Dynamic Electrophoretic Mobility in Concentrated Dispersed Systems. Cell Model

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Electroacoustic characterization of concentrated dispersed systems requires an adequate theory of dynamic electrophoretic mobility which takes into account particle–particle interaction. The concept of the "cell model" provides convenient and comprehensive means for creating this theory. There are two different versions of the electrokinetic cell model. The first one was introduced by Levine and Neale, the second one by Shilov and Zharkikh. The Levine–Neale cell model gives a large discrepancy with experimental data as it was shown by O'Brien and Hunter. We suggest several reasons indicating that the Shilov–Zharkikh cell model is more adequate than the Levine–Neale one. First of all, it gives transition to the Smolichowski law for electroosmosis which is valid for concentrated systems. The Shilov–Zharkikh cell model yields a symmetrical Onsager relationship between kinetic coefficients as well as the Maxwell–Vagner law for electric conductivity. In addition, the Shilov–Zharkikh cell model predicts much stronger volume fraction dependence of dynamic electrophoretic mobility. Such strong dependence corresponds to O'Brien–Hunter experimental data which could not be explained by the Levine–Neale cell model. We developed two versions of the theory using different constrains. The first version is valid only at low frequency, but it takes into account surface conductivity. The second version neglects surface conductivity. At the same time this second version takes into account inertia effects which makes it valid at high frequencies. We do not address a question of the appropriate frame of references for the dynamic electrophoretic mobility. All calculations are performed in the frame of references which is associated with the liquid.

Introduction

Electroacoustics is a relatively new technique for characterizing concentrated dispersed systems. This technique requires a theory which connects measured electroacoustic parameters such as the colloid vibration current (CVI)[1] or electrosonic amplitude (ESA)[2] with properties of the given dispersed system including ζ-potential and particle size. This theory must take into account particle–particle interaction which is an essential feature of the concentrated systems. Unfortunately, the general theory like this does not exist yet.[3]

At the same time there is an intermediate theory which is valid in concentrated systems and connects measured electroacoustic signals with "dynamic electrophoretic mobility" μ_d. This theory has been created by O'Brien.[4] It yields the following general relationship:

$$\text{ESA(CVI)} = C\sigma\varphi\mu_d \qquad (1)$$

where C is a cell constant, σ is the density contrast, φ is the volume fraction of the solid; ESA corresponds to the case when the electric field E is a driving force. The gradient of the pressure is a drving force in the case of CVI.

Dynamic electrophoretic mobility can be used as a useful system characteristic. It is sufficient, for instance, for determining the isoelectric point. However, dynamic electrophoretic mobility provides only partial, approximate characterization. Detailed, complete characterization includes information about particle size distribution, ζ-potential, and other surface properties.

There are several theories describing relationship between dynamic mobility and other properties of the dispersed system. The most known theories were created by O'Brien[4] for a thin double layer and by Babchin with co-authors[5,6] for any double-layer thickness. These theories do not take into account particle–particle interaction. As a result, they are valid only in the dilute case with the volume fraction below 5%.

There are two different approaches for incorporating particle–particle interaction into the electrokinetic theory. The first approach explores a "cell model" concept. It was applied to the electroacoustic theory initially by Marlow[1] and later generalized by Ohshima.[7] Both these theories use the Levine–Neale version of the cell model.[8]

There is the second completely different approach to deriving the expression for dynamic mobility. It was suggested by Rider and O'Brien.[9] They used an expansion of the dynamic mobility on the volume fraction. Only the first term of the expansion was retained which made this theory suitable only for sufficiently low volume fraction. It turned out that this approach is associated with big

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mathematical complications even for the first term of the expansion. It does not look promising to include further terms of the volume fraction expansion which would be necessary for a wider range of the solid content. That is why we concentrate our attention on further development of the cell model approach.

It is important to mention that there is a certain doubt about the validity of the cell model concept in the electroacoustics. This doubt comes from the O'Brien, Rowlands, and Hunter experimental work[10] where they tested electroacoustic theory based on the Levine—Neale cell model. They discovered a big discrepancy between theory and experiment. This experimental test discouraged further development of the cell model electroacoustic theories. The failure of the Levine—Neale cell model does not mean that a complete cell model concept is wrong.

There are several pure hydrodynamic cell models which are successfully applied for solving complicated hydrodynamic problems in concentrated systems. Electrokinetic cell models are the results of some generalization of the hydrodynamic cell models. There are many ways to perform this generalization and, correspondingly, many ways to create different electrokinetic cell models.

The difference between electrokinetic cell models is related to the description of the electric characteristics. The relationship between macroscopic experimentally measured electric properties and local electric properties calculated using cell concept varies for different cell models. For instance, the Levine—Neale cell model specifies this relationship using one of the many possible analogies between local and macroscopic properties. Macroscopic properties are current density $\langle I \rangle$ and electric field strength $\langle E \rangle$. They are related to local electric current density I and electric field $\nabla \phi$ according to the Levine—Neale cell model with the following expressions:

$$\langle I \rangle = \frac{I}{b \cos \theta_{r=b}} \tag{2}$$

$$\langle E \rangle = - \frac{1}{\cos \theta} \frac{\partial \phi}{\partial r_{r=b}} \tag{3}$$

where radius b is a cell radius:

$$b^3 = \frac{a^3}{\varphi} \tag{4}$$

a is a particle radius, φ is a volume fraction, and r and θ are spherical coordinates associated with the particle.

Relationships 2—3 are not unique. There are many other ways to relate macroscopic and local fields. It means that we need a set of criteria to select a proper cell model. These criteria have been suggested in the electrokinetic cell model created by Shilov and Zharkikh.[11] Their two criteria determine a proper choice of the macroscopic "fields" and "flows".

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The first criteria is a well-known Onsager relationship[14] which constrain values of the macroscopic particles velocity relative to the liquid $\langle V \rangle$, macroscopic pressure $\langle P \rangle$, electric current $\langle I \rangle$, and field $\langle E \rangle$:

$$\frac{\langle V \rangle}{\langle I \rangle_{\langle \Delta P \rangle = 0}} = \frac{\langle E \rangle}{\langle \Delta P \rangle_{\langle I \rangle = 0}} \tag{5}$$

This relationship requires a certain expression for entropy production Σ:

$$\Sigma = \frac{1}{T}(\langle I \rangle \langle E \rangle + \langle V \rangle \langle \Delta P \rangle) \tag{6}$$

Shilov and Zharkikh used this relationship between "fields", "flows", and entropy production in order to derive the cell model condition for macroscopic properties. It turned out that the expression for the macroscopic field strength is different comparing to that of Levine—Neale:

$$\langle E \rangle = \frac{\phi}{b \cos \theta_{r=b}} \tag{7}$$

whereas the expression for the macroscopic current is the same in both models.

This cell model was criticized by Kozak and Davis[12] because according to them this model does not reduce to the Smoluchowski law.

Smoluchowski law is a very important test for any electrokinetic theory because it is valid for any geometry and volume fraction. Failure to satisfy the Smoluchowski law test is a clear indication that the theory is not correct. However, Shilov and Zharkikh wrote in their paper that their theory met Smoluchowski law requirement. They even made a stronger conclusion that it was the Levine—Neale cell model which did not reduce to the Smoluchowski law. We address this difference in opinions in the next section. We show that this difference comes from the misunderstanding of the Smoluchowski law in the case of concentrated systems. The version of Smoluchowski's law which is valid in concentrated systems confirms the Shilov—Zharkikh cell model.

We use this cell model for characterizing dynamic electrophoretic mobility in the concentrated systems. We will derive two expressions for dynamic electrophoretic mobility using different simplifying constrains. The first one will be valid only at low frequencies but it includes surface conductivity contribution. The second one neglects surface conductivity effects but it will be valid at low and high frequencies.

These expression predicts much stronger dependence of the dynamic mobility from the volume fraction than the Levine—Neale cell model. This explains the results of the O'Brien, Rowlands, and Hunter experimental test.[10]

We conclude that the Shilov—Zharkikh cell model provides consistent basis for electroacoustic theory in concentrated systems.

Smoluchowski Laws for Electrophoresis and Electroosmosis

The Smoluchowski law for electrophoresis expresses static electrophoretic mobility μ through dielectric permittivity ϵ and viscosity η of media and ζ-potential of particles:

$$\mu = \frac{\epsilon \epsilon_0 \zeta}{\eta} \tag{8}$$

There are two conditions restricting applicability of Smoluchowski law. The double-layer thickness must be much smaller than the particle radius a:

$$\kappa a \gg 1 \qquad (9)$$

where κ is the reciprocal Debye length.

The second condition requires a surface conductivity κ^σ contribution to be negligibly small. It happens when dimensionless Dukhin number Du introduced by Lyklema[13] is sufficiently small:

$$Du = \frac{\kappa^\sigma}{K_m a} \ll 1 \qquad (10)$$

where K_m is a conductivity of the medium outside the double layer.

Smoluchowski law for electrophoresis (8) is usually derived for a single particle in the infinite liquid. The electrophoretic mobility μ is defined in (8) as the ratio of field-induced particle velocity V to homogeneous field strength E_{ext} in liquid at a large distance from the particle:

$$\mu = \frac{V}{E_{ext}} \qquad (11)$$

The Smoluchovski law (8) is applicable to any geometrical form of the particle. Independence of applicability of (8) on the particle's geometry makes it applicable to the arbitrary system of particles, including the cloud of particles, or concentrated suspension.

But, to apply Smoluchovski's law in form (8) to concentrated suspension, one should take into account the difference between the external electric field in free liquid outside the suspension E_{ext} and the averaged electric field inside the dispersion $\langle E \rangle$. Static mobility in (8) and (11) is determined with respect to field strength in free liquid outside the suspension.

There is another form of Smoluchivski's law, more common in the case of concentrated suspensions, in which figured another value $\langle \mu \rangle$ of electrophoretic mobility (or electroosmotic velocity), defined with respect to $\langle E \rangle$:

$$\langle \mu \rangle = \frac{\epsilon \epsilon_0 \zeta}{\eta} \frac{K_s}{K_m} \qquad (12)$$

where K_s, the macroscopical conductivity of the dispersed system and

$$\langle \mu \rangle = \frac{V}{\langle E \rangle} \qquad (13)$$

Smoluchowski's electroosmosis law was expressed in this form by many authors including Kruyt and Overbeek,[14] Dukhin,[15] and O'Brien.[16] This law is valid under the same conditions, (9) and (10).

These two definitions of the electrophoretic mobility are identical if we take into consideration the well-known[17] relationship between E_{ext} and $\langle E \rangle$:

$$\frac{\langle E \rangle}{E_{ext}} = \frac{K_m}{K_s} \qquad (14)$$

Both expressions, (8) and (14), specify electrophoretic mobility μ and $\langle \mu \rangle$ independently on the volume fraction and system geometry. It means that the comparison with Smolchowski's law (in the limiting cases when conditions 9 and 10 are valid) is a validity test of the cell model which pretends to describe the volume fraction dependence of the electrokinetic effects in concentrated suspensions. Both versions of Smoluchowski's law can be used for this purpose. However, expression 12 is more appropriate for this test comparison because it emphasizes the relations between the fields and flows inside the concentrated disperse system.

We will show later in this paper that the Levine–Neale cell model for limiting case (9) and (10) gives

$$\langle \mu \rangle = \frac{\epsilon \epsilon_0 \zeta}{\eta} \qquad (15)$$

which is neither (12) nor (8) and thereby appears to be unable to describe the volume fraction dependence of $\langle \mu \rangle$ given by the factor K_s/K_m in exact Smoluchovski's law (12).

Disregarding the existence of two different definitions of electrophoretic mobility may lead sometimes to erroneous conclusions. For instance, Kozak and Davis[12] meant mistakenly expression (15) when they declared that the Shilov–Zharkikh cell model does not meet Smoluchowski's law requirement. Actually, the Shilov–Zharkikh cell model transfers to expression 12 and predicts much stronger dependence on volume fraction than expression 8. These stronger volume fraction effects were confirmed experimentally using electroosmosis. There is a review of these experimental works published by Dukhin and Derjaguin.[15]

To specify volume fraction dependence, one must express the conductivity of system K_s through the conductivity of medium K_m, conductivity of particle K_p including surface conductivity and volume fraction φ. There are several ways to do this. One of them was used by O'Brien.[16] We suggest that the Maxwell–Vagner[17] theory be used, which is one of the versions of the cell model. This theory gives the following relationship between conductivities:

$$\frac{K_s}{K_m} = \frac{1 - 2\varphi F^*}{1 + \varphi F^*} \qquad (16)$$

where

$$F^* = \frac{K_m - K_p}{2K_m + K_p} \qquad (17)$$

It is important to mention that the Shilov–Zharkikh cell model yields the same results for conductivity as the Maxwell–Vagner theory. It makes this version of the cell model self-consistent.

In the case of the nonconducting particles with a weak surface conductivity ($Du \ll 1$) function $F^* = 0.5$ and expressions 13 and 12 give the following result for electrophoretic mobility:

$$\langle \mu \rangle = \frac{\epsilon \epsilon_0 \zeta}{\eta} \frac{(1 - \varphi)}{(1 + 0.5\varphi)} \qquad (18)$$

This expression is a low-frequency limit for dynamic electrophoretic mobility with negligible surface conductivity effects.

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Shilov–Zharkikh Cell Model at Low Frequencies

Dynamic electrophoretic mobility in general depends on the frequency of the driving field ω (electric field or a sound wave). It happens because of the particles and fluid inertia. However, this dependence disappears at the sufficiently low frequency. This frequency should be low enough for allowing sufficient time for electric and hydrodynamic fields to reach a stationary configuration. It means that ω must be much less than the frequency of hydrodynamic relaxation ω_h and frequency of electrodynamic relaxation ω_e:

$$\omega \ll \omega_h = \frac{2\eta}{\rho_m a^2} \tag{19}$$

$$\omega \ll \omega_e = \frac{K_m}{\epsilon} \tag{29}$$

where ρ_m is the density of the medium.

At the same time we restrict the frequency from below assuming that it is above the concentration polarization limit ω_c. This condition is certainly valid for the electroacoustic technique which operates with frequencies in the MHz range. It means that the frequency should satisfy the following restriction as well:

$$\omega \gg \omega_c = \frac{2D}{a^2} \tag{21}$$

where D is the effective diffusion coefficient.

It is known that if the frequency exceeds ω_c the concentration of the electrolyte remains constant. There is no need to consider ion fluxes separately at this high frequency, which simplifies mathematics dramatically.

There is also one restriction which we apply on the particle size. We assume that the wavelength is much larger than the particle size which means that

$$\omega \ll \frac{c}{a} \tag{22}$$

where c is a sound speed.

This restriction allows one to consider liquid as incompressible.

The electrokinetic phenomena in the specified above range of low frequencies arise because of the mutual coupling of the three nonreversible local fields: fluid velocity v, hydrodynamic pressure P, and electric potential ϕ. The space distribution of these fields is described by the following system of equations within the specified frequency range:

$$\eta \Delta v = -\nabla P \tag{23}$$

$$\nabla v = 0 \tag{24}$$

$$\Delta \phi = 0 \tag{25}$$

This system of equations has the following general solution in the spherical coordinate system (r, θ) associated with the center of the given particle:

$$v_r = \frac{D}{a} \cos \theta \left(A_1 - 2A_2 \frac{a^3}{r^3} + 0.1 A_3 \frac{r^2}{a^2} + A_4 \frac{a}{r} \right) \tag{26}$$

$$v_\theta = \frac{D}{a} \sin \theta \left(-A_1 - A_2 \frac{a^3}{r^3} - 0.2 A_3 \frac{r^2}{a^2} - 0.5 A_4 \frac{a}{r} \right) \tag{27}$$

$$P = \frac{D\eta}{a^2} \cos \theta \left(A_3 \frac{r}{a} + A_4 \frac{a^2}{r^2} \right) \tag{28}$$

$$\phi = \frac{RT}{F} \cos \theta \left(A_5 \frac{r}{a} + A_6 \frac{a^2}{r^2} \right) \tag{29}$$

where R is a gas constant, T is the absolute temperature, and F is the Faraday constant.

To determine unknown constant A_i, we must specify boundary conditions on the particle surface at $r = a$ and on the cell surface at $r = b$ where b is the cell radius (4).

Boundary conditions on the particle surface reflect the following facts: (1) Liquid cannot penetrate through the particle surface

$$v_r(r = a) = 0 \tag{30}$$

(2) electroosmotic slip

$$v_\theta(r = a) = \frac{\epsilon \epsilon_0 \zeta}{\eta} \frac{\partial \phi}{\partial \theta_{r=a}} \tag{31}$$

(3) compensation of the normal current by surface current $I_s = \kappa^\sigma \nabla \phi$

$$K_m \nabla \phi = \text{div}_s I_s \tag{32}$$

Cell boundary conditions reflect hydrodynamic particle interaction. For instance, the hydrodynamic condition can be used as suggested by Kuvabara:

$$\text{rot } v_{r=b} = \left[\frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} - \frac{\partial v_r}{r \partial \theta} \right]_{r=b} = 0 \tag{33}$$

There are two more cell conditions which specify values of the two acting thermodynamic forces (∇P and $\nabla \phi$) on the cell surface for particular electrokinetic phenomena. For instance, in the case of electrophoresis the gradient of pressure equals zero:

$$\nabla P_{r=b} = \frac{\eta D}{a^3} 3\varphi A_4 = 0 \tag{34}$$

There has been no difference so far between the Shilov–Zharkikh and Levine–Neale cell models. The next condition which specifies electric field brings up this difference. According to Shilov and Zharkikh, this condition is

$$\frac{\phi}{b \cos \theta_{r=b}} = -E \tag{35}$$

The system of the boundary conditions (30–35) yields the following values of unknown parameters A_i:

$$A_1 = 2A_2$$

$$A_2 = \frac{\epsilon \epsilon_0 \zeta a E}{\eta D} \frac{1}{2(1 + Du) + \varphi(1 - 2Du)}$$

$$A_3 = A_4 = 0$$

$$A_5 = 2A_6 \frac{1 + Du}{1 - 2Du}$$

$$A_6 = \frac{aFE}{RT} \frac{1 - 2Du}{2(1 + Du) + \varphi(1 - 2Du)}$$

The last step is the calculation of the average liquid volume flow I_v and average electric charge flow I_e.

According to Shilov and Zharkikh, these flows are expressed through the corresponding local fields on the cell surface:

$$I_\mathrm{v} = \frac{v_r}{\cos\theta_{r=b}} \qquad (36)$$

$$I_\mathrm{e} = -K_\mathrm{m}\frac{\nabla_r\phi}{\cos\theta_{r=b}} \qquad (37)$$

Kinetic coefficients for electrophoresis and electric conductance are defined as a ratio of corresponding flow divided by the electric field strength. As a result, we obtain the following expressions for the dynamic electrophoretic mobility and conductivity:

$$\langle\mu\rangle = \frac{\epsilon\epsilon_0\zeta}{\eta}\frac{(1-\varphi)}{(1+Du+0.5\varphi(1-2Du))} \qquad (38)$$

$$\frac{K_\mathrm{s}}{K_\mathrm{m}} = \frac{1+Du-\varphi(1-2Du)}{1+Du+0.5\varphi(1-2Du)} \qquad (39)$$

It is important to mention that formulated here is system of thermodynamic forces (∇P and $\nabla\phi$) and thermodynamic flows (I_v and I_e) that satisfies the Onsager reciprocal relationship. It is possible to show that

$$\frac{I_v}{E_{\nabla P=0}} = \frac{I_\mathrm{e}}{\nabla P_{E=0}} \qquad (40)$$

It is an additional important argument confirming validity of the Shilov–Zharkikh cell model.

Shilov–Zharkikh Cell Model Including Inertia Effects

To take into account inertia effects, we eliminate restriction 19 on the frequency. It means that we will consider here nonstationary hydrodynamic effects and use nonstationary Navier–Stocks law:

$$\eta\,\mathrm{rot}\,\mathrm{rot}\,v + \nabla P = -\rho_\mathrm{m}\frac{\partial V}{\partial t} \qquad (41)$$

which is to replace eq 23 from the previous section.

We also neglect effects related to the surface conductivity χ^σ, which means according to Lyklema[13] that we assume the Dukhin number to be much less than 1:

$$Du \ll 1 \qquad (42)$$

It allows us to replace the particle surface boundary condition (32) with the condition of the zero current through the particle surface:

$$\frac{\partial\phi}{\partial r}_{r=a} = 0 \qquad (43)$$

The particle velocity is calculated from the balance of forces acting on the particle:

$$\iint\Pi_{ik}\,dS = \frac{4}{3}\pi a^3\rho_\mathrm{p}\frac{dv_\mathrm{p}}{dt} \qquad (44)$$

The solution of the bulk equations with the specified boundary conditions yields the following expression for

$$\mu_\mathrm{d}^\mathrm{m} = \frac{3\epsilon_\mathrm{m}\epsilon_0\zeta}{2\eta(1+0.5\varphi)}\frac{(1-\varphi)H(\alpha)+I(\alpha,\beta)}{1.5H(\alpha)-\sigma I(\alpha,\beta)} \qquad (45)$$

where $\alpha = a\sqrt{\omega/\nu}$, $\beta = b\alpha/a$, ν is the kinematic viscosity, and ω is the frequency.

$$H(\alpha) = \frac{ih(\alpha)}{2\alpha}\left(\frac{idh(x)}{2dx}\right)_{x=\alpha}$$

$$I(\alpha,\beta) = \int_\alpha^\beta h(x)\left(1-\frac{x^3}{\beta^3}\right)dx$$

$$h(x) = h_1(x)h_2(\beta) - h_1(\beta)h_2(x)$$

$$h_1(x) = \frac{\exp(-x)}{x}\left[\frac{x+1}{x}\sin x - \cos x + i\left(\frac{x+1}{x}\cos x + \sin x\right)\right]$$

$$h_2(x) = \frac{\exp(x)}{x}\left[\frac{x-1}{x}\sin x + \cos x + i\left(\frac{1-x}{x}\cos x + \sin x\right)\right]$$

This expression determines the dynamic electrophorewtic mobility in the frame of reference related to the liquid.

Figure 1 illustrates the frequency dependence of this dynamic electrophoretic mobility expressed in mV for different volume fractions. The dynamic mobility shown in Figure 1, μ_d^1, corresponds to the mobility $\mu_\mathrm{d}^\mathrm{m}$ assuming the following normalization:

$$\mu_\mathrm{d}^1 = \mu_\mathrm{d}^\mathrm{m}\frac{2\eta}{3\epsilon\epsilon_0}$$

Figure 1 corresponds to the density of particles 2.2 g/cu·cm and·particle size 1 μm.

Conclusions

A comparison of the two existing cell models for electrokinetics (Levine–Neale and Shilov–Zharkikh) confirms a significant difference between them. There are several arguments indicating that the Shilov–Zharkikh model is more adequate.

(1) Electrophoretic mobility calculated using the Shilov–Zharkikh model reduces at weak surface conductivity (Du
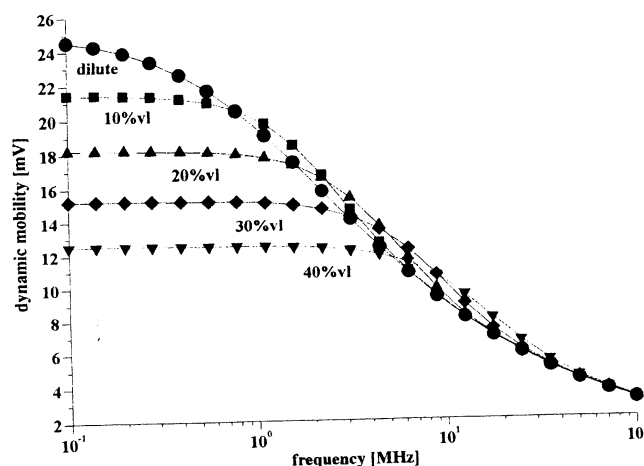

Figure 1. Dynamic electrophoretic mobility versus frequency for various volume fractions. Particle density is 2.2 g/cu·cm;

≪ 1) to the Smoluchowski law derived for electroosmosis which is valid in concentrated systems.

(2) The Shilov−Zharkikh cell model yields in addition to electrophoretic mobility an expression for electric conductivity which correlates with the Maxwell−Vagner−O'Konski theory.

(3) The Shilov−Zharkikh cell model satisfies Onsager resiprocal relationship.

(4) The Shilov−Zharkikh cell model predicts much stronger dependence of the dynamic electrophoretic mobility from the volume fraction. It explains the observed discrepancy between the theory and experiment observed by O'Brien with co-authors.[10]

All these arguments lead to the conclusion that the Shilov−Zharkikh cell model is suitable for developing consistent electroacoustic theory. The expression for dynamic electrophoretic mobility derived in this paper describes particle motion relative to the liquid. It is not sufficient for experimental interpretation because the measured electroacoustic signal is sensitive to the motion of both liquid and particle. The problem of the adequate frame of references is not considered in this paper. It will require an additional theoretical consideration. We have just shown here that the Shilov−Zharkikh cell model can be used as a convenient and adequate basis for further theoretical development.

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