PHYSICAL REVIEW B VOLUME 30, NUMBER 6 15 SEPTEMBER 1984

High-density jellium-model calculation of force between half-planes of a nearly-free-electron metal at small separation

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(Received 11 January 1984)

The high-density limit of the jellium model is used to study the kinetic energy $T(z)$ of the electron gas as bulk jellium is separated into two half-planes at distance z. It is shown that, for $qz \ll 1$, where q^{-1} is the Thomas-Fermi screening length, the Taylor expansion of $T(z)$ around $z=0$ contains, in particular, a quadratic term with a coefficient proportional to $r_s^{-11/2}$, where r_s is the mean interelectronic separation. Using the virial theorem, this same r_s dependence is shown to appear in the quadratic term in the expansion of the total energy $E(z)$. It is thereby argued that in the limit $r_s \rightarrow 0$ the constant in the force $F(z)=Az$ for small z in real metals, calculated from phonon-dispersion relations, must tend to a limit proportional to $r_s^{-11/2}$. Possible implications of this result for prediction of the surface energy of simple metals are briefly considered.

I. INTRODUCTION

The study of the surface energy of simple metals based on the jellium model is of long standing, and was brought to full fruition in the fully self-consistent calculations of the density profile of a semi-infinite electron fluid by Lang and Kohn.[1,2] They clearly recognized that difficulties arose in the high-density limit, which were connected with the fact that discrete ions had to be introduced for the metal to be in equilibrium under the action of purely Coulomb forces.

Different approaches have been explored by a variety of workers, in which the surface energy is calculated by integrating the force $F(z)$ between half-planes at separation z in order to obtain the surface energy σ:

$$\sigma=\tfrac{1}{2}\int_0^\infty F(z)dz \ . \tag{1.1}$$

One might mention the earlier studies of Friedel,[3] in which all attention was focused on the small-z form of F, namely,

$$F(z)=Az \ , \tag{1.2}$$

the work of Schmit and Lucas,[4] who started from the large-separation result

$$F(z)=\frac{C}{z^3} \ , \tag{1.3}$$

and more importantly the later studies of Zaremba[5] and of Kohn and Yaniv,[6] who interpolated $F(z)$ between (1.2) and (1.3).

Whereas, for a nearly-free-electron metal, it is known that C takes the form

$$C=\gamma\hbar\omega_p \ , \quad \gamma=1.79\times10^{-3} \tag{1.4}$$

where ω_p is the electronic plasma frequency; the fundamental theory of A in Eq. (1.2), given by Zaremba[5] and Kohn and Yaniv,[6] requires knowledge of phonon-dispersion curves for its evaluation.

It has hitherto been supposed that this model must fail at small separation because the jellium model is known not to satisfy the relation (1.2) at small z since $F(z)\rightarrow F(0)\neq 0$.[7] In this paper, we shall nevertheless focus attention first on the variation of the kinetic energy $T(z)$ between two semi-infinite half-planes described by the jellium model in the extreme high-density limit $r_s \rightarrow 0$. We shall argue that, notwithstanding the lack of equilibrium in jellium, the constant A in Eq. (1.2) can be calculated in that limit from the curvature of $T(z)$ at $z=0$, since this can be related to the curvature of the total energy $E(z)$ at $z=0$ by the virial theorem. We combine A and C for this jellium model, using the scaling used by Kohn and Yaniv,[6] to calculate the surface energy from Eq. (1.1).

Since we start from a constant density bulk-jellium model, with density ρ_0, and separate the bulk jellium into two half-planes at separation z, the density will have very small gradients, and the Thomas-Fermi approximation, which becomes exact in a high-density uniform gas, is the appropriate starting point. Thus in Sec. II below we set up this theory for the electron density, and show thereby that the electron density scales according to

$$\rho(x,z,r_s)\equiv\rho(r_s,qx,qz) \ , \tag{1.5}$$

where q^{-1} is the Thomas Fermi screening radius given by

$$q^2=\frac{4k_F}{\pi a_0} \ , \quad a_0=\hbar^2/me^2 \ . \tag{1.6}$$

In Sec. III we calculate the kinetic energy $T(z)$ by an expansion in z up to and including the term of order z^2, from the electron density (1.5). In Sec. IV we then obtain the total energy $E(z)$ to $O(z^2)$, by means of the virial theorem, while in Sec. V we consider the high-density jellium formula for A in relation to the numerical results of Zaremba for real metals.

Section VI is concerned with an interpolation formula for jellium (following Kohn and Yaniv) in which, however, equilibrium is imposed, i.e., we assume $F(0)=0$. Thereby an approximate formula for surface energy in the high-density limit is obtained. In regimes other than the high-density limit $r_s \rightarrow 0$ considered here, exchange and correlation must also be treated.

II. THOMAS-FERMI DENSITIES FOR HALF-PLANES AT SEPARATION z

We take the x axis perpendicular to the half-planes, which are at separation z. The starting point is the Thomas Fermi theory of the density $\rho(x,z,r_s) \equiv \rho(x)$. This is given in terms of the self-consistent potential energy $V(x)$ and the Fermi energy (chemical potential) μ by the usual result

$$\rho(x)=\frac{8\pi}{3\hbar^3}(2m)^{3/2}[\mu-V(x)]^{3/2} . \tag{2.1}$$

The geometry is specified in Fig. 1, with regions I—III. We take these in order.

A. Region I

Since we deal throughout with very small separation z, it is clear that in region I the electron density $\rho(x)$ differs from the bulk density $\rho_0=(8\pi/3\hbar^3)(2m)^{3/2}\mu^{3/2}$ by only a small quantity. This allows us immediately to linearize Eq. (2.1) to read

$$\rho(x)=\rho_0(1-\tfrac{3}{2}V/\mu) . \tag{2.2}$$

Now we invoke the Poisson equation

$$\nabla^2 V=4\pi e^2[\rho_0-\rho(x)] \equiv q^2 V , \quad q^2=\frac{6\pi e^2 \rho_0}{\mu} . \tag{2.3}$$

This evidently has a solution

$$V_{\rm I}(x)=V_{\rm I}(0)\exp(qx) , \quad x \leq 0 \tag{2.4}$$

the second solution of (2.3) diverging as $x \rightarrow -\infty$. The corresponding density is evidently

$$\rho_{\rm I}(x)-\rho_0=-\frac{3}{2}\frac{\rho_0}{\mu}V_{\rm I}(0)\exp(qx) . \tag{2.5}$$

Region III is completely similar, yielding

$$V_{\rm III}(x)=V_{\rm III}(z)\exp[-q(x-z)] , \quad x \geq z \tag{2.6}$$

and

$$\rho_{\rm III}(x)-\rho_0=-\frac{3}{2}\frac{\rho_0}{\mu}V_{\rm III}(z)\exp[-q(x-z)] , \quad x \geq z . \tag{2.7}$$

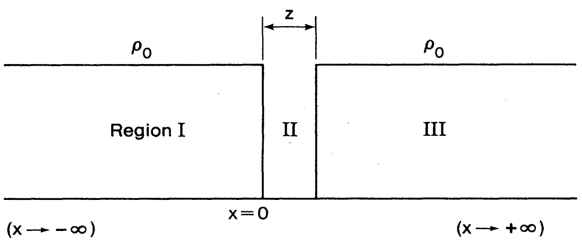

FIG. 1. Showing regions I—III of two identical half-planes separated by distance z for metal of bulk density ρ_0.

B. Region II

Evidently,

$$\rho_{\rm II}(x)=\rho_0(1-\tfrac{3}{2}V_{\rm II}/\mu) , \quad 0 \leq x \leq z \tag{2.8}$$

while the Poisson equation is modified in this region of zero positive charge to read

$$\nabla^2 V_{\rm II}=-4\pi e^2 \rho_0+q^2 V_{\rm II} , \quad 0 \leq x \leq z . \tag{2.9}$$

The general solution of Eq. (2.9) in this region is

$$V_{\rm II}=\frac{4\pi e^2 \rho_0}{q^2}+\gamma_1\exp(-qx)+\gamma_2\exp(qx) . \tag{2.10}$$

Hence

$$\rho_{\rm II}(x)=\rho_0-\frac{3}{2}\frac{\rho_0}{\mu}\left[\frac{4\pi e^2\rho_0}{q^2}+\gamma_1\exp(-qx)+\gamma_2\exp(qx)\right] . \tag{2.11}$$

C. Continuity equation for potential and its first derivative

Continuity of V and $\partial V/\partial x$ at $x=0$ $[V_{\rm I}(0)=V_{\rm II}(0)$ and $\partial V_{\rm I}(x)/\partial x\,|_{x=0}=\partial V_{\rm II}(x)/\partial x\,|_{x=0}]$ gives immediately

$$V_{\rm I}(0)=\frac{4\pi e^2\rho_0}{q^2}+\gamma_1+\gamma_2 \tag{2.12}$$

and

$$qV_{\rm I}(0)=-q\gamma_1+q\gamma_2 . \tag{2.13}$$

Similarly, the continuity at $x=z$ between regions II and III yields

$$V_{\rm III}(z)=\frac{4\pi e^2\rho_0}{q^2}+\gamma_1\exp(-qz)+\gamma_2\exp(qz) \tag{2.14}$$

and

$$-qV_{\rm III}(z)=-q\gamma_1\exp(-qz)+q\gamma_2\exp(qz) . \tag{2.15}$$

These equations are readily solved to give

$$\gamma_1=-\frac{2\pi e^2\rho_0}{q^2}\equiv-\frac{\mu}{3} , \quad \gamma_2=\gamma_1\exp(-qz) , \tag{2.16}$$

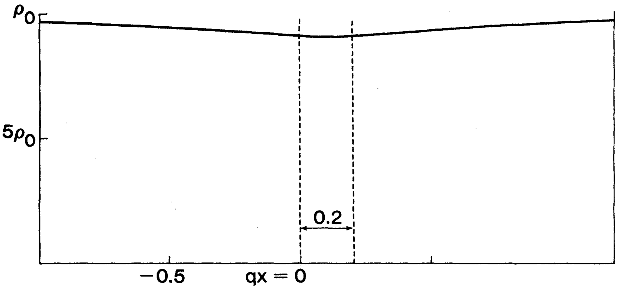

FIG. 2. Electron density $\rho(x,z)$ for case of $qz = 0.2$, and the bulk density $\rho_0 = 3/4\pi r_s^3$ is appropriate to Al with $r_s = 2.07a_0$, with a_0 the Bohr radius.

as well as

$$V_{\mathrm{I}}(0) = \gamma_1[\exp(-qz) - 1] = V_{\mathrm{III}}(z) \ . \tag{2.17}$$

To show the nature of the variation of the electron density with x, Fig. 2 shows $\rho(x)$ versus x for the case when $qz = 0.2$, and $r_s = 2.07$ as appropriate to Al metal.

III. CHANGE OF ELECTRONIC KINETIC ENERGY AS A FUNCTION OF SEPARATION z

We turn to the calculation of the total electronic kinetic energy $T(z,r_s)$ of the composite system at separation z, always remembering that the present treatment, because of neglect of exchange and correlation in the simple Thomas-Fermi model used, is a high-density theory which will only become exact in the limit $r_s \to 0$. The usual expression for the kinetic energy in this approximation is

$$T(z) = c_k \int [\rho(x,z)]^{5/3} d\tau \ , \quad c_k = \frac{3h^2}{10m}\left[\frac{3}{8\pi}\right]^{2/3} . \tag{3.1}$$

Evidently, since ρ varies only with x, the volume element $d\tau$ can be replaced by dx, with the understanding that $T(z)$ is then to be interpreted per unit area. Apparently, we must split the x integrations into the sum of the three regions I—III treated in Sec. II. Furthermore, we again make use of the fact that, at the small separation z with which we are concerned, $\rho(x)$ deviates from the bulk density ρ_0 by only a small quantity. Hence we can again linearize as in Sec. II. Then the contribution to $T(z)$, for example, from region I, is explicitly

$$T_{\mathrm{I}}(z) - T_{0\mathrm{I}} = -\frac{5}{2}\frac{c_k V_{\mathrm{I}}(0)\rho_0^{5/3}}{q\mu} \ , \tag{3.2}$$

where $T_{0\mathrm{I}}$ is simply obtained from the bulk density, integrated through region I, and is clearly independent of z. For region III, the contribution is identical to Eq. (3.2), while for region II we find

$$T_{\mathrm{II}}(z) = \tfrac{2}{3}c_k\rho_0^{5/3}z - \frac{5}{2\mu}\frac{c_k\rho_0^{5/3}\gamma_1}{q}[1 - \exp(-qz)] - \frac{5}{2\mu}\frac{c_k\rho_0^{5/3}\gamma_2}{q}[\exp(qz) - 1] \ . \tag{3.3}$$

Although we have written Eq. (3.3) fully above, the theory is limited in its range of validity to $qz \ll 1$, and hence, expanding the exponentials, including that appearing in γ_2 in Eq. (2.16), we find,

$$T_{\mathrm{II}}(z) = \tfrac{2}{3}c_k\rho_0^{5/3}z + \frac{5}{3}\frac{c_k\rho_0^{5/3}}{q}\left[-qz + \frac{q^2z^2}{2} + O(z^3)\right] . \tag{3.4}$$

Adding the three contributions to obtain $T(z)$, we finally form $\partial^2 T/\partial z^2 |_{z=0}$, with the result

$$\left.\frac{\partial^2 T(z)}{\partial z^2}\right|_{z=0} = \tfrac{10}{3}c_k\rho_0^{5/3}q \equiv \frac{t}{r_s^{11/2}} \ , \quad t = \frac{1}{2^{11/3}}\left[\frac{3}{\pi}\right]^{8/3} . \tag{3.5}$$

This is the basic result of the present calculation. We shall show below that, in the high-density limit $r_s \to 0$, Eq. (3.5) is sufficient for determining $\partial^2 E/\partial z^2 |_{z=0}$ where E is the total energy of the composite system, by use of the virial theorem.

IV. USE OF VIRIAL THEOREM TO DETERMINE CURVATURE OF TOTAL ENERGY $E(z)$ AT ZERO SEPARATION

We recall first that for bulk jellium the virial theorem reads[8]

$$T + E = -r_s\frac{dE}{dr_s} \ , \tag{4.1}$$

which shows that for arbitrary r_s the jellium system is not in equilibrium under the action of purely Coulombic forces.

In the system considered in the present paper, we must clearly add to Eq. (4.1) the virial of force acting between the half-planes at separation z, the modification of Eq. (4.1) being then

$$T + E = -r_s\frac{dE}{dr_s} - z\frac{dE}{dz} \ . \tag{4.2}$$

Substituting the Taylor expansions

$$T(z) = T(0) + zt_1 + \frac{z^2}{2}\left.\frac{\partial^2 T(z)}{\partial z^2}\right|_{z=0} + \cdots \tag{4.3}$$

and

$$E(z) = E(0) + z\left.\frac{\partial E}{\partial z}\right|_{z=0} + \frac{z^2}{2}A + \cdots \tag{4.4}$$

into the virial theorem (4.2), and using the form (3.5), which yields

$$\frac{t}{r_s^{11/2}} = -\left.\frac{3\partial^2 E(z,r_s)}{\partial z^2}\right|_{z=0} - r_s\frac{\partial}{\partial r_s}\left.\frac{\partial^2 E(z,r_s)}{\partial z^2}\right|_{z=0} \tag{4.5}$$

with t constant, we obtain by straightforward integration of this first-order differential equation in r_s the result

$$\left.\frac{\partial^2 E(z,r_s)}{\partial z^2}\right|_{z=0} \equiv A \equiv \frac{2}{5}\frac{t}{r_s^{11/2}} = \frac{0.0278}{r_s^{11/2}} \text{ a.u.} \ , \tag{4.6}$$

with r_s measured in units of the Bohr radius. This is the basic result of the electronic theory developed here. In the next section, we shall endeavor to relate this high-density jellium result to results for real, nearly-free-electron metals.

V. COMPARISON OF RESTORING FORCE AT SMALL z WITH RESULTS FROM PHONON DISPERSION RELATIONS IN NEARLY-FREE-ELECTRON METALS

Though it is clearly not possible to relate the theoretical prediction (4.3) directly to experiment, we next note that the constant A in formula (2.1) can be expressed in terms of experimentally measured phonon dispersion relations, following Zaremba[5] and Kohn and Yaniv.[6] Since the work of Ref. 6 differs in numerical values of A given by Zaremba by ~20 to 40%, for our present semiquantitative purposes we have used the tabulated values of Zaremba in attempting to make contact with Eq. (4.3).

In fact, in Fig. 3 the *ordinate plotted is proportional* to $r_s^{11/2}A$, using the Zaremba values of A. The abscissas we have chosen as the valency Z; this is motivated by the fact that other physical quantities, namely, the velocity of sound and vacancy-formation energy, have been fruitfully plotted, when deduced by jellium predictions, against valency.[9,10] Though the above is the basic reason for making the plot in Fig. 3, it should be noted that the present work neglects electron-ion interaction and is therefore a small Z, as well as a high-density limit. That there is no conflict can be seen as follows. An ion of charge Ze results in an electron at distance r from it experiencing a potential energy $-(Ze^2/r)\exp(-qr)$. Taking q^{-1} as a characteristic distance at which to measure this perturbing potential energy, its absolute value is $\sim Ze^2q$, which must be small compared with the Fermi energy E_F to validate the jellium prediction, i.e., $Ze^2q/E_F \ll 1$. Since in terms of r_s the left-hand side of the inequality involves the combination $Zr_s^{3/2}$, there is, as already mentioned, no conflict between small Z and small-r_s limits. The result is that Fig. 3 is the best plot for our extrapolation purposes. In particular, though the scatter for the monovalent metals is huge, it is quite clear that the general trend with Z is nevertheless consistent with a finite value as $Z \rightarrow 0$, as predicted by Eq. (4.3). We shall not attempt further quantitative tests of this equation directly, as it is a high-density-limit formula. However, in the following section, we shall use the interpolation method of Kohn and Yaniv, in conjunction with formulas (4.3), (1.3), and (1.4), to make a theoretical prediction of the surface energy σ of metals in the extreme high-density limit $r_s \rightarrow 0$.

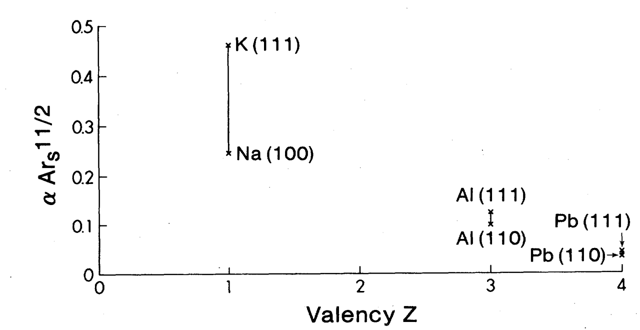

FIG. 3. Shows Zaremba constant A times $r_s^{11/2}$ versus valency Z. A is taken from Ref. 6, ordinate being simply proportional to $Ar_s^{11/2}$. The spread of values for the monovalent metals omits the extreme value of A for one face of Rb metal. The extremities in the spread of $Ar_s^{11/2}$ are otherwise labeled by metal and face.

VI. PREDICTION OF HIGH-DENSITY LIMIT OF SURFACE ENERGY

We have already noted that straightforward use of the self-consistent theory of jellium in Refs. 1 and 2 leads to nonphysical negative values for the surface energy σ as $r_s \rightarrow 0$. This problem was corrected by Kohn and Lang by introducing discrete ions, by means of appropriate pseudopotentials, to restore equilibrium.

Below, we shall merely assert that the lack of equilibrium in the jellium model is corrected by insisting that the force must have the correct equilibrium form in Eq. (1.2) as $Z \rightarrow 0$. Following the interpolation method of Kohn and Yaniv we then obtain

$$\sigma = (AC)^{1/2} \times \text{const} , \qquad (6.1)$$

the constant depending on the detailed interpolation procedure. We immediately see from Eqs. (4.3), (1.3), and (1.4) that $\sigma \propto r_s^{-7/2}$, which is to be compared with the Lucas-Schmit collective mode treatment of $r_s^{-5/2}$, and with a prediction from experiment of r_s^{-3}. This seems satisfactory, though we recognize that it rests on the validity of Eq. (6.1).

VII. SUMMARY

The main achievements of the present paper lie in determining the curvature of the kinetic energy $T(z)$ and hence the total energy $E(z)$, in the high-density jellium limit, at $z=0$. We have argued that, in spite of the equilibrium condition not being fulfilled in jellium, and hence $F(z)$ tends to $F(0) \neq 0$. Provided we insist on the physical small-z form (1.2), the high-density limit of A, the force constant, is given by Eq. (4.3). The relation of the predicted r_s dependence, $A \propto r_s^{-11/2}$, to Zaremba's values obtained from measured phonon-dispersion relations is satisfactory. Combined with the Kohn-Yaniv interpolation procedure, the present work predicts, by using the jellium model only to obtain the high-density limit of the force constant A, that for nearly-free-electron metals the surface energy σ will vary as $r_s^{-7/2}$ as $r_s \rightarrow 0$.

ACKNOWLEDGMENT

One of us (N.H.M.) is grateful for the hospitality and financial support from the Department of Physics, University of Alberta, Edmonton, where this work was undertaken.

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