# Shape Dependence of the Work Function of Small Metallic Clusters

Minoru YOSHIDA, Masato AOKI and Hideji YAMADA

Department of Physics, Faculty of General Education, Gifu University

(Received November 4, 1988)

**Abstract**

The shape dependence of the work function of small metallic clusters is studied by taking into account the effect of image forces. A general expression of the work function for prolate and oblate spheroidal clusters is obtained. It is shown that the work functions for the prolate and oblate spheroidal clusters are smaller and larger than that for the spherical cluster with the same volume, respectively.

The studies on small clusters have recently become one of the most interesting fields on the solid state physics. By the aggregation of atoms, a crystal grows to form the ultimate extended solid structure and physical properties of the intermediate states between the atom and the solid are particularly taken an interest in to understand how the extended solid develops from the growing cluster aggregate. Then, the stability of the atomic configurations, electronic structures and ionization potentials of the small clusters have so far been studied intensively [1].

The observations of the mass spectra and the ionization potentials for the small clusters are strong experimental methods to study their electronic structures. It was found that the observed ionization potentials for small sodium and potassium clusters are larger than the bulk work function and vary with the cluster size [2, 3]. An appreciable amount of the additional energy $q^2/2C$ is required to charge up the very small conducting clusters, where $q$ and $C$ are the charge on the cluster and the electric capacity, respectively. The work function $W$ is then given by

$$W = W_b + \frac{1}{2}\frac{e^2}{C}, \tag{1}$$

where $W_b$ is the work function for the bulk medium and $e$ is the electron charge. The capacity $C$ and then $W$ for small conducting clusters depends strongly on the size of the cluster through the second term in eq. (1). For example, the capacity $C$ for a spherical conductor with radius $R$ is equal to $R$.

On the other hand, various results of experiment and theory show that the coefficient 1/2 in the second term of eq. (1) seems to be rather large. This coefficient is reduced when the details of the charge removal from the cluster, including the effect of image forces, are taken into account. For a spherical cluster, Smith [4] and Wood [5] showed that the coefficient 1/2 in eq. (1) is reduced to 3/8 due to the effect of image forces. In this short paper, the shape dependence of the work function $W$ for small metallic clusters is discussed by taking into account the effect of image forces.

For the prolate and oblate spheroidal clusters, the Laplace's and Poisson's equations for the potential can be solved by using the prolate and oblate spheroidal coordinates $(\xi, \eta, \phi)$, respectively [6]. In the prolate spheroidal coordinates, the work required to remove an electron from a position $(\xi_0, \eta_0, \phi_0)$ outside of the cluster to infinity is given by

$$W(\xi_0, \eta_0; \xi_1) = \frac{2e^2}{a}\left\{Q_0(\xi_0) - \frac{[Q_0(\xi_0)]^2}{2Q_0(\xi_1)} + \frac{1}{2}\sum_{n,m}(2n+1)\varepsilon_m \right. \\ \left. \times(-i)^m\left[\frac{(n-m)!}{(n+m)!}\right]^2 [P_n^m(\eta_0)Q_n^m(\xi_0)]^2 \frac{P_n^m(\xi_1)}{Q_n^m(\xi_1)}\right\}, \tag{2}$$

where the surface of the cluster is the prolate spheroid given by $\xi=\xi_1$ with interfocal distance $a$, $\varepsilon_m$ is the Neumann factor ; $\varepsilon_0=1$, $\varepsilon_m=2$ for the positive integer $m$, and $P_n^m$ and $Q_n^m$ are associated Legendre functions of the first and second kinds, respectively. In the oblate spheroidal coordinates, the expression of $W(\xi_0, \eta_0 ; \xi_1)$ is the same as eq. (2) when $a$, $\xi_0$ and $\xi_1$ are replaced with $2a/i$, $i\xi_0$ and $i\xi_1$, respectively, where $a$ in the oblate spheroid denotes the radius of the focal ring. The details of the derivation of eq. (2) will be published elsewhere.

The expression of $W(\xi_0, \eta_0 ; \xi_1)$ given by eq. (2) is very complicated. For the sake of simplicity, we put $\eta_0=1$, that is, we discuss the work required to remove an electron only from a point on $z$-axis of the spheroid. In this case, $P_n^m(1)=\delta_{m0}$ and we get

$$W(\xi_0, 1 ; \xi_1) = \frac{2e^2}{a}\left\{Q_0(\xi_0) - \frac{[Q_0(\xi_0)]^2}{2Q_0(\xi_1)} + \frac{1}{2}\sum_n(2n+1)[Q_n(\xi_0)]^2\frac{P_n(\xi_1)}{Q_n(\xi_1)}\right\} \tag{3}$$

for a prolate spheroidal cluster. For an oblate spheroidal cluster, the same expression as eq. (3) is obtained again by the replacements of $a$, $\xi_0$ and $\xi_1$ as mentioned above.

For $\xi_0$ and $\xi_1 \gg 1$, Legendre functions $P_n(\xi_1)$, $Q_n(\xi_0)$ and $Q_n(\xi_1)$ in eq. (3) can be expanded in a power series of the inverse of $\xi_0$ and $\xi_1$. Up to the second order terms with respect to $\xi_0^{-1}$ and $\xi_1^{-1}$, we get for the prolate spheroidal clusters

$$W(\xi_0, 1 ; \xi_1) = \frac{e^2}{4d} + \frac{3}{8}\left(1 - \frac{2}{9\xi_1^2}\right)\frac{e^2}{R^*} \tag{4}$$

in the limit of the small distance $d=a(\xi_0-\xi_1)/2$ of the electron above the pole ($\xi=\xi_1$ and $\eta=1$) of the prolate spheroid, where $R^*$ is the radius of the equivalent sphere. For the oblate spheroidal clusters, we get

$$W(\xi_0, 1 ; \xi_1) = \frac{e^2}{4d} + \frac{3}{8}\left(1 + \frac{2}{9\xi_1^2}\right)\frac{e^2}{R^*} \tag{5}$$

in the limit of the small distance $d=a(\xi_0-\xi_1)$ of the electron above the pole ($\xi=\xi_1$ and $\eta=1$) of the oblate spheroid, where $R^*$ is the radius of the equivalent sphere again.

The values of $\xi_1$ in eqs. (4) and (5) for prolate and oblate spheroidal clusters are given in terms of the axially symmetric distortion parameter $\delta$ defined by Clemenger [7] as $\xi_1=(2+\delta)/2^{3/2}|\delta|^{1/2}$, where $\delta$ is positive for the prolate distortion and negative for the oblate distortion, respectively. Then, eqs. (4) and (5) are rewritten as

$$W(\xi_0, 1 ; \xi_1) = \frac{e^2}{4d} + \frac{3}{8}\left(1 - \frac{4}{9}\delta\right)\frac{e^2}{R^*} \tag{6}$$

for both of the prolate and oblate spheroidal clusters. Our result of eq. (6) can be shown to coincide with that for the spherical cluster obtained in refs. [4] and [5] when $\delta=0$.

The first term in eq. (6) is the same as the work required to remove an electron just above the surface of the bulk medium and then it is included into the bulk work function $W_b$ in eq. (1). The work $e^2/4d$, which is derived by the classical electrostatic theory, becomes infinity when $d$ tends to zero. However, the image force is a part of the change in the quantum mechanical exchange-correlation energy when an electron leaves the cluster and the classical theory breaks down in the limiting case of $d=0$ [1]. Anyhow, the work, $e^2/4d$, can be attributed to the bulk work function $W_b$ in eq. (1).

On the other hand, the electric capacity $C$ in eq. (1) for prolate and oblate spheroidal clusters can be shown to be the same as that for the spherical cluster with the same volume up to the order of $\xi_1^{-2}$. Therefore, the shape dependence of the capacity for the conducting clusters does not take part in the work function $W$ in eq. (1) within the present approximation.

In this short paper, the work function for the small metallic clusters has been shown explicitly to depend on their shapes. We have discussed it only for the special position just above the surface of clusters on the $z$-axis, i.e., $\eta_0=1$ in the prolate and oblate spheroidal coordinates. However, it can be easily understood that eq. (4) is the smallest value for the prolate spheroidal cluster and eq. (5) is the largest value for the oblate spheroidal cluster, because the work function becomes small when the curvature of the surface becomes sharp. An electron will be emitted near from the position where the work function is the smallest and the cluster is ionized. Therefore, it is concluded that the work function for small metallic clusters depends strongly not only on the size of the cluster but also on the shape of the cluster.

Furthermore, it can be pointed out that some informations on the shape of clusters may be obtained from the observed value of the coefficient in the second term of eq. (1). Recently, this coefficient was observed to be 0.33 for the potassium clusters [3], which is a little smaller than 3/8 for spherical clusters. This reduction of the coefficient may be explained by the distortion of the clusters as shown in the present paper.

## References

[1] W. A. de Heer, W. D. Knight, M. Y. Chou and M. L. Cohen, *Solid State Physics*, ed. H. Ehrenreich and D. Turnbull, vol. 40 (Academic Press, Inc., New York, 1987) p. 93.

[2] E. J. Robbins, R. E. Leckenby and P. Willis, Adv. Phys. 16 (1967) 739 ; K. I. Peterson, P. D. Dao, R. W. Farley and A. W. Castleman, Jr., J. Chem. Phys. 80 (1984) 1780.

[3] W. A. Saunders, Ph. D. Thesis, University of California, (1986).

[4] J. M. Smith, AIAA J. 3 (1965) 648.

[5] D. M. Wood, Phys. Rev. Lett. 46 (1981) 749.

[6] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, New York, 1953) p. 1252.

[7] K. Clemenger, Phys. Rev. B 32 (1985) 1359.

*Note added in proof.* —— Recently, Y. Ishii (Solid State Commun. 61 (1987) 227.) has discussed independently the ionization potential of the conducting spheroidal clusters. When $\eta=0$ and $Z=-1$, eq. (8) in his paper coincides exactly with our results of eqs. (4) and (5).