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Adhesion between simple metal surfaces

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Abstract. The adhesive energies and forces between surfaces of identical simple metals (Al, Mg and Na) modelled by a semi-infinite stabilized jellium have been calculated self-consistently as functions of their separation. The calculated binding energies agree well with the experimental surface energies and a good agreement is found between the maximum adhesive forces and the empirical fracture strength.

1. Introduction

The strong adhesive bonding which takes place at intimate contact between two metal surfaces is of great significance in many surface phenomena such as friction, crack formation and fracture. At large separations the wave functions of electrons belonging to metallic pieces do not overlap appreciably and the interaction is dominated by the van der Waals forces [1, 2]. For small separations between two identical metals the electrons tunnel through the symmetric barrier and a nonvanishing charge distribution in the separation gap produces a short-range bonding.

The early (not self-consistent) calculations of the charge redistribution at the interface [3, 4] employed density functional theory, including the fourth-order density gradient corrections to the kinetic energy [5], and assumed a simple overlap of the metal–vacuum electron distributions associated with the individual metals. In these calculations the electron-density distributions and potentials were calculated using a jellium model which served as a first step in the studies of the properties of the inhomogeneous electron gas near the surface of simple metals [6, 7]. The necessity of inclusion of the electron–ion-lattice interaction into the calculation of adhesive energies and forces was recognized quite early by Ferrante and Smith [4] who incorporated the lattice effects via the first-order perturbation theory [6]. An attempt has been also made [2] to account for the contributions coming from both the short-range and the van der Waals forces acting at larger separations. These studies were followed by fully self-consistent calculations of adhesive energies [8–10] and forces [11, 9], where the discrete lattice effects were taken into account in a perturbative way.

The effects of crystallinity can be included from the beginning of the calculations in a structureless pseudopotential or *stabilized-jellium* model [12]. In this model the simplicity of jellium is retained and the forces at the jellium surface are equilibrated by taking into account the discrete lattice effects in an averaged way. The model has proven to provide calculated surface quantities which are much more realistic than those given using the ordinary jellium model and, moreover, comparable with or even superior to those yielded by perturbative

jellium calculations [13]. By modifying the electron-density profile, stabilization should have an important effect on the adhesive binding between two metal surfaces brought into proximity.

In this paper we present the results of self-consistent calculations of adhesive energies and forces acting between two identical surfaces of simple metals. The calculated adhesive energies are compared with those resulting from the ordinary jellium model. The recently proposed asymptotic expression for the van der Waals interaction energy [14] is briefly discussed.

2. The model

The adhesive energy $E_{\text{ad}}(d)$ of two pieces of metal separated by a distance d can be defined as the work required to increase the distance from d to infinity divided by twice the cross sectional area:

$$E_{\text{ad}}(d) = \frac{E(d) - E(\infty)}{2A}. \quad (1)$$

Here $E(d)$ is the total energy of the system at separation d and A is the surface area of the fragments. For identical metals initially at zero separation, E_{ad} is the negative of the surface energy σ .

The total energy of the metal as a functional of the electron density $n(\mathbf{r})$ is given by

$$E[n(\mathbf{r})] = T_s[n] + E_{\text{xc}}[n(\mathbf{r})] + \int v(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + \frac{1}{2} \sum_{i,j} \frac{Z^2}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (2)$$

where the energy terms describe the kinetic, exchange–correlation and electrostatic energy, respectively. Here, $v(\mathbf{r})$ is the ionic potential and the last term in equation (2) describes the mutual interaction of ions of charge Z at positions \mathbf{R}_i . The Hartree atomic units are used throughout. In the jellium model, which can be applied as the zeroth approximation to our system, the ion charges are smeared out in the volume of the metal to create a uniform positive background of density $n_+(\mathbf{r}) = n_0$, and all of the electrostatic energy contributions can be grouped into one term. However, jellium appears to be mechanically unstable for the bulk electron densities characterizing most of the metals. This deficiency can be remedied by reintroducing the interaction of electrons with the discrete ions. The latter can be reintroduced in a perturbative way by replacing the electron–ion interaction potentials by weaker pseudopotentials. Consequently, the difference potential $\delta v(\mathbf{r})$ of the array of pseudopotentials and the electrostatic potential due to the uniform positive background system

$$\delta v(\mathbf{r}) = \sum_i w_{\text{ps}}(\mathbf{r} - \mathbf{R}_i) + \int \frac{n_+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \quad (3)$$

can be treated as a first-order perturbation contributing to the energy. Taking into account the Madelung interaction between discrete ions leads to the so-called classical cleavage energy term in the adhesive energy [4, 6].

In the stabilized-jellium model adopted in this work, the discrete lattice effects are represented by structureless averages and the total energy of a system as a functional of the electron density $n(\mathbf{r})$ and of the positive background density can be written in the form [12]

$$E[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + \frac{1}{2} \int \phi(\mathbf{r})[n(\mathbf{r}) - n_+(\mathbf{r})] d\mathbf{r} + B \int d^3r n_+(\mathbf{r}) + \int d^3r \langle \delta v \rangle_{\text{WS}} \Theta(\mathbf{r})[n(\mathbf{r}) - n_+(\mathbf{r})]. \quad (4)$$

The first three terms represent the standard jellium energy (i.e., the kinetic, exchange–correlation and electrostatic energy contributions) [7]. The remaining two terms originate from the corrections which are needed to transform metal built up of spherical Wigner–Seitz jellium cells into a more realistic model—stabilized jellium [12]. The constant B present in the first of them is a sum of the average value of the Madelung energy of point ions embedded in a uniform negative background and the average of the repulsive part of the ionic pseudopotential. This term contributes to the metal bulk energy. The second of the new terms represents a surface correction to the energy of the jellium due to the stabilizing lattice potential. Here, $\langle \delta v \rangle_{\text{WS}} \Theta(\mathbf{r})$ is a step potential vanishing outside the positive background region with the difference potential being averaged over the spherical Wigner–Seitz cell.

Employing the metal bulk stability condition, $\langle \delta v \rangle_{\text{WS}}$ can be expressed [12] as a structureless average depending upon the bulk electron density $n_0 = 3/4\pi r_s^3$ alone, to give

$$\langle \delta v \rangle_{\text{WS}} = -n_0 \frac{d\varepsilon(n_0)}{dn_0} \quad (5)$$

where $\varepsilon(n_0)$ is the total (kinetic + exchange + correlation) energy per particle of the uniform electron gas of density n_0 . The Ceperley–Alder values of the correlation energy as parametrized by Perdew and Zunger [15] have been employed in this work. Note that $\langle \delta v \rangle_{\text{WS}}$ gives the bulk electronic pressure divided by n_0 .

For the symmetric positive charge-density distribution of two semi-infinite metals separated by a distance d , the ground-state electron density $n(z)$ is constructed from the solution of the Kohn–Sham equations [6] with the effective potential

$$v_{\text{eff}}[n; z] = \phi[n; z] + v_{xc}[n; z] + \langle \delta v \rangle_{\text{WS}} \Theta\left(\pm z - \frac{d}{2}\right) \quad (6)$$

which is symmetric with respect to zero. The electrostatic potential $\phi(z)$ is obtained from the Poisson equation and the exchange–correlation potential, $v_{xc}(z)$, is evaluated in the local density approximation (LDA). The form of the effective one-particle potential for stabilized jellium differs from that for ordinary jellium only in the appearance of the last term on the r.h.s. of equation (6). This allows the quasi-one-dimensional character of the set of self-consistent equations which were solved following the procedure described by Nieminen [11] to be retained.

The adhesive force acting between two fragments can be obtained by differentiating the energy dependence with respect to the distance. Alternatively, for two interacting jellium surfaces, the force (per unit area) can be calculated directly from the simple expression derived by Budd and Vannimenus [16]:

$$F_{\text{ad}}(d) = F_0 + n_0[\phi(\pm d/2) - \phi(\pm\infty)] \quad (7)$$

where F_0 is the bulk pressure exerted by the uniform electron gas of density n_0 .

The stabilized-jellium model replaces the so-called pseudopotential and cleavage corrections, which have to be added to F_{ad} and E_{ad} in the perturbative treatment of the lattice effects [9, 11], by the stabilization term. This extra term in F_{ad} which should appear on the r.h.s. of equation (7) equals $n(\pm d/2)\langle \delta v \rangle_{\text{WS}}$ and compensates exactly the bulk electronic pressure F_0 for the zero-separation limit.

3. Results and discussion

The numerical calculations have been performed for three (Al, Mg, Na) pairs of like metal surfaces represented by the stabilized-jellium model. The self-consistency of the calculations has been checked through the application of the Budd–Vannimenus theorem [16] which was obeyed to a very good accuracy for all of these metals. In all three cases the stabilizing potential $\langle \delta v \rangle_{\text{WS}}$ is negative [13], ranging from -2.49 eV for Al to -0.06 for Na. This means that the calculated electron-density profiles are more confined in the metal and fewer electrons spill out into the separation gap. Consequently, for the stabilized-jellium surface the bond charge density has a similar monotonic character to that for ordinary jellium but it is reduced in magnitude. For example, in the case of Al the relative bond charge density $n(0)/n_0$ at the middle of the separation gap is reduced by some 10–20% at short separations ≤ 2.5 au, and by a factor of two or more for $d \geq 7$ au. For Na, where the stabilizing potential is very weak, this reduction is small.

The surface electrostatic barrier $\Delta\phi$ as well as the total barrier (the difference between the effective potentials at the surface and in the bulk metal) behave qualitatively as their counterparts for ordinary jellium and monotonically attain their asymptotic limits of the single-surface case. The electrostatic barrier is lower whereas the total barrier is higher, approximately by the magnitude of $\langle \delta v \rangle_{\text{WS}}$, than the corresponding ones for ordinary jellium.

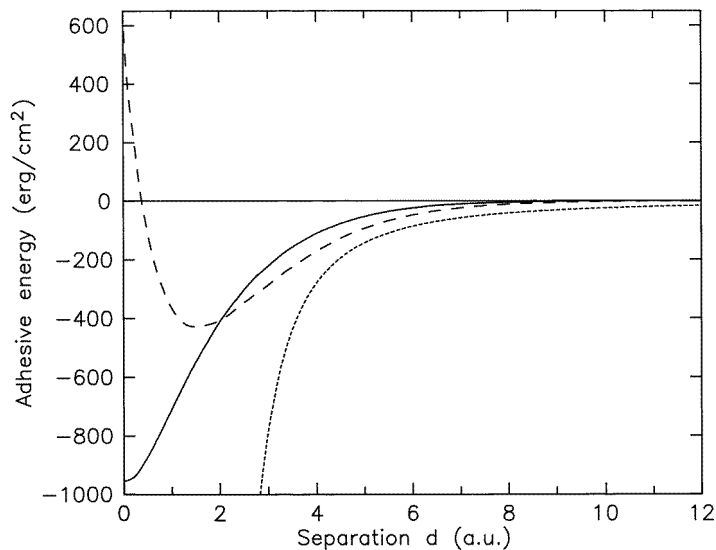


Figure 1. Adhesive binding energy curves for two parallel Al surfaces as functions of their separation. Full line: stabilized jellium; dashed line: ordinary jellium; dotted line: the van der Waals interaction energy.

Figure 1 shows the adhesive energy plotted versus the separation between two Al surfaces represented by jellium and stabilized-jellium models. The shapes of the two curves differ markedly as regards the position of the minimum and its depth. For both models the magnitudes of the adhesive energy at zero separation agree well with the values of the negative of the surface energy calculated for single surfaces [13]. However, in the case of ordinary jellium the position of the minimum is distant by about 1.2 Bohr from $d = 0$. Like in the perturbational treatment of Ferrante and Smith [4, 9], the effect of crystallinity,

inherently included in the stabilized-jellium model, allows one to change the magnitude of the adhesive energy curve and to shift the minimum to $d = 0$. Similar character of the adhesive energy curves is observed for Mg surfaces. For Na–Na contact the effect of crystallinity is small and the two curves (for jellium and stabilized jellium) do not exhibit big differences in the magnitudes and the positions of the minimum.

The effect of atomic corrugations on the single-crystal planes can be accounted for in a variant of the stabilized-jellium model [12] by adding an extra crystal-face-dependent term to $\langle \delta v \rangle_{\text{WS}}$. Consequently, the latter should be replaced by $\langle \delta v \rangle_{\text{face}}$ in the respective equations [13]. The difference between the surface energy of the flat Al surface and that of Al(111), calculated in the stabilized-jellium model [13], amounts to only about 10 erg cm^{-2} , so the adhesive energy curve for Al(111) is very close to that for a flat surface of Al and for reasons of clarity is not drawn in figure 1.

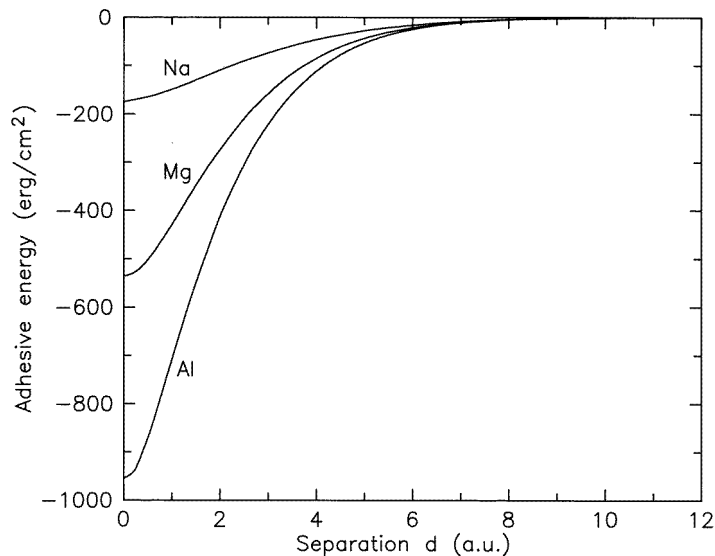


Figure 2. Adhesive binding energies calculated in the stabilized-jellium model for two parallel metallic surfaces of the same metal.

The calculated adhesive energy curves can be compared with the van der Waals interaction energy. Recently Lundqvist *et al* [17, 18] have proposed an extension to the density functional theory to include the dispersion interactions. For the two interacting parallel surfaces a modified expression for the van der Waals interaction energy has been proposed [14] which, for large separation, can be written in the form

$$E_{\text{vdW}} = -\frac{C_{\text{vdW}}}{(d - Z_1 - Z_2)^2}. \quad (8)$$

C_{vdW} is the van der Waals constant and Z_1 and Z_2 are the van der Waals reference planes of two metals. In figure 1 the interaction energy for Al(111) surfaces represented by stabilized jellium calculated from equation (8) with $C_{\text{vdW}} = 0.00225$ and $Z_1 = Z_2 = 0.75 \text{ au}$ is compared with the charge overlap energies. It is seen that the dispersion energies dominate for all separations. This is contrary to previous findings [19, 2, 11] where, considering the classical Lifshitz formula, it was found that van der Waals interactions prevail only for larger separations. The above-given value of the van der Waals constant [20] and that

used in references [2, 11] for Al agree within 3%, so it is the van der Waals reference plane position which increases the magnitude of the interaction by reducing the separations appearing in the denominator of equation (8).

In figure 2 we have plotted the adhesive energies versus separation for the three metals represented by stabilized jellium. As can be seen, each of these curves shows a minimum at $d = 0$. The depths of the minima agree to a very good accuracy with the negative of the surface energies calculated [13] for a flat surface of stabilized jellium. Also the zero-separation adhesive energies calculated in this work in the LDA for Al and Mg show better agreement with the experimental surface energies (1143 erg cm^{-2} for Al and 785 erg cm^{-2} for Mg [21]) than those resulting from the application of perturbation theory to the ordinary jellium [9]. For Na the result of a perturbative treatment agrees better with the experimental data (261 erg cm^{-2} [21]). Only a small part of these differences arises from the different parametrization of the correlation energy employed in this paper [15].

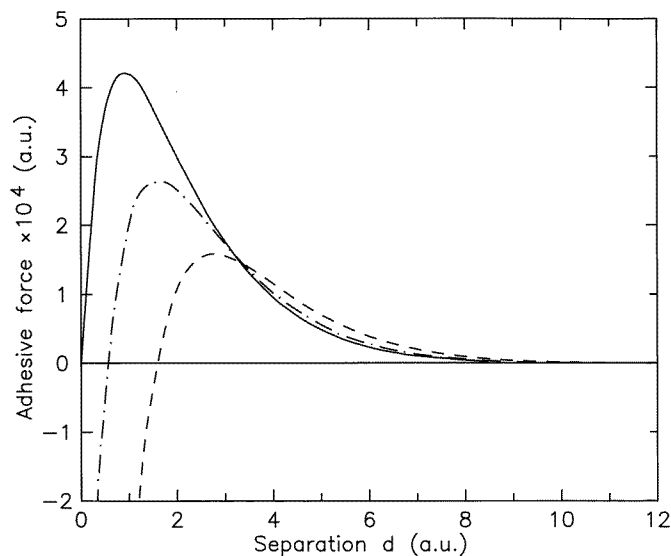


Figure 3. The adhesive force per unit area between two parallel Al surfaces as a function of their separation. The full curve represents the flat-surface stabilized-jellium model. The chain line shows the results for Al(111) in the face-dependent stabilized jellium. The dashed line represents ordinary jellium.

In figure 3 we show the adhesive force for the contact of two Al surfaces. For the jellium model the adhesive force at zero separation is equal to the bulk pressure of the homogeneous electron gas. For a flat surface of stabilized jellium the zero-separation force vanishes because it is compensated by the stabilization term. For small separations the force rises linearly. The linear force constant can be compared with that calculated in terms of the static dielectric function of the homogeneous electron gas [16, 19, 22]. The inclusion of the face dependence in the stabilized-jellium model disturbs its stability. This can be seen in the case of two Al(111) surfaces in contact. On adding to the average of the difference potential $\langle \delta v \rangle_{\text{WS}}$ an extra contribution due to the atomic corrugations, its magnitude changes from -2.49 eV , for a flat surface, to -1.75 eV , for the (111) face of Al. This has a relatively small effect on the adhesive energy curve but it is clearly visible in the force curve plotted in figure 3. As can be seen, the adhesive force for the Al(111) surface crosses zero at

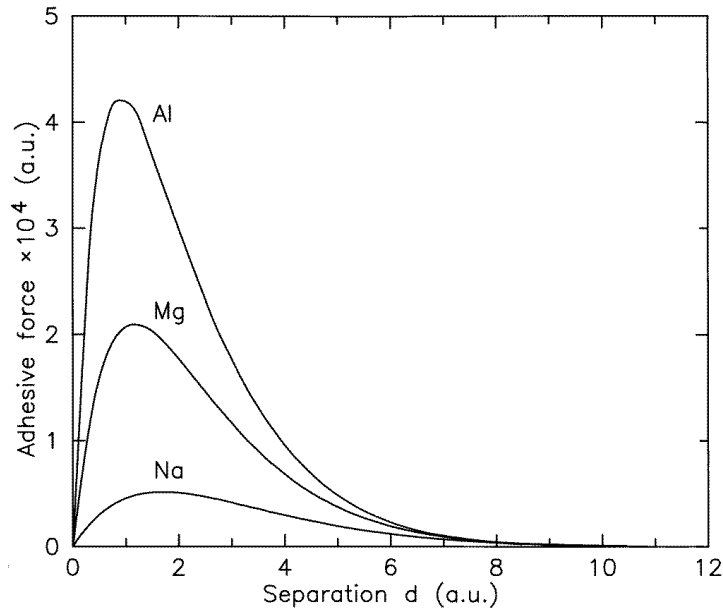


Figure 4. The force per unit area acting between two parallel metallic surfaces calculated in the stabilized-jellium model.

about a 0.4 Bohr separation and is negative for $d = 0$. The adhesive force calculated for flat surfaces of Al, Mg and Na is plotted versus separation in figure 4. For small separations and all three metals the adhesive force rises approximately linearly and attains its maximum at about 1 Bohr. With the decrease of the average electron density in the bulk metal, the position of the maximum shifts toward larger separations.

The maximum in the adhesive force can be associated with the ideal fracture strength of the metal, which is an important parameter in the phenomenological theories of fracture. The present calculations for the flat surface of stabilized jellium give $F_{\max}(\text{Al}) = 4.2 \times 10^{-4} \text{ au} = 1.24 \times 10^{11} \text{ dyn cm}^{-2}$ and $F_{\max}(\text{Mg}) = 2.1 \times 10^{-4} \text{ au} = 6.2 \times 10^{10} \text{ dyn cm}^{-2}$. The value for Al is twice that reported in references [2, 11] and compares reasonably well with the value $1.72 \times 10^{11} \text{ dyn cm}^{-2}$ which results from a crude estimation using Orowan's formula [2]. A similar estimation for Mg gives $1.14 \times 10^{11} \text{ dyn cm}^{-2}$ which is almost twice the value given by F_{\max} . However, considering the very approximate character of this estimation involving empirical parameters—Young's modulus and the surface energy—and the uncertainty in the experimental values of the latter, the agreement might be considered very good.

In summary, using the stabilized-jellium model, we have calculated self-consistently the adhesive energies and forces for the contacts of identical simple metals. The stabilized jellium, by its definition, does not suffer from the principal drawback of the jellium model: the calculated adhesive forces go to zero with the separation tending to zero, and the minimum in the binding energy curves appears at zero separation. There is a pressing need for an adhesion theory which can consistently connect the two regions of the short-range and the long-range (van der Waals) interactions. The substantial progress that has been made recently in describing the van der Waals interactions on the basis of density functional theory [17, 18] makes it look hopeful that such a unifying theory may be established quite soon.

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