

INTERACTING LATTICE GAS APPROACHES TO SPACE CHARGE DISTRIBUTIONS

J. Ross Macdonald, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, N.C. 27514; D. R. Franceschetti, Department of Physics, Memphis State University, Memphis, TN 38152; and A. P. Lehnen, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, N.C. 27514

Two different lattice gas models of the diffuse space-charge layer at a blocking electrode are discussed and their predictions compared to those of the conventional continuum Gouy-Chapman approach and to recent Monte Carlo results for the primitive model of an aqueous electrolyte. Self-consistent results of both lattice gas approaches can differ appreciably from Gouy-Chapman predictions but may be made to agree well with the Monte Carlo calculations.

The ionic diffuse double layer (DDL) plays an important role in the electrical behavior of solid and liquid electrochemical systems, colloids, and living cells. The conventional Gouy-Chapman (GC) theory of the equilibrium DDL in ionically conducting liquids and solids involves a continuum treatment of point charges and is well known to be inaccurate at high charge concentrations. Several complex treatments of the DDL have recently appeared^{1,2,3} but seem difficult to extend to high concentrations and potentials. Here we discuss a much simpler liquid lattice gas model^{4,5} (LLGM) which extends up to close packing and yields excellent agreement with recent Monte Carlo DDL results.⁶

A lattice gas treatment of the space charge in an ionic single crystal is appropriate when the charged defect concentration is not negligible compared to the normal concentrations of atom or anion or cation sites in the crystal. This condition may occur in a superionic conductor, where the undisturbed relative bulk charge concentrations can be very high, and/or it can occur in the interface diffuse double layer region of an ionic crystal when an applied potential difference leads to a high concentration there of positive or negative charge. Here we are concerned with equilibrium space charge distributions appropriate for a semi-infinite material with a completely blocking electrode. We compare lattice gas results obtained without detailed interactions between charges but which, of course, satisfy Poisson's equation, with those where mean field or Bragg-Williams interactions are included as well.^{5,7}

Because accurate experimental results for the dependence of the integrated charge in the DDL, q_d , vs. the potential across it, ψ_d , are unavailable, theoretical results must be compared with Monte Carlo (MC) calculations. The only ones available thus far are for the primitive model of an aqueous electrolyte: a model which involves a collection of mobile positive and negative spherical ions of equal diameter d in surroundings defined entirely by the unsaturated room-temperature dielectric constant of water,

$\epsilon_p = 78.5$. It is unfortunate that no appropriate DDL lattice gas MC results are yet available for comparison. But recent MC results⁸ show only relatively small differences between the average potential per ion in the bulk found for a continuum (liquid) MC calculation and for a lattice MC calculation with ions of the same size. Further, a lattice approximation has also been successfully employed for bulk calculations of ionic solutions.⁹ We thus expect that our fitting of lattice gas theoretical results to continuum MC results will alter some of the derived parameters somewhat but will not lead to qualitatively incorrect conclusions. If so, the present relatively simple LLGM theory will be of value for both liquid and single crystal situations.

In the LLGM we use the mean-field correction to account for any residual interactions not already incorporated in Poisson's equation; some of these residual effects arise from the difference between the potential of mean force on an ion and the average electrostatic potential, ψ , used in Poisson's equation.

In the LLGM with mean-field interactions (LLGM/MF), let α be the normalized pair interaction energy between charges of like sign; when $\alpha < 0$, such residual interactions between like-sign pairs are attractive.^{5,7,10,11} We assume the normalized pair interaction energy between charges of unlike sign to be $-\alpha$. The quantity α involves, for example, all nearest like-sign neighbor interactions or can also be considered to include all mean field residual interactions of a given charge and its like-sign near and far neighbors.

Let N be the LLGM site concentration. For FCC close packing of spheres of diameter D , $N = \sqrt{2}/D^3$. Since N will be used as a fitting parameter, we have made a distinction here between d and D . When the molarity of an ionic solution is M , the common bulk concentration of positive and negative ions, c_0 , is $6.022 \times 10^{20} M \text{ cm}^{-3}$. Finally, define the fractional bulk concentration

$\delta \equiv c_0/N \approx 4.26 \times 10^{-4} D^3 M$, where D is in Å. Then the LLGM/MF yields for the normalized local charge density,^{5,7,10,11} $\rho^* \equiv \rho/eN$,

$$\rho^* = -2\delta \sinh(\phi_1) / [1 - 2\delta + 2\delta \cosh(\phi_1)] \quad (1)$$

where $\phi_1 \equiv \phi + \alpha \rho^*$, and $\phi \equiv e\psi/kT$, the normalized local potential. The total normalized charge in the diffuse layer is

$$Q_d \equiv q_d/\sigma_n = -\text{sgn}(\phi_d) [\delta^{-1} \int_0^{\phi_d} \rho^*(\phi) d\phi]^{1/2} \quad (2)$$

where ϕ_d is the total normalized p.d. across the diffuse layer, $\sigma_n \equiv 2ecL_D$, and L_D is the bulk Debye length. Note that iteration of Eq. (1) to find the converged, self-consistent value of ρ^* is usually required for each ϕ value of interest and thus Q_d must be calculated using numerical integration. When $\alpha = 0$ and $N \rightarrow \infty$ so $\delta \rightarrow 0$, however, $\rho \rightarrow -2ec \sinh(\phi)$ and $Q_d \rightarrow -2 \sinh(\phi_d/2)$, the usual GC results. Alternatively, when $|\phi_1| \ll 1$, $\rho^* \approx -2\delta\phi/[1 + 2\delta\alpha]$ and for $|\phi_d| \ll 1$ as well, $Q_d \approx -\text{sgn}(\phi_d)\phi_d^2/[1 + 2\delta\alpha]$, and no iteration is required.¹⁰

Figure 1 shows a comparison of LM liquid-like MC results⁶ and the LLGM/MF with various values of α .¹¹ Here we took $D = d = 4.25 \text{ \AA}$, so $N = 1.84 \times 10^{22} \text{ cm}^{-3}$ and $\delta \approx 0.033$. The $\alpha = -3$ curve yields agreement with the MC points to within one standard deviation of these values. Incidentally, when $\alpha \lesssim -4$, Eq. (1) becomes triple valued over a finite ϕ range, indicating instability and a phase change.¹⁰ Although $\alpha < 0$ introduces positive feedback, the system is still stable at $\alpha = -3$. The negative value of α required here implies that the continuum Poisson equation solution (marked MGC on Fig. 1) overcompensates for the ion-ion Coulomb interactions and this must be cancelled by the like-ion residual attraction introduced by negative α . The curvature in the $\alpha = -3$ curve for $\phi_d > 3$ arises from the approach to close packing of ions of the same sign in the part of the diffuse layer closest to the blocking electrode. But even for smaller ϕ_d values one sees very significant differences between the MC and MGC results. Clearly a theory is required which both corrects for interaction overcompensation and for the finite size of ions, as does the LLGM/MF. None of the more complicated DDL theories has yet been able to be extended to charges and p.d.'s as large as considered here. Thus the present theory is both the simplest and the only one yet available which can yield agreement with the full span of the MC results.

But the present approach will be of value only if it applies for arbitrary M as well as $M = 1$. Unfortunately, there are fewer MC points currently available at $M < 1$ than at $M = 1$ but some comparison is still possible. If one keeps $D = d$, then at $M = 0.1$ and 0.01 , $\delta \approx 3.27 \times 10^{-3}$ and 3.27×10^{-4} , respectively. With α still at -3 , one finds poor agreement with the MC results,⁶ especially for $M = 0.01$. At $M = 0.1$, reasonably good agreement is obtained with $\alpha = -3.4$. But it seems more appropriate to keep α independent

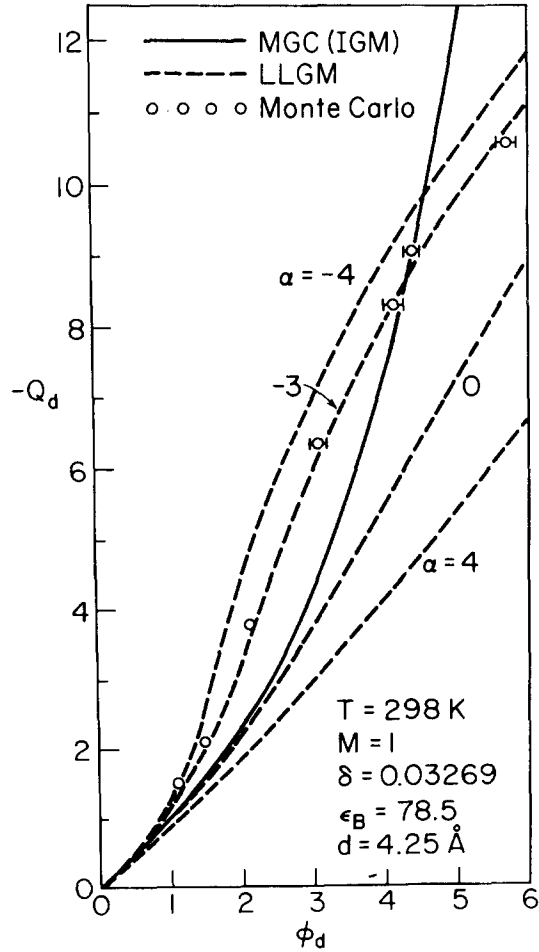


Figure 1: Integrated diffuse double layer charge as a function of layer potential difference from MC and LLGM/MF calculations; LM solution.

of M and let N (and thus D) vary with M as necessary. With $\alpha = -3$, one then finds quite good agreement with the few MC points available. The best-fit values of δ are 5.2×10^{-3} and 1.6×10^{-3} for $M = 0.1$ and 0.01 . Note that δ here varies very closely as M^2 rather than M in this range. The two associated values of D are about 4.96 \AA and 7.22 \AA . It appears that approximating a liquid space charge situation by a lattice gas theory requires that the lattice spacing increase as the mean separation between charges increases. This is at least a reasonable direction for the variation, and further MC results should allow one to pin down more closely the dependence of N (and possibly α) on M , T , d , and ϵ_B . The LLGM/MF approach is appropriate for Schottky-defect single crystal situations as

well as liquids and needs only minor modifications for Frenkel defect materials.^{4,5,7}

The MGC and LLGM approaches are only reasonable for single crystals when there are many crystal planes contained within a local Debye length. But in high concentration materials or regions near an electrode, this requirement is often unsatisfied. Let $\Delta \equiv a/L_D$, where a is the planar spacing perpendicular to the electrode and L_D is the bulk Debye length. It occurred to us⁷ that it might be reasonable to treat $\Delta > 0.01$ situations by means of a two-dimensional lattice gas, with or without mean-field corrections, for each separate plane, and to apply Gauss' law to pass from plane to plane. We shall term this the quasi-discrete lattice gas model (QDLGM). The average charge density in a plane for the QDLGM will be $q = \rho a$. Let the index i denote the i th plane with $i = 0$ for the electrode, charge q_i ; $i = 1$ for the first plane of the crystal parallel to the electrode, etc. Now normalizing all planar charges with σ_m , we find^{4,5,10} $Q \equiv (q/\sigma_m) = \Delta \cdot \rho^*/2\delta$ and, for the normalized charge in the i th plane ($i \geq 1$) where the normalized electrostatic potential is ϕ_i ,

$$Q_i = \frac{-\Delta(1-\eta\delta_s)\sinh(\phi_{ei})}{1-2\delta_s(1-\eta\delta_s) + 2\delta_s(1-\eta\delta_s)\cosh(\phi_{ei})}, \quad (3)$$

where $\phi_{ei} \equiv \phi_i + \alpha Q_i$, $\delta_s \equiv \Gamma/\Gamma_s$ is the fractional bulk concentration of charge of either sign in the absence of space charge, and Γ_s is the two-dimensional site concentration. For simplicity we shall use δ hereafter, however, to represent either $\delta \equiv c_0/N$ or δ_s . The quantity η in Eq. (3) is zero for the LLGM and unity for the Schottky defect lattice gas model (SLGM). Unless $\delta \gtrsim 0.1$, there will be little difference between the LLGM and the SLGM. Equation (3) applies for $i > 1$; for $i = 0$ the appropriate normalized charge is Q_0 , the charge on the metal electrode; thus we may define $Q_0 = Q_m$.

It will be noted that when $\alpha \neq 0$, Eq. (3) again requires iteration to obtain the self-consistent Q_i , given ϕ_i . But there is a further complication in the present theory. It is necessary for a completely blocking electrode that $Q_m + Q_d = 0$, where $Q_d \equiv \sum_{i=1}^{\infty} Q_i$, the entire charge in the diffuse layer. If we define $Q_{smi} \equiv \sum_{j=0}^i Q_j$, it is thus necessary, for specified Q_d , to pick a Q_0 such that $Q_{smi} \rightarrow 0$ as $i \rightarrow \infty$. We have solved this problem by an iterative shooting method and generally find that with double precision calculations it is practical to find a $Q_m(\phi_d)$ which leads to Q_i values essentially correct for 15 or more Debye lengths. By this point, where $i \geq 15/\Delta$, Q_i is negligibly small.

It only remains to find ϕ_i . Let $\phi_0 \equiv \phi_m$ and $\phi_1 = \phi_d$. Then Gauss' law yields the normalized relation $\phi_{i+1} = \phi_i + \Delta \cdot Q_{smi}$, $i = 0, 1, 2, \dots$. Here ϕ_i is the normalized potential at the i th plane whose charge is Q_i . We have here implicitly assumed that the effective separation be-

tween the electrode equipotential plane and the charge centroids of the first charge layer is a , but this assumption is readily generalized. If one specifies ϕ_m as an input, one solves the modified LGM, a solution which approaches that of the MGC model when $\Delta \rightarrow 0$, $\delta \rightarrow 0$, and $\alpha \rightarrow 0$. In keeping with the approach of the first part of this work, however, we shall take ϕ_d as the input value rather than ϕ_m . It is worthwhile to point out that specific ionic adsorption effects (or intrinsic Frenkel space charge layers) can be added to the present approach by replacing $\phi_{e1} = \phi_1 + \alpha Q_1 = \phi_d + \alpha Q_1$ by $(\phi_d + \phi_s + \alpha Q_1)$, where the constant ϕ_s determines the amount of space charge present when $\phi_d = 0$.

Figure 2 shows how the normalized local potential varies with $X \equiv x/L_D$ for $\eta = 1$, $\alpha = 0$, $\Delta = 1$, and $\delta = 10^{-3}$. Distance is measured from the blocking electrode at $x = 0$. Between planes the normalized potential ϕ decreases linearly, but this leads to the curved sections in this semi-log plot. It is clear that the larger ϕ_d the larger the proportion of ϕ_d which appears between the first and second layers (at $X = 0$ and 1). From the third layer onwards the potential at each plane decreases very nearly proportional to $\exp(-X)$, just as in the continuum GC solution.

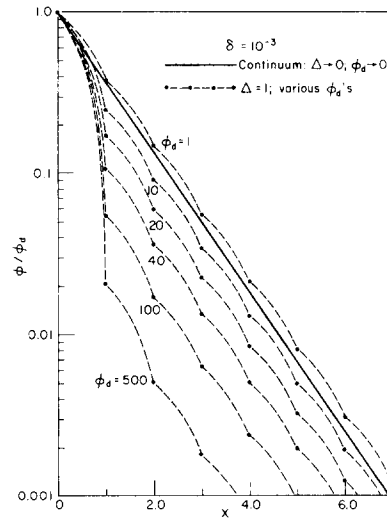


Figure 2: Normalized potential vs normalized distance for the QDLGM.

For comparison with Fig. 1, Fig. 3 shows how Q_d depends on ϕ_d for $\eta = 1$, $\alpha = 0$, $\Delta = 1$, and various δ values. As shown, for small ϕ_d the curves lie to the left of the MGC curve. Thus the present approach needs no $\alpha < 0$ values to achieve compensation of the excess Coulomb interaction effects incorporated in the continuum GC model. On the other hand, there is no

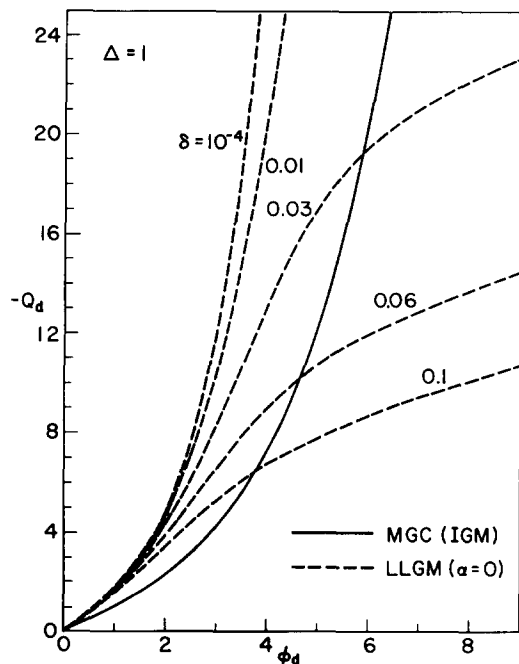


Figure 3: Integrated diffuse double layer charge as a function of layer potential difference for QDLGM; $\Delta = 1$ and δ variable.

guarantee that a given Δ value will give the correct compensation with $\alpha = 0$. As an example, the present model with $\alpha = 0$ was fitted to the $M = 1$ MC results⁶ by nonlinear least squares, yielding a good fit with $\delta \approx 0.0608$ and $\Delta = 0.843$. If one takes a HCP array of $d = 4.25$ Å ions, $\Gamma_s = 2/\sqrt{3}d^2 \approx 6.39 \times 10^{14}$ cm⁻². But if we write $\delta = \delta_s = \Gamma/\Gamma_s = ac/\Gamma_s$ and remember that $\Delta = a/L_D$, where $L_D^s = 3.04/\sqrt{M}$ Å for the aqueous primitive model used in the MC calculations, we see that we have two expressions with which to calculate a . The first yields $a \approx 6.45$ Å and the second 2.56 Å, very poor agreement. Further, the second value is less than the sterically imposed minimum value of a , $d\cos(30^\circ)$, 3.68 Å. Although the QDLGM can also fit the $M = 0.1$ and 0.01 MC results, again the Δ and δ values lead to ambiguous results. It appears that when the present LGM for a crystalline solid is applied to liquid MC results, one can't interpret the values of Δ and δ obtained from a sensible physical point of view but must just use them as fitting parameters. Possibly with a $\neq 0$ (and positive) more consistent and physically plausible results could indeed be obtained but this option has not yet been investigated.

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