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Observation of sol–gel transition for carbon nanotubes using electroacoustics: Colloid vibration current versus streaming vibration current

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Received 30 November 2006; accepted 8 January 2007

Abstract

Propagation of ultrasound through a porous body generates an electric signal, similarly to the well-known electroacoustic effect in dispersions of mobile particles. This obscure version of electroacoustics has been known since 1948, when M. Williams published his paper on electrokinetic transducers [Rev. Sci. Instrum. 19 (10) (1948) 640–646]. We observe this effect in a 1 wt% aqueous dispersion of carbon nanotubes. Magnitude and phase of the electroacoustic signal, as well as conductivity, are sensitive to sonication and mixing. Sonication with no mixing leads to phase rotation by up to 180° comparing to the traditional colloid vibration current (CVI) in sols. This is explained by the fact that sonication terminates motion of the carbon nanotubes by building up a continuous network gel. Propagation of ultrasound through the immobile carbon nanotube network generates a streaming vibration current (SVI), but not a CVI, which requires free motion of the particles relative to the liquid. Theoretical analysis indicates that the SVI has 180° difference in phase from the CVI. The magnitude of the SVI after sonication with no mixing depends on the shifts of the measuring probe position. Apparently this occurs due to inhomogeneity of the carbon nanotube gel, which might have clusters with higher density and gaps with no solids at all. This effect can be used for testing homogeneity of the carbon nanotube gel. Sonication with continuous mixing also affects the electroacoustic signal and conductivity. However, the electroacoustic phase does not reach 360°, which corresponds to the SVI in gel. The measured signal is the vector sum of the CVI and SVI under these conditions. It is possible to use data on the electroacoustic phase to monitoring the number of carbon nanotube segments that retain independent motion.
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Keywords:

1. Introduction

We observed the effect that is described in this paper accidentally. One of the potential users of our electroacoustic ζ-potential probe DT-300 asked us to verify the applicability of this instrument for characterizing carbon nanotubes. The results were very surprising and forced us to look at the literature. It turned out that similar effects had been observed much earlier. The earliest relevant work that we found was published by Williams in 1948 [1]. It was experimental, but with useful and completely forgotten industrial application. Theoretical model was developed about 30 years later [2]. There has been no follow-up for the past 30 years. We consider the observed effect quite useful, because it opens up a new way of characterizing porous bodies. The scope of electroacoustic ζ-potential probes can be expanded substantially by including porous bodies for characterization of their electric surface properties.

This paper presents results of our more detailed investigation that followed up our initial findings.

Our customer provided us with dry carbon nanotubes. We prepared aqueous dispersions at 1 wt% and performed a set of measurements using various schemes of sample handling. In the original setup we inserted the probe into the beaker with the sample, which could be either immobile or mixed with a magnetic mixer. In the later setup we used the sample chamber of our instrument DT-1200, which allowed mounting electroacoustic and conductivity probes in the walls and pumping the sample through.

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doi:10.1016/j.jcis.2007.01.018

Results of the measurements turned out to be very sensitive to the sample handling. This is unusual. Normal stable dispersions exhibit practically the same electroacoustic signal independent of the method of the probe mounting, unless sedimentation does not affect stability. This is clearly not the case with structured carbon nanotubes dispersion. Electroacoustic measurement apparently is quite sensitive to the structure, and can even be used for monitoring the homogeneity of the structure. Illustration of this statement is one of this paper's purposes.

However, the most surprising discovery was the behavior of the electroacoustic phase. It corresponded to a positive surface charge of the carbon nanotubes, whereas independent tests indicated that they are negatively charged. To explain the meaning of this contradiction, we present electroacoustic measurements in some detail.

We measure the electroacoustic signal as an alternating current at a frequency of 3 MHz. This current comes as a result of ultrasound propagation through the system. It was shown 70 years ago by Debye that propagation of ultrasound through a liquid that contains charged species, ions or colloid particles, generates an electric response [3]. In the case of colloidal particles this is called colloid vibration current (CVI).

This signal, like all alternating signals, can be characterized by magnitude and phase. The magnitude of CVI depends on the volume fraction, the ζ-potential of the dispersed phase, and some other parameters. A detailed theory is given in the book [5].

The phase of CVI reflects first of all the sign of the particles' surface charge. There is a convention relating CVI phase with ζ-potential sign. Positive ζ-potential yields CVI phase values around 360°, whereas negative ζ-potentials are associated with CVI phases around 180°. Theory predicts that increasing particle size might affect CVI phase as well, but no more than 45°.

We have consistently measured the electroacoustic phase of sonicated immobile structured carbon nanotube dispersions as 360° with a few degrees variation. According to the well-known, well-tested, and widely accepted electroacoustic theory, this points toward positively charged particles.

However, microelectrophoretic measurement tells us unambiguously that carbon nanotubes are negatively charged in 0.001 M KCl solution, such as we prepared the dispersion in.

Existing electroacoustic theory does not know any effect that would alter electroacoustic phase by 180°, other than the sign of the surface charge. This means that existing electroacoustic theory cannot explain our experimental data for carbon nanotubes. We have been forced to look for a new electroacoustic theory.

We found the first clue when measuring stirred samples. There has also been a phase shift, but not as big as 180°. The phase was in the range of 250°–320°. Mixing destroys the carbon nanotube network. This points toward this structure as a reason for the phase shift.

It is possible that carbon nanotubes linked into the network become completely immobile and even ultrasound cannot move or shake them.

Existing electroacoustic theory assumes that ultrasound moves particles relative to the liquid due to the density contrast. This assumption might be not valid for structured carbon nanotube dispersions. Ultrasound would still go through the structured network, but carbon nanotube segments would not move relative to the laboratory frame of references

This does not mean yet that termination of the carbon nanotubes' motion would eliminate relative motion of the liquid. The gradient of the pressure in the ultrasound wave would move the liquid relative to the immobile carbon nanotubes. It would squeeze the liquid as in the case of a membrane. This motion would drag ions of the carbon nanotubes' double layer. This motion of ions would be registered by our probe as an electroacoustic signal.

This situation is well known in classical colloid science [6]. Electric current generated by a gradient of pressure is called streaming current.

We are coming to the conclusion that ultrasound can generate a streaming current when it propagates through the network of immobile carbon nanotubes. We suggest calling it a streaming vibration current (SVI) to reflecting that it is alternating with a frequency identical to the ultrasound frequency. Similar effect had been predicted and observed many years ago for membranes [1,2,5].

A simple analysis presented below in Appendix A indicates that the phase of the SVI is 180° reversed from the phase of the CVI.

Our experimental data presented below can be interpreted as a result of transition from CVI to SVI. Structuring of carbon nanotubes causes this transition. It can be controlled by application of ultrasound and/or mixing.

When the measured phase is 360°, the measured signal is only SVI. When the measured phase is much below 360°, measured signal is a vector sum of the CVI and SVI.

At the end we suggest several potential applications of this effect.

2. Materials

We use carbon nanotubes produced by Jeio Co., Ltd., Seoul, Korea and received through our supplier.

A dispersion is prepared as 1 wt% of these carbon nanotubes in a 0.001 M KCl aqueous solution. This and other potassium chloride (KCl) solutions are prepared using powder produced by J.T. Baker Chemical Co.

For chemical modification of the carbon nanotubes we use sodium hexametaphosphate from Fluka, UK.

For calibrating the electroacoustic probe we use silica Ludox TM-50 produced by Grace–Davison and purchased from Sigma–Aldrich. The original dispersion contains 50 wt% silica. We dilute it down to 10 wt% using a 0.01 M KCl solution. Silica has ζ-potential −38 mV in this solution.

Calibration of the conductivity probe has been done using distilled water and two KCl solutions with concentrations 0.01 and 0.1 mol/l.

3. Experimental techniques

We used an instrument manufactured by Dispersion Technology Inc., Model DT-300. It has electroacoustic sensors as

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Fig. 1. Images of the conductivity and electroacoustic probes used in these experiments. The sound beam of the electroacoustic probe propagates into the liquid through the central gold electrode. It determines the diameter of the beam.

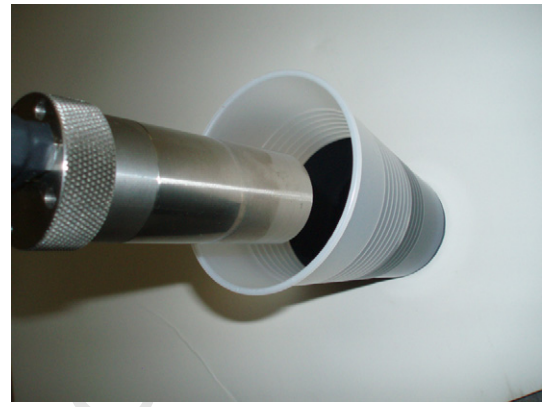

Fig. 2. The electroacoustic probe can simply be inserted into the sample. In this case it is a black 1 wt% carbon nanotube dispersion in the cup. This is Setup 1 for the experimental protocol.

well as a built-in conductivity probe. Details are available on the Web site www.dispersion.com and in the book [4]. Photographs of both probes are shown in Fig. 1. It is essential for our subject that these probes can be used deep in and permanently mounted in the wall of the sample chamber.

Both probes function at 3 MHz. This eliminates electrode polarization for conductivity measurement and allows very simple probe design (see Fig. 1).

Precision of both the conductivity and electroacoustic measurements is about 1%.

The electroacoustic method is much less known. That is why we present some details below.

Debye [3] first predicted an electroacoustic effect 70 years ago. In either electrolyte solutions or dispersions, the effect is related to coupling between electrodynamic and mechanical phenomena. For instance, the transmission of ultrasound through an electrolyte solution or dispersion generates a current, which is usually referred to as an ion/colloid vibration current. In the case of the DT-300 this ultrasound is generated with a piezoelectric transducer inside the probe. It converts an electrical tone burst signal to a sound pulse that is then transmitted to the front face of the probe and into the colloid. This sound pulse generates an electroacoustic signal in front of the probe, which is measured as a current between a central gold electrode and a surrounding annular electrode.

The experimental output of the electroacoustic measurement is the CVI magnitude and phase. They are usually converted to the dynamic electrophoretic mobility and/or ζ-potential, which are considered as outputs of the electroacoustic technique. This conversion procedure requires a proper theory. The simplest version, which is valid for sufficiently small particles with thin DL and negligible surface conductivity, is

$$\frac{CVI_{\omega\to 0}}{\nabla P} = \frac{\varepsilon_{\mathrm{m}}\varepsilon_0\zeta\Phi K_{\mathrm{s}}}{\eta K_{\mathrm{m}}}\frac{(\rho_{\mathrm{p}}-\rho_{\mathrm{s}})}{\rho_{\mathrm{s}}}, \tag{1}$$

where P is pressure in the sound wave, ε_{m} and ε_0 are dielectric permittivities of the media medium and vacuum, Φ is volume fraction of the dispersed phase, η is dynamic viscosity, ρ_{p}, ρ_{m}, and ρ_{s} are densities of the particle, media medium, and dispersion, and K_{s} and K_{m} are conductivities of the system and medium.

In this paper we do not convert electroacoustic signal into ζ-potential. We report just the magnitude of the electroacoustic signal, which is normalized by the intensity but not the pressure gradient of the ultrasound. There are also some dimensionless corrections involved in calculation of this magnitude, for instance, reflection of ultrasound at the probe–sample interface. Final units of this magnitude after calibrating out dimension constants, such as dielectric permittivity of vacuum, are $mV\sqrt{s/g}$.

The second experimental parameter is the phase of the electroacoustic signal. The calibration procedure with negatively charged silica Ludox assigns 180° values to this phase for all negative particles. It is assumed to be close to 0° or 360° for positive particles. This assumes that general electroacoustic theory is valid.

We use a PenKem 501 microelectrophoretic instrument to verify the sign of the carbon nanotubes' surface charge.

4. Experimental protocols

We used two different sample handling setups.

In the first one we placed a sample in the beaker and inserted conductivity and electroacoustic probes into it. Fig. 2 illustrates this setup.

In the second setup we mounted both probes in the standard sample chamber of DT-1200 with built-in magnetic mixer—see Fig. 3.

There have been various tests performed with each setup. We measured three different samples of the same carbon nanotubes using each setup to test reproducibility of the data.

As a first step after calibrating the sensors, we prepared 10 g of the 1 wt% carbon nanotube dispersion by adding powder to 0.001 M KCl solution and mixing it till all powder became wetted. Then we stopped mixing and let the sample sit till sedimentation separated the supernatant and deposit. This allows us to measure the electroacoustic signal generated by the ions. It is a background signal that can mask contributions from particles.

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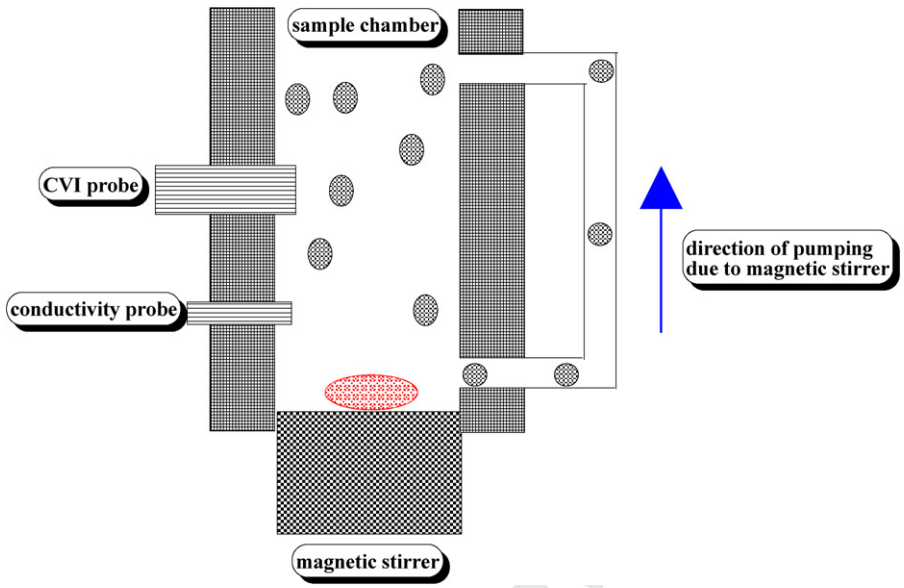

Fig. 3. Scheme of the DT-1200 sample chamber. Probes are mounted in the left wall of the chamber. The magnetic stirrer on the bottom creates extra pressure that pumps the sample from the bottom to the top over the plastic tube that connects bottom and top ports. This is Setup 2 for the experimental protocol.

4.1. Supernatant measurement

For performing supernatant measurement the electroacoustic probe and conductivity probe are not inserted deeply, only into the supernatant.

4.2. Deposit measurement

As a next step we inserted the probes deeper, into the deposit. This allowed us to measure the electroacoustic signal coming from rather undisturbed carbon nanotubes.

4.3. Sonication effect

After this we took the probes out and sonicated the sample. Sonication for 1 min makes the sample look like a gel. It is still possible to insert probes into this gel and make measurements.

Then we removed the probes and sonicated the sample for another minute with the following measurement.

4.4. Reproducibility test

After 3 min sonication we just left the probes inside of the sample and made 500 continuous measurements. Each measurement took about half a minute.

4.5. Homogeneity test

After about 15 h of continuous measurement we tested the sensitivity of the measurement to the position of the probes inside the sample. This would be a test of the gel homogeneity. We just shifted the probes' position in the horizontal plane without interrupting the measurements.

Instead of placing the sample in the beaker we filled it into the DT-1200 sample chamber and turned the mixer on. We set software for multiple continuous measurements.

Table 1
Magnitude of electroacoustic signal when probe is inserted into the sample and no mixing is applied

Sample	Magnitude of electroacoustic signal $[mV\sqrt{s/g}]$.
Distilled water	51.860
0.001 M KCl	8.164 ± 3.373
Supernatant of 1 wt% carbon nanotube dispersion	15.021 ± 4.938
Deposit of 1 wt% carbon nanotube dispersion	68.711 ± 5.026

4.6. Sonication test

We can insert sonication probe directly into the sample chamber and sonicate sample during mixing.

4.7. Surface modification test

We added a certain amount of surfactant directly into the sample without interrupting measurements and mixing.

5. Results

Results of all tests are summarized in Table 1 and Figs. 4–7. We present here only the features of these measurements that have been reproducible from sample to sample. We also discuss reasons for poor reproducibility in some experimental setups.

Results of the measurements using Setup 1 for supernatant and deposit are shown in Table 1. We also show the electroacoustic signal in the 0.001 M KCl solution and distilled water for comparison. It is seen that there is practically no difference between the supernatant and the 0.001 M KCl solution. This indicates that carbon nanotubes did not change the ionic composition of the liquid when we added them to the KCl solution.

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Conductivity measurement confirms this conclusion. Conductivity of the supernatant is 0.0136 at 24 °C, which is very close to the conductivity of the 0.001 KCl solution at this temperature.

The magnitude of the electroacoustic signal in the deposit exceeds that of the electroacoustic signal from the supernatant by almost 5 times. This proves that we can measure the electroacoustic signal generated by carbon nanotubes.

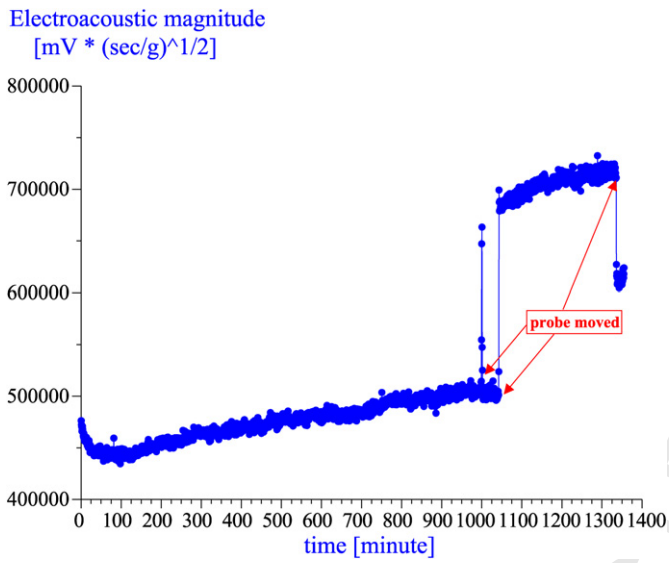

Fig. 4. Multiple measurements of the electroacoustic signal magnitude for 1 wt% carbon nanotube dispersion after 3 min of sonication using Setup 1. Arrows indicate time moments when probe was shifted horizontally in the cup.

The phase of the electroacoustic signal in the deposit was about 250°. This is the first indication that the electroacoustic signal that we measure is not colloid vibration current.

Sonication changes measured the electroacoustic signal. It became much greater in magnitude. Phase increased as well, approaching a value of 360°.

Unfortunately, results of sonication turn out to be very poorly reproducible. Each 1-min sonication cycle could change the magnitude of electroacoustic signal by tens of percent and the phase by tens of degrees. This was puzzling, with no real explanation at this point. That is why we decided to make con-

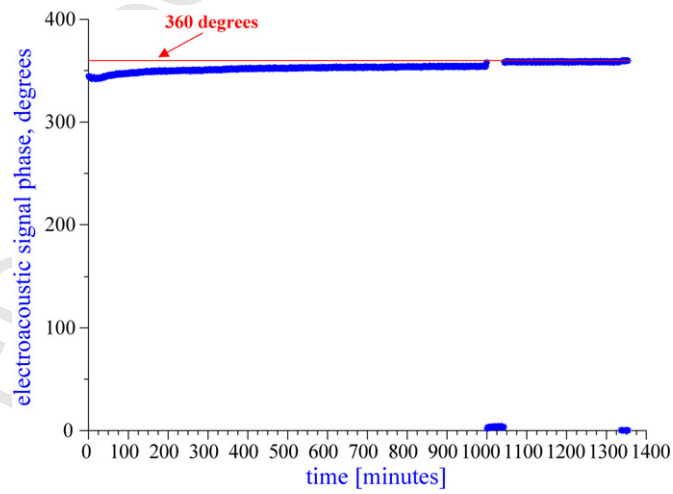

Fig. 5. Multiple measurements of the electroacoustic signal phase for 1 wt% carbon nanotube dispersion after 3 min of sonication using Setup 1.

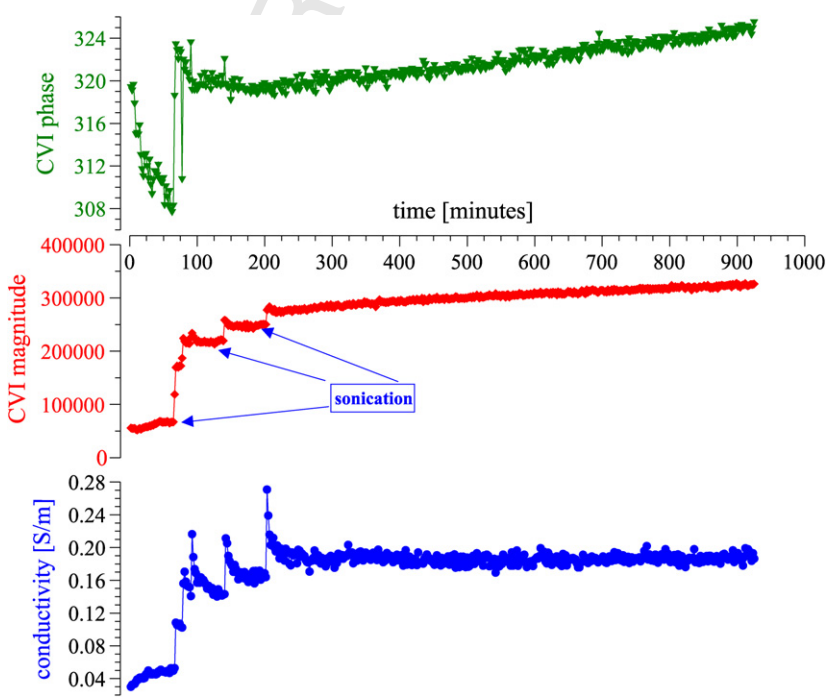

Fig. 6. Multiple measurements of the conductivity and electroacoustic signal magnitude and phase for 1 wt% carbon nanotube dispersion using Setup 2. Arrows indicate time moments when sample was sonicated.

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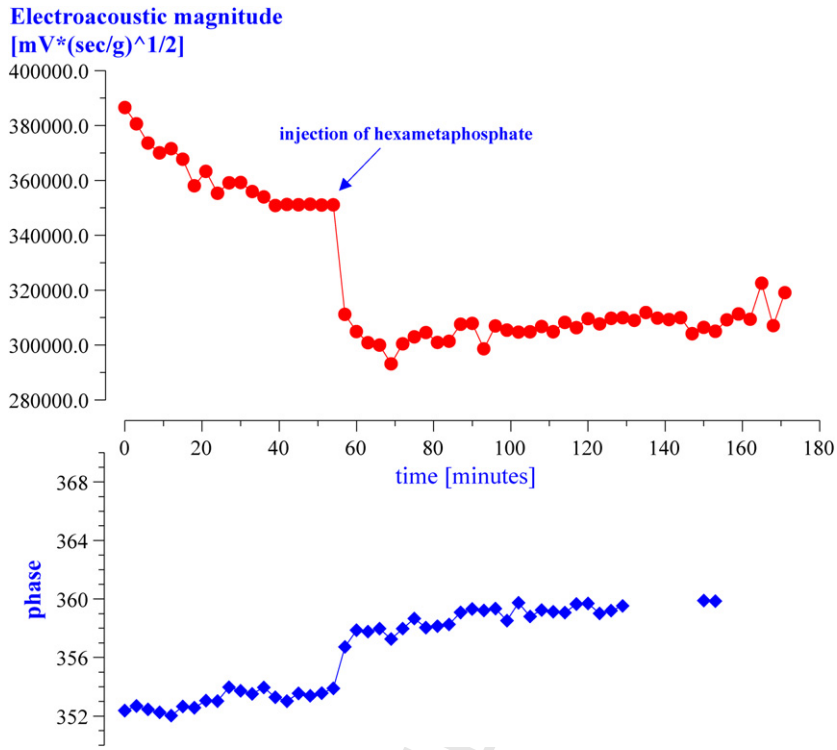

Fig. 7. Multiple measurements of the electroacoustic signal magnitude for 1 wt% carbon nanotube dispersion after a week since preparation and sonication using Setup 1. Arrow indicates injection of the hexametaphosphate.

tinuous measurements after making three poorly reproducible sonication tests.

Figs. 4 and 5 illustrate results of this continuous test.

The magnitude of the electroacoustic signal increases almost 10 times after 3 min of sonication. This measurement is quite reproducible if the probe is fixed in the sample.

The moving probe in the sample after 1000 min of equilibration still causes very large and irreproducible changes in the magnitude of the electroacoustic signal. One can see that magnitude might increase or decrease after the probe has been moved.

In contrast, the phase of the electroacoustic signal is not sensitive to the position and movement of the probe in the sensor.

The value of the phase is very surprising. It is 360° for the negatively charged carbon nanotubes. We verified the sign of the carbon nanotubes' surface charge using a microelectrophoretic instrument. The direction of the motion corresponds to that of the negatively charged particles.

This value of the phase also indicates that the electroacoustic signal that we measure is not colloid vibration current. According to the instrument calibration, CVI value of the negatively charged particles must be above 180° and less than 225°.

Measurements using Setup 2 when sample was being pumped through the measuring chamber confirm the importance of sonication. Fig. 6 presents the results of this test. The initial value of the measured electroacoustic signal before sonication is almost the same as in the immobile deposit. This means that mixing only does not affect carbon nanotubes. The observed effect of increasing the magnitude and phase of the electroacoustic signal requires higher energy, such as is provided by sonication.

Sonication directly in the chamber increases the magnitude of the electroacoustic effect and conductivity.

It is interesting that all three measured parameters in Fig. 6 exhibit a gradual increase with time.

Measurements of the same samples after several days indicate that this increase leads eventually to the phase of the electroacoustic signal becoming around 360° degrees and the magnitude almost independent of sonication. This is shown in Fig. 7.

We also tried to modify surface carbon nanotubes by adding hexametaphosphate. It is known that this substance enhances the negative charge of the surfaces. Results of this test are inconclusive. In some cases we observed a substantial increase of the electroacoustic signal magnitude; in some cases, as in Fig. 7, it was decreasing.

6. Discussion and explanation of the experimental data

We think that the observed peculiarities of the electroacoustic measurement are related to the structure built up by carbon nanotubes. It is known (see Appendix A) that there is a large difference in the electroacoustic signal produced either by mobile particles or by particles that cannot move in the sound field due to the gel structure. Mobile particles generate CVI, whereas structured immobile particles generate SVI.

Theory predicts a 180° phase difference between these two cases. This correlates with our observations of the carbon nanotubes after sonication, when the structure is well developed.

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Apparently in this case nanotube segments are completely locked into the network.

A smaller phase shift for the deposit can be an indication that the structure has not yet formed completely. Some segments retain their independent motion, which generates CVI. Other segments that are interlocked already generate SVI. The measured signal is a vector sum of these two. The phase of this sum vector can be in the range around 250°–300° if the phase of the CVI is not exactly 180°, or the phase of the SVI is not exactly 360°.

We do know the SVI phase from the measurement of the completely formed gel. It is very close to 360°.

This means that the CVI phase must differ from 180°.

Rotation of the CVI vector away from 180° might occur due to the Maxwell–Wagner relaxation effect. There is an expression in Appendix A (Eq. [illegible]) that determines the frequency of the double-layer relaxation. It turns out that this frequency almost exactly equals the ultrasound frequency for these measurements with 0.001 M KCl solutions,

$$\omega_{\mathrm{MW}} = \kappa^2 D_{\mathrm{eff}\ 0.001\ \mathrm{M\ KCl}} \approx 3\ \mathrm{MHz}, \tag{2}$$

where all parameters are defined in Appendix A.

The maximum phase shift from very low to very high frequency due to the Maxwell–Wagner relaxation is 90°. In this case, when we are in the middle of this relaxation range, we could expect a phase shift of around 45°.

The positions of these two vectors and their sum are shown in Fig. 8.

A similar explanation can be applied to the continuously mixing dispersion, which also exhibits a smaller phase shift.

Another relaxation effect mentioned in Appendix A, hydrodynamic relaxation, seems unimportant in this case. The critical hydrodynamic frequency many times exceeds the frequency of the ultrasound,

$$\omega_{\mathrm{hd}} = \frac{2\nu\Phi}{a}^{2}_{a=10\ \mathrm{nm},\Phi=0.01} \approx 100\ \mathrm{MHz}, \tag{3}$$

where all parameters are defined in Appendix A and we assume the radius of the carbon nanotubes to be 10 nm.

However, this conclusion would be valid only for a homogeneous gel. In this case the average distance between carbon nanotubes would be much shorter than the hydrodynamic depth at 3 MHz, which is about 1 μm. This allows us to consider the hydrodynamic field between carbon nanotube segments as being completely developed, the same as under stationary conditions.

In the case of an inhomogeneous gel, hydrodynamic relaxation might be important. Carbon nanotubes can build clusters with rather large distances from one cluster to another. If this distance exceeded the hydrodynamic depth, which is about 1 μm in this experiment, there would be no signal coming from these gaps between clusters. The measured SVI would become a function of cluster numbers in front of the measuring electroacoustic probe. Moving the probe inside of the sample could expose it to different numbers of such clusters. This would cause variation in the magnitude of the measured SVI.

The spreading of this SVI variation would depend not only on the size of the clusters, but also on the average distance between them and the size of the sound beam. The diameter of the sound beam of the DT-300 is about 5 mm. Substantial variations of SVI magnitude occur only when the average distance between clusters is comparable with the size of the sound beam. The number of clusters in front of the probe would be small and this would allow large deviations due to probe shifts in the sample.

This simple analysis yields an explanation of the observed instability in the magnitude of the measured SVI when Setup 1 was used for sample handling. Apparently gels built up by sonication are not homogeneous enough, at least at the beginning. The scale of the gel density variations is from hundreds of micrometers to millimeters, which would be comparable with the diameter of the sound beam.

It is possible that carbon nanotubes become more homogeneous with time. We observed that the SVI signal becomes less sensitive to the probe shifts after several days. This would require further systematic investigation.

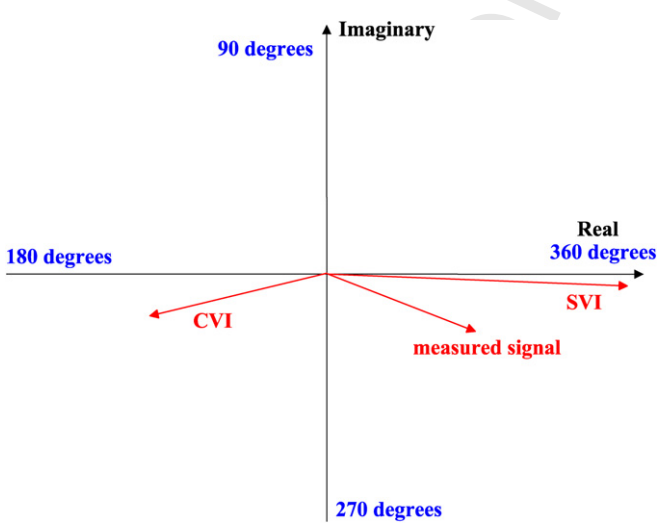

Fig. 8. Illustration of the CVI and SVI as vectors. The SVI phase is close to 360°, according to the experiment. The CVI phase is more than 180° in order for the net vector to have a phase of around 300°, which would correspond to the measurement with Setup 2.

7. Conclusions

The electroacoustic effect exists not only in dispersions of mobile particles, but in porous bodies as well. Pressure gradients in ultrasound waves move ions of diffuse layers relative to the solid surface. This motion creates a measurable electric current. We suggest calling this effect a streaming vibration current.

We measure SVI in dispersion of carbon nanotubes. The phase of the electroacoustic signal reflects the degrees of freedom of the carbon nanotube segments. The closer the phase is to 360°, the fewer nanotube segments retain their mobility.

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The magnitude of the electroacoustic signal can be used to monitoring the homogeneity of the gel on the scale of hundreds of micrometers to millimeters. Position shifts of the electroacoustic probe in the sample would create variation in the measured electroacoustic signal if the gel were inhomogeneous.

Electroacoustic measurement can be used to monitor relative values of the surface electric charges when position shifts of the probe do not affect the signal magnitude and the gel is homogeneous. It is possible that measurement of the potential, instead of the current, would yield certain advantages for monitoring electric surface properties. This can be achieved by terminating the measuring probe with a high external impedance, similarly to traditional streaming potential measurement.

Electroacoustic measurement in the dispersion of nanotubes might be useful, first of all, for characterizing microrheological properties of the dispersion, instead of electric surface properties, as for traditional colloids. This conclusion might be valid for other systems where particles build up gel structures. Termination of the particles' motion in gels rather than the traditional dispersions or sols leads to the transition of the electroacoustic measurement from the colloid vibration current mode in sols to the streaming vibration current mode in gels.

Appendix A. Theoretical description of the colloid vibration current transition into a streaming vibration current due to termination of the particles' motion

Propagation of ultrasound through a liquid containing charged objects (ions, colloid particles, etc.) generates an electric response, according to Debye [3]. This response is associated with the motion of these objects relative to the liquid. The name of the electric signal reflects the nature of the moving objects—ion vibration current for ions, colloid vibration current for colloid particles, etc.

In the case of CVI it is assumed that colloidal particles move relative to the liquid under the influence of ultrasound. However, it is also known that this condition is not necessary for creating an electric response. There are several old papers dedicated to ultrasound propagation through membranes [1,2,5]. It turns out that there is a certain electric response, which is similar to the streaming potential or streaming current [6]. We suggest calling this effect streaming vibration current/potential (SVI/SVP) in order to reflect the alternating nature of this effect, its relationship to the ultrasound. It should exist when ultrasound propagates through gels, membranes, and other systems with immobile particles.

There is a close relationship between CVI and SVI, which, as far as we know, has never been described or observed before. For further analysis it is helpful to have a simple qualitative description of the mechanism that links together mechanical and electrical forces in liquids with charged objects.

It turns out that it is easier to create such a description for the case when the electrical force is driving, not ultrasound. This reverse electroacoustic effect is referred to as electric sonic amplitude (ESA) [7]. We present here a description of the ESA effect following original paper by O'Brien, who created the first theory [7]. The theory of ESA assumes that particles move relative to the laboratory frame of reference under the influence of an electric field. The opposite case of immobile particles corresponds to the nonstationary electroosmosis. We use this transition "ESA–electroosmosis" to illustrate the role of the particles' motion.

As a next step we employ Onsager relationship [8,9] for expanding derived conclusions on the "CVI–SVI" relationship. In addition, we present some results from an old theoretical paper on streaming vibration current, which confirms our conclusions [2].

At the end, we discuss some limitations of theory with regard to the frequency domain.

A.1. ESA versus nonstationary electroosmosis

Fig. A.1 illustrates how an applied electric field generates ultrasound. Charged particles would move relative to the laboratory frame of reference due to the electric forces that an external field exerts on their surface charges. This particle motion generates a certain mechanical momentum flux, M_p. The value of this flux can be estimated as a product of the particles' volume flux, V_Ω, multiplied by the particles density, ρ_p:

$$M_p = V_p \rho_p. \tag{A.1}$$

This flux is not a single one in the system. Motion of the particles generates an opposite liquid flow. This flow of the liquid also causes a certain volume flux, V_m, and associated with it a momentum flux, M_m. These two fluxes are related to a medium density ρ_m as multiplier:

$$M_m = -V_m \rho_m. \tag{A.2}$$

The net momentum flux M generates a pressure that acts on the sensing element. It equals

$$M = M_p + M_m = V_p \rho_p - V_m \rho_m. \tag{A.3}$$

A very significant simplification that becomes possible if we assume the liquid to be incompressible. This assumption should be valid for a sample layer that contains a representative number of particles on one side and is much thinner than the wavelength on the other side. The measurement frequency of the DT-300 is 3 MHz, which corresponds roughly to 50 μm wavelength. This means that for particles that are smaller than 10 μm the liquid incompressibility assumption can be considered valid.

In the case of an incompressible liquid, the volume fluxes of the particles and liquid are equal, but momenta are not, due to the difference in densities. The total momentum flux in this case equals

$$M = V_m(\rho_p - \rho_m). \tag{A.4}$$

This equation eventually leads to the final expression of the O'Brien theory, which links together the ESA signal normalized by the pressure gradient ∇P with density contrast $(\rho_p - \rho_m)/\rho_m$, volume fraction of particles Φ, and dynamic electrophoretic mobility μ_d:

$$\mathrm{ESA} \propto \Phi \frac{\rho_p - \rho_m}{\rho_m} \mu_d. \tag{A.5}$$

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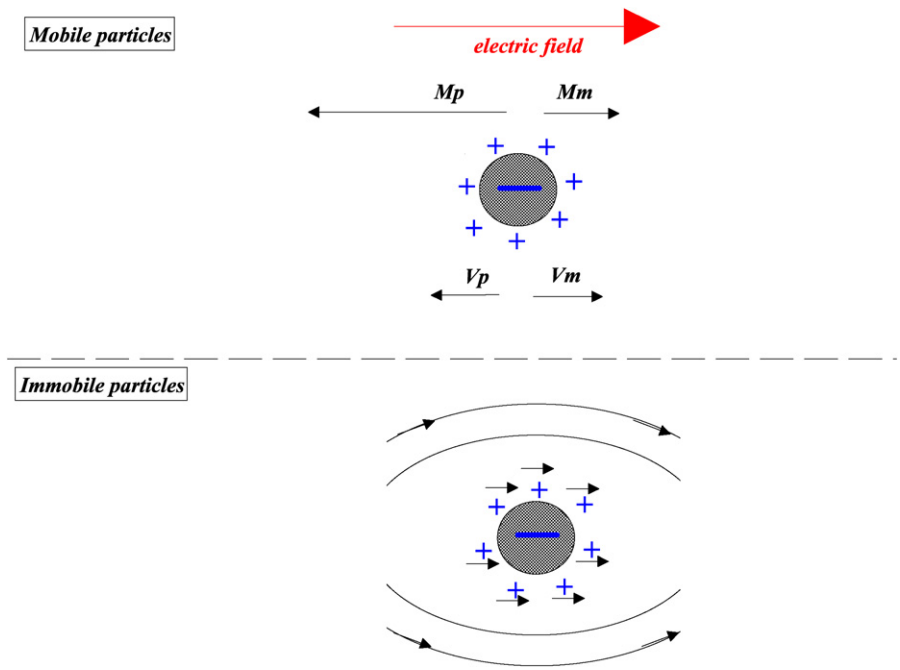

Fig. A.1. Illustration of ultrasound generation by the particles' motion under the influence of the electric field E, when the particles are mobile. Immobile particles causes an electroosmotic flow that would also generate an ultrasound pressure wave.

The direction of the ESA vector depends on the sign of the particles' charge and the sign of the density contrast. For instance, negatively charged particles, as in Fig. A.1, move against the electric field, from the right to the left. Let us assume that they are heavier than the liquid. This means that the pressure force due to the net momentum would be directed against the electric field, with a phase shift of 180°. Positively charged particles would generate an ESA signal in phase with the electric field, which means its phase would be 0° or 360°. Reversal of the density contrast sign would reverse this ESA phase.

One can see that all this analysis is based on the assumption that particles move relative to the laboratory frame of reference under the influence of the electric field. What would happen if they were not moving? This question is relevant for systems where particles' motion is terminated by networking by specific forces. Carbon nanotube gel is an example.

Let us assume that particles in Fig. A.1 do not move relative to the laboratory frame of reference. Does this mean that application of the electric field will not cause any mechanical effect? Obviously, it will generate one. The electric field generates an electroosmotic flow on particles' surfaces. This flow generates a momentum flux, which in turn causes a pressure gradient on the sensor element surface.

There is an electroacoustic effect even in the case of mobile particles, but its properties are quite different from those of the traditional ESA.

First of all, there is no dependence on the density contrast. Electroosmotic flow exists even at a perfect match of the particle and liquid densities.

Second, the direction and related phase of the effect are different. The direction of the electroosmotic flow would depend on the sign of the diffuse layer charges. In the case of the negative particle in Fig. A.1, the diffuse layer is positive. Therefore, electroosmotic flux would be in phase with the external electric field.

This leads us to the conclusion that termination of particle motion relative to the laboratory frame of reference reverses the phase of the electroacoustic signal by 180° and eliminates dependence on the density contrast.

A.2. CVI versus SVI

The theoretical analysis given above has been performed for an electric field as a driving force. It is well known that there is a reciprocal effect, which occurs when the pressure gradient is the driving force. It is symmetrical to ESA, following the Onsager principle [8,9]. In traditional electroacoustics this effect is called colloid vibration current [5]. Our analysis indicates that propagation of ultrasound through a sample with immobile particles would also generate an electric current. It occurs due to the motion of the diffuse layers in the gradient of pressure. This effect is well known in general colloid science—streaming current [6]. In the case where it is generated by ultrasound, it is streaming vibration current.

There is a theory of the streaming vibration current/potential developed for membranes almost 25 yr ago by Dukhin et al. [2]. Unfortunately, it is not directly applicable to the case of gels built up by fibers. Its final model expressions had been derived either for membranes with cylindrical capillaries or for packed spheres. However, there are some conclusions that can be directly applied to this study.

The first part of the paper [2] presents a phenomenological treatment of the problem. It simply declares proportionality between current density in the membrane, I, and the pressure drop

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over the membrane, p:

$$p = p_0 \sin \omega t, \tag{A.6}$$

$$i = i_0 \sin \omega t, \tag{A.7}$$

$$i_0 = I p_0. \tag{A.8}$$

There is no clarification of the parameter I initially. The membrane is assumed to be a homogeneous object with a certain resistance, R_m. This resistance is connected to the external resistance of the measuring device, R_h. Solution of the electrodynamic equations for this simple model makes it possible to derive expressions for the experimentally measured parameters. The final expressions can be simplified for two extreme cases:

(a) Resistance of the measuring device is much smaller than membrane resistance, $R_h \ll R_m$.
(b) Resistance of the measuring device is much larger than membrane resistance, $R_h \gg R_m$.

Case (a) corresponds to the conditions where the measured current equals the streaming vibration current. This is also the case when the colloid vibration current is measured for the dispersion of the moving particles. The measuring probe is designed with an impedance that is much smaller than the impedance of the dispersion [4].

Case (a) corresponds to the experimental setup of the current study.

The important conclusion derived in the paper [2] is that there is no phase difference between electric current and pressure in the ultrasound waves for case (a). We have concluded the same from simple qualitative analysis of the ESA effect for immobile particles.

This means that the theory predicts a 180° shift of the measured electric current generated by ultrasound due to termination of the particles' motion.

The second step of the theory in the paper [2] was calculation of the kinetic coefficient I for two different models of the membrane: cylindrical capillaries for packed spheres. Neither of them is applicable to this study.

In the case of low or zero frequency the classical theory of the streaming current/potential can be useful. It yields the following expression for the streaming current I_{str} in the constant–pressure gradient,

$$I_{str} = \frac{\varepsilon_0 \varepsilon A \zeta}{\eta} \nabla P, \tag{A.9}$$

where ε_0 and ε are dielectric permittivities of vacuum and liquid, η is dynamic viscosity, and ζ is electrokinetic potential. Parameter A reflects the geometry of the system. For instance, it is a simple cross-section in the case of a single capillary.

Comparing Eqs. (A.9) and (A.10), one can derive a simple expression for the parameter I in the theory of SVI [2] that would be valid for low frequencies only:

$$I = \frac{\varepsilon_0 \varepsilon A \zeta}{\eta}. \tag{A.10}$$

Classic theory [6] predicts that measurement of the current might be not optimum for characterizing surface properties of the dispersed phase. This is because of the dependence on the geometrical factor A in Eq. (A.10). This parameter is not known for real systems. In contrast, streaming potential is independent of this factor, at least when surface conductivity is negligible and double layers are not overlapped. That is why measuring potential instead of current might be more advisable for characterizing electric surface properties. This can be achieved by making the external resistance R_h much higher than the resistance of the dispersed system.

Measurements of the current, on the other side, can be used for characterizing the microstructure of the system, assuming unchanged electric surface properties.

There is one more important feature that is different for CVI and SVI. Colloid vibration current depends on the density contrast between the dispersed phase and the dispersion medium. It decreases when this parameter becomes smaller.

In contrast, SVI is independent of the density contrast. It would exist even the density of the particles and media matched perfectly.

We observe transition from CVI to SVI for the very-low-volume fraction in the case of carbon nanotubes. This is not the case for traditional suspensions, emulsions, nanocolloids, etc. However, one should take into account that increasing the volume fraction would eventually restrict the motion of the particles. Existing cell model theory for CVI [5] takes this effect into account to a certain degree. It cannot describe all transitions from CVI to SVI. Deviation of the theoretical phase from the experimentally measured values would be an indication that particles' motion has been retarded more than the existing model predicts.

A.3. Frequency ranges

There are two major restrictions on the frequency for applying classical stationary streaming potential/current theory to the nonstationary SVI or SVP.

When a pressure gradient wave propagates through the network of particles, the last ones disturb the generated hydrodynamic flow. These distortions reach steady state if the average distance between particles (d) is much smaller than the hydrodynamic depth penetration (δ). The expression for hydrodynamic penetration depth is well known; see [4,6]. It yields the following condition for the steady state SVI,

$$d \ll \delta = \sqrt{\frac{2\nu}{\omega}}, \tag{A.11}$$

where ν is the kinematic viscosity of the medium.

We can express the average distance between the particles, assuming that they are fibers with diameter (a), and much, much greater length. This model would work for carbon nanotubes or paper fibers. As a next step, we assume that the fibers are placed in perfect order with equal distances d between them. This distances for such a simple model would be equal:

$$d \approx \frac{a}{\sqrt{\Phi}}. \tag{A.12}$$

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Combining Eqs. (A.11) and (A.12), we derive the first restriction on the ultrasound frequency for validity of the classical theory for SVI:

$$\omega \ll \omega_{\mathrm{hd}} = \frac{2\nu\Phi}{a^2}. \tag{A.13}$$

The second restriction comes from the Maxwell–Wagner theory of double-layer relaxation [10,11]. Variation of the ultrasound should be slow enough to allow DL adjustment. This requires that ultrasound frequency must be lower than the so-called Maxwell–Wagner frequency ω_{MW},

$$\omega \ll \omega_{\mathrm{MW}} = \kappa^2 D_{\mathrm{eff}}, \tag{A.14}$$

where κ is the reciprocal Debye length and D_{eff} is the effective diffusion coefficient of the electrolyte.

References

[1] M. Williams, Rev. Sci. Instrum. 19 (10) (1948) 640–646.
[2] S.S. Dukhin, N.A. Mischuk, B.B. Kuz'menko, B.I. Il'in, Colloid J. 45 (5) (1983) 875–881.
[3] P. Debye, J. Chem. Phys. 1 (1933) 13–16.
[4] A.S. Dukhin, J.P. Goetz, Ultrasound for Characterizing Colloids: Particle Sizing, Zeta Potential, Rheology, Elsevier, [illegible], 380 pp.
[5] J.N. Graves, A.R. Gears, J. Colloid Interfa[illegible]i. 53 (1) (1975) 83.
[6] J. Lyklema, Fundamentals of Interface and Colloid Science, vol. 1, Fundamentals, Academic Press, London/Toronto, 2000.
[7] R.W. O'Brien, J. Fluid Mech. 190 (1988) 71–86.
[8] L. Onsager, Phys. Rev. 37 (1931) 405.
[9] L. Onsager, Phys. Rev. 38 (1931) 2265.
[10] J.C. Maxwell, Electricity and Magnetism, vol. 1, Clarendon, Oxford, 1892.
[11] K.W. Wagner, Arch. Elektrotech. 2 (1914) 371.

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