# FINITE LENGTH EFFECTS IN A LATTICE GAS TREATMENT OF AN IONIC CRYSTAL HAVING FRENKEL OR SCHOTTKY DISORDER

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A continuum lattice gas model is applied to a finite slab of monovalent ionic crystal exhibiting either Schottky or Frenkel disorder. Under the condition of a completely blocking electrode attached at one end and an ohmic electrode at the other, expressions are derived for the diffuse layer differential capacitance. Results are presented both for arbitrary fractional bulk defect concentration and diffuse-layer surface potential; our results agree with earlier work in the limits of low concentrations and low potentials. For sufficiently thin crystals the expected geometric capacitance is recovered, while at large crystal lengths the deviation of the differential capacitance from its semi-infinite approximation becomes exponentially small. For surface potentials at least 2.89 times larger than the thermal voltage conventional Gouy-Chapman theory predicts a crystal length at which the differential capacitance goes through a minimum before exhibiting the behavior of the geometric capacitance. Analytic tion and increasing surface potential, the effect of finite ion size embodied in the lattice gas statistics eliminates the length-dependent minima and increases the crystal length necessary for the semi-infinite results to be valid.

## I. INTRODUCTION

In an earlier paper<sup>1</sup> the equilibrium space charge and differential capacitance associated with semiinfinite monovalent ionic crystals exhibiting Schottky or Frenkel disorder were analyzed. The purpose of the present work is to generalize this continuum lattice gas treatment to crystals of finite length with a blocking electrode at the left and an ohmic electrode at the right. In particular, the behavior of the diffuse double layer differential capacitance as a function of crystal length, applied potential, and bulk defect concentration is investigated.

The introduction of non-interacting lattice gas statistics reflects some of the consequences of finite ion size, yet it maintains most of the conceptual and mathematical simplicity of the conventional Gouy–Chapman Theory.<sup>2,3</sup> An immediate consequence of the lattice gas model is a maximum allowed defect concentration. Such a limitation, while only relevant in the bulk for a system with a large defect concentration, becomes very important for large applied potentials in the vicinity of the blocking electrode, where a region of constant charge density develops when defects of both sign are mobile. This region causes a drastic reduction in the diffuse differential capacitance when compared to the corresponding Gouy-Chapman expression.

Recent work by Georgiev, Martinov, and Ouroushev<sup>4,5,6</sup> is closely related to this study since it attempts to construct space charge waves from the Gouy-Chapman solutions applied to finite-length boundary conditions. Unfortunately, as we mention in Section II and demonstrate in Appendix A, their analysis contains several errors which invalidate most if not all of their conclusions.

The effects of finite crystal length for the electrode conditions considered here have, to our knowledge, never been extensively studied, even for the Gouy-Chapman case. Hence, this work establishes the results appropriate both for low defect concentrations as well as the regime where lattice gas statistics dominate. From this analysis one obtains a quantitative estimate of the accuracy of approximating the differential capacitance of a finite crystal with the intrinsic (length independent) result appropriate for a semiinfinite system.

It should, however, be pointed out that the present work is still a continuum approach, which requires that many crystal lattice planes be contained within a Debye length of the material. In addition, recent calculations,<sup>7</sup> using a heuristic Frumkin-like<sup>8</sup> correction to model the detailed microscopic interactions between the charged defects, indicate that deviations from simple lattice gas results can be expected.

To place this analysis in perspective and connect it to earlier research, a conscious effort is made to reduce results to both the limits of low defect concentration and low surface potential. Thus, the domains of validity of the standard treatments become more apparent.

The contents of this paper are divided into the following four sections. In Section II the model is set up and the basic definitions are introduced. Section III contains the relevant electrostatics, asymptotic expressions for the charge on the ohmic electrode as a function of crystal length, and a derivation of the equations of the diffuse differential capacitance. A detailed treatment of the differential capacitance for infinite length systems is presented in Section IV. While this was the focus of much of the earlier work, it is repeated here for completeness and to make the finite length results comprehensible. In addition, several new analytic approximations are introduced which yield a simple characterization of the curves of differential capacitance vs potential as the fractional bulk defect concentration varies from 0 to 1.

The actual finite-length crystal analysis is done in Section V. There it is shown that for small lengths one recovers the geometric capacitance, while for large lengths the deviation of the differential capacitance from its semi-infinite value becomes exponentially small. For the Gouy-Chapman limit one has for large enough potentials that the differential capacitance goes through a minimum when considered as a function of crystal length. Numerical results are presented which seem to indicate that such minima might be measured for an AgCl single crystal at various temperatures. Finally, the effects of lattice gas statistics on both these minima and the approach to semi-infinite behavior are analyzed.

### **II DESCRIPTION OF THE MODEL**

For the purposes of this paper the crystal is assumed to be a laterally infinite slab of continuous material starting at position x = 0 and ending at x = l. In addition the system is imagined to be connected to a blocking electrode at the left of zero. An ohmic electrode is attached at x = l and is joined via an external emf to the blocking electrode. The electrostatic potential is designated by  $\psi(x)$  with  $\psi(0) \equiv \psi_d$ . Let  $\sigma_0$  be the total charge per unit area for x < 0 and  $\sigma_l$  the surface charge density of the ohmic electrode. Charge conservation then demands that

$$\sigma_0 + \sigma_d + \sigma_l = 0, \tag{1}$$

where  $\sigma_d$  is the net charge per unit area in the region 0 < x < l.

The condition and properties of the blocking electrode-material interface and any associated surface charge density are not considered in this paper; thus only diffuse layer effects are dealt with. For Frenkel systems, a model involving surface kink sites was developed in our earlier paper.<sup>1</sup> There it was shown that one could characterize the total differential capacitance by an equivalent circuit involving separate contributions of surface and diffuse charge distributions. In this work only the latter is treated.

Let N denote the concentration of anion (or cation) sites and  $c_0$  the common bulk concentration of positive and negative space charge. For Schottky systems these  $c_0$  charge concentrations are associated with negative and positive ion vacancies, respectively. For Frenkel disorder the positive charge density is due to cation interstitials, while the negative charge density is produced by the resulting cation vacancies. In order to condense the formalism the convention is adopted that the negative and positive defect concentrations are designated by  $c_1(x)$  and  $c_2(x)$ , respectively. The presence of the ohmic electrode requires that

$$c_i(l) = c_0, \quad i = 1, 2.$$
 (2)

Since we assume two interstitials per cation site, structure factors  $s_i$  are defined with  $s_1 = 1$  always, and  $s_2 = 1$  for Schottky disorder and  $s_2 = 2$  for Frenkel disorder.

An important parameter in characterizing the system is the fractional bulk defect concentration given by

$$\delta \equiv c_0/N. \tag{3}$$

An appropriate free energy minimization employing lattice gas statistics and coarse-grained potential interactions leads<sup>1,9</sup> to the following

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normalized charge distributions:

$$C_{i}(X) \equiv \frac{c_{i}(x)}{Ns_{i}}$$
$$= \left\{ 1 + \left(\frac{s_{i}}{\delta} - 1\right) \exp\left[(-1)^{i}\phi(X)\right] \right\}^{-1}.$$
(4)

Here  $\phi(X)$  is the normalized electrostatic potential,

$$\phi(X) \equiv \frac{\psi(x)e}{kT} \tag{5}$$

with e being the unit of positive electric charge, k the Boltzmann constant, and T the absolute temperature. The normalized position variable X is measured in units of Debye length,

$$X \equiv x/L_D, \qquad (6)$$

where for bulk dielectric constant  $\varepsilon_{\rm B}$ ,

$$L_{\rm D} = [\varepsilon_{\rm B} kT/8\pi e^2 N\delta]^{1/2}.$$
 (7)

The crystal slab is then contained in the region  $0 \le X \le L$ , with

$$L \equiv l/L_D. \tag{8}$$

The continuum approach inherent in the derivation of Eq. (4) is valid only if  $L_D$  is much larger than the crystal lattice spacing.

### III FIELD EQUATIONS AND DIFFERENTIAL CAPACITANCE

The Eq. (4) distributions give the potential dependence of the space charge concentrations. To obtain spatial dependence one must use Poisson's equation, which in the bulk material has the form,

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi e}{\varepsilon_B} [c_2(x) - c_1(x)]. \tag{9}$$

The appropriate boundary conditions found by a simple application of Gauss's law are

$$\left. \begin{cases} \frac{\varepsilon_{\rm B}}{4\pi} \, \psi'(0) = -\sigma_0 \\ \frac{\varepsilon_{\rm B}}{4\pi} \, \psi'(l) = \sigma_l \end{cases} \right\}, \tag{10}$$

where the prime denotes differentiation with respect to x. However, in addition one already has

the relations

$$\begin{cases} \boldsymbol{\psi}(0) = \boldsymbol{\psi}_d \\ \boldsymbol{\psi}(l) = 0 \end{cases} .$$
 (11)

Since only two of these four boundary conditions can be arbitrarily specified, one concludes that of the four physical variables  $\psi_d$ ,  $\sigma_0$ ,  $\sigma_l$ , and l only two are independent. By definition one has

$$\sigma_d = e \int_0^t [c_2(x) - c_1(x)] \, dx, \qquad (12)$$

and it is of course true that from (9) and (10) Eq. (1) follows immediately and does not constitute an additional constraint.

In normalized form Eqs. (9) through (11) can be written as

$$\frac{d^2\phi}{dX^2} = -\frac{1}{2\delta} [s_2 C_2(X) - s_1 C_1(X)]$$
(13)

$$\frac{d\phi}{dX}\Big|_{X=0} = -Q_0 \\
\frac{d\phi}{dX}\Big|_{X=L} = -\mathcal{E}_l \\
\phi(0) = \phi_d \\
\phi(L) = 0 \\
\end{cases},$$
(14)
(15)

where we have introduced the following definitions:

$$\begin{array}{l}
Q_{0} \equiv \frac{\sigma_{0}}{2c_{0}eL_{D}} \\
\mathscr{E}_{l} \equiv \frac{-\sigma_{l}}{2c_{0}eL_{D}} \\
\phi_{d} \equiv \frac{e\psi_{d}}{kT}
\end{array}$$
(16)

Here the parameter  $\mathscr{E}_l$  is simply the normalized electric field at the ohmic electrode. The normalized bulk charge can be defined similarly as

$$Q_{d} \equiv \frac{\sigma_{d}}{2c_{0}eL_{D}}$$
$$= \frac{1}{2\delta} \int_{0}^{L} [s_{2}C_{2}(X) - s_{1}C_{1}(X)] dX. \quad (17)$$

In solving the system of Eqs. (12) through (14), the solution can be considered to be a function

of  $\delta$  and any two of  $\phi_d$ , L,  $Q_0$ , and  $\mathcal{E}_l$ . Physically it seems most appropriate to take L as given; however, it is more convenient mathematically to take  $\phi_d$  and  $\mathcal{E}_l$  as explicitly free and to calculate all other parameters from these two.

Using Eq. (4) one sees that Eq. (13) is equivalent to the following first-order system:

$$\frac{d}{dX} \begin{pmatrix} \phi \\ \eta \end{pmatrix} = \begin{pmatrix} \eta \\ h(\phi, \delta) \end{pmatrix}$$
$$\equiv \begin{pmatrix} \frac{d\phi}{dX} \\ -\frac{1}{2\delta} \left[ \frac{s_2}{1 + \left(\frac{s_2}{\delta} - 1\right) \exp(\phi)} \\ -\frac{s_1}{1 + \left(\frac{s_1}{\delta} - 1\right) \exp(-\phi)} \right] \end{pmatrix}.$$
(18)

Here  $-h(\phi, \delta)$  is just the normalized charge density. Except for Schottky systems with  $\delta = 1$ (whose solution is treated separately later in this section), the flow associated with Eq. (18) has its only fixed point at the origin of the  $\phi - \eta$  plane. The eigenvalues of the Jacobian matrix,  $\partial(\eta, h)/\partial(\phi, \eta)$ , evaluated at (0, 0) are

$$\lambda_{\pm} = \pm \lambda \equiv \pm \left[ 1 - \frac{\delta}{2s_1 s_2} (s_1 + s_2) \right]^{1/2},$$
 (19)

leading to  $\lambda = \sqrt{1-\delta}$  for Schottky systems and  $\lambda = \sqrt{1-(\frac{3}{4})\delta}$  for Frenkel disorder. Thus (0, 0) is a saddle point<sup>10</sup> of the system described by Eq. (18), and in the resulting phase space ( $\phi - \eta$  plane) portrait of the flow there is a trajectory which tends to the origin with increasing X only in the quadrants for which  $\phi$  and  $\eta$  differ in sign. Thus, given a non-zero  $\phi_d$ , there is a unique solution to Eqs. (13) to (15) only for  $\mathscr{E}_l = 0$  or sgn ( $\mathscr{E}_l$ ) = sgn ( $\phi_d$ ), where sgn (x) = x/|x|. The choice  $\mathscr{E}_l = 0$  is exactly the  $L = \infty$  case, and in this situation for large X,  $\phi$  is proportional to exp ( $-\lambda X$ ).

To proceed further in solving Eq. (13) one notes that

$$\frac{d\eta}{dX} = \frac{1}{2} \frac{d}{d\phi} (\eta)^2, \qquad (20)$$

and

$$h(\phi, \delta) = \frac{1}{2\delta} \frac{d}{d\phi} \\ \times \left\{ s_2 \ln \left[ \exp\left(-\phi\right) + \left(\frac{s_2}{\delta} - 1\right) \right] \\ + s_1 \ln \left[ \exp\left(\phi\right) + \left(\frac{s_1}{\delta} - 1\right) \right] \right\}.$$
(21)

Hence, on integrating  $d\eta/dX$  from  $\phi = 0$  (X = L) to  $\phi(X)$  one finds

$$\eta^{2} = \mathscr{C}_{l}^{2} + \delta^{-1} \ln \left[ 1 + R_{J} (\phi, \delta) \right].$$
 (22)

Here the index J stands for either s (Schottky) or f (Frenkel) with

$$R_{s}(\phi, \delta) = 4\delta(1-\delta)\sinh^{2}(\phi/2) \qquad (23)$$

and

$$R_{f}(\phi, \delta) = 4\delta \sinh^{2}(\phi/2) \times \left[ (1 - \delta/2)^{2} + \frac{\delta(1 - \delta)}{4} \exp(-\phi) \right]. \quad (24)$$

Since  $0 \le \delta \le 1$ , both  $R_f$  and  $R_s$  are strictly non-negative.

For the limiting case of  $\phi_d = 0$  one sees from Eq. (22) and Rolle's theorem<sup>11</sup> that if  $\mathscr{C}_l \neq 0$ there is no solution to Eq. (13) which satisfies the boundary conditions of Eqs. (14) and (15). Hence, the only solution with  $\phi_d = 0$  has  $\mathscr{C}_l = 0$ and  $\phi(X) \equiv 0$ .

In the dilute concentration limit where  $\delta$  tends to 0, the lattice gas distributions of Eq. (4) reduce to Boltzmann distributions. For this case, hereafter referred to as the Gouy-Chapman limit<sup>2,3</sup>, one sees that  $h(\phi, \delta = 0)$  simplifies to the familiar form<sup>9,12</sup> of sinh ( $\phi$ ), while  $\delta^{-1} \ln [1 + R_J(\phi, \delta)]$  for both Schottky and Frenkel disorders becomes  $4 \sinh^2 (\phi/2)$ .

The case of "total dissociation",  $\delta = 1$ , requires special examination only for Schottky systems where  $R_s(\phi, 1) \equiv 0$  and  $(d\phi/dX)^2 \equiv \mathscr{E}_1^2$ . Thus Eqs. (13) and (15) have the unique solution

$$\phi(X) = \phi_d [1 - (\mathscr{E}_l / \phi_d) X]$$
(25)

with  $L = \phi_d / \mathcal{E}_l$  and  $Q_0 = \mathcal{E}_l$ . For  $\phi_d \neq 0$  and  $\mathcal{E}_l = 0$ or sgn  $(\mathcal{E}_l) \neq$  sgn  $(\phi_d)$  there is no solution.

For the more general case of  $\phi_d \neq 0$  and a Frenkel system with  $0 \le \delta \le 1$  or a Schottky system with  $0 \le \delta < 1$ , one can further characterize the solutions. From Eq. (22) it is obvious that only for  $\mathscr{C}_l = 0$  (the semi-infinite case) could

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 $\eta(X_0) = 0$  for a finite value of  $X_0$ . However, this would still imply that  $R_I(\phi, \delta) = 0$ , which requires  $\phi(X_0) = 0$ . Since (0, 0) is a fixed point of Eq. (18), one concludes that  $\phi(X) \equiv 0$ , which is impossible for  $\phi_d \neq 0$ . Therefore,  $\eta(X)$  can only vanish at  $X = \infty$ . As a simple corollary one sees that  $\phi$  can vanish only at X = L. For if at some  $X_1$  it is true that  $0 < X_1 < L$  and  $\phi(X_1) = 0$ , then by Rolle's theorem there must exist an  $X_2$  with  $X_1 < X_2 < L$  and  $\eta(X_2) = 0$ . This agrees with the analysis of Grimley<sup>13</sup> who, although he considered different boundary (electrode) conditions, showed that a lattice gas treatment does not allow the charge density to vanish at any point inside a finite crystal. Thus,  $|\phi(X)|$  (or equivalently,  $\phi(X)/\phi_d$  is a strictly monotone decreasing function of X for  $0 \le X \le L$ . Therefore, one has that

$$\frac{d\phi}{dX} = -\text{sgn}(\phi_d) \left| \frac{d\phi}{dX} \right|.$$
 (26)

From Eqs. (22) and (26) one deduces the result,

$$-\frac{d\phi}{dX} = \operatorname{sgn}(\phi_d) \left[ \mathscr{E}_l^2 + \frac{\ln\left[1 + R_J(\phi, \delta]\right]}{\delta} \right]^{1/2}$$
$$\equiv F_J(\phi, \mathscr{E}_l, \delta), \qquad (27)$$

which with Eq. (14) yields

$$Q_0 = F_J(\phi_d, \mathscr{E}_l, \delta). \tag{28}$$

One can now unambiguously solve for X as a function of  $\phi$ . The result is that

$$X(\phi, \mathscr{E}_{l}, \delta) = \int_{\phi}^{\phi_{d}} \frac{dy}{F_{J}(y, \mathscr{E}_{l}, \delta)}.$$
 (29)

From Eqs. (4) and (29) one obtains implicit equations (through  $\phi$ ) for the space charge concentrations as a function of position. Letting  $\phi$ tend to 0 in Eq. (29), one obtains L in terms of  $\phi_d$ ,  $\mathcal{E}_l$  and  $\delta$ ,

$$L(\phi_d, \mathscr{C}_l, \delta) = \int_0^{\phi_d} \frac{dy}{F_J(y, \mathscr{C}_l, \delta)}.$$
 (30)

For the situation where the surface potential,  $\psi_d$ , is much less than the thermal voltage, kT/e, one can make a small  $\phi_d(|\phi_d| \leq 0.2)$  expansion of  $R_I(\phi_d, \delta)$  and evaluate the resulting integral. After some manipulation one arrives at the following:

$$\mathscr{E}_l \simeq \lambda \phi_d \operatorname{csch}(\lambda L),$$
 (31)

$$\phi(X)/\phi_d \simeq \sinh[\lambda(L-X)]\sinh(\lambda L).$$
 (32)

In the limit that  $\phi_d$  goes to 0, Eq. (32) becomes exact, while for the semi-infinite system one gets  $\phi(X)/\phi_d \simeq \exp(-\lambda X)$ .

In the Gouy-Chapman limit one can integrate Eq. (30) to give the result

$$L(\phi, \mathscr{C}_{l}, \delta = 0) = \int_{0}^{|\phi|} \frac{dy}{\sqrt{\mathscr{C}_{l}^{2} + 4\sinh^{2}(y/2)}}$$
$$= \frac{2}{|\mathscr{C}_{l}|} F\left(\sin^{-1}\left[\tanh\left(\frac{|\phi|}{2}\right)\right], [1 - 4/\mathscr{C}_{l}^{2}]^{1/2}\right). \quad (33)$$

Here F is the incomplete elliptic integral of the first kind.<sup>14</sup> From Eqs. (23) and (24), one sees for  $\delta \neq 0$  that as  $|\phi_d| \rightarrow \infty$ ,  $F_I$  diverges like  $|\phi_d|^{1/2}$ . Hence, for large potentials  $(|\phi_d| \ge -\ln \delta) L$  increases like  $|\phi_d|^{1/2}$ . This is in sharp contrast to the Gouy-Chapman result of Eq. (33), which predicts the finite result  $L(\phi_d = \infty, \mathscr{E}_l, \delta = 0) =$ K(k). Here K is the complete elliptic integral of the first kind and  $k = [1 - (\mathcal{E}_l^2/4)]^{1/2}$ . Therefore, the limit as  $\delta \to 0$  of  $L(|\phi_d| = \infty, \mathscr{E}_l, \delta)$  is not the same as the limit as  $|\phi_d| \rightarrow \infty$  of  $L(\phi_d, \mathcal{E}_t, \delta = 0)$ . This discontinuity is a direct consequence of the finite size of the lattice defects. For  $\delta > 0$ , defect size restriction is built into the lattice gas distributions of Eq. (4) which, regardless of potential, never permit  $c_i(x)$  to exceed Ns<sub>i</sub>. If one goes to the Gouy-Chapman limit, this is equivalent to letting  $N = \infty$  and thus allows charge to accumulate without limit on a planar surface within the material.

Georgiev, Martinov, and Ouroushev<sup>4.5.6</sup> start with the lattice gas distribution of Kliewer and Koehler.<sup>12</sup> They then make the conventional Gouy-Chapman approximation and note that  $L(\phi_d = \infty, \mathcal{E}_l, \delta = 0)$  is finite. From this fact they attempt to construct periodic space charge waves within the bulk. However, if they had retained their original distribution functions, their spatial period would diverge. In addition, they make a major sign error in their analysis which causes them to erronously conclude that in the Gouy-Chapman limit their wave-like solutions are thermodynamically stable. A more complete discussion of their calculation is given in Appendix A.

Since  $X(\phi, \mathcal{E}_{l}, \delta) = L(\phi_{d}, \mathcal{E}_{l}, \delta) - L(\phi, \mathcal{E}_{l}, \delta)$  one can invert Eq. (33) to eventually arrive at the result true for the Gouy-Chapman limit,

$$\phi(X) = \ln \left\{ \frac{dn(L-X,k) + (|\mathcal{E}_1|)/2sn(L-X,k)}{dn(L-X,k) - (|\mathcal{E}_1|/2)sn(L-X,k)} \right\}.$$
(34)

Here dn and sn are the usual Jacobi elliptic functions.<sup>14</sup> Essentially this result has been given earlier by Franceschetti and Macdonald;<sup>15</sup> however, in Ref. 15 Eqs. (21) and (22) have an incorrect factor of  $\frac{1}{2}$ , while Eq. (26) should have a factor of 2 in the argument of the ctnh term. In the present Eq. (34) the potential is given as a function of L and  $\mathscr{C}_l$  with  $\phi_d$  being the value at X = 0. If  $\phi_d$  and  $\mathscr{C}_l$  (or  $\phi_d$  and L) are known, the remaining unknown, L (or  $\mathscr{C}_l$ ), is given implicitly by the equation  $\phi(0) = \phi_d$ . For the semi-infinite crystal ( $\mathscr{C}_l = 0$ ) the above analysis simplifies considerably to yield the result again true for the Gouy-Chapman limit,<sup>16</sup>

$$\phi(X) = 2 \ln \{ [1 + \exp(-X) \tanh(\phi_d/4)] \} / [1 - \exp(-X) \tanh(\phi_d/4)] \}. (34)'$$

From a small y expansion of  $R_J(y, \delta)$  in Eq. (30) one obtains the asymptotic representation that as  $L \rightarrow \infty$ 

$$\mathscr{E}_{l} \simeq g(\phi_{d}, \delta) \exp(-\lambda L);$$
 (35)

the coefficient g is defined for sgn  $(t) = \text{sgn}(\phi_d)$ as  $\phi_d$ 

$$g(\phi_d, \delta) = \lim_{t \to 0} 2\lambda t \exp\left[\lambda \int_{t}^{t} \frac{dy}{F_J(y, 0, \delta)}\right].$$
(36)

For small  $|\phi_d|$  Eq. (36) gives  $g(\phi_d, \delta) \approx 2\lambda\phi_d$  in agreement with Eq. (31). Simplification of Eq. (36) also results for the following two cases:

$$g(\phi_d, \delta = 0) = 8 \tanh(\phi_d/4),$$
 (37)

 $|\phi_d| \gg -\ln \delta$ ,  $g(\phi_d, \delta) \simeq g_0(\delta, \operatorname{sgn}(\phi_d), J) \times \exp[\lambda g_J(\phi_d, \delta)]$ . (38)

Here  $g_0$  is a function of  $\delta$  and the algebraic sign of  $\phi_d$  (but not of  $|\phi_d|$ ) which has, in general, a different form for Schottky and Frenkel systems. The function  $g_f$  is defined as follows:

 $g_J(\phi_d, \delta) = 2\sqrt{\delta} \times \sqrt{\sqrt{|\phi_d| - c}}$ 

$$\begin{cases}
\sqrt{|\phi_d| - c_s} & \text{for } J = s \\
\sqrt{|\phi_d| - c_+} & \text{for } J = f \text{ and } \phi_d > 0 \\
\sqrt{\frac{|\phi_d| - c_-}{2}} & \text{for } J = f \text{ and } \phi_d < 0 \\
\end{cases}$$
(39)

with

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$$c_{s} \equiv -\ln \left[ \delta(1-\delta) \right] c_{+} \equiv -\ln \left[ \delta(1-\delta/2)^{2} \right] c_{-} \equiv -\ln \left[ \delta \frac{\sqrt{1-\delta}}{2} \right]$$
(40)

From Eq. (37) one sees in the dilute or Gouy-Chapman limit for large and fixed L that the charge on the ohmic electrode saturates at large potentials. In contrast, for  $|\phi_d|$  large enough the effects of finite size contained in Eq. (38) for  $\delta > 0$  cause  $|\mathscr{C}_l|$  to grow rapidly with increasing  $|\phi_d|$ . These results simply reflect the fact that a finite  $\delta$  (i.e., N not infinite) implies that a system of length L can accommodate only so much bulk charge  $Q_d$ . Hence, as one increases  $|\phi_d|$  and therefore  $|Q_0|$ , the excess charge necessary to achieve equilibrium must reside on the ohmic electrode.

The differential capacitance per unit area of a fixed length, l, of bulk material with electrodes as described above may be defined as

$$C_{\rm DO} = \left(\frac{\partial \sigma_0}{\partial \psi_d}\right)_l \equiv C_d \times C_{\rm DON}, \qquad (41)$$

where  $C_d \equiv \varepsilon_B/4\pi L_D$ . Here  $C_{DON}$  is the normalized "diffuse double layer" differential capacitance,

$$C_{\rm DON} = \left(\frac{\partial Q_0}{\partial \phi_d}\right)_L.$$
 (42)

Because  $\delta$  is assumed here to be a function of temperature, but not of potential, it is implicit that all variations are made at constant  $\delta$ .

With the choice of  $\phi_d$  and  $\mathcal{E}_l$  as independent variables rather than  $\phi_d$  and L,  $C_{DON}$  will consist of two terms,

$$C_{DON}(\phi_d, \mathcal{E}_l, \delta) = A_J(\phi_d, \mathcal{E}_l, \delta) + B_J(\phi_d, \mathcal{E}_l, \delta)$$
(43)

with

$$A_{J}(\phi_{d}, \mathscr{C}_{l}, \delta) = \left(\frac{\partial F_{J}}{\partial \mathscr{C}_{l}}\right)_{\phi_{d}} \left(\frac{\partial \mathscr{C}_{l}}{\partial \phi_{d}}\right)_{L}$$
(44)

$$B_{J}(\phi_{d}, \mathscr{E}_{l}, \delta) = \left(\frac{\partial F_{J}}{\partial \phi_{d}}\right)_{\mathscr{E}_{l}}.$$
 (45)

The evaluation of the second factor in Eq. (44) can be done in the standard manner,<sup>17</sup>

$$\left(\frac{\partial \mathscr{E}_l}{\partial \phi_d}\right)_L = -\left(\frac{\partial L}{\partial \phi_d}\right)_{\mathscr{E}_l} / \left(\frac{\partial L}{\partial \mathscr{E}_l}\right)_{\phi_d}.$$
 (46)

Hence, from Eq. (30) one obtains

$$A_{J}(\phi_{d}, \mathscr{E}_{l}, \delta) = \left\{ [F_{J}(\phi_{d}, \mathscr{E}_{l}, \delta)]^{2} \times \int_{0}^{\phi_{d}} \frac{dy}{[F_{J}(y, \mathscr{E}_{l}, \delta)]^{3}} \right\}^{-1}.$$
 (47)

The evaluation of Eq. (45) is straight-forward and the results are

$$B_{s}(\phi_{d}, \mathscr{C}_{l}, \delta) = (1 - \delta) \sinh(\phi_{d}) \\ \times \{F_{s}(\phi_{d}, \mathscr{C}_{l}, \delta)[1 + R_{s}(\phi_{d}, \delta)]\}^{-1}$$
(48)

 $B_f(\phi_d, \mathscr{C}_l, \delta) = \{\sinh(\phi_d)\}$ 

$$\times \left[ (1 - \delta/2)^2 + \frac{\delta(1 - \delta)}{4} e^{-\phi_d} \right]$$

$$- \frac{\delta(1 - \delta)}{8} [1 - \exp(-\phi_d)]^2 ]/$$

$$\{F_f(\phi_d, \mathcal{E}_l, \delta) [1 + R_f(\phi_d, \delta)] \}.$$
(49)

From Eqs. (47) through (49) one sees that both  $A_J$  and  $B_J$  can never be negative for  $0 \le \delta \le 1$ . It is apparent from Eqs. (23), (24), (48), and (49) that  $B_s$  and  $A_s$  are symmetric with respect to change of sign of the potential, while  $A_f$  and  $B_f$  are not. This latter asymmetry reflects the basic asymmetry between  $s_1$  and  $s_2$  for Frenkel systems. In the strict Gouy-Chapman limit of  $\delta = 0$  the expressions for  $C_{DON}$  become identical for both Frenkel and Schottky systems, while for small but finite  $\delta$  ( $\delta \le 0.1$ ) the expressions are in close agreement for positive potentials.

### IV DIFFERENTIAL CAPACITANCE OF THE SEMI-INFINITE CRYSTAL

The case  $L = \infty$  corresponds to letting  $\mathscr{C}_l = 0$ . One then has  $A_J(\phi_d, 0, \delta) \equiv 0$ , so that

 $C_{DON}(\phi_d, L = \infty, \delta) = B_J(\phi_d, \mathscr{C}_l = 0, \delta) \quad (50)$ 

The expressions given by Eqs. (48) and (49) for  $\mathscr{C}_l = 0$  agree with our earlier work<sup>1</sup> on semiinfinite systems.

Plots of  $C_{DON}$  vs  $\phi_d$  for Frenkel systems with  $L = \infty$  and various values of  $\delta$  are given in Figure 1. At these values of  $\delta$  one could not distinguish the right half of the symmetric Schottky curves from the positive potential portions of the results shown here.

The general "two-humped" shape of these curves is characteristic of both Frenkel and



FIGURE 1 Plots of the normalized diffuse layer differential capacitance vs normalized potential for a semi-infinite Frenkel system. The various curves are for different values of the bulk fractional defect concentration.

Schottky systems for  $\delta$  not exceeding about 0.1. In fact by a rather straight-forward analysis one can characterize the qualitative features of  $C_{DON}$ as a function of  $\phi_d$  and  $\delta$  for  $L = \infty$ .

Making a large  $\phi_d(|\phi_d| \ge -2 \ln \delta)$  expansion of Eqs. (48) and (49) leads one to the following asymptotic result:

$$B_J(\phi_d, \mathscr{C}_l = 0, \delta) \simeq [g_J(\phi_d, \delta)]^{-1}$$
 (51)

where  $g_J$  is given by Eq. (39). The feature for Frenkel systems that  $C_{DON}(-|\phi_d|, \mathcal{E}_l = 0, \delta) \approx \sqrt{2}$  $C_{DON}(|\phi_d|, \mathcal{E}_l = 0, \delta)$  is quite well obeyed in the region  $|\phi| \geq -2 \ln \delta$ . Furthermore, for small  $\delta$  ( $\delta \leq 0.1$ ) all three expressions in Eq. (40) reduce to  $c \sim -\ln \delta$ . The decrease in  $C_{DON}$  like  $|\phi_d|^{1/2}$  for large potentials is interpreted<sup>1</sup> to be due to a build-up of a region of constant charge density extending from X = 0 to a point inside the bulk material. The length of this region increases like  $|\phi_d|^{1/2}$ .

Probably the most prominent feature of the curves in Figure 1 are the two local maxima located to the left and right of  $\phi_d = 0$ . If Eq. (51) is extrapolated beyond its domain of validity, one might guess that these maxima occur at approximately  $\phi_d = \pm \ln \delta$ . While this guess has the right qualitative features as  $\delta$  varies from 0 to 1, it underestimates the actual location of the maxima by about fifteen to twenty per cent. In addition, using these estimates, one would predict from Eqs. (48) and (49) that the maximum value of  $C_{\text{DON}}$  at positive potential is approximately  $0.300/\sqrt{\delta}$ . However, from the numerical

analysis which led to Figure 1, the right-most maximum is well approximated by  $0.319/\sqrt{\delta}$ .

To obtain a more accurate location of the maxima one should look at the zeroes of  $\partial C_{DON}/\partial \phi_d |_{L=\infty}$ . From Eq. (45) one sees that

$$B_{J}(\phi_{d}, \mathscr{C}_{l}=0, \delta) = \frac{1}{2} \operatorname{sgn}(\phi_{d}) \left(\frac{\partial R_{J}}{\partial \phi_{d}}\right)$$
$$\times [1 + R_{J}(\phi_{d}, \delta)]^{-1} [\delta \ln [1 + R_{J}(\phi_{d}, \delta)]^{-1/2}.$$
(52)

A little manipulation of Eq. (52) soon confirms the identity,

$$\frac{\partial C_{DON}}{\partial \phi_d} \bigg|_{L=\infty} = \frac{1}{F_J(\phi_d, \mathcal{E}_l = 0, \delta)} \\ \times \bigg\{ \frac{1}{2\delta} \frac{\partial^2 R_J}{\partial \phi_d^2} [1 + R_J(\phi_d, \delta)]^{-1} \\ - [C_{DON}(\phi_d, L = \infty, \delta)]^2 \\ \times [1 + 2\ln(1 + R_J(\phi_d, \delta))] \bigg\}.$$
(53)

Therefore, at any potential  $\phi_m$  where  $(\partial C_{DON}/\partial L)|_{L=\infty}$  vanishes, one has

$$C_{\text{DON}}(\phi_{d} = \phi_{m}, L = \infty, \delta) = \sqrt{\frac{\partial^{2} R_{J}}{\partial \phi_{d}^{2}}} \Big|_{\phi_{d} = \phi_{m}}$$

$$\times \{2\delta[1 + R_{J}(\phi_{m}, \delta)]$$

$$\times [1 + 2\ln(1 + R_{J}(\phi_{m}, \delta))]\}^{-1/2}. \quad (54)$$

Equation (54) is of course less general than Eq. (50) but with Eq. (50) provides an implicit transcendental equation for the location of  $\phi_m$ . One can solve this equation for  $\delta \ll 1$  and  $\exp(|\phi_d|) \gg$ 1. The result is that  $|\phi_m| \cong \ln[s_i p/\delta]$ , where i = 1 for maxima at positive potential, and i = 2 for the negative potential maxima. The number  $p \cong$  2.51286242 is the positive root of the transcendental equation,  $\chi = 2 \ln[1+\chi]$ . These results for  $\phi_m$ , when inserted into either Eq. (50) or (54), give  $(s_i p/2\delta)^{1/2}/(1+p) \cong 0.3191(s_i/\delta)^{1/2}$  as the approximate value of  $C_{DON}$  at  $\phi_m$ . Thus, for  $\delta < 10^{-2}$  the maximum values of  $C_{DON}$  are well approximated by the formula

 $C_{DON} \approx \frac{0.319}{\sqrt{\delta}} \times \begin{cases} \sqrt{s_1} \text{ for the right most maximum} \\ \sqrt{s_2} \text{ for the left most maximum.} \end{cases}$ (55)

For  $\delta < 0.1$  there is a region between the maxima where  $\delta \exp(|\phi_d|)$  is small. Making a small  $\delta$  expansion of Eq. (50) gives for both Frenkel and Schottky systems the symmetric result,

$$C_{\text{DON}}(\phi_d, L = \infty, \delta = 0) = \cosh\left(\frac{\phi_d}{2}\right).$$
 (56)

This of course is just the familiar Gouy-Chapman<sup>2,3</sup> expression derived in earlier work.<sup>1,18</sup>

Taken together, Eqs. (51), (55) and (56) allow one to "sketch"  $C_{DON}$  vs  $\phi_d$  for small  $\delta$  without any detailed calculation based on Eq. (50). However, what is measured experimentally is  $C_{DO}$ . From Eqs. (41) and (7) one sees that

$$C_{\rm DO} = \sqrt{\frac{\varepsilon_{\rm B} e^2 N}{2 \pi k T}} \left( \sqrt{\delta} \, C_{\rm DON} \right).$$

The first factor is a rather showly varying function of temperature, while the second exhibits the explicit  $\delta$  dependence. In Figure 2  $\sqrt{\delta} C_{DON}(\phi_d, L = \infty, \delta)$  is plotted vs  $\phi_d$  for a Frenkel system and three values of  $\delta$ . These curves show that the measured differential capacitance is not nearly as sensitive a function of  $\delta$  as Figure 1 might have indicated. For a given material the variation with temperature of  $C_{DO}$  vs  $\phi_d$  would be different from that indicated



FIGURE 2 Plots of the normalized diffuse layer differential capacitance multiplied by  $\sqrt{\delta}$  vs normalized surface potential for a semi-infinite Frenkel system at different bulk fractional defect concentrations. The unnormalized differential capacitance is given by  $\sqrt{\epsilon_B e^2 N/2\pi kT} \times (\sqrt{\delta}C_{DON})$ , where the symbols are explained in Section II of the text.

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by Figure 2 because of the temperature dependence of  $\sqrt{\epsilon_B/T}$ . However, for the same N,  $\epsilon_B$  and temperature, Figure 2 illustrates how the measured differential capacitance might change with various materials having different bulk defect concentrations.

One can understand several features of Figure 2 directly from Eqs. (51) and (55). For large  $|\phi_d|$  all of the curves converge to  $\sqrt{s_i}/2\sqrt{|\phi_d|}$ , while at its maximum values  $\sqrt{\delta} C_{DON}$  approaches  $0.32\sqrt{s_i}$ . Here  $s_1$  and  $s_2$  refer to the positive and negative potential parts of the curve, respectively.

For most physical systems where the continuum lattice gas treatment might be expected to be appropriate, the relevant values of  $\delta$  are small.<sup>1</sup> However, for completeness and to see the full implications of the model, the regime where  $\delta$  tends to 1 is discussed in Appendix B.

#### V DIFFERENTIAL CAPACITANCE OF FINITE CRYSTALS

Equations (30) and (43) together give an implicit equation (through  $\mathscr{C}_l$ ) for calculating  $C_{DON}(\phi_d, L, \delta)$ . As with the  $L = \infty$  case, for  $\phi_d =$ 0 and  $\delta$  small enough, the calculated  $C_{DON}$  for Frenkel and Schottky systems become identical. Furthermore, because of the Schottky symmetry relation  $s_1 = s_2$ , one has  $C_{DON}(\phi_d, L, \delta) =$  $C_{DON}(-\phi_d, L, \delta)$  for such systems.

From Eqs. (30) and (27) it is apparent that as  $\mathscr{E}_1 \to \infty$ ,  $L \to \phi_d/\mathscr{E}_1$ , while a similar analysis if Eq. (47) reveals that  $A_J(\phi_d, \mathcal{E}_l, \delta) \rightarrow \mathcal{E}_l/\phi_d$ . Furthermore, from Eqs. (48) and (49) one sees that as  $\mathscr{E}_l \to \infty$ ,  $B_J(\phi_d, \mathscr{E}_l, \delta) = 0(1/|\mathscr{E}_l|)$ . The 0 notation used here is the standard one.<sup>19</sup> Hence,  $B_J$  tends to 0 while  $A_J$  (and therefore  $C_{DON}$ ) tends to 1/L. This is of course just the normalized geometric capacitance,  $C_{gN} \equiv (\varepsilon_B/4\pi l)/C_d$ , which should dominate for sufficiently small L. In some sense, one might then say that  $A_J$  contains the finitelength part of the differential capacitance, while  $B_I$  represents the behavior of the diffuse layer. However, such a division is both arbitrary and misleading since it fails to recognize that at intermediate values of  $\mathscr{E}_{l}$  (ie., L) both terms contribute. For the case of very small  $|\phi_d|$  one can use a more direct approach. By combining Eqs. (28) and (31) one has for fixed L as  $\phi_d$  tends to 0 that

$$Q_0 \simeq \lambda \phi_d \coth(\lambda L). \tag{57}$$

Hence, from Eq. (42) one deduces the limiting result that

$$C_{\text{DON}}(\phi_d = 0, L, \delta) = \lambda \coth(\lambda L).$$
 (58)

this agrees with earlier work<sup>15,16,20</sup> on the Gouy-Chapman limit where  $\lambda = 1$ . The fact that  $C_{DON}(\phi_d = 0, L = \infty, \delta) = \lambda$  is also seen from the results of Appendix B.

From Eq. (35) one sees that as  $\mathscr{E}_l$  tends to 0, L diverges like  $\ln [g(\phi_d, \delta)/|\mathscr{E}_l|]^{1/\lambda}$ . In this same small  $|\mathscr{E}_l|$  limit one determines from Eqs. (47), (48) and (49) that

$$\Delta C_{N}(\phi_{d}, L, \delta) \equiv C_{DON}(\phi_{d}, L, \delta) - C_{DON}(\phi_{d}, L = \infty, \delta)$$

$$= \left[\frac{\mathscr{E}_{l}}{F_{J}(\phi_{d}, 0, \delta)}\right]^{2} \times \left[\lambda - \frac{C_{DON}(\phi_{d}, L = \infty, \delta)}{2}\right] + 0(\mathscr{E}_{l}^{4}),$$
(60)

From Eqs. (31), (35), (37), (38), (51) and (56) one obtains the following asymptotic representations for large L:

$$\phi_d \to 0 \Delta C_N(\phi_d, L, \delta) \simeq 2\lambda \exp(-2\lambda L)$$
 (61)

$$C_N(\phi_d, L, \delta = 0) \approx 4 [1 - \frac{1}{2} \cosh(\phi_d/2)]$$
  
  $\times [\cosh(\phi_d/4)]^{-4} \exp(-2L)$  (62)

$$|\phi_d| \gg -\ln \delta, \ \Delta C_N(\phi_d, L, \delta) \simeq [g_0(\delta, \operatorname{sgn}(\phi_d), J)]^2$$

$$\times P_{J}(\phi_{d}, \delta) \left[ \lambda - \frac{1}{2g_{J}(\phi_{d}, \delta)} \right]$$

$$\times \exp \left\{ -2\lambda \left[ L - g_{J}(\phi_{d}, \delta) \right] \right\},$$
(63)

where

$$P_{J}(\phi_{d}, \delta) = \delta \times \begin{cases} \frac{1}{|\phi_{d}| - c_{s}} & \text{for } J = s \\ \frac{1}{|\phi_{d}| - c_{+}} & \text{for } J = f, \phi_{d} > 0 \\ \frac{1}{2[|\phi_{d}| - c_{-}]} & \text{for } J = f, \phi_{d} < 0. \end{cases}$$
(64)

It is easily verified that Eq. (61) agrees with Eq. (58), while for large potentials the Gouy-Chapman limit of Eq. (62) tends to  $-16 \exp(-2L - |\phi_d/2|)$ . From Eqs. (60) through (62) one can see how, at fixed large L, changes in  $\delta$  or  $\phi_d$  will affect the approach of  $C_{DON}$  to its limiting semi-infinite value.



FIGURE 3 Plots of the normalized diffuse layer differential capacitance of a Frenkel system vs crystal length, normalized in units of Debye length for different normalized surface potentials,  $\phi_d$ . For  $\delta \approx 8.599 \times 10^{-6}$  the continuous and single-dashed curves represent positive and negative  $\phi_d$ , respectively, while the dash-dot-dash curves are the Gouy-Chapman limit for which  $\delta = 0$ . The normalized geometric capacitance is given by  $C_{\rm gN} = 1/L$ .

In Figures 3 through 6 plots of  $C_{DON}$  vs L for fixed  $\phi_d$  and  $\delta$  are shown for a Frenkel system. Each figure is for a different value of  $\delta$ , while the values of  $\phi_d$  are indicated on the graph. For Frenkel systems, as before, there is an asymmetry between positive and negative potentials,



FIGURE 4 Plots of the normalized diffuse layer differential capacitance of a Frenkel system vs crystal length, normalized in units of Debye length for different values of  $\phi_d$  and  $\delta = 1.0 \times 10^{-3}$ .



FIGURE 5 Plots of the normalized diffuse layer differential capacitance of a Frenkel system vs crystal length, normalized in units of Debye length for different values of  $\phi_d$ , and  $\delta = 0.1$ .

and the latter are shown as dotted lines in the figures. The choice of  $\delta$  for Figure 3 is appropriate for an AgCl crystal (a typical Frenkel material) at T = 500 K.<sup>1</sup> The "dash-dot-dash" curves of Figure 3 are plots of  $C_{DON}(\phi_d, L, \delta = 0)$ . For  $|\phi_d| \leq 8$  this Gouy-Chapman limit can not be distinguished (on this graph) from the corresponding  $\delta = 8.599 \times 10^{-6}$  results. For the three smallest values of  $\delta$ , the associated Schottky



FIGURE 6 Plots of the normalized diffuse layer differential capacitance of a Frenkel system vs crystal length, normalized in units of Debye length for different values of  $\phi_d$  and  $\delta = 0.5$ .

curves are also indistinguishable from the positive potential Frenkel ones. For  $\delta = 0.5$ , the Schottky  $\phi_d = 1.0$  and  $\phi_d = 0$  curves have an  $L = \infty$  intercept below the corresponding Frenkel results by 0.02 and 0.08 respectively; however, by L = 1.0, the Frenkel and Schottky values have merged.

All four figures illustrate the approach to the normalized geometric capacitance,  $C_{gN} = 1/L$ , for sufficiently small L. The relative ordering of the curves with respect to  $\phi_d$  as  $\delta$  varies is a reflection of going from the "two-humped" (Figures 3 through 5) to the "one-humped" (Figure 6) behavior of the  $L = \infty$  curves discussed in Section IV. Also apparent for Frenkel systems in all four figures is the factor of  $\sqrt{2}$  between  $C_{DON}(-|\phi_d|, L, \delta)$  and  $C_{DON}(|\phi_d|, L, \delta)$  for  $|\phi_d| \gg -\ln \delta$ .

The approach of  $C_{DON}$  to its  $L = \infty$  asymptotic limit is clearly seen. Many of the qualitative features of this approach can be explained by Eqs. (61) through (64). For example, if  $\delta =$  $8.599 \times 10^{-6}$  Eq. (62) predicts that  $C_{DON}(\phi_d =$  $10, L, \delta)$  attains† its  $L = \infty$  value at a smaller L then  $C_{DON}(\phi_d = 7, L, \delta)$ . This is confirmed in Figure 3. Similarly, Eq. (63) explains why for  $\delta = 0.5$ , the  $\phi_d = 30$  curve "turns up" at a larger L than either the curves at smaller  $|\phi_d|$  or  $\phi_d =$ -30.

From Eq. (51) for  $|\phi_d|$  large and increasing one has that  $C_{DON}(\phi_d, L = \infty, \delta)$  tends to 0 like  $|\phi_d|^{-1/2}$ , so that the transition to  $C_{gN}$  must occur at increasingly larger L just as Eq. (63) predicts. Thus at large  $|\phi_d|$  the lattice gas statistics implicit in Eq. (63) have a marked effect on the adequacy of approximating the diffuse differential capacitance by its intrinsic semi-infinite limit. For example, in the Gouy–Chapman limit with  $\phi_d = 30$ ,  $|\Delta C_N(\phi_d, L, \delta = 0)/C_{DON}(\phi_d, L = \infty, \delta = 0)|$  is less than  $3.02 \times 10^{-4}$  for all L larger than  $3 \times 10^{-4}$ . In contrast, from Figures 3, 5, and 6 one sees that for this same potential and  $\delta$  having the values  $8.60 \times 10^{-6}$ ,  $10^{-1}$ , and 0.5, that  $C_{DON}$  has already begun to "break away" from its  $L = \infty$ limit for L as large as 0.04, 1.4, and 9.0, respectively. This difference for large  $|\phi_d|$  in the nature of the transition of  $C_{DON}$  to its semi-infinite

value is another reflection of the build-up of a region of constant charge density. When the length of this region becomes comparable to the overall length of the crystal, large deviations from semi-infinite behavior are to be expected. This connection is illustrated by a comparison between Figure 4 and Figure 11 of Ref. 1, where a plot of normalized charge density vs X for a Frenkel system at  $\delta = 10^{-3}$  is presented.

As a rough approximation for large  $|\phi_d|$ , one might expect the semi-infinite result to be valid until  $B_J(\phi_d, \mathcal{E}_l = 0, \delta)$  becomes comparable to  $C_{gN}$ . From Eq. (51) this gives a transition length equal to  $g_J(\phi_d, \delta)$ .

In summary, over the range of both  $\delta$  and  $\phi_d$  presented in Figures 3 through 6 a length of about L = 10 is required to validate the semiinfinite approximation to the differential capacitance.

Probably one of the most surprising features of Figures 3 and 4 is the existence of a distance  $L_0$ where at fixed  $\phi_d$  and  $\delta$ ,  $C_{DON}(\phi_d, L, \delta)$  has a minimum. These minima only become apparent at small  $\delta$  ( $\delta \leq 10^{-2}$ ) and potential in the range  $-\ln \delta \ge |\phi_d| \ge 3$ . Thus, in some sense, they are an aspect present only in the Gouy-Chapman limit. In this limit one can determine precisely the smallest  $|\phi_d|$  necessary for a minimum to occur. From Eq. (62) one sees that at large L,  $\Delta C_N$  will be negative and thus  $C_{DON}$  as a function of L must have a minimum, if and only if  $|\phi_d| >$  $2 \ln [\sqrt{5}+2] \approx 2.8873$ . A detailed consideration of  $\partial C_{DON}/\partial L|_{\phi_4}$  in Appendix C shows that in the Gouy-Chapman limit of  $\delta \exp(|\phi_d|) \ll 1$ , one has the following approximation valid for  $|\phi_d| \ge 6$ :

$$L_0 \approx |\phi_d| \sqrt{\frac{2}{r(|\phi_d|)}} \exp(-|\phi_d|/2)$$
 (65)

$$\Delta C_{N}(\phi_{d}, L_{0}, \delta = 0) \simeq \frac{-\exp(|\phi_{d}|/2)}{2} \times \{1 - [\sqrt{1 + \frac{1}{2}r(|\phi_{d}|)} + [r(|\phi_{d}|)]^{3/2}/(\sqrt{2} |\phi_{d}|)] / [1 + \frac{1}{2}r(|\phi_{d}|)]\}$$
(66)

where

$$r(x) = \left(\frac{x}{2} - 3\right) + \sqrt{\left(\frac{x}{2} - 3\right)^2 + x}.$$
 (67)

From Eq. (56) one has in this regime that the ratio  $-\Delta C_N(\phi_d, L_0, \delta = 0)/C_{DON}(\phi_d, L = \infty, \delta = 0)$  is just the term in the braces of Eq. (66). Even if  $\delta$  is small enough so that  $\delta \exp(|\phi_d|) \ll 1$ , at large potentials Eq. (65) gives unphysical results when

<sup>&</sup>lt;sup>†</sup>Of course, it is in general not true that for finite L that one can have equality between  $C_{DON}(\phi_d, L, \delta)$  and  $C_{DON}(\phi_d, L = \infty, \delta)$ . However, for a given positive number  $\epsilon$ one can define  $L_{\epsilon}(\phi_d, \delta)$ , such that whenever  $L > L_{\epsilon}$ ,  $|\Delta C_N(\phi_d, L, \delta)| < \epsilon$ . Thus the above comparisons are made at small but finite  $\epsilon$ .

Calculated location and depth of minima of diffuse differential capacitance of an AgCl crystal at different temperatures and potentials. The first column gives the temperature and some temperature dependent parameters.

	$\phi_d$	$\psi_d$ volts	$C_{\rm DO}(L=\infty) \\ \mu F/\rm cm^2$	l <sub>o</sub> Å	$\frac{\Delta C_{\rm N}(L_0)}{C_{\rm DON}(L=\infty)}$
T = 350  K $\delta = 6.67 \ 10^{-9}$ $L_D = 2.58 \times 10^3 \text{ Å}$ $C_d = 0.0427 \mu \text{ F/cm}^2$	7 10	0.211 0.302	0.708 3.17	$\begin{array}{c} 4.30 \times 10^2 \\ 1.01 \times 10^2 \end{array}$	0.1342 0.2291
T = 273  K $\delta = 8.09 \times 10^{-12}$ $L_{D} = 6.56 \times 10^{4} \text{ Å}$ $C_{d} = 1.69 \times 10^{-3} \mu F/\text{cm}^{2}$	7 10 13	0.165 0.235 0.306	0.0280 0.125 0.561	$1.09 \times 10^{4}$ $2.58 \times 10^{3}$ $6.15 \times 10^{2}$	-0.1342 -0.2291 -0.3006
T = 200  K $\delta = 1.12 \times 10^{-16}$ $L_D = 0.151 \text{ cm}$ $C_d = 7.32 \times 10^{-6} \mu \text{F/cm}^2$	20 25	0.345 0.431	0.0806 0.982	$\begin{array}{c} 4.92 \times 10^{3} \\ 4.40  10^{2} \end{array}$	-0.4131 -0.4672

 $l_0 \equiv L_0 \times L_D$  becomes comparable to the crystal lattice spacing. At such small distances any result based on a continuum treatment makes little sense.

Using data appropriate for AgCl<sup>1</sup> the transition from the intrinsic diffuse differential capacitance associated with the semi-infinite crystal to the minimum at finite length described by Eqs. (65) and (66) is presented in Table I. As can be seen, the drop in  $C_{DO}$  from its semi-infinite value can be appreciable. Furthermore, the values of  $l_0$  and  $C_{DO}$  seem large enough so that this effect would be measurable. In addition for the temperatures given,  $L_D$  seems large enough to justify a continuum approach, while  $\delta$  is small enough to validate the Gouv-Chapman limit for the potentials considered. If such effects are not observed, this may reflect the inadequacy of ignoring detailed microscopic (Coulombic) interactions even at the small concentrations considered here.

One problem which should be noted is that  $\psi_d$  can not be measured or controlled directly, and, in general,<sup>1</sup> the potential drop across the diffuse material is much less than the applied (left electrode) potential. Similarly, changes in the total differential capacitance of the electrode plus diffuse region can be somewhat insensitive to changes in  $C_{DO}$ .<sup>1</sup>

The effect of lattice gas restrictions as seen in Figures 3 through 6 is to begin supressing these length-dependent minima as  $|\phi_d|$  becomes comparable to  $-\ln \delta$ . For finite  $\delta$  and  $|\phi_d|$  large

enough, the approach of  $C_{DON}$  to  $C_{gN}$  is essentially monotonic, and as noted in the discussion of Eqs. (62) and (63) the transition from intrinsic to manifestly length-dependent  $C_{DON}$  occurs at much larger values of L than the Gouy-Chapman model predicts.

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## Appendix A

## STABILITY OF SPACE CHARGE WAVES IN THE GOUY–CHAPMAN LIMIT

In their recent work<sup>4</sup> Georgiev, Martinov and Ouroushev (hereafter referred to as GMO) construct periodic space charge wave solutions to the Poisson-Boltzmann equation (Eq. (13) in the Gouy-Chapman limit). They conclude, for parthe spatial ticular values of period or "wavelength", that such waves are thermodynamically stable and should lead to an ordered condensation of charged defects within the bulk of the material. While they claim that their analysis is valid for both intrinsic and impurity situations, we limit our discussion to the former.

The basic starting point of the GMO analysis is to ignore the lattice gas restrictions on defect size and to consider that the  $\delta \rightarrow 0$  limit is valid everywhere in the crystal regardless of the magnitude of the electrostatic potential. The normalized Poisson-Boltzmann equation is given by

$$\frac{d^2\phi}{dX^2} = \sinh{(\phi)}.$$
 (A1)

If one requires a solution which vanishes at X = L, one is led, as in Section II, to Eq. (34). As an additional boundary condition GMO take  $\phi(0) \equiv \phi_d = \infty$ . They then correctly deduce that the solution is given by

$$\phi(X) = \ln \{ [1 + cn(X, k)] / [1 - cn(X, k)] \}$$
  
= 2 ln {cn(X/2, k)/[sn(X/2, k)dn(X/2, k)]},  
(A2)

where as before cn, sn, and dn are Jacobi elliptic functions<sup>14</sup> and

$$k = \left[1 - \left(\frac{d\phi}{dX}\Big|_{L} / 2\right)^{2}\right]^{1/2}$$

The solution given by Eq. (A2) diverges like

 $-2\ln(X)$  as  $X \rightarrow 0$  and like  $2\ln(2L - X)$  as  $X \rightarrow 2L$ . As was shown in Section II, for  $\phi_d = \infty$ one has that L = K(k), with K the complete Jacobi elliptic function. Now, the largest domain<sup>21</sup> over which one can find a real-valued solution to Eq. (A1) which diverges at X = 0 is the open interval 0 < X < 2L. However, GMO, by extending Eq. (A2) to the complex variable Z = X + iY, obtain a solution of the differential equation  $d^2\phi/dZ^2 = \sinh(\phi)$ . The solution is a doubly-periodic meromorphic function (i.e., an elliptic function in the most general sense<sup>22</sup>)  $\tilde{Z}_{mn} = 2mK(k) +$ which has poles at  $i2nK([1-k^2]^{1/2})$ , where m and n run over all integer values. Hence, along the real (X) axis this is an analytic continuation of Eq. (A2) with a period,  $\Lambda$ , equal to 4 K(k). At the singularities, 2mK(k), the potential  $\phi$  is "seemingly continuous" with  $\phi(2mK(k)-\varepsilon) = \phi(2mK(k)+\varepsilon)$  for all  $\varepsilon$  in the interval  $0 < \varepsilon < 2K(k)$ , while  $d\Phi/dX$ discontinuous, with  $\Phi'(2mK(k)+\varepsilon) =$ is  $-\Phi'(2mK(k)-\varepsilon)$ . According to GMO the origin of these singularities is in the point charge character of the defect distribution functions, and they expect that finite size effects will result in a "cut-off" of the singular potentials. However, if they had kept the original lattice gas distributions of Kliewer and Koehler,<sup>12</sup> which embody finite size restrictions, then, as was shown in Section II, the wavelength of their periodic structure would be infinite. The material would then exhibit no periodic space charge wave behavior at all.

Despite the above objections, one might still feel that these space charge wave calculations have some merit, and may indeed be a first approximation in describing physical phenomena within a bulk ionic material. In fact, if  $\phi(X)$  as given by Eq. (A2) leads to a lower energy than the conventional solution, where  $\phi$  is zero in the bulk (corresponding in our notation to Kliewer and Koehler's bulk potential of  $\Phi_x$ ), then their calculation might have some validity. Unfortunately, this is not the case. In their calculation of the free energy, GMO make an error in going from their Eq. (32) to their Eq. (34). Essentially, over a wavelength of their space charge waves, they deduce that

$$\int_{0}^{\Lambda} [\phi \sinh \phi] dX = \int_{0}^{\Lambda} -\left(\frac{d\phi}{dX}\right)^{2} dX; \quad (A3)$$

but for real  $\phi$ , the first integral is positive definite, while the second is negative definite. Hence, Eq. (A3) is true only for  $\phi \equiv 0$ . The error made by GMO was in their assumption that the surface term which appears on the right hand side of Eq. (A3) is zero due to periodicity. However, the discontinuity in  $d\phi/dX$  causes this term to diverge to  $+\infty$ . Thus, instead of being thermodynamically stable compared to the bulk charge neutrality state, GMO's space charge waves are inherently unstable.

In our earlier paper,<sup>1</sup> we presented a treatment based on Poeppel and Blakely's<sup>9</sup> model of surface charge in terms of surface kink sites in an ionic crystal having Frenkel disorder. Following the notation of that paper and, in particular of its Appendix A, one finds that inserting the minimizing distributions (i.e., the lattice gas distributions) back into the expression for the free energy (Eq. (A1) of Ref. 1) gives the following result:

$$[G - W(l)]/(kTc_0L_D)$$

$$= -Q_m\phi_m - Q_s\phi_s - 2Q_{sm} \ln \{4/[1 - (Q_{sr})^2]\}$$

$$-2(Q_m + Q_l)\{\phi_s + \ln [(1 + Q_{sr})/(1 - Q_{sr})]\}$$

$$+ \int_0^L f_B(\phi(X), \delta) dX. \qquad (A4)$$

Here G is the Gibbs free energy per unit area at constant temperature and pressure; W(l) is the binding energy of the defect-free crystal;  $Q_m$  is the normalized blocking electrode charge density;  $Q_s$  is the normalized surface layer charge density;  $Q_{sm}$  is the normalized maximum allowed surface layer charge density;  $\phi_m$  is the normalized potential of the left (blocking) electrode; and  $\phi_s$  is the normalized surface layer potential. In addition one has  $Q_l = -\mathscr{E}_l$  and  $Q_{sr} = Q_s/Q_{sm}$ .

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Finally,  $f_{\rm B}$  is given by

$$f_{\rm B}(\phi, \delta) \equiv \frac{\phi}{2} \{ [\exp(\phi)/t_1(\phi, \delta)] \\ - [\exp(-\phi)/t_2(\phi, \delta)] \} \\ - \frac{1}{\delta} \ln \{ t_1(\phi, \delta)/[1-\delta] \} \\ - \frac{s_2}{\delta} \ln \{ t_2(\phi, \delta)/[1-(\delta/s_2)] \}, \quad (A5)$$

where

$$t_1(\phi, \delta) \equiv 1 + \delta[\exp(\phi) - 1]$$
  

$$t_2(\phi, \delta) \equiv 1 + (\delta/s_2)[\exp(-\phi) - 1].$$
(A6)

In Eq. (A4), the term G - W(l) represents the free energy change caused by the presence of the defects.

Now, if we confine our attention to the Gouy-Chapman limit, one has the following simplification,

$$f_{\rm B}(\phi, \delta = 0) = \phi \sinh(\phi) - 2\cosh(\phi). \quad (A7)$$

To make connection to the work of GMO we consider the material in zero external field, so  $Q_m = Q_l = 0$ . Then Eq. (A4) reduces to the following,

$$[G - W(l)]/(kTc_0L_D) = -Q_s\phi_s - 2Q_{sm} \ln \{4/[1 - (Q_{sr})^2]\} + \int_{0}^{\infty} f_B(\phi(X), \delta = 0) dX.$$
(A8)

The term involving  $Q_{sm}$  is the energy associated with the particular kink site model we employed; apart from this term, Eq. (A8) is essentially equivalent to Eq. (9) given by GMO in Ref. 4. The bulk or large X behavior of the potential affects the free energy through the integral term. It is elementary to show that

$$\left.\frac{\partial f_{\rm B}}{\partial \phi}\right|_{\delta=0} = \sum_{n=1}^{\infty} \frac{(2n)(\phi)^{2n+1}}{(2n+1)!}.$$
 (A9)

This means that

$$\frac{\partial f_{\mathbf{B}}}{\partial \phi}\Big|_{\delta=0} = \operatorname{sgn}(\phi) \left|\frac{\partial f_{\mathbf{B}}}{\partial \phi}\right|_{\delta=0} |;$$

hence,  $f_B(\phi = 0, \delta = 0)$  is the absolute minimum of  $f_B(\phi, 0)$ . Thus, a potential which tends to zero in the interior of the material always gives a

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lower free energy than any other solution of the Poisson-Boltzmann equation. In particular, the space charge waves of GMO even with some cut-off of their singular potentials, would give a very large positive free energy change. Thus as stated previously, such space charge waves are thermodynamically unstable. A zero potential of course corresponds (c.f. Eq. (18) of this work) to a net charge density of zero. Hence, the result shown above that  $\phi$  should be zero in the bulk of the crystal, is consonant with the original conclusion of Kliewer and Koehler that "electrical neutrality within the bulk of the crystal is a consequence of thermal equilibrium."<sup>12</sup>

## **Appendix B**

## DIFFUSE DIFFERENTIAL CAPACITANCE FOR LARGE BULK DEFECT CONCENTRATIONS

The purpose of this appendix is to investigate the behavior of the diffuse differential capacitance of semi-infinite Schottky and Frenkel systems for large bulk fractional defect concentration,  $\delta$ . For Frenkel systems a detailed small  $\phi_d$  expansion of Eq. (50) yields the result that

$$C_{DON}(\phi_d, L = \infty, \delta) = \sqrt{1 - \frac{1}{2}\delta} \times \left[ 1 - \frac{\delta(1 - \delta)}{4 - 3\delta} \phi_d + 0(\phi_d^2) \right].$$
(B1)

Hence as  $\delta$  tends to 1, one has that  $C_{\text{DON}}(\phi_d = 0)$ ,  $L = \infty, \delta$ ) tends to  $\frac{1}{2}$ . For large  $\phi_d$ , however,  $C_{DON}$  still falls off proportional to  $|\delta \phi_d|^{-1/2}$ . The result is that the two maxima present for small  $\delta$  converge to a single maximum at about  $\delta = 0.2$ . This single maximum is located at a small  $(|\phi_d| < 2)$ negative potential which tends to 0 as  $\delta$  tends to 1. As  $\delta$  increases beyond 0.9 two maxima again appear. One is still at about  $\phi_d = 0$ , and the second is at a negative potential whose distance from  $\phi_d = 0$  increases as  $\delta$  tends to 1. To understand these phenomena one need only look at Eqs. (51) and (40). As  $\delta$  approaches 1, it is apparent that  $c_+$  goes to  $\ln 4$ , while  $c_-$  diverges like  $-1/2 \ln (1-\delta)$ . Therefore, for  $\delta$  close to 1, one expects to see a maximum at  $\phi_d =$  $O(\ln [1-\delta])$ . In the extreme limit of  $\delta = 1$ , this secondary maximum has disappeared (moved out to  $-\infty$ ), and one is left with the symmetric curve described by

$$B_{f}(\phi_{d}, \mathscr{E}_{t} = 0, \, \delta = 1) = \frac{1}{2\sqrt{2}} \\ \times |\tanh(\phi_{d}/2)| / \{\ln[\cosh(\phi_{d}/2)]\}^{1/2}.$$
(B2)

The large  $\delta$  behavior of Schottky defect systems is quite different. From Eqs. (23) and (50) one sees that for small  $\phi_d$ ,

$$C_{DON}(\phi_d, L = \infty, \delta) = \sqrt{1 - \delta}$$
$$\times \left\{ 1 + 3 \left( \frac{\phi_d}{2} \right)^2 [\frac{1}{6} - \delta(1 - \delta)] + 0(\phi_d^4) \right\}.$$
(B3)

Thus, in contrast to Frenkel systems  $\phi_d = 0$  is either a maximum or a minimum of  $C_{DON}$ . From Eq. (59) one sees that for  $0 < \delta < \frac{1}{2} - 1/\sqrt{12} \approx$ 0.2113248, the origin is a local minimum. This corresponds to the "double-humped" curves of Figure 1. For

$$\frac{1}{2} - 1/\sqrt{12} < \delta < \frac{1}{2} + 1/\sqrt{12} \approx 0.7886572$$

one has an absolute maximum (single hump) at  $\phi_d = 0$ . Finally, for  $\frac{1}{2} + 1/\sqrt{12} < \delta < 1$ , the doublehumped pattern returns. Because only the combination  $\delta(1-\delta)$  appears in Eq. (23), the shape of the  $C_{DON}$  versus  $\phi_d$  curves for Schottky systems is symmetric about  $\delta = \frac{1}{2}$ . In fact it is not difficult to show from Eq. (50) that for a Schottky system

$$\frac{C_{DON}(\phi_d, L = \infty, \delta)}{C_{DON}(\phi_d = 0, L = \infty, \delta)} = \frac{C_{DON}(\phi_d, L = \infty, 1 - \delta)}{C_{DON}(\phi_d = 0, L = \infty, 1 - \delta)}.$$
 (B4)

Hence, a plot of  $C_{DON}$  vs  $\phi_d$  for an  $L = \infty$ Schottky system with  $\delta = 1 - \varepsilon$  would be identical in shape to a similar curve for  $\delta = \varepsilon$ , with  $\frac{1}{2} \ge \varepsilon >$ 0. As predicted from Eq. (25), the  $\delta = 1$  limit for Schottky systems gives the rather uninteresting results that  $B_i(\phi_d, \mathcal{E}_l, \delta = 1) \equiv 0$  and  $A_i(\phi_d, \mathcal{E}_l, \delta = 1) = 1/L$ .

# Appendix C

### LOCATION OF LENGTH-DEPENDENT MINIMA IN THE DIFFERENTIAL CAPACITANCE

For  $\phi_d$  and  $\delta$  fixed a necessary condition that  $C_{DON}(\phi_d, L, \delta)$  has a minimum as a function of L is that  $(\partial C_{DON}/\partial L)|_{\phi_d} = 0$ . Treating  $\phi_d$  and  $\mathscr{E}_l$  as the independent variables, then one has

$$\left(\frac{\partial C_{DON}}{\partial L}\right)_{\phi_d} = \left(\frac{\partial C_{DON}}{\partial \mathcal{E}_l}\right)_{\phi_d} / \left(\frac{\partial L}{\partial \mathcal{E}_l}\right)_{\phi_d}.$$
 (C1)

If one defines the following integrals

$$I_{J}(\phi_{d}, \mathcal{E}_{l}, \delta; \alpha) \equiv \operatorname{sgn}(\phi_{d}) \times \int_{0}^{\phi_{d}} \frac{dY}{\left[\frac{\ln\left[1 + R_{J}(Y, \delta)\right]}{\delta} + \mathcal{E}_{l}^{2}\right]^{\alpha}}, \quad (C2)$$

then Eqs. (30) and (47) can be expressed as

$$L(\phi_d, \mathscr{E}_l, \delta) = I_J(\phi_d, \mathscr{E}_l, \delta; \frac{1}{2})$$
(C3)

 $A_{J}(\phi_{d}, \mathscr{E}_{l}, \delta) = \{I_{J}(\phi_{d}, \mathscr{E}_{l}, \delta; \frac{3}{2}) \\ \times F_{J}(\phi_{d}, \mathscr{E}_{l}, \delta)^{2}\}^{-1}.$ (C4)

After some manipulation on Eqs. (30), (48), (49), and (C3) one arrives at the result

$$\begin{pmatrix} \frac{\partial C_{\text{DON}}}{\partial L} \end{pmatrix}_{\phi_d} = -[I_J(\phi_d, \mathcal{E}_l, \delta; \frac{3}{2})]^{-3} \\ \times F_J(\phi_d, \mathcal{E}_l, \delta)^{-2} \times \{3I_J(\phi_d, \mathcal{E}_l, \delta; \frac{5}{2}) \\ -2I_J(\phi_d, \mathcal{E}_l, \delta; \frac{3}{2})F_J(\phi_d, \mathcal{E}_l, \delta)^{-2} \\ -B_J(\phi_d, \mathcal{E}_l, \delta)[I_J(\phi_d, \mathcal{E}_l, \delta; \frac{3}{2})]^2\}.$$
(C5)

In the limit of  $|\phi_d| \ll 1$ , one can make the usual small  $\phi_d$  expansion of  $R_J(\phi_d, \delta)$  and evaluate the resulting integrals. After some calculation one finds that

$$\left(\frac{\partial C_{\rm DON}}{\partial L}\right)_{\phi_{\rm d}} \approx -\mathscr{E}_{\rm l}^2/\phi_{\rm d}^2.$$

The validity of this result depends only on  $|\phi_d|$  being small and is true for all  $\mathcal{E}_l$ . In particular, from Eq. (31) one sees in the limit of  $\phi_d$  going to 0 that  $(\mathcal{E}_l/\phi_d)^2 = \lambda^2 \operatorname{csch}^2(\lambda L)$ , so that the above asymptotic expression for  $\partial C_{\text{DON}}/\partial L$  agrees with Eq. (58). At  $\phi_d$  and  $\delta$  fixed, to use Eq. (C5) to find directly the value  $\mathcal{E}_l^0(L_0)$  at which  $C_{\text{DON}}$  has

a minimum would in general involve more computation than an implicit calculation of  $C_{DON}$  vs L such as was performed in generating the data of Figures 3 through 6. However, as these figures indicate, the minima occur at small L (large  $\mathscr{E}_{l}$ ). Hence if one assumes that

$$(\mathscr{E}_l^0)^2 \gg \frac{\ln\left[1+R_J(\phi_d,\delta)\right]}{\delta},$$

then the integrals can be approximated by their upper bounds as  $I_J(\phi_d, \mathcal{E}_l, \delta; \alpha) \simeq |\phi_d|/|\mathcal{E}_l|^{2\alpha}$  and, for fixed  $\phi_d$  and  $\delta$ , the zeroes of Eq. (C5) occur approximately for  $\mathcal{E}_l^0$  which satisfies

$$\begin{bmatrix} 1 + \frac{3\ln\left[1 + R_J(\phi_d, \delta)\right]}{\delta(\mathscr{E}_l^0)^2} \end{bmatrix} \frac{|\phi_d|}{|\mathscr{E}_l^0|^3} - \beta_J(\phi_d, \delta) \\ \times \frac{\phi_d^2}{|\mathscr{E}_l^0|^5} \left[ 1 + \frac{\ln\left[1 + R_J(\phi_d, \delta)\right]}{\delta(\mathscr{E}_l^0)^2} \right]^{1/2} = 0, \quad (C6)$$

where

$$B_{J}(\phi_{d}, \delta) \equiv B_{J}(\phi_{d}, \mathscr{E}_{l}, \delta) |F_{J}(\phi_{d}, \mathscr{E}_{l}, \delta)|.$$
(C7)

In the limit that  $\ln [1 + R_J(\phi_d, \delta)] / \delta(\mathscr{C}_l^0)^2 \ll 1$ , one gets the result that

$$\mathscr{E}_l^0 \simeq \operatorname{sgn}(\phi_d) [\beta_J(\phi_d, \delta) |\phi_d|]^{1/2}. \quad (C8)$$

To investigate the consistency of this approximation, it is necessary to know under what conditions (values of  $\phi_d$  and  $\delta$ ) it is true that  $\ln[1 + R_J(\phi_d, \delta)]/[\delta\beta_J(\phi_d, \delta) |\phi_d|]$  is small compared to 1. As  $\phi_d$  tends to 0, this ratio tends to 1. Similarly for  $|\phi_d| \ge -\ln \delta$  the desired inequality is not satisfied. For  $\phi_d$  in the range  $|\phi_d| \ge 6$  and  $\delta \exp(|\phi_d|) \ll 1$  one has that

$$\frac{\ln\left[1+R_{J}(\phi_{d},\delta)\right]}{\delta\beta_{J}(\phi_{d},\delta)\left|\phi_{d}\right|} \approx \frac{2}{\left|\phi_{d}\right|}$$

So in the Gouy-Chapman limit with  $|\phi_d| \ge 6$ , Eq. (C8) gives at least a qualitative estimate of  $\mathscr{E}_l^0$ . In this limit one has that

$$\mathscr{E}_{l}^{0} \simeq \operatorname{sgn}(\phi_{d}) \sqrt{\frac{|\phi_{d}|}{2}} \exp(|\phi_{d}|/2). \quad (C9)$$

While accurate to within about 10% for  $|\phi_d| \ge 25$ (assuming of course that  $\delta \exp(|\phi_d|) \ll 1$ ), Eq. (C9) needs improvement for smaller potentials. In the Gouy-Chapman limit Eq. (C6) reduces to

the following:

$$(\mathscr{E}_{l}^{0})^{2} \left[ 1 + \frac{3 \exp(|\phi_{d}|)}{(\mathscr{E}_{l}^{0})^{2}} \right] - \frac{|\phi_{d}| \exp(|\phi_{d}|)}{2} \left[ 1 + \frac{\exp(|\phi_{d}|)}{(\mathscr{E}_{l}^{0})^{2}} \right]^{1/2} = 0. \quad (C10)$$

By expanding the square root, one has as an approximation to Eq. (C10) an equation quadratic in  $(\mathscr{C}_l^0)^2$ . Upon taking the positive root one obtains the result that

$$\mathcal{E}_{l}^{0} \simeq \operatorname{sgn}(\phi_{d}) \sqrt{\frac{r(|\phi_{d}|)}{2}} \exp(|\phi_{d}|/2), \quad (C11)$$

where r(x) is defined by Eq. (67). By approximating Eq. (C3) as  $|\phi_d/\mathscr{E}_1^0|$ ,  $L_0$  is given by Eq. (65). In the limit of very large  $|\phi_d|$ ,  $r(|\phi_d|)$  tends to  $|\phi_d|$  and Eqs. (C9) and (C11) become identical. To estimate  $\Delta C_N(\phi_d, L_0, \delta = 0)$  one first notes that

$$F_J(\phi_d, \mathscr{E}^0_l, \delta = 0) \simeq \operatorname{sgn}(\phi_d) \exp(|\phi_d|/2) \sqrt{1 + \frac{r(|\phi_d|)}{2}}.$$

Hence, if one approximates  $I_J(\phi_d, \mathscr{E}_l^0, \delta; \frac{3}{2})$  by  $|\phi_d|/|\mathscr{E}_l^0|^3$ , Eq. (66) follows directly from Eqs. (48) and (C4).

Comparison of the results of Eqs. (65) and (66) with a detailed numerical determination of the minima reveals that Eq. (65) is accurate to within 1.2% for  $|\phi_d| \ge 7$  with the discrepancy less than 0.33% by  $|\phi_d| = 25$ . The agreement of Eq. (66) is not quite as good, being only 14.7% at  $|\phi_d| = 7$ . However, by  $|\phi_d| = 25$  the difference is less than 0.3%.

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