THERMAL STABILITY OF AN ADSORBED ARRAY OF CHARGES IN THE EINSTEIN APPROXIMATION

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ABSTRACT

For an infinite hexagonal array of ions adsorbed on a conducting plane of infinite extent, the thermal fluctuation from strict lattice ordering in the neighborhood of a given adion is considered. The ions are imaged in the uniform, conducting adsorbent and are assumed to move freely in the plane; they thus arrange themselves in a perfect hexagonal array at absolute zero temperature. By use of the accurate planar potential seen by one adion moving in the field arising from an infinite number of fixed hexagonally arrayed surrounding ions, the root-mean-square (r.m.s.) amplitude of planar vibration of the ion relative to its neighbors is approximately determined for several values of nearest neighbor distances between ions, r_1. On the basis of these results, we find, for example, that for a distance, β, between the center of charge of an ion and the imaging plane of 3 Å, an ionic valence z_v of unity, and an effective dielectric constant of ϵ, a hexagonal array with $r_1 = 15$ Å is stable up to a temperature, T_0, of approximately $1760/\epsilon$ °K while one with $r_1 = 21$ Å is stable up to about $760/\epsilon$ °K. Results apply to adsorption from either a gas or liquid phase and, as well, to an array of real dipoles adsorbed on a nonconducting surface. The appropriate values for ϵ are of the order of 2 and 6, respectively, for adsorption from gas or from aqueous electrolytes. For various r_1's, explicit expressions for T_0 are obtained which depend on ϵ, β, and z_v.

INTRODUCTION

In many treatments (1–7) of the adsorption of ions from a gas phase onto a conducting plane adsorbent, it is assumed that the adions are strongly bound to the surface by physical or chemisorption forces but are free to move in the plane. If the adsorbent surface is relatively uniform and without many discrete, strongly preferred adsorption sites, then the mutual repulsion between adions will tend to make each such ion move as far away from every other ion as possible, leading, at absolute zero temperature and for surface coverage of a monolayer or less, to the establishment of a fixed hexagonal array of discrete charges, the configuration that minimizes the electrostatic energy of interaction in the plane. As the concentration of adions is quasi-statically increased, a hexagonal array will be maintained but with decreasing nearest-neighbor distance, r_1. Finally, a full hexagonally arranged monolayer of adsorbed ions will be reached when steric forces prohibit the addition of further adions in the first adsorbed layer.

At non-zero temperature, planar thermal vibrations of adsorbed ions will tend to destroy the long range order of the fixed hexagonal array. As the coverage is decreased, mutual repulsion between adions weakens because r_1 increases and, at a given non-zero temperature, a coverage will be reached where thermal energy and interaction energy are comparable and the order represented by the hexagonal array substantially disappears. Alternatively, at fixed coverage, increasing temperature will eventually lead to "melting" of the two-dimensional adsorbed structure and again the order will degrade.

This paper is concerned with establishing approximate but reasonably quantitative conditions for the loss of quasi long range order (defined later), primarily in the case of ions electrically imaged in a conducting adsorbent surface. Such imaging leads to the formation of nonideal discrete dipoles which can again form ordered hexagonal arrays at low temperatures or sufficiently high coverages. This situation of ordered dipolar arrays

has received much attention in treatments of adsorption from a gas phase, although the dipoles are usually approximated as ideal (1–6). Elsewhere, we (see ref. 8, hereafter referred to as II) have treated the situation of hexagonally arrayed, nonideal dipoles in considerable detail and have also discussed the error to be expected from using the classical electrostatic image potential. For most cases of interest, the error is small, and the classical imaging formula was used there and will also be employed herein since we shall make use here of planar potentials calculated by the methods of II.

The question of thermal stability of a hexagonal array of adions is also of importance in adsorption of ions from a liquid phase. In a number of treatments of the electrolyte double layer (9–13), it has again been assumed that at least above some minimum surface coverage, the ions adsorbed on the electrode (usually a mercury drop) arrange themselves in a fixed hexagonal array. In this situation, there is the possibility of imaging of adions in the diffuse double layer as well as in the electrode (10–13). Such imaging leads to an infinite array of image charges perpendicular to the adsorbent surface and has been termed infinite imaging (13). When the imaging in the diffuse layer is assumed to be incomplete, the situation is termed partial imaging, whose limit is the present single-imaging situation (8) when imaging in the diffuse layer (if it exists) is absent or negligible. Bell, Levine, and Mingins (14) have considered the thermal stability problem for a partial-imaging situation nearly approximating infinite imaging. Their results and method, which is based on more approximate planar potentials and calculations than those used herein, will be discussed later.

The results of the present treatment, which apply to adsorption from a gas phase and, perhaps to a somewhat lesser extent, to adsorption from an electrolyte, may be used to show under what conditions the single-imaging, hexagonal-array treatment of nonideal dipoles referred to earlier (8) is a good representation of the actual situation for an adsorbed layer of ions. Buff and Stillinger (15) have constructed a cluster integral theory of the double layer in which in treating the adsorbed ionic layer they properly account for short range forces. Hence, in their treatment the tendency of the adsorbed ions to form a lattice under conditions approaching close packing, as a result of the steric effects arising from such short range forces, is a natural consequence of the theory. It is important to recognize that the long range forces between the ions will also play a part in creating array structures. These arrays have nothing to do with steric effects and so are quite different from any arrays consistent with the Buff and Stillinger treatment. In the present work, we are concerned with the long range interaction type of array and ignore short range forces entirely. Our interest is to determine under what conditions such arrays are essentially undestroyed by thermal motion and therefore under what conditions arrays are adequate as models for the adsorbed layer. It should be pointed out that in those circumstances where the long range forces lead to array structures, the Buff and Stillinger theory loses validity: The reason for this is that in their theory (eqs. [33] et seq.) the long range forces are treated as a small perturbation—all Mayer f-bonds are linearized in the long range interaction and, consistent with this, contributions from the long range forces to clusters higher than first order are ignored. It is precisely in the regime where long range forces lead to array structures that such approximations become poor, however. Clearly, the treatments of Buff and Stillinger and those which assume an array model ab initio are complementary, but one should know where the crossover occurs, and this question, while not considered by Buff and Stillinger, is approximately answered by this paper. As we shall see, even for infinite imaging (13), where adsorbed concentrations must be somewhat

higher than for single-imaging situations in order that a hexagonal array will be formed and maintained at the usual experimental temperatures, there is an appreciable range of surface concentration less than the maximum experimentally observed concentration over which the hexagonal array seems to be a good model. The Buff and Stillinger approach seems more appropriate only at rather small adsorbed concentrations where quasi long range order has completely disappeared and where the effect of adsorption itself on measured quantities such as double-layer differential capacitance is still small.

THERMAL AVERAGING CALCULATION

Before actually attempting to estimate the degree of thermal disorder present in a lattice, it is desirable to present a physical picture of the system as the temperature is raised from absolute zero. Consider the surroundings of a given particle: At any finite temperature, the correlation between the position of that particle, taken to define the origin, and the position of any other particle is a steadily decreasing function of distance. In fact, for sufficiently large arrays there will be a distance beyond which the fluctuations of particle positions relative to the particle at the origin will be comparable to or greater than the zero-temperature lattice separation between nearest neighbors. It is consequently only within such distances that the lattice structure is a good concept. Within this distance, the environment of a particle is that of a two-dimensional "microcrystal"; beyond this distance are other particles in motion, essentially uncorrelated with the given particle and belonging to their own microcrystals. As a particle moves over the surface, some particles remote from the given one gradually leave this microcrystal and are replaced by other particles. Thus, after a sufficiently long time the original microcrystal will disappear and new microcrystals will have formed. In this respect, our two-dimensional system is different from the usual concept of a solid, three-dimensional lattice and resembles more the case of liquid crystals. Nonetheless, it is important to recognize that at any time the environment of any particle may be considered as a crystal of possibly very many lattice spacings in size. Now as the temperature is increased, the correlations between particle positions decrease and accordingly the sizes of the microcrystals decrease. Of course, provided the interaction potential between particles asymptotically falls off faster than the inverse square of the distance, all particles sufficiently remote from a given one will play an arbitrarily minor role in influencing that particle or its immediate surroundings. Accordingly, we shall say that quasi long range order exists provided the size of the microcrystals is sufficient that negligible change would result in the neighborhood of a given particle by taking the size of the microcrystals as infinite. In the present work, we shall, in fact, use the potential appropriate for an infinite array in carrying out thermal averaging.

As the temperature is raised further, quasi long range order begins to deteriorate and the particles become so agitated that eventually even the short range order, correlations between the positions of near neighbors, has dropped to a point where fluctuations play a significant role in determining even the local environment of a given particle. When the microcrystals have become only a few lattice spacings in linear dimension, a further raising of the temperature will finally destroy the obvious lattice structure and the n-body correlations remaining will become sufficiently small to be considered as mere perturbations upon a highly randomized system, as in Buff and Stillinger's (15) treatment of long range forces.

As has already been pointed out, the transition between the phase possessing indefinitely long range order and that described by microcrystals takes place at absolute zero. The

transition which concerns us here, however, is the one wherein the neighborhood of a particle ceases to resemble a lattice at all, that is, the melting of the microcrystals. It is this melting which truly affects the appropriateness of a lattice model of a particle array for practical purposes. We shall be concerned, therefore, with the regime in which this gradual phase transition takes place and shall use the term "quasi long range order" to indicate the order of a microcrystal having a minimum linear dimension sufficiently greater than r_1. Note that our treatment involves a gradual diminution of order and is not relevant to first order phase transitions which may possibly occur.

In describing melting phenomena of three-dimensional crystals, two types of criteria have been used: One of these involves macroscopic thermodynamic quantities such as chemical potentials and pressures of the two phases; the other approach (which should lead to the same results, of course) is the microscopic statistical method exemplified by the melting criterion of Lindemann. This criterion which provides that melting takes place when the root-mean-square (r.m.s.) displacement of a particle relative to its neighbors is of the order of the lattice spacing or thereabouts seems appropriate for the type of gradual loss-of-ordering transition considered here. In applying such a criterion to the present situation, the "critical" r.m.s. displacement is determined by the maximum amount of disorder deemed consistent with an array model. Thus, the value actually used amounts to a choice for which the ions fluctuate so strongly as to be somewhat weakly associated with their lattice sites but not so strongly as to destroy the appropriateness of such sites as estimates of particle positions, and hence of local potentials. Finally, some discussion is necessary regarding the basis for calculating the r.m.s. thermal motion of a given particle relative to its neighbors.

Let us consider a fixed hexagonal array of ions of charge e and their images in the plane, conducting adsorbent. Let β be the distance between the center of charge of an adion and the conducting plane and r_1 the nearest-neighbor distance for adsorbed ions. Take the origin of a rectangular coordinate system on the adsorbent surface between a given adion and its image, let x and y be in the plane, and take z positive along the outward perpendicular to the plane. For convenience define the normalized quantities $R_1 \equiv r_1/\beta$, $X \equiv x/\beta$, $Y \equiv y/\beta$, and $Z \equiv z/\beta$. Then $Z = 1$ will define the plane in which the centers of charge of the adions lie. There will be a charge at $(X, Y, Z) = (0, 0, 1)$, $(R_1, 0, 1)$, $(R_1/2, \sqrt{(3)}R_1/2, 1)$, etc.

An accurate treatment of thermal averaging should involve averaging in the plane with all adions subject to thermal motion. Since even the problem of determining the accurate potential at a given point in the $Z = 1$ plane arising from an infinite number of fixed, hexagonally arranged surrounding ions is itself quite difficult (8, 13), we shall consider the simpler problem in which the ion originally at $(0, 0, 1)$ is allowed to move, under thermal perturbation, in the potential arising from all other ions and their images, taken to be substantially at the regular lattice sites. The solution of this problem will approximate closer and closer to the full vibration problem above as the planar r.m.s. distance of vibration from the equilibrium position at $(0, 0, 1)$ decreases. For consistency as well as stability, of course, we demand that this r.m.s. vibration distance be sufficiently small. Since the criterion we shall use for melting of two-dimensional quasi long range order is not very precise, the accuracy and applicability of the solution of the simplified problem will be adequate for our purpose. This simplification was also made by Bell, Levine, and Mingins (14). In further support of the reasonableness of this approximation, we remark that the very same replacement of coupled particles by a system of individual particles, each

vibrating in the constant potential well representing the average interaction (calculated here as though at absolute zero) with its neighbors, was introduced by Einstein to calculate the vibrational energy of a solid (16) (see ref. 17 for an application of the Einstein model to adsorption). When Debye subsequently removed this approximation, it was seen that in spite of the introduction of coupled vibrations the Einstein and Debye theories predicted almost identical behavior except at temperatures very close to absolute zero. When we realize that except for a multiplicative constant these thermal energies predicted so accurately by the Einstein model are identical to the mean-square-displacement of the particles relative to their neighbors, we gain some optimism regarding the usefulness of our approach.

To carry out two-dimensional averaging conveniently, we need an analytic expression for the potential $\psi_a(X, Y, 1) \equiv \psi_a$ at the point $(X, Y, 1)$ arising from all charges but that originally at $(0, 0, 1)$. Although such an expression was obtained in II, it is too complicated to lend itself readily to the weighted double integration needed in two-dimensional averaging. Thus, here we shall initially consider one-dimensional averaging along certain selected lines in the plane, then apply these results to consideration of two-dimensional motion.

Bell, Levine, and Mingins (14) have carried out their thermal stability, partial-imaging treatment using a fixed-array planar potential arrived at by two distinct types of approximation. First, only terms in the potential quadratic in x and y have been kept. Second, the doubly infinite sums remaining in the expression for the potential have been approximated by finite sums: only contributions from ions and their images lying relatively near the origin have been included. The quadratic approximation allows the integrals arising in the averaging problem to be carried out analytically. Another consequence of retaining only terms through quadratic is that to this order of approximation the potential becomes circularly symmetric. This is very convenient in determining the r.m.s. thermal displacement from the origin in the two dimensions of the planar array inasmuch as each degree of freedom contributes equally, reducing the complexity of the problem to that of one dimension. In the present calculation, however, higher order terms destroy the circular symmetry and present us with an essentially two-dimensional problem which is not so easily reduced to one dimension. Thus, we have been led to the method of studying motion along selected lines. As it turns out, the potential for single imaging in the neighborhood of the origin ($r \equiv (x^2 + y^2)^{1/2} \lesssim 0.3r_1$) is fairly well approximated by the circularly symmetric form when a hexagonal array itself is a good approximation. We shall later see in the present single-imaging case how much difference is obtained between results calculated with the quadratic approximation and the results obtained when this approximation is not made.

Figure 1 shows the potential difference $\xi \equiv \psi_a(X, Y, 1) - \psi_a(0, 0, 1)$ plotted versus the normalized distance l for several values of R_1 and several specific lines in the plane indicated by the heavy lines and arrows in the diagrams. These curves were calculated by the method described in II using $\beta = 3$ Å, $\epsilon = 1$, and positive adions of unit valence. Here ϵ is the dielectric constant in the neighborhood of adsorbed charges and l is the distance from an assumed center of one-dimensional vibration normalized by the basic triangle height $h \equiv (\sqrt{(3)}/2)r_1$. Thus for the line to which the solid curves apply, $l \equiv 2r/\sqrt{(3)}r_1 \equiv 2R/\sqrt{(3)}R_1 \equiv 4x/3r_1$, where $R \equiv r/\beta$. This particular line, a binary axis (and its five other half-line equivalents under the symmetry of the hexagonal lattice), is that along which vibration can occur most readily because the potential increases most slowly along
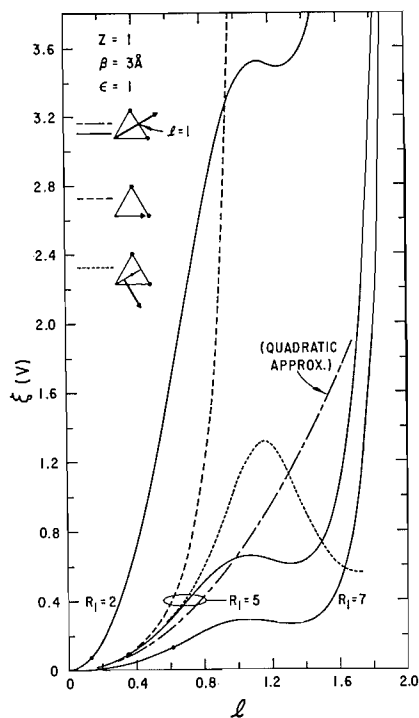
FIG. 1. The quantity $\xi \equiv \psi_a(X, Y, 1) - \psi_a(0, 0, 1)$ versus normalized distance: $l = |4X/3R_1|$, $l = (\sqrt{(3)}/2)|X/R_1|$, and $l = (1/\sqrt{3})|(4X/R_1) - 1|$, respectively, for the three directions indicated. The distance l is measured along the heavy directed lines in the diagrams.

this line. Thus, it is of the most immediate interest to obtain the r.m.s. distance, $\overline{(r^2)}^{\frac{1}{2}}$, of vibration along this line. It will be termed line 1.

Let us define $L \equiv \overline{(r^2)}^{\frac{1}{2}}/h$ as the normalized r.m.s. vibration amplitude. Then

[1]
$$L^2 = \frac{\displaystyle\int_0^\infty l^2 \rho(\xi) \exp\left(-e\xi/\epsilon kT\right) d\xi}{\displaystyle\int_0^\infty \rho(\xi) \exp\left(-e\xi/\epsilon kT\right) d\xi}$$

$$= \frac{\displaystyle\int_0^{l_{max}} l^2 \exp\left(-e\xi/\epsilon kT\right) dl}{\displaystyle\int_0^{l_{max}} \exp\left(-e\xi/\epsilon kT\right) dl}.$$

The second form follows because the weighting factor $\rho(\xi) \propto (d\xi/dl)^{-1}$. The quantity l_{max} is the value of l for which $\xi = \infty$ provided such an l exists, and is infinite otherwise; $l_{max} = 2$ for line 1. The dielectric constant enters (1) because ξ was calculated with $\epsilon = 1$.

The introduction of ϵ is itself an approximation; it has been discussed at length elsewhere (6, 8, 13). For adsorption from a gas phase, there will be no material between adions and ϵ can arise only from adion polarizability itself. Therefore, in this case ϵ will vary with coverage and will lie between approximately 1 and 3 or 4 at most. In the single-imaging

electrolyte case, it has been found (8) that there is a very high field in the inner region of the double layer where ions are adsorbed and this field (for constant ϵ) varies only slightly with adsorbed ion concentration (itself a function of electrode charge). The field is large enough to produce almost entire dielectric saturation of the dipolar contribution of water molecules between adions. Thus, in this case the appropriate dielectric constant is probably 6 or less (8, 18) and will not vary much with coverage until the contribution from ionic polarizability outweighs that from water-molecule polarizability when the coverage approaches that of a monolayer. There is a feedback mechanism at work here which tends to ensure complete saturation. If the field is large enough to produce some dielectric saturation, the consequent reduction in ϵ will increase the effective field, reducing ϵ further and so on. The final self-consistent value of field and dielectric constant may not be that for complete saturation—this depends on the details of the dielectric constant-field dependence—but in the electrolyte single-imaging case, saturation is apparently virtually complete (8). In the present calculations, we shall use $\epsilon = 6$; remember, however, that ϵ and T enter the equations together. Thus, the lower ϵ appropriate for gas phase adsorption can be associated with a higher temperature than the 20 °C we shall use in the electrolyte situation.

Since the potential is an even function of l, it must involve l^{2n}, $n = 1, 2, 3 \ldots$, not l^n. To carry out the integrations in [1] numerically, we found it convenient to fit $\xi(l^2)$ by rational approximations of the form

[2]
$$\xi \cong [l^2/f(l^2)] \sum_{i=0}^{3} \alpha_i l^{2i} \Big/ \sum_{i=0}^{3} \beta_i l^{2i},$$

where $f(l^2)$ varies in form with the line considered. For line 1, $f(l^2) = l^2 - 4$; for line 2, a bisectrix axis (associated with the dashed curve in Fig. 1), $f(l^2) = l^2 - 4/3$, $l_{max} = \sqrt{(4/3)}$; and for line 3 (associated with the dotted curve in Fig. 1), $f(l^2) = 1$, $l_{max} = \infty$. The constants α_i and β_i were determined for given β and R_1 from numerical values of $\xi(l^2)$ calculated by the methods of II. A Chebyshev type of rational fitting* was used in finding best values for α_i and β_i. This is an equi-ripple method which minimizes the absolute error between the original (or transformed) data and the approximation. Typical values obtained for $\beta = 3$ Å and $R_1 = 5$ were, for line 1, $\alpha_0 = 121.2885$, $\alpha_1 = -29.07516$, $\alpha_2 = -25.75952$, $\alpha_3 = 12.05564$, $\beta_0 = -45.52907$, $\beta_1 = 33.67155$, $\beta_2 = -29.53773$, and $\beta_3 = 1$. With ξ available to very high accuracy in the form of eq. [2], the integrals of [1] could be readily evaluated numerically.

It is of interest to note that when $\xi(l^2) \cong \chi l^2$, where χ is a constant, the integrals can be evaluated analytically and yield

[3]
$$L_0 = (\epsilon k T/2e\chi)^{1/2} \equiv (\phi_1/\chi)^{1/2},$$

where $\phi_1 \equiv \epsilon k T/2e$. This quadratic approximation has been evaluated in several cases using χ values obtained from an accurate fit of $\xi(l^2)$ near the origin. The dash–dot curve of Fig. 1 is the result for $R_1 = 5$ and line 1. For the quadratic approximation, as pointed out by Bell, Levine, and Mingins (14), who used only this approximation with $2\phi_1$ rather than ϕ_1 since two-dimensional vibrations were envisaged, the average value $\bar{\xi} = \epsilon k T/2e = \phi_1$. Since the original ξ was defined with $\epsilon = 1$, we must divide the above result by ϵ to obtain the average potential difference appropriate to a non-unity value of ϵ.

*Programmed for computer by E. L. Jones of this laboratory.

RESULTS OF CALCULATIONS

The single-imaging curves of Fig. 2 were calculated for line 1 using eqs. [1] and [3]. Clearly, terms in ξ higher than l^2 cause L to be less than L_0 provided the peak and valley parts of the ξ curves have negligible effect in the averaging. When they do become important, for $R_1 > 4.5$, the moving ion can vibrate further, on the average, and $L > L_0$. The dotted curve in Fig. 2 has been derived from the results of Levine, Mingins, and Bell (14) by transforming from the value $\epsilon = 10$ they used to $\epsilon = 6$, more appropriate for the electrolyte situation, by changing the normalization to agree with our convention, and by dividing their results by $\sqrt{2}$ to change (within the framework of the quadratic approximation) from two-dimensional to one-dimensional motion and averaging. It is evident that the ion can vibrate considerably more freely in the nearly infinite-imaging case than in the single-imaging case. For $\epsilon = 2$, more appropriate for adsorption from a gas phase, the curves of Fig. 2 apply to a temperature of about 790 °K.
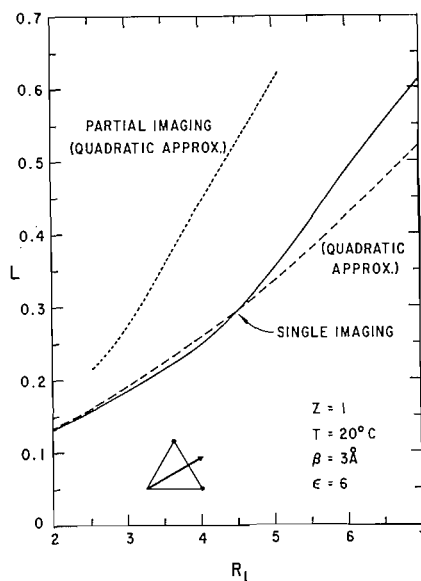

FIG. 2.   The normalized r.m.s. vibration amplitude $L \equiv [3\overline{(X^2 + Y^2)}/4R_1{}^2]^{1/2}$ versus normalized nearest-neighbor distance $R_1 \equiv r_1/\beta$.

The superiority of two-dimensional over one-dimensional averaging depends on the ratio of the normalized distance l_0, over which circular symmetry is a good approximation, to L. If both these numbers are small enough that a hexagonal array is well maintained, two-dimensional averaging using the quadratic approximation will be the more appropriate provided $l_0/L \gtrsim 1$. When vibration along a particular line, such as line 1, is greatly favored over all other directions of vibration, l_0/L will be much less than unity and the assumption of circular symmetry will be very poor.

Figures 1 and 2 show that $l_0/L \approx 1$ for $R_1 = 5$. The ratio will be even larger for smaller R_1. Thus, for the input parameters shown in Fig. 2, two-dimensional averaging will be a somewhat better approximation than one dimensional for $R_1 \gtrsim 5$. If a criterion is established for the maximum one-dimensional L for which we may expect maintenance of a hexagonal array, then the criterion is divided by $\sqrt{2}$ to obtain that appropriate for

circular symmetry and two-dimensional averaging. It seems to us reasonable to pick $L \gtrsim 0.5$ as a rough criterion for hexagonal array (microcrystal) stability. This is somewhat more stringent than that used by Bell, Levine, and Mingins (14) when transformed to the same basis for comparison. The two-dimensional criterion is thus $L_2 \gtrsim 0.35$. It is of interest to compare this figure with the corresponding one for the melting of single-crystal solids: In the latter case the value ~ 0.1 has been found to be appropriate (19); however, it is important to realize that the case considered here is actually quite different from that of solids insofar as first order phase transitions are not treated and the forces are the long range repulsions of the similarly charged adions and their images rather than the crystal-binding fields of an ionic crystal or the short range forces found in metals and covalent crystals. We should accordingly not expect the analogous values to carry over from one situation to the other. Although we have here used the stability criterion $L_2 \gtrsim 0.35$, Fig. 2 may be used in conjunction with any other reasonable value to obtain the limiting value of R_1 appropriate to the new criterion.

Since $L \simeq 0.35$ from Fig. 2 for $R_1 = 5$, this value of R_1 seems, according to the above criterion, to be at or near the limit of hexagonal stability for the choices $\beta = 3$ Å, $z_v = 1$, $\epsilon = 6$, and 20 °C. Further, Fig. 1 shows that for $l \gtrsim 0.35$, circular symmetry is a fair approximation for $R_1 = 5$. In fact, the values of L obtained for lines 1, 2, and 3 were 0.351, 0.268, and 0.344, respectively, for $R_1 = 5$. The fair correspondence of these figures indicates the approximate validity of the circular symmetry assumption for $R_1 \gtrsim 5$ under the conditions of Fig. 2. The quadratic approximation for $R_1 = 5$ leads to $L_0 \simeq 0.336$, again showing that this further approximation is also not too bad for this value of R_1. Note that the heavy solid circles on the curves of Fig. 1 indicate the calculated values of L for the conditions of Fig. 2. It is worth noting that these conditions lead for $R_1 = 5$ to an adsorbed charge density, q_1, of 8.22 μC/cm², a nearest-neighbor distance of 15 Å, and an area per adsorbed ion of about 195 Å².

When the present two-dimensional averaging stability criterion is applied to the partial-imaging curve of Fig. 2, one obtains a limiting R_1 of about 3.5. In turn, this leads to a limiting area per ion of about 106 Å², almost exactly the criterion for loss of hexagonal order derived by Bell, Levine, and Mingins for the partial-imaging case. This agreement is somewhat fortuitous since the effect of our more stringent criteria for loss of quasi long range order is offset by the present use of $\epsilon = 6$ rather than 10. Comparison of the present results for partial and single imaging shows that the hexagonal array is appreciably more rigid for single imaging, and quasi long range order is not lost until ionic nearest-neighbor distance is appreciably greater in the single-imaging case than for partial imaging. Note especially that since the circular symmetry assumption is not very well met for $R_1 = 5$, the criteria for melting should actually lie between the two values 0.35 and 0.5, leading to a larger limiting R_1 than 5 (and accordingly even poorer applicability of the assumption of circular symmetry) for stability calculations at 20 °C.

Finally, Fig. 3 shows how L depends on ϕ_1 for several values of R_1. The temperature scale shown at the top is appropriate for $\epsilon = 6$; its values should be multiplied by 3 for the choice $\epsilon = 2$ more appropriate in the gas adsorption situation. In this case, we see that even the array with $R_1 = 7$ will be stable at room temperature. For $\epsilon = 3$, it will be stable only below about -20 °C. We may write the temperature at which stability tends to disappear according to the present two-dimensional criterion as $T_0 \sim 1760/\epsilon$ or $760/\epsilon$ °K for $r_1 = 15$ Å or 21 Å, respectively, when $\beta = 3$ Å. Note that since the $R_1 = 2$ curve is exactly proportional to $\sqrt{\phi_1}$, the circular symmetry and quadratic approximations are completely valid for this curve.
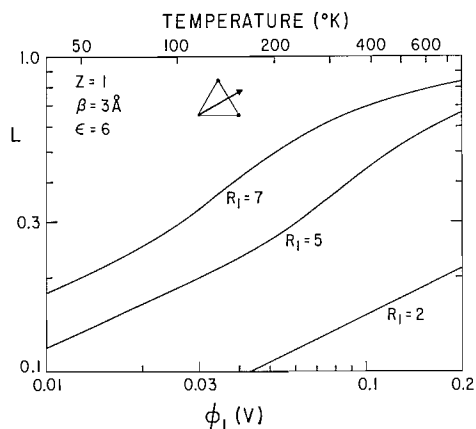
FIG. 3. The normalized r.m.s. amplitude L versus $\phi_1 \equiv \epsilon kT/2e$. The temperature scale at the top applies for $\epsilon = 6$.

Thus far, we have considered only adions of valence $z_v = 1$. When z_v is different from unity, our ϕ_1 becomes ϕ_1/z_v^2. Thus, for adions of valence 2, for example, the instability temperature is four times greater than that for $z_v = 1$. Further, when $R_1 \gtrsim 5$, it turns out (8) that $\psi_a(0, 0, 1)$, for example, may be well approximated by β times the field at $(0, 0, 1)$ derived by replacing all nonideal dipoles by ideal dipoles (6). In this case, ξ will be proportional to β^2, and our present L curves, derived with $\beta = 3$ Å, may be transformed to apply to arbitrary β by replacing a given ϕ_1 by ϕ_1/β^2. In the present work we have used $\beta = 3$ Å since this value seems most appropriate for most electrolyte double layer situations of interest. In adsorption from a gas phase, β may frequently be somewhat smaller even when the imaging plane is taken ≈ 0.5 Å behind the "physical" surface of the conducting adsorbent (8, 16). When $R_1 \gtrsim 5$, the effective ϵ appropriate for adsorption from a gas phase is probably (6) appreciably less than 2. For $r_1 = 15$ Å, we may finally write $T_0 \sim 1760(z_v\beta/3 \text{ Å})^2/\epsilon$ °K. A similar expression for $r_1 = 21$ Å is $T_0 \sim 760(z_v\beta/3 \text{ Å})^2/\epsilon$ °K.

No information seems currently available concerning the sharpness of melting of two-dimensional order with temperature increase or increase in nearest-neighbor distance. It is clear, however, that if quasi long range order has disappeared by the time R_1 has reached a certain value, say R_{10}, R_1 must be somewhat smaller than R_{10} before the order will reestablish itself. Further, R_1 must be larger than R_{10} before the cluster theory of Buff and Stillinger (15) is a good approximation. If $R_{10} = 5$, for example, corresponding to a q_1 of 8.22 μC/cm², a q_1 of 10 or 12 μC/cm² might be required before hexagonal order were regained, and a value of q_1 as small as 5 or 6 μC/cm² might be required before the Buff–Stillinger approach would be applicable. As an example, for 1.0 N KI ($z_v = -1$), the results of Grahame (20) indicate that the charge on the electrode, q, might have to be less than ~ -9 μC/cm² for the Buff–Stillinger approach to apply and greater than ~ -6 μC/cm² for the hexagonal lattice model to apply. Between -9 and -6 μC/cm² neither model would theoretically apply well but the gap might be bridged reasonably accurately by extrapolation between the results of the two approaches. Grahame's data extends to $q_{max} = 18$ μC/cm² and $|q_{1(max)}| \cong 42.61$ μC/cm², indicating that the hexagonal model applies, at 20 °C, $\epsilon = 6$, and $z_v = \pm 1$, over a much greater and more important part of the $|q_1|$ range than does the Buff–Stillinger approach.

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