On dissociation in weakly doped ice

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Currently, there is some ambiguity in the problem of decay of a single donor into charged fragments. Thus, in the well-known Ostwald approximation used for semiconductors (ice being one of them) the donor dissociation degree of tends to its maximum value (i.e., unity) as the doping impurity concentration approaches zero. At the same time, the statistical theory of atom reveals within the Thomas–Fermi (or Debye–Hückel) approximation the existence of a thermodynamically equilibrium state of a single multi-electron atom (donor) where charged nucleus keeps the number of counterions just necessary for its neutralization. These scenarios do not show the atom dissociation at all. Discussed in the present paper is the alternative between the full dissociation of a single donor (i.e., dissociation degree equals unity) in a semiconducting media (ice, water, semiconductor) and zero dissociation degree.

Decay of a neutral donor into charged fragments, which is typical of semiconducting media, is a reversible reaction obeying the law of mass action (MAL) [1]. Its application to *n*-type semiconductors leads to a formula (Ostwald law) which yields an important characteristic of the solution, the ionization (dissociation) degree α of the donors [1,2]:

$$K(T) = \frac{\alpha^2 C}{1-\alpha}, \qquad (1)$$

where C is the doping impurity concentration, $\alpha(C)$ is defined as the ratio of the number of ionized donor molecules to their total number, $K(T)$ is the ionization constant which does not depend on C but is very sensitive to temperature T.

Table 1. Data on the dissociation of a weak water solution of acetic acid for a wide range acetic acid concentrations (taken from Refs. 3, 4).

C, mole/l	α	K, mole/l
0.000028	0.539	$1.77 \cdot 10^{-5}$
0.000111	0.328	$1.78 \cdot 10^{-5}$
0.000218	0.248	$1.78 \cdot 10^{-5}$
0.001030	0.124	$1.80 \cdot 10^{-5}$
0.05	0.019	$1.84 \cdot 10^{-5}$
0.10	0.0135	$1.85 \cdot 10^{-5}$

The degree to which K appearing in the Ostwald law is actually constant for weakly doped semiconductors is illustrated by the data of Table 1 on dissociation of weak solutions of acetic acid in water [3,4]. Actually, this example referring to electrolytes does not affect the general nature of Eq. (1) which holds for any semiconducting media. Liquid solutions are much more convenient (compared to solid semiconductors) for varying the parameter C, especially for the case $C \to 0$. According to these data, the independence of K on C does take place in a wide range of donor concentrations. As to strong (anomalous) electrolytes, no quantitative statements on the dissociation degree are made here with the MAL. As a rule, the dissociation degree of strong electrolytes is assumed to have the maximum value, i.e., unity.

Equation (1) allows us to trace the behavior of the dissociation degree of a dilute solution of a weak electrolyte in the limit $C \to 0$ where properties of the doped solution are practically unaffected by Coulomb correlations:

$$\alpha_c \simeq (1-4C/K), \quad 4C/K < 1, \quad \alpha(C)_{C\to 0} \to 1. \quad (2)$$

For α_{uks}, i.e., taking into account the real value of constant K_{uks} from the Table 1, the range (2) begins when C reaches the values $C \leq 10^{-5}$–10^{-6} mole/l. Data reported in Table 1 is cut off at exactly these values of C, which does not allow to verify Eq. (2) in the domain $4C/K < 1$.

At the same time, there also exist approaches yielding results different from those presented by Eq. (2). One of them, the Thomas–Fermi approximation for a single multi-electron atom, leads to a statistically equilibrium confinement of Z electrons by a nucleus containing Z protons [5]. The same result is suggested by the known statistically equilibrium solution of the Poisson equation in the form of the Yukawa potential for a single Coulomb center whose field is screened at the Debye length R_D by counterions available in the electrolyte [1]. Both examples refer to the properties of a single donor (acceptor) in vacuum or inside the intrinsic electrolyte, i.e., deal exactly with the case (2) with a qualitatively different behavior of $\alpha(C)$

$$\alpha(C)_{C \to 0} \to 0. \tag{3}$$

The Thomas–Fermi approximation for a single multiple-charged donor is one of the building blocks of the hopping conductivity theory for *n*-type semiconductors (e.g., see Ref. 6). The assumption of confinement within the Debye radius around a positively charged center of electrons which are sufficiently numerous for its complete screening lies at the basis of the calculations of correlative corrections to the energy of systems with Coulomb interaction (see Ref. 1 with applications to osmotic pressure in charged solutions). If one literally follows these widely known statements, the rule $\partial K/\partial C = 0$, experimentally found to be valid in doped semiconductors, should be violated within almost the entire range of concentrations C presented in the Table.

Detailed discussion of the properties of dilute charged solutions in the limit providing, in particular, the answer to the alternative (2), (3), is given in the present report.

1. Basic assumptions on the properties of the components involved in dissociation are qualitatively important. In the generally accepted scheme the strong Coulomb interaction between dissociation fragments is taken into account by introducing a finite binding energy between them (derived from a quantum-mechanical treatment of the problem). As to the properties of emerging components, the charged particles are assumed to be noninteracting. This leads to the Ostwald law relating the dissociation degree of a single donor α and the doping impurity concentration [1]. A modification where spin is also taken into account is known as the Sakha law [1]. In both cases the dissociation degree of a single donor α grows with decreasing doping component concentration C reaching the limit $\alpha \to 1$ at $C \to 0$.

The major advantages of the Ostwald formula are in its relative simplicity and physically understandable behavior of the function $\alpha(C)$. Qualitatively, this law means that any potential well with a finite depth confines the charge localized in its vicinity provided that density of these wells is finite (proportional to C). In the limit of small $C \ll 1$ Eq. (1) implies Eq. (2) which tells us that for $C \ll K$ all wells lose localized charges.

2. The alternative (3) arises when one turns to results obtained in the statistical theory of atoms. First of all, the well known statistical Thomas–Fermi approximation for the electron shell of a many-electron atom should be considered [5] where the actual electron density distribution around the Z-charged nucleus is replaced with approximate one $n(r)$ derived from the requirement of constant electrochemical potential for electron gas of density $n(r)$ in a Coulomb field at all distances $0 < r < \infty$ from the nucleus. The resulting nonlinear relation between $n(r)$ and $\varphi(r)$

$$n(r) = F[\varphi(r)] \tag{4}$$

is not actually accurate both at small and large distances. The approximate nature of the model is partly compensated for by applying special boundary conditions for the Poisson equation

$$\Delta\varphi = \frac{4\pi}{\varepsilon}\sigma(r), \quad \sigma(r) = en(r) = eF[\varphi(r)], \tag{5}$$

$$r\varphi(r)|_{r \to 0} \to Z, \quad \varphi(r)|_{r \to \infty} \to 0, \tag{6}$$

where Z is the number of charges at the cluster center, ε is the medium dielectric constant (for comments, see Refs. 4, 5). The resulting self-consistent density distribution provides a general idea on the electron density and on the possibility of formulating the problems involving $n(r)$ (e.g., finding the plasma oscillations spectrum in a charged cloud with density $n(r)$).

A disadvantage of the Thomas–Fermi model when applied to the dissociation processes is its failure at large distances $r \gg r_B$ (r_B being the effective Bohr radius). At these distances the chemical potential of electrons becomes classical, $\zeta(n) \propto \ln n$, and the second condition in Eq. (6), $\varphi(r)|_{r \to \infty} \to 0$ proves to be incompatible with the requirement $n(r)|_{r \to \infty} \to 0$. As a result, a single multi-electron atom in vacuum cannot be statistically equilibrium.

In the classical formulation [1], the problem of the atom equilibrium structure reduces to solving the equation

$$\Delta\varphi = \frac{4\pi}{\varepsilon}\sigma(r), \quad \sigma(r) = |e|[n_+(r) - n_-(r)], \tag{7}$$

$$n_\pm(r) = n_0 \exp[e_\pm\varphi(r)/T]. \tag{8}$$

Conditions (6) here are consistent with Eq. (8): for the limiting behavior $\varphi(r)|_{r \to \infty} \to 0$ it is sufficient to demand that $[n_+(r) - n_-(r)]|_{r \to \infty} \to 0$ provided that at large distances each fraction $n_\pm(r)$ retains its finite density. Thus, in principle, every external charge in the electrolyte can be assumed to be screened to within (6), (7), (8), confirming therefore the feasibility of the limit (3). The difficulties in the classical approach start when the requirement

$$\int [n_+(r) - n_-(r)]d^3\mathbf{r} = Z = ?? \tag{9}$$

is considered with $n_\pm(r)$ from Eq. (8) together with the solution (8) for $\varphi(r)$. For $e\varphi(r)/T \gg 1$, the condition (9)

has not yet been verified because of absence of an analytical solution to the set (6), (7), (8). One can only stress that the second order equation (7), (8) has two boundary conditions (6) on $\varphi(r)$ allowing to assume the uniqueness of the solution. In that sense the requirement (9) is actually redundant. By chance, it can be satisfied automatically. If not, the relevant solution has some problems preventing it from being considered as a statistically equilibrium one.

The correlational Debye–Hückel approach to the problem (6), (7), (8) contains quite reasonable, at a first glance, assumptions. Clearly, the relatively large Coulomb correlations are mainly related to the long-range nature of the problem. The properties of $\varphi(r)$ important for correlations are determined by large distances (the actual values of relevant distances should be derived from the analysis of the final solution) where the ratio $e\varphi(r)/T \ll 1$ becomes small. Under these conditions, one can linearize the equation set (7), (8) with respect to the parameter $e\varphi(r)/T \ll 1$ without loss of generaluty. This yields

$$\Delta\varphi = \varphi/\lambda_D^2, \quad \lambda_D^{-2} = \kappa_D^2, \quad \kappa_D^2 = \frac{8\pi e^2}{\varepsilon T}n_{aq}, \quad (10)$$

together with the boundary conditions (6). When applied to water, $n_{aq} \equiv n_0$ is the equilibrium water ions density, n_0 is the constant from Eq. (8).

The solution to Eq. (10) in the form of Yukawa potential

$$\varphi(r) = e\exp(-\kappa_D r)/r, \quad \kappa_D^2 = \frac{8\pi e^2}{\varepsilon T}n_{aq},$$

$$e\varphi(r) < T, \quad Z = 1, \quad (11)$$

is qualitatively correct at both small and large distances allowing to speak of the possibility of complete screening of a point charge by ions of the intrinsic semiconductor (water). For $T \simeq 300\,\text{K}$, $\alpha_{aq} \simeq 10^{-7}$ [3], $n_{aq} \simeq 10^{+23}\,\text{cm}^{-3}$, $\varepsilon \sim 80$ [3] one has the estimate $\kappa_{aq}^2 \sim (10^6\text{–}10^7)\,\text{cm}^{-2}$. An additional argument in favor of Eq. (11) is the positive answer to the test (9).

Equation (11) is the basis of the Debye–Hückel correlation theory [1]. It also provides the idea on the structure of a neutral donor in semiconducting media, solving the alternative between Eqs. (2) and (3) in favor of Eq. (3). However, linearization of Eqs. (7), (8) which allowed obtaining Eq. (11) destroys qualitatively important details in the behavior of $\varphi(r)$ thus leaving the alternative between Eqs. (2) and (3) an open question.

3. The point is that the nonlinearity of the problem (7), (8) proves to be important not only at small (compared to Debye length $R_D \sim \kappa_D^{-1}$) distances. It also governs the behavior of $\varphi(r)$ for $r \gg R_D$. This circumstance is established in the discussion of the possibility of confinement the screening cloud of counter ions by external potentials $V(r)$ of different dimensionality and strength. The available answers confirm this detail, which is not quite obvious.

Thus, in one-dimensional case (the problem of calculating properties of 2D charged layers in heterostructures) where the screening of a charged plane involves formation of a potential $\varphi(x)$ of arbitrary strength, including those for which $e\varphi(x) \gg T$, the density distribution $n(x)$ is [7,8]

$$n(x) \propto \left(\frac{a}{a+x}\right)^2. \quad (12)$$

Here the constant a plays the role of the screening length. Obviously, the behavior of nonlinear solution (12) at large distances $x \gg a$ (12) has nothing to do with exponentials which could be expected from the arguments leading to Eqs. (10), (11). The integral like (9) with $n(x)$ (12) proves to be convergent, suggesting that one-dimensional Coulomb potentials $V(x)$ can be classified as those confining their counterions.

It is rather instructive that the two-dimensional case (DNA molecules in a solution [9], edge dislocations in semiconductors [10]) also allows a detailed nonlinear analysis. Let us start with the approximation which also proves to be useful in 3D geometry. By employing the potential $\varphi(\rho)$ (ρ being the two-dimensional radius) in the form

$$\varphi(\rho) \simeq \frac{2q}{\varepsilon}\ln(\rho/b), \quad (13)$$

where q is the charge density per unit thread length and b is the thread core radius, one obtains the counterions density $n(\rho)$ (8) in the form

$$n(\rho) = C\exp\left(-\frac{e\varphi}{T}\right) = C\left(\frac{b}{\rho}\right)^{(2qe)/(\varepsilon T)}. \quad (14)$$

The normalization constant C is fixed by the condition

$$2\pi\int_b^\infty n(\rho)\rho\,d\rho = q/e, \quad (15)$$

which is similar to Eq. (9).

For $qe/(\varepsilon T) > 1$ the integral (15) converges and the constant C is nonzero. Here the density $n(\rho)$ (14) decays faster than ρ^{-2}. This is again a nonexponential behavior as in (11) but the decay is sufficiently fast to provide confinement of counterions near the charged thread. On the contrary, for $qe/(\varepsilon T) < 1$ the integral (15) diverges, the constant C tends to zero, counterions go to infinity from the charged thread, suggesting a dissociation.

A consistent solution to the nonlinear axially symmetric problem confirms the tendency of countreions to leave the neighborhood of the charged thread and feasibility of the approximate approach (13)–(15).

Arguing by analogy with (13)–(15), one can construct density (8) for a spherically symmetric center by employing $\varphi(r) \simeq Ze/\varepsilon r$

$$[n_+(r) - n_-(r)] \propto \sinh\left(\frac{Ze^2}{\varphi Tr}\right). \quad (16)$$

At large distances this density behaves as

$$[n_+(r) - n_-(r)]_{r>>r_B} \propto \left(\frac{Ze^2}{\varepsilon Tr} \right), \qquad (17)$$

leaving no chances for convergence of the integrals (9) or (15).

4. Summary. The alternative (2), (3) contains actually two questions. An answer to one of them: is there a threshold in the behavior of $\alpha(C \to 0)$? — is directly related to the properties of the statistical model of atom (donor). If the answer is positive (the answer obtained within the Thomas–Fermi or Debye–Hückel approximations) the threshold does exist (as in the hopping conduction [6]). The above arguments favor the conclusion that a singly equilibrium spherically symmetric donor cannot exist in a semiconductor medium. Therefore, the dependence $\alpha(C \to 0)$ does not contain any threshold.

A separate question on the behavior of $\alpha(C)$ in the limit $C \to 0$ remains open. The linear asymptote (2) is rather naive. It can be corrected in a consistent solution of the problem taking into account the behavior of counterions leaving the neighborhood of the donor central charge.

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