Statistical mechanics of an ion ensemble adsorbed at a metal-insulator interface

M. A. Vorotyntsev and S. N. Ivanov

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow

(Submitted 30 August 1984)
Zh. Eksp. Teor. Fiz. **88**, 1729–1737 (May 1985)

The free energy of a $2D$ system of adsorbed ions ("adions") and the correlation properties of the system are analyzed as functions of the coverage of the interface by ions. Because of the broad range of values for the distance between adions in which the energy of their binary interaction obeys a "Coulomb" law, which gives way at large distances to a more rapid decay, this system will undergo a change from a slightly nonideal gas into a classical $2D$ plasma as its density is increased. As the density is increased further, the system will go into a condensed state. The reason for the very broad range of densities of the system in which the component of the chemical potential corresponding to the interaction of adions is a linear function of the density is determined. The reason for the large coefficient in this functional dependence is also determined.

1. INTRODUCTION

Recent years have seen a sharp increase in the number of studies of phenomena in $2D$ systems—at the free surfaces of solids and liquids, at interfaces, in thin films, in layered solids, etc. Such systems have several features which are unusual from the the standpoint of the more conventional "three-dimensional physics." To some extent these distinctive features stem directly from the change in the dimensionality of the system (cf., e.g., Refs. 1–3). Other effects arise from the change in the nature of the interaction between particles as they approach interfaces. One of the most important examples is the screening of the interaction between charged particles (ions or electrons) near the surfaces of media with mobile carriers. This screening increases the rate with which potential $U(R)$ decays, to R^{-3} instead of R^{-1}. As a result there is a fundamental change in the statistical-mechanics properties of the ensemble of charged particles, and the Coulomb system goes over to a short-range system.

An important example of such systems is a $2D$ layer of adsorbed ions ("adions") on an interface between a metal and an insulating liquid (an electrolytic solution). Experiments have been carried out on such properties of these systems as the shape of the adsorption isotherm and the dependence of the parameters of this isotherm on the characteristics of the adion, the metal, and the solvent; the ionic strength and composition of the solution; the charge of the metal; etc.[4,5] For inorganic ions adsorbed on *sp* metals, the "virial isotherm" has been used widely; i.e., the chemical potential (μ) of the adions has been written as a function of the surface density of these ions, $\Gamma = N/S$, in the following way:

$$\mu/kT = \ln\Gamma + 2v\Gamma + \text{const}, \qquad (1)$$

where N is the number of adions, S is the area of the interface, and v is the so-called attraction constant.

Our purpose in the present paper is to study the statistical-mechanical properties of an ensemble of adions. For a long time, analyses of this sort have been based on the "image-method" expression for the binary potential of the interaction between adions, according to which we have $U(R) \propto R^{-3}$ at distances greater than the characteristic atomic distances. Recently, however, it has been found that for real metal-insulator interfaces the potential $U(R)$ is more complicated. There exists a broad range of distances between adions within which $U(R)$ has a "Coulomb" behavior ($U \propto R^{-1}$), with the more rapid decay beginning only at far greater distances. We show below that this behavior of $U(R)$ gives rise to quite different results for the thermodynamic and correlation characteristics of such systems. At low densities ($\Gamma \ll \Gamma_*$), we can use virial expansions for these characteristics, but the coefficients are very large, and the values of the "transition" density Γ_* are correspondingly low. At higher densities ($\Gamma_* \ll \Gamma \ll \Gamma_B$) the system acquires the properties of a $2D$ single-component plasma with a screening length R_Γ which depends on the density according to $R_\Gamma \sim \Gamma^{-1}$. At $\Gamma \sim \Gamma_B$, the average interaction energy of the adions is comparable to the thermal energy, and a transition to a $2D$ condensed state takes place.

Our analysis also reveals that there is an extremely broad region within which expression (1) holds; in particular, in this region the component of the chemical potential corresponding to the ion-ion interaction, $2v\Gamma kT$, is linear. This expression is found to hold not only in the virial region ($\Gamma \ll \Gamma_*$) but also at far higher densities ($\Gamma_* \lesssim \Gamma \lesssim \Gamma_B$), and the coefficient v is the same.

The results derived below can be used to study other classical $2D$ systems of charged particles, both ions and electrons, if their binary interaction potential has an "intermediate Coulomb asymptotic behavior" ($U \propto R^{-1}$) which gives way at greater distances to a more rapid decay.

2. FORMULATION OF THE PROBLEM

The following expression for the binary interaction potential of charged particles is widely used to describe the properties of these particles near a metal-insulator interface:

$$U(R) = \frac{(ze)^2}{\varepsilon R} - \frac{(ze)^2}{\varepsilon (R^2+4a^2)^{1/2}} \approx (ze)^2 \frac{2a^2}{\varepsilon R^3} \qquad (R \gg 2a), \qquad (2)$$

where ze is the charge of the particle, R is the distance between particles along the interface, ε is the dielectric constant of the medium in contact with the metal, and a is the distance from the center of the charge to the surface of the

0038-5646/85/051028-05$04.00

metal. Applied to an ensemble of adions, this approach makes it possible to derive expression (1) on the basis of a Mayer expansion for a weakly nonideal $2D$ gas, with

$$v=\pi\int_0^\infty R\,dR\{1-\exp[-U(R)/kT]\}. \tag{3}$$

The use of the conventional expression (2), however, directly contradict experimental results:

1) The actual values of the attraction constant v are far larger than the estimate of this constant given by (3). Specifically, the experimental data yield values ranging from 100 to 1500 Å^2, in contrast with the theoretical predictions, which range from 20 to 40 Å^2 for $a = 1$ Å. Attempts to reconcile these figures by increasing the distance (a) between the adion and the metal lead to physically impossible values—from 3 to 20 Å.

2) According to the Mayer theory, the linear approximation of the component of the chemical potential due to the ion-ion interaction ($\mu - kT\ln\Gamma\sim\Gamma$) is valid only at low coverages, for which $2v\Gamma\ll 1$. For real systems, in contrast, a linear dependence with the same coefficient v is observed over a broad interval of surface concentrations of adions, at both $2v\Gamma\ll 1$ and $2v\Gamma\gg 1$.

Our purpose in the present paper is to show that these discrepancies are not chance occurrences but instead consequences of a fundamental inadequacy of the conventional expression (2) for the interaction energy of charges at a metal-insulator interface.

The binary interaction potential $U(R)$ of adions has recently been analyzed in detail[7–9] with allowance for the structure of the interface, a finite screening length for the static electric field in the metal and the quantum features in the dielectric constant of the metal, the spatial structure of the insulator, the penetration of the electron tail of the metal into a surface layer of the insulator, screening of the field of the adions by the electrolyte, etc. It has thus become possible to set about deriving a systematic theory of an ensemble of adions. In the present paper we take this ensemble to be a $2D$ system of particles with an interaction potential $U(R)$ in which the particles obey the laws of classical statistical mechanics. In taking this approach we are ignoring the discrete nature of the ion framework of the metal, which plays an extremely important role in adsorption on transition metals. Incorporating this ion framework would cause the coordinate $\mathbf{R}$ to depend on the energy $[V(\mathbf{R},a)]$ of the single-particle external field which is acting on each adion. This factor may also be seen in adsorption on *sp* metals, where the change in V along the surface is apparently small in comparison with the thermal energy, but primarily at comparatively high surface coverages, in ordered $2D$ phases.

The single-particle potential $V(a)$ has a deep adsorption minimum. Although the amplitude of the thermal vibrations of an adion in this well along the direction normal to the surface of the metal is small (much smaller than 1 Å), its value may strongly influence the properties of the system. We will not discuss this effect in the present paper.

According to Refs. 7–9, the potential of the interaction between adions begins to fall off according to a Coulomb law at a distance of a few angstroms:

$$U(R)\approx 2(ze)^2\Delta^2/\varepsilon R. \tag{4}$$

The parameter Δ is determined by the dielectric properties of the interface and by the characteristics of the individual adion; it is usually slightly less than unity.[9,10] A sharp distinction between (4) and the expressions for $U(R)$ which follow, on the one hand, and the conventional representations, (2) and (3), on the other, stems from the existence of a region near the interface in which the potential varies sharply because of a decrease in the effective dielectric constant (the spatial dispersion of the dielectric constants of the media in contact, the distortion of the structure of the insulator, etc.). That such a region exists follows[8,9] directly from measurements of the capacitance of an interface.

At a very low concentration of the electrolytic solution, in particular, at a metal-insulator contact without mobile charges, the Coulomb law (4) gives way to a sharper decay:

$$U(R)\approx(ze)^2\Delta^2(2\varepsilon L_H{}^2/R^3). \tag{5}$$

The transition from (4) to (5) occurs at $R\sim\varepsilon L_H$, where ε is the bulk value of the dielectric constant of the medium in contact with the metal, $L_H = (4\pi C_H)^{-1}$, and C_H is the capacitance of the interface. From the experimental values of this capacitance we find values on the order of tens of angstroms for the distance εL_H. For a contact between mercury and an aqueous solution, e.g., we find $\varepsilon L_H\approx 24$ Å.

Since, within the range of applicability of expressions (4) and (5), $U(R)$ is dominated by the interaction of the adions along the lines of force which penetrate a distance on the order of R into the interior of the insulator, the presence of an electrolyte in the insulator leads to an exponential decay of the potential, $\exp(-R/L_D)$, at distances greater than the Debye length L_D. Depending on the relation between the lengths εL_H and L_D, we could find from the general expression

$$U(R)\approx(ze)^2\Delta^2\frac{4}{\pi\varepsilon}\int_\varkappa^\infty\frac{t(t^2-\varkappa^2)^{1/2}K_0(tR)}{t^2-\varkappa^2+(\varepsilon L_H)^{-2}}\,dt,\qquad \varkappa=L_D{}^{-1}, \tag{6}$$

expressions (4) and (5) and other asymptotic expressions for $U(R)$ (Ref. 8; see Ref. 9 for the case in which the metal has a nonzero charge).

The most important point for the analysis below, of the statistical-mechanics properties of the ensemble of adions, is the existence of a broad range of distances between the adions, $R<R_* = (\varepsilon^{-1}L_H^{-1}+L_D^{-1})^{-1}$, in which the potential falls off slowly, while outside this interval the potential decreases far more rapidly: $U\propto R^{-3}$ or $U\propto\exp(-R/L_D)$. Another important point is that the "Bjerrum distance" R_B, at which the transition form the strong interaction to the weak interaction $[U(R_B)=kT]$ occurs, lies within the Coulomb distance interval: $R_B = 2(ze)^2\Delta^2/\varepsilon kT\ll R_*$, i.e., $R_B\sim 5$–10 Å for aqueous solutions.

These features of the behavior of $U(R)$ rule out direct use of the results of the two most important approximate approaches, namely, the virial expansion for a weakly nonideal gas and an expression in powers of the plasma parameter. In the former case, the problem is that it is not clear just what we are to understand as the characteristic interaction radius R_0 with which we are to compare the average distance between particles, $\langle R\rangle\sim\Gamma^{-1/2}$. a) If $U(R_0)\sim kT$, i.e., $R_0\sim R_B$, then at $R\sim R_0$ the potential cannot be assumed to be a short-range potential; b) if $R_0\sim R_*$, then the potential is a short-range potential, but—as simple estimates show—the component of the chemical potential from the adion interaction can be ignored altogether at $\langle R\rangle\sim\Gamma^{-2}\gtrsim R_0$. It becomes necessary to carry out a special analysis and to use the techniques which are employed in the theory of a classical plasma. Although expression (4) does hold at $U(R)\sim kT$, an attempt to restrict the analysis to the Coulomb region, i.e., to let R_* go to infinity, leads to a divergence in the expression for the chemical potential of the adions. This divergence does not occur in a classical plasma because of its overall electrical neutrality. The divergence can be eliminated by adding a uniformly smeared background of opposite charges to the system of adions. However, as we will see below, this approach would lead to a completely incorrect adion adsorption isotherm.

In the sections which follow we will accordingly analyze the structure of power-series expansions in these parameters of both the free energy of the system and the binary correlation function or, more precisely, the potential of the average force.

3. VIRIAL EXPANSION

The expansion of the free energy in cluster integrals can be written[11]

$$F=F_{id}-kTN\sum_{n\geqslant 2}B_n\Gamma^{n-1},\quad F_{id}=N(kT\ln N/eS+\text{const}),\tag{7}$$

where F_{id} is the free energy of an ideal $2D$ gas, and the virial coefficients B_n can be expressed in terms of irreducible integrals. In particular, we can write

$$B_2=\frac{1}{2}\int f(R)\,d\mathbf{R}=\pi\int_0^\infty f(R)R\,dR,$$

$$f(R)=\exp\left(-\frac{U(R)}{kT}\right)-1.\tag{8}$$

Because of the slow decay $U(R)\propto R^{-1}$ in the region $R_B\ll R\ll R_*$, the integral over R is dominated by the region $R\sim R_*$, where $f(R)\approx-U(R)/kT$, so that we have $B_2\sim R_BR_*\gg R_B^2$. A more precise calculation using (6) leads to the expression

$$B_2\approx-\pi R_BR_*+O\left(R_B{}^2\ln\frac{R_*}{R_B}\right).$$

The leading correction comes from the second term in the expansion of the exponential function in (8), which falls off as R^{-2}.

Among the irreducible integrals which appear in the following virial coefficients B_n, those which are largest in order of magnitude are the ring diagrams: $B_n\sim R_B^nR_*^{-2}$. The introduction of an additional k couplings between vertices reduces the size of the diagram by a factor of $(R_*/R_B)^k$ to $R_B^{2n-3}R_*$; then come terms of order $R_B^{2n-2}\ln R_*/R_B$ and R_B^{2n-2}.

Expansion (7) in powers of the density is actually parametrized in terms of $\Gamma R_BR_*\equiv\Gamma/\Gamma_*$. This parameter originates from the slow rate of decay of $U(R)$ at $R<R_*$, so that the leading integrals are dominated by the region $R\sim R_*$, where the Mayer function in (9) is small: $f\approx-R_B/R$. An increase in the number of (n) of vertices in the diagram in (7) thus adds a factor of order $\Gamma R_*^2R_B/R_*$. As a result, the system may be treated as a slightly nonideal gas when the average distance between particles exceeds the critical length $(R_BR_*)^{1/2}$. Because of the particular features of the functional dependence $U(R)$, the role of the critical length is played not by the Bjerrum distance R_B, where we have $U\sim kT$, and not by the distance R_*, where $U(R)$ changes, but by a combination of the two.

On the other hand, as for systems with a conventional short-range potential $U(R)$, the condition for the applicability of the virial expansion can be written

$$\mu_{int}\equiv\partial(F-F_{id})/\partial N\sim kT\Gamma/\Gamma_*\ll kT.$$

4. REGROUPING AND PARTIAL SUMMATION OF THE MAYER DIAGRAMS

When the transition density $\Gamma\sim\Gamma_*\equiv(R_BR_*)^{-1}$ is reached, all the leading terms of expansion (7) are of the same order of magnitude: $B_3\Gamma^2\sim B_4\Gamma^3\sim\ldots\sim R_B/R_*\ll 1$. The contribution of the second virial term, on the other hand, is substantially larger: $B_2\Gamma\sim 1$. This result demonstrates that expression (1) for the chemical potential of the adions is applicable at both low and transitional surface coverages, $\Gamma\lesssim\Gamma_*$. The attraction constant v is $-B_2\approx\pi R_BR_*$.

To move to higher coverages, $\Gamma\gg\Gamma_*$, we can regroup the terms within diagrams with a given number (n) of vertices and then sum over the n different types of diagrams. In particular, a summation of the ring diagrams yields

$$\Sigma^{(r)}\equiv\sum_{n=3}^{\infty}B_n^{(r)}\Gamma^{n-1}$$

$$=\frac{1}{4\pi\Gamma}\int_0^\infty K\,dK\left\{\ln[1+\Gamma f(K)]-\Gamma f(K)+\frac{1}{2}\Gamma^2f^2(K)\right\};\tag{9}$$

$$f(K)=2\pi\int_0^\infty R\,dR\,J_0(KR)f(R).$$

It follows from this expression that at moderate surface coverages ($\Gamma_*\ll\Gamma\ll\Gamma_B\equiv R_B^{-2}$) this sum $\Sigma^{(r)}$ increases more slowly ($\Sigma^{(r)}\sim\Gamma R_B^2\ln\Gamma R_BR_*$) than at small Γ, $\Sigma^{(r)}\sim\Gamma^2R_B^3R_*$, and at all $\Gamma\lesssim\Gamma_B$ it remains a correction in comparison with $B_2\Gamma$: Their ratio does not exceed $R_BR_*^{-1}\ln R_*R_B^{-1}$. At moderate densities of the system, $\Sigma^{(r)}$ is dominated by multiple binary ion-ion collisions at short distances, $R_*\gtrsim R\gtrsim R_\Gamma$, where $R_\Gamma=(\Gamma R_B)^{-1}$, according to (9). This result means that at $\Gamma\sim\Gamma_*$ there is a change in the correlation properties of the system: Collective modes arise in the system. We will show below that the new parameter R_Γ determines the screening length.

5. METHOD OF COLLECTIVE VARIABLES

Since a multiparticle screening arises in the system at adion surface coverages greater than the transition value ($\Gamma > \Gamma_*$), we will use the method of collective variables[12,13] for a systematic study of the statistical characteristics of this system. This method permits a successful description of both an ensemble of the slightly-non-ideal-gas type and an ensemble with collective excitations. At low and moderate densities of the system $\Gamma \ll \Gamma_*$ and $\Gamma_* \ll \Gamma \ll \Gamma_B$, respectively, where $\Gamma_B \equiv R_B^{-2}$), the potential $U(R)$ is conveniently broken up into long-range and short-range parts, $U = U_l + U_s$, in the following way: $U_l \equiv 0$ at $R < R_B$ and $U_s \equiv 0$ at $R > R_B$. The free energy is written as the series[13]

$$F = F_{id} + F_{\mathrm{HTL}} + F_{\mathrm{RPA}} - kT \sum_{n \geqslant 2} B_n', \tag{10}$$

where

$$F_{\mathrm{HTL}} = \frac{1}{2} N^2 S^{-1} \int U_l(R)\, d\mathbf{R}$$

is the average energy of the long-range part of the interaction in the case of a uniform distribution of particles (the "high-temperature limit"), while the contribution from ion-ion interactions in the random phase approximation in the presence of a uniformly smeared background of the opposite charge is

$$F_{\mathrm{RPA}} = -\frac{1}{2} kT {\sum_K}' \{\alpha(K) - \ln[1 + \alpha(K)]\},$$
$$\alpha(K) = N(SkT)^{-1} \nu(K), \quad \nu(K) = \int U_l(R) e^{i\mathbf{KR}} d\mathbf{R}. \tag{11}$$

The group intervals B_2', B_3',..., are expressed[13] in terms of the potentials $U_l(R)$ and $U_s(R)$.

We can use expressions (5)–(7) for $U_l(R)$ to find estimates of the terms in series (10) for all $\Gamma \lesssim \Gamma_B$:

$$F_{\mathrm{HTL}} \approx N\Gamma kT \pi R_B R_*,$$
$$F_{\mathrm{RPA}} \sim N\Gamma kT R_B^2 \ln [R_B^{-1} \min (R_*, R_\Gamma)], \tag{12}$$
$$B_n' \leqslant N[\Gamma R_B^2 \ln \min (R_* R_B^{-1}, R_\Gamma R_B^{-1})]^{n-1}, \quad R_\Gamma = (\Gamma R_B)^{-1}.$$

Consequently, at all $\Gamma \ll \Gamma_B$, expansion (10) is dominated by the term F_{HTL}. The contribution F_{RPA} is small, on the order of the parameter $R_B/R_* \ll 1$, and as we go from F_{RPA} to the terms of the type of kTB_n' we find an additional cofactor $\sim (\Gamma R_B^2)^{n-2} = (\Gamma/\Gamma_B)^{n-2} \ll 1$. When the Bjerrum density $\Gamma \sim \Gamma_B$ is reached, all the correction terms in series (10) become comparable in magnitude (NkT); i.e., they remain small in comparison with $F_{\mathrm{HTL}} \sim NkTR_*/R_B$. This result means that, within small quantities on the order of R_B/R_*, the expression for the chemical potential of the system given in (1) remains valid over the entire region of moderate coverages, $\Gamma_* \lesssim \Gamma \lesssim \Gamma_B$, and the value of the attraction constant v is the same as at low densities.

The breakup of $U(R)$ into long-range and short-range components which we carried out above does not allow us to find the chemical potential at high densities of the system, $\Gamma \gg \Gamma_B$, since, according to (12), the quantities B_n' increase with index n in accordance with $(\Gamma R_B^2)^{n-1} = (\Gamma/\Gamma_B)^{n-1} \gg 1$. However, there is a different way to choose the point at which to break up $U(R)$ into U_l and U_s. Calculations show that the smallest correction terms in (10) are found if the boundary $R_{s/l}$ is allowed to depend on the density: $R_{s/l} \sim (\Gamma R_B)^{-1}$. In this case we again have estimate (12) for F_{HTL}, but for F_{RPA} we have the new expression

$$F_{\mathrm{RPA}} \sim kTB_2' \sim kTB_3' \sim \ldots \sim NkT\Gamma R_B^2.$$

Since the latter quantity is small in comparison with F_{HTL}, and since the potential $U(R)$ is purely repulsive, it may be suggested that expression (1) remains approximately correct even at these coverages. We can expect this expression to become incorrect at coverages close to the limiting coverage, at which, at an average distance $\langle R \rangle \sim \Gamma^{-1/2}$ between adions, the potential $U(R)$ becomes a non-Coulomb potential because of, e.g., a short-range repulsion.

6. BINARY DISTRIBUTION FUNCTION AND AVERAGE-FORCE POTENTIAL

Using some analogous asymptotic estimates we can show that at low surface coverages ($\Gamma \ll \Gamma_*$), i.e., in the region of the applicability of the Mayer group expansion, the situation is dominated by binary collisions of adions, so that we have

$$F_2(R) \approx \exp[-U(R)/kT],$$

and the contributions of the other particles to $F_2(R)$ amount to small corrections: Even at large distances, $R \gg R_*$, they do not exceed $O(\Gamma R_B^2 R_*^3/R^3)$ and are thus small in comparison with unity, $O(R_B/R_*)$, even at $R \sim R_*$ and $\Gamma \sim \Gamma_*$. A similar result is found for the average-force potential $W(R) = -kT \ln F_2(R)$, i.e., for the interaction energy of two adions when the other particles have an equilibrium distribution. The largest correction is observed at $R \gg R_*$:

$$W(R) \approx U(R)[1 + O(\Gamma R_B R_*)].$$

When the transition density $\Gamma \sim \Gamma_* = (R_* R_B)^{-1}$ is reached, the long-range interaction of the adions becomes a multiparticle interaction: $W(R)$ begins to differ substantially from $U(R)$. At moderate surface coverages ($\Gamma_* \lesssim \Gamma \ll \Gamma_B$) we can use the method of collective variables. As a result we have $W(R) \approx U(R)$ at $R \ll R_\Gamma = (\Gamma R_B)^{-1}$ and $W(R) \approx g_l(R)$ at $R \gg R_B$, where the "screened potential" $g_l(R)$ is determined in terms of $u_l(R)$ from (13) and (11):

$$g_l(R) = \frac{1}{S} \sum_{\mathbf{K}} \nu(K) e^{i\mathbf{KR}} \left[1 + \frac{N}{SkT} \nu(K)\right]^{-1}. \tag{13}$$

Analysis of the expression for $W(R)$ shows that a new characteristic distance has arise in the system: the $2D$ screening length $R_\Gamma = (\Gamma R_B)^{-1}$. Its size is determined by the size ($R \sim R_\Gamma$) of the region in which the field of the adion of interest, $U(R) \propto R^{-1}$, induces a screening charge of the opposite sign:

$$ze \sim \int_0^{R_\Gamma} R\,dR\, ze\Gamma\{1 - \exp[-U(R)/kT]\} \sim ze\Gamma R_\Gamma R_B.$$

Inside this region ($R \ll R_\Gamma$), the field produced by the induced charge is weak in comparison with $U(R)$, so that we hae $W(R) \approx U(R)$. At $R \gtrsim R_\Gamma$ the average-force potential differs sharply from $U(R)$: $W(R)/kT \approx R_B R_\Gamma^2/R^3$. At moderate densities the screening length lies in the Coulomb region: $R_B \ll R_\Gamma \ll R_*$. At such surface coverages the system therefore converts into a classical plasma. Because of the $2D$ nature of the system, the multiparticle screening of the interactions results in an R^{-3} decay of these interactions at $R > R_\Gamma$, not the exponential decay $\exp(-R/R_\Gamma)$ of the $3D$ case.

When the Bjerrum density $\Gamma \sim \Gamma_B$ is reached, the perturbed region in $W(R)$ reaches $R \sim R_B$. As can be seen from the series for $W(R)$ in the collective-variable method, all the terms of the series become comparable in magnitude. It can be expected that the system will undergo a phase transition in this region to a "condensed" state, accompanied by a sharp change in the binary correlation function.

7. DISCUSSION OF RESULTS

The analysis above reveals the complicated behavior of the statistical-mechanics properties of $2D$ system of adions as functions of the density of the system, Γ.

At low densities the behavior of the system is analogous to that of a slightly nonideal $2D$ gas, but, in contrast with ordinary ensembles of this type, the leading group integrals (the ring diagrams) are dominated not by the Bjerrum distance R_B, where $U \sim kT$, but by the region in which the Coulomb law (4) for the functional dependence $U(R)$ gives way to the sharper decay described by (5): $R \sim R_*$. Consequently, the virial coefficients B_n in (7) are far larger than the Bjerrum interaction cross sections; for example, we have $-B_2 \approx \pi R_B R_* \gg \pi R_B^2$. Substituting in some typical lengths $R_B \sim$ 5-15 Å and $R_* \sim$ 10-100 Å, we can explain the experimental result that a substantial repulsion of adions occurs even at $\Gamma \sim \Gamma_* \sim (0.5\text{–}5)\cdot 10^{-3}$ Å^{-2}.

In this density interval (at $\Gamma \sim \Gamma_* = (R_* R_B)^{-1}$) there is a change in the correlation properties of the system: While the interaction of adions at $\Gamma \ll \Gamma_*$ occurs by a binary-collision mechanism, at $\Gamma \gg \Gamma_*$ we find a screening of the interaction by collective excitations of a plasma type at distances $R \sim R_\Gamma = (\Gamma R_B)^{-1}$. Because of the $2D$ nature of the system, the decay of the average-force potential $W(R)$ at $R \gg R_\Gamma$ occurs in accordance with $W \sim R^{-3}$.

When Bjerrum densities are reached, $\Gamma \sim \Gamma_B = R_B^{-2}$, and the interaction of the adions at a distance $R \sim \langle R \rangle = \Gamma^{-1/2}$ reaches a level on the order of kT, we can expect a transition to a condensed $2D$ phase accompanied by a sharp change in the correlation properties of the system.

This analysis has also revealed the strikingly wide range of applicability of expression (1) for the chemical potential of the adions: The contribution of the ion-ion interaction of μ depends linearly on Γ over the range from extremely low coverages ($\Gamma \ll \Gamma_*$) all the way up to Bjerrum densities (and even higher), and the coefficient in this linear relation is the same, $2vkT$, where $v \approx \pi R_B R_*$. This result, which agrees with experimental data, is a consequence of the circumstance that the distribution of adions around a given charge is substantially perturbed only in the Bjerrum region, $R \lesssim R_B$, while the basic contribution to the interaction with the other adions, $F_2(R)U(R)dR$, comes at $R \sim R_*$ even if these adions have a uniform distribution, $F_2(R) \equiv \text{const}$. Consequently, deviations from expression (1) can be expected only at densities for which the average distance between adions, $\langle R \rangle = \Gamma^{-1/2}$, becomes comparable to the radius of their short-range repulsion (in this region we should also modify the entropy contribution to the chemical potential).

We are indebted to D. N. Zubarev, V. N. Lutskiĭ, V. L. Pokrovskiĭ, A. A. Rukhadze, and Yu. A. Chizmadzhev for a useful discussion of these results.

[1] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, Nauka, Moscow, 1976 (Statistical Physics, Pergamon Press, Oxford).

[2] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Fluktuatsionnaya teoriya fazovykh perekhodov (Fluctuation Theory of Phase Transitions), Nauka, Moscow, 1982.

[3] I. F. Lyuksyutov, Ukr. Fiz. Zh. **28**, 1281 (1983).

[4] U. V. Pal'm and B. B. Damaskin, Itogi nauki. Élektrokhimiya (Scientific Progress. Electrochemistry), VINITI, Moscow, Vol. 12, 1977, p. 99.

[5] B. B. Damaskin and R. V. Ivanova, Usp. Khim. **48**, 1747 (1979).

[6] R. H. Fowler and E. A. Guggenheim, Statistical Thermodynamics, Cambridge Univ. Press (1939) (Russ. transl. IIL, Moscow, 1949).

[7] M. A. Vorotyntsev and A. A. Kornyshev, Zh. Eksp. Teor. Fiz. **78**, 1008 (1980) [Sov. Phys. JETP **51**, 509 (1980)].

[8] M. A. Vorotyntsev, Élektrokhimiya **16**, 1350 (1980).

[9] M. A. Vorotyntsev, V. Yu. Izotov, and A. A. Kornyshev, Poverkhnost': Fizika, khimiya i makhanika **7**, 97 (1983).

[10] M. A. Vorotyntsev, Research Inst. Catalysis, Vol. 30, Hokkaido Univ., 1982, p. 167.

[11] J. E. Mayer and M. Goeppert-Mayer, Statistical Mechanics, Wiley, New York, 1940 (Russ. transl. Mir, Moscow, 1980).

[12] D. N. Zubarev, Dokl. Akad. Nauk SSSR **95**, 757 (1954).

[13] I. R. Yukhnovskiĭ and M. F. Golovko, Statisticheskaya teoriya klassicheskikh ravnovesnykh sistem (Statistical Theory of Classical Equilibrium Systems), Naukova Dumka, Kiev, 1980.

Translated by Dave Parsons