.

In general, we may say that the quasi-homogeneous model, being independent of the particle's shape and poly-

dispersity, provides good accuracy for characterizing concentrated dispersions with κa almost up to unity.

6. Conclusions

We have established the possibility of developing an analytical electroacoustic theory for concentrated colloids in the range of low and moderate κa values. This κa range corresponds to a variety of aqueous nanocolloids and practically all nonaqueous colloids.

There are two simplifying conditions that could be used for this development. The first one restricts κa by requiring double layers of particles to be strongly overlapped. This version of the theory is mathematically simple. It is valid for particles with any shape and polydispersity, which makes it similar to the Smoluchowski theory. It applies no restriction on the ultrasound frequency. It is valid for κa values up to almost 1.

The second version restricts frequency of ultrasound to the range much above Maxwell–Wagner frequency. It is mathematically more complicated, but it applies no restriction on κa. The last feature of this theory allowed us to estimate the validity range of the first version.

We have also stressed here a major difference in the "surface charge-ζ-potential" relationship between cases of "thin DL" and "thick DL." In the case of the "thin DL" both parameters are volume fraction independent and can be used for characterizing surface. In the case of "thick DL" there is a volume fraction multiplier relating these parameters. As a result it is imperative to specify which one of them is volume fraction independent and can be used for characterizing surface properties.

We give here mathematical expressions and analyze them for both cases, constant surface charge and constant ζ-potential.

Acknowledgment

Appendix A

Solution of the first problem for the case of 1-1 electrolyte includes the following steps.

First, the Poisson–Boltzman equation with respect to the distribution of dimensionless electric potential $\tilde{\Phi}_0(r) = F\Phi_0(r)/RT$ in the equilibrium diffuse double layer, surrounding particles. In the frame of the cell model this potential depends only on one space coordinate, namely on the distance r from the center of the cell:

$$\nabla^2 \tilde{\Phi}_0(r) = \kappa^2 \sinh\left[\tilde{\Phi}_0(r)\right]. \tag{A.1}$$

The surface condition on the particle surface, represented as sphere with radius a, is

$$\tilde{\Phi}_0(r)|_{r=a} = \frac{F}{RT}\zeta. \tag{A.2}$$

The surface condition at the outer surface of the cell reflects the electroneutrality of suspension:

$$\left.\frac{d\Phi_0(r)}{dr}\right|_{r=b} = 0. \tag{A.3}$$

This problem was solved in [32,33] for the case of Debye approximation, which consists in replacing the right-hand side of the Poisson–Boltzman equation with the first term of its power series: $\sinh[\tilde{\Phi}_0(r)] \to \tilde{\Phi}_0(r)$. The solution has the next form:

$$\Phi_0(r) = \zeta \frac{a(\kappa b \cosh[\kappa(b-r)] - \sinh[\kappa(b-r)])}{r(\kappa b \cosh[\kappa(b-a)] - \sinh[\kappa(b-a)])}. \tag{A.4}$$

This solution for the surface charge yields the following expression for the surface charge density of the particle, $\sigma = \varepsilon_m \frac{d\Phi_0(r)}{dr}|_{r=a}$:

$$\sigma = \frac{\varepsilon_m \zeta}{a} \frac{\kappa(b-a)\cosh[\kappa(b-a)] + (\kappa^2 ab - 1)\sinh[\kappa(b-a)]}{\kappa b \cosh[\kappa(b-a)] - \sinh[\kappa(b-a)]}. \tag{A.5}$$

For the limiting case of a strongly overlapped diffuse layer (quasi-homogeneous approximation) $\kappa(b-a) \ll 1$ this equation reduces to

$$\sigma = \frac{\varepsilon_m \zeta}{3}\frac{1-\varphi}{\varphi}\varepsilon_m a \kappa^2 \zeta. \tag{A.6}$$

The more general form of the expression for σ, without linearity assumption with respect to ζ-potential, and even without using the cell model (i.e., for arbitrary geometry of disperse phase) may be obtained in the frame of quasi-homogeneous approximation directly from suspension electroneutrality, as is shown in Section 3.

Appendix B

The mathematical formulation of the problem describing a sound-induced distribution of $\vec{v}(\omega, \vec{r})$ in the frame of the cell model consists of the well-known system of the Stocks equation and matter conservation equation for incompressible liquid with a zero slip condition at the particle surface:

$$i\omega\rho_m \vec{v}(r, \theta, \omega) = \eta\, \text{rot}\, \vec{v}(r, \theta, \omega) + \text{grad}\, P(r, \theta, \omega), \tag{B.1}$$

$$\text{div}\,\vec{v} = 0, \tag{B.2}$$

$$v_r|_{r=a} = 0, \tag{B.3}$$

$$v_\theta|_{r=a} = 0. \tag{B.4}$$

The surface condition at the cell's outer surface connects the distribution of the normal component of the local velocity with the value of the sound-induced macroscopic velocity, Eq. (28):

$$v_r|_{r=b} = \langle \vec{v} \rangle_z = \frac{\rho_p - \rho_s}{\rho_s + i\omega(1-\varphi)\frac{\varphi}{\gamma}\rho_p\rho_m}\langle \nabla P \rangle_z. \tag{B.5}$$

The second outer-surface condition, which is specific for the Kuwabara model [31], reflects the irrotational nature of the current of free liquid outside the dispersion:

$$\operatorname{rot}\vec{v}(r,\theta,\omega)|_{r=b}=0. \tag{B.6}$$

It can be transformed to the following form:

$$\frac{1}{r}\left(\frac{d}{dr}\big(rv_{\theta}(r)\big)-\frac{dv_r(r)}{dr}\right)\bigg|_{r=b}=0. \tag{B.7}$$

The solution of Eqs. (B.1) and (B.2) with the surface conditions (B.3)–(B.7) with regard to the distribution of the components of the local velocity in vibrated dispersion is

$$\frac{v_r(r,\omega)}{|\langle\vec{v}\rangle|}=\frac{\frac{2\tilde{a}^4}{9\tilde{b}^3}\left(\frac{\tilde{b}^3}{\tilde{a}^3}-1\right)\left(1-\frac{\tilde{b}^3}{\tilde{r}^3}\right)+\frac{2}{3}\int_{\tilde{r}}^{\tilde{b}}\left(1-\frac{x^3}{\tilde{r}^3}\right)h(x)\,dx}{-\frac{2\tilde{a}^4}{9\tilde{b}^3}\left(\frac{\tilde{b}^3}{\tilde{a}^3}-1\right)^2+\frac{2}{3}\int_{\tilde{a}}^{\tilde{b}}\left(1-\frac{x^3}{\tilde{r}^3}\right)h(x)\,dx}-1, \tag{B.8}$$

$$v_{\theta}(r,\omega)=-\left(v_r+\frac{r}{2}\frac{dv_r}{dr}\right), \tag{B.9}$$

where

$$\tilde{a}^2=a^2\omega\rho_m/2\eta_m, \qquad \tilde{b}^2=b^2\omega\rho_m/2\eta_m,$$

$$\tilde{r}^2=r^2\omega\rho_m/2\eta_m. \tag{B.10}$$

$\langle\vec{v}\rangle$ is the macroscopic drag velocity of liquid disperse phase with respect to dispersed particles,

$$\gamma=\omega\rho_m\varphi\left[\frac{3}{4I}\left(-\frac{dh}{dx}+\frac{h}{x}\right)_{r=a}-2j\right], \tag{B.11}$$

$$h(x)=h_1(x)h_2(\tilde{b})-h_1(\tilde{b})h_2(x), \tag{B.12}$$

$$h_1(x)=\frac{\exp(-x)}{x}\left[\frac{x+1}{x}\sin x-\cos x\right.$$
$$\left.+j\left(\frac{x+1}{x}\cos x+\sin x\right)\right], \tag{B.13}$$

$$h_2(x)=\frac{\exp(x)}{x}\left[\frac{x-1}{x}\sin x+\cos x\right.$$
$$\left.+j\left(\frac{1-x}{x}\cos x+\sin x\right)\right], \tag{B.14}$$

$$\int_{\tilde{r}}^{\tilde{b}}\left(1-\frac{x^3}{\tilde{r}^3}\right)h(x)\,dx=\frac{e^{-(1+j)(\tilde{r}+\tilde{b})}}{2\tilde{r}^3b^2}$$
$$\times\begin{pmatrix}3je^{(2+2j)\tilde{b}}\big(1+(1+j)\tilde{r}\big)\big(-1+(1+j)\tilde{b}\big)-\\3je^{(2+2j)\tilde{r}}\big(-1+(1+j)\tilde{r}\big)\big(1+(1+j)\tilde{b}\big)+\\(4+4j)e^{(1+j)(\tilde{r}+\tilde{b})}\big(\tilde{b}^3-\tilde{r}^3\big)\end{pmatrix}. \tag{B.15}$$

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