Theory of Metal Surfaces: Work Function*

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In a recent paper we presented a contribution to the theory of metal surfaces with emphasis on the shape of the electron-density distribution and the surface energy. The present paper extends this analysis to a consideration of the work function. Some general theoretical relationships are established. Effects of the ions are included using a simple pseudopotential theory, permitting the calculation of the variation of the work function from one crystal face to another. For simple metals (Li, Na, K, Rb, Cs, Al, Pb, Zn, and Mg), agreement with available experimental data is good (5–10%); for the noble metals, the computed work functions are 15–30% too low.

I. INTRODUCTION

The present paper represents a sequel to one concerned primarily with metal-surface charge densities and surface energies.[1] In the earlier paper we presented, first of all, a theory of the electronic structure of a model metal surface in which the lattice of positive ions was replaced by a uniform background charge. Exchange and correlation effects were included using the self-consistent version of the theory of the inhomogeneous electron gas.[2,3] Following this, the effect of the actual ionic structure on the surface energy was taken into account by calculating exactly a purely electrostatic contribution (similar to a Madelung energy), and by evaluating the interaction of the electrons with the ion cores using first-order pseudopotential theory.

In the present paper, we shall follow a similar plan in developing a theory of the work function. This quantity, denoted by Φ, and defined precisely in Sec. II in terms most useful for theoretical analysis, is equal to the minimum work that must be done to remove an electron from the metal at $0\,°K$.

We give first a rigorous demonstration that

$$\Phi = \Delta\phi - \bar{\mu}, \tag{1.1}$$

where $\Delta\phi$ is the rise in mean electrostatic potential across the metal surface and $\bar{\mu}$ is the bulk chemical potential of the electrons relative to the mean electrostatic potential in the metal interior. In spite of its simple form, this expression includes all many-body effects, in particular, that of the image force.

For the uniform-background model we evaluate $\Delta\phi$ from the electronic charge density $n(\vec{r})$, com-

puted in LK-I, and we take $\bar{\mu}$ from the available theory of exchange and correlation of a uniform electron gas. This yields the work function Φ_u of this model as a function of the mean bulk density $\bar{n}$ (or of the Wigner-Seitz radius r_s).[4] These results are compared with experiment and with the theoretical calculations of Smith, who used a similar approach but did not carry out a fully self-consistent calculation.[5]

Finally, we incorporate the effect of the actual ion cores. We show first that when the difference between the pseudopotentials of the ion cores and the electrostatic potential of the uniform charge background is treated as a small perturbation $\delta v(\vec{r})$, the change of the work function of a particular crystal face due to this perturbation is given to first order by the following rigorous expression:

$$\delta\Phi = \int \delta v(\vec{r})\, n_\sigma(\vec{r})\, d\vec{r}. \tag{1.2}$$

Here the integral is carried out over a slab whose surface consists overwhelmingly of the face in question; and $n_\sigma(\vec{r})$ is the change of the electron density, calculated in the uniform-background model, following the removal of one electron from the system. This electron deficiency is of course localized near the metal surface. We have calculated the charge density n_σ by a method analogous to that of LK-I, except that we have now had to look for self-consistent solutions with a zero mean electric field deep inside the metal but a small finite field outside it.

Since $n_\sigma(\vec{r})$ depends in fact only on the distance x from the nominal surface, it is possible to reduce (1.2) to a one-dimensional quadrature. In this way we have calculated the total work function

$$\Phi = \Phi_u + \delta\Phi \tag{1.3}$$

for the principal faces of nine simple metals – Al, Pb, Zn, Mg, Li, Na, K, Rb, Cs – and the noble metals Cu, Au, and Ag. Experimental data are generally available only for polycrystalline samples of unknown surface structure. This makes a detailed comparison between theory and experiment impossible. Nonetheless, we can state the following conclusions.

Simple metals: The measured work functions range over 2.1–4.3 eV. With the possible exception of Li (where there is considerable uncertainty both in the experimental data and in the pseudopotential), agreement between the full theory and experiment is typically within 5–10%. The ionic lattice contributions $\delta\Phi$, which are characteristically of the order of 10% of the total work functions, contribute to establish this rather good agreement. Anisotropies among the different faces are typically also of the order of 10% of the mean work function. In accordance with the arguments of Smoluchowski,[6] we find the lowest work function to be associated with the least densely packed face among those considered [(110) for fcc, (111) for bcc].

Noble metals: In view of the success with simple metals, we have applied the same technique to the noble metals to learn about the limits of validity of our theory. Here the experimental work functions range over 4.0–5.2 eV, and the calculated values are 15–30% too low. It may be assumed that the presence of the filled d bands not far from the Fermi level makes our highly simplified theory, based on the inhomogeneous-electron-gas model with small pseudopotential corrections, much less appropriate for these metals.

In summary, the theory we have outlined appears to describe well the work functions of simple metals. Additional reliable experimental data for this class of metals would be highly desirable, particularly data on the work functions of single-crystal faces. In the case of the noble metals, on the other hand, where, for metallurgical reasons, the experimental data are much more consistent and reliable, the present theory is less successful, and further theoretical work is needed. There is need also for additional theoretical studies on the transition metals, which are not discussed in this paper.[7]

II. RIGOROUS EXPRESSION FOR WORK FUNCTION

Qualitative considerations, in the spirit of the Sommerfeld electron theory of metals, strongly suggest that the work function is given by the expression

$$\Phi = \Delta\phi - \bar{\mu} . \tag{2.1}$$

Here $\Delta\phi$ is the change in electrostatic potential across the dipole layer created by the "spilling out" of electrons at the surface, and $\bar{\mu}$ is the chemical potential of the electrons in the bulk metal rel-
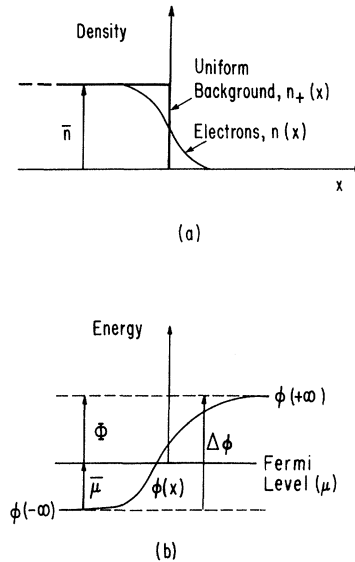

FIG. 1. Schematic representation of (a) density distributions at a metal surface and (b) various energies relevant to a study of the work function.

ative to the mean electrostatic potential there (see Fig. 1). It is important to know if this expression includes properly all many-body effects, in particular, the work done against the image force in removing an electron from the metal. This is in fact the case. As we have not found any rigorous demonstration of Eq. (2.1) in the literature, we present one in this section.

Since we are interested in removing one electron from the metal at 0 °K, we first develop a simple extension of the theory of Hohenberg and Kohn (HK)[2] to allow for a variable number of electrons,[8] and then use this theory in establishing the validity of Eq. (2.1).

In HK, it was shown that for a fixed number of electrons N and arbitrary static external potential $v(\vec{r})$, there exists an energy expression[9]

$$E_v[n] = \int v(\vec{r})n(\vec{r}) \, d\vec{r} + \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}\,'$$

$$+ G[n] , \tag{2.2}$$

with the following properties: (a) $G[n]$ is a universal functional of $n(\vec{r})$, not explicitly dependent on $v(\vec{r})$, given by

$$G[n] \equiv (\Psi_n, [T + U]\Psi_n) - \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}', \tag{2.3}$$

where the wave function Ψ_n refers to the (unique) electron ground state with density $n(\vec{r})$, and T and U are, respectively, the kinetic- and interaction-energy operators; (b) $E_v[n]$ is equal to the correct

ground-state energy for a given $v(\vec{r})$ when the correct density $n(\vec{r})$, corresponding to v, is used on the right-hand side of the equation; (c) the first variations of $E_v[n]$ about this density, consistent with the restriction

$$\delta N \equiv \int \delta n(\vec{r}) \, d\vec{r} = 0 , \qquad (2.4)$$

vanish:

$$\delta E_v[n] = 0 . \qquad (2.5)$$

Now consider an ensemble of macroscopic electronic systems at the absolute zero of temperature, specified by the external potentials $v(\vec{r})$ and the chemical potentials μ. The subsidiary condition (2.4) will no longer be imposed on the density variations of interest. We define

$$\Omega_{v,\mu}[n] \equiv E_v[n] - \mu \int n(\vec{r}) \, d\vec{r} . \qquad (2.6)$$

Clearly, for a first variation of the density $\delta n_1(\vec{r})$ which does satisfy the condition (2.4),

$$\delta_1 \Omega_{v,\mu}[n] = \delta_1 E_v[n] = 0. \qquad (2.7)$$

Now let $n_{\mu,v}(\vec{r})$ and $n_{\mu+\delta\mu,v}(\vec{r})$ be the correct electron densities corresponding to a given $v(\vec{r})$ and, respectively, to μ and $\mu+\delta\mu$. These two chemical potentials describe two systems whose total numbers of particles differ by δN:

$$\delta N = \int [n_{\mu+\delta\mu,v}(\vec{r}) - n_{\mu,v}(\vec{r})] \, d\vec{r} \equiv \int \delta n_2(\vec{r}) \, d\vec{r} . \qquad (2.8)$$

The corresponding first-order change of $\Omega_{v,\mu}$ is given by

$$\delta_2 \Omega_{v,\mu}[n] = E_v[n_{\mu+\delta\mu,v}] - E_v[n_{\mu,v}] - \mu\delta N = 0 , \qquad (2.9)$$

where the vanishing follows from the thermodynamic definition of the chemical potential at $T = 0$ °K. Since an arbitrary small variation δn is a (unique) sum of variations of the types δn_1 and δn_2, it follows that, in general,

$$\delta \Omega_{v,\mu}[n] = 0. \qquad (2.10)$$

We now apply this theory to the work function. We consider a neutral slab of metal, all of whose dimensions are macroscopic but whose surface consists overwhelmingly of two parallel faces the work function of which we wish to consider (the physical properties of these two surfaces are taken to be identical). Let $n(\vec{r})$ be the correct electron density corresponding to the given nuclear potential, the chemical potential μ, and a total number of electrons N. By (2.6), (2.2), and (2.10) we have, for a small variation in density $\delta n(\vec{r})$,

$$\int \left(\phi(\vec{r}) + \frac{\delta G[n]}{\delta n(\vec{r})} \right) \delta n(\vec{r}) \, d\vec{r} - \mu\delta N = 0 , \qquad (2.11)$$

where

$$\phi(\vec{r}) \equiv v(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' \qquad (2.12)$$

is the total electrostatic potential. Now consider first a particle-conserving, but otherwise arbitrary, variation δn. Equation (2.11) then gives

$$\phi(\vec{r}) + \delta G[n]/\delta n(\vec{r}) = \mu' , \qquad (2.13)$$

where μ' is some constant, independent of $\vec{r}$. Next, consider a particle nonconserving variation; from (2.11) and (2.13) we then see that

$$\mu = \mu' = \phi(\vec{r}) + \delta G[n]/\delta n(\vec{r}) . \qquad (2.14)$$

The work function is, by definition,

$$\Phi = [\phi(\infty) + E_{N-1}] - E_N , \qquad (2.15)$$

where $\phi(\infty)$ is the total electrostatic potential far from the slab considered above and E_M is the ground-state energy of the slab with M electrons (but still with N units of positive charge). [Both $\phi(\infty)$ and E_M depend on the choice of energy zero, but the combination (2.15) does not.] Using the definition of the chemical potential and Eq. (2.14), this can also be written as

$$\Phi = \phi(\infty) - \mu = [\phi(\infty) - \bar{\phi}] - \bar{\mu} , \qquad (2.16)$$

where

$$\bar{\phi} \equiv \langle \phi(\vec{r}) \rangle ,$$

$$\bar{\mu} = \mu - \bar{\phi} = \langle \delta G[n]/\delta n(\vec{r}) \rangle . \qquad (2.17)$$

Here $\langle \rangle$ denotes an average over the metal. $\bar{\mu}$ is the bulk chemical potential relative to the mean interior potential; its independence of this potential may be verified from the definition (2.3) of $G[n]$. Equation (2.16) is equivalent to the postulated Eq. (2.1).

All many-body effects are contained in the exchange and correlation contributions to $\bar{\mu}$ and in their effect on the barrier potential $\Delta\phi$. In particular, the image-force effect on Φ may be regarded as contained in the disappearance of part of the correlation energy when one electron is moved away from the metal surface.

III. UNIFORM-POSITIVE-BACKGROUND MODEL

We consider in this section a model of a metal surface in which the positive ions are replaced by a uniform positive charge background filling the half-space $x \le 0$.[10] The electron density in this model is shown schematically in Fig. 1(a).

We consider first the quantity $\bar{\mu}$ in Eq. (2.1). Since deep in the metal interior the electron density has a constant value $\bar{n}$, $\bar{\mu}$ takes on the simple form

$$\bar{\mu} = \tfrac{1}{2} k_F^2 + \mu_{xc}(\bar{n}) . \qquad (3.1)$$

Here $k_F = (3\pi^2 \bar{n})^{1/3}$ is the bulk Fermi wave number

TABLE I. The work function Φ_u of the uniform-background model, and its bulk and surface-barrier components. The Wigner-Seitz radius r_s characterizes the interior density. $\Phi_u = \Delta\phi - \bar\mu$, where $\bar\mu = \frac{1}{2}k_F^2 + \mu_{xc}$. The barrier term $\Delta\phi$ is given with a self-consistency of 0.03 eV or better (this is a somewhat greater self-consistency than that of the preliminary report, Ref. 4).

r_s	$\frac{1}{2}k_F^2$ (eV)	μ_{xc} (eV)	$\bar\mu$ (eV)	$\Delta\phi$ (eV)	Φ_u (eV)
2	12.52	-9.61	2.91	6.80	3.89
2.5	8.01	-7.90	0.11	3.83	3.72
3	5.57	-6.75	-1.18	2.32	3.50
3.5	4.09	-5.92	-1.83	1.43	3.26
4	3.13	-5.28	-2.15	0.91	3.06
4.5	2.47	-4.78	-2.31	0.56	2.87
5	2.00	-4.38	-2.38	0.35	2.73
5.5	1.66	-4.04	-2.38	0.16	2.54
6	1.39	-3.76	-2.37	0.04	2.41

and $\mu_{xc}(\bar n)$ is the exchange and correlation part of the chemical potential of an infinite uniform electron gas of density $\bar n$. μ_{xc} is given by the relation

$$\mu_{xc}(n) = \frac{d}{dn}[n\epsilon_{xc}(n)], \qquad (3.2)$$

with ϵ_{xc} the exchange and correlation energy per particle of the uniform gas. In our computations, we have used the expression[11]

$$\epsilon_{xc}(\bar n) = -(0.458/r_s) - 0.44/(r_s + 7.8) \qquad (3.3)$$

from Wigner's classic analysis of the electron gas; here the Wigner-Seitz radius r_s is given by

$$\tfrac{4}{3}\pi r_s^3 = 1/\bar n. \qquad (3.4)$$

Other, more recently suggested, forms of the correlation energy give substantially similar results.[12]

The quantity $\bar\mu$ and its two components $\frac{1}{2}k_F^2$ and μ_{xc} are shown in Table I for r_s in the metallic range 2–6. By Eq. (2.1), $-\bar\mu$ can be regarded as the bulk contribution to Φ. It will be seen from Table I that, for metals of low electron density (K, Rb, and Cs with $r_s = 4.96$, 5.23, 5.63, respectively), $-\bar\mu$ is much larger than the other term $\Delta\phi$. The rather good agreement with experiment (see Table II) constitutes therefore a good confirmation of the expression (3.3) for ϵ_{xc}. This is especially meaningful since the theory of the correlation energy is most difficult at low electron densities.

We turn now to the double-layer contribution $\Delta\phi$. By Poisson's equation,

$$\Delta\phi = \phi(\infty) - \phi(-\infty) = 4\pi \int_{-\infty}^{\infty} x[n(x) - n_+(x)]\,dx, \qquad (3.5)$$

with $n(x)$ and $n_+(x)$, respectively, the electron- and positive-background densities in the uniform model. $n(x)$, calculated in LK-I with a self-consistency of better than 1% of $\bar n$, was recalculated for the present work to an accuracy of 0.2% or better. The resulting values of $\Delta\phi$ are listed in Table I, as is the total work function in the uniform model

$$\Phi_u = (\Delta\phi - \bar\mu)_{\text{uniform}}. \qquad (3.6)$$

It will be noted that while $\Delta\phi$ is negligible for metals of low electron density, it becomes dominant for high-electron-density metals. It is also striking that while $\bar\mu$ and $\Delta\phi$ separately change by 5.3 and 6.8 eV, respectively, over the metallic

TABLE II. Theoretical and experimental work functions of nine simple metals. Φ_u is the work function for the uniform-background model; $\delta\Phi$ is the first-order pseudopotential correction; $\Phi = \Phi_u + \delta\Phi$ (rounded to the nearest 0.05 eV). The pseudopotential core radii r_c are taken from the work of Ashcroft and Langreth (Refs. 18–20). In the cases in which these authors give two possible values of r_c for a metal, the choice which yields agreement with experiment for a wider range of bulk properties is marked with an asterisk. Experimental values Φ_{expt} for polycrystalline samples were taken from Refs. 25–27 (see text for details of selection). [The most densely packed faces for the various structures are: fcc (111), hcp (0001), bcc (110).]

Metal	Structure	r_s	Φ_u (eV)	r_c	$\delta\Phi$ (eV)			Φ (eV)			Φ_{expt} (eV)
					(110)	(100)	(111)	(110)	(100)	(111)	(polycrystalline)
Al	fcc	2.07	3.87	1.12	-0.21	0.32	0.19	3.65	4.20	4.05	4.19
Pb	fcc	2.30	3.80	1.12	0	0.13	0.06	3.80	3.95	3.85	4.01
				1.47*	0	0.72	1.33	3.80	4.50	4.15	
Zn	hcp	2.30	3.80	1.27	0.36 for (0001) face			4.15 for (0001) face			4.33
Mg	hcp	2.65	3.66	1.39	0.38 for (0001) face			4.05 for (0001) face			3.66
Li	bcc	3.28	3.37	1.06*	0.19	-0.05	-0.13	3.55	3.30	3.25	2.32, 3.1
				2.00	-0.99	-0.95	-1.05	2.40	2.40	2.30	
Na	bcc	3.99	3.06	1.67	0.03	-0.29	-0.39	3.10	2.75	2.65	2.7
K	bcc	4.96	2.74	2.14	0.01	-0.34	-0.40	2.75	2.40	2.35	2.39
Rb	bcc	5.23	2.63	2.61	-0.45	-0.53	-0.60	2.20	2.10	2.05	2.21
				2.13*	0.03	-0.26	-0.34	2.65	2.35	2.30	
Cs	bcc	5.63	2.49	2.93	-0.23	-0.61	-0.67	2.25	1.90	1.80	2.14
				2.16*	0.10	-0.21	-0.27	2.60	2.30	2.20	

density range, the total work function, given by their difference, varies only from 2.4 to 3.9 eV. [13]

The values of Φ_u given in Table I are similar to those obtained by Smith,[5] although Smith did not include in his calculations the Friedel density oscillations near the surface. The reason for this is the following: The contribution $-\bar{\mu}$ to Φ_u is identical in both calculations. For high electron densities, $\Delta\phi$ is substantial, but since the Friedel oscillations at these densities are rather small,[1] Smith's calculations give similar results to ours. For low electron densities, the Friedel oscillations are important and our $\Delta\phi$ is substantially smaller than that of Smith (by about a factor of 2 for Cs), but at these densities $\Delta\phi$ is negligible compared with $-\bar{\mu}$.

Figure 2 compares the computed values of Φ_u with recent experimental data on the work functions of polycrystalline simple metals. There is rather good agreement between theory and experiment for these metals, to which the uniform-background model would be expected to be best applicable. A more realistic treatment of the positive ions, presented in Sec. IV, improves this agree-
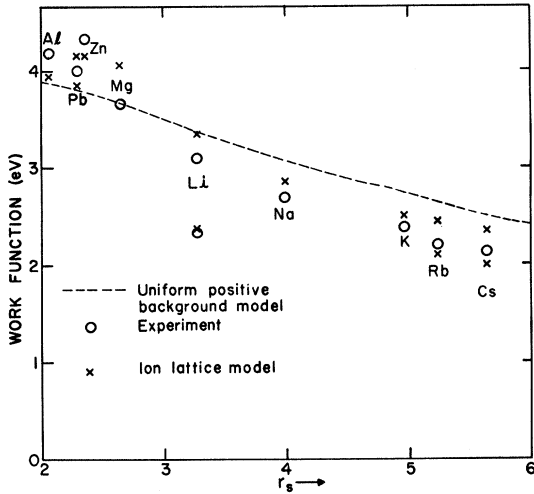
FIG. 2. Comparison of theoretical values of the work function with the results of experiments on polycrystalline samples (open circles). (The reason for the presence of two experimental points for Li is discussed in the text.) Φ_u, the work function in the uniform-background model, is shown as a dashed curve. The Φ values in the ion-lattice model were computed for the (110), (100), and (111) faces of the cubic metals and the (0001) face of the hcp metals (Zn and Mg). For qualitative purposes, the simple arithmetic average of these values for each metal is indicated by a cross (two crosses are shown for the cases in which there were two possible pseudopotential radii). The experimental and theoretical points for Zn should be at $r_s = 2.30$; they have been shifted slightly on the graph to avoid confusion with the data for Pb.

ment somewhat and also permits calculation, for a given metal, of the anisotropy of Φ, i.e., the variation of Φ from one crystal face to another.

IV. ION-LATTICE MODEL

A. Theory

When we pass from the idealized uniform-background model to a more realistic model in which the effect of each metal ion on the conduction electrons is represented by a pseudopotential, a straightforward attempt to calculate Φ from Eq. (2.1) would involve the prohibitively difficult task of solving self-consistently a system of equations which no longer separate, but which are truly three-dimensional. To avoid this problem we shall use the fact that the replacement of the uniform background by the ion pseudopotentials represents a small perturbation $\delta v(\vec{r})$. To first order in δv, the change of the work function $\delta\Phi$ will be shown to be given by the expression

$$\delta\Phi = \int \delta v(\vec{r}) n_\sigma(\vec{r}) \, d\vec{r}, \tag{4.1}$$

which has already been explained in Sec. I [Eq. (1.2)], and which avoids the solution of three-dimensional wave equations.[14]

To derive (4.1) we begin with the definition (2.15) of the work function

$$\Phi = [\phi(\infty) + E_{N-1}] - E_N = E_N' - E_N, \tag{4.2}$$

where the system in question is a large metal slab whose surface consists almost entirely of two parallel faces of a given orientation relative to the crystal axes. E_N is the ground-state energy of the neutral slab, containing N electrons; and E_N' is the energy of an excited state of the N-electron system in which $(N-1)$ electrons reside in the lowest possible state in the metal, while one electron is at rest at infinity. The first-order change of Φ due to δv is then, by standard perturbation theory,

$$\delta\Phi = \int \delta v(\vec{r}) n_N'(\vec{r}) \, d\vec{r} - \int \delta v(\vec{r}) n_N(\vec{r}) \, d\vec{r}, \tag{4.3}$$

where n_N' and n_N are the electron densities in the uniform model, associated with E_N' and E_N, respectively. Now since $\delta v(\infty) = 0$, the "escaped" electron does not contribute to the first integral and we may rewrite (4.3) as

$$\delta\Phi = \int \delta v(\vec{r}) n_\sigma(\vec{r}) \, d\vec{r}, \tag{4.4}$$

where

$$n_\sigma(\vec{r}) = n_{N-1}(\vec{r}) - n_N(\vec{r}), \tag{4.5}$$

with n_{N-1} the density distribution of the $(N-1)$ electrons in their ground state. Clearly the density deficiency n_σ satisfies the normalization

$$\int n_\sigma(\vec{r}) \, d\vec{r} = -1. \tag{4.6}$$

Now in the $(N-1)$-electron ground state, associated with E_{N-1}, the electric field $\vec{\mathscr{E}}$ inside the metal is zero, and outside each of the two parallel faces is given by $\vec{\mathscr{E}} = 4\pi/2A$ (directed along the outward normal), with $2A$ the total surface area. Let us take the x axis to have its origin in one of the faces and point outwards [see Fig. 1(a)]. Then n_σ is a function of x only. Further, let us denote the y-z average of $\delta v(\vec{r})$ by

$$\delta v(x) \equiv \int_A \delta v(x, y, z)\, dy\, dz / \int_A dy\, dz . \quad (4.7)$$

Then, using (4.6), Eq. (4.4) reduces to

$$\delta\Phi = A \int_{-\infty}^{\infty} \delta v(x) n_\sigma(x)\, dx$$

$$= - \int_{-\infty}^{\infty} \delta v(x) n_\sigma(x)\, dx / \int_{-\infty}^{\infty} n_\sigma(x)\, dx$$

$$= - \int_{-a}^{\infty} \delta v(x) n_\sigma(x)\, dx / \int_{-a}^{\infty} n_\sigma(x)\, dx , \quad (4.8)$$

where a is a length large compared with a screening length but small compared with the thickness of the slab. In the last step both numerator and denominator have been reduced by a factor of 2. Since (4.8) is homogeneous in n_σ, $n_\sigma(x)$ can now be taken to be the surface-charge density in the semi-infinite uniform-background model induced by an arbitrary weak electric field $\vec{\mathscr{E}}$ perpendicular to the surface.

B. Calculations

To evaluate (4.8) we require $n_\sigma(x)$ and $\delta v(x)$. $n_\sigma(x)$ was determined as the difference between two self-consistent densities: one corresponding to a neutral metal with vanishing field outside, and the other corresponding to a metal with a small surface charge and finite field $\vec{\mathscr{E}}$ outside. The method used was the same as that described in LK-I, and $n_\sigma(x)$ was evaluated for r_s between 2 and 6.[15] The functions $n_\sigma(x)$ for $r_s = 2, 4,$ and 6 are shown in Figs. 3(a), (b), and (c), respectively. They are rather wide density distributions, which outside the metal drop to half their maximum value at approximately 2–3 a. u. (or 1.0–1.5 Å) from the nominal surface.[16]

The perturbation potential $\delta v(x)$, Eq. (4.7), was obtained, as explained in LK-I, Appendix D,[17] using pseudopotentials of the form employed by Ashcroft and Langreth[18-20]:

$$v_{ps}(r) = \begin{cases} 0, & r \le r_c \\ - Z/r, & r > r_c \end{cases} . \quad (4.9)$$

These authors have determined the radius r_c for each metal to give a good description of bulk properties.

C. Results and Comparison with Experiment – Simple Metals

Our calculated results for Φ_u, $\delta\Phi$, and $\Phi = \Phi_u + \delta\Phi$ are given in Table II for nine simple metals. For
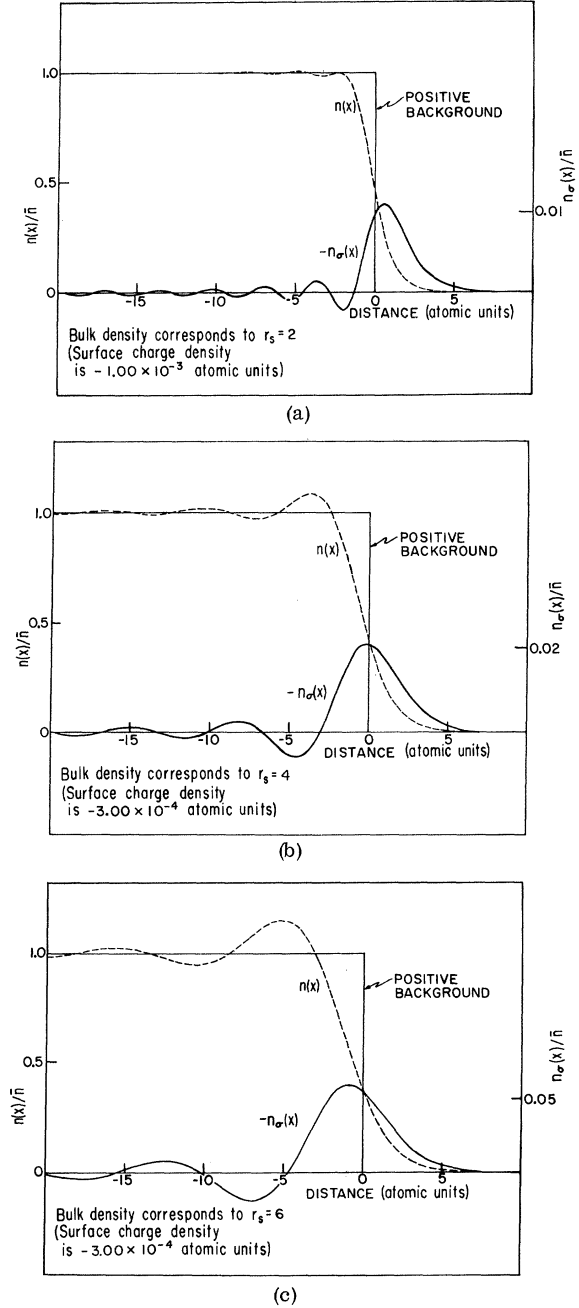

(a)

(b)

(c)

FIG. 3. The change $n_\sigma(x)$ in the electron-density distribution $n(x)$ of the uniform-background model, induced by a weak external electric field along the outward normal to the surface (i.e., along $+x$). Curves are shown for (a) $r_s = 2$, (b) $r_s = 4$, and (c) $r_s = 6$. $\bar{n}$ is the mean electron density deep in the metal.

the cubic crystals the calculations were done for the (111), (100), and (110) crystal faces,[21] and for hcp crystals, for the (0001) face. In the cases for which Ashcroft and Langreth give two possible

choices for the pseudopotential radius r_c, we have carried out the computation for both. In these instances, the r_c value marked with an asterisk in the table is generally found to yield agreement with experiment for a wider range of bulk properties than the other.[19,20] There exist at present practically no experimental data on the work functions of single-crystal faces of the metals listed. Of those few recent data which we could find,[22] almost none were determined by more than one group of workers and some appear to disagree with accepted results for polycrystals. We therefore felt that comparison of our results with single-crystal measurements was premature. We remark however that the general trend of a decrease of the calculated Φ with decreasing density of ions in the lattice plane[23] is in keeping with the arguments of Smoluchowski[6] and with the extensive body of single-crystal work on metals such as W, Mo, and Ni.[24] For the polycrystalline data we have, so far as possible, used recent results which agreed substantially with earlier measurements. With the exception of Li, we have used only experimental data obtained by the photoemission or Kelvin contact-potential-difference methods.[25] These methods are in wide use, they yield the work function in a direct way, and they avoid high temperatures. For Li, however, the most frequently quoted result was obtained over 20 years ago, by a type of contact-potential-difference method,[26] and disagrees seriously with that of a very recent field-emission experiment by Ovchinnikov and Tsarev.[27] In this case we have included both experimental results. The reader is referred to the article by Rivière for a general review of the experimental situation.[28]

The measured work function of a polycrystalline sample represents a certain average over various crystal faces, which depends on the technique used, the conditions of the measurement (e.g., temperature), and the relative proportion of each face on the surface.[29] For qualitative orientation the simple arithmetic average of the Φ values computed for the several faces of each metal is shown in Fig. 2 as a cross (there are two crosses for the cases in which there were two r_c values).

However, it should be remarked that for higher-density metals, theory predicts that the more closely packed faces will have substantially lower

surface energies than the others,[1] and therefore should be preferentially present. These surfaces have the highest work functions. Thus, in the cases of Al and Pb, for which the work-function measurements were made on evaporated films, the appropriate theoretical estimates are probably somewhat higher than the crosses. For Zn and Mg (whose experimental work functions were also obtained using evaporated films) the crosses already correspond to the most closely packed faces, which were the only ones calculated.

It should also be mentioned that photoemission measurements weight the low-Φ faces most strongly. This effect is probably of greatest importance for the lower-density alkali metals whose quoted work functions were obtained by this method and for which the surface-energy anisotropy is small. Hence, for these metals, the appropriate theoretical estimates are probably somewhat lower than the crosses.

In view of the uncertainties concerning the correct crystal-face average for polycrystalline materials, it is not possible to state just how much, if at all, the ion-lattice corrections $\delta\Phi$ to the uniform model improve the agreement with experiment. However, we note (see Fig. 2) that for the alkalis, for which $\Phi_u > \Phi_{expt}$, the average $\delta\Phi$ is negative, as it should be, and of the right order of magnitude, while for Al, Pb, and Zn, $\Phi_u < \Phi_{expt}$, and the average $\delta\Phi$ is properly positive and again of the right order. (For Mg, Φ_u agrees exactly with Φ_{expt}, and the addition of $\delta\Phi$ produces a 10% error.) Thus it appears that, all in all, the inclusion of the ion potential in the theory improves the agreement with experiment to within 5–10%.[30]

D. Results and Comparison with Experiment - Noble Metals

Our calculated results for the noble metals Cu, Ag, and Au are given in Table III. Again we have used local pseudopotentials of the simple form (4.9), with values of r_c taken from Ref. 19.[31] The calculated work functions are seen to be 15–30% too low compared with experiment,[32] the absolute discrepancies being in the vicinity of 1 eV. For these metals the experimental data are consistent and appear to be reliable, so that this error is almost certainly due to the theory. We do not know at present how this error is apportioned between

TABLE III. Theoretical and experimental work functions of the three noble metals. See Table II for explanation of symbols. Experimental values for polycrystalline samples were taken from Ref. 32.

Metal	Structure	r_s	Φ_u (eV)	r_c	$\delta\Phi$ (eV)			Φ (eV)			Φ_{expt} (eV)
					(110)	(100)	(111)	(110)	(100)	(111)	(polycrystalline)
Cu	fcc	2.67	3.65	0.81	−0.08	0.14	0.26	3.55	3.80	3.90	4.65
Au	fcc	3.01	3.49	0.81	0	0.18	0.30	3.50	3.65	3.80	5.22
Ag	fcc	3.02	3.49	1.04	−0.15	0.07	0.19	3.35	3.55	3.70	4.0

$-\bar{\mu}$ and the barrier potential $\Delta\phi$. (Significant outward movement of the last layer of atoms would reduce $\Delta\phi$ and thus further increase the error.[33]) It is not clear whether more sophisticated pseudopotential theory would remove most of the discrepancy or whether these metals, with hybridized s-d bands, require a different approach.

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[1] N. D. Lang and W. Kohn, Phys. Rev. B $\underline{1}$, 4555 (1970); this paper will be denoted as LK-I.

[2] P. Hohenberg and W. Kohn, Phys. Rev. $\underline{136}$, B864 (1964).

[3] W. Kohn and L. J. Sham, Phys. Rev. $\underline{140}$, A1133 (1965).

[4] A preliminary account of this part of the calculation has been given in N. D. Lang, Solid State Commun. $\underline{7}$, 1047 (1969).

[5] J. R. Smith, Phys. Rev. $\underline{181}$, 522 (1969).

[6] R. Smoluchowski, Phys. Rev. $\underline{60}$, 661 (1941).

[7] An example of a semiempirical study of the work function using an approach very different from that taken in this paper is given by D. Steiner and E. P. Gyftopoulos, in Proceedings of the Twenty-Seventh Annual Conference on Physical Electronics, Massachusetts Institute of Technology, Cambridge, Mass., 1967 (unpublished).

[8] The extension of HK to the grand canonical ensemble at arbitrary temperatures has already been given by N. D. Mermin, Phys. Rev. $\underline{137}$, A1441 (1965). [On the right-hand sides of Eq. (9) and the second unnumbered equation of this paper, the term $-\mu \int n(\vec{r})d\vec{r}$ must be added.] We present de $novo$ the specially simple case of zero temperature.

[9] We use atomic units, with $|e| = m = \hbar = 1$. In this system the unit of energy is 27.2 eV.

[10] The first wave-mechanical computation of the work function using this model was given by J. Bardeen, Phys. Rev. $\underline{49}$, 653 (1936).

[11] For this corrected form, see Eq. (3.58) of D. Pines, $Elementary$ $Excitations$ in $Solids$ (Benjamin, New York, 1963).

[12] See, e. g., K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B $\underline{1}$, 1044 (1970).

[13] One can easily show that in the high-density limit the leading terms of $\bar{\mu}$ and $\Delta\phi$ are both $\frac{1}{2}k_F^2$; they diverge individually but cancel each other in (3.6). We conjecture that in the uniform model the work function tends to a finite limit (in the vicinity of 4 eV) as the interior electron density becomes infinite.

[14] In connection with the material of this section we note that the effect of an array of planar δ-function potentials on the double-layer moment has been considered by A. J. Bennett and C. B. Duke, Phys. Rev. $\underline{188}$, 1060 (1969).

[15] The values of $\vec{\mathscr{E}}$ were chosen large enough that $n_\sigma(x)$ was well above the "noise level" associated with lack of self-consistency, and small enough to be in the linear-response region. These conditions were checked by repeating the calculations with the values of $\vec{\mathscr{E}}$ doubled. The entire theory of this section was also checked by

using an artificial small $\delta v(x)$ localized near the surface, and doing a direct self-consistent calculation of $\Delta\phi$ and hence of $\Phi = \Delta\phi - \bar{\mu}$ for this case. The result for $\delta\Phi$ agreed within a few percent with the perturbation result (4.8).

[16] The surface-charge distributions $n_\sigma(x)$ also play an important role in theories of the image force and of small-gap condensers, which will be discussed in a forthcoming paper.

[17] The case $r_c > \frac{1}{2}d$ (d is the spacing of the lattice planes), which did not occur in LK-I, does occur in some of the present calculations.

[18] N. W. Ashcroft and D. C. Langreth, Phys. Rev. $\underline{155}$, 682 (1967).

[19] N. W. Ashcroft and D. C. Langreth, Phys. Rev. $\underline{159}$, 500 (1967).

[20] N. W. Ashcroft, J. Phys. C$\underline{1}$, 232 (1968).

[21] Of these three faces, the (111) face is the most closely packed and the (110) face the least closely packed for the fcc structure; for the bcc structure the roles are reversed.

[22] Al [(111), (100)]: B. Sieroczynska-Wojas, Fiz. Tverd. Tela $\underline{10}$, 693 (1968) [Soviet Phys. Solid State $\underline{10}$, 544 (1968)]; Zn (0001): L. P. Mosteller, T. Huen, and F. Wooten, Phys. Rev. $\underline{184}$, 364 (1969); K[(110, (100)]: J. C. Richard and P. Saget, J. Phys. Suppl. $\underline{31}$, C1 155 (1970). Professor G.-A. Boutry (private communication) has described current work on the (110) faces of K, Rb, and Cs. Single-crystal data on the noble metals Cu, Au, Ag [(111), (100)] is given by P. Vernier, E. Coquet, and E. Boursey, Czech. J. Phys. $\underline{B19}$, 918 (1969); see also, for Cu, P. Köhler, Z. Angew. Phys. $\underline{21}$, 191 (1966).

[23] Note, however, the exceptions to this trend for the (100) faces of Al and Pb.

[24] For example, W, Mo: O. D. Protopopov, E. V. Mikheeva, B. N. Sheinberg, and G. N. Shuppe, Fiz. Tverd. Tela $\underline{8}$, 1140 (1966) [Soviet Phys. Solid State $\underline{8}$, 909 (1966)]; Ni: A. Kashetov and N. A. Gorbatyi, Fiz. Tverd. Tela $\underline{10}$, 2135 (1968) [Soviet Phys. Solid State $\underline{10}$, 1673 (1969)].

[25] Al: J. C. Rivière, Proc. Phys. Soc. (London) $\underline{B70}$, 676 (1957) (as corrected in Ref. 28); Pb: F. Baumann, Z. Physik $\underline{158}$, 607 (1960) (as quoted in Ref. 28); Zn: R. Suhrmann and G. Wedler, Z. Angew. Phys. $\underline{14}$, 70 (1962); Mg: R. Garron, C. R. Acad. Sci $\underline{258}$, 1458 (1964); Na: R. L. Gerlach and T. N. Rhodin, Surface Sci. $\underline{19}$, 403 (1970), and private communication (value used is average of high-coverage-limit work functions for Na deposited on three different faces of Ni); K, Rb, Cs: G.-A. Bountry and H. Dormount, Philips Tech. Rev. $\underline{30}$, 225 (1969).

[26] P. A. Anderson, Phys. Rev. $\underline{75}$, 1205 (1949) (as corrected in Ref. 28).

[27] A. P. Ovchinnikov and B. M. Tsarev, Fiz. Tverd. Tela $\underline{9}$, 3512 (1967) [Soviet Phys. Solid State $\underline{9}$, 2766

(1968)]. Value used is average of high-coverage-limit work functions for Li deposited on various faces of W and Re.

[28]J. C. Rivière, in *Solid State Surface Science*, edited by M. Green (Dekker, New York, 1969), Vol. 1.

[29]C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949).

[30]It might be mentioned that T. Schneider [Phys. Status Solidi 32, 323 (1969)] has shown second-order effects in δv to reduce $-\bar{\mu}$, the bulk contribution to the work function, by 0.1–0.2 eV for the alkalis and by 0.3 and 0.8 eV for Al and Mg, respectively. The second-order effect of δv on the surface term $\Delta\phi$ must be determined, however, before any conclusions can be drawn concerning

the net importance of $(\delta v)^2$ terms in Φ.

[31]Reference 19 gives also a second, much larger, value of r_c for each of these metals, which leads to somewhat less satisfactory results for bulk properties. The work functions calculated with these r_c's are about 1 eV lower than those corresponding to the preferred set, giving an even greater discrepancy with experiment.

[32]Cu and Ag: D. E. Eastman, Phys. Rev. B 2, 1 (1970); Au: E. E. Huber, Appl. Phys. Letters 8, 169 (1966).

[33]There is some theoretical evidence suggesting the existence of occupied surface states in the noble metals; this could of course also affect $\Delta\phi$. See F. Forstmann and J. B. Pendry, Z. Physik 235, 75 (1970).

Some Formal Aspects of a Dynamical Theory of Diffusion*

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A classical dynamical theory of diffusion is presented in which the reaction coordinate and its critical value are expressed in terms of a $3N$-dimensional vector $\underline{R}$. The Slater approximation to the Kac equation is shown to be exact for classical statistics, and the jump rate is calculated accordingly. The jump rate can be expressed in terms of the vector $\underline{R}$ and the dynamic matrix; this leads to a frequency factor different from that obtained from the reaction-rate theory, and an indication that the system does not jump through the relaxed saddle-point configuration. The self-diffusion isotope effect is also considered. It is shown explicitly that the migration energy is mass independent, and that the effect may be expressed simply in terms of the reaction coordinate. In terms of the phonons, the isotope effect depends on a weighted average of the fraction of the energy carried by the jumping atom in each mode. Quantum corrections are discussed and a connection is made between the isotope effect and thermomigration.

I. INTRODUCTION

There has been increasing interest in recent years in formulating the theory of diffusion jump rates in a way that avoids some of the conceptual difficulties of the absolute-rate theory.[1] The rate theory was applied to diffusion by Wert and Zener,[2] and elegantly formulated by Vineyard[3] to show explicitly how the motions of many atoms are involved in the jump process. This can be seen in Vineyard's form for the preexponential or frequency factor

$$\frac{\omega_0}{2\pi} = \prod_{i=1}^{3N} \nu_i \Big/ \prod_{i=2}^{3N} \nu_i' \tag{1.1}$$

in which ν_i and ν_i' are the normal-mode frequencies of the equilibrium and saddle-point configurations, respectively, with the unstable "mode" of the saddle point left out of the product in the denominator. The many-body nature is also apparent in the identification of the migration energy with the potential-energy difference of the relaxed saddle-point and

equilibrium configurations.

The troubling aspect of rate theory is that it focuses so strongly on properties of the relaxed saddle-point configuration. In a quantum-mechanical theory it would not only be impossible to treat positions and velocities independently, but, more significantly, it would be completely inappropriate to speak of the properties of the intermediate state, as has been pointed out by Flynn and Stoneham.[4]

Attempts to circumvent these difficulties have been made by several authors.[5–8] These "dynamical" theories view the jump process as resulting from a special kind of fluctuation from equilibrium, and attempt to calculate the frequency of such fluctuations. In the earlier work, fluctuations were considered that carried the system to a definite configuration, e.g., the relaxed saddle-point configuration. Glyde[7] has shown that, for this case, the dynamical and rate theories have the same formal content. More recently, Flynn[8] has considered fluctuations in a reaction coordinate, made up of a linear combination of particle displacements,