

## Brief Reports

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### Stabilized jellium model for the average electron density

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Employing the stabilized jellium model [J. Perdew *et al.*, *Phys. Rev. B* **42**, 11 627 (1990)] without the bulk stability condition, the bulk cohesive properties and surface energy of a simple metal are calculated. In the calculations the core-radii values are taken from the pseudopotential theory. Good agreement with experimental data is achieved.

The present paper concerns the recently proposed stabilized jellium (SJ) model.<sup>1</sup> In this model, based on the energy functional of jellium, the spurious electrostatic self-interaction of the positive background of each "ion" of radius  $r_0 = z^{1/3} r_s$  ( $z$  being the valence and  $r_s$  the density parameter given by the uniform positive background density  $\bar{n} = 3/4\pi r_s^3$ ) is subtracted and a constant potential which acts on the valence electrons only inside the metal is added. This constant potential, representing the average difference between the external potential of an array of pseudopotentials and that of the jellium background is expressed in terms of pseudopotential "core radius"  $r_c^0$  adjusted to achieve bulk stability at the observed valence-electron density

$$\left. \frac{\partial \epsilon(r_s, z, r_c)}{\partial r_s} \right|_{r_c = r_c^0} = 0. \quad (1)$$

In (1)  $\epsilon$  is the average energy per valence electron in the bulk. It is the sum of kinetic and exchange-correlation,  $\epsilon_{xc}(\bar{n})$ , contributions for a uniform electron gas of density  $\bar{n}$  and of the average value of the repulsive part of pseudopotential  $w_R$  and of the average Madelung energy  $\epsilon_M$ .

Equation (1) gives the dependence between  $r_c^0$ ,  $z$ , and  $r_s$  treated as the equilibrium density parameter, from which the core radius  $r_c^0$  may be determined for every metal as a function of its valence and  $r_s$  [see Eq. (26) of Ref. 1].

In the present paper we accept all assumptions of the SJ model except the assumption (1) which we do not use, and perform all calculations taking for the core radii  $r_c$  of the Ashcroft empty-core pseudopotential<sup>2</sup> their values fitted to measured bulk properties of the individual metals. Such procedure follows from the fact that the values of  $r_s$  are a measure of the observed density of individual

metal and  $r_c$  are deduced from its metallic properties.<sup>3</sup>

In this paper we compute, for  $r_s$ ,  $r_c$ , and  $z$  (Table I) characterizing simple metals, the binding energy  $-\epsilon(r_s, r_c, z)$  per valence electron<sup>1</sup>

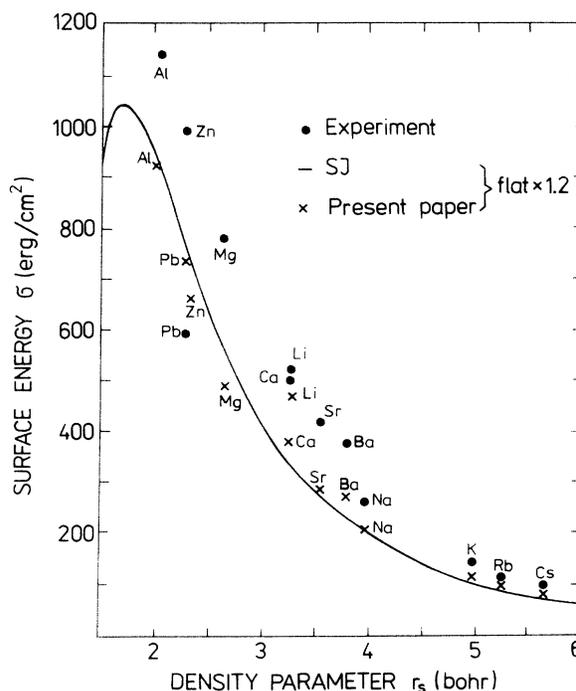


FIG. 1. Intrinsic surface energy  $\sigma$  vs density parameter  $r_s$ . Full line denotes  $\sigma(r_s)$  calculated in Ref. 1. Crosses denote the values calculated in the present paper. All calculated values are multiplied by the corrugation factor 1.2 (Ref. 12). The experimental values of the intrinsic surface energy, denoted by dots, are the zero-temperature extrapolation of the liquid-metal surface tension (Ref. 13).

$$\epsilon(r_s, r_c, z) = \frac{3}{10} \left[ \frac{9\pi}{4} \right]^{2/3} \frac{1}{r_s^2} - \frac{3}{4\pi} \left[ \frac{9\pi}{4} \right]^{1/3} \frac{1}{r_s} + \epsilon_c(\bar{n}) + \frac{3}{2} \frac{r_c^2}{r_s^2} - \frac{9}{10} \frac{z^{2/3}}{r_s}, \quad (2)$$

and the bulk modulus  $B$ , or the inverse compressibility<sup>4</sup>

$$B = -V \left[ \frac{\partial P}{\partial V} \right]_N = \frac{1}{12\pi} \left[ \frac{1}{r_s} \frac{\partial^2 \epsilon}{\partial r_s^2} - \frac{2}{r_s^2} \frac{\partial \epsilon}{\partial r_s} \right]. \quad (3)$$

Table I displays the values so determined as well as the ones calculated in Ref. 1, and experimental data. It is seen from this table that the values calculated in the present work are very similar to those obtained in Ref. 1. It has to be noted that the agreement between the values calculated and the measured data is generally better for

the binding energy than for bulk modulus. The present calculation give excellent agreement between the calculated and measured binding energy for Pb, Mg, Na, K, and Rb. It is expected that if the  $r_c^0$  values are used in these cases in the calculations of other metallic properties, worse results will be obtained than in the case of using the standard values<sup>3</sup> of Ashcroft core radii. On the other hand, however, as it is seen from Table I, the assumption (1) accepted in Ref. 1 gives similar values  $r_c^0$  for  $r_c$  values, for many metals.

We have also performed calculations of the surface properties in the framework of the SJ model, rejecting assumption (1). The results of such calculations for the work function are given in Ref. 5, where it is shown that also in this case the calculations done in the spirit of the present paper give similar, and even better, agreement with experiment than obtained in Ref. 1. The calculated

TABLE I. Bulk cohesive properties of simple metals. The binding energy per valence electron,  $-\epsilon$ , and the bulk modulus  $B$  are compared for the stabilized jellium (Ref. 1), present calculations, and experiment. Values in parentheses in the third column are the  $r_c^0$  (in bohr units) calculated in Ref. 1 while the values in the fourth column, given in parentheses, are the Ashcroft core radii (in bohrs).

| $r_s$ (bohr) | $-\epsilon$ (eV)   |                 |  | $B$ (Mbar)         |               |                |       |
|--------------|--------------------|-----------------|--|--------------------|---------------|----------------|-------|
|              | Stabilized jellium | Present calc.   | Experiment   | Stabilized jellium | Present calc. | Experiment     |       |
| Al           | 2.07               | 19.10<br>(1.11) | 19.05<br>18.93<br>(1.131) <sup>b</sup>                         | 18.88              | 1.577         | 1.611<br>1.677 | 0.722 |
| Pb           | 2.30               | 20.57<br>(1.46) | 23.51<br>(1.120) <sup>a</sup><br>20.47<br>(1.470) <sup>c</sup> | 24.68              | 1.288         | 0.044<br>1.334 | 0.430 |
| Zn           | 2.30               | 13.95<br>(1.07) | 13.65<br>(1.110) <sup>b</sup>                                  | 14.35              | 0.819         | 0.948          | 0.598 |
| Mg           | 2.65               | 12.38<br>(1.31) | 12.12<br>(1.358) <sup>b</sup>                                  | 12.10              | 0.487         | 0.562          | 0.354 |
| Ca           | 3.27               | 10.33<br>(1.74) | 10.48<br>(1.700) <sup>d</sup>                                  | 9.91               | 0.222         | 0.200          | 0.152 |
| Li           | 3.28               | 7.38<br>(1.33)  | 8.14<br>(1.06) <sup>a</sup><br>7.25<br>(1.374) <sup>c</sup>    | 7.02               | 0.149         | 0.038<br>0.167 | 0.116 |
| Sr           | 3.57               | 9.56<br>(1.94)  | 9.74<br>(1.890) <sup>d</sup>                                   | 9.22               | 0.160         | 0.139          | 0.116 |
| Ba           | 3.71               | 9.24<br>(1.94)  | 9.41<br>(1.984) <sup>d</sup>                                   | 8.56               | 0.138         | 0.121          | 0.103 |
| Na           | 3.99               | 6.26<br>(1.76)  | 6.26<br>(1.758) <sup>c</sup>                                   | 6.25               | 0.072         | 0.072          | 0.068 |
| K            | 4.96               | 5.19<br>(2.33)  | 5.34<br>(2.230) <sup>d</sup>                                   | 5.28               | 0.032         | 0.026          | 0.032 |
| Rb           | 5.23               | 4.95<br>(2.49)  | 5.07<br>(2.400) <sup>d</sup>                                   | 5.03               | 0.026         | 0.022          | 0.031 |
| Cs           | 5.63               | 4.64<br>(2.72)  | 4.76<br>(2.627) <sup>d</sup>                                   | 4.70               | 0.020         | 0.016          | 0.020 |

<sup>a</sup>Reference 7.

<sup>b</sup>Reference 8.

<sup>c</sup>Reference 9.

<sup>d</sup>Reference 10.

<sup>e</sup>Reference 11.

surface energy values for the flat surface are marked by crosses in Fig. 1. From this figure we observe that the present calculations give better agreement with experimental data in the case of many simple metals.<sup>6</sup>

Concluding, one has to state that the condition given by Eq. (1) is not a necessary condition for the bulk stability of simple metals which is already guaranteed by the in-

troduction of the short-range part of the pseudopotential. A more exact understanding of the role of this condition in the metallic equilibrium state requires further research.

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<sup>1</sup>J. P. Perdew, H. Q. Tran, and E. D. Smith, *Phys. Rev. B* **42**, 11 627 (1990).

<sup>2</sup>N. W. Ashcroft, *Phys. Lett.* **23**, 48 (1966).

<sup>3</sup>V. Heine and D. Weaire, *Solid State Phys.* **24**, 262 (1970).

<sup>4</sup>All equations are expressed in atomic units. The unit of distance is 1 bohr =  $0.5292 \times 10^{-8}$  cm, the unit of energy is 1 hartree = 27.21 eV and 1 hartree/bohr<sup>3</sup> = 294.2 Mbar.

<sup>5</sup>K. F. Wojciechowski and H. Bogdanów, *Acta Phys. Pol. A* **85**, 875 (1994).

<sup>6</sup>The calculation of the surface energy of the flat planar surface employs the procedure given in Ref. 1 [Eqs. (40)–(44) and (21)] by the use of core-radii  $r_c$  determined in pseudopotential theory (Refs. 7–11) instead of the “equilibrium” radii  $r_s^0$

determined by Eq. (26) of Ref. 1.

<sup>7</sup>N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **155**, 682 (1967).

<sup>8</sup>W. M. Shyn and G. D. Gaspari, *Phys. Rev.* **170**, 687 (1968).

<sup>9</sup>N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **159**, 500 (1967).

<sup>10</sup>J. M. Wills and W. A. Harrison, *Phys. Rev. B* **28**, 4363 (1983).

<sup>11</sup>J. M. Lopez and J. A. Alonso, *Phys. Status Solidi B* **104**, 307 (1981).

<sup>12</sup>J. P. Perdew, Y. Wang, and E. Engel, *Phys. Rev. Lett.* **66**, 508 (1991); see also C. Fiolhais and J. P. Perdew, *Phys. Rev. B* **45**, 6207 (1992).

<sup>13</sup>W. R. Tyson and W. A. Miller, *Surf. Sci.* **62**, 267 (1977).