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The Application of the Modified Gouy-Chapman Theory
to an Electrical Double Layer Containing Asymmetric Ions

by

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The modified Gouy-Chapman Theory is applied to 1:1, 2:1 and 1:2 electrolytes of unequal sizes near a flat electrode. This model features a potential of zero charge in the absence of specific adsorption.

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INTRODUCTION

The accumulation of ions near a charged electrode, resulting in a so-called electrical double layer, has been the subject of considerable recent interest. Both integral equation methods[1-5] and Monte Carlo simulations[6] have been applied to this problem.

The classical theory of the electric double layer is the Poisson-Boltzmann theory of Gouy[7] and Chapman[8] in which the solvent is assumed to be a uniform dielectric medium whose dielectric constant is ε.

In the Gouy-Chapman (GC) theory, the ion cores are neglected. It is a theory for point ions. However, if the ionic profiles are displaced by $\sigma/2$, where σ is the ionic diameter, so that the distance of closest approach is $\sigma/2$ rather than zero, the GC profiles for monovalent ions are reasonably good. We refer to this modification as the modified Gouy-Chapman (MGC) theory. In the MGC theory, the hard-core interactions among the ions are neglected, but the hard-core interaction of an ion with the electrode is not neglected. The MGC is less satisfactory for multivalent ions but is still of interest because it is a useful starting point for more accurate interactive procedures based on integral equations.

The GC theory was originally applied to symmetric ions.[7,8] The extension to 2-1 and 1-2 electrolytes was obtained by Grahame.[9] Recently, Valleau and Torrie[10] have applied the MGC theory ions which are symmetric in charge and asymmetric in diameter. In this note, we apply the MGC theory to ions which are asymmetric in both diameter and charge.

THEORY

The starting point of the GC is the one-dimensional Poison-Boltzmann equation

$$\frac{d^2\phi}{dx^2} = \frac{4\pi e}{e} \sum_{i=1}^{m} z_i\rho_i \exp\{\beta z_i e\phi(x)\} ,$$ (1)

where $\phi(x)$ is the mean electrostatic potential at a distance x from the electrode, e is the magnitude of the electronic charge, z_i and ρ_i are the valence (including the sign) and number density of ions of species i, $\beta=1/kT$, k is the Boltzmann constant, and T is the temperature. The parameter m is the number of species of ions in the region of space to which Eq. (1) is being applied. If m=0, the RHS of Eq. (1) is zero and Eq. (1) becomes Laplace's equation for charge free space.

Independently of the value of m≥1, Eq. (1) can be integrated to give

$$\frac{d\phi}{dx} = -\left[\frac{8\pi kT}{e} \sum_{i=1}^{m} \rho_i \exp\{\beta z_i e\phi(x)\} + A\right]^{1/2} ;$$ (2)

where A is a constant of integration.

To obtain $\phi(x)$, Eq. (2) must be integrated. This can always be done numerically. However, results in closed form have been obtained only for m=0, 1 and 2 with either all the z_i equal (symmetric charge) or with $z_1=1$ and $z_2=2$, or equivalently, $z_1=2$ and $z_2=1$. Therefore, we restrict ourselves to n-n, 1-2 and 2-1 binary solutions.

The geometry of a general binary system is shown in Fig. 1. There are three regions to consider: $0\leq x\leq\sigma_1/2$, $\sigma_1/2\leq x\leq\sigma_2/2$ and $x=\sigma_2/2$, where $\sigma_1<\sigma_2$ and σ_2 are the diameters of the two species of ions. In these three regions, there are, respectively, no ions present, only ions of one species, or both species of ions.

In the first region ($m=0$), $0 \leq x \leq \sigma_1/2$ and integrating Eq. (2) we get

$$\phi(x) = \phi(0) + x\phi'(0) . \tag{3}$$

where $\phi'(0)$ is the derivative of $\phi(x)$ at the electrode. In the second region ($m=1$), $\sigma_1/2 \leq x \leq \sigma_2/2$,

$$\frac{d\phi}{dx} = -\left[y_1^2 \exp\{\beta z_1 e\phi(x)\} + A\right]^{1/2} , \tag{4}$$

where $y_1^2 = 8\pi k T \rho_1/\varepsilon$. Integrating gives

$$\beta z_1 e\phi(x) = \begin{cases} \ell n\left\{\dfrac{A}{y_1^2}\left[\left(\dfrac{1+B \exp\{-\beta z_1 e\phi(x)\}}{1-B \exp\{-\beta z_1 e\phi(x)\}}\right)^2 - 1\right]\right\} , & A>0 \\[3ex] \ell n\left\{-\dfrac{A}{y_1^2}\left[1+ \tan^2(B-x\beta z_1 e\sqrt{-A}/2)\right]\right\} , & A<0 , \end{cases} \tag{5}$$

where B is a constant of integration.

The solution for $\phi(x)$ in the third region ($m=2$), $x>\sigma_2/2$, is well known. For symmetric charge, $|z_i|=z$, the result is[7,8]

$$\tanh\left[\frac{\beta z e\phi(x)}{4}\right] = \tanh\left[\frac{\beta z e\phi(\sigma_2/2)}{4}\right] e^{-\kappa x} \tag{6}$$

For the unsymmetric 2-1 and 1-2 case, the result is[9]

$$\exp[\beta e\phi(x)] = \begin{cases} \dfrac{3}{2}\left[\dfrac{1+Ce^{-\kappa y}}{1-Ce^{-\kappa y}}\right]^2 - \dfrac{1}{2} & \text{(7a)} \\[3ex] -\dfrac{3}{2}\left[\dfrac{1+Ce^{-\kappa y}}{1-Ce^{-\kappa y}}\right]^2 + \dfrac{1}{2} , & \text{(7b)} \end{cases}$$

4

where

$$c = \frac{x_0 - \sqrt{3}}{x_0 + \sqrt{3}} \tag{8}$$

with

$$x_0 = \begin{cases} \{2 \ \exp \ [\beta e \phi(\sigma_2/2)] + 1\}^{1/2} & \text{(9a)} \\ \\ \{2 \ \exp \ [-\beta e \phi(\sigma_2/2)] + 1\}^{1/2} & \text{(9b)} \end{cases}$$

In Eqs. (6) and (7), $y = x - \sigma_2/2$, and

$$\kappa^2 = \frac{4\pi\beta e^2}{\varepsilon} \sum_{i=1}^{2} z_i^2 \rho_i \ . \tag{10}$$

In obtaining Eqs. (6) and (7), we have employed the condition $\phi(x)$, $\phi'(x) \to 0$ as $x \to \infty$. Equations (7a) and (9a) apply to the case where the electrode has a positive charge and Eqs. (7b) and (9b) apply to the case where the electrode has a negative charge.

The constants of integration are determined by requiring that $\phi(x)$ and $\phi'(x)$ be continuous at $x = \sigma_1/2$ and $\sigma_1/2$ and $\phi(0)$ be equal to the applied potential. In principle, analytical expressions could be developed for these constants of integration. However, in practice, we found it convenient to satisfy the boundary conditions by an iterative procedure.

RESULTS

The potential drop across the double layer (measured from $x=0$) is plotted in Figs. 2-5 as a function of the charge density on the electrode. As would be expected at large charge densities, the potential drop is largely determined by the counterions since the co-ions are excluded from the vicinity of the electrode. Consequently, the results for

positive charge densities are insensitive to the value of σ_1/σ_2 since, for positive charge densities, the counterion always has the diameter $\sigma_2 = 4.25\text{Å}$.

For negative charge densities on the electrode, there is a wider variation in the potential since the counterions now have a variable diameter $\sigma_1 < \sigma_2$. At large negative charge densities, the potential, as expected, approaches that of a symmetric electrolyte of the same charge and diameter as the counterion.

At small charge densities on the electrode, the smaller ions can approach the wall more closely. This results in a separation of charge for ions of unequal diameter even at zero charge on the electrode and a resulting nonzero potential difference across the double layer. This has already been noted by Valleau and Torrie[10] for ions which have a symmetric charge.

The charge profile and concentration profiles for a 0.5M solution with $\sigma_1/\sigma_2 = 0.1$ are plotted in Figs. 6 and 7 for the case where the potential drop across the double layer is zero. The potential profile is not monotonic, as is the case when $\sigma_1 = \sigma_2$ or when the potential drop is appreciably different from zero. The concentrations profile of the smaller ions is also nonmonotonic at $V = 0$.

As is seen from Figs. 8 and 9, even for the relatively small potential, $|V| = 0.026$ volts, the concentration profiles are rather similar to those for the equal diameter case. At large potential drops, the concentration profiles near the electrode will approach those of the symmetric electrolyte whose charge and diameter are equal to those of the counterions.

CONCLUSIONS

The MGC theory has been applied to electrolyte which are asymmetric in charge and size. Within the MGC theory, the most interesting results are obtained in the region of very small potential drop and very small charge density on the electrode because at large potentials or charge densities, the co-ions are excluded from the vicinity of the electrode. Consequently, the counterions dominate and the double layer properties approach these of a symmetric electrolyte whose charge and diameter are equal to those of the counterion.

If the ions differ in size, then the smaller ions can penetrate closer to the electrode than the larger ions. At large charge densities, this effect would be negligible compared to the coulombic effects. However, this effect is significant at small charge densities. In particular, charge separation and a nonzero potential can occur even when there is not charge on the electrode.

It is conventional to interpret experimental results in terms of the GC theory in which ion diameters do not appear. As a result, noncoulombic effects such as specific adsorption, are required to explain such phenomena as a nonzero potential at zero charge on the electrode. It is not necessary to invoke such effects since unequal ion sizes can also give rise to such phenomena. This is not to say that specific adsorption is not an important phenomena in double layer studies. However, estimates of the importance of specific adsorption obtained by subtracting equal diameter Gouy-Chapman results from experimental studies may well be misleading. if there are sizeable differences in ionic radii

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FIGURE CAPTIONS

Figure 1. Double layer geometry.

Figure 2. Potential drop across a double layer as a function of the charge density on the electrode for the case where $z_1=1$, $z_2=-1$, $\varepsilon=78.5$, T=298K, $\sigma_2=4.25$Å and $\sigma_1/\sigma \dashv 1$, 0.5 and 0.1. The solid and broken curves give the MGC results for concentrations of $\quad$ M and 0.05M, respectively.

Figure 3. Potential drop across a double layer as a function of the charge density on the electrode for the case where $z_1=1$ and $z_2=-2$. The other parameters have the same values as in Fig. 2 and the curves have the same meaning as in this figure.

Figure 4. Potential drop across a double layer as a function of the charge density on the electrode for the case where $z_1=2$ and $z_2=-1$. The other parameters have the same values as in Fig. 2 and the curves have the same meaning as in this figure.

Figure 5. Potential drop across a double layer as a function of the charge density on the electrode for the case where $z_1=2$ and $z_2=-2$. The other parameters have the same values as in Fig. 2 and the curves have the same meaning as in this figure.

Figure 6. Potential profiles for the case where V=0 and where $\sigma_2/\sigma_2=0.1$ and $z_1=2$, $z_2=-1$ and $z_1=1$, $z_2=-2$. The concentration is 0.5M. The other parameters have the same values as in Fig. 2.

Figure 7. Concentration profiles for the case where $V=0$ and where $\sigma_1/\sigma_2 = 0.1$ and $z_1 = 2$, $z_2 = -0.1$ and $z_1 = 1$, $z_2 = -2$. The concentration is 0.5M. The other parameters have the same values as in Fig. 2.

Figure 8. Concentration profiles for the case where $V=0.026$ volts and where $\sigma_1/\sigma_2 = 0.1$ and $z_1 = 2$, $z_2 = -1$ and $z_1 = 1$, $z_2 = -2$. The concentration is 0.05M. The other parameters have the same values as in Fig. 2.

Figure 9. Concentration profiles for the case where $V=-0.026$ volts and where $\sigma_1/\sigma_2 = 0.5$ and $z_1 = 1$, $z_2 = -2$ and $z_1 = 2$, $z_2 = -1$. The concentration is 0.5M. The other parameters have the same values as in Fig. 2.
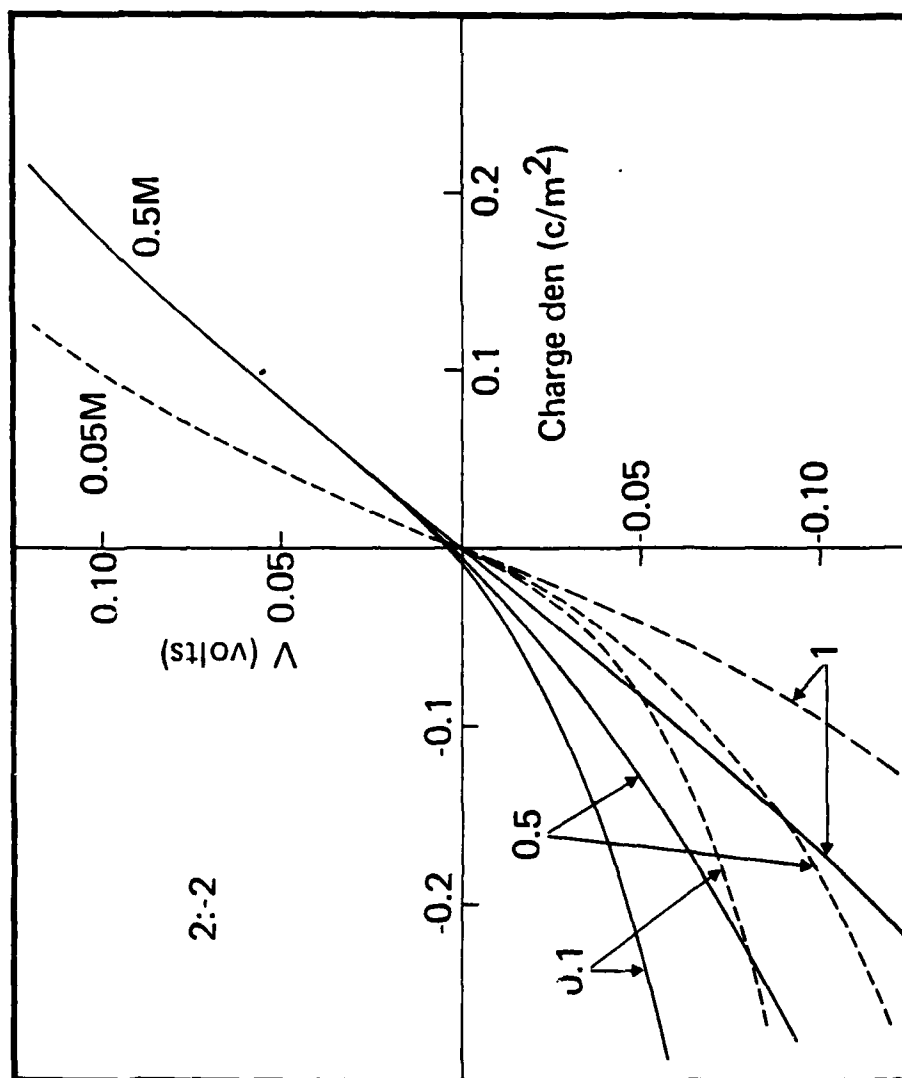
$\sigma_1/2$ $\sigma_2/2$

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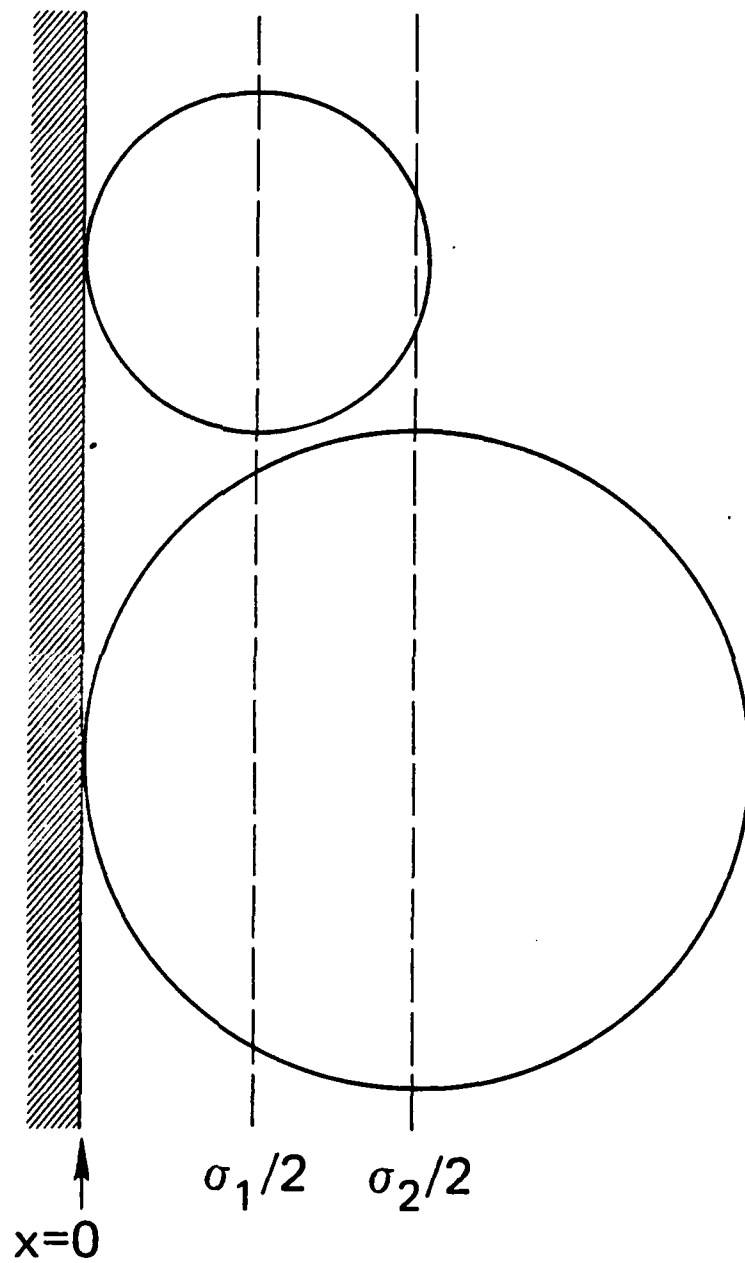
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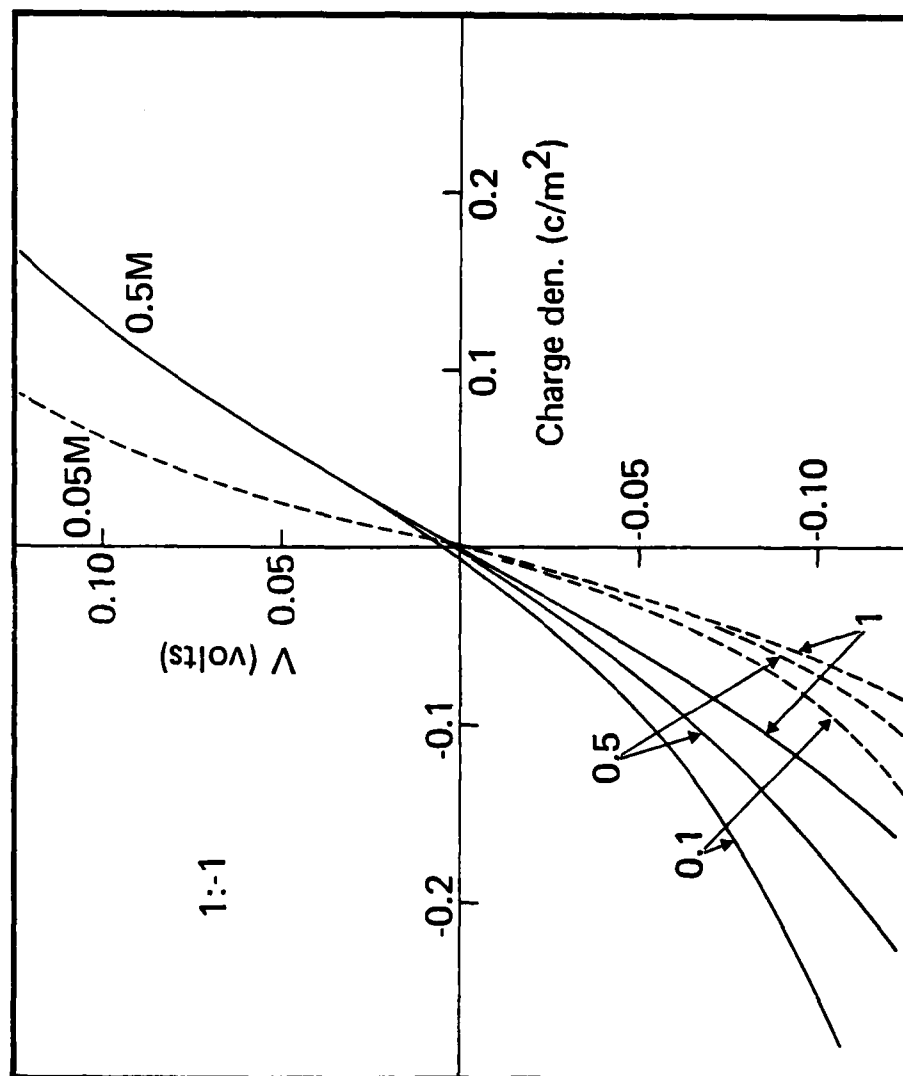
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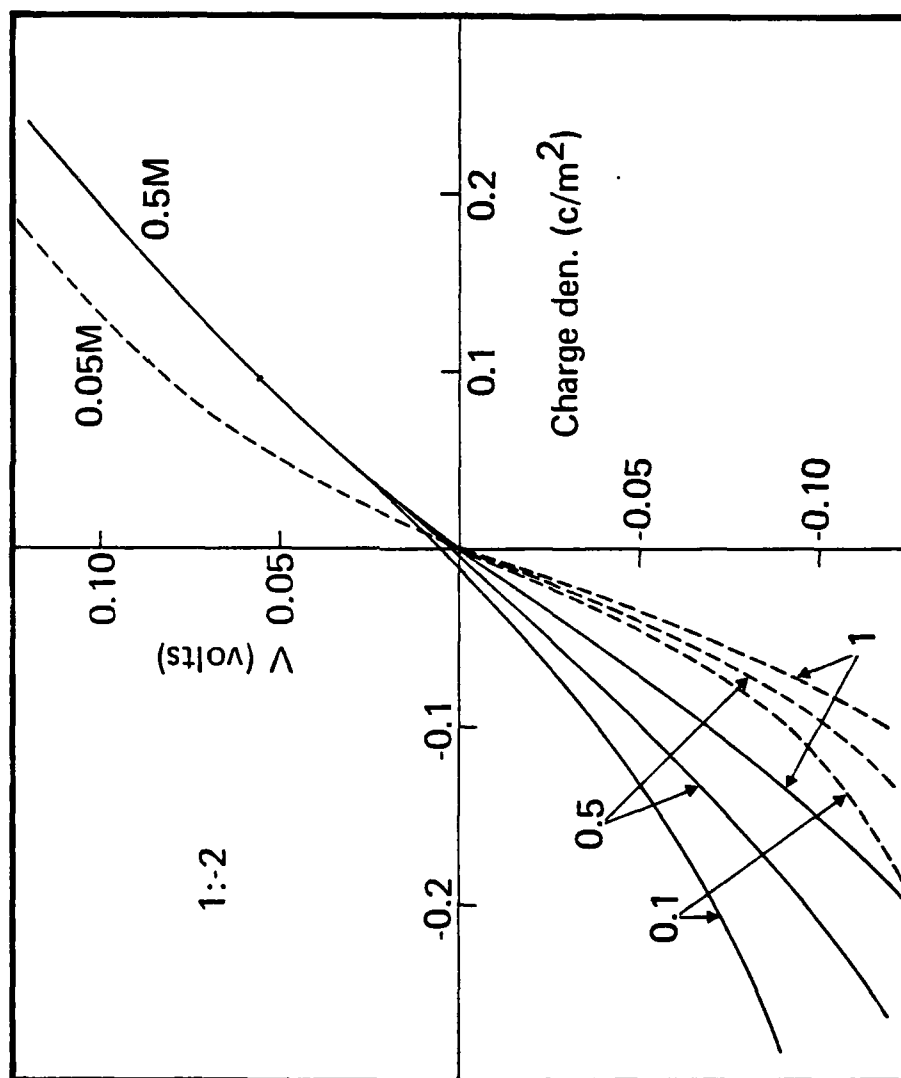
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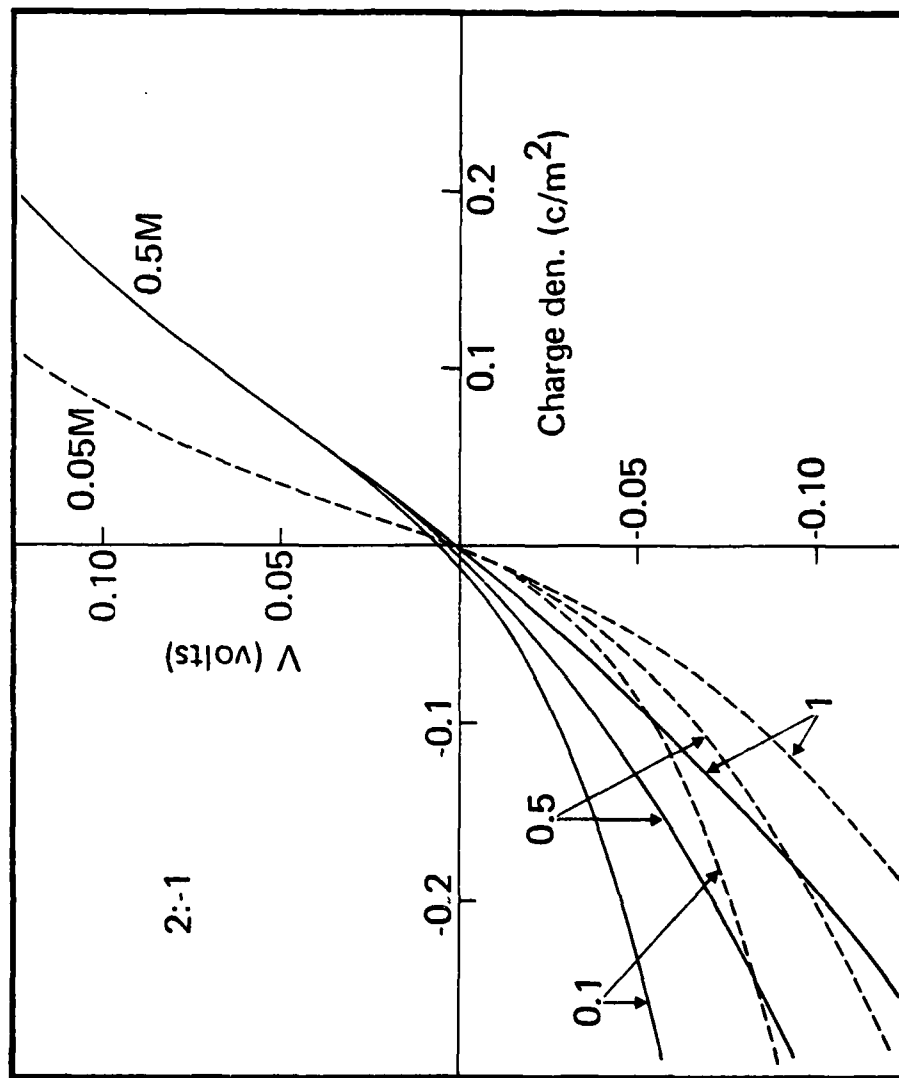
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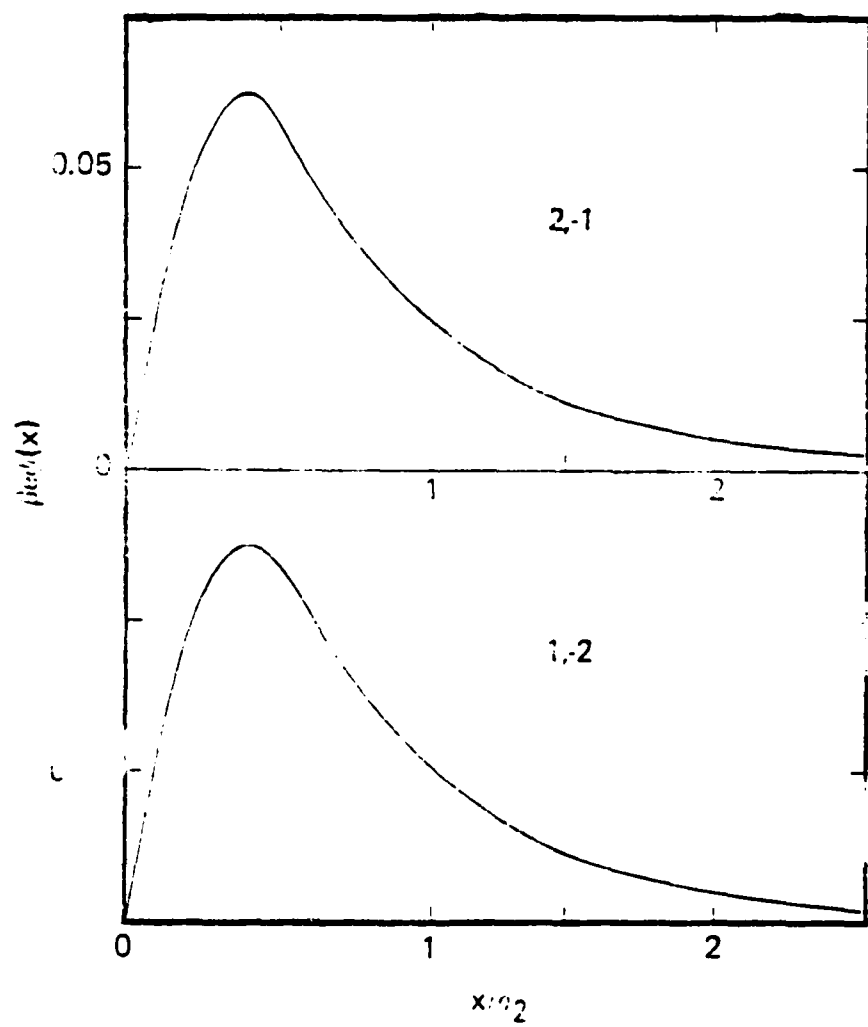
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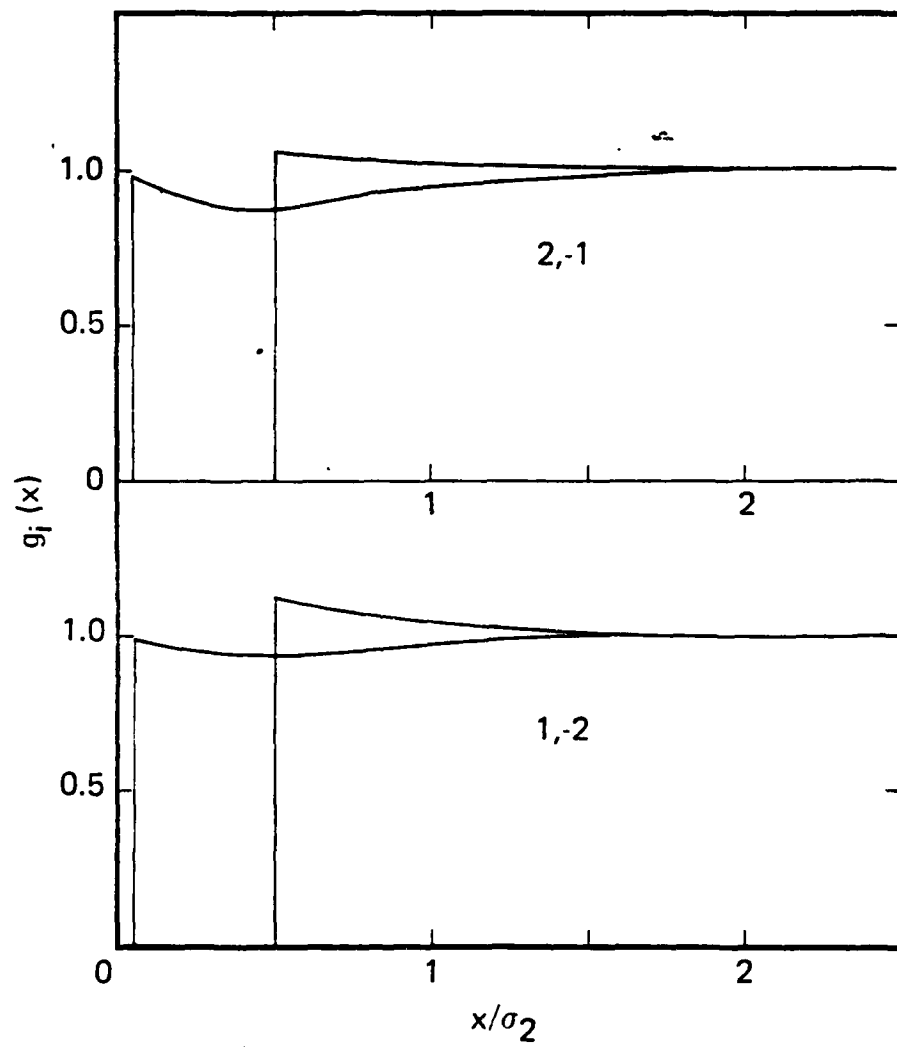
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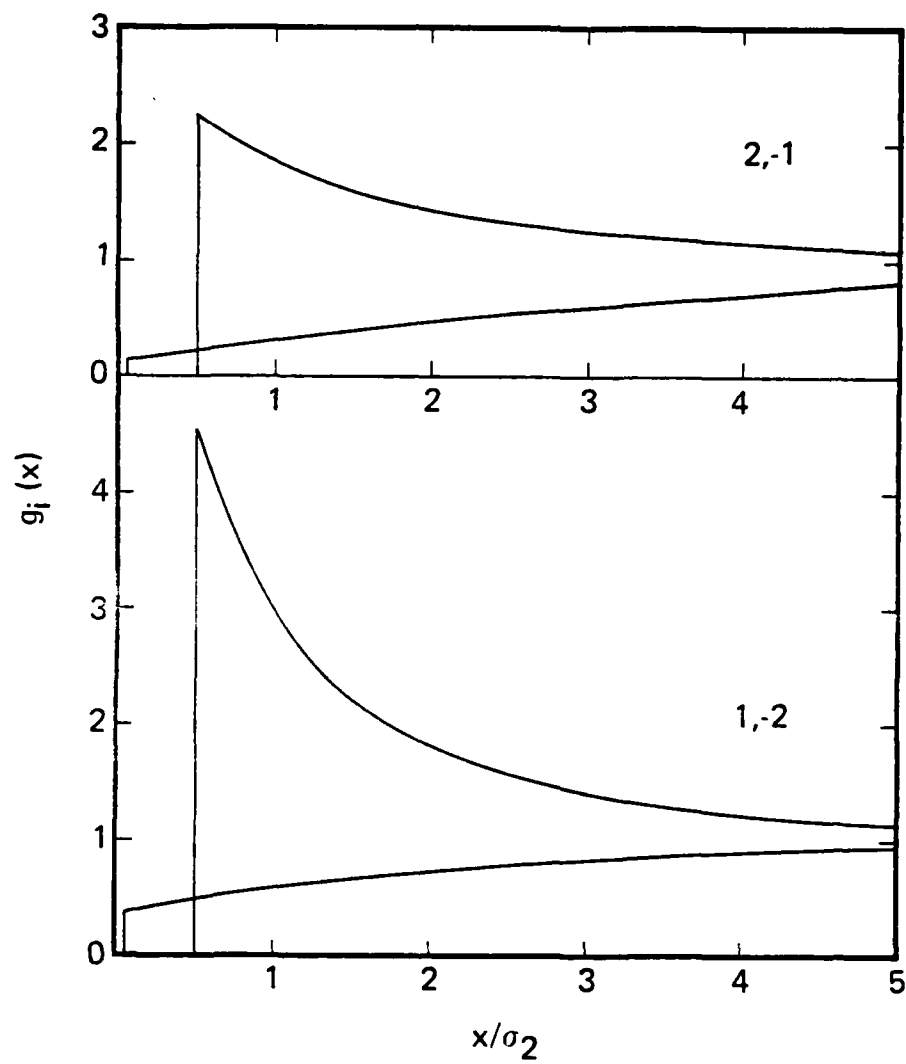
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