A GENERAL THEORY OF THE SURFACE PHOTOELECTRIC EFFECT AT A METAL – ELECTROLYTE INTERFACE

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The external photoelectric effect at a metal–vacuum interface has been thoroughly studied, both experimentally and theoretically [1-4]. Systematic studies on the photoelectric effect at a metal–electrolyte interface did not, however, begin until very recently [5-8]. These studies have considerable interest for the general theory of the photoelectric effect and surface phenomena as well as for practical application of photoemission. This fact largely traces back to the structure of the interface [9] which is such that the application of a relatively small external potential can radically alter the electrode photoemission.

We will be concerned with the details of the so-called surface photoelectric effect at a metal–electrolyte interface, and will show that the semi-empirical theory developed by Fowler [2] cannot be applied here in the manner proposed in [5, 6]. We start from the following natural assumptions: 1) the field associated with the external electromagnetic wave is much weaker than either the interatomic or the intermolecular field; 2) the distance over which inelastic collision occurs between the fast moving photoelectrons and the solvent of the solution (moderation) is large in comparison with the interatomic separation. The illumination frequency, ω, will, moreover, be assumed low enough to eliminate the possibility of the bulk photoelectric effect in the metal, this being only weakly related to surface phenomena. The interesting range of frequencies will therefore generally be $\hbar\omega = 1$ to 10 eV. Here the effect of the magnetic field of the impinging wave on the electron movement can be neglected.

On this basis, the general expression for the photoemission current from the metal can be written as:

$$I = \int j(E, \mathbf{p}_\parallel A)\, F(\mu, E)\, \rho(E, \mathbf{p}_\parallel)\, dE\, d\mathbf{p}_\parallel. \tag{1}$$

Here A is the potential vector for the electromagnetic wave; E and $p_{||} = \{ p_x, p_y \}$ are the initial values of the energy and the momentum component parallel to the surface, as given by the electron functions for the metal, from which one develops j, the current density, asymptotic as $z \to \infty$ and averaged over the metal surface (z is the coordinate normal to the surface); F is the Fermi function with the chemical potential μ, and $\rho(E, p_{||})$ is the density distribution function. Integration is to range over the entire phase space.* To find the current in any case, it is necessary to solve the complex quantum mechanical problem of relating j to the interfacial properties; this we will treat in a special communication. Certain significant conclusions can, however, be drawn from Eq. (1), which can also serve as a basis for general statements as to the structure of the expression for the current density, j.

Most of the electrons emitted into the liquid will have energies considerably greater than kT, and their motion in the liquid will be that of particles of effective mass m in a mean potential well of depth V, the latter dependent on the liquid properties (in the case of vacuum emission, V = 0). In this respect, particle motion in a polar liquid is not different from particle motion in a polar crystal [10]. We limit discussion to cases involving the absorption of a single photon. In view of conservation of energy and momentum, one has for the z momentum component of the emitted electron at points far removed from the metal:

$$p = \sqrt{2m(E + V + \hbar\omega) - \mathbf{p}_\parallel^2}. \tag{2}$$

It follows from the form of the quantum mechanical current density operator [11] that the expression for $j(E, \mathbf{p}_\parallel A)$ will be

$$j(E, \mathbf{p}_\parallel A) = e\frac{p}{m}|\psi_f|^2\,\theta(p_f^2). \tag{3}$$

* It is to be emphasized that the form of Eq. (1) is not dependent on the particular model chosen for the metal.

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Here ψ_f is the value of the electron wave function in an electromagnetic field at the limit $z \to \infty$, $\theta(p^2)$ is a theta function defined by the conditions, $\theta(x) = 0$, when $x < 0$, and $\theta(x) = 1$ when $x > 0$. The following statements can be made concerning the function $|\psi_f|^2$. First, it is smooth over the region of integration, the latter being bounded because of the θ function of Eq. (3); second, it behaves like a constant as $p \to 0$, provided the surface potential fall-off is sufficiently rapid. Estimates similar to those made for threshold sections (see, for example, [12]) show that $|\psi_f|^2$ can always be considered as constant when the energy $\hbar\omega$, and the corresponding final electron kinetic energy, $p^2/2m$, is less than $\hbar^2/2m\delta^2$, δ being a parameter measuring the fall-off in the surface forces. For the case in question here, this interval of final energies covers several electron volts, and thus includes almost the entire range of surface photoelectric effect energies.

The situation in regard to electron emission in vacuum, or in a dielectric with dielectric constant close to unity, is quite different; there one has long-range image forces, so that $|\psi_f|^2 \sim 1/p$ when the energy is low. This fact justifies the substitution in Eq. (1) of a constant when $p^2 > 0$ and zero when $p^2 < 0$, rather than the expression of Eq. (3), when calculating the vacuum threshold current. This is the procedure of the Fowler theory mentioned above.

Substituting Eqs. (2) and (3) in Eq. (1), and taking account of the preceding remarks, one finds for the present case:

$$I = \frac{e}{m} \int_{-\hbar\omega-U}^{\infty} dE\, F(\mu, E) \int_0^{\sqrt{2m(E+V+\hbar\omega)}} p\,|\psi_f|^2 \rho \cdot 2\pi\, |p_\parallel|\, d|p_\parallel|$$

$$= \frac{2\pi e}{3m} \overline{|\psi_f|^2 \rho} \int_{-\hbar\omega-U}^{\infty} \frac{dE}{e^{(E-\mu)/kT}+1} [2m(E+V+\hbar\omega)]^{3/2}. \qquad (4)$$

Here $\overline{|\psi_f|^2\rho}$ is the mean value of the function $|\psi_f|^2\rho$, a quantity which depends only weakly on E over an integration range of $\hbar\omega$ values limited in the above sense.

At T = 0, it is reasonable to speak of the threshold frequency for the single-photon photoelectric effect (red edge). The corresponding value of ω_0 is to be determined from the condition $\hbar\omega_0 = W$, where W, the work function for passage of an electron from the Fermi surface into the liquid, is given, in the present case, by $W = -(\mu + V)$. Over the interval of frequencies close enough to ω_0 so that $\hbar|\omega - \omega_0| < \varepsilon_F$, ε_F being the Fermi energy of the metal calculated from the bottom of the conduction band, one can use the approximation $\overline{|\psi_f|^2\rho} = |\psi_f|^2\rho|_{E=\mu}$.

Carrying out a change of variables in Eq. (4), $p_\parallel = 0$, $x = (\hbar\omega + E + V)/kT$, one can rewrite the expression for I in the form:

$$I = A_0 (kT/\varepsilon_F)^{1/2} T^2 \chi B(\beta). \qquad (5)$$

Here A_0 is the Sommerfeld constant, as given by the equation $A_0 = 4\pi e k^2 m_e/(2\pi\hbar)^3 = 120$ A/(cm^2 · deg^2) (m_e is the mass of the electron), χ is a dimensionless function depending on the properties of the metal and the interface, and $\beta = \hbar(\omega - \omega_0)/kT$. The general function $B(\beta)$ of Eq. (5) is defined by

$$B(\beta) = \int_0^{\infty} \frac{x^{3/2}}{e^{x-\beta}+1}\, dx. \qquad (6)$$

It is to be emphasized that the derivation of Eq. (5) involves no assumptions concerning the form of the potential barrier, other than it fall off rapidly, and none at all concerning the properties of the Fermi surface. This is in distinction to the work of [1-3] which was based on the free electron model and an assumed rectangular potential barrier. The function $B(\beta)$ has been studied earlier in connection with the calculation of the mean energy of the electron gas. It follows from Eqs. (5) and (6) that when T = 0, one has

$$I = 0 \qquad \text{if} \quad \omega \leqslant \omega_0; \qquad (7)$$

$$I = A_0 \chi \frac{2}{5k^{3/2}\varepsilon_F^{1/2}} [\hbar(\omega - \omega_0)]^{5/2} \qquad \text{if} \quad \omega \geqslant \omega_0. \qquad (8)$$

Equation (8) indicates that the photocurrent from a monochromatic source follows a 5/2 law at T = 0. The concept of the red edge becomes vague when $T \neq 0$ since there is then a photocurrent even if $\omega < \omega_0$. However, with increasing frequency, the temperature dependency rapidly disappears if $\hbar(\omega - \omega_0) \gg kT$, and when $\beta \gg 1$ the photocurrent will once more be described by Eq. (8), as can be seen from Eq. (6).

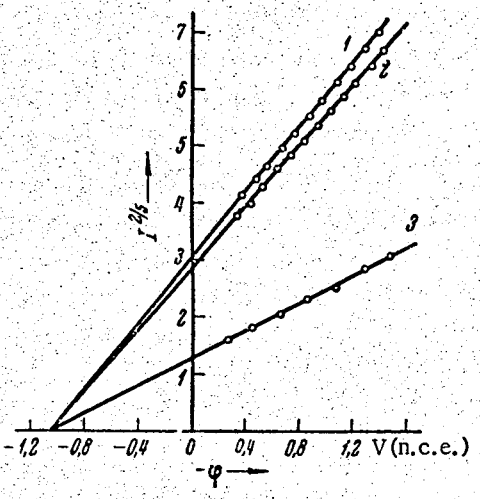

Fig. 1. The relation between the photocurrent $I^2/_5$ (relative units) and the electrode potential, $-\varphi$, in volts (recalculation of the data of [5]). Wave length of light, λ, 2537 Å. Solution composition: 1) 0.2 M KCl, saturated with N_2O; 2) 0.2 M NaF, saturated with N_2O; 3) 0.2 M KCl and $3.3 \cdot 10^{-3}$ M N_2O.

We will now consider the frequency dependence of the surface photocurrent when $\hbar(\omega - \omega_0) > \varepsilon_F$. When the frequencies, and corresponding values of p, are high, and the surface potential falls off rapidly, ψ_f proves to be the p-th Fourier component of the bounded square integrated function. It then follows from the known properties of the Fourier transform that the value of $|\psi_f|^2$ will diminish as p increases (with $|\psi_f|^2 \to 0$ and $p \to \infty$). This indicates that departures from Eq. (8) will be in the direction of diminished values of I as ω increases. The general form of the $I(\omega)$ function up to the beginning of the bulk effect must be that of a curve with a maximum (or maxima) at $\hbar(\omega - \omega_0) \sim \varepsilon_F$.

It is to be emphasized that the situation here is different from that of [4, 13, 14], in that Eq. (8) contains the factor $(\omega - \omega_0)$ raised to the 5/2 rather than the second power,* our calculation having taken account of the additional fall-off in the current as $\omega \to \omega_0$. The temperature dependence of I in the neighborhood of the threshold frequency must naturally be different from that given by the Fowler theory.

Establishment of a potential difference, φ, between the metal and the electrolyte (electrode polarization) changes the depth of the potential well, V, by the amount $e\varphi$, and brings about a corresponding shift in the red edge for the photoelectric effect

$$\hbar\omega_0(\varphi) = \hbar\omega_0(0) + e\varphi. \qquad (9)$$

Here $\omega_0(0)$ is the value of the threshold in the absence of any additional polarization, φ, of the electrode. The relations obtained for I combined with Eq. (9) fix the volt–ampere characteristics of the metal–electrolyte system under the electronic photoelectric effect, provided the effect of an alteration of the potential on the electron density of the metal can be neglected.

As an illustration of the theory, the experimental data of Barker et al. on mercury [5] have been reworked with the aid of Eqs. (8) and (9). It is seen from Fig. 1 that the agreement with the theory is quite good, the straight lines of the family passing through a single point. Knowing the potential of this point of intersection of the wave length of the radiation used in the experiment [5], Eq. (9) was used to determine the work function for the passage of rapid electrons from mercury to water at the null charge of W = 3.3 eV. Similar results have been obtained on reworking other data [6].

It follows from symmetry considerations that it is only the z component of the electric field, E_z, that can give rise to this kind of quantum transfer. From this one concludes that in first order perturbation theory, $\psi_1 \sim E_z$ and $\chi \sim E_z^2$. Thus the photoemission current resulting from polarized light depends not only on the angle of incidence, but is also proportional to the second power of the sine of the angle between the plane of polarization and the plane of incidence. The experimentally observed close dependence of the photocurrent and the light polarization points to the presence of a surface photoelectric effect, this type of dependence being foreign to other mechanisms which have been advanced to account for the photocurrent in the metal – electrolyte system. By using polarized light sources, one could hope to separate the surface and bulk components of the photoelectric effect at high energies. This should give additional significant information concerning surface effects. In particular, the "point of departure" from the 5/2 law is related to the range of action of the surface forces.

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* We note that the 5/2 law was also obtained in [3] for the special model of the electron gas and a rectangular potential well. The approach of [3] is not, however, suitable for the present case of photoemission in vacuum, since long-range image forces always come into play there.

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