Dependence of metal surface properties on the valence-electron density in the stabilized jellium model

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Abstract

The stabilized jellium model is the simplest model which yields realistic results for the physical properties of simple metals. For the surface properties, its single input is the valence-electron density, which is described by the density parameter r_s. We remark that the surface energy and the work function as a function of r_s, within that model, are reasonably approximated by power laws and compare that behaviour with similar descriptions found in the literature and with experiment. We also present a simple relationship between the surface energy and the bulk modulus, which is well fitted by the power $-\frac{7}{2}$ of the density parameter (when the effective valence is taken to be $z^* = 1$). Another simple relationship between the work function and the bulk modulus is shown. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The stabilized jellium model [1] has been successfully applied to understand the physics of surfaces [2], slabs [3] and clusters [4] of simple metals. This model has been recently reviewed in Ref. [5].

The surface properties of stabilized jellium are independent of the valence z. They are determined only by the average valence electron density in the bulk $\bar{n} = 3/(4\pi r_s^3)$, with r_s the density parameter or Seitz radius.

The surface energy σ and the work function W can be obtained from Lang–Kohn type [6] calculations for the planar surface of stabilized jellium [2], in the local density approximation for exchange and correlation. Within that approach, the surface energy and the work function depend continuously on r_s in a non-analytical way. However, we remark here that both results are well approximated by r_s-power laws. We compare ours with similar power law descriptions found in the literature (some of them having a theoretical justification), and with experiment.

Sixteen simple or sp-bonded metals are considered: Be ($r_s = 1.87$), Al ($r_s = 2.07$), Ga ($r_s = 2.19$), Sn ($r_s = 2.22$), Pb ($r_s = 2.30$), In ($r_s = 2.41$), Tl ($r_s = 2.48$), Mg ($r_s = 2.65$), Li ($r_s = 3.24$), Ca

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$(r_s = 3.27)$, Sr $(r_s = 3.57)$, Ba $(r_s = 3.71)$, Na $(r_s = 3.93)$, K $(r_s = 4.86)$, Rb $(r_s = 5.20)$, and Cs $(r_s = 5.62)$. The r_s values are all given in bohr.

The stabilized jellium model with effective valence $z^* = 1$ predicts also the realistic bulk moduli B for all simple metals, which are well fitted by a $r_s^{-7/2}$ law [7]. We remark that the adimensional ratio Br_s/σ, within that model, is nearly constant for the range of metallic densities. The same happens with the adimensional ratio Br_s^3/W.

2. Results

The stabilized jellium surface energy σ (in erg/cm^2) as a function of the density parameter r_s is represented in Fig. 1. Our calculations for the 16 simple metals are well described by the function $\sigma = 6937 \times r_s^{-2.7}$ obtained by a least-squares fit (solid line). This result should be compared with similar fits made by other authors. For example, some ab initio calculations [8] have been fitted by $\sigma \sim r_s^{-3}$, a result which may be understood on the basis of Miedema's model of metal cohesion [9].

On the other hand, the law $\sigma \sim r_s^{-2.5}$ has appeared several times in the literature being presented as a kind of empirical law (see, for example, Ref. [10]). A theoretical justification, based on zero-point energy of plasmons, has been given in Ref. [11], but received strong criticism [12]. The power $-\frac{5}{2}$ of the density parameter ($\sigma = 5709 \times r_s^{-2.5}$) is displayed in Fig. 1 by the dashed line, showing that it also gives a good account of our results.

We have obtained $\sigma = 8134 \times r_s^{-2.6}$ (not displayed in the figure) as the best fit to the experimental data taken from Ref. [13].

Recently, in Ref. [14], experimental and theoretical surface energies of simple and transition metals have been systematically examined and the case has been made to describe them by $\sigma \sim r_m^{-4}$, where r_m is the effective density parameter of Ref. [15]. This r_m correlates with r_s although not in a simple, analytical way.

Fig. 2 shows separately the four contributions to the stabilized jellium surface energy: exchange-correlation (σ_{xc}), pseudopotential correction (σ_{pseudo}), electrostatic (σ_{es}), and non-interacting kinetic (σ_{kin}). The best fits which we have obtained (not dis-
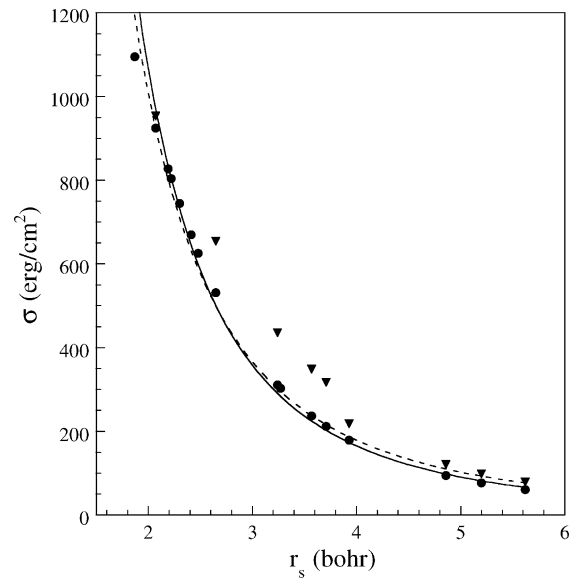

Fig. 1. Surface energy σ as a function of the density parameter r_s. The black circles represent Lang–Kohn results, within the stabilized jellium model, for different simple metals (Be, Al, Ga, Sn, Pb, In, Tl, Mg, Li, Ca, Sr, Ba, Na, K, Rb, and Cs in ascending order of r_s). The solid line represents the power function of r_s which better describes those results: $\sigma = 6937 \times r_s^{-2.7}$. The dashed line shows the best power $-\frac{5}{2}$ fit ($\sigma = 5709 \times r_s^{-2.5}$). The black triangles are experimental surface energies taken from Ref. [13].

displayed in the figure) for those contributions are: $\sigma_{xc} = 3.001 \times 10^4 \times r_s^{-3.4}$, $\sigma_{pseudo} = 2.584 \times 10^5 \times r_s^{-7.0}$, $\sigma_{es} = 1.160 \times 10^4 \times r_s^{-4.1}$, and $\sigma_{kin} = -1.554 \times 10^5 \times r_s^{-5.1}$. We recall that in the ordinary jellium model, the exchange and kinetic contributions are given by $\sigma_x \sim r_s^{-3.5}$ and $\sigma_{kin} \sim r_s^{-4.5}$ [16].

Let us now examine the work function. Fig. 3 shows the work function (in eV) as predicted by the stabilized jellium model. The best density scaling law $W = 6.756 \times r_s^{-0.6}$ is indicated by the solid line. As a consequence $\sigma r_s^2/W \sim r_s^{-0.1}$ is almost independent of the density.

The power $-\frac{1}{2}$ of the density parameter was obtained in a recent theoretical study of the work function [17] on the basis of Brodie's definition [18]. We have also tried this power: the dashed line in Fig. 3, representing the best fit $W = 6.077 \times r_s^{-0.5}$, does not reproduce well our values, namely for the lowest densities.
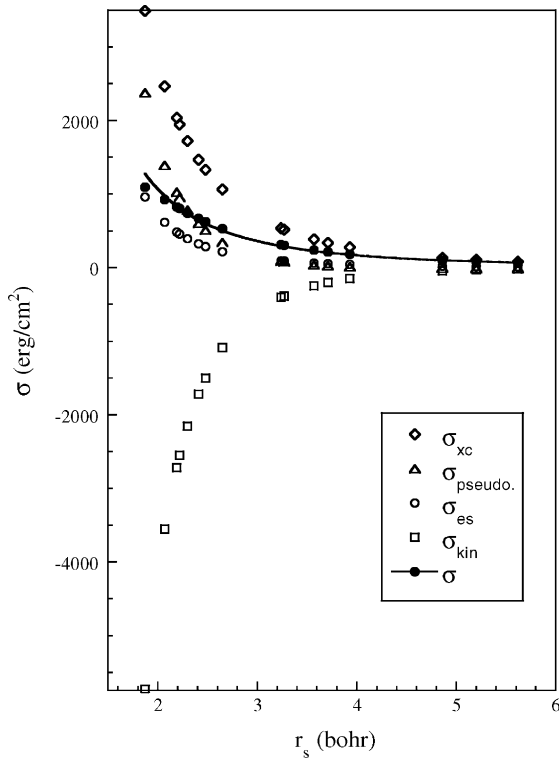
Fig. 2. Surface energy σ for different simple metals as predicted by the stabilized jellium model (same as the solid line in Fig. 1) and its decomposition in four contributions: exchange-correlation σ_{xc}, pseudopotential correction σ_{pseudo}, electrostatic σ_{es}, and non-interacting kinetic σ_{kin}.
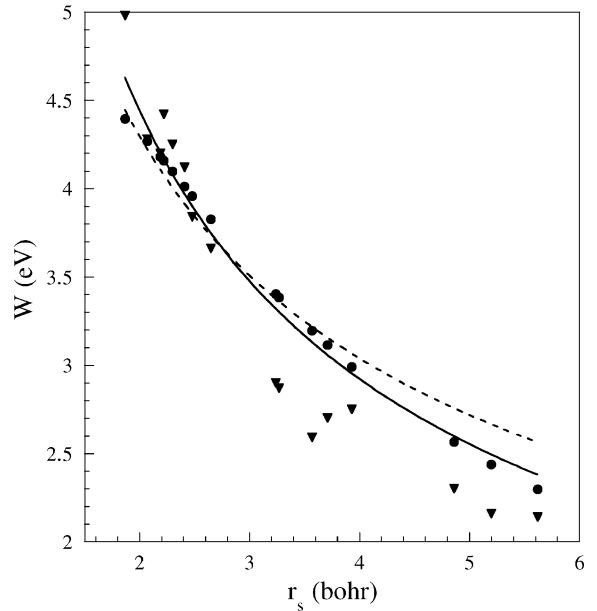

Fig. 3. Work function W as a function of the density parameter r_s. The black circles represent Lang–Kohn results, within the stabilized jellium model, for different simple metals. The solid line represents the power function of r_s which better describes those results: $W = 6.756 \times r_s^{-0.6}$. The dashed line shows the best power $-\frac{1}{2}$ fit ($W = 6.077 \times r_s^{-0.5}$). The black triangles are experimental work functions taken from Ref. [19].

We have obtained $W = 7.937 \times r_s^{-0.8}$ (not displayed in the figure) as the best fit to the experimental data (polycrystalline samples) taken from Ref. [16].

The stabilized jellium model with effective valence $z^* = 1$ describes correctly the real dependence of the bulk moduli (or the inverse compressibilities) upon r_s. Within that model, the bulk moduli are well fitted by $B \sim r_s^{-7/2}$ [7]. Similar simple power laws can be found in the literature for other kinds of materials. For example, in Refs. [20,21] it is shown that the bulk modulus in covalent materials depends only on the nearest neighbours separation d: $B \sim d^{-7/2}$.

It is interesting to relate the bulk and surface problems, analyzing the adimensional ratios Br_s/σ and Br_s^3/W. From Fig. 4, we observe that Br_s/σ is nearly constant, approximately equal to 9. This result agrees with earlier empirical observations that the ratio of the surface energy to the bulk modulus depends only weakly on the material [22,23]. A justification for the validity of $Br_s/\sigma \simeq$ constant has been given in Ref. [24] using density functional theory in the Thomas–Fermi–Dirac–Weizsäcker approach. On the other hand, the ratio Br_s^3/W, also displayed in Fig. 4, is remarkably close to 0.143 for all simple metals.

3. Conclusions

In the stabilized jellium model, treated in the framework of Lang–Kohn method using the local density approximation, the surface energy and work function are complicated functions of the density parameter r_s.

We have shown here that these functions can be well approximated, in the range of metallic densities, by power laws (respectively $\sim r_s^{-2.7}$ and
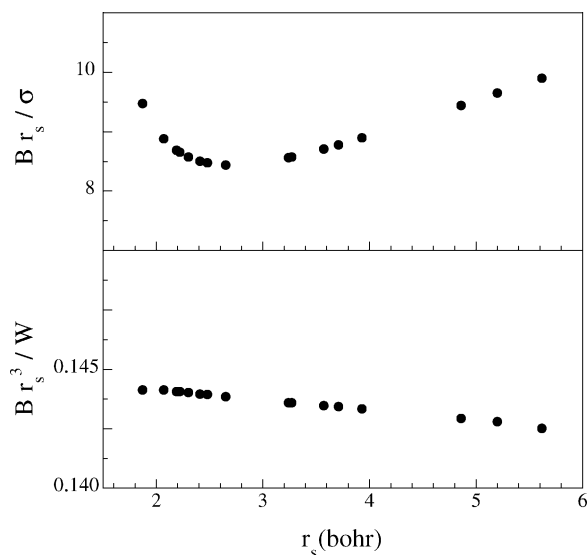
Fig. 4. Adimensional ratios Br_s/σ and Br_s^3/W for the simple metals as predicted by the stabilized jellium model, where B is the bulk modulus (calculated with effective valence $z^* = 1$), r_s the density parameter, σ the surface energy, and W the work function.

$\sim r_s^{-0.6}$). These relationships, although not exact, are useful to describe the gross trends of surface properties. Of course, they fail outside the range of densities of real metals. For instance, for $r_s \leqslant 1.6$ both the surface energy and the work function have maxima.

Since the bulk modulus, in the same model, has also been found to follow a simple power law (with exponent $-\frac{7}{2}$), it is possible to combine bulk and surface properties in a way that it is independent of the density. The dimensionless ratios Br_s/σ and Br_s^3/W have been found to be approximately constant. Theoretical explanations for these simple results are being investigated.

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