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# Surface Forces and the Jellium Model

H. F. Budd
*Centre National de la Recherche Scientifique, New York Office,* New York, New York 10021*

and

J. Vannimenus
*Groupe de Physique des Solides, Ecole Normale Supérieure, 75231 Paris, France*

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Analytic results are derived for the surface properties of jellium. The surface potential relative to its bulk value is determined exactly in terms of the bulk properties of the uniform electron gas. This result is independent of any assumption concerning the electron energy density functional in an inhomogeneous system and depends only on the energy density in the homogeneous solid. We discuss the basic inapplicability of dispersion-type calculations of the surface energy.

While progress has recently been made in understanding the surface properties of solids, no exact results have been obtained in this area. Elaborate numerical calculations of the electronic ground state in the fixed background potential of the ions have been presented.[1,2]

In this Letter we present the first exact result relevant to the surface properties of the jellium model. We calculate the surface potential of the jellium relative to its bulk value exactly. No use is made of an approximate form for the energy density functional of the inhomogeneous electron system. Our results depend only on the bulk properties of the jellium, and we obtain explicit results for an arbitrary form of the bulk energy density.

We now consider the jellium model, with the jellium background split into two parts separated by a distance $2D$, as in Fig. 1. The force acting on an infinitesimal slab of background charge is simply $q\vec{E}$, where $q$ is the total charge of the slab and $\vec{E}$ is the expectation value of the electric field at the slab position.[3] This is the well-known result of the Feynman-Hellman theorem.[4] Since the electric field is generally nonzero, the jellium cannot conceivably be in equilibrium. If in fact we had considered a fixed discrete ionic background, the ion positions would be determined by just this condition, namely that they be at potential energy minima.

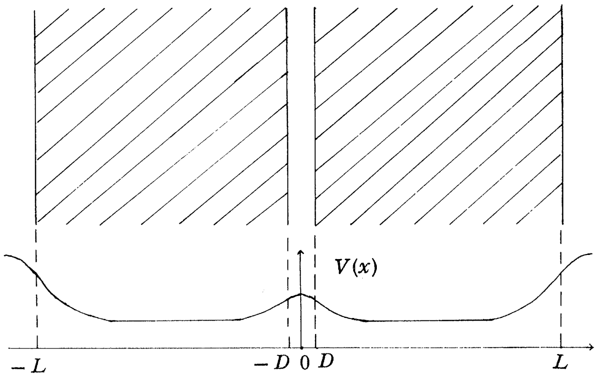

FIG. 1. Schematic representation of two parts of a solid separated by a gap $2D$. Lower curve represents electron electrostatic potential energy.

The force that one half of the split jellium ex-

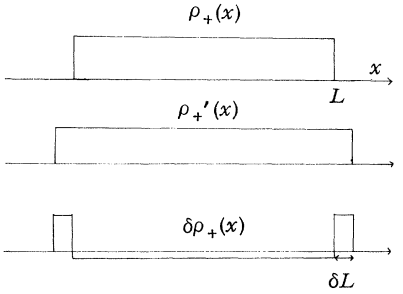

FIG. 2. Schematic representation of positive jellium background stretched from initial state (upper figure) to final state (center figure). Bottom figure shows charge difference between the two.

erts on the other is simply obtained by summing the force acting on each slab of charge. This leads directly to the following expression for the attractive force per unit area:

$$F/A = -\rho[V(L,D) - V(D,D)] \equiv -\rho\Delta V(D), \qquad (1)$$

where $\rho$ is the jellium density and $V(x,D)$ is the electron electrostatic potential energy at point $x$ when the separation is $2D$. We note that $V(L,D)$ is independent of $D$ for a macroscopic sample, and that the variation of the force with distance is given by the variation of $V(D,D)$, the potential energy at the inner surface. The latter obviously tends to $V(L,D)$ as $D$ tends to infinity. We note that this force is repulsive for the barrier shape shown in Fig. 1. This is quite simple to understand physically: Since this barrier shape corresponds to an electric field which contains the electrons, it acts to expel the positive charge near the surfaces.

We can in fact calculate this force exactly at zero distance, and it is simply given by minus the pressure:

$$F_0/A = \partial E/\partial\Omega, \qquad (2)$$

where $E$ and $\Omega$ are the total energy and volume, respectively, and the subscript 0 denotes $D=0$. This pressure can be calculated from a knowledge of the bulk properties of the jellium, which then provides a relation between the surface and bulk properties via Eq. (1). This is our principal result:

$$\Delta V(0) \equiv V(L,0) - V(0,0) = -\frac{1}{\rho}\frac{\partial E}{\partial\Omega} = \rho\frac{\partial f}{\partial\rho}, \qquad (3)$$

where $f$ is the energy per electron for the *uniform* electron gas. Obviously for a real solid this pressure would be zero by definition, while for jellium it is not. This is the basic reason for obtaining negative surface energies in the jellium model, since at high electron density the kinetic energy is dominant and decreases with increasing volume. This corresponds to a repulsive force, Eq. (2). We wish to emphasize that Eq. (3) is *exact* and that no assumption has been made concerning the form of $f(\rho)$.

To derive Eq. (2) we formally consider an infinitesimal expansion of the jellium background, which is performed by stretching the jellium as shown in Fig. 2. The corresponding energy change is, by the Feynman-Hellman theorem,

$$\begin{aligned}\frac{\partial E}{\partial\Omega} = \frac{1}{2A}\left\langle\Psi\left|\frac{\partial H}{\partial L}\right|\Psi\right\rangle &= -\frac{1}{2}\int_{-\infty}^{\infty} dx\,\frac{\partial\rho_+(x)}{\partial L}V(x,0)\\ &= -\rho[V(L,0) - V(0,0)]\\ &= F_0/A, \end{aligned} \qquad (4)$$

where in the last line we have replaced the average potential by its bulk value, which is exact for a macroscopic sample, i.e., $L\to\infty$.

It is interesting to compare our exact result for $\Delta V(0)$ with the work of Lang and Kohn,[1] who have carried out a detailed numerical analysis of jellium in the Kohn-Hohenberg-Sham[5] formalism. The principal approximation used by Lang and Kohn is the assumed form of the exchange-correlation energy functional, which is taken to be that of the uniform electron gas evaluated at the local electron density. Within this approximation the electron density is calculated self-consistently, with due regard to the details of the Friedel oscillations in the electron density.

To make this comparison we use the same bulk energy density function as that used by Lang and Kohn. This provides a meaningful test of their local exchange and correlation function, since our result is completely independent of this assumption. Inserting the same bulk $f(\rho)$ as used by Lang and Kohn in Eq. (3), we obtain

$$\Delta V(0) = 0.4 - 0.0829r_s - \frac{0.0796r_s^3}{(r_s+7.8)^2}, \qquad (5)$$

where $\Delta V(0)$ is measured in units of the free-electron Fermi energy and $\frac{4}{3}\pi r_s^3\rho a_0^3 = 1$ defines $r_s$ in the usual way in units of $a_0$, the Bohr radius. As $r_s$ tends to zero this yields the usual Thomas-Fermi result,[6] while for finite $r_s$ we compare our results with the numerical calculations of Lang and Kohn in Table I. The first two columns are the electrostatic potential energies reported by these authors, while the third represents the corresponding $\Delta V(0)$. The fourth column gives the values derived from Eq. (5). The agreement is remarkable. The last column presents slightly refined values of $\Delta V(0)$ obtained in more recent calculations by Lang.[7] These yield even closer agreement. Thus despite the local energy density functional used by Lang and Kohn, excellent agreement is obtained between our exact results and their numerical calculations. This is a more sensitive test than is the surface energy itself, since Smith's results[8] for the latter are in rough agreement with those of Lang and Kohn, even though his assumed form for the electron density profile is quite different from that obtained by Lang and Kohn. This is particularly true at large $r_s$, where the Friedel oscillations become quite large.

We can go one step further with the jellium by calculating $V(D, D)$ for small but finite distances $D$. In this case we treat the small separation between the two portions as a perturbation on the intact jellium. This consists of adding a negative slab of charge of width $2D$ at the center of the whole jellium, and a compensating positive slab at its far end. The induced charge density in the bulk is readily calculated, from which we obtain the change in the potential energy at $x = D$,

$$V(D, D) - V(0, 0) = 2e^2\rho\int_{-\infty}^{\infty} dq \, \sin 2qD/q^3\epsilon(q), \tag{6}$$

where $\epsilon(q)$ is the dielectric constant of the uniform electron gas. This is exact as $D$ tends to zero so that we obtain the exact variation of the force at small distance:

$$\frac{1}{A}\frac{dF}{dD} = 4e^2\rho^2\int_{-\infty}^{\infty}\frac{dq}{q^2\epsilon(q)}. \tag{7}$$

TABLE I. Comparison of exact electron electrostatic potential energies with numerical calculation. First two columns give values obtained in Ref. 1, while the third column represents their difference. Fourth column gives values calculated from Eq. (5). Last column gives refined values of Ref. 7.

| $r_s$ | $V(L)$, Ref. 1 | $V(0)$, Ref. 1 | $\Delta V(0)$, Ref. 1 | $\Delta V(0)$, Exact Eq. (5) | $\Delta V(0)$, Ref. 7 |
|---|---|---|---|---|---|
| 2 | − 0.0032 | − 0.2324 | 0.2292 | 0.2276 | 0.2275 |
| 3 | 0.3472 | 0.2126 | 0.1346 | 0.1329 | 0.1332 |
| 4 | 0.7145 | 0.6872 | 0.0273 | 0.0318 | 0.0322 |
| 5 | 1.103 | 1.186 | − 0.083 | − 0.0752 | − 0.068 |
| 6 | 1.492 | 1.704 | − 0.212 | − 0.1877 | − 0.197 |

As we pointed out following Eq. (1), the force between the two segments of the jellium is indeed repulsive for the barrier shape shown in Fig. 1, which is qualitatively the case at high densities. This makes plausible the negative surface energies calculated in Ref. 1 for small $r_s$. It was only after explicitly including the discrete nature of the ionic background that positive surface energies were obtained.

Other approaches to calculating surface energies have been presented which are modifications or derivatives of the Lifshitz[9] theory of dispersion forces. These lead to positive surface energies in an apparently simple fashion.

There is however a fundamental objection to the dispersion-type theories as is apparent in the Lifshitz[9] expression for the attractive force per unit area between two macroscopic bodies (Fig. 1),

$$\frac{F}{A} = \frac{\hbar}{16\pi^2(2D)^3} \times \int_0^\infty dx\int_0^\infty dy\,\frac{x^2}{[(\epsilon+1)/(\epsilon-1)]^2 e^x - 1}, \tag{8}$$

where $2D$ is the separation between the two macroscopic parts of the body under consideration, and $\epsilon(y)$ is its dielectric constant along imaginary frequency axis $\omega = iy$. We note that spatial dispersion is neglected in this expression, as are retardation effects. The effects of spatial dispersion are expected to be important at small separations, and it is only at large separations that one can hope to use the local dielectric theory of Lifshitz. This apparent in Eq. (8) where the force is seen to be always *attractive,* and *divergent* at small separations. If in fact the separated segments in Fig. 1 are considered to be extremely rarefied, the Lifshitz result is identical to summing the usual pairwise Van der Waals interaction over the two half-spaces. This expression obviously neglects any short-range forces.

The energy difference between the infinitely separated bodies and that at zero distance is readily obtained by integrating Eq. (8) over $D$. This yields twice the surface energy, since two new surfaces are created by this procedure.

This obviously yields a divergent result because of the inadequacy of this theory at short distance.

The energy difference between the infinitely separated bodies and that at *finite* separation, as obtained from Eq. (8), can be cast into the form of the energy difference between the zero-point energies of the collective modes in the two configurations.[10] This method has been used by Schmidt and Lucas[11] to obtain surface energies. These authors obviously encounter the divergence problem discussed above, and they introduce a cutoff procedure to obtain a finite surface energy. This is unsatisfactory since the final result depends critically on the cutoff used.[12,13] We wish to stress that need for a cutoff procedure emphasizes the importance of short-range forces, for which the dispersion-type theory is basically inapplicable.

It is of course possible to express the surface energy in terms of generalized response functions and thus to obtain formal expressions for the surface energy. This has indeed been done by Peuckert[14] and by Craig.[15] Here of course one is forced to introduce approximations in order to calculate explicitly the response function for a nontranslationally invariant medium. This at least formally eliminates the need to introduce arbitrary cutoff procedures, but still requires a correct description of the short-range forces. In addition, one also requires a knowledge of the electron density profile, which appears explicitly in the formalisms of Refs. 14 and 15. Needless to say, the electron density profile is extremely difficult to calculate.

In summary, then, we have presented the first analytic results concerning the surface potential of the jellium model for an arbitrary energy density function. Our theory is exact and establishes a relation between the surface potential and the bulk energy density. The excellent agreement of our theory when applied to the model of Kohn and Lang shows that their local exchange-correlation approximation leads to surprisingly good results in this case. We hope that this Letter will stimulate further analytical work in this area, particularly in obtaining an exact expression for the remaining portion of the potential between the surface and the vacuum level.

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