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Energies of curved metallic surfaces from the stabilized-jellium model

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In the liquid-drop model, the total energy of a system is expanded as a sum of volume, surface, and curvature terms. We derive an expression for the curvature energy of a metal in terms of the electron-density profile for a planar surface, and show that the resulting values agree with the fits of calculated or measured total energies to the liquid-drop expansion. In particular, this expansion accurately describes the formation energies of microscopic voids (including monovacancies) in metals. In our calculations, the curvature energy is determined by the bulk density. It is nearly the same for restricted trial density profiles as for self-consistent Kohn-Sham profiles, for the fourth-order gradient expansion as for the exact kinetic energy, and for jellium as for stabilized jellium. We also report Kohn-Sham results for the surface energy and work function. The stabilized-jellium model, while retaining the simplicity and nonempirical character of jellium, gives a significantly more realistic description of the simple metals, especially those with high bulk densities.

I. INTRODUCTION

Within the liquid-drop model,[1,2] the total energy E of an extended system with volume V and surface area A is expanded as

$$E=\alpha V+\sigma A+\tfrac{1}{2}\gamma\int dA\,\mathcal{R}^{-1}\,, \tag{1}$$

where α, σ, and γ are intrinsic volume, surface, and curvature energies, and $\mathcal{R}^{-1}$ is the local curvature of area element dA (i.e., the arithmetic mean of the principal-axis values $\mathcal{R}_1^{-1}$ and $\mathcal{R}_2^{-1}$). While the accuracy of Eq. (1) for finite systems (nuclei, metallic clusters) is limited by shell-structure oscillations, this expansion is surprisingly accurate for monovacancy-formation energies (Sec. V) and crystal-face-dependent surface energies in metals of infinite volume.[2] Thus we seek *a priori* values of σ and γ for metals, to compare with phenomenological values.[2]

The qualitative physics of the liquid-drop expansion (1) is simple. If the extended metal is stable at the bulk density $\bar{n}$, then each atom will require an environment that is as bulklike as possible. The energy will minimize when the surface is as small in area (for a given volume) and as concave (for a given area) as possible, i.e., the surface energy σ and curvature energy γ will be positive.[2] Moreover, the bulk stability is the result of a competition between the electronic kinetic energy (which tries to reduce $\bar{n}$) and the potential energy (which tries to increase $\bar{n}$). At the electronic surface, the electrons "spill out" as their density goes continuously to zero, and this effect lowers the kinetic energy while increasing the potential energy. Thus the kinetic-energy components of σ and γ are negative.

Lang and Kohn[3] showed how to calculate the metallic surface energy σ, using density-functional theory[4] and the electron-density profile of a planar surface. Here we will do the same for the metallic curvature energy γ, following the leptodermous expansion[5] of nuclear physics. After our work was completed, we learned of the similar theory of Pogosov,[6] who derived a curvature-energy expression which is a special case of ours. (Pogosov also studied size effects on the ionization energy and electron affinity, as did other authors.[7,8])

The volume energy α and surface energy σ of a simple metal are determined largely by the average valence electron density in the bulk

$$\bar{n}=3/4\pi r_s^3=k_F^3/3\pi^2\,, \tag{2}$$

and the same can be expected of the curvature energy γ. The "stabilized-jellium model" of Perdew, Tran, and Smith[9] displays this behavior, and provides realistic first-principles estimates for α and σ. In this model, the total energy as a functional of the electron density $n(\mathbf{r})$ is

$$\begin{aligned}E[n,n_+]=&T_s[n]+E_{xc}[n]\\&+\tfrac{1}{2}\int d^3r\,\phi([n,n_+],\mathbf{r})[n(\mathbf{r})-n_+(\mathbf{r})]\\&+B\int d^3r\,n_+(\mathbf{r})\\&+\frac{C}{\bar{n}}\int d^3r\,n_+(\mathbf{r})[n(\mathbf{r})-n_+(\mathbf{r})]\,.\end{aligned} \tag{3}$$

Here T_s and $E_{\rm xc}$ are the noninteracting kinetic and exchange-correlation energies of the electrons, and

$$\phi([n,n_+],\mathbf{r})=\int d^3r'[n(\mathbf{r}')-n_+(\mathbf{r}')]/|\mathbf{r}'-\mathbf{r}| \tag{4}$$

is the electrostatic potential. The positive background density $n_+(\mathbf{r})$ equals the constant $\bar{n}$ inside a sharp surface, and vanishes outside. For a neutral metal,

$$\int d^3r\,n_+(\mathbf{r})=\int d^3r\,n(\mathbf{r})\,. \tag{5}$$

With $B=C=0$, Eq. (3) reduces to the jellium model, for which the bulk metal is stable (i.e., obeys the zero-pressure condition) only at $r_s=4.2$. Away from this density, the jellium model develops unphysical features (e.g., negative surface energies for metals with $r_s\lesssim 2.5$). These difficulties are removed[3] by the Madelung and pseudopotential corrections to jellium. In the stabilized-jellium model,[9] those corrections are simply approximated by the structureless averages displayed in the last two terms of Eq. (3), where the constants B and C are determined by the condition of bulk stability. B contributes only to the volume energy, and so for present purposes we set $B=0$. When $\bar{n}$ is the equilibrium bulk density (the only case of interest here),

$$C=-k_F^2/5+k_F/4\pi+(r_s/3)d\varepsilon_c/dr_s \ , \tag{6}$$

where $\varepsilon_c(\bar{n})$ is the correlation energy[10] per electron in a uniform gas of density $\bar{n}$. (All equations are in atomic units, in which $\hbar=e^2=m=1$; the atomic units of energy and distance are hartrees and bohrs, respectively.) C is negative for $r_s<4.2$ and positive for $r_s>4.2$.

The exchange-correlation energy in the local-density approximation[4] is

$$E_{\mathrm{xc}}[n]=\int d^3r\, n(\mathbf{r})\varepsilon_{\mathrm{xc}}(n(\mathbf{r})) \ , \tag{7}$$

where $\varepsilon_{\mathrm{xc}}(n)=-3(3\pi^2 n)^{1/3}/4\pi+\varepsilon_c(n)$. The kinetic energy may be constructed exactly by the Kohn-Sham method[4]

$$T_s[n]=\sum_i \int d^3r\, \tfrac{1}{2}|\nabla\psi_i(\mathbf{r})|^2 \ , \tag{8}$$

$$n(\mathbf{r})=\sum_i |\psi_i(\mathbf{r})|^2 \ , \tag{9}$$

where the ψ_i are self-consistent orbitals. Continuum density-functional approximations include the gradient expansion:[4]

$$T_s[n]=T_0[n]+T_2[n]+T_4[n] \ , \tag{10}$$

$$T_0[n]=\int d^3r\, \tfrac{3}{10}(3\pi^2)^{2/3}n^{5/3} \ , \tag{11}$$

$$T_2(n)=\int d^3r\, \tfrac{1}{72}\frac{|\nabla n|^2}{n} \ , \tag{12}$$

$$T_4[n]=\int d^3r\frac{(3\pi^2)^{-2/3}}{540}n^{1/3} \times\left[\left[\frac{\nabla^2 n}{n}\right]^2 -\frac{9}{8}\left[\frac{\nabla^2 n}{n}\right]\left|\frac{\nabla n}{n}\right|^2+\frac{1}{3}\left|\frac{\nabla n}{n}\right|^4\right] . \tag{13}$$

The density which minimizes $E[n,n_+]$ is found approximately by variation of parameters, or exactly by solution of the Euler equation

$$\delta E[n,n_+]/\delta n(\mathbf{r})=\mu \ , \tag{14}$$

where the Lagrange multiplier μ is the chemical potential.

Equations (7) and (10) constitute the Thomas-Fermi-Dirac-Gombas-Weizsäcker-4 (TFDGW4) approximation. Simpler approximations include TFDGW (neglect of T_4) and TF (neglect of $E_{\mathrm{xc}}+T_2+T_4$).

II. PLANAR-SURFACE EXPRESSIONS FROM THE LEPTODERMOUS EXPANSION

Let the sharp surface of the positive background be a sphere of radius R, where R is much bigger[5] than the thickness of the electronic surface, and expand the energy in inverse powers of R. The expansion is formally the same whether the system is a solid sphere in vacuum ($\mathcal{R}=R$) or a spherical void in an infinite metal ($\mathcal{R}=-R$). The former case will be discussed below, although some assumptions behind the expansion may be more appropriate to the latter. (In particular, we ignore the compression[5] of the interior density which occurs in nuclei and real metallic clusters as a result of surface tension. In other words, we study a metal with a *rigid,* uniform positive-charge background density. Because of the long range of the electrostatic interaction, the bulk compressibility of the electrons in such a metal vanishes, and so does the compressive contribution[5] to its curvature energy.)

The "nonvolume" contribution to the total energy is

$$\Delta_R=E_R[n_R,n_+]-\varepsilon\int_0^\infty dr\, 4\pi r^2 n_R(r) \ , \tag{15}$$

where $\varepsilon=\alpha/\bar{n}$ is the bulk energy per electron. The subscript R reminds us that both the energy functional E and the electron-density profile n depend upon R. Define the distance from the surface

$$z=r-R \ , \tag{16}$$

and note that

$$n_+(z)=\begin{cases}\bar{n} & (z<0)\\ 0 & (z>0),\end{cases} \tag{17}$$

$$n_R(r)=n(z)+f(z)/R+O(R^{-2}) \ , \tag{18}$$

where $n(z)$ is the electron-density profile for the planar surface of the semi-infinite ($R\rightarrow\infty$) metal. From Appendix A of Ref. 7 (or from Ref. 6),

$$\int_{-\infty}^{\infty} dz\, f(z)=\frac{1}{2\pi}\phi([n,n_+],-\infty) \ . \tag{19}$$

Here $\phi([n,n_+],z)$ is the electrostatic potential for the planar surface, with

$$\phi([n,n_+],\infty)=0 \ . \tag{20}$$

Functional Taylor expansion of Eq. (15) about the planar-surface profile, combined with the Euler equation (14), yields

$$\Delta_R=E_R[n,n_+]-\varepsilon\int_{-R}^{\infty} dz\, 4\pi(R+z)^2 n(z) +(\mu-\varepsilon)\int_{-R}^{\infty} dz\, 4\pi(R+z)^2\frac{f(z)}{R}+O(R^0) \ , \tag{21}$$

where μ is the chemical potential in the limit $R\rightarrow\infty$.

The energy functional for the sphere, evaluated for the planar-surface profile, is

$$E_R[n,n_+]=\int_{-R}^{\infty} dz\, 4\pi(R+z)^2 e_R([n,n_+],z) \ , \tag{22}$$

where the energy density must also be expanded:

$$e_R([n,n_+],z)=e([n,n_+],z)+g([n,n_+],z)/R+O(R^{-2}) \ . \qquad (23)$$

Neglecting discrete-level effects that may arise for a solid sphere but not for a spherical void, we assert that $n-n_+$, $e-\varepsilon n$, f, and g vanish rapidly away from the surface, and thus

$$\Delta_R=4\pi R^2\sigma+4\pi R\frac{\gamma}{2}+O(R^0) \ , \qquad (24)$$

where

$$\sigma=\int_{-\infty}^{\infty}dz[e([n,n_+],z)-\varepsilon n(z)] \ , \qquad (25)$$

$$\tfrac{1}{2}\gamma=\int_{-\infty}^{\infty}dz\,2z[e([n,n_+],z)-\varepsilon n(z)]+(\mu-\varepsilon)\int_{-\infty}^{\infty}dz\,f(z)+\int_{-\infty}^{\infty}dz\,g([n,n_+],z) \ . \qquad (26)$$

Equation (25) is a standard expression[3] for the surface energy, and Eq. (26) is a general expression for the curvature energy (valid for any kind of particle, so long as the bulk density is uniform). The leading term on the right of Eq. (26) is the first moment[5] of the surface contribution to the energy density. For stabilized jellium, the second term simplifies with the help of Eq. (19) and the displaced-profile expression[11] for the work function

$$W=-\mu=-\phi\ ([n,n_+],0)-\varepsilon+C[n(0)/\bar{n}-1] \ . \qquad (27)$$

We find

$$(\mu-\varepsilon)\int_{-\infty}^{\infty}dz\,f(z)=\frac{1}{2\pi}\phi([n,n_+],-\infty)\times\{\phi([n,n_+],0)+C[1-n(0)/\bar{n}]\} \ . \qquad (28)$$

In Appendix A, we show that the electrostatic contribution to the final term of Eq. (26) is

$$\int_{-\infty}^{\infty}dz\,g_{\mathrm{es}}([n,n_+],z)=-\frac{1}{8\pi}[\phi([n,n_+],-\infty)]^2 \ . \qquad (29)$$

Within the TFDGW4 approximation for stabilized jellium,

$$e([n,n_+],z)=\tfrac{3}{10}(3\pi^2)^{2/3}n^{5/3}+\frac{1}{72n}\left[\frac{dn}{dz}\right]^2+\frac{(3\pi^2)^{-2/3}}{540}n^{1/3}\left[\left[\frac{1}{n}\frac{d^2n}{dz^2}\right]^2-\frac{9}{8}\left[\frac{1}{n}\frac{d^2n}{dz^2}\right]\left[\frac{1}{n}\frac{dn}{dz}\right]^2+\frac{1}{3}\left[\frac{1}{n}\frac{dn}{dz}\right]^4\right]$$
$$+n\varepsilon_{\mathrm{xc}}(n)+\tfrac{1}{2}[n(z)-n_+(z)]\phi([n,n_+],z)+C\frac{n_+(z)}{\bar{n}}[n(z)-n_+(z)] \ , \qquad (30)$$

$$\varepsilon=\tfrac{3}{10}(3\pi^2)^{2/3}\bar{n}^{2/3}+\varepsilon_{\mathrm{xc}}(\bar{n}) \ . \qquad (31)$$

Moreover, the curvature contribution to the Laplacian

$$\nabla^2=\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}=\frac{d^2}{dz^2}+\frac{2}{R}\frac{d}{dz}+O(R^{-2}) \qquad (32)$$

in T_4 makes a second (and final) contribution to the last term of Eq. (26)

$$\int_{-\infty}^{\infty}dz\,g_4([n,n_+],z)=\int_{-\infty}^{\infty}dz\frac{(3\pi^2)^{-2/3}}{540}n^{1/3}\times\left[\frac{4}{n^2}\left[\frac{dn}{dz}\right]\left[\frac{d^2n}{dz^2}\right]-\frac{9}{4n^3}\left[\frac{dn}{dz}\right]^3\right] \ . \qquad (33)$$

Thus the TFDGW4 expression for the curvature energy is Eq. (26), supplemented by Eqs. (28), (29)–(31), and (33). When the contributions from T_4 and C are neglected (i.e., within TFDGW for jellium), our Eq. (26) reduces to Eq. (22) of Pogosov,[6] since[3]

$$\int_{-\infty}^{\infty}dz\,z[n(z)-n_+(z)]=\frac{1}{4\pi}\{-\phi([n,n_+],-\infty)\} \ . \qquad (34)$$

In principle, our expressions require the density profile $n(z)$ which solves the Euler equation (14). However, they also accept the profile which minimizes (25) over a restricted class of trial densities. While the surface energy has the obvious variational accuracy of the total energy, the variational accuracy of the work function or curvature energy is more subtle: The work function of Eq. (27) is the difference[11] (divided by Σ) between total energies per unit area for the neutral surface and the surface with infinitesimal charge Σ, while the curvature energy is essentially the difference (divided by $\mathcal{R}^{-1}$) between total energies per unit area for the flat surface and the surface with infinitesimal curvature $\mathcal{R}^{-1}$.

Unlike the surface energy σ, the curvature energy γ turns out to be about the same for stabilized jellium as for jellium. This behavior might be expected from Eq. (26), which contains two contributions proportional to C:

$$2C\int_{-\infty}^{0}dz\,z[n(z)-n_+(z)] \qquad (35)$$

and

$$\frac{C}{2\pi}\phi([n,n_+],-\infty)[1-n(0)/\bar{n}] \ . \qquad (36)$$

These direct terms would cancel exactly for an antisymmetric trial charge distribution $\{[n(-z)-n_+(-z)]=-[n(z)-n_+(z)]\}$, leaving only the indirect effect of C upon $n(z)$. With a more realistic trial density, the situation is not so simple but the conclusion remains the same. (A similar argument explains why the work function W of Eq. (27) depends only weakly upon C; the argument follows from equating (27) to the Koopmans expression $W=-\phi([n,n_+],-\infty)-\bar{\mu}-C$, and leads to the estimate $W\approx\bar{\mu}-2\varepsilon$, where $\bar{\mu}=d[\bar{n}\varepsilon(\bar{n})]/d\bar{n}$.)

III. SIMPLE ANALYTIC MODEL

For simple, quasirealistic estimates of σ and γ from Eqs. (25) and (26), we use the trial density profile of Ref. 9:

$$n(z)=\bar{n}F(\beta k_s z)\ , \tag{37}$$

where β is a variational parameter of order 1 [fixed by minimizing the surface energy (25)],

$$k_s=(4k_F/\pi)^{1/2} \tag{38}$$

is the Thomas-Fermi screening wave vector, and

$$F(y)=\begin{cases}1-0.621e^{y}+0.08576e^{2.9889y} & (y<0)\\ 0.46476e^{-0.7847y} & (y>0)\end{cases} \tag{39}$$

The corresponding electrostatic potential is

$$\phi([n,n_+],z)=-\frac{k_F^2}{3\beta^2}\Phi(\beta k_s z)\ , \tag{40}$$

where

$$\Phi(y)=\begin{cases}1.36628-0.621e^{y}+0.00956e^{2.9889y} & (y<0)\\ 0.75486e^{-0.7847y} & (y>0)\end{cases} \tag{41}$$

The density of Eq. (37) matches the Thomas-Fermi (TF) density at $y=0$ and (with $\beta=1$) $y\ll 0$. Thus Eq. (37) becomes most realistic in the high-density limit $\bar{n}\to\infty$, where TF is exact. By construction, $n(z)$ and dn/dz are continuous, and the charge neutrality condition (5) is satisfied.

TABLE I. Curvature energy γ (in units of millihartree/bohr) for jellium in the TFDGW4 approximation. Values from Eq. (26) in the simple analytic model of Eq. (37) are compared to the results of fitting $E=\alpha 4\pi R^3/3+\sigma 4\pi R^2+\gamma 2\pi R$ to the total energies for jellium spheres with radii R.

r_s	Reference 12	Reference 7	Equation (26)
2	1.84	1.64	1.77
3	0.63		0.65
4	0.22	0.26	0.30
5	0.06		0.17
6	−0.01	0.07	0.10

This simple analytic model was used in Ref. 9 to estimate the surface energy σ and work function W for jellium and stabilized jellium. We apply it here to investigate some general features of the curvature energy γ for jellium (deferring more refined calculations to Secs. IV and VI).

Table I compares Eq. (26) for the curvature energy against fits of the liquid-drop expansion (1) to the total energies of neutral jellium spheres containing up to 10^6 electrons, all within TFDGW4. Seidl, Spina, and Brack[12] performed restricted variational calculations for the spheres, while Engel and Perdew[7] solved the Euler equation (14) numerically. The close agreement of the present results with the fits of Refs. 7 and 12 at high densities should be noticed. The agreement with the Engel-Perdew[7] fit would presumably be even closer if the density profile from Eq. (37) were replaced by that which solves the Euler equation for the planar surface. The origin of the negative curvature energy for $r_s=6$ in Ref. 12 is unknown.

Table II decomposes the TFDGW4 curvature energy of Eq. (26) into contributions of different physical origin. The individual components are large and tend to cancel one another, with no single component either dominant or negligible.

TABLE II. Components (in mhartrees/bohr) of the TFDGW4 curvature energy γ for jellium, evaluated from Eq. (26) in the simple analytic model of Eq. (37). "Moment" refers to the first moment of the surface energy density, i.e., the leading term of Eq. (26). For a critique of this decomposition, see Appendix B. The densities considered are those of Al ($r_s=2.07$), Na ($r_s=3.99$), and Cs ($r_s=5.63$).

		$r_s=2.07$ ($\beta=1.31$)	$r_s=3.99$ ($\beta=1.49$)	$r_s=5.63$ ($\beta=1.51$)
Kinetic	Moment	−2.33	0.02	0.05
	Eq. (33)	−0.40	−0.14	−0.07
	Total	−2.73	−0.12	−0.02
Exchange-Correlation	Moment X	2.86	0.31	0.11
	Moment C	0.44	0.07	0.03
	Total	3.30	0.38	0.14
Electrostatic	Moment	−3.93	−0.17	−0.04
	Eq. (28)	9.15	0.40	0.10
	Eq. (29)	−4.14	−0.18	−0.04
	Total	1.08	0.05	0.02
Total		1.65	0.31	0.14

Table III displays the curvature energy of jellium within the various density-functional approximations (TF, TFDGW, and TFDGW4) described at the end of Sec. I. The TF curvature energy is negative, and scales like r_s^{-4}. For comparison, the TF surface energy[13] is also negative, and scales like $r_s^{-9/2}$. These facts, together with Eq. (1), show that the TF metal is unstable against evaporation. The curvature energy is systematically increased by inclusion of $E_{\mathrm{xc}}+T_2$(TFDGW) and T_4(TFDGW4). The TFDGW values have also been reported by Iakubov *et al.*[14] We will argue in Sec. VI that the TFDGW4 values are essentially correct.

Table IV compares the TFDGW4 surface properties of jellium with those of stabilized jellium. Besides the surface energy σ and curvature energy γ, we also display the work function W of Eq. (27) and the surface dipole moment

$$D=-\phi([n,n_+],-\infty)=4\pi\int_{-\infty}^{\infty} dz\, z\,[n(z)-n_+(z)]\ . \quad (42)$$

Although the correction to jellium has a substantial effect on σ and D, it has only a weak effect on W and γ, as explained at the end of Sec. II.

IV. KOHN-SHAM SURFACE ENERGY AND WORK FUNCTION

In Kohn-Sham theory,[4] the gradient expansion (10) is replaced by the exact noninteracting kinetic energy (8), and the Euler equation (14) is replaced by a self-consistent one-electron Schrödinger equation for the orbitals $\psi_i(\mathbf{r})$. Only the exchange-correlation energy is approximated, as in Eq. (7). Lang and Kohn[3] solved the Kohn-Sham problem for the electron density, surface energy, and work function of jellium. Monnier and Perdew[15] solved the Kohn-Sham problem for the jellium surface with external potential $\tilde{C}n_+(z)/\bar{n}$, where $\tilde{C}$ was a variational parameter adjusted to minimize the surface energy of a crystalline metal. Thus the Monnier-Perdew computer code is well suited for both jellium ($\tilde{C}=0$) and stabilized jellium ($\tilde{C}=C$), and we have employed an enhanced version[16] of this code in our present calculations.

TABLE III. Curvature energies γ (in mhartrees/bohr) of jellium, evaluated from Eq. (26) in the simple analytic model of Eq. (37), within various density-functional approximation described at the end of Sec. I. [The curvature energies in Table 2 of Ref. 14 are incorrect. We have computed the correct values from Eq. (13) and Table 1 of Ref. 14. Note that the last column of Table 1 should be labeled $C_g^j\times 10^3$, and that the first term on the right of Eq. (13) should be $C_q^j n_+^2 b^{-3}$.]

	$r_s=2.07$	$r_s=3.99$	$r_s=5.63$
TF	-2.35	-0.17	-0.04
TFDGW (Ref. 14)		0.20	0.07
TFDGW	1.48	0.20	0.06
TFDGW4	1.65	0.31	0.14

Deferring the curvature energy γ to Sec. VI, the other properties are straightforwardly evaluated, with the results displayed in Table IV. These results from Kohn-Sham theory may be compared with those of Table IV from the cruder TFDGW4 approximation, which is seen to work reasonably well apart from its overestimation of the surface dipole moments of the low-density metals (for which the Kohn-Sham density exhibits strong Friedel oscillations[3]). Table V compares the exact kinetic-energy component of the Kohn-Sham surface energy against the gradient expansion applied to the Kohn-Sham density profile, and shows the improvement coming from T_4. A similar comparison (but for non-self-consistent densities) was made by Ma and Sahni.[17]

Table VI compares our Kohn-Sham surface energies and work functions for jellium and stabilized jellium against experimental values[18,19] for simple metals. Especially for the high-density metals, the stabilized-jellium model gives a significantly more realistic account of both properties than does the jellium model. For Al, there is perfect agreement between theory and experiment. However, this perfect agreement may be accidental, since the stabilized-jellium model neglects band-structure effects which can contribute to surface properties. Moreover, the local-density approximation is not exact.

TABLE IV. Surface energy σ, work function W, surface dipole moment D, and curvature energy γ (1 hartree/bohr$^2=1.5569\times10^6$ erg/cm^2; 1 hartree$=27.21$ eV). TFDGW4 results within the simple analytic model of Eq. (37) are compared with Kohn-Sham (KS) results, for jellium and stabilized jellium.

	$r_s=2.07$		$r_s=3.99$		$r_s=5.63$	
	TFDGW4	KS	TFDGW4	KS	TFDGW4	KS
Jellium						
σ (erg/cm^2)	-642	-605	156	164	71	71
W (eV)	3.62	3.74	2.81	2.91	2.33	2.35
D (eV)	6.21	6.06	1.29	0.88	0.63	0.13
γ (mhartrees/bohr)	1.65	1.77	0.31	0.36	0.14	0.13
Stabilized						
σ (erg/cm^2)	801	953	163	171	59	60
W (eV)	3.83	4.24	2.83	2.92	2.24	2.24
D (eV)	4.16	4.02	1.26	0.84	0.69	0.27
γ (mhartrees/bohr)	1.42	1.82	0.30	0.35	0.13	0.13

TABLE V. Test of the gradient expansion (10) applied to the self-consistent Kohn-Sham density profile of jellium. σ_s is the exact kinetic-energy component of the Kohn-Sham surface energy (erg/cm^2).

	$r_s=2.07$	$r_s=3.99$	$r_s=5.63$
σ_0	-5195	-218	-37
$\sigma_0+\sigma_2$	-4766	-173	-23
$\sigma_0+\sigma_2+\sigma_4$	-4699	-158	-17
σ_s	-4644	-140	-10

V. KOHN-SHAM CURVATURE ENERGY FROM FITS TO THE TOTAL ENERGY

Before we discuss the Kohn-Sham calculation of the curvature energy γ from Eq. (26) (Sec. VI), we pause to extract γ for jellium from fits to Kohn-Sham total energies. The results will serve as a standard of comparison in Sec. VI. More importantly, they will expose the validity, but also the limitations, of the liquid-drop expansion (1).

Perdew *et al.*[2,7] proposed that γ could be extracted from the formation energy Δ_R of a spherical void of radius R, which Eq. (1) predicts to be

$$\sigma 4\pi R^2-\gamma 2\pi R \ . \tag{43}$$

Manninen and Nieminen[20] have calculated this energy for jellium, and reported the results as a graph of $\sigma_R=\Delta_R/4\pi R^2$. From (43), the quantity

$$\gamma_R=2R(\sigma-\sigma_R) \tag{44}$$

should be independent of R. We test this prediction in Table VII, using values of σ_R and N provided by Manninen. Here N is the number of "atoms" removed to create the void, i.e., $R=(Nz)^{1/3}r_s$, where z is the valence. Table VII provides a striking confirmation of the accuracy of the liquid-drop expansion (1) for even the smallest physical voids (monovacancies with $N=1$). Indeed, for $N\geq 1$ the values of γ_R from Eq. (44) are very close to the $R\to\infty$ predictions of Eq. (26), as displayed in Table IV.

In the jellium model, of course, a void can have any radius R. For $r_s=2.07$, Manninen and Nieminen[20] also considered the subatomic radius $R=1.30$ (Table VII). Their energies for this bulk density can be represented by the Padé form

$$\sigma_R=\sigma\frac{1+\left[-\dfrac{\gamma}{2\sigma}-1.068\right]R^{-1}}{1-1.068R^{-1}+1.931R^{-2}} \ , \tag{45}$$

which has the shape of Fig. 5 of Ref. 20 and effectively sums the leptodermous expansion to all orders in R^{-1}. (That $\sigma_R\sim R$ as $R\to 0$ follows from a theorem of Lehmann and Ziesche.[21]) From (45), the first correction to the right-hand side of the leptodermous expansion (1) for $r_s=2.07$ jellium is the constant -3.5 mhartrees, but adding just this term actually worsens the resulting estimate of the monovacancy formation energy.

For a *solid* sphere of jellium, the total energy E_R from Eq. (1) is

$$\alpha\frac{4\pi}{3}R^3+\sigma 4\pi R^2+\gamma 2\pi R \ . \tag{46}$$

Thus, a plot of $(E_R-\alpha 4\pi R^3/3)/R$ versus R should yield a straight line

$$\sigma 4\pi R+\gamma 2\pi \ , \tag{47}$$

with slope $4\pi\sigma$ and intercept $2\pi\gamma$. (More precisely, one uses the straight-line extrapolation of the large-R asymptote.) This analysis has been applied to the Kohn-Sham energies of jellium spheres by Utreras-Díaz and Shore,[22]

TABLE VI. Intrinsic surface energy σ and work function W for simple metals. The jellium (J) and stabilized-jellium (SJ) values computed in Kohn-Sham theory are compared to experimental values (expt.). The experimental value for the intrinsic surface energy σ is the zero-temperature extrapolation of the liquid-metal surface tension (Ref. 18), divided by the corrugation factor 1.2 (Ref. 2). The experimental work function is the polycrystalline value (Ref. 19).

		σ (erg/cm^2)			W (eV)		
Metal	r_s	J	SJ	expt.	J	SJ	expt.
H	1.58	-5161	1186		3.77	4.41	
Al	2.07	-605	953	953	3.74	4.24	4.28
Zn	2.30	-103	741	828	3.62	4.02	4.33
Mg	2.65	168	536	654	3.46	3.77	3.66
Li	3.28	220	303	435	3.21	3.33	2.9
Sr	3.57	199	238	349	3.08	3.09	2.59
Ba	3.71	188	211	317	3.02	3.01	2.7
Na	3.99	164	171	218	2.91	2.92	2.75
K	4.96	100	89	121	2.53	2.49	2.30
Rb	5.23	87	75	98	2.45	2.40	2.16
Cs	5.63	71	60	79	2.35	2.24	2.14

TABLE VII. Curvature energy γ for jellium, extracted from Kohn-Sham void formation energies (Ref. 20). See the discussion around Eq. (44). Here σ_R and $\sigma=\sigma_\infty$ are from the calculation of Ref. 20.

	N	$R=(Nz)^{1/3}r_s$ (bohr)	$\sigma_R\equiv\Delta_R/4\pi R^2$ (erg/cm^2)	$\gamma_R\equiv 2R(\sigma-\sigma_R)$ (mhartrees/bohr)
	0.083	1.30	-860	0.56
$r_s=2.07$	1	2.99	-920	1.52
$z=3$	4	4.74	-805	1.70
$\sigma=-525$ erg/cm^2	6	5.43	-770	1.71
	13	7.02	-730	1.85
	19	7.97	-695	1.74
	38	10.04	-660	1.74
$r_s=3.93$	1	3.93	98	0.42
$z=1$	9	8.17	142	0.41
$\sigma=181$ erg/cm^2	15	9.69	150	0.39
	27	11.79	155	0.39

who found an oscillatory correction to Eq. (47)—presumably a shell-structure effect due to the high degeneracy of the one-electron levels in a spherical potential. If this oscillatory correction survives undamped in the limit $R\to\infty$, then there is a breakdown of the leptodermous expansion in the Kohn-Sham description of solid spheres. Stocker and Farine[23] have suggested that such a breakdown could arise from a failure of Eq. (18) due to oscillations of amplitude $\sim R^{-1}$ in the density $n_R(r)$ near the center of the sphere.[24]

Because of the oscillation, Utreras-Díaz and Shore could obtain only a rough estimate of the curvature energy for jellium ($\gamma\approx 5.1$ mhartrees/bohr at $r_s=2.07$, and 0.66 mhartrees/bohr at $r_s=3.99$). They also studied "pseudojellium," a semiempirical relative of our stabilized-jellium model, and found curvature energies close to those they found for jellium.

VI. CURVATURE ENERGY FROM THE KOHN-SHAM DENSITY PROFILE

Within the Kohn-Sham method of Eqs. (8) and (9), there is no obvious way to determine the kinetic-energy contribution to the function $g([n,n_+],z)$ of Eqs. (23) and (26). Following a suggestion of Stocker and Farine,[23] we tried to evaluate Eq. (26) by dropping g and using Eq. (8) for the kinetic-energy density; this ansatz gave a curvature energy that was an order of magnitude too big. Thus, to calculate the curvature energy γ from Eq. (26), we apply the fourth-order gradient expansion of Eq. (10) to the Kohn-Sham density. We expect this hybrid approach to be adequate for γ, as it would be for the surface energy σ, because the kinetic-energy component of either is most important in the high-density metals, for which the relative error of the gradient expansion is smallest. Tables II, IV, and V support this argument. *A posteriori,* the hybrid approach is justified by the close agreement between its "Kohn-Sham" curvature energies for jellium (Table IV) and the true Kohn-Sham values from void formation energies (Table VII).

The main qualitative difference between the Kohn-Sham and TFDGW4 planar-surface density profiles is the Friedel oscillation[3] of the Kohn-Sham density: As $z\to-\infty$,

$$n(z)\to\bar{n}[1+3\cos(2k_Fz-\delta_F)/(2k_Fz)^2+0(z^{-3})]\ , \tag{48}$$

where δ_F is a phase shift. This oscillation does not invalidate the leptodermous derivation of Eqs. (25) and (26), nor does it create any special difficulty for the evaluation of the required integrals. In our calculations, we evaluate the integrals numerically for $z>z_c\approx-3(2\pi/k_F)$, and analytically for $z<z_c$. For example,

$$\int_{-\infty}^{z_c} dz\, 2z\{e([n,n_+],z)-\varepsilon n(z)\}$$
$$\approx(\bar{\mu}-\varepsilon)\int_{-\infty}^{z_c} dz\,(2z)3\bar{n}\cos(2k_Fz-\delta_F)/(2k_Fz)^2\ , \tag{49}$$

where $\bar{\mu}=d[\bar{n}\varepsilon(\bar{n})]/d\bar{n}$. The contributions from $z<z_c$ are found to be small.

In Table VIII, we compare our calculated curvature energies γ against phenomenological values.[2] The latter have been extracted from measured monovacancy formation energies ε_{vac} and surface energies σ, using Eq. (43):

$$\varepsilon_{\text{vac}}=\sigma 4\pi(z^{1/3}r_s)^2-\gamma 2\pi(z^{1/3}r_s)\ . \tag{50}$$

As we have shown in Table VII, Eq. (50) can be highly

TABLE VIII. Curvature energies γ for simple metals. The jellium (J) and stabilized-jellium (SJ) values computed from the Kohn-Sham density via Eq. (26) are compared to phenomenological values (expt.) from vacancy-formation energies (Ref. 2).

		γ (mhartrees/bohr)		
Metal	r_s	J	SJ	expt.
H	1.58	2.6	3.2	
Al	2.07	1.8	1.8	2.3
Zn	2.30	1.4	1.4	2.0
Mg	2.65	1.0	1.0	1.2
Li	3.28	0.6	0.6	1.2
Na	3.99	0.4	0.4	0.5
K	4.96	0.2	0.2	0.3
Rb	5.23	0.1	0.1	0.3
Cs	5.63	0.1	0.1	0.3

accurate. In comparison with the phenomenological values, the calculated curvature energies are somewhat too low. There is essentially no difference between the values calculated for jellium and for stabilized jellium.

Rose, Vary, and Smith[25] have proposed a scaling relation $\gamma/\sigma r_s \approx 1.7$ for stable systems, but our results for stabilized jellium in the metallic range $2 \le r_s \le 6$ can be fitted by

$$\frac{\gamma}{\sigma r_s} \approx 2.7 r_s^{-7/8} . \tag{51}$$

An otherwise stable metal will also be stable against vacancy formation, provided that Eq. (50) is positive, i.e.,

$$\frac{\gamma}{\sigma r_s} < 2z^{1/3} . \tag{52}$$

This condition is satisfied by the stabilized-jellium model for all the metals in Tables VI and VIII except monatomic hydrogen, which is in fact unstable against dimerization.

VII. CONCLUSIONS

The liquid-drop expansion (1) gives a remarkably accurate account of metallic total energies, even when the surface is structured on the atomic scale. This suggestion from Refs. 2 and 7 is dramatically confirmed by Table VII for the case of microscopic voids in jellium.

We have derived an expression for the metallic curvature energy [Eq. (26)] in terms of the electron-density profile for the planar surface, and shown that the resulting values agree with fits of Eq. (1) to calculated or measured total energies. We find that the curvature energy is determined largely by the bulk density $\bar{n}$. It is nearly the same (Table IV) for restricted trial density profiles as for self-consistent Kohn-Sham densities, nearly the same within the Thomas-Fermi-Dirac-Gombas-Weizsäcker-4 approximation as within Kohn-Sham theory, and nearly the same for jellium as for stabilized jellium.

We have also reported self-consistent Kohn-Sham results (Table VI) for the surface energy and work function of jellium and of stabilized jellium. We find that the stabilized-jellium model gives a reasonable description of simple metals over the full range of bulk densities $\bar{n}$, and is significantly more realistic than jellium for the high-density metals.

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APPENDIX A: DERIVATION OF EQ. (29)

As show in Appendix A of Ref. 7, the electrostatic potential for the neutral sphere of radius R is

$$\phi_R([n_R,n_+],z)=\phi([n,n_+],z)+h(z)/R+O(R^{-2}) , \tag{A1}$$

where

$$h(z)=-\int_{-\infty}^{z} dz_1 \int_{-\infty}^{z_1} dz_2 \left(2\frac{d\phi}{dz_2}([n,n_+],z_2) + 4\pi f(z_2) \right) + h(-\infty) \tag{A2}$$

and $f(z)$ is defined by the expansion (18). By Eq. (19), $h(z)$ tends to a constant limit as $z \to +\infty$; $h(-\infty)$ is chosen to make this constant equal to zero.

But the expansion (23) requires the electrostatic potential of a *charged* sphere of radius R, in which the density profile is that of the planar surface:

$$\phi_R([n,n_+],z)=\phi([n,n_+],z)+\tilde{h}(z)/R+O(R^{-2}) . \tag{A3}$$

Aside from an irrelevant additive constant, $\tilde{h}$ is just the first term of (A2):

$$\tilde{h}(z)=-2\int_{-\infty}^{z} dz_1 \{\phi([n,n_+],z_1)-\phi([n,n_+],-\infty)\} . \tag{A4}$$

Note that $\tilde{h}$ decreases linearly with z as $z \to +\infty$, as befits the electrostatic potential outside a charged planar surface.

Now the electrostatic contribution to Eq. (23) gives

$$g_{\text{es}}([n,n_+],z)=\tfrac{1}{2}[n(z)-n_+(z)]\tilde{h}(z) . \tag{A5}$$

Finally, we integrate by parts:

$$\begin{aligned}\int_{-\infty}^{\infty} dz\, g_{\text{es}}([n,n_+],z) &= -\int_{-\infty}^{\infty} dz\,[n(z)-n_+(z)]\int_{-\infty}^{z} dz'\{\phi([n,n_+],z')-\phi([n,n_+],-\infty)\} \\ &= \int_{-\infty}^{\infty} dz\{\phi([n,n_+],z)-\phi([n,n_+],-\infty)\}\int_{-\infty}^{z} dz'[n(z')-n_+(z')] \\ &= \int_{-\infty}^{\infty} dz\{\phi([n,n_+],z)-\phi([n,n_+],-\infty)\}\left(-\frac{1}{4\pi}\right)\frac{d}{dz}\{\phi([n,n_+],z)-\phi([n,n_+],-\infty)\} ,\end{aligned} \tag{A6}$$

where the last step follows from Gauss's law for the planar surface. Evaluation of the integral (A6) [with application of Eq. (20)] yields Eq. (29).

APPENDIX B: COMPONENTS OF THE CURVATURE ENERGY

All terms of the surface energy (25), and most terms of the curvature energy (26), have a transparent physical origin, but the contribution from Eq. (28) is an exception. For convenience in Table II, we have assigned the first term of Eq. (28) to the electrostatic energy, and the second to the pseudopotential energy. But in fact Eq. (28) contributes to other components of the curvature energy. For example, its contribution to the kinetic-energy component of $\gamma/2$ is

$$\int_{-\infty}^{\infty} dz[\delta T_s/\delta n(z)-\tfrac{3}{10}(3\pi^2)^{2/3}\bar{n}^{2/3}]f(z) \ . \tag{B1}$$

Only when $f(z)$ of Eq. (18) assumes (or is constrained to) the displaced-profile[11] form

$$f^{\mathrm{DP}}(z)=-\frac{\phi([n,n_+],-\infty)}{2\pi\bar{n}}\left[\frac{dn(z)}{dz}\right] \tag{B2}$$

is our decomposition of Table II fully correct. Under this assumption, terms like (B1) vanish.

The components of the curvature energy shown in Table II are less meaningful than the total. They are also more sensitive to the density profile and to the difference between jellium and stabilized jellium.

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