

## Electrode-Electrolyte Interface Simulation in Microbubble Distillation: Role of (DDLs) as Electrochemical Cell

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### Abstract

The proposed dielectric mediums of a hot microbubble interface experience different behaviours due to the electrical mobility of carriers (electron and ion) within their domains. The responses of such mediums towards the initial and average mobility of these carriers can be classified as the linear and nonlinear responses. These two kinds of response define and categorize these mediums as the linear homogeneous isotropic and nonlinear heterogeneous anisotropic dielectric mediums. Accordingly, the categorization of mediums into two classes and their responses towards the mobilities of carriers motivate the approach of electrochemical phenomena within their domains. Furthermore, the restricted boundaries for these mediums are specified by the formation of dipole-double layers (DDLs) within the shell zone of this interface. Therefore, the electrochemical phenomena are implemented in COMSOL Multiphysics for simulating (modelling) the gas-liquid interface of a hot microbubble and its shells as the electrode-electrolyte interface due to the assumed behaviour of microbubble or its shells as an electrode in a specific electrolyte (the bulk of liquid). The computational model determines the current distribution throughout these mediums (DDLs) and calculating their resistance because every electrochemical cell is already assessed by these two important factors besides its resultant voltage. This model treats the solvation process for the dissolving of air (solute) inside the bulk of liquid BTX mixture (solution). In general, the diffusion according to *Nernst-Einstein* relation, convection, and the independent migration of species according to the limiting molar conductivity by *Kohlrausch's law* are investigated as the driving force for the transport phenomena within the imposed interface of a hot microbubble and its shells. Hence, the mass balance (mass flux) and current flux are estimated in this model by the implementation of tertiary current distribution by *Nernst-Planck* equation in COMSOL Multiphysics. Furthermore, the initial and *averaging* cases of charge distributions within these categorized mediums are originally investigated to simulate the reaction kinetics and their effects on the *mechanisms* of transported species from the bulk of liquid (electrolyte) towards the surface of a hot microbubble (electrode) according to their attractiveness due to their polarity.

**Keywords:** Dipole-double layers (DDLs), electrochemical cell, fuel cell, electrode-electrolyte interface, and ion hydration.

### Introduction

A hot microbubble distillation can experience an electrochemical system during the governing *mechanisms* of its progress. As a result of the occurrence of electrons and ions as the carriers, the proposed mediums of the gas-liquid interface of a hot microbubble and the formed (DDLs) show the self-entirety skills to be such a system. Both carriers are equivalently treated in this investigating modelling. Thereby, any related parameters for both carriers are analogously computed or defined. The electrical mobility of each of these carriers is computed to simulate their effects on the characteristics of those electric mediums which are categorized as the linear homogeneous isotropic and nonlinear heterogeneous anisotropic. These categorizations of those mediums in association with these carriers drive the gas-liquid interface of a hot

microbubble and the formed (DDLs) to be an electrode-electrolyte interface. Particularly, the only way to simulate these behaviours of mediums and the computations of related factors and boundary conditions is by implementing the interface of tertiary current distribution by the *Nernst-Planck relations* in COMSOL Multiphysics. Accordingly, the main contributions of this approach of such an interface are:

- 1) Describing the current distribution (balance) according to the *Nernst-Planck relation* (tertiary distribution), calculating the mass flux of the solute (species *i*) in the electrolyte (the bulk) in terms of the three species transport phenomena: diffusion, independent migration, and convection; describing the reaction kinetics of the solvation process through the computations of the reaction rates and the electrochemical overpotentials within the mediums

of the interface, and investigating the characteristics of the (DDLs) formed.

- 2) Describing the effects of the Boltzmann distribution at equilibrium (velocity distribution of carrier) to reach the actual energy distribution during the proposed interface of a hot microbubble.
- 3) Providing the computations of the harmonic perturbations and investigating their effects on the medium behaviour of the proposed interface.
- 4) Providing exclusive evidence for the emergence of *chromophores* for different molecules through the computation of the initial and average effective elementary charges and their roles in the evolution of the species separation *mechanisms* under the effects of *quantum field theory*.
- 5) Calculating the electric and magnetic resistance of interfacial mediums based on the actual currents in both phases (electrode-electrolyte).
- 6) Investigating the effects of the existences for the cations and anions on the stability of the (DDLs) formed near the interface. Also, the exploring of the ion hydration due to these existences of the cations and anions.
- 7) Identifying a robust methodology for expressing the roles of the blackbody radiation and impingement light of a hot microbubble interface through the computation of the collision frequency between every two carriers. This allows the computation of the reaction cross-section due to the collision of the carrier species.

### **The Methodology of Investigation (Simulation)**

For better comprehension about the proposed computational model of electrochemical approach in the interface of a hot microbubble and (DDLs), the following procedure can achieve such illustration. The main important factors, initial and *averaging* boundary conditions, and the key steps of the model are briefly described to facilitate the achievement of these objectives of the computational model.

The electric mobility of each carrier is computed and applied to compute the diffusion coefficient and the limiting molar conductivity of cations within each curvature. These two factors are applied in the implemented interface of the tertiary current distribution by the *Nernst-Planck* equations for simulating the behaviour of the gas-liquid interface of a hot microbubble and (DDLs) as an electrode-electrolyte interface. Either the electrode or the electrolyte has its initial and *averaging* governing equations. Mass flux, current density, energy source, and the amplitudes of the

harmonic perturbations are computed for the electrolyte side. Whereas the current density, energy source, effective charges, and power are computed for the electrode side. Furthermore, from the interface of electrode-electrolyte, the capacitance of the proposed (DDLs) is computed for the two cases of the charge distributions within their domains. All these resultant factors have been utilized to compute several important factors which are the electric current of cations, electrolyte molar conductivity, actual electric current, the resistance of the interface, and effective collision frequency. Eventually, all the computed factors are achieved for both cases of charge distributions within the proposed interface of a hot microbubble and (DDLs).

### **Theory**

The transfer of electrons and ions, i.e. the carriers of elementary charge, within the mediums of the curvatures of the gas-liquid interface of a hot microbubble and (DDLs) rises the electrochemical phenomena. Such phenomena, in turn, drive these mediums to behave as an electrochemical system (Martinez-Vega, 2010). Accordingly, this behaviour of these mediums can be enhanced by the potentiality of the chemical potentials occurrences for these species besides the solute species due to the solvation process and the convection within the medium and outside its domain. Thus, the internal (within the microbubble) and external (in the liquid-side shells) mixing in the two-phase system due to the terminal velocity of the injected microbubble in the organic mixture is induced. This results in collisions between the transported species, supporting the adoption of the *Boltzmann distribution* and the *Brownian motion* theories emerging from molecular-level effects. These continuum level theories, in turn, lead to the computations of the thermodynamic factors such as the *Gibbs free energy*, entropy production, and ... etc.

On the other hand, the electronic interactions between the microbubble and its bulk liquid environment are dominated by the *fluctuation-dissipation theory* (Bustamante *et al.*, 2005); where the flow is dynamically varied but still the laminar state where chaotic dynamics occur (Gallavotti, 1998). Thermodynamically, the ensembles of non-equilibrium, thermal fluctuations, different (magnetic, electric, and frequency) perturbations, and the chaotic dynamics are the transients which determine the state variation from the linear to the nonlinear during the proposed mediums of a hot microbubble interface which manifest electrochemical properties. Furthermore, these properties of (DDLs) around the hot microbubble ought to be calculated where

their actual state is transient and unstable. Therefore, these computations are not conducted by usual methods unless it obeys to the principles of *quantum mechanics* which in turn support or explain the *fluctuation-dissipation mechanisms* during these layers. Briefly, the transition from the linear to the nonlinear final state for the characteristics of (DDLs) defines this electrochemical system.

Consequently, the gas-liquid interface of a hot microbubble and (DDLs) behaves as an electrode in a specific electrolyte (the bulk). Precisely, such an interface can be assumed as an electrode-electrolyte interface.

### The Preliminary Factors

The preliminary mobility, diffusion coefficients, and limiting molar conductivity of carriers are estimated as follow:

#### 1) The Mobility of Carriers

The electrical mobilities of species ( $\mu_{e(0,avg)i}$ ) specify the influence of the occurred electric fields in the gas-liquid interface of a hot microbubble. The drift velocity ( $v_{dt}$ ) of these species in association with the electric field ( $E_0$ ) are defined to compute the electrical mobility of species. Typically, modelling the mobility of ions (is) or even of the electrons (e) largely depends on the *averaging* of the electric field and the drift velocity, in order to show the differences between the initial and the *averaging* cases of every carrier when they are excited. Moreover, *Einstein* thermodynamically defines a significant mobility relation (Smirnov, 1967). The *kinetic theory* in term of the *Boltzmann distribution* and the diffusion coefficient of species in the gas phase are involved in the *Einstein relation*. The first computes the mobility while the second *Nernst-Einstein* relation determines the diffusion coefficients for each component (i) of the organic mixture during each formed layer of the interface including the microbubble. However, both cases of the initial and *averaging* electrical mobilities are similarly computed with respect to spatial and temporal variations, as follow:

$$\mu_{e(0,avg)(is,e)i}(\Delta r, \Delta t) = \frac{v_{dt(is,e)i}(\Delta r, \Delta t)}{E_{(0,avg)(is,e)i}(\Delta r, \Delta t)} \quad (1)$$

#### 2) The Diffusion Coefficients of Carriers

The computations of the diffusion coefficients represent the main components in the charge and material balances in the electrochemical computational model. These important parameters are calculated by the *Nernst-Einstein relation*. In a similar way to the mobility

computation, the initial and *averaging* diffusion coefficients are computed but depend on the initial and *averaging* elementary charge of each carrier ( $Q_{(0,avg)}(\Delta r, \Delta t)_i$ ). The *averaging* charges are computed according to a specific approach depends on the *Gaussian* continuous distributions and the mixed distributions (continuous and discrete) distributions that based on *Dirac delta function* as an indicator to the role of *quantum field theory* in this investigation.

$$D_{(0,avg)(is,e)i}(\Delta r, \Delta t) = \frac{\mu_{e(0,avg)(is,e)i}(\Delta r, \Delta t)}{Q_{(0,avg)}(\Delta r, \Delta t)} \quad (2)$$

#### 3) The Limiting Molar Ionic Conductivity of Carriers

The electrolyte conductivity is a factor used to compute the molar conductivity when the individual ions are considered in dilute solutions. The individual contribution of each ion is determined in terms of the independent migration of ions. Therefore, the limiting molar ( $\lambda_{(0,avg)(is,e)i}^+(\Delta r, \Delta t)$ ) is an important factor used to specify the independent migration term in the equations of charge and mass balances simultaneously. *Kohlrausch's law* of independent ionic migration computes the initial and *averaging* limiting molar conductivity of each carrier (cation) in the interface of a hot microbubble and based on the charge number ( $z_i$ ), mobility ( $\mu_{e(0,avg)i}$ ), and *Faraday constant* ( $F$ ), as follows:

$$\lambda_{(0,avg)(is,e)i}^+(\Delta r, \Delta t) = z_i F (\mu_{e(0,avg)(is,e)i}(\Delta r, \Delta t)) \quad (3)$$

### COMSOL Models

The computational model of electrochemical behaviour (self-entity) of the gas-liquid interface of a hot microbubble and (DDLs) is divided into two models. The first is simulating the initial case of steady-state of charge distributions in this interface while the *averaging* case is adopted for simulating the unsteady state of these charges in terms of mixed distributions. The second case arises due to the proposed oscillation, collision, and/or excitation for each carrier within these categorized mediums. Hence, these models are defined with their related governing equations, factors, and boundary conditions in the next sections.

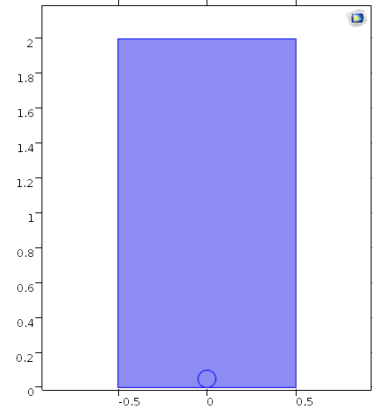
The behaviours of different potential mediums for the two-phase system of a hot microbubble and (DDLs) motivate the notion of such an interface as an electrode-electrolyte interface. The only way to model this hypothesis is by determining the current distribution throughout these mediums and calculating their resistance because every electrochemical cell is already assessed by these two important factors besides its

resultant voltage. Furthermore, the assumption of the solvation process for the air dissolved inside the bulk of liquid, i.e. the electromigration of species, influences these computations. Also, the diffusion due to the mobility of the charged solute species (ions) and their convection state are both involved in this model. These three cases of the transition of the charged solute species (ions) are typically used to compute their flux (mass balance). Thereafter, these fluxes altogether compute the total flux in the electrolyte (bulk) in this computational model according to the *Nernst-Planck* equation. Therefore, the current distribution is implemented by COMSOL Multiphysics based on these cases of the species transferred between the microbubble (electrode) and the bulk of liquid mixture (electrolyte).

A single hot microbubble is assumed to be injected in the liquid BTX mixture with different radii to investigate the variations in the electrochemical properties of the varied volumes of microbubble and (DDLs) (mediums), as the responses due to variation in its composition. A 2D space domain is specified for such microbubble dynamics modelling. Imposing 2D space domain reduces the computational intensity from full 3-D models, which is a reasonable assumption in the laminar flow where there is no clear symmetry-breaking bifurcation known a priori. The solution methods are selected for the two assumed cases with transient initialization for the initial case and the time-dependent evolution for the *averaging* case.

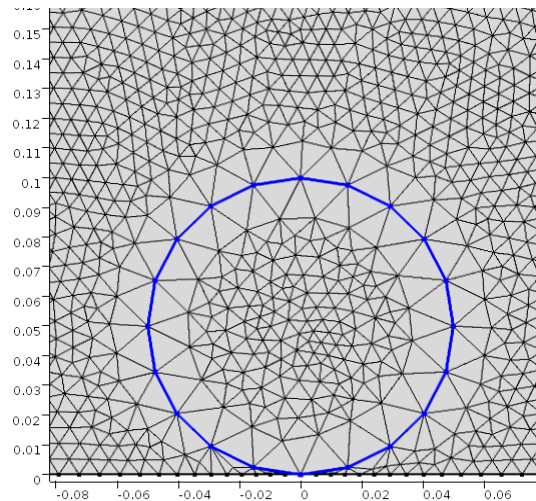
Figure (1) shows the computational domain of the current distribution interface in the gas-liquid interface of a single hot microbubble which is illustrated in the 2D space domain.

Additionally, the mesh element size in this model has been calibrated for the fluid dynamics. The element size has been selected as an extremely fine size with a distribution mode. The distribution properties have been specified as the predefined distribution type with 5 numbers of elements and 1 element ratio. Also, the distribution method is selected to be the geometric sequence of symmetric distribution. These specifications of mesh are selected for supporting all the prerequisites of this computational model such as the better assessment for the assumed electrochemical approach for a hot microbubble interface. Furthermore, the customizing for the wrong element size parameters can be avoided by these selections where the main interfaces of the simulation are highly complicated and interplayed.



**Figure (1): The 2D space configuration for the computational model of the tertiary current distribution by *Nernst-Planck* equations in the gas-liquid interface of a hot microbubble.**

Figure (2), which focusses on the near microbubble domain, displays the element size of the mesh for the current distribution as achieved by COMSOL. The computational model of the electrochemical approach has a complete mesh consists of 127908 domain elements and 922 boundary elements due to the association with the other interfaces of the main model. However, the required time for such calculations of this huge number of domain elements was roughly about (1h:48m:36s) on a computer with RAM (8G) and running Microsoft Windows.



**Figure (2): The extremely fine element size of the adopted mesh for the interface of the tertiary current distribution by *Nernst-Planck* equations in the gas-liquid interface of a hot microbubble.**

### **The Governing Equations of the Tertiary Current Distribution (*Nernst-Planck* Equations)**

The *Nernst-Planck* governing equations are selected in the COMSOL model to describe the current distribution, a branch of electrochemistry. This general set of equations has several options which are:

- 1) Electrolyte,
- 2) Electrode surface includes the electrolyte current density as a dependent variable to determine the current amplitude perturbation,
- 3) Electrode power to compute the power density in the interface, and

In fact, these options are applied in sense of *Bruggeman* (Bruggeman, 1935 and Ordóñez-Miranda *et al.*, 2010) decreasing diffusion coefficients in the electrolyte and decreasing conductivities of the electrode due to the tortuosity of the porous matrix and the lower volume fractions of each phase. *Bruggeman* effective transport corrections are used for the particle systems with a distribution of shapes and sizes too (Goncharenko, 2003). Consequently, these 9 options of the model are described by important relations and depending on several boundary conditions. However, these interfaces are explicitly implemented in COMSOL Multiphysics to compute some of the properties of the (DDLs) such as its electric capacitance. Further, other layer properties can be computed such as the quantum properties of (DDLs) which remain under investigation so far. The governing equations of treating these electrochemical phenomena fully detailed in the next subsections.

### The Initial (Steady-State) Model

The tertiary current distribution described by the *Nernst-Planck equations* is used to treat the current and potential distribution in an electrochemical cell. The basis of these model equations is the individual transport of species in the electrolyte, where the condition of electroneutrality in the electrolyte is assumed. The *Butler-Volmer* expression is predefined to describe the electrode kinetics for the charge transfer where significant concentration gradients of the current-carrying species are implicitly modelled, e.g. the local current of ions (Hughes *et al.*, 2010 and Bauer *et al.*, 2011).

The selected equations involve all the major current-carrying ions, namely diffusion, independent migration, and convection based on the assumption of electroneutrality underpinning the *Nernst-Planck equations*. The supporting of electrolyte is also considered by this treatment due to a combination of a secondary current distribution and imposing a mass transport model for the individual species. This combination is often used to describe the transfer of the

major part of charges by ions whose concentration is assumed to be constant. Initially, the flow of currents inside and outside the electrode (microbubble) is supported by a combination of a charge balance with *Ohm's law* where the neutral and charged species are transported within the (liquid) electrolyte. Therefore, the *Nernst-Planck* model is employed to describe the solvation of the different neutral solute species in the electrolyte (the bulk liquid).

In summary, all these specifications of the selected model equations for different multiphysics phenomena are defined for the initial (steady-state) of the charge continuous distribution (*Gaussian* distribution) throughout the two-phase system of a hot microbubble. The governing equations of the initial tertiary current distribution (Hughes *et al.*, 2010) are solved by the transient initialization numerical method (Bauer *et al.*, 2011). Explicitly, the equations are divided into two categories. The continuity equation is used to compute the material balance for the charged solute species ( $i$ ) in the electrolyte while the *Nernst-Planck* equation computes the total mass flux for these species. However, these species include the dry air and the BTX constituents according to the assumption that is 'these constituents are initially occupying the microbubble at the first moment of its generation'. Thus, all the components species are employed where their diffusion coefficients ( $D_{0i}$ ), concentrations ( $C_{0i}$ ), limiting molar conductivity ( $\lambda_{0(T,b,f)(is,e)i}^+(r)$ ), the initial electrolyte potential ( $\phi_{0bulk}$ ), and the fluid velocity ( $u_i$ ) are all substituted in the following equations of this model.

### 1) The Electrolyte

The following *Nernst-Planck equation* (4) determines the initial total flux ( $(N)_{0(f)(is,e)i}(r)$ ) in an electrolyte (bulk liquid) for the charged solute species that are transferred by the three driving *mechanisms*: diffusion, independent migration and convection. However, the fluid velocity near the surface of the microbubble is generally computed based on the slip model which is considered as a boundary condition. Therefore, the velocity component of the fluid would be normal to the wall of the microbubble. But, the initial case of the charge distribution allows the fluid velocity of the microbubble has not yet reached its terminal rise. Accordingly, the value of the fluid velocity is roughly zero ( $u_i = 0$ ) initially. Consequently, convection is not involved in the initial estimation of the charge distribution.

$$(N)_{0(f)(is,e)i}(r) = -(D_{0(f)(is,e)i}(r))(\nabla(c_1)_{i,m}) - (\lambda_{0(f)(is,e)i}^+(r))((c_1)_{i,m})\nabla((\phi_{bulk})_{0(f)(is,e)i}) \quad (4)$$

From this flux, the model computes the net current density in the electrolyte. Initially, the charge distribution is attributed to the continuous *Gaussian* distribution only. Furthermore, (DDLs) represent the transition region between the electrode and the electrolyte. The diffusion term has a higher influence than the independent migration and convection terms. Isotropic diffusion results in a linear. With the initial actual current density in the electrolyte ( $(I)_{l_0(f)(is,e)i}(r)$ ) computed based on diffusion and independent migration only, it is expressed as follows:

$$(I)_{l_0(f)(is,e)i}(r) = F \sum_{i=1}^{i=6} z_i (-D_{0(f)(is,e)i}(r)) (\nabla(c_i)_{i,m}) - (\lambda_{0(f)(is,e)i}^+(r)) ((c_i)_{i,m}) \nabla((\phi_{bulk})_{0(f)(is,e)i}) \quad (5)$$

Similarly, the following equation computes the initial actual reaction rate for the species within the shell region ( $(R_{10})_{i(f)(is,e)i}(r)$ ), already taken as (DDLs) between the microbubble and the bulk of the liquid:

$$(R_{10})_{i(f)(is,e)i}(r) = \nabla \cdot ((N)_{0(f)(is,e)i}(r)) \quad (6)$$

## 2) The Electrode

The part of the computational model that relates to the electrode is divided into six features of the computational model which are starting with the electrode surface and end with the electrode power. The six features are implemented in COMSOL as “Multiphysics interfaces” where each PDE interface is defined as its governing equations and boundary conditions. These electrode types support the electrochemical modelling approach such as the modelling for the proposed “electrode-electrolyte interface” between the hot microbubble and its surrounding environment. Actually, these sections of electrode represent the definition for the actual boundary conditions that are used to solve the general governing equations of the electrochemical approach. The solution of these types is achieved by transient initialization, see the COMSOL user’s manual, to show the initial state of the electrode properties.

### A) The Electrode Surface

The electrode surface implements the electrode-electrolyte interface, electrode reactions (solvation process), and (DDLs) capacitance. Furthermore, this is individually applied so as to define the outer boundaries of the electrolyte domain. However, it also provides better handling of the initial total current amplitude perturbation ( $\Delta l_{l_0,total}$ ) in the frequency domain through the involvement of the harmonic perturbation section in this interface. The computation of the current amplitude

perturbation is obtained from different initial boundary conditions. The first important boundary condition is the initial actual total current ( $(I)_{l_0,total}$ ), usually called the current flux in the outer surface of the electrolyte. This total current density is determined in a 2D domain from the initial property of the out-of-plane thickness and the vector form for the initial actual current density in the electrolyte ( $n \cdot (I)_{l_0(is,e)i}(r)$ ).

Hence, this total current density represents the summation of the initial actual local current densities (reaction currents) of all the solute species in the electrolyte ( $i_{loc0,i}$ ), i.e. the linearized *Butler-Volmer* kinetics expression, and the initial current density of (DDLs) from the electrolyte side ( $i_{l_0(d-d1),i}$ ). The (DDLs) current density is set to zero at the initial steady state. This kinetic expression is typically applied for the initial tertiary current distribution when the overpotential is small for the reaction.

Basically, the local currents are varied according to the variations of the overpotential because the linearized expression includes the anodic and cathodic. In other words, the vector form of ( $I_{l_0,total}$ ) is integrated over the whole electrolyte domain to determine the initial total current perturbations ( $l_{l_0,total}$ ) within its boundaries. Precisely, the vector form of ( $I_{l_0,total}$ ) represents the computed free current for each solute species ( $I_{(f)i}$ ); therefore, the initial current perturbations are computed as follow:

$$l_{l_0,total} = \int_{\partial\Omega} (I)_{l_0(is,e)i}(r) \cdot n \, dl = I_{(f)i}(r) \cos(\theta_{orth}) \quad (7)$$

Ultimately, the initial current amplitude perturbation is computed as the difference of the initial current perturbations between every two shell boundaries (curvatures) such as between the microbubble and the first inner surface of the shell zone.

$$\Delta l_{l_0,total} = (l_{l_0,total})_2 - (l_{l_0,total})_1 \quad (8)$$

In fact, this current amplitude of initial actual perturbations is computed to match the constraints proposed by intermolecular forces. Furthermore, this current amplitude perturbation allows constructing constitutive models of the molecular properties within the proposed (DDLs).

Subsequently, the second boundary condition is the external initial electric potential ( $\phi_{s0,ext}$ ) equals the external electric potential of the microbubble ( $(\phi_{mo})_{0(is,e)i}$ ). This electrode surface permits computing the Ohmic resistance causing additional potential drop at the electrode-electrolyte interface.

Hence, the definition of the film resistance in this electrode surface will be done by specifying the reference film (layer) thickness ( $s_0$ ), the difference of the thickness ( $\Delta s_0$ ) which represents the displacements within the shell zone, and the film conductivity (the medium conductivity  $\sigma_{0(f)(is,e)i}(\mathbf{r})$ ). Precisely, this section of the electrode surface computes the initial actual surface resistivity ( $R_{0film(f)(is,e)i}(\mathbf{r})$ ) based on a thickness of the film (layer), as follows:

$$R_{0film(f)(is,e)i}(\mathbf{r}) = \frac{s_0 + \Delta s_0}{\sigma_{0(f)(is,e)i}(\mathbf{r})} \quad (9)$$

Consequently, the initial actual surface resistivity in combination with the initial actual total current produces the initial actual difference of the external surface electric potential ( $\Delta\phi_{s0film(f)(is,e)i}(\mathbf{r})$ ) in the electrolyte side, as follows:

$$\Delta\phi_{s0film(f)(is,e)i}(\mathbf{r}) = (R_{0film(f)(is,e)i}(\mathbf{r}))(I_{l0,total}) \quad (10)$$

A possible reaction of the transferred charges throughout the boundaries of the electrode-electrolyte interface is implemented through the electrode reaction interface which specifies the electrode kinetics due to such reaction. The entire sections in the electrode reaction are specified according to the user-defined option. The equilibrium potential and its temperature derivative are defined as ( $E_{0eq(f)(is,e)i}(\mathbf{r}) = E_{0(f)(is,e)i}(\mathbf{r})$ ) and ( $dE_{0eq(f)(is,e)i}(\mathbf{r})/dT = dE_{0(f)(is,e)i}(\mathbf{r})/dT_b$ ), respectively. The temperature derivative parameter supports the calculation of reversible heat source of the electrode reaction. However, it is applied to achieve the coupling with the heat transfer in this model. Thereby, the computation of the activation overpotential ( $\eta_{l0(f)(is,e)i}$ ) for the possible reaction in the electrode-electrolyte boundary (electrolyte side) is achieved by the following main equation:

$$\eta_{l0(f)(is,e)i} = \phi_{s0,ext} - \Delta\phi_{s0film(f)(is,e)i}(\mathbf{r}) - (\phi_{bulk})_{0(f)(is,e)i} - E_{0eq(f)(is,e)i}(\mathbf{r}) \quad (11)$$

The electrode kinetics are specified to describe the initial actual local current density throughout the electrode-electrolyte interface where different expressions for these kinetics are available. Since the convection term of the charged solute species is not included in the initial case, the ideal expression of such reaction kinetics is linearized *Butler-Volmer* due to the expected smaller activation overpotential. Additionally, this expression usually targets the low-field approximation in the region of the proposed interface, i.e. near to equilibrium. Furthermore, the anodic ( $\alpha_a$ ) and cathodic ( $\alpha_c$ ) transfer coefficients are involved in this expression too. Due to the occurrence of the equilibrium state, these coefficients

are equally defined, and they are in default equal to (0.5). Another term is required to compute the initial actual local current densities for all the species in the electrode-electrolyte interface. This term is the exchange current density which measures the kinetic activity of the reaction for the individual species. In the initial state, this exchange current density is adopted to be ( $i_{0,i} = J_{(f)(is,e)i}(\mathbf{r})$ ). Thus, the initial actual local current ( $i_{loc0,i}$ ) is:

$$i_{loc0,i} = i_{0,i} \left( \frac{(\alpha_a + \alpha_c)F}{RT_b} \right) \eta_{l0(f)(is,e)i} \quad (12)$$

However, the initial actual total current will vary due to the variation of the local current densities. The cause of this variation is related to the activation overpotential of possible reaction in the electrolyte side. Since the computed overpotential actually depends on the defined equilibrium potential, the variation of this total current density is prominent at the equilibrium state. Therefore, the total current density is:

$$I_{l0,total} = \sum_{m=1}^{m=(n_T)_i} (i_{loc0,i})_m \quad (13)$$

Because of such variation in the local currents, the initial actual total reaction rate is the sum of the individual rates for each constituent. The individual rate is calculated from the local current density, stoichiometric coefficient ( $\nu_i$ ), and the number of electrons participating from each constituent within the interface. These significant variations influence the capacitance of (DDLs) formed in the interface region. Although the electrode surface also includes this capacitance, it could not specify its internal boundary conditions because this section solely defines the outer boundary conditions to the electrolyte domain. Therefore, the internal electrode surface is implemented to define the internal boundary conditions and to describe the capacitance of (DDLs) in a hot microbubble interface.

## B) Electrode Power

The pertinent boundary condition that describes the amount of drawn or added power density for the electrode (microbubble) is specified by the governing equations for the electrode power interface in COMSOL Multiphysics.

Whether the electrode is a porous or not, a specific amount of power density releases from the combination of the electric potential difference and current which are applied or produced in the whole system. Therefore, the determinant for whether the case is added or drawn power density is the preliminary electric potential of the external electrode boundary, i.e. the (DDLs) zone.

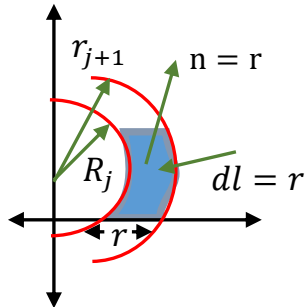
Precisely, the external electric potential of the electrode is considered as the main controller for the amount, type, and direction of the power density. Further, the power density in the 2D space depends on the out-of-plane thickness. All these basic conditions must be acquired to estimate such power while its type and direction depend on the flow direction through the electrode domain. Since the fluid flow is either inflow or outflow throughout the microbubble interface, the total power may be inserted or drawn from the electrode. For instance, when the flow of fluid is inflow, the electrode (microbubble) will be hotter than its initial generation state due to the added amount of power.

In the initial case, the initial total power density ( $P_{w0, total(f)(is,e)i}$ ) is determined by the integration for both electric potential difference and the current density vector over the whole external boundary of the electrode. The difference in the electric potential for the electrode surface is assumed to be the difference between the potential of the container wall ( $\phi_w$ ) and the external electric potential ( $(\phi_{mo})_{0(f)(is,e)i}$ ) of the hot microbubble.

$$P_{w0, total(f)(is,e)i} = \int_{\partial\Omega} ((\phi_{mo})_{0(f)(is,e)i} - \phi_w) (n \cdot (I)_{s0(f)(is,e)i}(r)) dl \quad (14)$$

$$\therefore P_{w0, total(f)(is,e)i} = ((\phi_{mo})_{0(f)(is,e)i} - \phi_w) \int_{R_j}^{r_{j+1}} n \cdot dl \quad (15)$$

The last term of integration represents the whole area of (DDLs) in the 2D space domain. In this case, the area bounded by these potential and current density can be expressed in the polar coordinates due to the spherical shape of the microbubble and each layer of (DDLs). Figure (3) shows the definition of (DDLs) area in term of the polar coordinates.



**Figure (3): The specification of the out-of-plane thickness as the area of (DDLs) in the 2D space domain.**

Thus, the integral can be rewritten in the following polar coordinates form:

Consequently, the initial total power density and after the neglect of ( $\phi_w$ ) becomes:

$$\therefore P_{w0, total(f)(is,e)i} = 2\pi((\phi_{mo})_{0(f)(is,e)i}) ((I)_{s0(f)(is,e)i}(r))(r_{j+1} - R_j)^2 \cos(\theta_{orth}) \quad (16)$$

Actually, this total power density initially represents the mean of the total power for the whole distributed species in this layer within the thickness of the out-of-plane. In summary, the total power initially equals the average power density in the whole region outside the electrode (microbubble).

### The Averaging (Unsteady State) Model

In the average case of the charge distributions, the continuous *Gaussian* and discrete distributions are mixed to display the actual situation of the excited (oscillation) carriers. From this point of view, especially, in the *quantum field theory*, it is very important to describe the real state of each carrier when the transported species in the two-phase system experience different effects. Such effects are the electric, magnetic, thermal, and frequency perturbations in the interface domain of a hot microbubble as well as the thermal fluctuations. The easier way to achieve such description is by investigating the reaction kinetics of those transported species in their unsteady state, especially, in the two-phase region of a hot microbubble. Because the injected hot microbubble provides some thermal energy at its initial state of generation, thermal fluctuations, the first type of effect, occur. Since the initial current and voltage amplitudes of the harmonic perturbations are also excited, consequently, the second type of these effects occurs as well. Whereas the third type of effect is the occurrence of different initial electric and magnetic dipoles such as the *multipoles* or *Hertzian* dipoles, eEDM, and eMDM. These effects generate oscillations of their carriers – exciting the frequency domain in a hot microbubble interface. Consequently, the tertiary current distribution by *Nernst-Planck equations* is implemented by COMSOL Multiphysics to describe the current and potential for the mixed distributions (*averaging case*) of charges in a hot microbubble interface.

The selected Multiphysics interface involves all the major current-carrying ions: diffusion, independent migration, and convection based on the implicitly applied condition of electroneutrality in *Nernst-Planck equations*. The electrolyte constituency is also considered due to a combination of a tertiary current distribution and mass transport interfaces. This combination is employed to describe the transfer of the major part of the average charges by ions whose concentration is assumed to be non-constant. In the



initial case of the charge distribution, a charge balance and *Ohm's law* are combined to define the flow of currents inside and outside the electrode (microbubble). Due to such combination, both charged and neutral species are transferred to the electrolyte. Thereby, *Nernst-Planck* model is the only possible model to describe the solvation of the neutral solute species (dry air) in the electrolyte (bulk liquid) by using the equations for secondary current distribution. However, in the average case of charge distribution, the same equations are used but for the tertiary current distribution due to two significant factors. The first factor is the state of the transported species transitioning from equilibrium to non-equilibrium because of the mixed distributions. The second factor is both a time-dependent concentration gradient and the dominant convection term occur simultaneously due to the occurrences of the three types of effects mentioned above. In other words, the transport phenomena in terms of the flow of heat, mass, and momentum evolve under the simultaneous principles of thermodynamics and polarity within the two-phase region of a hot microbubble.

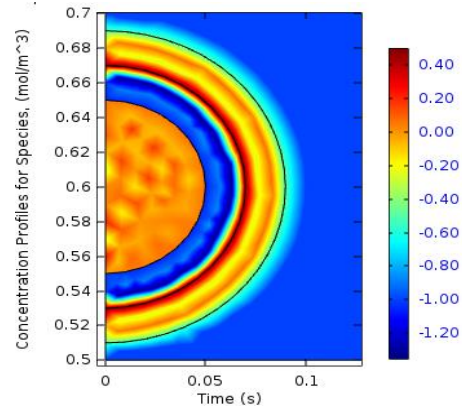
Consequently, all these specifications of the implemented interface for the average (unsteady state) of the charge mixed distribution throughout the two-phase system of a hot microbubble are similarly defined to the initial state. The equations selected for this interface of the average tertiary current distribution are solved by the time-dependent finite element model for fluid transport. In a similar way to the initial case, the equations are also divided into two categories. The continuity equation is used to compute the average material balance for the whole charged solute species ( $i$ ) in the electrolyte while the *Nernst-Planck equation* computes the average total flux for these species. All the species of dry air and BTX constituents are employed, where their average diffusion coefficients ( $D_{avg,i}$ ), concentrations ( $C_{avg,i}$ ), limiting molar conductivity ( $\lambda_{avg(T,b,f)(i,s,e)}^+(\Delta r, \Delta t)$ ), the average electrolyte potential ( $\phi_{avg,bulk}$ ), and the fluid velocity ( $u_l$ ) are all substituted in these similar equations of this model.

## Simulation Results

The results due to these two most similar sets of governing equations of this simulation are briefly listed in this paper, while the applications of the related factors to the electrochemical phenomena are applied in other different models for other studies such as the mass transfer by the transport of diluted species. In fact, the initial and *averaging* models are showing similar results.

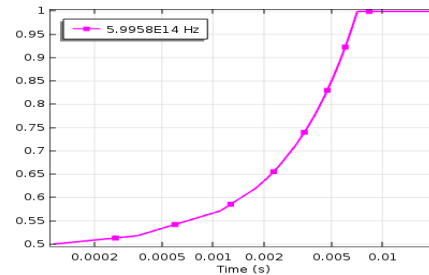
These results, therefore, automatically represent a comparison between both models.

Based on that, the results are generally displayed for the concentration of polar and nonpolar species in the second and fifth layer of (DDLs), the linear response (the current distribution within the formed layers of (DDLs)), and the nonlinear response (the current distribution within the formed layers of (DDLs)). In fact, the following results are computed under the effects of different perturbations which are represented by the frequency of  $5.9958E14$  Hz as the main predominant perturbation by comparison with other types. Hence, the concentration profiles of species in (DDLs) is displayed in figure (4).



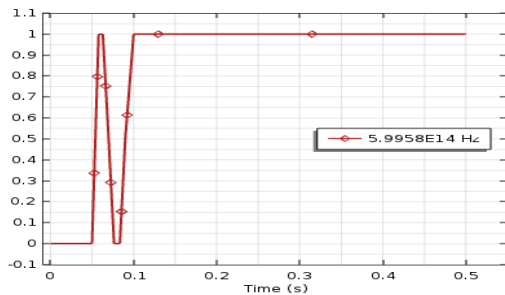
**Figure (4):** The formation of the (DDLs) around a hot microbubble including the linear-nonlinear nonequilibrium concentration profile for the assembled species, at the time  $< 1$  s and frequency  $5.9958E14$  Hz in the scatter field with the effects of thermal and frequency harmonic perturbations in the 2D space.

The linear response for the initial model is displayed in figure (5). This figure shows the current distribution for the initial steady model of charge distribution within (DDLs).



**Figure (5):** The linear non-equilibrium electric current profile for the assembled species in the formed layer of (DDLs), at the milliseconds of time ( $< 0.46$  s) and the frequency of  $5.9958E14$  Hz in the scatter field without the effects of the thermal perturbations in the 2D axisymmetric space.

The nonlinear response to the *averaging* model is displayed in figure (6). This figure shows the current distribution for the average unsteady model of charge distribution within (DDLs).



**Figure (6): The nonlinear non-equilibrium electric current profile for the assembled species in the formed layer of (DDLs), at the milliseconds of time ( $< 0.98s$ ) and the frequency of  $5.9958E14$  Hz in the scatter field with the effects of the thermal perturbations in the 2D axisymmetric space.**

## Conclusions

A brief conclusion is: such a model contributes to explain other phenomena such as the blackbody radiation in terms of monochromatic electromagnetic radiation and visible light to excite *chromophores* due to the electric and magnetic field oscillations within a specific medium, or another phenomenon such as the flow of spectral energy flux density in the far-field from this interface domain. Such energies are the kinetics energies result from the oscillation of electrodynamic fields. Additionally, this model can facilitate the investigating of formed (DDLs) in the separation process of organic mixtures such as the azeotropic or multicomponent mixtures through the computations of chemical potentials within (DDLs) boundaries. This model provides evidence for ion hydration process which can prove the occurrence of electronic interactions in (DDLs) of a hot microbubble and shells. Finally, such a model can enhance the fuel cells such as batteries depends on the current and voltage distributions throughout the restricted distance between the center of a hot microbubble and the edge of the bulk of the liquid.

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