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**“Phantom ion effect” and the contact potential of the water-vapor interface**Yan Levin<sup>a)</sup>*Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970, Porto Alegre, Rio Grande do Sul, Brazil*

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The contact (junction) potential between water-vapor and water-oil interfaces is studied theoretically. Unlike the previous studies, we show that ionic contribution to the contact potential vanishes when the concentration of aqueous electrolyte goes to zero. The incorrect prediction of a large ionic contribution to the junction potential in the infinite dilution limit, obtained in the earlier studies, is traced back to the inappropriate use of the grand-canonical ensemble for strongly inhomogeneous Coulomb systems. It is shown that for these systems, the thermodynamic limit is not reached even when the number of particles is astronomically large, on the order of  $10^{24}$ . There is, therefore, no equivalence between statistical ensembles. For realistic, finite size systems, canonical calculation predicts a vanishing ionic contribution to the junction potentials of water-vapor and water-oil interfaces even for very concentrated electrolyte solutions. © 2008 American Institute of Physics. [DOI: 10.1063/1.2982244]

**I. INTRODUCTION**

Electrical structure of the water-vapor interface is of fundamental importance for ionic solvation thermodynamics and for interfacial reactivity.<sup>1–5</sup> Yet our understanding of the interfaces between immiscible liquids, as well as, between water and its vapor is far from complete. One quantity that, in particular, is of fundamental interest is the so-called contact electrostatic potential. This potential is the difference between the inner (liquid) Galvani electrostatic potential and the outer (vapor) Volta electrostatic potentials. The precise value of the contact potential for a pure water-vapor interface remains controversial,<sup>6</sup> with values ranging from  $-1.1$  to  $+0.5$  V. Simulations using simple point charge/extended water<sup>1</sup> place this value at  $-546$  mV, while the full *ab initio* molecular dynamics simulations<sup>6</sup> predict a much smaller value of  $-18$  mV. The situation is further complicated by a curious paper published by Zhou, Stell, and Friedman (ZSF) 20 years ago.<sup>7</sup> In that paper ZSF argued that presence of electrolyte strongly modifies the value of the junction potential. However, what is really curious is that ZSF calculations show that the electrolyte contribution to the contact potential persists, even when the concentration of electrolyte is vanishingly small. In the words of Lawrence Pratt “the ionic contribution is there even though the ions are not.”<sup>8</sup> Like the Cheshire Cat of Alice in Wonderland, ions disappear, but leave their electrostatic potential behind.

The contribution to the contact potential due to the “phantom ions”<sup>6</sup> is quite large—in the hundreds of millivolts, as compared to  $-18$  mV for pure water-vapor interface, found in the *ab initio* simulations. If true, this finding could be of a paramount importance, providing a possible justification for the long sought “water memory”—the under-tow of homeopathy. The situation is so unsettling that the authors of a recent review expressed their hope that “future

studies should quantify this *phantom ionic effect* to determine its actual relevance to the electrochemical potential.”<sup>6</sup> The purpose of this paper is to provide precisely such quantification. In Sec. II. I will briefly review the basic idea behind the ZSF model. I will then discuss its limitations and introduce an alternative “canonical” calculation,<sup>9,10</sup> which will allow me to precisely quantify the contribution of the phantom ions to the contact potential.

**II. THE ZSF MODEL**

ZSF used the MacMillan–Mayer theory of solutions to calculate the equilibrium distribution of electrolyte and the resulting equilibrium junction potential of two immiscible solvents in contact.<sup>7</sup> The electrolyte ions were modeled as hard spheres with a point charge located at the center, while the solvent was represented by dipolar hard spheres. The calculations were performed using the mean spherical approximation. Since I am only interested in highly diluted electrolytes instead of repeating the full ZSF analysis, I will use a much simpler Born model<sup>11</sup> to calculate the ionic solvation energy. For simplicity I will also restrict my attention to 1:1 electrolyte although all the calculations can be easily extended to more general electrolyte systems.

Consider two immiscible solvents in contact. Suppose that the dielectric constant of solvent one is  $\epsilon_1$  and the dielectric constant of solvent two is  $\epsilon_2$ . If some electrolytes are dissolved in the two solvents, when the equilibrium is established it will partition itself between the solvents in such a way as to have a constant electrochemical potential. The equality of the electrochemical potentials can be expressed as

$$k_B T \ln(\rho_+^{(1)} \Lambda^3) + \mu_+^{(1)} + q\psi^{(1)} = k_B T \ln(\rho_+^{(2)} \Lambda^3) + \mu_+^{(2)} + q\psi^{(2)}, \quad (1)$$

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$$k_B T \ln(\rho_{\pm}^{(1)} \Lambda^3) + \mu_{\pm}^{(1)} - q\psi^{(1)} = k_B T \ln(\rho_{\pm}^{(2)} \Lambda^3) + \mu_{\pm}^{(2)} - q\psi^{(2)}. \quad (2)$$

In the equations above  $\rho_{\pm}^{(i)}$  is the concentration of  $\pm$  ions in the solvent  $i$ ,  $\psi^{(i)}$  is the electrostatic potential of solvent  $i$ ,  $q$  is the elementary charge,  $\mu_{\pm}^{(i)}$  is the solvation free energy of a  $\pm$  ion inside solvent ( $i$ ),  $T$  is the temperature, and  $\Lambda$  is the de Broglie thermal wavelength. Since I am interested in very dilute solutions, the interaction between ions can be neglected and the solvation free energy of each ion can be approximated by the Born form

$$\mu_{\pm}^{(i)} = \frac{q^2}{2R_{\pm}} \left( \frac{1}{\epsilon_i} - \frac{1}{\epsilon_0} \right), \quad (3)$$

where  $R_{\pm}$  is the ionic radius of  $\pm$  ions and  $\epsilon_0$  is the vacuum permittivity constant. Subtracting Eq. (2) from Eq. (1) and using the fact that in the thermodynamic limit the two phases must be charged neutral, I arrive directly at the principal ZSF result

$$\Delta\psi \equiv \psi^{(2)} - \psi^{(1)} = \frac{q}{4} \left( \frac{1}{R_+} - \frac{1}{R_-} \right) \left( \frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right). \quad (4)$$

Since  $\Delta\psi$  does not depend on the concentration of electrolyte, we are forced to conclude that the ionic contribution to the junction potential is there “even though the ions are not.”<sup>8</sup> Certainly this seems like a strange state of affairs. Is it possible that the calculation presented above is missing some important ingredient? To see what has gone wrong we will now present a slightly different discussion of the same model.

### III. CANONICAL CALCULATION

The calculation presented in Sec. II is intrinsically grand canonical—one of the solvents can be thought of as being a reservoir of electrolyte for the other solvent. In a charge neutral system there must be equivalence between grand-canonical and canonical ensembles.<sup>9,10,12</sup> However, this equivalence exists only in the *thermodynamic limit*,  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ , while  $N/V$  is held fixed. Clearly in any experiment, the number of ions—although very large—will not be infinite. The long range nature of the Coulomb interaction demands a particular care in going to the thermodynamic limit. To see clearly the finite size effects we will now study a canonical version of the problem discussed above.

Suppose that we have two immiscible solvents confined in a beaker of volume  $2V$ . The lower half of the beaker is occupied by a solvent of large dielectric constant (water,  $\epsilon_1$ ), and the top half by a solvent of low dielectric constant (oil,  $\epsilon_2$ ). If  $N$  ion pairs of a strong electrolyte are dissolved in water, after some time a fraction of these ions will diffuse into the oil region. If the electrolyte is asymmetric with  $R_- > R_+$ , there will be an excess of anions in the oil phase—since the electrostatic energy penalty for going into the low dielectric phase for larger ions is smaller—and an excess of cations in the water phase. As a consequence of the Earnshaw theorem,<sup>13</sup> the excess charge in the two conducting phases will concentrate along the interface, establishing an electric field that will oppose a further charge build up. It

should be noted that the tendency of the excess charge to go to the surface is to a large extent a nonlinear and correlational effect,<sup>14</sup> not well accounted for in mean-field theories based on the linearized Poisson–Boltzmann equation. Thus, in general, such mean-field theories will overestimate the length scale on which the electrostatic potential varies in strongly inhomogeneous systems.

Following the original ZSF model, I will take the water-oil interface to be planar and rigid. The excess charge of the two phases will then form a double layer of width  $w = R_+ + R_-$  along the interface. After the equilibrium is established the ionic concentration in the two phases will be such as to minimize the Helmholtz free energy. Suppose that  $x$ -fraction of cation and  $y$ -fraction of anions are in the water phase. Then from the conservation of the total number of particles, the corresponding fractions in the oil phase will be  $1-x$  for cations and  $1-y$  for anions. Using the Gauss law, the electric field inside the oil portion of the double layer is found to be  $E_2 = 4\pi(x-y)Nq/\epsilon_2 A$ , and the electric field inside the water portion of the double layer is  $E_1 = 4\pi(x-y)Nq/\epsilon_1 A$ , where  $A$  is the cross-sectional area. Integrating the field energy density over the span of the double layer, we obtain the electrostatic contribution to the total free energy. The Helmholtz free energy for the whole system is

$$\begin{aligned} \beta F = & Nx \ln x + N(1-x)\ln(1-x) + Ny \ln y \\ & + N(1-y)\ln(1-y) + \frac{2\pi N^2(x-y)^2 q^2}{k_B T A} \frac{\epsilon_2 R_+ + \epsilon_1 R_-}{\epsilon_1 \epsilon_2} \\ & + Nx\beta\Delta\mu_+ + Ny\beta\Delta\mu_- + \text{const.} \end{aligned} \quad (5)$$

The first four terms of Eq. (5) are purely entropic, the  $(x-y)$  term is the contribution from electric field established at the interface, while the last two terms correspond to the difference in the solvation free energy for cations and anions in the two phases

$$\beta\Delta\mu_{\pm} = \frac{q^2}{2k_B T R_{\pm}} \left( \frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right). \quad (6)$$

Minimizing the free energy with respect to  $x$  and  $y$ , we find

$$\ln \frac{x}{1-x} + (x-y)\chi + \beta\Delta\mu_+ = 0, \quad (7)$$

$$\ln \frac{y}{1-y} - (x-y)\chi + \beta\Delta\mu_- = 0, \quad (8)$$

where

$$\chi \equiv \frac{q^2 N}{k_B T A} \frac{\epsilon_2 R_+ + \epsilon_1 R_-}{\epsilon_1 \epsilon_2}. \quad (9)$$

Equations (7)–(9) determine the partitioning of ions between the two phases. Integrating the electric field across  $w$ , the electrostatic potential difference between the two phases is found to be  $\beta q \Delta\psi = (y-x)\chi$ . In the limit  $N \rightarrow \infty$  ( $\chi \rightarrow \infty$ ), Eqs. (7) and (8) require that  $y \rightarrow x$ . Subtracting Eq. (7) from Eq. (8), we arrive at the ZSF result for the electrostatic potential difference  $\Delta\psi$ . In the thermodynamic limit the electrostatic potential difference between the two phases saturates at the value predicted by the grand-canonical calculation, Eq. (4).

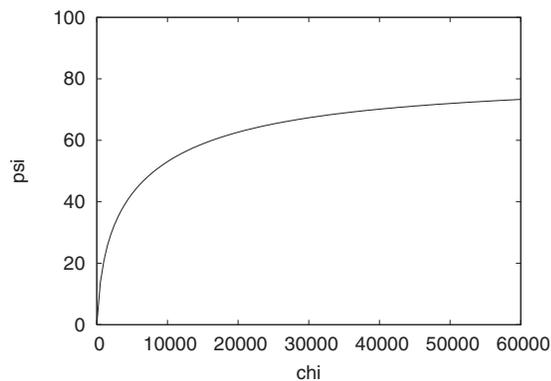


FIG. 1. Contact potential as a function of  $\chi$  for two immiscible liquids with dielectric constants  $\epsilon_1/\epsilon_0=80$  and  $\epsilon_2/\epsilon_0=10$ . The two solvents are inside a cylindrical 2 l bottle of cross-sectional area  $A=100$  cm<sup>2</sup>, each occupying half of its total volume. The ions of electrolyte have radius  $R_+=2$  Å, and  $R_-=4$  Å. The saturation value of  $\Delta\psi$  in this case is  $-81$  mV.

In the limit of vanishing ionic concentration  $N \rightarrow 0$ , however, we find a very different result. In this case the  $(x-y)$  term in Eqs. (7) and (8) becomes very small and the two equations decouple. The potential difference between the two phases becomes

$$\beta q \Delta\psi \approx (e^{\beta\Delta\mu_+} - e^{\beta\Delta\mu_-})\chi, \quad (10)$$

which clearly vanishes in the limit of infinite dilution. Depending on the value of the dimensionless parameter  $\chi$  there are, therefore, two distinct regimes of  $\Delta\psi$ : Linear and saturated. The crossover between the two occurs at

$$\chi_{\times} \approx \frac{\beta}{2} \left( \frac{\Delta\mu_+ - \Delta\mu_-}{e^{\beta\Delta\mu_+} - e^{\beta\Delta\mu_-}} \right). \quad (11)$$

Figure 1 shows the characteristic behavior of  $\Delta\psi$  as a function of  $\chi$  for two immiscible liquids with dielectric constants  $\epsilon_1/\epsilon_0=80$  and  $\epsilon_2/\epsilon_0=10$ .

Let us now consider a water-oil interface ( $\epsilon_1/\epsilon_0=80, \epsilon_2/\epsilon_0=3$ ) for an asymmetric electrolyte with  $R_+=2$  Å and  $R_-=4$  Å. Suppose that 1 mol of this electrolyte is first dissolved inside the water phase of  $V=1$  l and suppose that the cross-sectional area of our bottle is 100 cm<sup>2</sup>. Once the equilibrium is established what will be the junction potential across the water-oil interface? Let us first see whether for these parameters, the electrostatic potential is in the saturation or in the linear regime. Using Eq. (9) we find that  $\chi = 5.9 \times 10^9$ , on the other hand the crossover value is  $\chi_{\times} = 1.24 \times 10^{11}$  so we are well inside the linear regime. Using Eq. (10) I then calculate the ionic contribution to the contact potential to be  $\Delta\psi = -14$  mV, while the result of the grand-canonical calculation (the saturation value) is  $\Delta\psi = -297$  mV. For a water-vapor interface ( $\epsilon_1/\epsilon_0=80, \epsilon_2/\epsilon_0=1$ ) the situation is even worse. In this case I find the contact potential is  $-5.9 \times 10^{-20}$  mV, while the grand-canonical calculation predicts 913 mV. For water-vapor interfaces, the grand-canonical formalism errs by some 22 orders of magnitude.

## IV. CONCLUSIONS

It is quite common to use canonical or grand-canonical formalisms of statistical mechanics interchangeably, guided simply by convenience. The equivalence between ensembles, however, exists only in the thermodynamic limit,  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ . For systems with short range interactions, the thermodynamic limit is reached very quickly with a few hundreds of particles. However, for Coulomb systems this is no longer the case. The contact potential between the water-vapor interfaces is a dramatic demonstration of this dichotomy. In this case we see that the thermodynamic limit is not reached even when the number of particles is stupendously large, on the order of  $10^{24}$  ions. If one uses the grand-canonical formalism to calculate the contact potential of the water-vapor interface, one comes to the conclusion that at vanishing dilution of electrolyte, the ionic contribution to the junction potential is some hundreds of millivolts, meaning that any impurity, or even the dissociation of water into  $H^+$  and  $OH^-$  will significantly contribute to the interfacial electrostatic potential. The ionic contribution appears to be there even though the ions are not.<sup>8</sup> In reality, the canonical calculation shows that the ionic contribution to the junction potential of the water-vapor interface is always very small. At "infinite" dilution it is of the order of  $\sim 10^{-27}$  mV. There is no "phantom ion effect" for water-vapor interfaces. On the other hand, if water is placed in contact with a solvent of sufficiently large dielectric constant, say  $\epsilon_2/\epsilon_0=40$ , even a vanishingly small concentration of electrolyte on the order of  $10^{-6}$  M (for the system discussed above) would produce a  $-11.5$  mV compared to the saturation value of  $-11.56$  mV contribution to the junction potential. In this case, the grand-canonical formalism will work just fine. The range of validity of the grand-canonical ensemble is delimited by the value of  $\chi_{\times}$ . Finite size effects are fundamentally important as long as the number of ions in the systems is such that  $\chi \ll \chi_{\times}$ .

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