CONTRIBUTION OF COLLECTIVE EXCITATIONS TO THE SURFACE ENERGY OF METALS

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We report an RPA-calculation of the high-frequency contribution to the surface energy of metals. Further, on the same basis, we derived the Lifshitz expression for the Van der Waals energy between metallic half-spaces.

RECENT work on the electronic properties of metallic surfaces shows that the 'variational'[1] and the 'single'[2] particle'[2] treatment of the Hohenberg–Kohn–Sham[3,4] theory (HKS) for a jellium model leads to negative surface energies if $r_s < 2.5$. Two approaches have been carried out in order to correct this discrepancy: 1. Lang and Kohn[2] modified the jellium model by introducing (non-selfconsistently) the pseudopotential of the surface ions, which, for the materials considered, leads to (positive) surface energies of the correct magnitude. 2. On the other hand Schmit and Lucas[5] and Craig,[6] within the jellium model added surface plasmon contributions (obtained in a semi-quantitative way) to the HK-energy functional in order to complete its non-local part. This treatment leads also to reasonable results, although a number of details have been criticized.[7-9]

Presumably, both surface structure and surface plasmons play an important role. The fact, however, that jellium HK-theories of the image potential and of Van der Waals forces (both surface plasmon effects) also fail[2,10] suggest to study the surface plasmon contributions to the surface energy in more detail. In the present work we report an RPA-calculation of the high-frequency contributions to the surface energy which leads to the result of reference 5 and shows some of its underlying assumptions. The details of the calculation will be published elsewhere. We start

from the following expression[6] for the interaction energy of an inhomogeneous electron system

$$E_{int} = \frac{1}{2} \sum_K \frac{1}{2\pi i} \int dz \int_{\mathcal{C}} d\omega\, \alpha_K(z, z, \omega) \quad (1)$$

where K is a wave vector parallel to the surface, z is the direction perpendicular to the surface and $\mathcal{C}$ is a contour around the positive ω-axis. Here α is the linear density response function defined through the following relation:

$$\delta\rho(1) = \int d2\, \alpha(1, 2)\, \delta\rho_{ext}(2) \quad (2)$$

where $\delta\rho_{ext}$ is an external test-charge and $\delta\rho$ is the induced charge in the system.

The function α can be related to a linear density response function $\beta(1, 2)$ defined by

$$\delta\rho(1) = \int d2\, \beta(1, 2)[\delta\rho_{ext}(2) - \delta\rho(2)] \quad (3)$$

through the following integral equation:

$$\alpha_K(z, z') = \beta_K(z, z') - \int dz''\beta_K(z, z'')\, \alpha_K(z'', z') \quad (4)$$

where we have Fourier-transformed α and β in a direction parallel to the surface. If we now replace, in equation (4), β by the density response function α^0 of the non-interacting system we obtain an integral equation for α in the RPA.[11] This equation contains already the effects of the collective excitations.

Restricting ourselves to frequencies higher than the single-particle excitations one is able to express α^0 by its high frequency limit[12]. At this respect we

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are able to show that the high frequency limit[13−15] of α^0 can be written as

$$\lim_{\omega \to \infty} \omega^2 \alpha^0(\mathbf{r}_1, \mathbf{r}_2; \omega) =$$

$$- \omega_p^2 \left(n(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) - \nabla_1 n(\mathbf{r}_1) \nabla_1 v(\mathbf{r}_1 - \mathbf{r}_2) \right) \quad (5)$$

where $\omega_p^2 \equiv 4\pi n_1 e^2/m$. v is the coulomb potential and $n(\mathbf{r}) = \rho_0(\mathbf{r})/n_\star$ is the reduced density of the non-interacting system.

It is now convenient to split α into two parts

$$\alpha = \alpha^B + \alpha^S \quad (6)$$

in which α^B and α^S correspond to a bulk and surface term as it will become apparent in equations (13) and (14) below. Here

$$\alpha^B \equiv - \frac{N(z)}{1 - N(z)} \, \delta(z - z') \quad (7)$$

where

$$N(z) \equiv (\omega_p^2/\omega^2) n(z).$$

Thus, combining (4), (5), (6), and (7) we obtain within the RPA the following integral equation for α^S:[16]

$$\alpha^S(z, z') = - \frac{1}{2} \frac{N'(z)}{(1 - N(z))} \frac{\text{sgn}(z - z')}{(1 - N(z'))} e^{-K|z - z'|}$$

$$+ \frac{1}{2} \frac{N'(z)}{1 - N(z)} \int_{-\infty}^{-\infty} d\zeta \, \text{sgn}(z - \zeta) e^{-K|z - \zeta|} \alpha^S(\zeta, z') \quad (8)$$

where the coulomb potential v has been already Fourier-transformed in the direction parallel to the surface and $N'(z) \equiv dN(z)/dz$.

For an arbitrary K one obtains α_K^s to be complex corresponding to a decay of surface plasmons into electron−hole pairs. A solution of (8) leading to stable surface excitations and thus to a well defined surface energy can be obtained if we confine our attention to:

(i) a charge density profile described by

$n(z) = 1$ for $z < -a$

$n(z) =$ arbitrary decaying function   for $-a \leqslant z \leqslant 0$

where a is a measure of the surface diffuseness.

(ii) values of K and a such that

$$Ka \ll 1 \quad (9)$$

Under these conditions the integral equation (8) can

be written as

$$\alpha_K^S(z, z') = - \frac{1}{2} \frac{N'(z)}{(1 - N(z))} \frac{1}{1 - N(z')}$$

$$[\theta(z - z') e^{Kz'} - \theta(z' - z) e^{-Kz'}]$$

$$+ \frac{1}{2} \frac{N'(z)}{1 - N(z)} \int_{-a}^{0} d\zeta \, \text{sgn}(z - \zeta) \alpha_K^S(\zeta, z') \quad (10)$$

This integral equation can be transformed into a first order differential equation which can be solved immediately to give

$$\alpha_K^S(z, z') = \frac{N'(z)}{(1 - N(z))^2} \left[\theta(z' - z) - \frac{1}{2 - N(-\infty)} \right] \quad (11)$$

for $-a \leqslant z \leqslant 0$ and $-a \leqslant z' \leqslant 0$. The constant appearing in the solution of the first order differential equation has been determined directly through (10).

In the expression (1) for the energy

$$\alpha_K^S(z, z) = \frac{-N'(z)}{2(1 - N(z))^2} \frac{N(-\infty)}{2 - N(-\infty)} \quad (12)$$

is required.

Insertion of α^B and (12) into (1) and integration along the contour leads to the following expression for the energy as a functional of the density:

$$E_{\text{int}} = \frac{1}{2} \int dz \sum_k$$

$$\left[\frac{\hbar \omega_p}{2} \sqrt{n(z)} \, \delta(0) - \frac{\hbar \omega_p}{16} \frac{n'}{\sqrt{n}(\sqrt{n} + 1/\sqrt{2})^2} \right]. \quad (13)$$

Integration over z gives correspondingly

$$E_{\text{int}} = \frac{1}{2} \sum_k \frac{\hbar \omega_p}{2} \delta(0) L + \frac{1}{2} \sum_k \frac{\hbar \omega_p}{2\sqrt{2}} \left(1 - \frac{1}{\sqrt{2}} \right) \quad (14)$$

where L represents the dimension of the system in the direction perpendicular to the surface. Here the first term is the well known bulk energy term. The second term is the surface energy and it originates from the term proportional to n' in equation (13).

Thus, if we are allowed to introduce a cut-off wavenumber K_c in the second term of (14) this will become identical to the result obtained in reference 5 by intuitive arguments. In addition we would like to emphasize that this quantity is not composed of bulk and surface contributions as suggested in reference 7.

Further we report that we have applied the same procedure as above to calculate the Lifshitz-formula[17] for the attraction energy of two metallic half-spaces separated by a distance d. The functional form (corresponding to (13)) turns out to be quite complicated. However, since in the expression for the energy the weight of the terms with K do not contribute appreciably we are able to write the functional corresponding to the Van der Waals energy approximately as

$$E_{int} = -\int dz \sum_k \frac{\hbar\omega_p}{16} e^{-2kd} \frac{n'((7\sqrt{2}/8) + \sqrt{n})}{(\sqrt{n} + 1/\sqrt{2})^4} \quad (15)$$

If we further assume that the sum over K is limited by K_c and that $K_c d \gg 1$ one obtains the well known expression (see for example Krupp):[18]

$$E_{int} = -\frac{1}{2} \frac{\hbar\omega_p}{64\pi\sqrt{2}} \frac{1}{d^2} \quad (16)$$

(The total energies corresponding to (14) and (16), by use of Feynman's theorem, are twice the interaction energies.)

As summary we can say that in the calculation surface energies as presented here the basic assumptions are:

(i) the validity of the RPA,

(ii) a relatively sharp electron density profile, corresponding to $Ka \ll 1$

(iii) the validity of the high-frequency expansion of α^0.

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Im Rahmen der RPA-Näherung wurde der Hochfrequenzbeitrag zur Oberflächenenergie von Metallen und die Van der Waals Wechselwirkung von metallischen Halbräumen berechnet.