Impedance of the free surface of liquid electrolytes

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Abstract

A possibility for the observation of so-called structure resonances (SR) in electrolytes arising due to relative motion of the cluster charged nucleus and its solvation shell is demonstrated. The discussed method considers the resonant contribution of the SR to the frequency dependence of the reflection (transmission) coefficient of the electromagnetic wave interacting with the free electrolyte surface. Of special interest is the observation of SR for multiply charged particles in electrolyte providing direct information on the charge of single cluster. Also important are other not so prominent details of the wave interaction with mobile charged clusters in electrolyte related to the formation and complicated nature of the frequency dependence of the charged cluster associated mass.

1 Introduction

The term “surface impedance” usually refers to a complex-valued quantity whose knowledge allows one to calculate the electromagnetic wave reflection coefficient $R$ from the free surface of a conductor (e.g., liquid) as well as the absorption and transmission coefficients $A$ and $D$, respectively. Investigation of these properties of a free surface possesses a number of advantages deserving special attention. First of all, field approach minimizes the effects of metal electrodes (which are normally always present and introduce additional hydrolysis complications into kinetic problems). Further appealing point (related to non-symmetric electrolytes) is associated with the spatial separation multiply charged colloid particles and compensating ions in the field of image forces. These forces pushing charged particles from the free surface inside the liquid are known \cite{1} to be quadratic in the particle charge and, therefore, affect the equilibrium position of oppositely charged particles relative to the free surface in different ways. The arising double layer which has not yet been studied in detail (as it was already done, e.g. for solutions of charged colloids in gravity field \cite{2,3,4}) allows to assume that the motion of separated colloids and corresponding compensating ions along the liquid surface is to a large extent free from the
correlation phenomena complicating the linear dependence of electrolyte conductivity on the donor density \[5\]. Hence, the well-known impedance formalism \([1, 6]\) can be without any essential limitations transferred to liquid non-symmetric conducting media.

Bearing in mind the above arguments, discussed in the present paper is the impedance approach to the resonance phenomena of mainly structural origin for non-symmetric electrolytes. The first part considers the origin of the structure resonances on the whole and the details relevant to multiply charged clusters. The results expected here include the possibility of finding the charge of individual colloid cluster which is one of the most important its characteristics. The general formalism is also outlined together with the details of the impedance formalism. The concluding part of the paper contains results of calculations illustrating the details of the impedance behavior in a wide frequency range.

2 Frequency intervals

Dynamics of charged clusters in liquid electrolytes involves various frequency-dependent effects in a wide range of frequencies \(\omega\). To describe the details of the electrolyte surface impedance in various frequency ranges we start with a brief outline of relevant physics.

We start with the general equations of motion for a charged cluster in liquid medium in the presence of external electric field oscillating with frequency \(\omega\):

\[
-m_i\omega^2 x = -k_s(x - x_1) + eE_0, \\
-M\omega^2 x_1 = -k_s(x_1 - x) + F_{hyd}(\omega, V_1) \quad V_1 = -i\omega x_1.
\]

Here \(m_i\) is the charge bare mass (for simplicity, the charges of opposite signs are assumed to be identical in all the other parameters, which is not anyway an essential assumption), \(x(t)\) is its oscillating coordinate, \(M = 4\pi R_i^3 \rho_s/3, \rho_s > \rho_l\) is the effective mass of the neutral shell calculated for the case of a solidified sphere \((\rho_s\) and \(\rho_l\) being the density of solid and liquid, respectively), \(x_1(t)\) is the shell oscillating position, \(F_{hyd}(\omega, V_1)\) is the hydrodynamic force containing both the viscosity effects and the cluster frequency dependent associated mass, \(eE_\parallel(t) = eE_0 \exp(-i\omega t)\) is the local external field of the incident electromagnetic wave. According to (1) the field \(eE(t)\) acts on the particle with mass \(m_i\). As to the neutral part of the cluster with mass \(M\), it is driven through the elastic coupling \(k\) with the bare charge.

Equations (1)-(2) allow to roughly identify three interesting frequency ranges

\[
\omega_s > \omega_M > \omega_\eta.
\]

The first interval, \(\omega \sim \omega_s\), contains the so-called structure resonances for charged clusters in electrolyte. The frequency range \(\omega \sim \omega_M\) is indicated to highlight the mechanism of formation of the ideal associated mass. Finally, the third range \(\omega \sim \omega_\eta\) reveals interesting details in the behavior of the associated mass of viscous origin.

Following Ref. [7], we use the term “structure resonance” (SR) to identify the resonances occurring in the excitation of the relative motion between the cluster bare charge
and its neutral shell. According to Eqs. (1)-(2), the structure resonance position $\omega_s$ is given by the formulae

$$\tilde{\omega}_s^2 = \frac{1 + \gamma}{\gamma}, \quad \tilde{\omega}_s = \omega_s/\sqrt{k_s/m_i}, \quad \gamma = M/m_i$$

(4)

provided that the contribution of $F_{hyd}(\omega, V_1)$ into dynamics defined by Eqs. (1)-(2) is relatively small. Under these conditions the quantity $\tilde{\omega}_s^2$ varies from unity for $\gamma \gg 1$ up to two for $\gamma \simeq 1$, reproducing the properties of efficient mass well known from dynamics of a pair of coupled particles. We call the frequency (4) the dipole frequency since it can be excited by a uniform electric field. According to Ref. [8], $F_{hyd}(\omega, V_1)$ is small indeed if the cluster compressibility is characterized by the sound velocity $s_t$ substantially exceeding that of liquid solvent $s_l$ (or, equivalently, $\rho_s > \rho_l$).

For non-symmetric electrolytes the concept of structure resonance becomes more complicated. The compensating ion possess the SR of type (4) with the phenomenological constant $k_s$. As to the charged colloids, their structure resonance (referred to as $\Omega_s$ below) can be described in more detail. Here the SR involves a sort of plasma oscillations in the system of $N$ mobile charges of mass $m_c$ sliding (presumably) over the surface of the sphere with radius $R_c$. Simple calculations reveal that the dipole mode $\Omega_s$ of these oscillations has the scale

$$\Omega_s^2 \simeq \frac{8\pi e^2}{3\epsilon m_c R_c} n_s, \quad n_s = N/(4\pi R_c^2).$$

(5)

Here $\epsilon$ is the solvent dielectric constant.

Frequency $\Omega_s$ (5) contains three interesting poorly known characteristics of the complex: mass $m_c$, effective radius $R_c$, and total number of charges localized on an individual colloid particle. Therefore detection of the resonance frequency $\Omega_s$ allowing to estimate these parameters would be very useful.
Figure 2: \( \text{Im} v(\omega) \) (9) as a function of \( \omega \) for different values of the parameter \( \mu \). Inset shows \( \text{Im} v(\omega) \) for the Drude model (19).

Figure 3: Plots of \( \text{Im} v(\text{Re} v) \) (9) for the considered model and the Drude dynamics (inset).
Figure 4: $\text{Re} \, v(\omega)$ (8,11) as a function of $\omega$ for different values of the parameter $\mu$ for the Stokes hydrodynamic force.

Figure 5: $\text{Im} \, v(\omega)$ as a function of $\omega$ for different values of the parameter $\mu$ for the Stokes hydrodynamic force.
The next two frequency ranges defined by classification (3) can be considered by employing in Eqs. (1) and (2) suitable asymptotic expressions for $F_{hyd}(\omega, V)$. For example, for $\omega \sim \omega_M$ [8]

$$F_{hyd}(\omega) \rightarrow F_{id}(\omega) = \frac{4}{3} \pi R_i^3 \rho_l \omega V \left[ -q^3 R_i^2 + i (2 + q^2 R_i^2) \right] \left[ 4 + q^4 R_i^4 \right], \quad \omega \simeq sq,$$  \hspace{1cm} (6)

where $s$ is the sound velocity, $q$ is the wave number (the dispersion $\omega(q)$ is assumed to be linear), $V$ is the velocity amplitude of the cluster as a whole.

The corresponding associated mass is then

$$M^*(\omega) \simeq F_{id}(\omega)/(-i\omega V). \hspace{1cm} (7)$$

In the limit $q^2 R_i^2 \ll 1$ the general definition (7) reduces to $M_0^* = 2\pi R_i^3 \rho_l/3$. On the contrary, for $q^2 R_i^2 \geq 1$ the associated mass $M^*(\omega)$ begins to demonstrate a noticeable frequency dependence. According to Eq. (6), in both limits oscillations of a sphere in ideal liquid are accompanied by energy dissipation due to emission of sound waves.

According to the classification (3) and comments to Eq. (6), the SR position and the range of noticeable mass dispersion are separated to the extent that the sound velocity in solid exceeds that in liquid. This circumstance can be used to simplify the problem of finding the behavior of $M^*(\omega)$ by neglecting the effects of structure resonances in the frequency range $\omega \sim \omega_M$. This is formally possible in the limit $k \rightarrow \infty$. In that case the set of equations (1), (2), and (6) reduces to a single equation

$$-(m_i + M)\omega^2 x_1 = F_{id}(\omega, V) + eE_0, \quad V = i\omega x_1, \hspace{1cm} (8)$$

where $F_{id}(\omega, V)$ is taken from Eq.(6) and $\rho_s > \rho_l$ is the efficient density of the neutral cluster part, or, in dimensionless variables (frequency $\omega$ normalized $\omega_0 = s_l/R_i$ and velocity $v$ normalized to $v_0 = eE_0/(M_0^* \omega_0)$),

$$i\mu \omega v = f_{id}(p, v) + 1, \hspace{1cm} (9)$$

Figure 6: Plots of $\text{Im}\, v(\text{Re}\, v)$ for the Stokes hydrodynamic force.
\[ \mu = (m_i + M)/M_0, \quad f_{id}(p, v) = 2\omega v \frac{[-p^3 + i(2 + p^2)]}{(4 + p^4)}, \quad p = qR_i. \]

Equations (8,9) allow finding the real and imaginary parts of the velocity

\[ \text{Re} v = \frac{2 + (qR)^4/2}{\omega} \frac{(qR)^3}{(qR)^6 + (2 + (qR)^2 + \mu(2 + (qR)^4/2))^2}; \quad (10) \]
\[ \text{Im} v = \frac{2 + (qR)^4/2}{\omega} \frac{2 + (qR)^2 + \mu(2 + (qR)^4/2)}{(qR)^6 + (2 + (qR)^2 + \mu(2 + (qR)^4/2))^2}. \quad (11) \]

Thus, we have derived all the quantities required to calculate the electrolyte impedance in the frequency range of \( \omega \sim \omega_M \).

The frequency range \( \omega \sim \omega_\eta < \omega_M \) is interesting because of unusual viscosity effects on the associated mass. Here the ideal associated mass is already fully developed and one can employ the concept of liquid viscosity \( \eta \). In this case the solution of the Navier-Stokes equation yields the following frequency representation for the force \( F_{\text{hyd}}(\omega) \rightarrow F_s(\omega, V) \) [8]:

\[ F_s(\omega, V) = 6\pi\eta R_c \left(1 + \frac{R_s}{\delta(\omega)}\right) V(\omega) + 3\pi R_s^2 \sqrt{\frac{2\eta \rho}{\omega}} \left(1 + \frac{2R_s}{9\delta(\omega)}\right) i\omega V(\omega), \quad (12) \]

Here \( V \) is the sphere velocity as a whole and \( \delta(\omega) = (2\eta/\rho\omega)^{1/2} \) is the so-called dynamic penetration depth.

Equations of motion now acquire the form of (8) with \( F_{id}(\omega, V_1) \) from (6) replaced with \( F_s(\omega, V) \) (12). The coefficient at the imaginary part in Eq. (11) measuring inertia contribution (i.e., the associated mass) to the general expression for the force \( F_s \) proves to be divergent as \( \omega^{-1/2} \) with decreasing frequency. This fact deserves special attention in itself.

### 3 Impedance details

Going back to the details of the impedance, we start with a few general relations. If Ohm’s law in the medium is written as

\[ j = \alpha \dot{E} + \sigma E \quad (13) \]

where \( \alpha \) and \( \sigma \) are real constants, then its refraction index \( n \) and absorption index \( k \) can be expressed through \( \alpha \) and \( \sigma \) in the following way [1], [6]:

\[ (1 + 4\pi \alpha) = n^2 - k^2, \quad \sigma = nk\omega/2\pi \quad (14) \]

In its turn, the reflection coefficient \( R \) for the electrolyte surface is

\[ R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (15) \]
In all the preceding formulas (13–15) the electrolyte magnetic permeability was assumed to be equal to unit.

Current (13) in the medium is due to the motion of opposite charges preserving local neutrality. In three-dimensional problems local neutrality holds not only in the equilibrium, but also in the linear regime (13) under the applied vortex fields (in 3D systems the charge build up is associated with the violation of the condition $\text{div} E = 0$; in the transverse wave this condition is assumed to be satisfied). Thus, the problem of the wave interaction with semi-infinite electrolyte reduces to finding the constants $\alpha$ and $\sigma$ appearing in Eq. (12) from single-particle equations (1, 2).

The simplest variety of the interaction of the charged complex (1), (2) with the electromagnetic wave arises if one assumes that the shell motion is completely suppressed (large values of the mass $M$ or, which is more realistic, finite values of the solvent viscosity $\eta$, damping through the force $F_{\text{hyd}}(\omega, V_1)$ in Eqs. (1), (2) the free shell motion). In that case only the bare charge keeps its mobility so that the general picture proves to be essentially dielectric, and the problem (1), (2) for the oscillatory motion of a separate charge is reduced to the well known problem of dielectric constant dispersion in a homogeneous system of oscillators distributed with the spatial density $n_i$. The effective high-frequency conductivity in that case is

$$\tilde{\sigma} = \frac{n_i e^2}{m_i} \frac{\omega \exp[i(0.5\pi - \varphi)]}{\sqrt{(\omega_s^2 - \omega^2)^2 + \gamma^2 \omega^2}} = i\omega \alpha + \sigma. \quad (16)$$

Here $\omega_s$ is the SR position, $\gamma$ is the decay of the charge oscillations within the cluster, $\varphi$ is the current delay phase with respect to voltage. In accordance with Eq. (12), the refraction index can then be obtained as

$$n^2 - k^2 = 1 + \frac{4\pi n_i e^2}{m_i} \frac{(\omega_s^2 - \omega^2)}{(\omega_s^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad (17)$$

$$2nk = \frac{4\pi n_i e^2}{m_i} \frac{\gamma \omega}{(\omega_s^2 - \omega^2)^2 + \gamma^2 \omega^2}. \quad (18)$$

Assuming $(\omega_s^2 - \omega^2)^2 \gg \gamma^2 \omega^2$, one can take $k \to 0$, where $k$ is from (14). Then

$$n^2 \simeq 1 + \frac{4\pi n_i e^2}{m_i} \frac{1}{(\omega_s^2 - \omega^2)}, \quad (19)$$

which demonstrates the well known fact of the appearance of refraction index frequency dispersion in the ensemble of oscillators.

When dealing with the frequency $\Omega_s$ (5), it is reasonable not only to calculate the resonance position (19) but also find the imaginary part of $k$ defined by Eq. (18). This is useful for extracting from experimental data of both $N$ and the effective mass $m_c$. In that case the radius $R_c$ should be additionally obtained from low frequency measurements of the colloid mobility.

In the other frequency ranges ($\omega_M$ and $\omega_\eta$) indicated in Eq. (3) the finite cluster mass $M$ and solvent viscosity $\eta$ the shell mobility cannot be neglected. One should solve the
problem of cluster behavior in the external field more accurately, mainly in the sense of actual properties of the force $F_{\text{hyd}}(\omega, V_1)$. This approach (which was described in detail in the preceding part of the paper) allows one to immediately formulate the final results for frequency ranges defined by Eq. (3).

For convenience, in the frequency ranges $\omega \sim \omega_M$ and $\omega \sim \omega_\eta$ we consider the most significant and graphical (in our opinion) information concerning the structure of the corresponding hodographs expressing direct relations between $\text{Re}V$ and $\text{Im}V$ against the background of respective plots for the case of Drude dynamics,

$$m(-i\omega + \tau^{-1})v = eE_0.$$  \hspace{1cm} (20)

Here $m$ is some scalar mass and $\tau$ is the typical frequency independent relaxation time.

Frequency range $\omega \sim \omega_M$. Comparative plots for the frequency dependence $\text{Re}v$ and $\text{Im}v$ calculated for different values of the parameter $\mu = (m_i + M)/M_0^*$ (see Eq. 8) as well as the corresponding hodograph are shown in Figs. 1-3. This parameter reveals the role of the bare mass $M$ in the considered problem. In particular, the values $m_i = M = 0$, models the limit of zero bare mass and zero solidified neutral shell mass occurring for single-electron bubbles in liquid helium.

Frequency range $\omega \leq \omega_\eta < \omega_M$. Similar plots obtained by employing Eq. (8) with the hydrodynamical force defined by Eq. (11) are presented in Figs. 4-6.

Summary. Suggested is a resonance technique for the study of the structure of charged clusters in various electrolytes. The resonances, which were called structure resonances, arise in the course of excitation of relative motion of the bare charge and the neutral cluster shell, and contain interesting information on the strength of their elastic coupling. Within the framework of the developed formalism the problem of formation of “ideal” associated mass of oscillating sphere is discussed which is directly related to the behavior of structure resonances.

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