

## Jellium surfaces and interfaces

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Simplified derivations are presented for the work function of a jellium. Exact expressions are given for the interface potential relative to the bulk, for the contact between two metals as well as for the force between the two metals.

In a recent Letter<sup>1</sup> we presented the following exact relation for the potential difference between a jellium surface and its bulk:

$$V(0) - V(-\infty) = \rho \frac{df}{d\rho}, \quad (1)$$

where  $V(x)$  is the electron electrostatic potential energy in a jellium occupying the half-space  $x < 0$ , with surface at  $x = 0$ . Here  $f$  is the bulk energy per particle  $E = Nf$ , and  $\rho$  is the bulk density.

We also showed that the attractive force per unit area that one half of the jellium exerts on the other is given by

$$F = -\rho^2 \frac{df}{d\rho}. \quad (2)$$

These results establish a relation between the bulk and surface properties of the jellium.

The usual expression for the jellium work function  $W$  is given by<sup>2</sup>

$$W = V(\infty) - V(-\infty) - \mu; \quad \mu = \frac{d}{d\rho}(\rho f). \quad (3)$$

Combining this with our previous result, Eq. (1), we obtain

$$W = V(\infty) - V(0) - f. \quad (4)$$

Mahan and Schaich<sup>3</sup> have recently derived this expression for the work function.

This same result can also be derived as follows, without recourse to either Eq. (1) or Eq. (3). The work required to remove an infinitesimal slab of background charge, of unit total charge, from the jellium surface to infinity is given by

$$V(0) - V(\infty). \quad (5)$$

This follows directly from first-order perturbation theory, or equivalently from the Feynman-Hellman theorem.<sup>4</sup> If we now remove an electron from the jellium, the additional work done is simply  $W$ , the work function. The total work done is given by

$$V(0) - V(\infty) + W. \quad (6)$$

The final system has the same density as the original jellium but has a reduced number of particles. We therefore have

$$V(0) - V(\infty) + W = -\left(\frac{\partial E}{\partial N}\right)_\rho = -f, \quad (7)$$

which is identical to Eq. (4).

For the sake of completeness we also derive Eq. (3) in the same direct fashion. Instead of removing the unit positive background charge from the surface, we remove it by uniformly decreasing the jellium density; i.e., we remove  $e/\Omega$  of charge from each point of the jellium, where  $\Omega$  is the volume. We then obtain for the work the analog of (5) for a macroscopic system:

$$V(-\infty) - V(\infty). \quad (8)$$

Now removing an electron, we obtain the analog of Eq. (7):

$$V(-\infty) - V(\infty) + W = \delta\rho \left(\frac{\partial E}{\partial \rho}\right)_\Omega = \frac{-d}{d\rho}(\rho f), \quad (9)$$

since the volume remains constant and  $d\rho = -1/\Omega$ . This is identical to Eq. (3).

We conclude this note by presenting the generalization of Eqs. (1) and (2) to the interface between two metals in contact at  $x = 0$  (see Fig. 1). The electron electrostatic potential energy at the free surface, bulk, and interface are denoted by  $V_1^s, V_1^b, V(0)$  for metal 1 and similarly for metal 2. From Eq. (1) we have

$$V_{1,2}^s - V_{1,2}^b = \left(\rho \frac{df}{d\rho}\right)_{1,2}. \quad (10)$$

The work done in transferring a unit slab of positive charge from the surface of metal 1 to the surface of metal 2 is simply  $V_1^s - V_2^s$ . The final state is one in which jellium 1 is shortened and jellium 2 is lengthened, both at constant density. This energy difference is simply  $f_2 - f_1$ . Equating the work done to the energy change, we obtain

$$V_1^s + f_1 = V_2^s + f_2. \quad (11a)$$

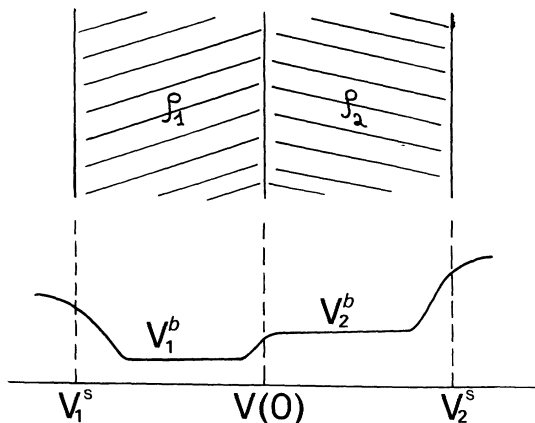


FIG. 1. Schematic representation of contact between two metals of different density. Lower figure illustrates spatial variation of electron electrostatic potential energy.

Using Eq. (4) this may be rewritten

$$V_1^b + \mu_1 = V_2^b + \mu_2, \quad (11b)$$

which is the familiar condition that the electrochemical potential be constant.<sup>2</sup>

We now derive a final equation from the Feynman-Hellman theorem. The force per unit area acting on metal 1 is given by

$$F_1 = \rho_1 [V(0) - V_1^s]. \quad (12)$$

Similarly the force acting on jellium 2 is given by

$$F_2 = \rho_2 [V_2^s - V(0)]. \quad (13)$$

Momentum conservation requires that the sum of these forces be zero:

$$\rho_1 [V(0) - V_1^s] + \rho_2 [V_2^s - V(0)] = 0. \quad (14)$$

We therefore obtain from Eqs. (10), (11), and (14)

$$V_1^b - V(0) = \rho_2 \frac{f_2 - f_1}{\rho_2 - \rho_1} - \rho_1 \frac{df_1}{d\rho_1}, \quad (15)$$

interchanging 1  $\rightleftharpoons$  2 gives  $V_2^b - V(0)$ .

Equation (15) reduces to our previous result, Eq. (1), when  $\rho_2$  tends to zero.

The attractive force per unit area between the two metals is given by

$$F = -\rho_1 \rho_2 \frac{f_2 - f_1}{\rho_2 - \rho_1}, \quad (16)$$

which reduces to our previous result, Eq. (2), for  $\rho_1 = \rho_2$ .

These relations give the potential difference between the interface and bulk of either jellium in terms of bulk jellium properties, as well as the force between the two systems. They represent a generalization of Eqs. (1) and (2), which describe the jellium-vacuum interface.

Fully self-consistent calculations of the potential distribution at the interface between two metals have not been presented; partially self-consistent results have been reported by Bennett and Duke.<sup>5,6</sup> The differences between their results and Eq. (15) are comparable to those for the metal-vacuum interface, Eq. (1).

Our treatment of the metal-metal contact has been based on the assumption of uniform electron densities in the bulk. For sufficiently low densities this assumption fails because of the occurrence of a Wigner transition.

At still lower densities in either of the metals, yet another difficulty is encountered for any slab of finite length. The electrons of this low-density system become concentrated at the interface between metals 1 and 2 and the system resembles a capacitor with net negative charge at the interface and an essentially unscreened uniform positive background charge extending out from the interface into the vacuum. In this case there are no bulk properties for jellium;  $f$  and  $V^b$  are no longer well defined, and the theory breaks down.

*Note added in proof.* Since this article was submitted, a self-consistent theory of the bimetallic junction has been given by J. Heinrichs and N. Kumar [Phys. Rev. B 12, 802 (1975); and Solid State Commun. 18, 961 (1976)].

<sup>1</sup>H. F. Budd and J. Vannimenus, Phys. Rev. Lett. 31, 1218 (1973); 31, E1430 (1973).

<sup>2</sup>Norton D. Lang, Solid State Phys. 28, 225 (1974); see p. 231.

<sup>3</sup>G. D. Mahan and W. L. Schaich, Phys. Rev. B 10, 2647 (1974).

<sup>4</sup>H. Hellman, Einführung in die Quantenchemie (Deuticke,

Leipzig, 1937); R. P. Feynman, Phys. Rev. 56, 340 (1939).

<sup>5</sup>A. J. Bennett and C. B. Duke, Phys. Rev. 160, 541 (1967); 162, 578 (1967).

<sup>6</sup>A. J. Bennett and C. B. Duke, in *Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (Wiley, New York, 1969), Chap. 25.