Drude-jellium model for the microwave conductivity of electrolyte solutions

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Abstract. The microwave conductivity characteristics of electrolyte solutions have attracted much interest of researchers because a good understanding of their properties plays a key role to study fundamental processes in biology and chemistry. In this work, we consider the solution of sodium chloride as a plasma consisting of ions with water background. Its plasmon frequency is calculated by the jellium theory. The linear dependence of the microwave conductivity on the ion concentration of the electrolyte solutions is explained by a microscopic approach and described by a combination of this plasmon relationship and the simplified Drude formula for dielectric constant. Furthermore, the dependence of the microwave conductivity on the frequency of the salt solution is also examined. We suggest that it obeys the logistic distribution. We found a good agreement between theoretical calculations and experimental data. The values of the damping coefficient $\gamma$ for the conductive solutions at low frequencies and the cutting frequency are estimated. The linear dependence of the diffusion coefficient on the temperature of the salt solution is also shown, in similarity with the result in the other model. The application of the Drude-jellium model could be done for the other electrolyte solutions in order to study theirs electro-dynamic properties.

1. Introduction

The important role of aqueous electrolyte solutions in biological systems is widely recognized. Researches on their characteristics could offer a key to investigate electrokinetic phenomena which happen in living cells, including charge transfer, electro-osmosis, electrophoresis [1] as well as electrochemical processes [2]. It is noticeable that the solvation of ions in aqueous media is a fundamental process in biology and chemistry [2–5]. A good understanding of the conductivity of aqueous electrolyte solutions at microwave frequencies could give a powerful way to investigate the dynamical processes in solution media [2, 6–8]. Researches on the microwave conductivity of electrolyte solution also help us have a deeper comprehension of the interaction mechanisms between electromagnetic waves and biological tissues surrounded by an aqueous buffer containing ions with different concentrations [9].

Electrical properties of electrolyte solution have been widely interested over the last 120 years [4]. Recently, the microwave conductivity of the salt solution was determined by measuring its dielectric constant via the combination of the Debye and Drude models [10]. The linear increase of the microwave conductivity of the sodium chloride solution at room temperature
versus its ion density was observed. This dependence was explained by the simplified Drude model. It is interesting that the microwave conductivity of the sodium chloride solution holds constant at low frequency (under 8 GHz) but it was higher than that in the static regime [11, 12]. In the opposite limit, the microwave conductivity of the solution obviously decreases as the frequency increases and reaches zero at high enough frequencies. However, the science behind the microwave conductivity behavior of the salt solution is poorly understood due to the absence of theoretical approaches. So, a further research to provide a microscopic model is needed for a good understanding of microwave conductivity behavior for the sodium chloride solution as well as the other electrolyte solutions.

In this paper, considering the electrolyte solution of sodium chloride as a plasma with water background, its plasmon frequency is calculated by the jellium theory. The concentration and frequency dependence of the microwave conductivity of the salt solution is described by a simple approach called the Drude-jellium model. The value of the damping constant of this solution in the regime of low frequency is estimated. The comparison between theoretical calculations and empirical data is performed to validate the Drude-jellium model. The dependence of the diffusion coefficient on the temperature of the salt solution at low frequencies is also considered by our model.

2. The jellium theory for electrolyte solution

2.1. Jellium theory

Let us consider the motion of one species of charged particles with density \( N \), charged \( e \) (\( e \) is the electron charge), and mass \( m \) in a neutralizing rigid continuous background of positive charge. If their mass is large, these charged particles have a classical dynamics. So, the motion of particles is affected by the Coulomb potentials \( \varphi = e^2 / 4 \pi \varepsilon_0 r \), where \( \varepsilon_0 \) is the electric constant and \( r \) denotes the distance between two charged particles. The jellium theory [12, 13] may be a useful tool to investigate dynamic processes which take place in the system. The Coulomb interaction in the jellium theory can be written as

\[
U = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \varphi(\mathbf{r} - \mathbf{r}') \delta n(\mathbf{r}) \delta n(\mathbf{r}'),
\]

where \( \delta n(\mathbf{r}) \) is a small disturbances of density at \( \mathbf{r} \). Let’s employ now Fourier representation for \( \delta n(\mathbf{r}) \) in its spatial Fourier coefficients at wavevector \( \mathbf{q} \)

\[
\delta n(\mathbf{r}) = \frac{1}{\sqrt{N_0}} \sum_{\mathbf{q}} \delta n(\mathbf{q}) e^{i\mathbf{q} \mathbf{r}},
\]

where \( N_0 = NV \) is the total number of charged particles containing in volume \( V \) and

\[
\delta n(\mathbf{q}) = \frac{N}{\sqrt{N_0}} \int d\mathbf{r} \delta n(\mathbf{r}) e^{-i\mathbf{q} \mathbf{r}}.
\]

Likewise, we also have

\[
\varphi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \varphi(\mathbf{q}) e^{i\mathbf{q} \mathbf{r}},
\]

where \( \varphi(\mathbf{q}) = \int d\mathbf{r} \varphi(\mathbf{r}) e^{-i\mathbf{q} \mathbf{r}} \). It is noticeable that \( \varphi(q) = e^2 / 4 \pi \varepsilon_0 q^2 \) is the Fourier representation of the Coulomb potential. Substituting (2) and (3) into (1), the Coulomb interaction for the system becomes

\[
U = \frac{1}{2N} \sum_{\mathbf{q}} \varphi(q) \delta n(\mathbf{q}) \delta n(-\mathbf{q}).
\]

It is possible to represent the small variation in the density \( \delta n = -N \text{div} \mathbf{u} \), where \( \mathbf{u} \) is the vector of displacement. This representation holds for the condition \( \mathbf{q} \mathbf{u}(\mathbf{r}) \ll 1 \). On the other hand,
the Coulomb interaction involves only longitudinal part of the displacement vector \( \mathbf{u}(\mathbf{q}) \) along the wavevector \( \mathbf{q} \), we may have \( \mathbf{u}(\mathbf{q}) = (q / q_0) \mathbf{u}(\mathbf{q}) \). Thus, we can write \( \delta n(\mathbf{q}) = -i N q \mathbf{u}(\mathbf{q}) \) with \( \delta n^*(\mathbf{q}) = \delta n(\mathbf{q}) \), \( \mathbf{u}^*(\mathbf{q}) = \mathbf{u}(\mathbf{q}) \), and \( u^*(\mathbf{q}) = -u(\mathbf{q}) \). The Coulomb interaction according to the relation (4) is given by

\[
U = -\frac{N}{2} \sum_\mathbf{q} q^2 \varphi(q) u(\mathbf{q}) u(-\mathbf{q}).
\]

Furthermore, the kinetic energy in the displacement wavevector representation for the system is defined by

\[
T = \frac{1}{2} \int d\mathbf{r} N m \dot{u}^2 = -\frac{1}{2} m \sum_\mathbf{q} \dot{u}(\mathbf{q}) \dot{u}(-\mathbf{q}).
\]

So, the equations of motion for the system derived from the Lagrange function are

\[
m\ddot{u}(\mathbf{q}) + N q^2 \varphi(q) u(\mathbf{q}) = 0,
\]

which gives the well-known plasma frequency \( \omega_p^2 = e^2 / \varepsilon_0 m \).

2.2. Plasma oscillation for the salt solution

We consider that the salt solution (NaCl) is a plasma consisting of two ionic species, cation \( \text{Na}^+ \) and anion \( \text{Cl}^- \) with the density of each ion being \( N \). The mass of cation \( \text{Na}^+ \) and anion \( \text{Cl}^- \) are denoted by \( m_1 \) and \( m_2 \), respectively. In this situation, we consider both ionic particles continuously distributed in a neutral continuous background of pure liquid water. Because of their large mass, the ions have a classical dynamics. We can apply the jellium model to describe the collective oscillation for the electrolyte solution of NaCl. Here, the equations of ionic motion can be derived by writing two equations, one for the displacement vector \( \mathbf{u}_1 \) of the cation \( \text{Na}^+ \) and another one for the displacement vector \( \mathbf{u}_2 \) of the anion \( \text{Cl}^- \). In similarity with the previous case, we limit ourselves to consider the motion of ions in the water under the action of the Coulomb potentials \( \varphi_{\text{Na}^- \text{Na}^+} = \varphi(q) \), \( \varphi_{\text{Na}^+ \text{Cl}^-} = -\varphi(q) \), and \( \varphi_{\text{Cl}^- \text{Cl}^-} = \varphi(q) \), where \( \varphi(q) = e^2 / 4\pi\varepsilon_0 q^2 \). As a result, the Coulomb interactions for the solution are defined by

\[
\begin{align*}
U_{\text{Na}^- \text{Na}^+} &= -\frac{N}{2} \sum_\mathbf{q} q^2 \varphi(q) u_1(\mathbf{q}) u_1(-\mathbf{q}), \\
U_{\text{Cl}^- \text{Cl}^-} &= -\frac{N}{2} \sum_\mathbf{q} q^2 \varphi(q) u_2(\mathbf{q}) u_2(-\mathbf{q}), \\
U_{\text{Na}^- \text{Cl}^-} &= N \sum_\mathbf{q} q^2 \varphi(q) u_1(\mathbf{q}) u_2(-\mathbf{q}).
\end{align*}
\]

The kinetic energy \( T_s \) of the system is represented by

\[
T_s = -\frac{1}{2} \left[ m_1 \sum_\mathbf{q} \dot{u}_1(\mathbf{q}) \dot{u}_1(-\mathbf{q}) + m_2 \sum_\mathbf{q} \dot{u}_2(\mathbf{q}) \dot{u}_2(-\mathbf{q}) \right].
\]

Consequently, the motions of both ions are written as

\[
\begin{align*}
m_1 \ddot{u}_1(\mathbf{q}) + N q^2 \varphi(q) u_1(\mathbf{q}) - 2N q^2 \varphi(q) u_2(\mathbf{q}) &= 0, \\
m_2 \ddot{u}_2(\mathbf{q}) + N q^2 \varphi(q) u_2(\mathbf{q}) - 2N q^2 \varphi(q) u_1(\mathbf{q}) &= 0.
\end{align*}
\]

The solution of these equations in the long wavelength limit \( \mathbf{q} \to 0 \) is

\[
\omega_p^2 = \frac{Ne^2}{\varepsilon_0} \left( \frac{1}{m_1} + \frac{1}{m_2} \right),
\]

which is considered as the plasmon frequency of the salt solution. According to this relation, for example, the plasmon frequency for the solution of sodium chloride with concentration 6.93% is approximately \( 10^{12} \) Hz.
It is possible to generalize this model to a system of multi-component plasma consisting of several ions labeled by $i$, each ionic species with the density $N_i$, charge $z_i e$ ($z_i$ is the reduced effective electron charge), and mass $m_i$. In similarity with the previous case, the plasmon frequency of such a system could be obtained in the following form [13]

$$\omega^2_p = \sum_i \frac{N_i z_i^2 e^2}{\varepsilon_0 m_i}. \quad (12)$$

3. Microwave conductivity of electrolyte solution in the Drude-jellium model

It is well-known that the relative permittivity $\varepsilon_D$ of metallic conductors obeys the Drude dispersion formula with the real part $\varepsilon'_D$ and the imaginary part $\varepsilon''_D$

$$\varepsilon_D(\omega) = \varepsilon'_D + j\varepsilon''_D = (1 - \frac{\omega_0^2}{\omega^2 + \gamma_e^2}) + \frac{j\omega_0^2 \gamma_e}{\omega \omega^2 + \gamma_e^2}, \quad (13)$$

where $\omega_0$ is the plasmon frequency of the system, $\gamma_e$ is the damping coefficient relating to the mean distance between subsequent collisions of an electron, and $\omega$ is the frequency. We note that the damping coefficient can be written by $\gamma_e = 1/\tau_e$, where $\tau_e$ is the relaxation time according to the average time between subsequent collisions of an electron. For electromagnetic waves whose frequency is satisfied with the condition $\omega \ll \gamma_e$, the Drude model for the relative permittivity of metal becomes simpler with the pure imaginary part, $\varepsilon(\omega) = \varepsilon''(\omega) = j\sigma^0/(\varepsilon_0 \omega)$, where $\sigma^0 = Ne^2/(m\gamma_e) = \omega_0^2 \varepsilon_0 /\gamma_e$ is the static conductivity of metal.

In similarity with the electron gas in the metal, the ions in the solution of sodium chloride are responsible for the conductivity with the water background. We assume that the interaction between ions and water molecules is negligible. Since the plasmon frequency of solution determined by (11), we have

$$\sigma^0_{solu} = \frac{Ne^2}{\gamma_0} \left( \frac{1}{m_1} + \frac{1}{m_2} \right), \quad (14)$$

where $\sigma^0_{solu}$ is called the static conductivity for the sodium chloride in the Drude-jellium model. In accordance with the relation (14), the static conductivity of solution is linearly proportional to the density of ion $N$ if the temperature is held constant. In fact, the concentration dependence plot for the static conductivity of the solution is a pure linearity [10] (the dashing line in the Fig. 1). It means that the damping constant $\gamma_0$ of the solution in the static regime is a constant at a definite temperature. According to the relation (14), its value can be estimated by determining the slop of the concentration dependence plot for the static conductivity of the solution, $\gamma_0 \approx 10^{14} s^{-1}$ [10], approximately the damping constant of metallic conductors [14].

It is well-known that the relation between the density of ion flow $J$ and the current density amplitude $I$ for the electrolyte solution of sodium chloride is given by $I = eJ$. The density of ion flow under the action of an external force could be written by the following expression [15]

$$J = J_D + J_\sigma, \quad (15)$$

where $J_D$ and $J_\sigma$ are the densities of the diffusion and convective flows, respectively. In addition, the diffusion flow counteracts the convective one. Thus, the relaxation time of solution is reduced in the presence of the diffusion flow. As an external field with microwave frequency is applied, the diffusion modes are too slow to follow the external field, resulting in the absence of the diffusion flow in the density of ion flow $J$. Only the convective flow survives, so the relaxation time of solution at low frequencies is higher than that in the static regime. We suggest that the damping constant of electrolyte solution at low frequency is invariable denoted $\gamma$, and, we have $\gamma < \gamma_0$. In fact, the motion or relaxation of most ions can respond effectively to the microwave field at low
The AC conductivity $\sigma_{\text{max}}^0$ at 1GHz of the sodium chloride solution in the Drude-jellium model versus the number of ions is shown by the solid line. The dashing line illustrates the concentration dependence of the static conductivity $\sigma_{\text{solute}}^0$ for the salt solution in Ref. 10. The experimental data [10] (symbols) are also represented to validate our Drude-jellium model.

frequencies. As a result, the microwave conductivity of the sodium chloride solution is invariable at low frequency and a definite temperature, denoted $\sigma_{\text{max}}^0$. Due to $\gamma < \gamma_0$, the microwave conductivity of solution at low frequencies (below 8 GHz) is higher than its static conductivity. This behavior has ever been observed by experiments [10,11]. Thus, the microwave conductivity of solution at low frequencies is defined by

$$\sigma_{\text{max}}^0 = \frac{Ne^2}{\gamma} \left( \frac{1}{m_1} + \frac{1}{m_2} \right).$$

(16)

In accordance with the formula (16), the microwave conductivity for the salt solution is independent of the frequency, but it linearly depends on the ionic concentration (the solid line in Fig. 1), resembling the behavior of the static conductivity mentioned above. In a similar way to derive the damping constant $\gamma_0$, the damping constant $\gamma \approx 0.78 \times 10^{14} \text{ s}^{-1} \approx 0.8\gamma_0$ is obtained for the salt solution at low frequencies. In the microwave regime, it is clear that the value of the damping coefficient is much higher than that of the frequency $\omega$. So, it proves the applicability of the Drude model in the simple form.

In addition, the response of ions to the alternative external electric field becomes more and more difficult with the increase in frequency due to their large mass. Consequently, an obvious decrease of the AC conductivity of solution to zero at high enough frequencies is observed. We suggest that $\omega_C$ is the maximum frequency at which most ions can be still responsible for the conductivity. Above this frequency, the ions are responsible for the conductivity function under the action of thermal fluctuation. It is clear to see that the number of ions being responsible for the conductivity of the sodium chloride solution is satisfied with the logistic function [16] which is used in a range of fields, including biology (especially ecology) [17, 18], physics (Fermi–Dirac statistics) [19], economics [20], linguistics [21], and statistics with the sigmoid’s midpoint $\omega_C$ and the variable $\omega$. In our opinion, the role of $\omega_C$ is similar to that of the cutoff frequency of physics and electrical engineering. According to the experimental data, the value of $\omega_C$ is approximately 12 GHz. As a result, the real part of the microwave conductivity $\sigma_{\text{solute}}(\omega)$ for the sodium chloride solution at room temperature $T_0 = 293 \text{ K}$ also obeys the logistic statistics with the curve’s maximum value $\sigma_{\text{max}}^0$

$$\sigma_{\text{solute}}(\omega) = \frac{Ne^2}{\gamma} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \frac{1}{1 + \exp[\alpha(\omega - \omega_C)]},$$

(17)
Figure 2. Frequency spectra of the microwave conductivity in the Drude-jellium model for the solution of sodium chloride with various concentrations: 2.96%, 6.93%, and 11.05%. Represented by the solid line, dot-dashed line, and dashed line, respectively. A good agreement between calculations made by formula (17) and experimental data [10] (symbols) is also shown.

where \( \alpha = 8.38 h/k_B T_0 \) \((k_B\) is the Boltzmann constant and \( h \) is the Planck’s constant) is corresponding to the steepness of the curve. In accordance with this relation, the microwave conductivity of the salt solution is invariable at low frequencies and it strongly decreases to zero at high enough frequencies. The linear concentration dependence of the microwave conductivity is also displayed. Furthermore, we found a good agreement between calculation results and experimental data in Ref. [10] (see Fig. 2). It is easily seen that the relation (17) in the Drude-jellium model describes well the frequency dependence of the microwave conductivity of the sodium chloride solution in a wide range of concentrations.

It is noticeable that the value of the cutoff frequency is much smaller than that of the plasmon frequency \( (\omega_C = 10^{-2} \omega_p) \). However, it is widely accepted that the value of the cutoff frequency is approximately equal to that of the plasmon frequency for the electron gas. In our opinion, it is the water background that has an impact on the ion motion resulting in the reduction in the value of the cutoff frequency in this case in comparison with the situation of the electron gas. Furthermore, it is the influence of the water background on the ion motion that also leads to a such value of the steepness of the logistic curve. Therefore, it is necessary to take into account the role of the water background in the jellium model for the electrolyte solution instead of ignoring its influence.

4. The diffusion coefficient of sodium chloride solution at low frequencies

It is well-known that the convection flow of ions in the salt solution looks like

\[
J_\sigma = NbF,
\]

where \( F = eE \) is the force caused by the alternative field \( E \) acting on ions, \( N \) is the ion density and \( b \) is the ion mobility. The ion mobility combines with the diffusion coefficient \( D_0 \) by the Einstein relation \( bk_B T = D_0 \), where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. We note that the diffusion coefficient is related to the ion concentration by the Fick’s first law \( J_D = -D_0 \text{grad} N \), where \( J_D \) denotes the diffusion flux vector.

As an external field with microwave frequency is applied, only the convective flow survives due to the absence of the diffusion flow in the flow density of ions \( J \). So the current density amplitude in the electrolyte solution is given by
Figure 3. The dependence of the diffusion coefficient on the temperature of the sodium chloride solution at low frequencies is exhibited by the Drude-jellium model.

\[ I = \frac{e^2 N D_0}{k_B T} E. \]  

Thus, the microwave conductivity of the sodium chloride solution is read by

\[ \sigma_{max}(\omega) = \frac{e^2 N D_0}{k_B T}. \]  

In comparison between (16) and (20), the diffusion coefficient at low frequency for the solution of sodium chloride is given by

\[ D_0 = \left( \frac{1}{m_1} + \frac{1}{m_2} \right) k_B T / \gamma. \]  

According to the relation (21), the diffusion coefficient of sodium chloride solution is a linear function of temperature. It is also independent of the solution concentration. This result is similar to that observed in experiment [11] and in agreement with the Stokes–Einstein equation. This is also an evidence to validate the Drude-jellium model for microwave conductivity of electrolyte solution suggested in the above section again.

5. Conclusion
In this work, we provided the jellium model for the electrolyte solution of sodium chloride, which was considered as a plasma consisting of ions with the water background. Its plasmon frequency was defined by our model. The linear dependence of the microwave conductivity on the ion concentration of the sodium chloride solution was pointed out by the combination of its plasmon frequency and the Drude formula in the simple form of dielectric constant. The decrease in the damping constant leading to the rise in the microwave conductivity of the solution at low frequencies in comparison with that in the static regime was interpreted due to the absence of the diffusion flow in the solution. In addition, the dependence of the microwave conductivity on the frequency of the salt solution was mentioned and explained by a microscopic approach. It obeys a famous distribution called the logistic statistics. According to our model, the microwave conductivity of the salt solution is almost dispersionless at low frequencies and it strongly decreases to zero at high enough frequencies. We found a good agreement between theoretical results and empirical data in a wide range of concentration. Furthermore, the linear dependence of the diffusion coefficient on the temperature of the solution at low frequencies being
similar to the famous Stokes–Einstein was also pointed out by our model. In addition, the value of the cutoff frequency is given, but it is much lower than that of the plasmon frequency due to the influence of the water background. However, the role of the water background has not been taken into account in our jellium model. This problem also leads to the poor understanding of the physical meaning of the constant according to the steepness of the logistic curve in this work. It is necessary to modify our jellium model to provide a new jellium model in which the role of the water background is taken into consideration.

Our research on the microwave conductivity of sodium chloride solution under ambient temperature is essential for an accurate description of molecular-level studies of tissues where the salt solution is an important component. Likewise, the application of this model could be done to study the frequency-dependent and the concentration-dependent behaviors for the microwave conductivity of the other electrolyte solutions in a wide range of concentrations and to estimate their several important parameters. However, the dependence of the microwave conductivity on the temperature of the sodium chloride solution has not been examined by the Drude-jellium model. This matter is rather interesting for our future research.

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