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# MEAN FIELD EFFECTS IN A LATTICE GAS MODEL OF IONIC SPACE CHARGE

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**Abstract**—Lattice gas models of the diffuse space charge layer in liquids and in ionic solids with Schottky or Frenkel disorder are considered with and without mean-field charge-interaction corrections. Even without explicit interaction corrections, the lattice gas model, by taking some account of charge carrier size in the liquid case and the actual lattice structure of the material in the case of single crystal solids, predicts a saturation in local charge density at high potentials, unlike the physically less realistic conventional Gouy-Chapman ideal gas, or independent particle model. Both unmodified and modified mean field corrections to the lattice gas basis are discussed and Coulombic interaction terms are considered in detail. The Monte-Carlo results obtained by other workers show that, as expected, the actual mean-field interaction terms required for fitting must be much smaller than those predicted by the unscreened Coulombic interaction. It is suggested that the mean field approach of Gurevich and Kharkats, who introduce an attractive mean field interaction between charges of like sign, is unlikely to be applicable over the entire space charge region of solid electrolyte systems and thus may not provide an explanation for the conductivity instability observed in $\alpha$-AgSbS$_2$. Some possible future directions of investigation for lattice gas models are also briefly discussed.

## 1. INTRODUCTION

Gurevich and Kharkats[1] (abbreviated hereafter as GK) have recently published a very interesting note in Solid State Communications which indicates that a lattice gas model[2] of space charge in a Frenkel-defect single crystal can, with the addition of mean-field nearest-neighbor interaction terms, exhibit an abrupt change in ionic conductivity as the electric field, or applied potential difference, is increased. For some time we have been independently investigating lattice gas models for space charge with and without mean-field corrections[3–7]. Unfortunately, we were ignorant of the earlier work of GK[8–11] in which some of our capacitance results had already been derived[8]. Luckily our work supplements theirs since we also consider surface adsorption effects and analyze in more detail then they a system of finite length with one blocking and one ohmic electrode[7].

Here we wish to deal with some of the implications of adding mean field interaction terms to the free energy in some specific lattice gas models, taking for simplicity a system with one blocking electrode at $x = 0$ and an ohmic one at infinity[3–5]. As in the earlier work[1–11], we shall consider a uni-univalent material with a single negative species of mobile charge, concentration $c_1$, and a single positive species of mobile charge, concentration $c_2$. The lattice gas models to be analyzed are of the liquid (e.g. aqueous electrolyte or possibly fused salt), Schottky defect, and Frenkel defect types. We shall assume in each case a face-centered cubic lattice.

## 2. ANALYSIS

In the liquid lattice gas model (LLGM) we assume that charges of both signs are to be found on a single FCC lattice. The lattice points have a concentration of $N$ points/cm$^3$ and may be unoccupied (or occupied by a neutral species), occupied by a negative charge carrier, or occupied by a positive charge carrier. When the two species of ions are of such different sizes that the larger blocks more than one site, one can readily modify the analysis to account for such blocking[2]; here we consider only situations where this is unnecessary. It is clear that a lattice gas model of a liquid is an approximation. Nevertheless, lattice gas models have been reasonably successful in the theory of liquids; at high charge concentration one would expect the formation of a lattice of finite-size charge carriers in a liquid[12]; and the lattice model, by taking some account of the finite size of charge carriers, should certainly be a better approximation than the conventional Gouy–Chapman[13, 14] model of the diffuse double layer which ignores ion size entirely. The Gouy–Chapman model is essentially an ideal gas model and will be abbreviated IGM.

In the lattice gas model for solids, which is certainly more physically based than the LLGM, one assumes that negative charges reside on a lattice of concentration $s_1N$ and positive ones on an interpenetrating lattice of concentration $s_2N$. Let $N_i = s_iN$. For the typical Schottky defect case (SLGM) where the charge carriers are vacancies in a crystal lattice of the NaCl type, $s_1 = s_2 = 1$, while for the usual Frenkel case (FLGM), where the carriers are cation interstitials and cation vacancies in a lattice of the AgCl type, $s_1 = 1$ and $s_2 = 2$. In both cases $N$ is the concentration of positive or negative ions in a perfect ionic crystal. GK[8] have also considered the $s_2 \gg s_1$ case.

Let $i = 1$ denote negative and $i = 2$ positive charge carriers and take $j \equiv 3 - i$ and $k$ independent of $i$. The common equilibrium bulk value of $c_1$ and $c_2$ in the region of electroneutrality is $c_0$. Let $C_i \equiv c_i/N_i$; $\delta \equiv c_0/N$, the fractional bulk concentration; and $\Delta_i \equiv \delta/s_i$. For maximum conciseness we define $s_1 = s_2 = 1$ for the LLGM as well as the SLGM. Let $\phi \equiv e\psi/kT$, where $\psi$ is the inner potential at some point $x$ in the material. The total applied potential difference between the beginning of the diffuse layer at $x = 0$ and an ohmic electrode at $x = \infty$ is, in normalized form, $\phi_d = e\psi_d/kT$. Thus $\phi(0) = \phi_d$ and $\phi(\infty) = 0$.

The actual applied p.d., $\Psi_m$, between a blocking electrode and the ohmic electrode is never exactly $\psi_d$ (when $\psi_d \neq 0$), as it may be in Gouy–Chapman IGM theory, because the finite size of charge carriers must be taken into account. The centroid of charge of each charge carrier in the first plane of the diffuse layer is necessarily separated from the equipotential plane of a blocking metal electrode by a distance which, in the LLGM, would be at least as large as the sum of about 0.5 A of field penetration into the electrode and a radius of an ion nearest the electrode. If this distance is denoted by $\beta$ and the capacitance of parallel planes a distance $\beta$ apart is defined as $C_\beta$, then $\psi_m$ must differ[6] from $\psi_d$ by the p.d. across $C_\beta$. It has recently been proved[15] under rather general conditions that $\psi_m$ is a monotonically increasing function of the total net charge density (charge/unit area) $q_d$ in the diffuse layer. This result does not, however, necessarily preclude the possibility of non-monotonic behavior of $\psi_d$ and $q_d$ such as that found by GK[1, 9–11].

To facilitate the presentation of results we define a quantity $\theta$, where $\theta = 1$ for the LLGM and $\theta = 0$ for the SLGM and FLGM cases. Minimization of the free energy for a lattice gas situation with mean field interactions between charge carrier pairs [1, 4, 5, 9–11] can be shown[4–6] to lead to the following distributions for the $C_i (i = 1, 2)$,

$$\frac{C_i}{1 - C_i - \theta C_j} = \frac{\Delta_i}{1 - \Delta_i(1 + \theta)} \exp(\phi_{ei}), \tag{1}$$

where

$$\begin{aligned} \phi_{ei} = (-1)^{i+1}\phi - \Gamma_{ii}(C_i - \Delta_i) \\ + \Gamma_{ij}(C_j - \Delta_j). \end{aligned} \tag{2}$$

The $\Gamma_{ii}$ and $\Gamma_{ij}$ terms arise from the interactions between the charge carriers, with $\Gamma_{ij} = \Gamma_{ji}$. For non-interacting lattice gas models $\Gamma_{ik} = 0$[2, 3, 6–8]. The signs in eqn (2) have been chosen so that all the $\Gamma_{ik}$ are positive when the net interaction between charges of like sign is repulsive and that between charges of unlike sign is attractive. Notice that when $\phi = 0$ (as at $x = \infty$), eqn (1) and (2) are consistent with the electroneutrality requirement $c_i \to c_0$ which implies $C_i \to \Delta_i$. The present normalization ensures that the maximum value of the $C_i$'s is unity.

For the $\theta = 0$ solid LGM cases GK[1, 9–11] obtain essentially the same results as those of eqns (1) and (2), but they take $i = 1$ for positive and $i = 2$ for negative carriers, the opposite of our choice. Further, they employ coefficients $\lambda_i$ and $\lambda_{12}$ which are related to our $\Gamma_{ik}$ by

$$\lambda_i = -kT\,\Gamma_{ii} \tag{3a}$$

and

$$\lambda_{12} = kT\,\Gamma_{12}. \tag{3b}$$

Thus, when their $\lambda_i$ coefficients are positive, charge carriers of the same sign are taken to have an attractive interaction.

### 3. SPECIFIC MEAN FIELD INTERACTION TERMS

Gurevich and Kharkats do not give a microscopic derivation of their $\lambda_i$ and $\lambda_{12}$ terms beyond stating that the interactions may be indirect. The form of the interaction terms in GK[9–11] and eqn (2) follows from a mean field or Bragg–Williams treatment of interactions[17–20]. This is an approximate approach which takes nearest neighbor interactions into account and in so doing assumes that "there is no short-range order apart from long-range order"[19]. It is strictly applicable only in the low density ($\delta \to 0$) limit, since it assumes in calculating the energy and entropy that the interacting entities are randomly distributed on their lattices. Further, for a given finite value of $\delta$ the approximation is best for interaction energies smaller than or comparable to $kT$ and becomes increasingly unreliable as the magnitude of the interaction energy increases.

The Bragg–Williams approximation was originally developed for binary alloys and has been applied to spins (e.g. Ising model) and to adsorbed atoms and molecules. In such situations the mean field corrections involve only two possible states for each lattice site. Here we are concerned with a three state model in which a lattice site may be empty (effectively uncharged) or occupied by a positive or negative charge carrier. While the mean field treatment of this three state case is mathematically straightforward, it is a somewhat uncertain step to apply it to charged entities because of their long range and quite strong Coulomb interactions. But as we shall see, comparison of LLGM predictions with diffuse-space-charge-layer Monte-Carlo results strongly suggests that the $|\Gamma_{ik}|$'s involved in a LLGM with mean field interactions can be considered to represent residual interactions only, with the bulk of the strong Coulomb interaction between charges already implicitly incorporated in the noninteracting ($\Gamma_{ik} \equiv 0$) IGM or LLGM solutions through their satisfaction of Poisson's equation. Because the required mean field corrections are thus small there is a good chance that they can yield a valid improvement over treatments without them. If one wishes to obtain an even better approximation and yet to retain the general form of the results of eqn (1) and (2), one will have to make the $\Gamma_{ik}$ coefficients dependent on the local concentration or field.

We shall first consider the $\Gamma_{ik}$ coefficients for the full Coulomb interaction and then compare numerical results with those obtained from the Monte-Carlo fitting. For a FCC ionic solid let $a_0$ be the conventional cell edge distance. Then $d = a_0/2$ is the lattice spacing (that between nearest unlike charges in a perfect cubic ionic crystal), and $d = (2N)^{-1/3}$. In the LLGM we shall here take $d$ as the diameter of an ion. We take the Coulomb interaction energy, $u_0$, between like charges a distance $d$ apart to be $e^2/4\pi\epsilon_0\epsilon d$, where $\epsilon_0$ is the permittivity constant for free space and $\epsilon$ is an effective dielectric constant. Although an effective $\epsilon$ should properly be obtained in a fully discrete treatment by taking the induced polarizability of each charge carrier directly into account[12], the use of an $\epsilon$ of the order of the index of refraction squared is probably a better approximation than taking $\epsilon$ either unity or $\epsilon_B$, where $\epsilon_B$ is the bulk dielectric constant. Finally we define $U_0 \equiv u_0/kT$.

Since there are no interactions assumed between empty sites or empty and charged sites, one finds that naive Bragg-Williams theory adds interaction terms to the Gibbs free energy of the system of the form $u_0\chi_{ik}c_ic_k$. Here $\chi_{ik}$ involves three factors: the number of nearest neighbor positions, the distance between $i$ and $k$ charges (in units of $d$), and a factor of 0.5 when $i = k$ and $-1$ when $i \neq k$. The factor of 0.5 takes account of duplicate counting for identical charge pairs. Minimization of the free energy involving both the ordinary lattice gas entropy term and the $ik = 11$, 12, and 22 interaction terms leads to the distributions of eqns (1) and (2). The specific values of the $\Gamma_{ik}$'s for arbitrary $U_0$ following for the liquid, Schottky and Frenkel lattice gas models are summarized in Table 1. For the LLGM we have taken positive and negative ions of equal diameter $d$, and assumed face centered cubic close packing. Then $N = \text{p.f.}/[4\pi(d/2)^3/3]$, where the FCC packing fraction $\text{p.f.} = \pi/3\sqrt{(2)}$. For $d = 3\,\text{Å}$, $N = 5.2\times10^{22}\,\text{cm}^{-3}$. For a fused salt one might consider a lattice of charge with few empty sites, but for an aqueous electrolyte of medium molarity, there would be many more "empty" (occupied by water molecules) than charged sites.

Now it turns out that for the LLGM and SLGM cases, the normalized charge density $\rho^* \equiv \rho/eN$ is given by the implicit equation[4, 5]

$$\rho^* = \frac{-2\delta[1-\eta\delta]\sinh[\phi+\alpha\rho^*]}{1+4\delta[1-\eta\delta]\sinh^2[(\phi+\alpha\rho^*)/2]}, \tag{4}$$

where $\eta \equiv 1-\theta$ and we have ignored the difference between $6\sqrt{(2)}$ and 6 in the SLGM and have thus taken $\alpha \equiv \Gamma_{11} = \Gamma_{12}$ for both models. A somewhat more complicated expression for $\rho^*$ is found for the Frenkel case. Actually, since the $\Gamma_{ik}$'s are different in both the Schottky and Frenkel cases, a set of two coupled equations must be solved to obtain the self-consistent value of $\rho^*$ for a given $\phi$. The behavior then found is not qualitatively different, however, from that following from eqn (4), where a single equation, showing negative feedback when $\alpha > 0$, must be solved self-consistently. When $\alpha = 0$, eqn (4) reduces to the ususal LLGM and SLGM results without interaction[2, 6], and as $\delta \to 0$, LLGM and SLGM results for $\rho^*$ become identical. Some $\alpha = 0$ results for various $\delta$ values are shown in Fig. 1. The dashed lines show the non-saturating Gouy-Chapman behavior.

Some $\alpha \neq 0$ curves are presented in Fig. 2. Since $\rho^*(\phi)$ saturates, we may formally introduce a new variable $z$ through $\rho^* \equiv \tanh(z)$. Then the feedback term is of the form $\alpha\tanh(z)$. But Fig. 1 shows that virtual saturation (charge of a single sign filling all available sites in a given region), occurs at relatively low applied p.d.'s. The physics of the situation suggests, however, that the approach to complete saturation should be much slower and that complete saturation, a condition where a crystal might

Table 1. Values of the interaction parameters $\Gamma_{ik}$ for three lattice gas models

| Parameter | Liquid | Schottky | Frenkel |
|---|---|---|---|
| $\Gamma_{11}$ | $12U_0$ | $6\sqrt{2}U_0$ | $6\sqrt{2}U_0$ |
| $\Gamma_{12}$ | $12U_0$ | $6U_0$ | $(8/\sqrt{3})U_0$ |
| $\Gamma_{22}$ | $12U_0$ | $6\sqrt{2}U_0$ | $3U_0$ |

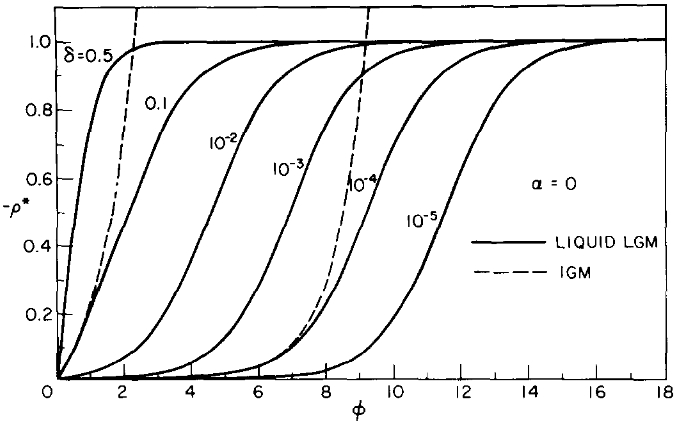


Fig. 1. Normalized charge density vs potential for liquid (noninteracting) lattice gas model and ideal gas model.

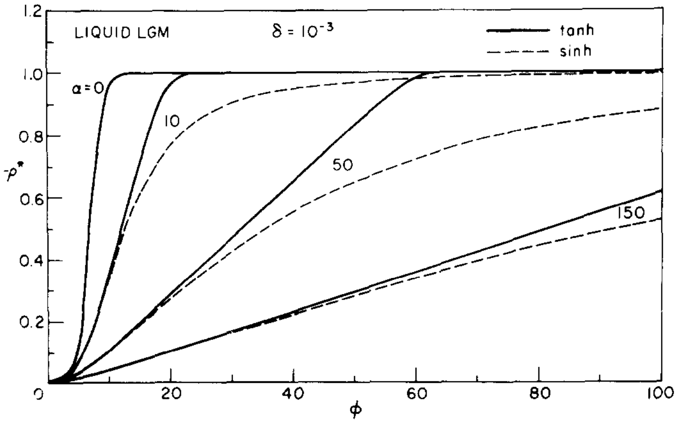


Fig. 2. Normalized charge density vs potential for liquid mean-field lattice gas model and proposed sinh modification.

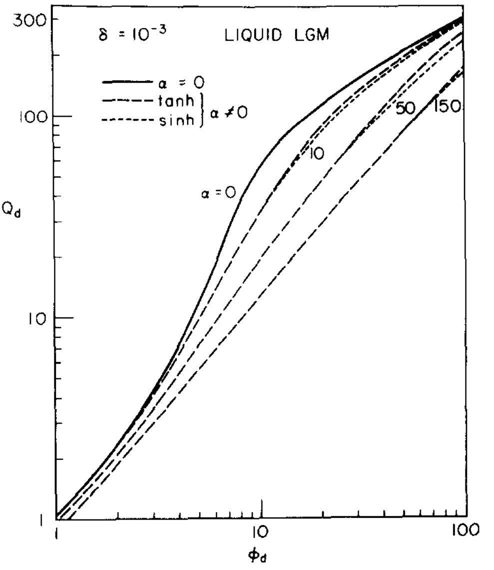
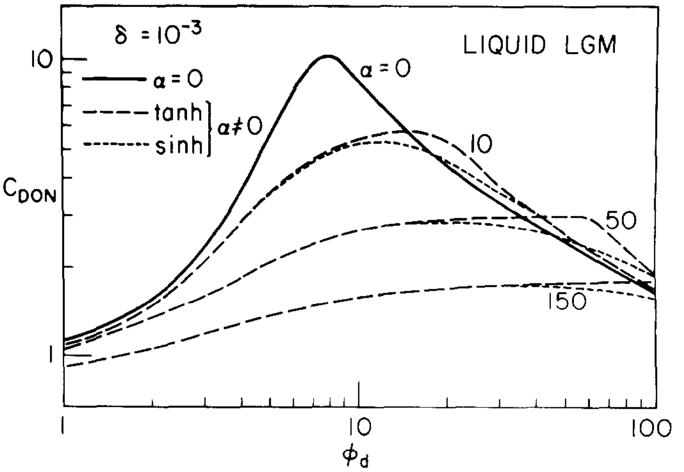


Fig. 3. Normalized integrated double layer charge vs double layer potential difference for noninteracting, mean field and sinh modification liquid lattice gas models.

fall apart, should be unreachable at finite applied p.d. A simple heuristic way to achieve this end when $\alpha > 0$ and to make little or no change far away from saturation is to replace the tanh $(z)$ term by sinh $(z)$ so that $\alpha\rho^*$ is replaced by $\alpha\rho^*/[1-(\rho^*)^2]^{1/2}$. Some tanh and sinh type interaction corrections are shown in Fig. 2 for several values of $\alpha$. The asymptotic approach to saturation for the sinh modification is evident. A more complex transformation would be required to achieve a similar approach to saturation for $\alpha < 0$.

Figure 3 shows the dependence of the normalized integrated charge in the double layer, $Q_d \equiv q_d/2ec_0L_D$, on the p.d. across the layer, $\phi_d$. Here $L_D$ is the two-mobile Debye length, which involves $c_0$. As we see, the sinh-modification results only differ from the tanh ones at high values of $\phi_d$. The normalized diffuse layer capacitance, $C_{DON} \equiv -\mathrm{d}Q_d/\mathrm{d}\phi_d \equiv C_{DO}/C_d$, where $C_d \equiv \epsilon_B/4\pi L_D$ is the $\phi_d \to 0$ limiting Gouy-Chapman capacitance per unit area, is shown in Fig. 4. It is important to note that the peak capacitance is essentially independent of $\delta$ when $\delta \leq 0.1$ for $\alpha$ either zero or non-zero. In the former case, the peak occurs at about[7] $\phi_d = \ln(2.51/\delta)$. This is somewhat more accurate than the value $\ln(2.75/\delta)$ given



Normalized diffuse double layer capacitance vs double layer potential difference for noninteracting, mean-field and sinh modification liquid lattice gas models.

by GK[8]. The $x = 0$ maximum value of $C_{DO}$ is about $0.319\ C_d/\sqrt{(\delta)}$, again when $\delta \leq 0.1$.

So far we have been using $\alpha$ as a rather arbitrary parameter. Now, however, let us evaluate it for Coulomb interactions in typical LLGM (NaF aqueous electrolyte) and SLGM (AgCl single crystal) situations. For the NaF electrolyte we shall approximate $Na^+$ and $F^-$ as sphere of 1 Å radius and consider that ions very close together either lose their hydration shells so that $d = 2$ Å or that they retain a single hydration sheath so that $d = 2(1\text{ Å} + 3\text{ Å}) = 8$ Å is the effective diameter of a hydrated ion approximated as a sphere. Now, the water molecules surrounding an ion are partly dielectrically saturated so that an appropriate value of $\epsilon$ to use in $u_0$ is about 15 in the second case[12] or 3 in the first. At $T = 298\ K$ the above values lead to $U_0 \simeq 93.5$ and 4.67 for the unhydrated and hydrated cases, respectively, and thus to $\alpha \simeq 1120$ and 56. The two values of $N$ are $1.77 \times 10^{23}\ \text{cm}^{-3}$ and $2.76 \times 10^{22}\ \text{cm}^{-3}$. For a 1 molar solution, the corresponding values of $\delta$ are about $3.4 \times 10^{-3}$ and 0.218. For AgCl near its melting point[6], $T = 700\ K$ and $\delta = 1.02 \times 10^{-3}$. Also for this material $N = 2.34 \times 10^{22}\ \text{cm}^{-3}$ and $d = 2.78$ Å. On using $\epsilon = 3$, one finds $U_0 \simeq 28.7$. If we take $\alpha$ as the average value of $\Gamma_{11}$ and $\Gamma_{12}$, one finds $\alpha = 7.24\ U_0 \simeq 208$.

Now we have already seen that $\alpha$ values even as small as 10 lead to appreciable differences between $\alpha = 0$ and $\alpha \neq 0$ results. Values of 200–1100 lead to much larger effects than are likely to occur. These results are direct indications of the inadequacy of naive mean field models with full Coulomb interactions. Further, it is important to note that significant difference may occur for all values of $\phi$. When $|\phi_{ei}|$ is so small that $\sinh(\phi_{ei}) \simeq \phi_{ei}$, eqn (4) may be solved directly to yield

$$\rho^* = -2\delta(1 - \eta\delta)\phi/[1 + 2\delta(1 - \eta\delta)\alpha]. \qquad (5)$$

The corresponding IGM result in the small $|\phi|$ region is just $-2\delta\phi$. For the LLGM, where $\eta = 0$, one sees that $\rho^*$ is altered by the factor $[1 + 2\delta\alpha]$, which may be appreciable. For the present unhydrated and hydrated LLGM situations one finds $2\delta\alpha \simeq 7.6$ and 24.4, while the SLGM AgCl results yield about 0.42. Even this last smaller value leads to difficulties.

There are some recent Monte-Carlo double layer results[21, 22] which involve 0.1 and 1 molar aqueous electrolyte solutions but only extend up to an equivalent $|\phi_d|$ of approx. 2. They give charge concentrations as a function of distance from a blocking electrode which appear to differ negligibly from IGM predictions. More recent Monte-Carlo calculations[23] give results for normalized $q_d$ vs $\phi_d$ up to nearly $\phi_d = 6$. These results differ appreciably from IGM predictions, even for $\phi_d = 1$. It has been shown[24] that these 1, 0.1 and 0.01 molar Monte-Carlo results can all be well fitted with $\alpha \simeq -3$. This value is much smaller in magnitude than predicted for Coulomb interaction and is negative, implying positive feedback. At room temperature it corresponds to a $|u_0|$ of only about $kT/4 \simeq 0.0064\ eV$. For one-molar conditions, $2\alpha\delta$ is of the order of $-0.2$, by no means negligible compared to unity.

Now GK[1, 9–11] have considered mean field interaction corrections to the LGM which involve $\Gamma_{ii}$ values both greater or less than zero. They do not calculate numerical values from a model but only consider qualitative behavior. They give little attention to the $\Gamma_{ii} > 0$ negative feedback situation which we have discussed in detail above. Instead, they are largely concerned with the $\Gamma_{ii} < 0$ case which involves attractive interactions between like charges. They find that for $\Gamma_{ii} < -4$ the resulting positive feedback leads to instability and a phase transition. This sort of instability has long been known in mean field treatments of attractive interactions between atoms or molecules[18, 25].

Gurevich and Kharkats seem to have been the first to apply a mean field theory of attractive interactions to ionic charges of the same sign, consistent with the above negative value of $\alpha$. The GK treatment predicts a phase transition from low to high conductivity only for a certain range of potentials, and thus it should occur only over a limited spatial region in the system. Further, GK state that the transition potential corresponds to a center of symmetry of the S-shaped concentration-potential curve. If indeed the $\Gamma_{ii} < -4$ situation were physically likely, we believe that the transition potential would have to be determined from minimization of the overall Gibbs free energy of the entire system and would not correspond to the center of symmetry, a concept not further defined by GK, but perhaps implying equal areas as in a Maxwell-type construction. Whatever the precise nature of the transition, one expects on qualitative physical grounds that the formation of a high concentration of mobile charge near an electrode would restrict most of the potential drop across the sample to a relatively thin double layer region at the electrode, leaving most of the electrolyte material in the original low conductivity state. Thus it seems somewhat doubtful that the treatment of GK provides an explanation of the observed instability of the conductivity of $\alpha$-$AgSbS_2$ as GK suggest.

For certain superionic conductor situations, work has been done involving attractive interactions between interstitials[26, 27] leading to $\Gamma_{ii} < 0$. Such interactions may arise from coupling to the strain field of the crystal[26] and lead to quite small ($10^{-2}$ to $10^{-1}$ eV.) contributions to the interaction energy. Although these contributions may play an important role in solids, the Monte-Carlo results which led to $\alpha \simeq -3$ are for a primitive model of a liquid, the reason the LLGM rather than the SLGM or FLGM was used. It thus appears that a negative value of $\alpha$ is required is such a situation to compensate for errors in the ordinary solution of Poisson's equation, errors introduced at least in part by the conventional replacement of the potential of mean force on an ion by the local continuum electrolyte potential. The negative value of $\alpha$ found suggests that the conventional solution overcompensates for Coulomb interactions and, e.g. in simplistic terms the ordinary attraction between charges of opposite sign must be reduced slightly by the mean-field-approach introduction of a small repelling force between them.

### 4. FUTURE DIRECTIONS

The Monte-Carlo results just discussed do not actually require that $2\delta\alpha$ be zero but only that it be relatively small in magnitude. Therefore, $\alpha$ may be used as a fitting parameter which can be accurately determined as Monte-Carlo results for a continuum or on a lattice become more accurate and are extended to higher $|\phi_d|$. Such fitting, if successful, should allow the dependence of $\alpha$ on $d$, bulk concentration, $\epsilon_B$, and other quantities to be determined, making the LGM of direct predictive value.

Most of the more complicated cluster and other approaches to the theoretical analysis of the diffuse double layer (e.g. those briefly mentioned in Refs.[21–23] cannot readily be extended to regions where $|\rho^*|$ is $\gtrsim 0.2$ or so and the approach to saturation begins to be felt. This suggests the usefulness of modifying a lattice gas approach, where saturation is an inherent feature, to better account for particle-particle Coulomb interactions. This was, in part, our own motivation for using a LGM in past work and considering mean-field corrections to it. In the future, one might modify the LGM with a more complex interaction-averaging approach, one such as the Bethe-Peierls approximation[19], which takes into account specific short range ordering.

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