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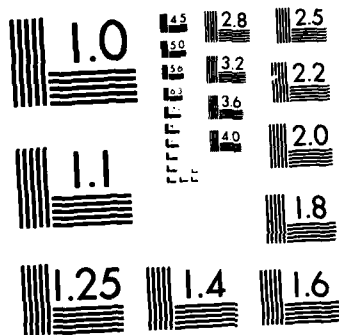
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A MICROSCOPIC MODEL FOR THE LIQUID METAL - IONIC SOLUTION INTERFACE

by

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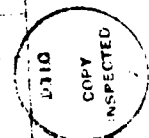
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20. (Abstract - cont'd)

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A MICROSCOPIC MODEL FOR THE LIQUID METAL - IONIC SOLUTION INTERFACE

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ABSTRACT

A microscopic model for the metal-solution interface is presented, which, for the first time, includes both a non-ideal treatment of the metal and a molecular model for the solution side. The metal is described by a jellium including electron-ion pseudopotential. The solution is treated as a mixture of hard spheres with point dipoles (solvent molecules) or point charges (ions). The statistical mechanics is solved using the mean spherical approximation. No a priori separation is introduced between compact and diffuse layers. A simplified version of the model is applied to the case of Hg-DMSO systems.

INTRODUCTION

The classical theories of the ideal polarized electrode are based on two premises :

a) The metal has no direct effect on the differential capacitance C , although it does determine the potential of zero charge and affects the orientation of solvent molecules. From an electrostatic point of view, every metal acts just the same, the only interaction being that of ideal images.

b) The solution side has two layers : the external, or diffuse layer, which can be described by such simple models as the Gouy-Chapman (G.C.) theory, and the internal, or compact layer, which in the absence of specific adsorption is formed only by solvent molecules.

These two premises are now being challenged. The important progress in the theory of metals and metal surfaces in recent times makes it hard to admit that the metal is totally unresponsive to changes in the electrolyte. The surface charge distribution in the metal must respond to local changes in the electrostatic field produced by modifications in the ionic and solvent distributions. Surely this will produce contributions to the differential capacitance, that will be different for each metal, since the response to an external field is different for each metal, and depends on details of the electronic structure near the surface. In previous work [1]- [3] an estimate of these effects was given. The solution side was represented by a layer of dielectric material. In a recent publication, W. SCHMICKLER [4] has discussed a similar model. His conclusions about the role of the metal are similar to ours.

On the solution side, recent advances in the treatment of molecular solutions [5][6], that is solutions in which the solvent is not treated as a continuum, have made it possible to treat the statistical mechanics of the solution side of the electrode interface. Although the approach, in principle, can handle realistic models of solvents and ions, the initial work has dealt with a model in which the solvent is represented by hard spheres with point

dipoles [7]. This work has revealed two important deficiencies of the classical treatment :

a) The separation of the inner and outer layers for the solvent orientation process (or better polarization) implies a violation of Maxwell's equations. The dipoles of the solvent are oriented wherever there is an electric field, that is, throughout the entire electric double layer.

b) The use of ^{local} dielectric constants is also unwarranted. Although this is a much more subtle problem, recent theoretical work [8] has shown that dielectric constants have a clear meaning only for large systems (thermodynamic limit) and not at the molecular level. The polarization is the local variable that is required.

In this work we present a comprehensive theory in which all of these concepts are included. In section 2 we review the models of the metal and solution sides of the interface. The potential drop and capacitance are then computed using a simple GMSA based model which has the obvious advantage of analyticity and simplicity.

In section 3 we discuss the electronic density profile of this model. We consider then a model in which the physical parameters are those of an alkali-ion in DMSO in the neighborhood of a mercury electrode.

In our model the point of zero charge is not the point of zero potential (which is the case in the restricted primitive model) : we discuss also the change in the surface potential of the metal induced by the presence of the solution. The influence of some of the parameters, and detailed comparison between Hg and Ga electrodes will be discussed in future work.

In the last section we examine possible improvements in our work.

of the metallic surfaces. Any model which does not include this layer leads to predictions which are incompatible with experiments [1][11].

In our model, the electrons can diffuse into the ionic solution. In actual practice, calculations show that both in the interface with the vacuum^[12], or with a dielectric film^[9], the electron density spill over is very small. However the change in the spill over with the electrode charge will give a direct contribution of the metal to the differential capacitance [1][4].

The metal electrons in the solution are subject to electrostatic interactions (electron-ion and electron-dipole) but also a repulsion due to the core electrons of ions and solvent molecules. These are represented by the Harrison repulsive potential [9].

There are several parameters in our model that are fixed a priori, but which should come out of a first principles calculation. One of these quantities is the distance of closest approach of the ions and solvent to the plane $z = 0$ (the metal surface). We will assume that it is just the sum of the molecular radius of the solvent or ions (which for this simple model are considered to be equal) and the radius of the metallic ion. In reality, this parameter should arise from a self-consistent density functional calculation [13].

In short, we will assume that there is an ideally smooth wall, located at $z = \delta$, which cannot be penetrated by either ions or solvent molecules. The distances of closest approach are

$$\begin{aligned} z_{\text{ion}} &= \delta + \sigma_i/2 && \text{for ions} \\ z_{\text{mol}} &= \delta + \sigma_d/2 && \text{for solvent molecules} \end{aligned}$$

There is also the problem of surface smoothness and structure. From recent experimental evidence, it is known that certain metal surfaces are subject to structural changes during chemisorption processes. In these cases the surface overlayer changes its structure. It is quite conceivable that in an intrinsically more labile environment such as that of liquid metals, the metal overlayer would also respond structurally to changes in potential.

Furthermore, the question of surface ripples (capillary waves) at the interface, and its effects on the structure and thermodynamics of the electrode is not discussed. We hope to address these and other questions in future work.

Summarizing, the ions and dipoles in the solution do not see simply a hard, charged surface, but rather the sum of a charged surface (located at $\delta + \sigma/2$) and a distribution of electron density beyond the plane of closest approach.

Even this simple model is not easily amenable to a complete numerical calculation. We will, therefore, in this first communication, use a simplified theory that has the advantage of giving explicit analytic expressions for the physically relevant quantities.

3. A SIMPLIFIED MODEL

For simplicity, we shall discuss only the restricted model in which $\sigma_i = \sigma_+ = \sigma_- = \sigma_d = \sigma$ (Although not in published form, the results for $\sigma_+ = \sigma_- \neq \sigma_d$ are also available). We neglect also the effects of the electron density on molecules and ions in the solution. We shall leave the discussion of the validity of this assumption for the future. The solution is represented by the MSA [5][6] which is only qualitatively correct. Near a charged interphase a simplified theory, valid presumably for dilute solutions, has been developed by Blum and Henderson [7]. In this theory, the dipolar interactions are decoupled from the ionic distributions, which are given by the modified Gouy-Chapman (MGC) theory. We are thus satisfying the electrostatic part of the contact density theorem. The simplified model of the interface is given on Fig. 1.

The charge density profile is given by

$$q_i(z) = -\kappa q_M e^{-\kappa(z-d_1)} \quad (1)$$

where κ is Debye's inverse length and

$$d_1 = \delta + \sigma/2$$

The total excess charge of the solution side is

$$q_s = \int_{d_1}^{\infty} dz q_i(z) = -q_M \quad (2)$$

The electronic density profile is postulated to be of the form [1][9] :

$$\begin{aligned} n(z) &= n \left[1 - \frac{1}{2} e^{\alpha(z-z_0)} \right] & z < z_0 \\ &= (n/2) e^{-\alpha(z-z_0)} & z > z_0 \end{aligned} \quad (3)$$

where n is the bulk metallic electron density. Clearly, the total excess charge on the metal side is

$$q_M = \int_{-\infty}^{\infty} dz [\rho\theta(-z) - n(z)] = -nz_0 \quad (4)$$

This last relation also defines z_0 .

For a given value of α , and q_M , the charge and polarization ($P(z)$) profiles are computed from the theory [7]. These in turn yield the potential $V(z)$ and electric field $E(z)$, which are obtained by solving Poisson's equation

$$\begin{aligned} \frac{\partial E(z)}{\partial z} &= -\frac{\partial^2 V(z)}{\partial z^2} = 4\pi [\rho\theta(-z) - n(z) \\ &+ \theta(z-d_1) \{ \kappa n z_0 e^{-\kappa(z-d_1)} - \frac{\partial P(z)}{\partial z} \}] \end{aligned} \quad (5)$$

The potential $V(z)$ is continuous in all space. Because of the discontinuities in the density profiles, $V(z)$ has a different form in the regions

- I) $-\infty < z \leq 0$
- II) $0 < z \leq d_1$
- III) $d_1 < z < \infty$

The solution of (5) is straightforward, and is explained in Appendix I. The total potential drop across the interface is

$$\Delta V = V(\infty) - V(-\infty) = \frac{4\pi n}{\alpha^2} \left[\alpha z_o (\alpha d_1 - \alpha z_o) + \frac{(\alpha z_o)^2}{2} - 1 \right] + \frac{4\pi n z_o}{\kappa} + 4\pi \int_{d_1}^{\infty} P(z) dz \quad (6)$$

The integral in this expression is explicitly known. The reader is referred to Ref. 7 (eq.15) for the derivation. The result is

$$4\pi \int_{d_1}^{\infty} dz P(z) = \lim_{s \rightarrow 0} \tilde{P}(s)$$

The Laplace transform $\tilde{P}(s)$ is

$$\begin{aligned} \tilde{P}(s) &= 4\pi \int_{d_1}^{\infty} dz e^{-sz} P(z) \\ &= \frac{4\pi \mu \rho_d}{\sqrt{3}} \left(\frac{\beta \mu 4\pi q_M}{\sqrt{3}} \right) \frac{1}{(\kappa + s) A(s)} \\ &\quad \times \frac{\beta_6^2}{\beta_3} \left\{ 1 - \frac{\kappa \sigma}{4} \frac{\beta_3}{\beta_{12}} \left[\frac{\beta_6^2}{\beta_3^2} + 2 \phi_1(s) \right] \right\} \end{aligned} \quad (7)$$

Here ρ_d is the bulk number density of solvent molecules. The coefficients β_3 , β_6 and β_{12} are functions of the bulk dielectric constant ϵ of the solvent, and are given through an auxiliary parameter λ

$$\beta_3 = \frac{3\lambda}{2 + \lambda} \quad ; \quad \beta_6 = \frac{3}{2 + \lambda} \quad ; \quad \beta_{12} = (3/2) \frac{1 + \lambda}{2 + \lambda} \quad (8)$$

The auxiliary parameter λ is computed from the equation

$$\epsilon = \frac{\lambda^2 (1 + \lambda)^4}{16} \quad (8')$$

The functions $\phi_1(s)$ and $A(s)$ are defined by

$$\phi_1(s) = 1/(s\sigma)^2 [1 - s\sigma - e^{-s\sigma}]$$

$$A(s) = 1 - 2\phi_1(s) (\lambda^2 - 1) - 4\phi_2(s) (\lambda^2 - \lambda)$$

with $\phi_2(s) = \frac{1}{s\sigma} [\phi_1(s) + \frac{1}{2}]$ (9)

Then

$$4\pi \int_{d_1}^{\infty} dz P(z) = \frac{-4\pi n z_0}{\kappa} \frac{\epsilon - 1}{\epsilon} \left[1 + \frac{\kappa\sigma}{2} \left(1 - \frac{1}{\lambda} \right) \right] \quad (10)$$

Substituting into equation (6) yields

$$\Delta V = -\frac{4\pi n}{\alpha^2} - 2\pi n z_0^2 + \frac{4\pi n z_0}{\kappa} \left\{ 1 + \kappa d_1 + \left(\frac{1 - \epsilon}{\epsilon} \right) \left[1 + \frac{\kappa\sigma}{2} \left(1 - \frac{1}{\lambda} \right) \right] \right\} \quad (11)$$

at the point of zero charge ($z_0 = 0$), this expression simplifies to

$$\Delta V = -\frac{4\pi n}{\alpha^2} \quad (12)$$

The potential drop across the interface is a function of only n and α , which are metal parameters. This however does not mean that the potential ΔV is equal to the surface potential of the metal-vacuum interface χ_m , since α is also a function of the solution parameters. In the limit $\alpha \rightarrow \infty$ the electronic profile tends to $n(z) = n \theta(z - z_0)$, and then Eq.(11) is not the same as the expression given in[14]. There are two reasons for this discrepancy. First, the term $2\pi n z_0^2$ does not exist in[14], because now the charge is not localized at the plane $z = 0$. Secondly, the third term in (11) is not that of[14]. However, if $d_1 = \sigma/2$ then they are identical. This means that an additional capacitance term appears because of the shift δ in the metal background profile.

The differential capacitance of the system is

$$\frac{1}{C} = \frac{\partial \Delta V}{\partial q_s} = -\frac{\partial \Delta V}{\partial q_M} = \frac{\partial \Delta V}{n \partial z_0} \quad (13)$$

using (11), we obtain

$$\begin{aligned} \frac{1}{C} = & \frac{4\pi}{\kappa\epsilon} \left[1 + \frac{\kappa\sigma}{2} \left(1 + \frac{\epsilon-1}{\lambda} \right) \right] + 4\pi[\delta - z_0] \\ & - 4\pi \frac{\partial}{\partial z_0} \left[1/\alpha^2 \right] + 4\pi z_0 \frac{\partial d_1}{\partial z_0} \end{aligned} \quad (14)$$

In this expression the first term of the right hand side is the result of the MSA [7][8]. If the solvent molecules are shrunk to point dipoles ($\sigma_d \rightarrow 0$), one should recover, from (14) the differential capacitance of the modified Gouy Chapman theory. Otherwise [14] one can define the effective dielectric constant.

$$\bar{\epsilon} = \frac{\epsilon}{1 + \frac{\epsilon-1}{\lambda}} \quad (15)$$

which then yields the MGC result with the effective dielectric constant $\bar{\epsilon}$. We must remark that in spite of the formal resemblance, the physics is different, since the solvent is polarized throughout the entire electric double layer.

The second term of (14) arises from the fact that the electrode charge is not localized at $z = 0$. The next term is due to changes in the dipolar surface layer of the metal as a function of the excess charge. And the last term reflects the fact that the distance d_1 is also a function of the excess charge. A detailed discussion of this fact can be found in [3]. At the point of zero charge this term vanishes.

Because of the intrinsic limitations of the MSA, we will limit ourselves to small surface charge densities around the point of zero charge.

Thus, for a given value of d_1 , we only need to compute α for the differential capacitance C .

4. ELECTRONIC DENSITY PROFILE

The ansatz (3) on the electronic density profile is particularly convenient since $n(z)$ only depends on the parameter α . We will compute this parameter by minimizing the surface excess energy U_s . The kinetic energy and the non-coulombic part of the electron - neutralizing background are not affected by the presence of the solution, and therefore we use the expressions given in Ref.[9] (Eq. 14 with $\alpha = \beta$).

$$U_{\text{Kin}} + U_{\text{exc}} + U_{\text{inh}} = \frac{n}{\alpha} [-1.6423 n^{2/3} + 0.25037 n^{1/3} + .006584] \quad (16)$$

$$+ \alpha n (\log 2) / 72$$

The pseudopotential contribution U_{ps} to the energy is given by (Eq. 10 of [1] with $\alpha = \beta$) :

$$U_{\text{ps}} = \frac{2\pi n^2}{\alpha^3} \left[e^{-\alpha|z_0|} - \frac{e^{-\alpha R_M}}{2} \left(A_0 R_M + \frac{A_0}{\alpha} + 1 \right) (e^{\alpha z_0} + e^{-\alpha z_0}) \right. \quad (17)$$

$$\left. + \alpha (|z_0| + A_0 z_0^2/2 - A_0 R_M^2/2 - R_M) \right] + \frac{A_0}{\alpha}$$

where A_0 and R_M are the pseudo potential parameters of Heine and Animalu (see also [1]).

The electrostatic energy is computed from the charge and polarization profiles, and the potential $V(z)$ which has been calculated in Appendix I. We find

$$U_{\text{es}} = \frac{\pi n^2}{2\alpha^3} \left[-8\alpha z_0 \theta(\alpha z_0) + 5 + 4\alpha z_0 e^{-\alpha(d_1 - z_0)} \right. \quad (18)$$

$$\left. - 4e^{-\alpha|z_0|} - \frac{2\alpha z_0 e^{-\alpha(d_1 - z_0)}}{1 + \kappa/\alpha} \right]$$

$$- \frac{2\pi n}{\alpha} \int_{d_1}^{\infty} dz P(z) e^{-\alpha(z - z_0)} + C_t$$

The last term C_t consists of the remaining contributions to the energy which are not functions of α , and thus irrelevant to our calculation.

The term before the last in (18) represents the interaction of the electrons with the local polarization of the solvent molecules in the solution. This contribution is easily calculated from the Laplace transform $\tilde{P}(s)$ (Eq. 7) :

$$- \frac{2\pi n}{\alpha} \int_{d_1}^{\infty} dz P(z) e^{-\alpha(z - z_0)} = - \frac{2\pi n}{\alpha} e^{\alpha z_0} \tilde{P}(\alpha) \quad (19)$$

There is also another contribution due to the repulsive interactions of the electrons and the electronic clouds of the ions and solvent molecules [9]. These interactions are represented by Harrison's pseudopotentials, with parameters λ_i (for ions), λ_d (for solvent). This interaction is independent from the ionic charge or solvent dipolar orientation, and because of the use of the MSA, it will depend only on the total density profile $\rho_o(z)$. Since all the particles are hard spheres of equal diameter, a single parameter $\bar{\lambda}$ (a weighted average of λ_i and λ_d) will be enough for our purposes. We get

$$U_B = \bar{\lambda} \int dr \int dz' n(z) \delta(r - r') \rho_o(z') \quad (20)$$

$$\bar{\lambda} = \frac{\lambda_d \rho_d + 2\lambda_i \rho_+}{\rho_d + 2\rho_+}$$

where ρ_d is the dipole concentration and ρ_+ is the (+) ion concentration. The integration is easily performed

$$U_B = \frac{\bar{\lambda} n}{2} \int_{d_1}^{\infty} dz e^{-\alpha(z-z_0)} \rho_o(z) \quad (21)$$

$$= \frac{\bar{\lambda} n}{2} e^{\alpha z_0} \tilde{\rho}_o(\alpha) \quad (21')$$

where $\tilde{\rho}_o(\alpha)$ is the Laplace transform of the total density distribution function ($\rho_o(z) = \rho_d(z) + \rho_+(z) + \rho_-(z)$). We get

$$U_B = \rho_o \frac{n\bar{\lambda}}{2} e^{-\alpha(d_1-z_0)} \frac{\beta_3^{(s)}}{\beta_6^{(s)}} \frac{1}{\alpha \tilde{Q}(i\alpha)} \quad (22)$$

$$\text{where } \beta_3^{(s)} = 1 + 2\eta \quad ; \quad \beta_6^{(s)} = 1 - \eta \quad ; \quad \beta_{12}^s = (1 + \eta/2)$$

$$\text{with } \eta = \frac{\pi}{6} (\rho_d + \rho_+ + \rho_-) \sigma^3$$

$$\text{and } \tilde{Q}(i\alpha) = 1 - 12 \phi_1(\alpha) \beta_{12}^{(s)} / (\beta_6^s)^2 - 12\eta \phi_2(\alpha) \beta_3^{(s)} / (\beta_6^s)^2$$

The functions $\phi_1(\alpha)$ and $\phi_2(\alpha)$ are defined by Eqs (9).

The total surface energy is then

$$U_s = U_{kin} + U_{exc} + U_{inh} + U_{ps} + U_{es} + U_B$$

Using Eqs (16-22) we get, finally

$$\begin{aligned} \frac{U_s}{\pi n^2} = & C_1/\alpha + C_2\alpha + \frac{1}{\alpha^3} \left[\frac{5}{2} - 2\alpha z_o - \left[1 + \frac{A_o}{\alpha} (1 + \alpha R_M) \right] e^{-\alpha R_M} (e^{\alpha z_o} + e^{-\alpha z_o}) \right. \\ & \left. - 2\alpha R_M + \frac{A_o}{\alpha} [2 + (\alpha z_o)^2 - (\alpha R_M)^2] \right] \\ & + e^{-\alpha(d_1 - z_o)} \left\{ \frac{E}{\alpha Q(i\alpha)} + \frac{\alpha z_o}{\alpha^3} \left[2 + \frac{\alpha}{\alpha + \kappa} \left[-1 + \frac{D}{A(\alpha)} \left[1 - \frac{\sigma}{1+1/\lambda} \left(\frac{1}{2\lambda^2} + \phi_1(\alpha) \right) \right] \right] \right] \right\} \end{aligned} \quad (23)$$

The coefficients C_1 , C_2 , E , D , are given in the Appendix 2.

In Equation (23), all the electrostatic interaction terms with the solution cancel at $z_o = 0$, the point of zero charge. The shift in the surface potential of the metal, when it is taken from the vacuum to the solution is due to the electron-solution repulsive interactions.

The minimization of U_s yields then α . This parameter is then used to compute the properties of the electrode with the aid of (11) and (19).

5. RESULTS

Clearly the MSA as a weak coupling parameter theory is not suited to describe the behaviour of hydrogen bonded solvents, such as water. However, an aprotic solvent like DMSO can be reasonably described by the MSA. Indeed, with the experimental values for the density ρ_d (14.05 M/dcm³ at room temperature) and the permanent dipole moment μ (~ 4 Debye), the MSA yields $\epsilon = 58$ instead of the experimental value 47.15 (see for instance [8] for the MSA expression of ϵ). From (8') this gives for λ respectively 2.49 and 2.39.

From (14) we see that the molecular contribution to the differential capacitance C depends only on ϵ , while from (23) α depends on λ (or ϵ), ρ_d and μ . We have checked that changing λ does not affect significantly the value of α which minimized U_s , and hence the metal contribution to the capacitance. Therefore we have used $\lambda = 2.39$ (i.e. $\epsilon = 47.15$) in the numerical computations.

We now choose the effective diameter of the DMSO molecule so that the parameter

$$\eta = \frac{\pi}{6} \rho_d \sigma^3 = 0.45$$

which is the value of the volume fraction characteristic of many liquids. This yields $\sigma = 8.81$ a.u. (4.66 Å), which is a little small, but not unreasonable for this molecule. The ionic diameters are taken also to be 8.81 a.u. Fig. 2 shows the corresponding MSA density profile for the molecules which have their dipole moment normal to the interface.

The electrode is liquid mercury, for which the parameters n , R_M and A_0 are taken from [9]. For the mercury-vacuum interface we found $\alpha_0 = 0.901$ u.a. and a surface potential $\chi_m = 5.34$ eV. Since we will also include some results for gallium, we refer the reader to our previous work [9].

Two of the parameters of the problem are free, and have to be selected using physical intuition. They are δ and $\bar{\lambda}$. It seems realistic

to choose the value of δ between 0 and R_c the crystallographic radius of the ions in the metal [9].

For water the parameter $\bar{\lambda}$ has been estimated to be ~ 15 . For DMSO we might expect an even higher value since there are 54 electrons in DMSO against 10 in water. In table I we show the influence of $\bar{\lambda}$ on α assuming that $d_1 = \sigma/2$ or $d_1 = R_c + \sigma/2$. As expected the repulsion term with the solution causes an increase in the values of α . This is similar to what we found previously [9]. In fig. (3) we have plotted the shift in the surface potential of the metal $\delta\chi_m = 4\pi n \left(\frac{1}{\alpha^2} - \frac{1}{\alpha_o^2} \right)$ calculated at the point of zero charge as a function of the distance d_1 . The corresponding case of gallium for $\bar{\lambda} = 30$ is also shown.

The repulsion from the solution is not enough to keep the electrons in the region $z < d_1$. There is always a small charge spillover, $-\delta q$, in the region $z > d_1$.

$$-\delta q = - \int_{d_1}^{\infty} dz \frac{n}{2} e^{-\alpha(z-z_o)} = - \frac{n}{2\alpha} e^{-\alpha(z-z_o)}$$

In fig. (4) we show $\delta q(d_1)$ for both Hg and Ga. The spillover δq is larger for Ga than for Hg.

In the simple model presented here, this effect has been neglected in calculating the charge distribution and the polarization in the solution. It is clear that this approximation is less justified for Ga than for Hg. However, the mathematical tools to include it are available and we will indeed discuss these effects in a near future.

The fact that there are electrons on the solution side even at the point of zero charge, indicates that the solvent molecules must be polarized at the interface even at the point of zero charge. Note that the ratio $\delta q(\text{Ga}) / \delta q(\text{Hg})$ is not simply the ratio of the electronic densities.

The differential capacitances for the mercury electrode are presented in table II. They were computed from the curve $\Delta V = f(q_M)$ by numerical

differentiation. With the parameters of this article the zero charge capacitance corresponding to an ideal metal would be

$$C_i = \frac{\kappa}{4\pi} \frac{\epsilon}{1 + \frac{\kappa\sigma}{2} \left(1 + \frac{\epsilon-1}{\lambda}\right)} = 7.94 \mu\text{F}/\text{cm}^2$$

We see that the total capacitance crucially depends on the distance d_1 .

When d_1 is large the value of C is greater than C_i but the effect of the non-ideality of the metal remains small. On the other hand, when the distance of closest approach decreases (for instance if there is interpenetration between the metallic ions and the particles of the solution) this effect becomes quite important and the influence of $\bar{\lambda}$ is not negligible (for comparison the experimental value is $18 \mu\text{F}/\text{cm}^2$ for LiClO_4 ions [15]).

First calculations show that the differential capacitance for Ga would be greater than for Hg, as observed experimentally.

6. CONCLUSIONS

We have presented a realistic model of the metal solution interface, in which the metal is not an ideal smooth metal, but a jellium model. A simple discussion of this model is given. The results confirm earlier calculations [1]-[4] that indicate that the metal makes an important contribution to the differential capacitance C .

The solution side of our model is a mixture of hard spheres with charges and point dipoles. No a priori separation of compact and diffuse layers is postulated in this model, and it also does not involve the use of local dielectric constants (a meaningless quantity). The calculations show that the solvent molecules are polarized even at the point of zero charge. This is so because of the spillover of electronic charge into the solution, which produces non zero electric fields in the metal-solution boundary layer. Although we have treated this effect only crudely, the recent work on the GMSA [16] of the ion dipole mixture allows a consistent calculation of this effect.

We show also that the distance d_1 of closest approach of the metal ions and the solution ions is a crucial parameter in the determination of the differential capacitance C . However this is also a drawback since the fact that d_1 is unknown makes the comparison of C with experiment a not very meaningful exercise. Indeed a value of d_1 which fits the experiments could be found.

However, the model that we have discussed here represents the most comprehensive one that we are aware of. We are undertaking a detailed study of the influence of various parameters, such as ionic concentration, density and dipole moment of the solvent, etc. on the differential capacitance. The results will be published in the near future.

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$\bar{\lambda}$	15	30	45
$d_1 = R_c + \sigma/2$	0.905	0.908	0.911
$d_1 = R_c$	0.916	0.932	0.947

Table I - Values of the profile parameter α (Hg) as a function of d_1 and $\bar{\lambda}$. For the bare surface $\alpha_0 = 0.901$ a.u.

$\frac{d_1}{\bar{\lambda}}$	$R_c + \frac{\sigma}{2}$	$\frac{\sigma}{2} + 1 \text{ \AA}$	$\frac{\sigma}{2}$
15	9	20.8	100
30	9	18.7	58.8
45	8.7	16.6	43.4

Table II - Differential capacitance of the interface ($\mu\text{F}/\text{cm}^2$) as a function of d_1 and $\bar{\lambda}$. The concentration is $c = 0.1 \text{ M/l}$.

FIGURE CAPTIONS

Fig. 1 : Simplified model of the interface.

δ position of the ideally smooth wall.

σ diameter of the ions and solvent molecules.

Fig. 2 : Jellium model and density profile of the dipoles normal to the interface.

Fig. 3 : Dependence of $\delta\chi_m$ on the parameter d_1 for different choices of $\bar{\lambda}$.

(1) Hg $\bar{\lambda} = 15$ (2) Hg $\bar{\lambda} = 30$

(3) Hg $\bar{\lambda} = 45$ (4) Ga $\bar{\lambda} = 30$.

Fig. 4 : Dependence of the charge spillover δq on the parameter d_1 for Hg and Ga.

($\bar{\lambda} = 30$ and $C = 0.1 \text{ M/l}$).

APPENDIX 1

Electrostatic Potential Profile

Integrating (5), we get, (using also (1) and (3))

a) For negative metal charge q_M ($z_0 > 0$)

$$V(z) = -\frac{2\pi n}{\alpha^2} e^{\alpha(z-z_0)} \quad (-\infty < z < 0)$$

$$V(z) = 2\pi n(z^2 - e^{+\alpha(z-z_0)} / \alpha^2) \quad (0 < z < z_0)$$

$$V(z) = 2\pi n[z_0(2z - z_0) - 2/\alpha^2 + e^{-\alpha(z-z_0)}/\alpha^2] \quad (z_0 < z < d_1)$$

$$V(z) = 2\pi n[z_0(2d_1 - z_0) - 2/\alpha^2 + e^{-\alpha(z-z_0)}/\alpha^2] + 4\pi n z_0 / \kappa \\ + 4\pi \int_{d_1}^z dz' P(z') - \frac{4\pi n z_0}{\kappa} e^{-\kappa(z-d_1)} \quad (z > d_1)$$

b) For positive q_M ($z_0 < 0$)

$$V(z) = -\frac{2\pi n}{\alpha^2} e^{\alpha(z-z_0)} \quad (-\infty < z < z_0)$$

$$V(z) = -2\pi n [(z - z_0)^2 + 2/\alpha^2 - e^{-\alpha(z-z_0)}/\alpha^2] \quad (z_0 < z < 0)$$

$$V(z) = 2\pi n [z_0(2z - z_0) - 2/\alpha^2 + e^{-\alpha(z-z_0)}/\alpha^2] \quad (0 < z < d_1)$$

For $d_1 < z < \infty$ the equations are those of the case $q_M < 0$.

APPENDIX 2

We give explicit formulas for the coefficients of Eq. 23

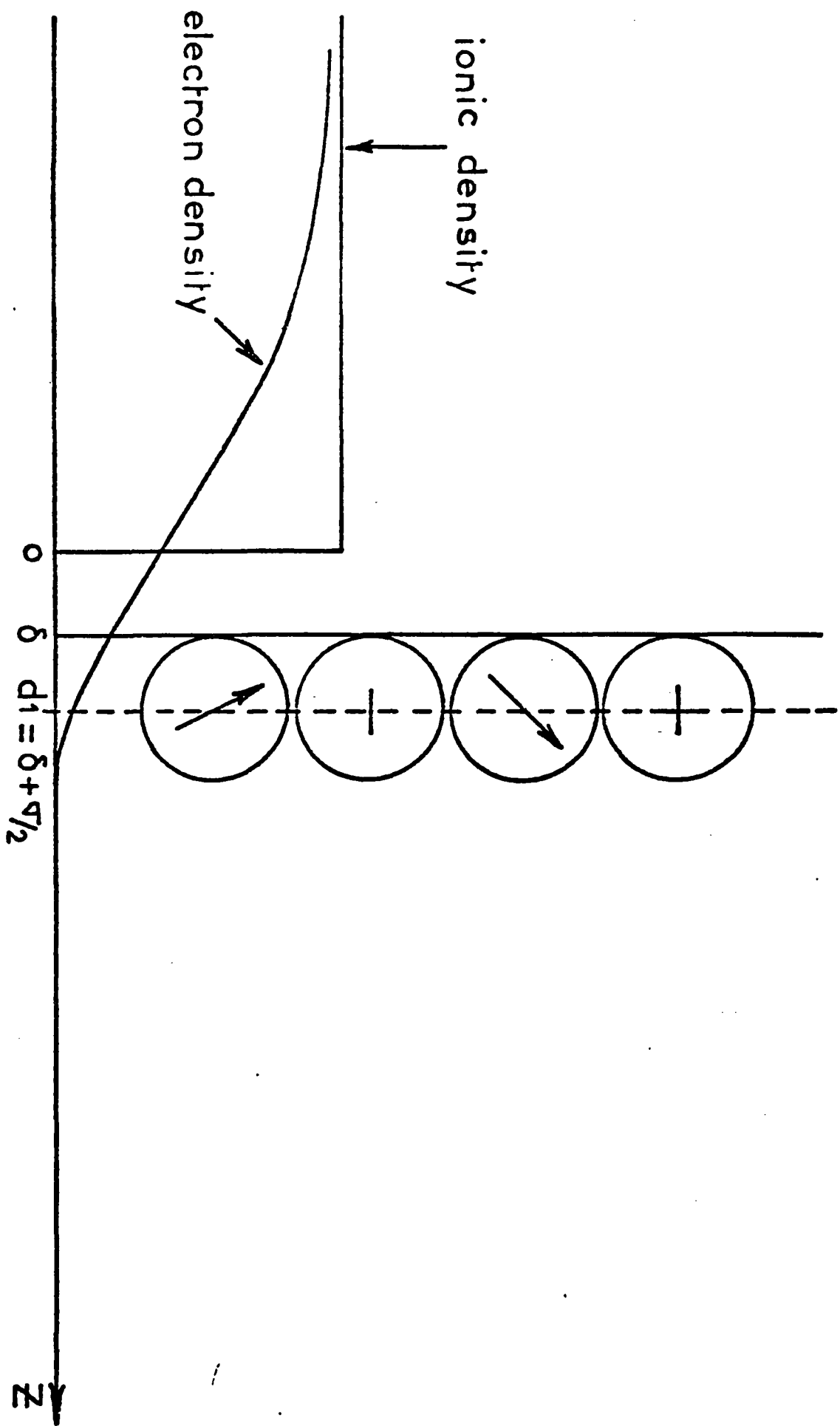
$$C_1 = \frac{1}{\pi n} [-1.6423 n^{2/3} + 0.25037 n^{1/3} + 0.006584]$$

$$C_2 = \frac{1}{\pi n} \frac{\log 2}{72}$$

$$E = \frac{\bar{\lambda}}{2\pi n} \rho_o \frac{(1 + 2\eta)}{(1 - \eta)^2}$$

$$D = \frac{8\pi \mu^2 \rho_d}{kT \lambda(2 + \lambda)}$$

These coefficients are computed once and for all for a given metal and solvent.



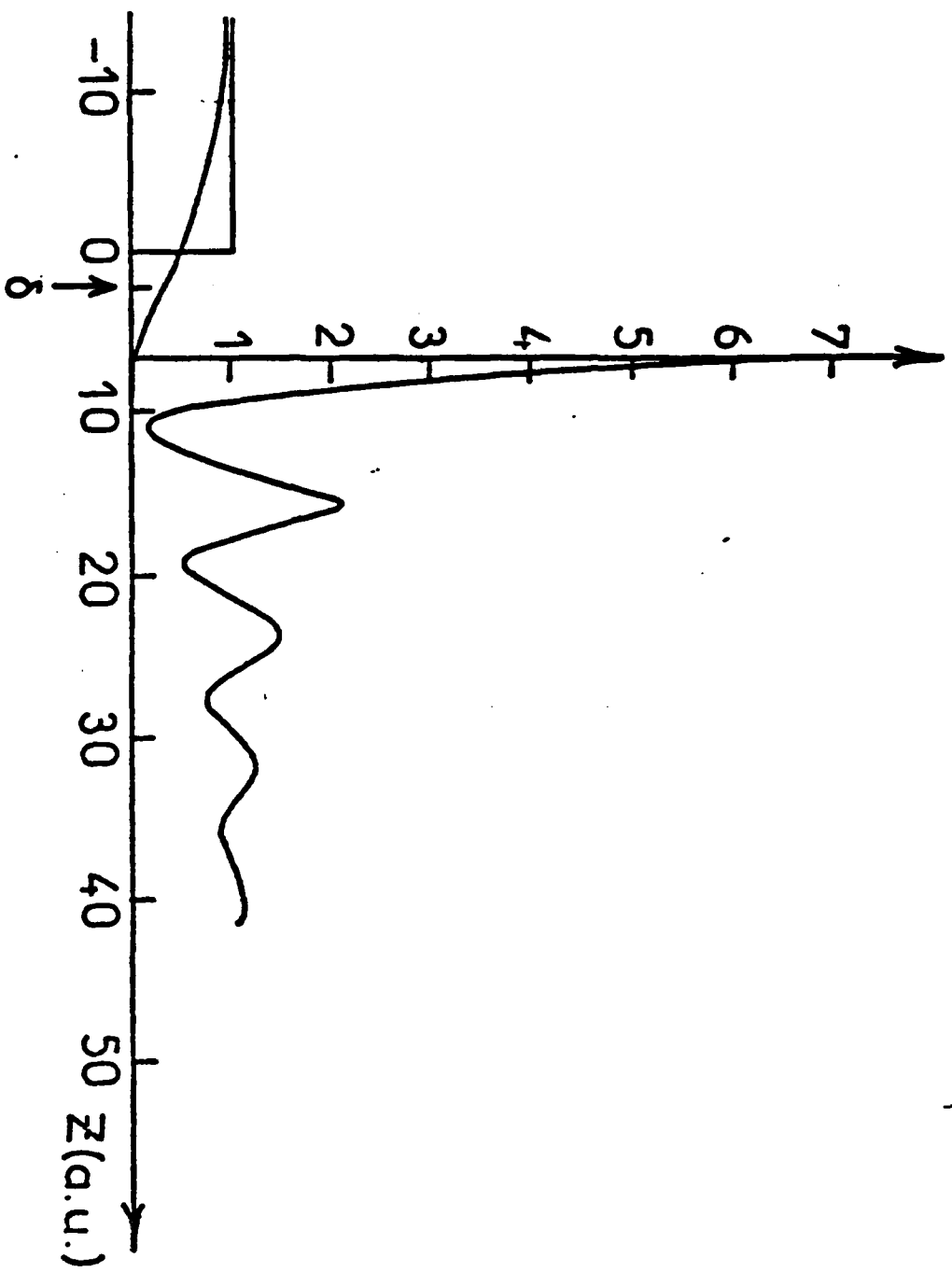
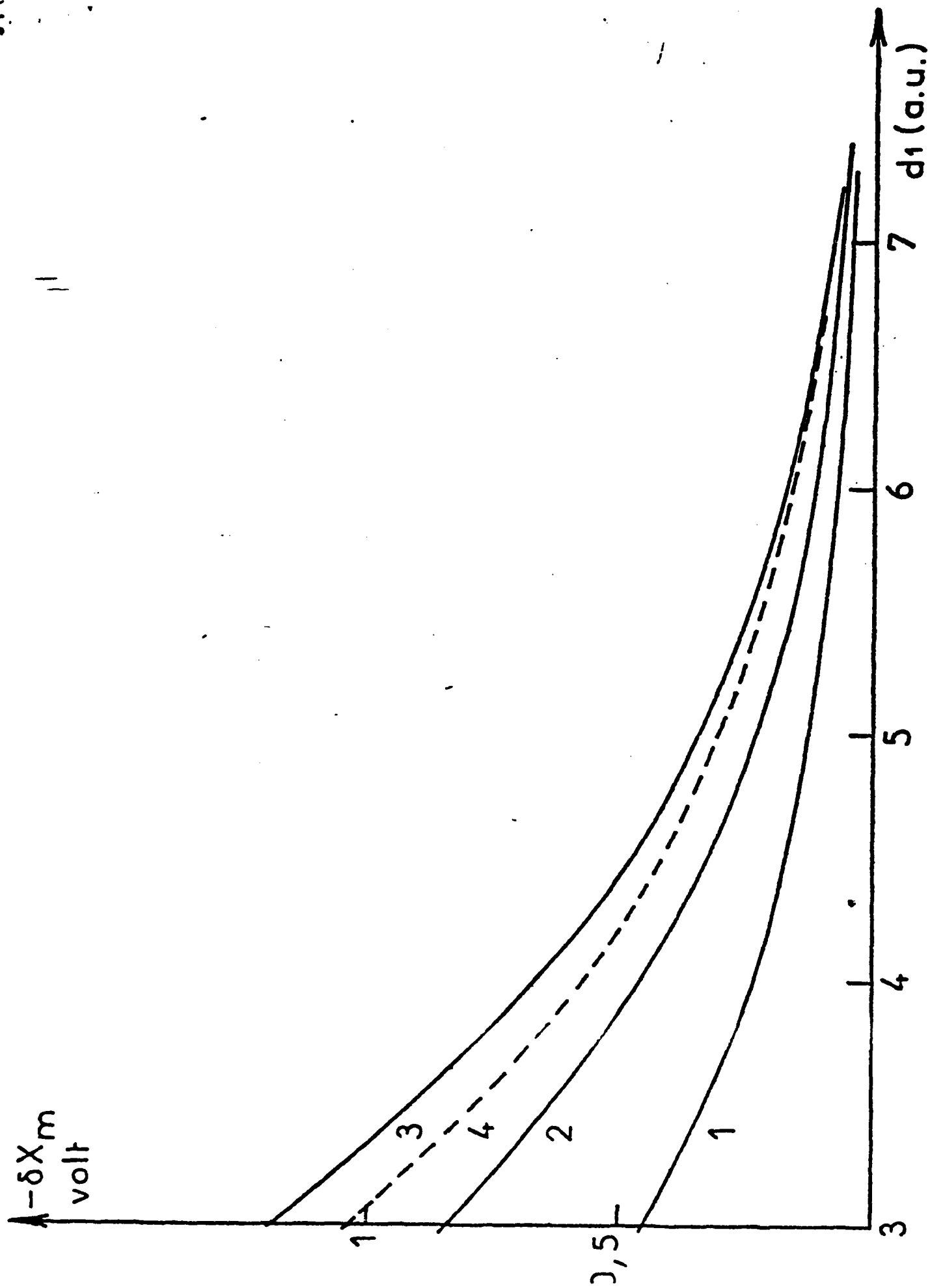
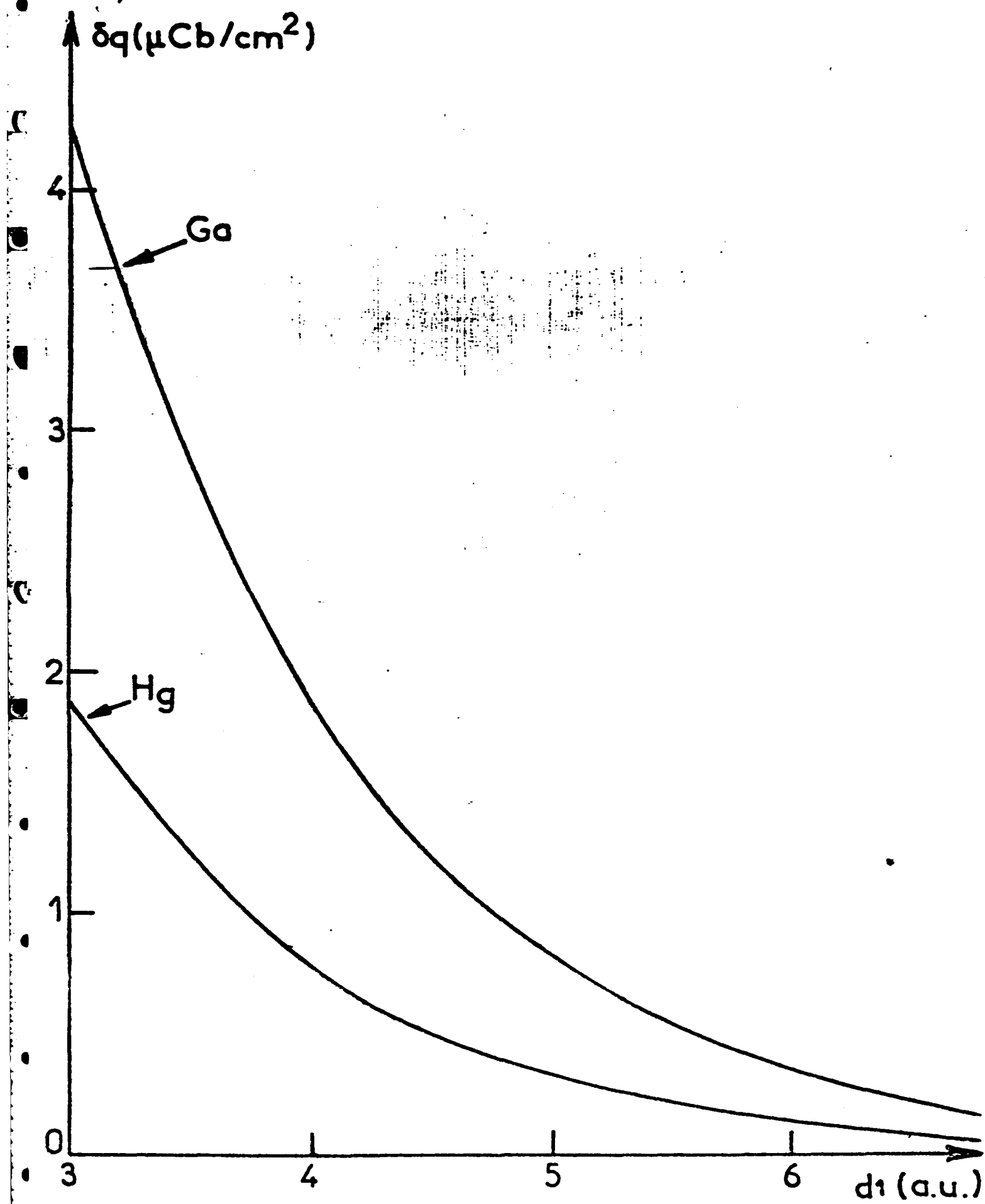


Fig 3





3-8

DT