

## Formation energies of metallic voids, edges, and steps: Generalized liquid-drop model

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The void formation energy is the work needed to create the curved surface of a void. For a spherical hole in a homogeneous metal (jellium or stabilized jellium), the void formation energy is calculated for large radii from the liquid-drop model (surface plus curvature terms), and for small radii from perturbation theory. A Padé approximation is proposed to link these limits. For radii greater than or equal to that of a single atom or monovacancy, the liquid-drop model is found to be usefully accurate. Moreover, the predicted monovacancy formation energies for stabilized jellium agree reasonably well with those measured for simple metals. These results suggest a generalized liquid-drop model of possible high accuracy and explanatory value for the energetics of stable metal surfaces curved on the atomic scale (crystal faces, edges, corners, etc.). The bending energy per unit length for an edge at angle  $\theta$  is estimated to be  $\gamma(\pi-\theta)/4$ , where  $\gamma$  is the intrinsic curvature energy. The step energy is estimated as  $(n-2+\pi/2)\sigma d$ , where  $\sigma$  is the intrinsic surface energy,  $n \geq 1$  is the number of atomic layers at the step, and  $d$  is the layer height.

### I. INTRODUCTION

The void formation energy is the energy of a macroscopic crystal with an  $N$ -atom hole, plus the energy of  $N$  bulk atoms, minus the energy of the perfect crystal. More simply, it is the work needed to create the curved surface of the void. Perdew, Wang, and Engel<sup>1</sup> have proposed that this energy, and the energies of other metallic surfaces curved on the atomic or larger scales, may be estimated from the liquid-drop model

$$\sigma A + \frac{1}{2}\gamma \int dA \mathcal{R}^{-1}, \quad (1)$$

where  $A$  is the area of an appropriately defined surface,  $\mathcal{R}^{-1}$  is the local curvature (negative for a concave surface), and  $\sigma$  and  $\gamma$  are intrinsic surface and curvature energies. Since Eq. (1) is in principle valid only for small curvature, it is necessary to assess the domain of its validity.

Equation (1) seems to be valid on the atomic and larger size scales for jellium, an idealized model in which the positive charge on the ions is smeared out into a uniform positive background. Fiolhais and Perdew<sup>2</sup> reached this conclusion by comparing

$$\sigma 4\pi R^2 - \gamma 2\pi R, \quad (2)$$

using first-principles values for  $\sigma$  and  $\gamma$ , against self-consistently calculated formation energies<sup>3</sup> for spherical voids of radius  $R = -\mathcal{R} > 0$  in jellium. However, the jellium model is unrealistic for high-density metals such as aluminum, where it incorrectly predicts negative values for the surface<sup>4</sup> and void formation energies.<sup>3</sup> A more

realistic approach to the simple metals is the stabilized jellium or structureless pseudopotential model,<sup>5,6</sup> for which self-consistent void formation energies have not yet been calculated.

In this work, we consider a spherical void in an otherwise homogeneous metal (with valence electron density  $\bar{n} = 3/4\pi r_s^3$ ; atomic units bohr =  $\hbar^2/me^2$  and hartree =  $me^4/\hbar^2$  are used throughout). We write the void formation energy for radius  $R$  as  $\sigma_R 4\pi R^2$ , where  $\sigma_R$  is the void formation energy per unit area. Here  $R = N^{1/3} z^{1/3} r_s$ , where  $z$  is the valence. For small  $R$ , we find

$$\sigma_R = aR + bR^3 + cR^4 + \dots \quad (3)$$

Note the absence of a term  $\sim R^2$ . For large  $R$ , the liquid-drop model of Eq. (2) predicts

$$\sigma_R = \sigma - \frac{\gamma}{2R} + \dots \quad (4)$$

Then we link these two limits by a simple Padé approximant

$$\sigma_R = \sigma \frac{1 + A_1 R^{-1} + A_2 R^{-2}}{1 + B_1 R^{-1} + B_2 R^{-2} + B_3 R^{-3}}. \quad (5)$$

All coefficients in Eqs. (3)–(5) are calculated from first principles in both the jellium and stabilized-jellium models, using the local-density approximation<sup>7</sup> for exchange and correlation. Within each model, these coefficients are functions of the electron-density parameter  $r_s$  alone; this parameter is fixed for each metal by the observed

valence-electron density. We then set  $R = r_0 \equiv z^{1/3} r_s$ , the radius of a single atom or monovacancy ( $N=1$ ), and compare the results of Eqs. (4) and (5) with each other and with measured monovacancy formation energies.

With a negative value of  $R$ , Eqs. (4) and (5) describe the nonoscillatory surface contribution to the energy of a spherical cluster (which can have no electron number less than 1, hence no radius smaller than  $r_s$ ).

## II. LARGE- AND SMALL- $R$ COEFFICIENTS

The surface energy  $\sigma$  and curvature energy  $\gamma$  have been computed for each model from self-consistent planar-surface electron-density profiles, by the approach of Ref. 2. The results are shown in Table I.

The small- $R$  coefficients for jellium are

$$a = -\frac{1}{3}\bar{n}^2 \frac{d\varepsilon}{d\bar{n}}, \quad (6)$$

$$b = \frac{4\pi}{15}\bar{n}^2, \quad (7)$$

$$c = \frac{4}{9}\bar{n}^2 \int_0^\infty dq \frac{4\pi\chi(q)}{q^2\tilde{\varepsilon}(q)}, \quad (8)$$

where  $\varepsilon$  and  $\tilde{\varepsilon}(q)$  are, respectively, the bulk energy per electron<sup>8</sup> and dielectric function<sup>9</sup> of jellium:

$$\tilde{\varepsilon}(q) = 1 - \frac{4\pi}{q^2}\chi(q)[1 - G(q)]. \quad (9)$$

The local-field correction

$$G(q) = -\frac{1}{4\pi} \frac{d^2}{d\bar{n}^2} (\bar{n}\varepsilon_{xc})q^2 \quad (10)$$

is evaluated in the local-density approximation.<sup>7</sup> Here  $\varepsilon_{xc}$  is the bulk exchange-correlation energy per electron,<sup>8</sup> which would vanish in the Hartree approximation for  $\varepsilon$  [i.e., in the Lindhard approximation for  $\tilde{\varepsilon}(q)$ ].

To derive Eqs. (6)–(8), imagine creating a small void at the center of a large jellium sphere of radius  $R_1 \rightarrow \infty$  by removing the positive background charge from a small sphere of radius  $R$ , and redistributing this charge uniformly over the outer surface of the jellium sphere. The resulting change  $\rho_v(\mathbf{r})$  in the background density will be small when  $R$  is small. It creates a perturbation term in the Hamiltonian,

$$\hat{H}_v = \int d^3r \frac{1}{4\pi} [\hat{\mathbf{E}}(\mathbf{r}) \cdot \mathbf{E}_v(\mathbf{r}) + \frac{1}{2} E_v^2(\mathbf{r})], \quad (11)$$

where  $\mathbf{E}_v(\mathbf{r})$  is the electric field due to  $\rho_v(\mathbf{r})$ . The electric field operator  $\hat{\mathbf{E}}(\mathbf{r})$  in Eq. (11) arises from the density

TABLE I. Planar surface energy  $\sigma$  and curvature energy  $\gamma$  for jellium ( $J$ ) and stabilized jellium (SJ) ( $r_s$  in bohr;  $\sigma$  and  $\gamma/2r_s$  in millihartree/bohr<sup>2</sup>). (1 millihartree/bohr<sup>2</sup> = 0.027 21 eV/bohr<sup>2</sup> = 1557 erg/cm<sup>2</sup>.)

Metal ( $r_s$ )	$\sigma$		$\gamma/2r_s$	
	$J$	SJ	$J$	SJ
Al (2.07)	-0.390	0.595	0.442	0.442
Na (3.93)	0.109	0.115	0.047	0.046
Cs (5.62)	0.045	0.038	0.016	0.012

$\bar{n}\theta(R_1 - r) - \hat{n}(\mathbf{r})$ , where  $\hat{n}(\mathbf{r})$  is the electron-density operator and  $\theta$  is the step function.

The coefficient  $b$  of Eq. (7) has a simple origin in the second term of Eq. (11) [the electrostatic self-energy of  $\rho_v(\mathbf{r})$ ]. The coefficients  $a$  and  $c$  of Eqs. (6) and (8) arise from the first term of Eq. (11), evaluated, respectively, to zeroth and first order in the linear response<sup>9</sup> of the electron density to the perturbation. The zeroth-order term arises only at the surface of the large jellium sphere, and is simplified with the help of the Budd-Vannimenus theorem<sup>10</sup>

$$\int_{-\infty}^0 dz E(z) = \bar{n} \frac{d\varepsilon}{d\bar{n}}. \quad (12)$$

Here  $E(z)$  is the electric field near the planar surface of a jellium whose positive background fills the half-space  $z < 0$ . Equation (12) is the first of a hierarchy of sum rules<sup>11–13</sup> leading from the bulk via surfaces and edges to corners.

Passing from jellium to stabilized jellium, the small- $R$  coefficients change by

$$\Delta a = \frac{1}{3}\bar{n}^2 \frac{d\varepsilon}{d\bar{n}}, \quad (13)$$

$$\Delta b = -\frac{4}{15}\bar{n}^3 \left[ \frac{d\varepsilon}{d\bar{n}} \right]^2, \quad (14)$$

$$\Delta c = \frac{8}{9}\bar{n}^2 \frac{d\varepsilon}{d\bar{n}} \int_0^\infty dq \frac{\chi(q)}{\tilde{\varepsilon}(q)} + \frac{1}{9\pi}\bar{n}^2 \left[ \frac{d\varepsilon}{d\bar{n}} \right]^2 \int_0^\infty dq \left[ 4\bar{n} + \frac{q^2\chi(q)}{\tilde{\varepsilon}(q)} \right]. \quad (15)$$

Note that  $a_s = a + \Delta a = 0$ , consistent with the zero-pressure condition for stabilized jellium. All stabilization corrections vanish at the equilibrium bulk density of jellium ( $d\varepsilon/d\bar{n} = 0$  at  $r_s = 4.19$ ).

To derive Eqs. (13)–(15), we begin with Eqs. (23) and (28) of Ref. 5 for a stabilized jellium whose background charge is held at its equilibrium bulk density. The perturbation created by a small void in a large stabilized jellium sphere is

$$\hat{H}_{sv} = \hat{H}_v - \frac{d\varepsilon}{d\bar{n}} \int d^3r \{ \rho_v(\mathbf{r}) [\hat{n}(\mathbf{r}) - \bar{n}\theta(R_1 - r)] - \rho_v(\mathbf{r}) \bar{n}\theta(R_1 - r) - \rho_v^2(\mathbf{r}) \} \quad (16)$$

[where the sum of all contributions following  $\hat{n}(\mathbf{r})$  integrates to zero]. When Eq. (16) is evaluated to zero order in the response of the electron density to  $\rho_v(\mathbf{r})$ , the result again arises only at the surface of the large jellium sphere. The resulting expression for  $a + \Delta a$  is simplified with the help of theorem

$$\int_{-\infty}^0 dz E_s(z) = [\bar{n} - n_s(0)] \frac{d\varepsilon}{d\bar{n}}, \quad (17)$$

where  $E_s(z)$  is the electric field of a half-space of stabilized jellium and  $n_s(0)$  is the electron density at its planar surface. Theorem (17) follows from Eq. (F14) of Ref. 14

TABLE II. Coefficients  $a$ ,  $b$ , and  $c$  of the small- $R$  expansion (3) for jellium ( $J$ ) and stabilized jellium (SJ) (in millihartree/bohr<sup>2</sup>).

Metal ( $r_s$ )	$ar_s$		$br_s^3$		$cr_s^4$	
	$J$	SJ	$J$	SJ	$J$	SJ
Al (2.07)	-1.698	0	5.383	4.851	-7.525	-12.848
Na (3.93)	-0.016	0	0.787	0.786	-1.446	-1.536
Cs (5.62)	+0.022	0	0.269	0.264	-0.582	-0.410

with  $C = -\bar{n} d\epsilon/d\bar{n}$  and  $X = 0$ .

The expressions for  $\Delta b$  and  $\Delta c$  arise from the linear response of the electron density to  $\rho_v(\mathbf{r})$ . To achieve Eqs. (14) and (15), an infinite contribution to the  $R^4$  term of Eq. (3) must be recast as a sum of finite contributions to the  $R^3$  and  $R^4$  terms:

$$\begin{aligned}
 R^4 \int_0^\infty dq g(qR) f(q) & \\
 &= R^4 \int_0^\infty dq g(qR) - R^4 \int_0^\infty dq g(qR) [1 - f(q)] \\
 &= R^3 \int_0^\infty dx g(x) \\
 &\quad - R^4 \int_0^\infty dq g(0) [1 - f(q)] + O(R^5), \quad (18)
 \end{aligned}$$

where  $f(q) \rightarrow 1$  as  $q \rightarrow \infty$ . Numerical results for the small- $R$  coefficients are presented in Table II.

We expect that the nonlinear response of the density does not contribute to Eq. (3) through order  $R^4$ , since the perturbation is of order  $R^3$  and its second-order or  $R^6$  contribution to  $\sigma_R 4\pi R^2$  formally requires<sup>9</sup> only the linear response of the density.

### III. RESULTS AND CONCLUSIONS

From the coefficients of Eqs. (3) and (4), evaluated in Sec. II, we obtain the coefficients for the Padé approximation of Eq. (5) by simple algebra.

In the case of jellium, the Padé representation for  $\sigma_R$  was plotted on top of the self-consistent local-density results in Fig. 5 of Manninen and Nieminen.<sup>3</sup> At the density of Na, no difference could be discerned. At the density of Al, the curves were qualitatively similar but the minimum occurred at  $-870$  ergs/cm<sup>2</sup> in the Padé and at  $-950$  ergs/cm<sup>2</sup> in the self-consistent result. (To make this comparison as fair as possible, we used the Gunnarsson-Lundqvist<sup>15</sup> electron-gas input here; the Perdew-Wang<sup>8</sup> input is used in all the tables of this paper.)

The results of the Padé approximation for stabilized jellium (where we find  $A_1 = A_2 = 0$ ) are displayed in Fig. 1. We believe that these curves should also describe nearly spherical voids in the simple or  $sp$ -bonded metals.

In Table III, we compare the liquid-drop model of Eq. (2) against the Padé representation for monovacancies (spherical voids of radius  $R = r_0 = z^{1/3} r_s$ ). The agreement is rather close, confirming that the domain of validity of the liquid-drop model for the simple metals extends down almost to the atomic scale of sizes. Moreover, the monovacancy formation energies predicted for stabilized jellium are in rough agreement with measured values<sup>16-18</sup>

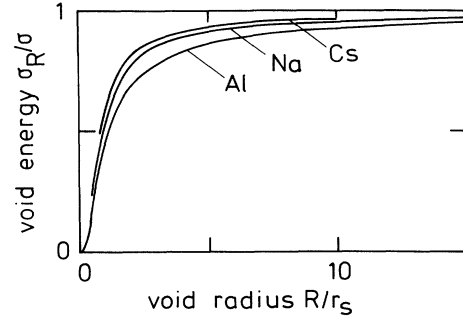


FIG. 1. Void formation energy per unit area  $\sigma_R$  vs void radius  $R$  for stabilized jellium with density parameter  $r_s$ . Padé approximation (5) with small- and large- $R$  coefficients  $a_s = a + \Delta a$ ,  $b_s = b + \Delta b$ , and  $c_s = c + \Delta c$ ,  $\sigma_s, \gamma_s$  from Tables I and II.

for the simple metals. (A recent detailed calculation<sup>19</sup> within the local-density approximation for Al yields vacancy formation energies  $0.83$  and  $0.73 \pm 0.10$  eV, respectively, without and with lattice relaxation.)

Our results suggest a generalized liquid-drop model for the energy of a stable metal surface curved on the atomic scale:

$$\int dA \frac{\sigma}{1 - B_1 \mathcal{R}^{-1} + B_2 \mathcal{R}^{-2} - B_3 \mathcal{R}^{-3}}, \quad (19)$$

where  $\mathcal{R}^{-1}$  is the local curvature. Equation (19) might effectively sum the curvature contribution to all orders. For greatest accuracy, the parameters  $B_1$ ,  $B_2$ , and  $B_3$  could be fitted to self-consistent stabilized-jellium void formation energies for  $|\mathcal{R}| > r_s$ , when those become available.<sup>20</sup> This procedure would yield an improved estimate of the curvature energy  $\gamma$  (currently evaluated<sup>2</sup> only with the help of the fourth-order gradient expansion for the kinetic energy), as well as higher-order terms in the leptodermous or large- $\mathcal{R}$  expansion. For detailed application of Eqs. (1) or (18) to real crystal faces, edges, corners, etc., the sharp surface of stabilized jellium should be warped on the atomic scale. This can be achieved by cutting along the surfaces of Wigner-Seitz cells and then rounding.<sup>1</sup> In the spirit of pseudopotential theory, the optimum warping might reproduce the valence-electron density of the real metal outside the surface.

Regardless of the ultimate accuracy that might be achieved by the approach of the preceding paragraph, the

TABLE III. Monovacancy formation energy of stabilized jellium in the liquid-drop model (without and with the curvature term) and in the Padé representation of Eq. (5), compared to experimental values for real metals. Here  $r_0 = z^{1/3} r_s$  is the void radius, and  $z$  is the valence. (Energies in eV.)

Metal ( $z$ )	$\sigma 4\pi r_0^2$	$\sigma 4\pi r_0^2 - \gamma 2\pi r_0$	$\sigma_{r_0} 4\pi r_0^2$	$E_{\text{vac}}^{\text{exper}}$
Al (3)	1.81	0.88	1.06	$0.66 \pm 0.02^a$
Na (1)	0.61	0.36	0.33	$0.42 \pm 0.03^b$
Cs (1)	0.41	0.28	0.24	$0.28^c$

<sup>a</sup>Reference 16.

<sup>b</sup>Reference 17.

<sup>c</sup>Reference 18.

explanatory value of these concepts now seems secure. The stabilized-jellium model shows how the average valence-electron density of a simple metal sets the size of  $\sigma$  and  $\gamma$ , while the liquid-drop model shows how  $\sigma$  and  $\gamma$  fix the energies of surfaces curved on the atomic scale. This model also explains<sup>21</sup> the effect on the cohesive energy of density-gradient corrections to the local-density approximation.

As another application of the liquid-drop model, we estimate the edge formation energy of a simple metal, omitting all atomistic detail. Imagine two *plane* faces of stabilized jellium meeting at an angle  $\theta$ . The most realistic edge is probably not pointed but rounded on the atomic scale, with principal curvature radii  $r$  and  $\infty$ , i.e., with curvature  $\frac{1}{2}r^{-1}$ . The precise value of  $r$  is unimportant, so long as it is large enough for the approximate validity of Eq. (1). From that equation, we find<sup>22</sup> that the energy per unit length needed to bend the edge is  $\gamma(\pi-\theta)/4$ , e.g.,  $+\gamma\pi/8$  for a  $90^\circ$  edge and  $-\gamma\pi/8$  for a  $270^\circ$  edge.

There is recent interest in steps<sup>23,24</sup> on planar surfaces. Since a step involves both a  $90^\circ$  and a  $270^\circ$  edge, the curvature contribution to the step formation energy may be small. But a step of height  $h$  also creates an additional surface area and thus an energy per unit length that varies between  $\sigma h$  for unrounded edges and  $(\pi/2-1)\sigma h$  for maximally rounded edges. For a monolayer step on

an Al(111) surface, with lattice constant  $a=7.52$  bohr and  $h=a/\sqrt{3}$ , these estimates are 2.6 and 1.5 millihartree/bohr, using  $\sigma=0.61$  millihartree/bohr<sup>2</sup> extrapolated from Table I. A detailed calculation by Scheffler, Neugebauer, and Stumpf<sup>24</sup> shows a formation energy of 0.24 eV per step atom, or 1.7 millihartree/bohr, using a distance  $a/\sqrt{2}$  between atoms along the step line.

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