

# On the differential capacitance of a double layer containing hard sphere ions and dipoles in the mean field approximation

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**Abstract.** The differential capacitance of an electric double layer containing a mixture of charged hard spheres and dipolar hard spheres is obtained using the mean field approximation. The results are qualitatively similar to experiment and to those obtained in the mean spherical approximation.

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A double layer of charge is formed at the interface of an electrolyte and an electrode. Capacitance measurements have very important and useful application in electrochemistry. The mean spherical approximation (MSA) capacitance of an aqueous electric double layer at various concentrations of the electrolyte have been recently calculated. [1] The results are in good, but no complete, agreement with the experimental curve [2] for a mercury/aqueous NaDP (sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4$ ) interface at 25°C.

The MSA expression for the inverse capacitance,  $C^{-1}$ , obtained for a double layer model of charged hard spheres and dipolar hard spheres next to a planar charged wall, and valid at low concentrations, is given by [3,4]

$$\frac{1}{C} = \frac{4\pi}{\epsilon\kappa} + \frac{2\pi}{\epsilon} \left[ d_1 + \frac{\epsilon - 1}{\lambda} d_D \right], \quad (1)$$

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where  $d_I$  and  $d_D$  are the diameters of the ions and the dipoles respectively,  $\epsilon$  the dielectric constant (of the pure dipolar liquid),  $\lambda$  being a parameter related to  $\epsilon$  through

$$\lambda^2(1 + \lambda)^4 = 16\epsilon, \tag{2}$$

and  $\kappa$  is the Debye-Hückel parameter

$$\kappa^2 = \frac{4\pi\beta}{\epsilon} \sum_i \epsilon_i^2 n_i^0. \tag{3}$$

Here  $\epsilon_i$  and  $n_i^0$  are the charge and average number density in the bulk of ions of species  $i$ ,  $\beta = 1/kT$ ,  $k$  being the Boltzmann constant and  $T$  the absolute temperature.

Note that  $C$  in Eq. (1) is both the integral and differential capacitance [3,4] since the MSA is a linear theory valid at or near zero surface charge density on the wall. In applying Eq. (1) in Ref. [1] the authors used  $d_I = d_D$  for simplicity and added an electrode contribution  $-2.6 \text{ m}^2\text{F}^{-1}$  (for a mercury electrode/aqueous 1:1 electrolyte) [5,6] to the right hand side of the equation. In this note we report a qualitatively similar result to that reported by Blum *et al.* [1] (Fig. 1 of Ref. [1]) using a mean field approach.

Outhwaite [7,8] has recently applied the mean field approach to the present interfacial model. We will now present a brief outline of the theory. The notation throughout this note closely follows that of Outhwaite. We write the Poisson equation for the mean electrostatic potential  $\psi(x)$  at a perpendicular distance  $x$  from the wall as

$$\frac{d^2\psi(x)}{dx^2} = -4\pi \sum_i \epsilon_i n_i(x) + 4\pi \sum_\alpha \int \vec{\mu}_\alpha \cdot \nabla n_\alpha(x, \vec{\omega}) d\vec{\omega} \tag{4}$$

Here  $\vec{\mu}_\alpha$  is the dipole moment of dipolar species  $\alpha$ ,  $\vec{\omega}$  are rotational coordinates,  $n_i(x)$  the average number density of the  $i$ th type ions at  $x$  and  $n_\alpha(x, \vec{\omega})$  the average number density of the  $\alpha$ th type dipoles at  $x$  and orientation  $\vec{\omega}$ .

Using the mean field approximation

$$n_i(x) = \begin{cases} 0 & x < \frac{d_I}{2} \\ n_i^0 e^{-\beta\epsilon_i\psi} & x > \frac{d_I}{2} \end{cases} \tag{5a}$$

and

$$n_\alpha(x, \vec{\omega}) = \begin{cases} 0 & x < \frac{d_D}{2} \\ n_\alpha^0 \exp(-\beta\vec{\mu}_\alpha \cdot \nabla\psi) & x > \frac{d_D}{2} \end{cases} \tag{5b}$$

and performing the necessary integrations over dipole orientations, Eq. (4) transforms to [7,8]

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} = & -4\pi H\left(x - \frac{d_I}{2}\right) \sum_i \epsilon_i n_i^0 e^{-\beta\epsilon_i\psi} \\ & - 4\pi H\left(x - \frac{d_D}{2}\right) \sum_\alpha n_\alpha^0 \mu_\alpha \frac{d}{dx} \left[ \frac{\theta_\alpha \cosh \theta_\alpha - \sinh \theta_\alpha}{\theta_\alpha^2} \right] \end{aligned} \quad (6)$$

In the above,  $H(x)$  is the Heaviside step function, and  $\theta_\alpha = \beta\mu_\alpha(d\psi/dx)$ . The boundary conditions that  $\psi(x)$  satisfies are,

$$\begin{aligned} \psi(x), \frac{d\psi}{dx} & \rightarrow 0 \text{ as } x \rightarrow \infty \\ \psi(x) & \text{ continuous in the region } x \geq 0, \end{aligned} \quad (7a)$$

$$\left. \frac{d\psi}{dx} \right|_{x=0^+} = -4\pi\sigma \quad (\sigma \text{ is the surface charge density}), \quad (7b)$$

and

$$\left. \frac{d\psi}{dx} \right|_{x=\frac{d_D^+}{2}} = \left. \frac{d\psi}{dx} \right|_{x=\frac{d_D^-}{2}} + 4\pi \sum_\alpha \int \mu_{\alpha x} n_\alpha \left(\frac{d_D}{2}, \vec{\omega}\right) d\vec{\omega} \quad (7c)$$

The last condition arises due to the discontinuity in  $d\psi/dx$  at  $x = d_D/2$ , the distance of nearest approach of the dipole to the wall. The above conditions will specify a unique value for  $\psi(x)$ .

Being non-linear, Eq. (6) is difficult to solve. By linearizing this equation with respect to both the ion and dipole terms, Outhwaite [7,8] has obtained analytical results for  $\psi(x)$  and has shown [8] that the expression for the inverse capacitance is analogous to that from the MSA, viz.,

$$\frac{1}{C} = \begin{cases} \frac{4\pi}{\epsilon\kappa} \left[ 1 + \kappa \frac{d_I}{2} + \kappa(\epsilon - 1) \frac{d_D}{2} \right] & d_D \leq d_I \\ \frac{4\pi}{\kappa_0} \left[ \kappa_0 \frac{d_I}{2} + \frac{\kappa + \kappa_0 \tanh \frac{\kappa_0}{2}(d_D - d_I)}{\kappa \tanh \frac{\kappa_0}{2}(d_D - d_I) + \kappa_0} \right] & d_I \leq d_D \end{cases} \quad (8a, b)$$

where

$$\kappa_0^2 = \epsilon\kappa^2, \quad (9)$$

$$\epsilon(x) = 1 + \frac{4}{3} \pi \beta H \left( x - \frac{d_D}{2} \right) \sum_{\alpha} \mu_{\alpha}^2 n_{\alpha}^0. \tag{10}$$

If the difference in diameters of the dipoles and the ions is small and if the concentration is not too high, expansion of Eq. (8b) to linear terms is possible and thus becomes identical to Eq. (8a). Note again that because of the linearizations,  $C$  above is both a differential and an integral capacitance.

Comparing Eqs. (1) and (8) for the case when the ions and the dipolar hard spheres have the same diameter,  $d_I = d_D = d$ , we obtain

$$f \left\{ d + \frac{\epsilon - 1}{\lambda} d \right\}_{\text{MSA}} = \left\{ d + (\epsilon - 1)d \right\}_{\text{Mean Field}} \tag{11}$$

where

$$f = \frac{\epsilon}{1 + (\epsilon - 1)/\lambda}. \tag{12}$$

For the system parameters utilized in the work of Blum *et al.* [1], viz., Symmetric 1:1 electrolyte with  $d = 2.76 \times 10^{-10}$  m,  $\epsilon = 78.4$  giving  $\lambda = 2.65$ , and at  $T = 298$  K, we obtain

$$\frac{2\pi}{\epsilon} \left\{ d + \frac{\epsilon - 1}{\lambda} d \right\}_{\text{MSA}} = 6.01 \text{ m}^2\text{F}^{-1}$$

and

$$\frac{2\pi}{\epsilon} \left\{ d + (\epsilon - 1)d \right\}_{\text{Mean Field}} = 15.6 \text{ m}^2\text{F}^{-1} \tag{13}$$

and thus  $f = 2.6$ . A plot of  $C^{-1}$  against  $4\pi/\epsilon\kappa$  therefore yields an intercept  $\sim 3.4$  on the  $C^{-1}$  axis (including an electrode contribution  $-2.6 \text{ m}^2\text{F}^{-1}$ ) in the MSA (see, for example, Fig. 1 of Ref. [1]) and an intercept of  $\sim 13.0$  in the mean field approach.

If we linearize Eq. (6) in the dipole terms only and set  $d_I = d_D = d$  we arrive at Eq. (24) of Ref. [7], that is:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi}{\epsilon(x)} \sum_{\mathbf{i}} e_{\mathbf{i}} n_{\mathbf{i}}^0 e^{-\beta e_{\mathbf{i}} \psi} H \left( x - \frac{d}{2} \right) \tag{14}$$

In this form the above equation is analogous to the non-linear Gouy [9]- Chapman [10] equation in the double layer literature. The boundary conditions are now as before, Eq. (7), with the exception of Eq. (7c) which now becomes

$$\epsilon \frac{d\psi}{dx} \Big|_{x=\frac{d^+}{2}} = \frac{d\psi}{dx} \Big|_{x=\frac{d^-}{2}}. \tag{15}$$



Solution of Eq. (14) considering the associated boundary conditions is now straightforward, and one obtains for a 1:1 electrolyte

$$\psi(x) = -4\pi\sigma x + 4\pi \left(\frac{d}{2}\right) \sigma + \frac{2}{\epsilon\beta} \sinh^{-1} \left[ \sigma \sqrt{\frac{\pi\beta}{2n^0\epsilon}} \right] \quad 0 \leq x \leq \frac{d}{2} \quad (16a)$$

and

$$\psi(x) = \frac{4}{e\beta} \tanh^{-1} \left[ \tanh \left( \frac{e\beta\psi(d/2)}{4} \right) e^{-\kappa(x-\frac{d}{2})} \right] \quad x \geq \frac{d}{2} \quad (16b)$$

where  $e$  and  $n^0$  are the electronic charge and average bulk number density of either ionic species.

The differential capacitance  $C_D$  may now be obtained from

$$\frac{1}{C_D} = \frac{d\psi(0)}{d\sigma} = 2\pi d + \frac{4\pi}{\epsilon\kappa} \frac{1}{\sqrt{1 + \sigma^2 \frac{\pi\beta}{2n^0\epsilon}}} \quad (17)$$

In the limit  $\sigma \rightarrow 0$ , Eq. (17) reduces to the expression

$$\frac{1}{C_D} = 2\pi d + \frac{4\pi}{\epsilon\kappa}, \quad (18)$$

which is the same result as that obtained in the linearized theory, as expected. From a theoretical point of view,  $C_D$  provides a real-world experimental test of the theory as opposed to simulating a model on the computer.

The results presented in this note are essentially Eqs. (16) and (17). Because of linearization of Eq. (6) in the dipole terms only, the differential capacitance depends on the surface charge density  $\sigma$ . The integral capacitance  $C_I$ , may be obtained from

$$\frac{1}{C_I} = \frac{\psi(0)}{\sigma} = 2\pi d + \frac{2}{e\beta\sigma} \sinh^{-1} \left[ \sigma \sqrt{\frac{\pi\beta}{2n^0\epsilon}} \right]. \quad (19)$$

In Figure 1 we have plotted the inverse capacitance  $C^{-1}$ , against  $4\pi/\epsilon\kappa$  for an aqueous 1:1 system at zero surface charge density, using Eqs. (1) and (8) ( $d_I = d_D = d$ ). The experimental points are the results of Parsons and Zobel. [2] The mean field capacitance is qualitatively similar to the MSA results and to experimental values at low concentrations. The discrepancy in the intercepts between the MSA and mean field theories is understandable. The  $\epsilon(x)$  given by Eq. (10) is only valid for rather low concentrations. This, in turn, is the result of the admittedly oversimplification introduced through the mean field approximation [Eq. (5)]. A full non-linear analysis to yield a better  $\epsilon(x)$  would be an improvement. In any case the qualitative nature of the work here reported is encouraging and suggests that the mean potential approach is reasonable.

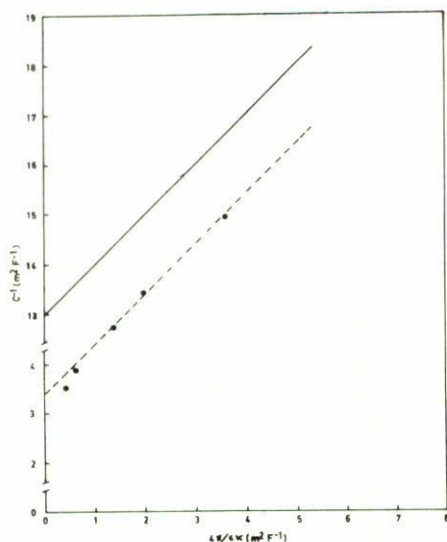


FIGURE 1. Plot of the reciprocal of the capacitance versus  $4\pi/\epsilon\kappa$  at zero surface charge density. The quantity  $\epsilon\kappa/4\pi$  is the diffuse layer capacitance. — mean field theory, - - - mean spherical approximation. The circles are the experimental results of Parsons and Zobel. [2]

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**Resumen.** Empleando la aproximación del campo medio se obtiene una expresión para la capacitancia diferencial de una capa eléctrica doble que contiene una mezcla de esferas duras cargadas y esferas duras dipolares. Los resultados son cualitativamente semejantes a los experimentales y a los obtenidos mediante la aproximación esférica media.