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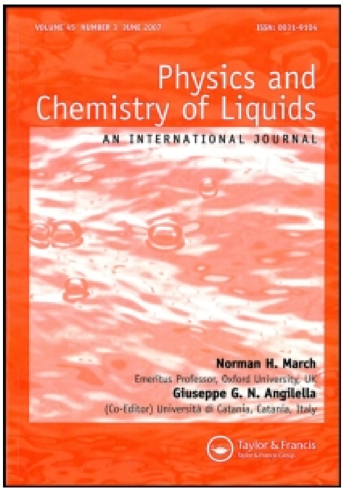

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ORIGIN OF CHARGE OSCILLATION OF SURFACE DENSITY PROFILES OF INHOMOGENEOUS CHARGED FLUIDS USING THE SQUARE-GRADIENT DENSITY FUNCTIONAL MODEL

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In order to clarify the origin of charge oscillation of the surface density profile of inhomogeneous charged fluids near an electrode observed in recent theoretical as well as computer simulation works, asymptotic density profiles of binary symmetric charged fluids are examined using a simple unified model based on the square-gradient (SG) density functional theory. The number density profile shows exponentially decaying monotonous tail expected from the SG approximation, while the charge density shows either monotonous or damped oscillating tail. Such charge oscillation is shown to arise from an interplay between the long-range Coulomb interaction and the short-range correlation of the charge density. Criterion of the appearance of an oscillatory tail based on the restricted primitive model model is examined.

KEY WORDS: Surface density profile, electrolyte, fused salt

1 INTRODUCTION

There have already been a number of works on the density profile of inhomogeneous charged fluid such as electrolytes or fused salts near an electrode because it is related to the surface dipole layer or the electrical double layer and has been one of the oldest and most fundamental electrical problems in electrochemistry[1–9]. Recent theoretical as well as computer simulation works[2–7] definitely demonstrated that there is a charge density oscillation in strongly coupled inhomogeneous charged fluids near an electrode. However, it seems that no explanation has been presented to clarify the origin of this oscillation.

In order to understand the density profile of charged fluids near an electrode qualitatively, in this report we are going to examine the asymptotic density tails of symmetric charged fluids using the simple square-gradient (SG) density functional theory.

2 SURFACE DENSITY PROFILE IN THE SQUARE-GRADIENT DENSITY FUNCTIONAL THEORY FOR SYMMETRIC CHARGED FLUIDS

The SG density functional theory for general charged fluids was already developed a decade ago[8]. For 1:1 electrolytes and fused salts, it is more convenient to use the number density N and the charge density Q defined by[6]

$$N = (n_+ + n_-)/2, \tag{2.1a}$$

$$Q = n_+ - n_-, \tag{2.1b}$$

instead of the local density of cation n_+ and anion n_- carrying electric charges $e_+ = e$ and $e_- = -e$. The density profiles N and Q are determined from the Euler-Lagrange equations[6]

$$\mu_N = \frac{\partial g_0}{\partial N} + \frac{\partial g_{2NN}}{\partial N} |\nabla N|^2 + \frac{\partial g_{2NQ}}{\partial N} \nabla N \cdot \nabla Q + \frac{\partial g_{2QQ}}{\partial N} |\nabla Q|^2$$
$$-2\nabla \cdot [g_{2NN} \nabla N + \tfrac{1}{2} g_{2NQ} \nabla Q] - \frac{1}{8\pi} \frac{\partial \varepsilon}{\partial N} |\nabla \Phi|^2, \tag{2.2a}$$

$$\mu_Q = e\Phi + \frac{\partial g_0}{\partial Q} + \frac{\partial g_{2NN}}{\partial Q} |\nabla N|^2 + \frac{\partial g_{2NQ}}{\partial Q} \nabla N \cdot \nabla Q + \frac{\partial g_{2QQ}}{\partial Q} |\nabla Q|^2$$
$$-2\nabla \cdot [g_{2NN} \nabla N + \tfrac{1}{2} g_{2NQ} \nabla Q] - \frac{1}{8\pi} \frac{\partial \varepsilon}{\partial Q} |\nabla \Phi|^2, \tag{2.2b}$$

and the Poisson's equation

$$\nabla \cdot (\varepsilon \nabla \Phi) = -4\pi e Q, \tag{2.3}$$

where g_0 is the Helmholtz free energy density of a uniform ionic mixture minus the electrostatic self-energy, ε is the dielectric constant of the medium and Φ is the electrostatic potential, and μ_N and μ_Q are the chemical potentials. The SG coefficients g_{2NN}, g_{2NQ} and g_{2QQ} are given by

$$g_{2NN} = g_{2++} + 2g_{2+-} + g_{2--}, \tag{2.4a}$$

$$g_{2NQ} = g_{2++} - g_{2--}, \tag{2.4b}$$

$$g_{2QQ} = (g_{2++} - 2g_{2+-} + g_{2--})/4. \tag{2.4c}$$

Using the non-Coulombic part of the Ornstein–Zernike direct correlation functions $\tilde{c}_{ij}(r)$ defined by

$$\tilde{c}_{ij}(r) = c_{ij}(r) + \frac{e_i e_j}{k_B T \varepsilon r}, \tag{2.5}$$

where $c_{ij}(r)$ is the direct correlation function of a uniform mixture with densities

$\{n_+, n_-\}$ and $\{i, j) = \{+, -\}$, the SG coefficients g_{2++}, g_{2--} and g_{2+-} are given by[8]

$$g_{2ij}(\{n_i\}) = \frac{k_B T}{12} \int \tilde{c}_{ij}(r) r^2 \, dr. \tag{2.6}$$

Asymptotic forms of above Euler–Lagrange equations (2.2a, b) and Poisson's equation (2.3) for a flat interface perpendicular to z direction can be written as

$$2g_{2NN} \frac{d^2M}{dz^2} - \frac{\partial^2 g_0}{\partial M^2} M = 0, \tag{2.7a}$$

$$2g_{2QQ} \frac{d^2Q}{dz^2} - \frac{\partial^2 g_0}{\partial Q^2} Q - e\Phi = 0, \tag{2.7b}$$

$$\varepsilon \frac{d^2\Phi}{dz^2} = -4\pi e Q, \tag{2.8}$$

where we have linearized the equations for $M = N - N_l$ and Q with N_l being the bulk liquid number density. We have also neglected density dependence of the dielectric constant ε. In order to decouple the equations for the number density $M = N - N_l$ and the charge density Q we have considered a symmetric case[6]

$$g_0(N, Q) = g_0(N, -Q), \tag{2.9a}$$

$$g_{2NQ}(N, Q = 0) = 0. \tag{2.9b}$$

All coefficients of the linear differential equations (2.7a)–(2.8), g_{2NN}, $\partial^2 g_0/\partial N^2$, g_{2QQ} and $\partial^2 g_0/\partial Q^2$, are those for the bulk densities $N = N_l$, and $Q = 0$. We should note that the external electrostatic field due to the uniform surface charge density σ on the planar electrode at $z = 0$ is already included in (2.7a, b) and (2.8) through the boundary conditions to the Poisson's equation[2–4]:

$$d\Phi/dz(0) = -4\pi\sigma/\varepsilon, \tag{2.10a}$$

$$\Phi(z \to \infty) = 0, \tag{2.10b}$$

where we have assumed that the fluid occupies a half space $z > 0$.

Using the relationships between the second derivatives of g_0 and the Fourier transforms $\tilde{c}_{ij}(q)$ for a symmetric ionic fluid[6]

$$\begin{aligned}\frac{\partial^2 g_0}{\partial N^2} &= k_B T\left(\frac{1}{n_+} + \frac{1}{n_-} - \tilde{c}_{++}(q=0) - \tilde{c}_{--}(q=0) - 2\tilde{c}_{+-}(q=0)\right), \\ &= 4/N_l^2 \chi_T, \end{aligned} \tag{2.11a}$$

$$\frac{\partial^2 g_0}{\partial N\,\partial Q} = \frac{k_B T}{2}\left(\frac{1}{n_+} - \frac{1}{n_-} - \tilde{c}_{++}(q=0) + \tilde{c}_{--}(q=0)\right),$$

$$= 0, \qquad (2.11\text{b})$$

$$\frac{\partial^2 g_0}{\partial Q^2} = \frac{k_B T}{4}\left(\frac{1}{n_+} + \frac{1}{n_-} - \tilde{c}_{++}(q=0) - \tilde{c}_{--}(q=0) + 2\tilde{c}_{+-}(q=0)\right), \qquad (2.11\text{c})$$

where χ_T is the isothermal compressibility, we can immediately obtain a monotonous exponential tail for the number density N from (2.7a) as

$$N(z) - N_l \sim \exp(-z/\lambda_N), \qquad (2.12)$$

with

$$\lambda_N = (N_l^2 g_{2NN} \chi_T/2)^{1/2}, \qquad (2.13)$$

corresponds to the bulk correlation length of the classical van der Waals theory. This result was already obtained by Telo da Gama *et al.*[9].

The charge density $Q(z)$ can be determined from a linear differential equation derived from (2.7b) and (2.8):

$$2g_{2QQ}\frac{d^4Q}{dz^4} - \frac{k_B T}{N_l'}\frac{d^2Q}{dz^2} + \frac{4\pi e^2}{\varepsilon}Q = 0, \qquad (2.14)$$

where we put

$$\partial^2 g_0/\partial Q^2 = k_B T/N_l', \qquad (2.15)$$

from (2.11c), and N_l' is an effective density corrected by the short-range correlation

$$N_l' = N_l/(1 - N_l\delta\tilde{c}(q=0)), \qquad (2.16\text{a})$$

with

$$\delta\tilde{c}(q=0) = (\tilde{c}_{++}(q=0) - \tilde{c}_{--}(q=0) + 2\tilde{c}_{+-}(q=0))/4. \qquad (2.16\text{b})$$

Since we consider the charge density under the influence of a planar electrode, a special solution $Q \equiv 0$ for the free liquid-vapor interface of exactly symmetric salts[9] will be excluded.

When $g_{2QQ} = 0$ and $N_l' > 0$ we have a monotonous exponential tail similar to the number density

$$Q(z) \sim \exp(-z/\sqrt{\Lambda_D}), \qquad (2.17)$$

where

$$\Lambda_D = [4\pi e^2 N_l'/\varepsilon k_B T]^{-1}, \tag{2.18}$$

is the square of an *effective* Debye-Hückel screening length. When $N_l' < 0$, on the other hand, we have a sinusoidal oscillating tail

$$Q(z) \sim \sin(z/\sqrt{|\Lambda_D|} + \theta), \tag{2.19}$$

with θ is an integration constant.

When $g_{2QQ} \neq 0$ we have three kinds of solution; oscillating, damped oscillating and exponentially decaying tails. Introducing a new square length scale

$$\Lambda_Q = 8g_{2QQ}N_l'/k_B T, \tag{2.20}$$

we have four regions for parameters Λ_D and Λ_Q and corresponding solutions:

(region I) $0 > \Lambda_Q \geqq \Lambda_D$ (Oscillating tail)

$$Q(z) \sim Q_+ \sin(-z/\mu_+ + \theta_+) + Q_- \sin(-z/\mu_- + \theta_-), \tag{2.21}$$

with

$$\mu_\pm = \sqrt{|\Lambda_Q|}/2/\sqrt{1 \pm \sqrt{1 - \Lambda_Q/\Lambda_D}}, \tag{2.22}$$

and $Q_\pm$ and $\theta_\pm$ are integration constants. This solution shows undamped layering similar to that expected in solid phase. When $0 > \Lambda_Q = \Lambda_D$, we have a critical tail

$$Q(z) \sim (Q_1 + Q_2 z)\sin(z/\mu + \theta), \tag{2.23}$$

with

$$\mu = \sqrt{|\Lambda_Q|}/2 = \sqrt{|\Lambda_D|}/2, \tag{2.24}$$

where Q_1, Q_2 and θ are integration constants.

(region II) $0 > \Lambda_D > \Lambda_Q$ (Damped oscillating tail)

$$Q(z) \sim Q_0 \exp(-z/\lambda)\sin(z/\mu + \theta), \tag{2.25}$$

where

$$\lambda = \sqrt[4]{\Lambda_Q \Lambda_D}/\sqrt{2}/\sqrt{1 - \sqrt{\Lambda_D/\Lambda_Q}}, \tag{2.26a}$$

$$\mu = \sqrt[4]{\Lambda_Q \Lambda_D}/\sqrt{2}/\sqrt{1+\sqrt{\Lambda_D/\Lambda_Q}}, \tag{2.26b}$$

and Q_0 and θ are integration constants. Surface density profile is a damped oscillating wave decaying into the bulk liquid phase with the decay length λ and the wavelength μ.

(region III) $0 < \Lambda_D < \Lambda_Q$ (Damped oscillating tail)

$$Q(z) \sim Q_0 \exp(-z/\lambda)\sin(z/\mu + \theta), \tag{2.27}$$

where

$$\lambda = \sqrt[4]{\Lambda_Q \Lambda_D}/\sqrt{2}/\sqrt{1+\sqrt{\Lambda_D/\Lambda_Q}}, \tag{2.28a}$$

$$\mu = \sqrt[4]{\Lambda_Q \Lambda_D}/\sqrt{2}/\sqrt{1-\sqrt{\Lambda_D/\Lambda_Q}}. \tag{2.28b}$$

(region IV) $0 < \Lambda_Q \leqq \Lambda_D$ (exponentially decaying tail)

$$Q(z) \sim Q_+ \exp(-z/\lambda_+) + Q_- \exp(-z/\lambda_-) \tag{2.28}$$

with

$$\lambda_\pm = \sqrt{\Lambda_Q}/2/\sqrt{1 \pm \sqrt{1-\Lambda_Q/\Lambda_D}}, \tag{2.29}$$

where $Q_\pm$ are integration constants. When $0 < \Lambda_Q = \Lambda_D$, we have a critical tail

$$Q(z) \sim (Q_1 + Q_2 z)\exp(-z/\lambda), \tag{2.30}$$

with

$$\lambda = \sqrt{\Lambda_Q}/2 = \sqrt{\Lambda_D}/2, \tag{2.31}$$

where $Q_{1,2}$ are integration constants.

Existence of such an oscillatory tail was already predicted in the SG density functional theory of charged fluids in general and applied to liquid metal surfaces[10,11]. Returning to (2.1b), the oscillation of charge density $Q(z)$ means that the oscillation of $n_+(z)$ and $n_-(z)$ are exactly out of phase, which seems to be implicit in theoretical results from more refined density functional models[7] and Monte Carlo simulations[5]. Finally we note that the decay length and the wave length of density oscillation are independent of the magnitude of the surface charge density on the electrode. This is certainly due to the crudeness of our model, however this model calculation indicates that those quantities will be relatively insensitive to the surface charge.

3 APPLICATION TO THE RESTRICTED PRIMITIVE MODEL

In order to see the condition of appearance of such an oscillating tail in more detail, we will consider a simple charged hard sphere mixture[12] of an equal hard sphere diameter σ called the restricted primitive model (RPM). In this model molecular interactions between i, j molecules are given by

$$V_{i,j}(r) = \begin{cases} \infty, & r < \sigma, \\ e_i e_j/\varepsilon r, & r > \sigma, \end{cases} \tag{3.1}$$

with $\{i, j\} = \{+, -\}$ and the direct correlation functions are written as[7]

$$c_{++}(r) = c_{--}(r) = c_S(r) + c_D(r), \tag{3.2a}$$

$$c_{+-}(r) = c_{-+}(r) = c_S(r) - c_D(r), \tag{3.2b}$$

where $c_S(r)$ describes the correlation of the number density while $C_D(r)$ describes that of the charge density. Writing[7]

$$c_D(\mathrm{r}) = -e^2/\varepsilon k_B \mathrm{Tr} + \delta c_D(r), \tag{3.3}$$

we have

$$g_{2QQ} = \frac{k_B T}{12} \int \delta c_D(r) r^2 \, d\mathbf{r}, \tag{3.4}$$

for (2.4c) and

$$\delta \tilde{c}(q = 0) = \delta c_D(q = 0) = \int \delta c_D(r) \, d\mathbf{r}, \tag{3.5}$$

for (2.16b).

The simplest "mean field" approximation[7] neglects the short range correlation of the charge density at all and sets $\delta c_D(r) \equiv 0$. In this case $g_{2QQ} \equiv 0$ and $N_l' = N_l > 0$, then we always have a monotonous charge density tail $Q(z)$ given by (2.17).

This means that both the short-range correlation and the long-range Coulomb interaction are necessary to induce the charge density oscillation, which therefore results from the competition between packing effect and screening.

A more realistic approximation which takes into account this short-range correlation is the mean spherical approximation (MSA)[12], which considers the hard sphere excluded volume effect to the electrostatic energy:

$$\delta c_D(r) = \begin{cases} \dfrac{e^2}{\varepsilon k_B \mathrm{Tr}} \left(1 - B\left(\dfrac{r}{\sigma}\right)\right)^2 & r < \sigma, \\ 0 & r > \sigma, \end{cases} \tag{3.6}$$

where

$$B = [1 + x - \sqrt{1 + 2x}]/x. \tag{3.7}$$

Using traditional non-dimensional coupling parameters Q^* and density ρ^* defined by[1,4,7]

$$Q^* = (e^2/\varepsilon\sigma k_B T)^{1/2}, \tag{3.8}$$

$$\rho^* = N_t\sigma^3, \tag{3.9}$$

the Debye–Hückel inverse screening length parameter x in (3.7) is given by

$$x = Q^*\sqrt{4\pi\rho^*}. \tag{3.10}$$

In this MSA we have

$$N_t\delta\tilde{c}(q = 0) = x^2 f(x), \tag{3.11a}$$

$$g_{2QQ} = (\pi k_B T Q^{*2}\sigma^5/3)g(x), \tag{3.11b}$$

with

$$f(x) = (6 - 8B + 3B^2)/12, \tag{3.12a}$$

$$g(x) = (15 - 24B + 10B^2)/60, \tag{3.12b}$$

then, we can express two characteristic square lengths Λ_Q and Λ_D as a function of x:

$$\Lambda_Q = \frac{2}{3}\frac{x^2 g(x)}{1 - x^2 f(x)}\sigma^2, \tag{3.13a}$$

$$\Lambda_D = \frac{1 - x^2 f(x)}{x^2}\sigma^2. \tag{3.13b}$$

Similarly all the decay lengths and the wave lengths $\lambda_\pm$, $\mu_\pm$, λ and μ in (2.22), (2.26), (2.28) and (2.29) are expressed as a function of x if we scale the length by the hard sphere diameter σ. Then the charged fluid system is characterized by a single parameter x ranging from the small electrolyte regime to the large fused-salt regime. According to the magnitude of x, the asymptotic density tail is classified as

(region II) $x > 1.8649$ (damped oscillating tail), and

(region III) $1.8649 > x > 1.2604$ (damped oscillating tail), where

$$\frac{\lambda}{\sigma} = \left(\frac{g(x)}{6}\right)^{1/4} \bigg/ \left(1 + \frac{(1 - x^2 f(x))}{x^2}\left(\frac{3}{g(x)}\right)^{1/2}\right)^{1/2}, \tag{3.14a}$$

$$\frac{\mu}{\sigma}=\left(\frac{g(x)}{6}\right)^{1/4}\Big/\left(1-\frac{(1-x^2f(x))}{x^2}\left(\frac{3}{g(x)}\right)^{1/2}\right)^{1/2}, \tag{3.14b}$$

(region VI) $x < 1.2604$ (exponentially decaying tail), where

$$\frac{\lambda_\pm}{\sigma}=\left(\frac{x^2g(x)}{6(1-x^2f(x))}\right)^{1/2}\Big/\left(1\pm\left(1-\frac{2x^4g(x)}{3(1-x^2f(x))^2}\right)^{1/2}\right)^{1/2}. \tag{3.15}$$

The oscillating density wave is expected when $x > 1.2604$. This is compared[12] with $x > \sqrt{6}$ which implies the existence of oscillations in the charge cloud about a fixed point ion[13]. The charge density oscillation is more easily excited for a planar perturbation. There is no solution for the inequality $0 > \Lambda_Q > \Lambda_D$ corresponding to the region I, and the solid-like charge density order is not expected.

In Figure 1 we have plotted the decay lengths $\lambda_\pm$ and λ, and the wavelength μ as a function of x. These results show generally narrow surface widths $\lambda_\pm$ and λ, which may be a common feature of the SG model. In the strong coupling region $x > 1.2604$, we expect density stratification, whose layer-layer width $\pi\mu \sim \sigma$ is reasonable magnitude. These results based on a very simple model can be used as a guide to predict qualitatively whether we observe strong surface density oscillation. Actually $x = 1.2604$ seems a reasonable estimate of the appearance of an oscillating tail because we usually have a monotonous tail for electrolytes for which $x < 1.2604$[1–4] while we have an oscillating tail for fused salts for which $x \gg 1.2604$[7].

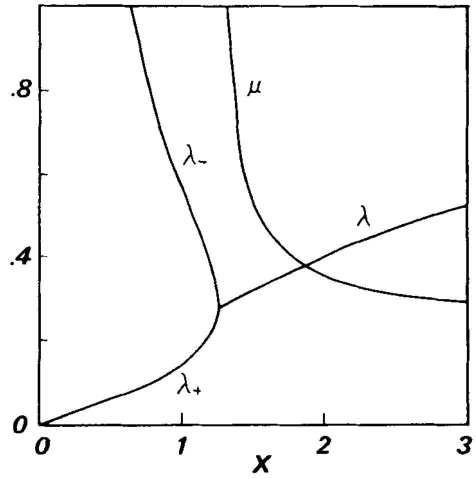

Figure 1 The decay lengths $\lambda_\pm$ and λ, and the wave length μ in unit of the hard sphere diameter σ as a function of the Debye-Hückel inverse screening length parameter x.

4 CONCLUDING REMARKS

We note that our analysis is based entirely on the so called square-gradient approximation and is naturally limited to the asymptotic region far into the bulk liquid phase or to the critical fluid. Although the existence of the long-range $\sim 1/r^6$ van der Waals interaction is known to produce $1/r^3$ tail[14] rather than the classical exponential tail (2.12), such a correction will be small for the tail of the charge density Q for which much stronger Coulomb interaction is dominant.

In the presence of an external hard wall, the surface density oscillation next to the wall is observed even in neutral single component fluids[15]. This oscillation does not arise from the long range Coulomb interaction considered in this paper but from the short range correlation of the number density originated in the packing effect[15,16]. Inclusion of such correlation will produce oscillation not in the charge density Q but in the number density N, which however is beyond the ability of continuum approximations such as the square-gradient approximation. More complicated non-local theory[17] is necessary to account for such a fine structure next to the wall.

Despite all these shortcomings our simple square-gradient model, we believe, did clarify the origin of layers of alternate positive and negative charged in charged fluids near an electrode.

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