Exact result for bimetallic interfaces

J. Heinrichs* and N. Kumar†

Institut de Physique, Université de Liège, Sart-Tilman, Belgium

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Exact analytic expressions for the change of electrostatic potential across either half of a bimetallic junction and across the metallic region of a metal-vacuum surface are derived in terms of bulk properties. The results for the bimetallic interface are compared in detail with numerical calculations based on the density-functional formalism. The result for the metal-vacuum surface coincides with the one obtained by Budd and Vannimenus using a different method.

The electrostatic dipole layer at a jellium-vacuum surface gives rise to a potential difference between the jellium boundary and the region deep inside the metal. Budd and Vannimenus[1] have derived an exact expression for this potential difference which, for a jellium system occupying the half-space $x < 0$ up to the plane $x = 0$, is given by

$$\rho \Delta V^0 = \rho[V^0(0) - V^0(-\infty)] = -p \ . \tag{1}$$

Here $V^0(x)$ denotes the electrostatic potential, ρ the uniform background charge density, and p the bulk electronic pressure. The numerical results of the microscopic theory of metal surfaces of Lang and Kohn[2] are in remarkable agreement with Eq. (1), which provides a useful test of the internal consistency of these calculations.[1]

In the present paper we derive results analogous to Eq. (1) for the important case of an interface between two metals in close contact. More precisely, we shall obtain exact expressions for the total electrostatic potential change across either half of the junction in terms of bulk properties of the two metals. The usefulness of these results lies primarily in the fact that they provide rigorous tests for the validity of self-consistent microscopic calculations of electronic properties at bimetallic interfaces.

For reasons which will become clear shortly, our results for the bimetallic case differ qualitatively from Eq. (1). We show however that the present analysis may also be applied to the metal-vacuum surface, in which case it leads back to Eq. (1). In fact, we believe our proof of Eq. (1) to be simpler and conceptually more satisfactory than the one given in Ref. 1 because it does not rely on a deformation of the jellium background; the latter is held rigidly fixed, just as in previous microscopic analyses.

Let $x = 0$ define the plane of contact between two metals 1 and 2 occupying the regions $x < 0$ and $x > 0$, respectively, and characterized by uniform background charge densities ρ_1, ρ_2. The electron number densities in the two regions are denoted by $n_1(x)$ and $n_2(x)$, respectively, and verify the conditions $\lim_{x \to \mp \infty} e n_{1,2}(x) = \rho_{1,2}$ ($-e$ = electron charge). The electrostatic dipole layer in the interface region is the source of a bounded electric field $E_{1,2}(x) = -dV_{1,2}(x)/dx$ which generates locally an electronic pressure gradient in the x direction. For an electron gas in equilibrium, the electronic pressure change dp across an element dx is balanced by the electrostatic force acting on the electron distribution in that element. This leads to the relations

$$dp_{1,2} = -e n_{1,2}(x) E_{1,2}(x)\, dx \ , \tag{2}$$

which are in fact a direct consequence of Newton's law as applied to the electron fluid in the presence of an electric field $E_{1,2}(x)$ acting as an externally applied field. These relations stand for the equation appropriate for region 1 when all indices are taken to be 1, and for the equation for region 2 when these indices are taken to be 2. The same notation will be used in some equations below. Since $dp_{1,2}$ is a perfect differential Eq. (2) combined with Poisson's equation

$$d^2V_{1,2}(x)/dx^2 = -4\pi[-e n_{1,2}(x) + \rho_{1,2}] \ , \tag{3}$$

may be directly integrated from points deep inside the solids to points x in the interface region. This leads to the results

$$p_{1,2}(x) = p_{1,2} + E_{1,2}^2(x)/8\pi + \rho_{1,2}[V_{1,2}(x) - V_{1,2}(\mp\infty)] \ . \tag{4}$$

Deep inside the metals where the system is uniform, the electronic pressures have well-known values denoted by $p_{1,2}$. Equation (4) defines the local electronic pressure at a distance $|x|$ from the bimetallic contact plane in terms of the values of the electric field and of the electrostatic potential at that distance. We note that the second term on the right-hand side of Eq. (4) gives the magnitude of the total electrostatic force per unit area (electrostatic energy density) acting at a plane placed parallel to the interface at a distance $|x|$. Therefore, the pressure at a point x is identified by Eq. (4) as the sum of three well-defined contributions. The first term represents the bulk electron gas pressures, which would be the true

pressures for all values of x if the electron gases in both regions were uniform right up to the plane $x=0$. The second term in Eq. (4) gives the *total* electrostatic contribution to the pressure and corresponds to the Coulomb attraction between the electrons which have been transferred from one metal to the other one and an equal amount of positive background charge which has been left behind. However, since the electronic pressure gradient in Eq. (2) involves only the force acting on the electrons, the actual electrostatic contribution in the pressure is given by the difference between the total electrostatic energy density and the change in the electrostatic energy of the positive background, $\rho_{1,2} \int_{\mp\infty}^{x} dx\, E_{1,2}(x)$, due to the electric field of the interface dipole layer.

In general, the explicit expressions for the pressures in Eq. (4) will be known only after the electric field and the electrostatic potential profiles have been determined from a self-consistent first-principles calculation. Of course, explicit forms for the pressures $p_{1,2}(x)$ are known, independently of Eq. (4), in some current approximations for inhomogeneous systems. In particular, in the local density approximation, $p(x)$ is given by the bulk pressure evaluated at the local density $n(x)$ of the system. In such a case Eq. (4) provides a test of the self-consistency of the microscopic calculations from which $n(x)$ and $E(x)$ are obtained. However, here we are mainly interested in deriving exact expressions for the electrostatic potential differences

$$\Delta V_{1,2} = V(0) - V_{1,2}(\mp\infty) , \qquad (5)$$

where $V(0)$ denotes the common value of $V_{1,2}(x)$ at $x=0$. A first equation relating ΔV_1 and ΔV_2 follows immediately from Eq. (4). Indeed by observing that the electric field, the electrostatic potential, and the pressure are continuous across the interface, we get from Eq. (4) at the contact plane $x=0$

$$p_1 + \rho_1 \Delta V_1 = p_2 + \rho_2 \Delta V_2 . \qquad (6)$$

In order to determine $\Delta V_{1,2}$, we need an additional relation which is obtained by requiring the electrochemical potentials deep inside the solids to be equal.[3] With the definitions (5) this condition may be written in the form

$$e(\Delta V_1 - \Delta V_2) = \mu_2 - \mu_1 , \qquad (7)$$

where μ_1 and μ_2 denote the bulk chemical potentials of the individual metals. By combining Eqs. (6) and (7) we then obtain explicitly

$$\Delta V_1 = \frac{1}{e(\rho_2 - \rho_1)} [\rho_2(\mu_2 - \mu_1) - e(p_2 - p_1)] , \qquad (8)$$

while ΔV_2 is obtained from ΔV_1, by changing indices $1 \rightleftarrows 2$. These equations are our basic results which

express $\Delta V_{1,2}$ in terms of properties of a bulk electron gas. While the total electrostatic potential difference across the bimetallic junction is fixed by Eq. (7), the way this difference is distributed between the two metal halves is determined by Eq. (8).

In order to estimate $\Delta V_{1,2}$ using Eq. (8), we first recall the necessary results for the homogeneous electron gas

$$\mu_i = \epsilon_{Fi} + \epsilon_{xc,i} - \frac{r_{si}}{3} \frac{d\epsilon_{xc,i}}{dr_{si}} , \qquad (9)$$

$$p_i = n_i \epsilon_{Fi} \left(\frac{2}{5} - \frac{r_{si}}{3\epsilon_{Fi}} \frac{d\epsilon_{xc,i}}{dr_{si}} \right) , \qquad (10)$$

where the index i refers to the ith species and where n_i is the electron number density, ϵ_{Fi} the Fermi energy, $\epsilon_{xc,i}$ the exchange-correlation energy per particle, and finally, $(r_{si}a_B)^3 = 3/4\pi n_i$. For the correlation energy, we use Wigner's interpolation formula which has usually been favored in connection with surface studies. In atomic units (where we put $e^2 = a_B = 1$), we thus have

$$\epsilon_{xc,i} = -\frac{0.458}{r_{si}} - \frac{0.44}{r_{si} + 7.8} , \quad i = 1, 2 , \qquad (11)$$

where the first and second terms are the exchange and correlation contributions, respectively. Using Eqs. (9)–(11), one may verify explicitly that the square bracket in Eq. (8) is proportional to $(\rho_2 - \rho_1)^2$ for $\rho_2 \rightarrow \rho_1$. This shows that the potential differences $\Delta V_{1,2}$ vanish, as they must, in the limit where the constituents of the junction are identical.

Numerical values for the electrostatic potential differences $\Delta V_{1,2}$, based on Eqs. (8) and (11), are listed in Table I. We have also studied the same quantities using other available expressions for the correlation energy,[4,5] and the results turn out to be similar to those of Table I. Our Eq. (8) may serve as useful tests for possible future calculations applying the density-functional formalism to bimetallic junctions with similar accuracy as the Lang-Kohn treatment[2] for metal-vacuum surfaces.

TABLE I. Numerical values of electrostatic potential change $10^2\Delta V_1$ across a metal 1 bounded by a metal 2, in atomic units. For given r_{s1} and r_{s2}, the value $10^2\Delta V_2$ of the potential change across metal 2 is given by the number occupying the symmetric position of ΔV_1, with respect to the principal diagonal.

r_{s1} \ r_{s2}	2	3	4	5	6
2	0	−7.40	−9.26	−9.90	−10.17
3	7.65	0	−1.84	−2.41	−2.62
4	9.36	1.73	0	−0.47	−0.58
5	9.54	1.98	0.36	0	−0.03
6	9.25	1.75	0.22	−0.049	0

We now wish to compare our results with recent calculations for a bimetallic interface by Bennett and Duke,[6-8] who applied the Hohenberg-Kohn-Sham formalism in an approximately self-consistent way and required Eq. (7) to be satisfied. Numerical results are given for a model junction[7,8] with $n_1 = 10^{22}$ cm^{-3}, $(r_{s1} = 5.44)$ and $n_2 = 10^{21}$ cm^{-3}, $(r_{s2} = 11.72)$, and are based on Eq. (11). From Fig. 5 of Ref. 7 and Fig. 2(c) of Ref. 8, we get, after subtraction of the exchange-correlation potential from the effective potential,[9] $\Delta V_1 = 0.0019$ a.u. and $\Delta V_2 = -0.021$ a.u. The corresponding exact values obtained from Eqs. (8) and (11) are $\Delta V_1 = 0.00478$ a.u. and $\Delta V_2 = -0.0173$ a.u. In this connection, we note that similar discrepancies exist between the results of Ref. 8 and the results of Ref. 2 for the electrostatic potential differences in the case of a metal surface bounded by vacuum (which we take to be region 2). Indeed, for the case $r_{s1} = 5.44$, one obtains from Fig. 2(a) of Ref. 8: $\Delta V_1^0 = 0.027$ a.u., $\Delta V_2^0 = 0.016$ a.u., while the averages of the values for the potential differences for $r_s = 5$ and $r_s = 6$ in Ref. 2 are $\Delta V_1^{av} = 0.0084$ a.u. and $\Delta V_2^{av} = 0.014$ a.u. On the other hand, the exact value of ΔV_1^0, given by Eqs. (1) and (11), is $\Delta V_1^0 = 0.0077$ a.u.

We now sketch our derivation of Eq. (1) of Budd and Vannimenus which is, in fact, a natural consequence of Eq. (4) as applied to the metal-vacuum case. The jellium is assumed to occupy region 1, and the electron distribution has a tail extending into the vacuum region 2. By applying the second of Eq. (4) to the electron gas in the vacuum region, we get

$$p_2(x) = E_2^2(x)/8\pi , \tag{12}$$

since $p_2 = \rho_2 = 0$ in this case. Equation (1) follows now by comparing Eq. (4) for region 1 with Eq. (12) at the contact plane $x = 0$, after noting that $p_1(0) = p_2(0)$ and $E_1(0) = E_2(0)$. The latter relations are a consequence of the continuity of the electronic pressure and of the electric field across the interface. The present derivation of Eq. (1) contrasts with the one given in Ref. 1 in that, in our case, the positive background is held rigidly fixed. One may note that, like Budd and Vannimenus, we are unable to give a general expression for the electrostatic potential change ΔV_2^0 across the vacuum region because Eq. (12) does not depend explicitly on $V_2^0(x) - V_2^0(\infty)$. We believe that the determination of this quantity and, consequent-

ly, of the work function of a jellium system[10] requires an explicit first-principles calculation.

As noted above, Eq. (4) for the jellium region and Eq. (12) for the vacuum region could be used in the local density approximation (where the functional dependence of $p(x)$ on the local density is known), in order to test numerical accuracy and self-consistency in obtaining the density profile $n(x)$ and the electric field in the calculations of Lang and Kohn.[2] This test is not inferior to a numerical test based on Eq. (1) because the latter equation turns out to be exactly verified in the local density approximation.[1] On the other hand, the fact that Eq. (1) is true in the local density approximation provides additional support for the validity of this approximation from a physical point of view.

We conclude our discussion of the metal-vacuum interface with two further remarks. The electronic pressure in the vacuum region, as defined by Eq. (12), is identical to the electrostatic energy density. Therefore the introduction of an electronic pressure may be somewhat superfluous in this case, since it may be replaced by a more familiar quantity, namely, the magnitude of the attractive force between the electronic charge which has leaked out of the jellium and the equal amount of positive background charge which is left behind. We also note that in a real system, the electrostatic pressure given by Eq. (12) is balanced by elastic restoring forces of the ions just as the electronic pressure in the jellium region. Indeed, from the point of view of equilibrium, there is no essential difference between electrons in region 2 and electrons moving between ion cores in region 1, although in the jellium model the electron gas in the vacuum region would appear to be unsupported by the positive background.

We conclude by emphasizing the difference between the bimetallic case and the metal-vacuum case. We note that if we were to consider the metal-vacuum case as a limiting case of a bimetallic interface in which r_{s2}, say, tends to infinity, we would not recover the result for this case, Eq. (1). This is because the equality of electrochemical potentials, Eq. (7), which is true for two metals in contact, no longer holds in the metal-vacuum limit. Indeed, in the metal-vacuum case, the difference between the electrochemical potentials in the two regions is precisely the work function of the metal.[10,3]

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