Electronic Supplementary Information for PCCP article:

3D Structure of the Electric Double Layer of Ionic Liquid-Alcohol Mixtures at the Electrochemical Interface

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I. IONIC POSITIONS FLUCTUATIONS: THEORETICAL DESCRIPTION

Let's suppose a situation where the ions are forming a two-dimensional triangular lattice in an ionic layer close to the electrodes. In a first approximation, we can calculate the probability of finding a given ion out of its equilibrium position at $\Delta\vec{r} = (\epsilon_x, \epsilon_y)$ (see Fig. A). This probability will be governed by the Boltzmann distribution. In our problem, the electrostatic potential energy plays a dominant role, so we can approximate this energy for the considered ion by the contributions of its first neighbours:

$$E_p = \frac{q^2}{4\pi\epsilon_r}\left(\frac{1}{\sqrt{\epsilon_x^2+(\epsilon_y-a)^2}} + \frac{1}{\sqrt{\epsilon_x^2+(\epsilon_y+a)^2}} + \frac{1}{\sqrt{\left(\epsilon_x-\frac{\sqrt{3}}{2}a\right)^2+(\epsilon_y-\frac{1}{2}a)^2}} + \frac{1}{\sqrt{\left(\epsilon_x-\frac{\sqrt{3}}{2}a\right)^2+(\epsilon_y+\frac{1}{2}a)^2}} \frac{1}{\sqrt{\left(\epsilon_x+\frac{\sqrt{3}}{2}a\right)^2+(\epsilon_y-\frac{1}{2}a)^2}} + \frac{1}{\sqrt{\left(\epsilon_x+\frac{\sqrt{3}}{2}a\right)^2+(\epsilon_y+\frac{1}{2}a)^2}}\right), \tag{1}$$

where q is the charge of the ions, ϵ_r the electric permitivity of the medium and a the lattice parameter of the model. It is straightforward to see that, since $(0,0)$ is a minimum of the potential, this expression can be approximated to the lowest order by:

$$E_p \approx \frac{3q^2}{2\pi\epsilon a} + \frac{9q^2(\epsilon_x^2+\epsilon_y^2)}{8\pi\epsilon a^3} + O(\epsilon_x^4, \epsilon_y^4). \tag{2}$$

Using this approximation of the energy together with the Boltzmann distribution, the probability of finding an ion out of its equilibrium position can be approximated by:

$$p(\epsilon_x, \epsilon_y) = \frac{1}{Z}e^{-\frac{E_p}{k_BT}} \approx \frac{1}{Z}e^{-\frac{q^2}{k_BT\pi\epsilon a}}e^{-\frac{3q^2(\epsilon_x^2+\epsilon_y^2)}{4\pi\epsilon a^3 k_BT}}, \tag{3}$$

where Z is the partition function, k_B the Boltzmann constant and T the temperature. As it can be seen, the probability of fluctuation in the positions of the ions is described by a Gaussian distribution function with the standard deviation

$$s_p = \frac{a^2}{q}\sqrt{\frac{2\pi\epsilon k_BT}{3a}} \propto \frac{\sqrt{T\epsilon}}{\sigma}, \tag{4}$$

where $\sigma = q/a^2$ is the surface charge density.

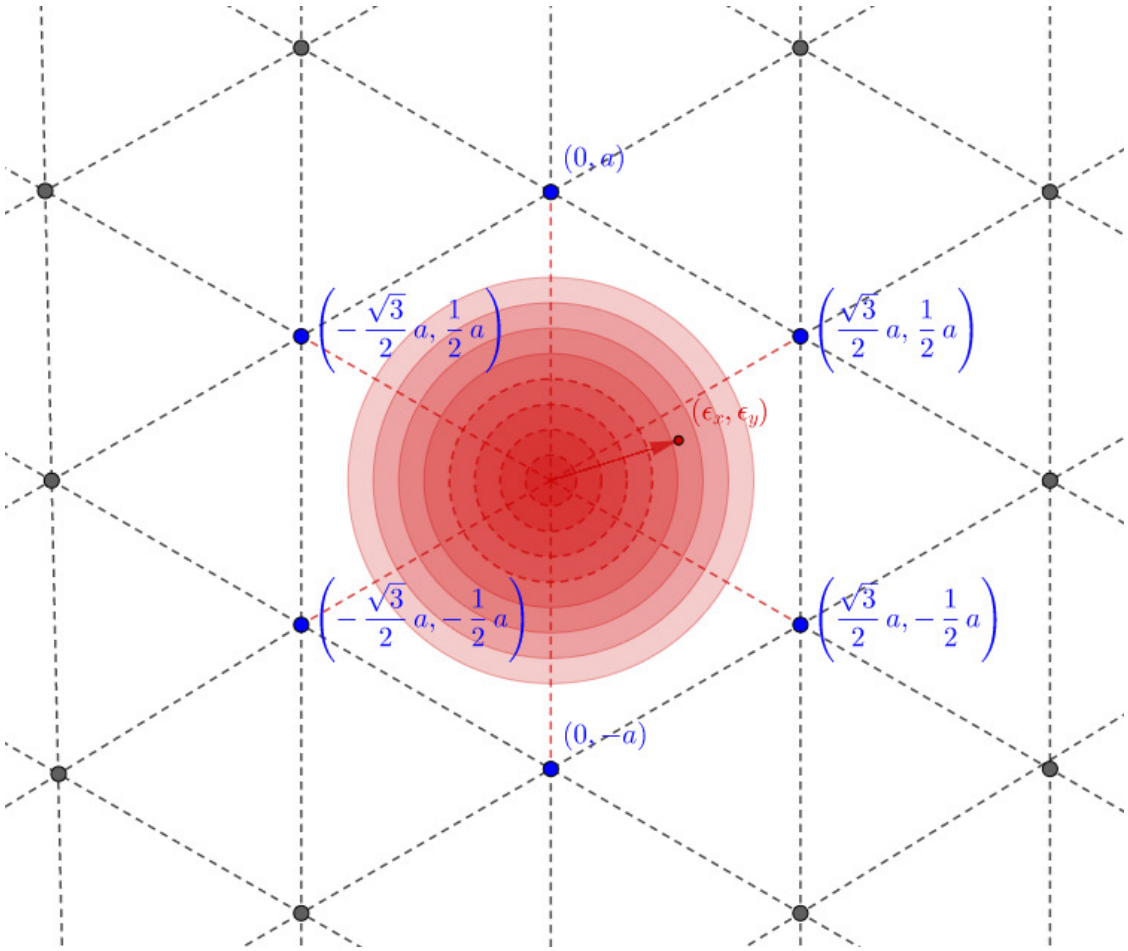

FIG. A: Scheme of the considered model for the calculation of the dispersion in the ionic position. The dots represents the ions positions, being a the lattice parameter. The considered ions for the energy calculation are those in blue.