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Theory of metallic clusters: Asymptotic size dependence of electronic properties

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For a spherical metallic cluster of large radius R, the total energy is $E=\alpha 4\pi R^3/3+\sigma 4\pi R^2+\gamma 2\pi R$, the chemical potential is $\mu=-W-c/R$, and the first ionization energy I and electron affinity A are $-\mu\pm 1/2(R+d)$. By solving the Euler equation within the Thomas-Fermi-Dirac-Gombas-Weizsäcker-4 approximation for jellium spheres with up to 10^6 electrons, we extract the surface energy σ, curvature energy γ, work function W, and constants c and d. The constant c is not zero, but neither is it $-\frac{1}{8}$, the prediction of the image-potential argument. We trace c to the second- and fourth-order density-gradient terms in the kinetic energy, which are present even in systems with no image potential. However, the constant d is found to be the distance from a planar surface to its image plane. In the absence of shell-structure oscillations, the asymptotic forms hold accurately even for very small clusters; this fact suggests a way to extract the curvature energy of a real metal from its surface and monovacancy-formation energies. We also discuss asymptotic R^{-1} corrections to the electron density profile and electrostatic potential of a planar surface.

I. INTRODUCTION AND SUMMARY

As a spherical metallic cluster grows, its properties evolve from those of a single atom to those of a bulk metal.[1,2] At first, the electronic properties oscillate with growing cluster radius R, reflecting the shell-structure of a finite system (Fig. 1). For large R, the valence-electron energy levels approach a continuum limit and the total energy E takes the asymptotic form

$$E=\alpha\frac{4\pi}{3}R^3+\sigma 4\pi R^2+\gamma 2\pi R\ , \tag{1}$$

where α, σ, and γ are the volume, surface, and curvature energies, respectively. The chemical potential $\mu=\partial E/\partial N$ becomes, to order R^{-1},

$$-\mu=W+c/R\ , \tag{2}$$

where W is the bulk work function. Since all the excess charge in a metal at equilibrium resides on the surface, the change in the electron number is $dN=-4\pi R^2 d\Sigma$, where Σ is the surface charge density. Thus

$$W=\frac{\partial\sigma}{\partial\Sigma} \tag{3}$$

$$c=\tfrac{1}{2}\frac{\partial\gamma}{\partial\Sigma}\ , \tag{4}$$

where Eq. (3) is well known.[3] To order R^{-2}, the first ionization energy I and electron affinity A approach[4,5]

$$I=-\mu+1/2(R+d)\ , \tag{5}$$

$$A=-\mu-1/2(R+d)\ , \tag{6}$$

where d is a microscopic distance. Thus,[5] to order R^{-1},

$$I=W+(\tfrac{1}{2}+c)/R\ , \tag{7}$$

$$A=W+(-\tfrac{1}{2}+c)/R\ . \tag{8}$$

The principal aim of the present study is to understand and evaluate the constant c in Eqs. (2), (7), and (8). Wood's image-potential argument[6-8] predicts $c=-\frac{1}{8}$, a value that seems to be confirmed by the recent photoemission study of Müller, Schmidt-Ott, and Burtscher.[9] This study of large clusters containing 5000–40 000 Ag atoms finds $c=-0.12\pm 0.06$, where the uncertainty arises from calibration of the cluster radius. However, the image-potential argument has been challenged by Makov, Nitzan, and Brus[10] and by Perdew,[4,5] who independently suggested that c might be zero. Here we will show that c is *not* zero, but neither is it exactly $-\frac{1}{8}$. Nonzero c arises from nonlocal (density-gradient) corrections[11] to the Thomas-Fermi *kinetic* energy, and thus is expected even in systems with no image potential (e.g., nonmetallic liquids or nuclei).

The outline of the paper is as follows. Section II reviews the shell-structure oscillation of I and A, and the derivation[4,5] of the asymptotic forms (5) and (6). Section III introduces the jellium model of a metallic cluster.[1,2,12] In order to suppress the strong shell-structure oscillation[12] of this model (which is much stronger than that of real metals), we make the Thomas-Fermi-Dirac-Gombas-Weizsäcker-4 (TFDGW4) approximation for the energy as a functional of the electron density. And in order to avoid possible artifacts of a restricted variational calculation or a limited data set, we numerically solve the TFDGW4 Euler equation for jellium spheres containing as many as 10^6 electrons. To our knowledge, this is the first study of asymptotic size dependence not hampered

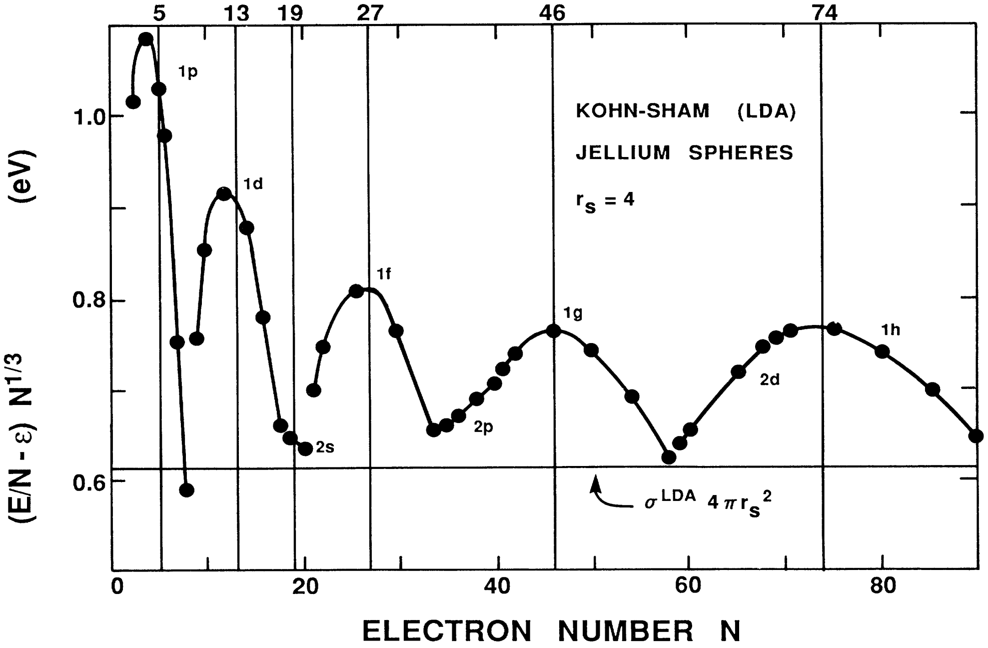

FIG. 1. Size dependence of the total energy E of a neutral jellium sphere with density parameter $r_s=4$. ε is the energy per electron in the bulk. The horizontal line is the $N\rightarrow\infty$ asymptote of the plotted quantity, which displays cusps at shell-closing numbers. Vertical lines indicate the half-filled shells, treating shells separated by small energy gaps as a single shell. [Data from the spin-unpolarized Kohn-Sham calculation of W. Ekardt (Ref. 1), who employed the local-density approximation with the Gunnarsson-Lundqvist correlation.]

by restrictions on the size of the system or the form of the solution.

Section IV presents our results for σ, γ, W, c, and d (which turns out to be the distance x_0 from the jellium edge to the centroid of excess charge at a planar surface, as suggested in Ref. 4). We confirm the asymptotic forms (1), (2), and (5), and find that they hold with remarkable accuracy even for the smallest metallic clusters. This result suggests a way to extract the unknown curvature energies of real metals from measured surface energies and monovacancy formation[13] energies. Finally, Sec. V identifies explicit curvature contributions to the kinetic-energy component of the chemical potential, which seem to make a dominant contribution to c of Eq. (2). The Appendix discusses the asymptotic R^{-1} corrections to the electron density profile and electrostatic potential of a planar surface. Our numerical method for the solution of the Euler equation is essentially that of Engel and Dreizler.[14]

Concurrently with our work, Spina, Seidl, and Brack[15] have made three-parameter variational calculations for large jellium spheres in the TFDGW4 approximation.[16] They find that asymptotically, with an error less than 1%,

$$I-A=1/R\ , \tag{9}$$

as implied by Eqs. (7) and (8).

In this paper, all equations are expressed in atomic units ($\hbar=e^2=m=1$). The unit of energy is 1 hartree$=27.21$ eV$=4.360\times10^{-11}$ erg, and the unit of distance is 1 bohr$=0.5292\times10^{-8}$ cm.

II. DERIVATION OF THE SIZE DEPENDENCE OF THE IONIZATION ENERGY AND ELECTRON AFFINITY

Consider a metal with bulk valence electron density

$$\bar{n}=3/4\pi r_s^3\ , \tag{10}$$

where r_s is the Wigner-Seitz radius or density parameter. A spherical cluster which contains N^* valence electrons at neutrality has a Gibbs surface of radius

$$R=r_s(N^*)^{1/3}\ . \tag{11}$$

The problem is to determine how the energy E of such a cluster, with $N^*+\Delta$ valence electrons, depends upon the excess electron number Δ. Crucial to the derivation is electronic relaxation, which places the excess charge on the surface.

Consider the Taylor expansion

$$E_\Delta=E_0+\Delta\left.\frac{\partial E}{\partial N}\right|_{N^*}+\frac{1}{2}\Delta^2\left.\frac{\partial^2 E}{\partial N^2}\right|_{N^*}+\cdots\ . \tag{12}$$

We shall work within the density-functional theory of Hohenberg, Kohn, and Sham.[17,18] The first derivative in Eq. (12) equals[19] $\varepsilon^{\mathrm{HO}}$ for $\Delta<0$, and $\varepsilon^{\mathrm{LU}}$ for $\Delta>0$, where $\varepsilon^{\mathrm{HO}}$ and $\varepsilon^{\mathrm{LU}}$ are the highest-occupied and lowest unoccupied Kohn-Sham orbital energies of the neutral cluster.

The exchange-correlation energy will be represented by a continuum approximation, such as the local-density approximation[18]

$$E_{\mathrm{XC}}[n]=\int d^3r\, n\varepsilon_{\mathrm{XC}}(n)\ , \tag{13}$$

where $\varepsilon_{\mathrm{XC}}(n)$ is the exchange-correlation energy per particle of an electron gas of uniform density n. This approximation usually gives a good account of ionization energies ($\Delta=-1$) and electron affinities ($\Delta=+1$). It fails to reproduce the behavior of the exact density-functional E_Δ for fractional Δ,[20] but that is of no concern here as we shall ultimately set $\Delta=\pm 1$. Within any continuum approximation for $E_{\mathrm{XC}}[n]$, the second derivative in Eq. (12) is dominated[4] by the electrostatic energy:

$$\left.\frac{\partial^2 E}{\partial N^2}\right|_{N^*}=\frac{1}{R+d}\ . \tag{14}$$

If the only contribution to Eq. (14) were electrostatic, and if all the infinitesimal excess charge on the particle were located at its radial centroid just outside the Gibbs surface, then $R+d$ would equal that radial centroid.[4] In fact, the distribution of excess charge has a finite width; moreover, the kinetic and exchange-correlation energies can contribute to order R^{-2}. These effects could "renormalize" the value of the microscopic distance d in Eq. (14). The first omitted term in Eq. (12) is of order Δ^3/R^4, and may be neglected.

The ionization energy I and electron affinity A are now, from Eq. (12) (Ref. 5)

$$I=E_{-1}-E_0=-\varepsilon^{\mathrm{HO}}+1/2(R+d)\ , \tag{15}$$

$$A=E_0-E_1=-\varepsilon^{\mathrm{LU}}-1/2(R+d)\ . \tag{16}$$

Note that the shell-structure oscillations in I and A are embedded in the Kohn-Sham orbital energies. Equations (15) and (16) have been tested[5] against self-consistent Kohn-Sham calculations[1,2] for jellium spheres, and thus confirmed.

In a *roughly* spherical cluster of large volume $4\pi R^3/3$, the energy difference between adjacent valence-band levels (and hence the amplitude of the shell-structure oscillations) varies as R^{-3}. Thus, to order R^{-2}, $\varepsilon^{\mathrm{HO}}$ and $\varepsilon^{\mathrm{LU}}$ in Eqs. (15) and (16) may be replaced by the single quantity μ, the chemical potential or Fermi level. This completes the derivation of Eqs. (5) and (6).

Kohn-Sham calculations[1,2] have been reported for jellium spheres containing up to about 10^2 electrons. The shell-structure oscillations of the ionization energy (see Fig. 4 of Ref. 5) are still substantial for $N^*=10^2$, so no conclusion can be drawn from them about the asymptotic size dependence of the chemical potential. For this purpose, we need a *continuum* approximation for the kinetic energy as a functional of the electron density, such as the density-gradient expansion described in Sec. II. Continuum approximations for the kinetic and exchange-correlation energies (but not necessarily the particular ones we shall use here) are justified asymptotically by the argument of the previous paragraph.

III. MODEL PROBLEM: JELLIUM SPHERES IN THE TFDGW4 APPROXIMATION

In the jellium model[1,2,12] of a spherical metallic cluster, the positive charge on the ions is smeared into a positive background of density

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

The valence electrons are then added to neutralize the cluster.

As a functional of the electron density $n(\mathbf{r})$, the total energy of the cluster is

$$E[n,n_+]=E_{\mathrm{es}}[n,n_+]+E_{\mathrm{XC}}[n]+T_s[n]\ . \tag{18}$$

The electrostatic energy is

$$E_{\mathrm{es}}[n,n_+]=\tfrac{1}{2}\int d^3r\,\phi([n,n_+];\mathbf{r})[n(\mathbf{r})-n_+(\mathbf{r})]\ , \tag{19}$$

where

$$\phi([n,n_+];\mathbf{r})=\int d^3r'[n(\mathbf{r}')-n_+(\mathbf{r}')]/|\mathbf{r}'-\mathbf{r}| \tag{20}$$

is the electrostatic potential. The exchange-correlation energy $E_{\mathrm{XC}}[n]$ is represented by the local-density approximation of Eq. (13), using accurate electron-gas input.[21]

The noninteracting kinetic energy $T_s[n]$ can be constructed exactly from Kohn-Sham orbitals, but we choose instead to use the density-gradient expansion truncated at fourth order:[11]

$$T_s[n]=T_0[n]+T_2[n]+T_4[n]\ , \tag{21}$$

$$T_0[n]=\tfrac{3}{10}(3\pi^2)^{2/3}\int d^3r\, n^{5/3}\ , \tag{22}$$

$$T_2[n]=\tfrac{1}{72}\int d^3r\frac{|\nabla n|^2}{n}\ , \tag{23}$$

$$T_4[n]=\frac{(3\pi^2)^{-2/3}}{540}\int d^3r\, n^{1/3}\left[\left(\frac{\nabla^2 n}{n}\right)^2-\frac{9}{8}\left(\frac{\nabla^2 n}{n}\right)\left|\frac{\nabla n}{n}\right|^2+\frac{1}{3}\left|\frac{\nabla n}{n}\right|^4\right]\ . \tag{24}$$

The optimum density $n(\mathbf{r})$ minimizes $E[n,n_+]$ subject to the constraint

$$\int d^3r\, n(\mathbf{r})=N\ . \tag{25}$$

It is found by solving the Euler equation

$$\frac{\delta E}{\delta n(\mathbf{r})}=\mu\ . \tag{26}$$

The required functional derivatives are

$$\frac{\delta E_{\mathrm{es}}}{\delta n(\mathbf{r})}=\phi([n,n_+];\mathbf{r}) , \tag{27}$$

$$\frac{\delta E_{\mathrm{XC}}}{\delta n(\mathbf{r})}=\frac{\partial}{\partial n}\left[n\varepsilon_{\mathrm{XC}}(n)\right] , \tag{28}$$

$$\frac{\delta T_0}{\delta n(\mathbf{r})}=\tfrac{1}{2}(3\pi^2)^{2/3}n^{2/3} , \tag{29}$$

$$\frac{\delta T_2}{\delta n(\mathbf{r})}=\frac{1}{72}\left[\frac{|\nabla n|^2}{n^2}-2\frac{\nabla^2 n}{n}\right] , \tag{30}$$

$$\frac{\delta T_4}{\delta n(\mathbf{r})}=\frac{(3\pi^2)^{-2/3}}{540}n^{-2/3}\left[2\frac{(\nabla^2)^2 n}{n}-\frac{53}{12}\frac{\nabla n\cdot\nabla\nabla^2 n}{n^2}-\frac{11}{4}\frac{(\nabla^2 n)^2}{n^2}-\frac{9}{8}\frac{\nabla^2|\nabla n|^2}{n^2}+\frac{68}{9}\frac{(\nabla^2 n)|\nabla n|^2}{n^3}\right.$$
$$\left.+\frac{14}{3}\frac{\nabla n\cdot\nabla|\nabla n|^2}{n^3}-\frac{22}{3}\frac{|\nabla n|^4}{n^4}\right] . \tag{31}$$

Equations (18)–(24) define the TFDGW4 approximation. Related approximations are generated by neglecting T_4 (TFDGW2), T_4 and T_2 (TFDG), or T_4, T_2, and E_{XC} (TF).

Within the TF approximation, all neutral systems have the same chemical potential, $\mu=0$, so the constant c of Eq. (2) is zero. Similarly, within the TFDG approximation, all neutral clusters with $r_s<4.2$ have the same chemical potential,[22,23] $\mu=-0.0775$ hartree, and again $c=0$. It is the gradient terms T_2 and T_4 which make $c\neq0$ in the TFDGW4 approximation.

There have been several TFDGW2 restricted variational calculations for jellium spheres with $N^*\leq10^4$. While Snider and Sorbello[24] find $c\approx-0.07$ at $r_s=4$, Makov *et al.*[10] seem to suggest that their own results could be consistent with an asymptotic value $c=0$. Clearly, a definitive determination of c requires an accurate solution for very large clusters.

IV. NUMERICAL RESULTS

We solve the TFDGW4 Euler equation (26) by the numerical method of Ref. 14, which directly yields the chemical potential μ and density profile $n(r)$. The total energy is then constructed from Eq. (18), and the first ionization energy is found from the total-energy difference of Eq. (15). For very large clusters ($N\approx10^6$), where there is loss of accuracy in the difference between two large energies, the ionization energy can be found more reliably from

$$I\approx\tfrac{1}{2}(\mu+\mu_+) , \tag{32}$$

where μ_+ is the chemical potential for the single positive ion. The quantities σ, γ, W, and c are obtained by fits to the asymptotic formulas (1), (2), and (5), while the distance x_0 from the Gibbs surface to the centroid of excess charge at a planar surface is obtained from the $R\rightarrow\infty$ limit of

$$-\int_{-R}^{\infty}dx\,4\pi(R+x)^2x\,\Delta n(R+x) , \tag{33}$$

where $\Delta n(r)$ is the change of electron density due to removal of one electron.

Measured ionization energies for metallic clusters are often analyzed[25–27] by plotting I-W (where W is the $R\rightarrow\infty$ limit of I) versus $1/R$. Figure 2 presents such an analysis of our theoretical data. Although the formulas of Wood[6] ($3/8R$) and Perdew[5] [$1/2(R+1.54)$] approximate the data for the large radii shown in Fig. 2 (and for the smaller radii not displayed), *neither* formula is asymptotically exact.

The results of our analysis are summarized in Tables I and II. Table I compares our TFDGW4 values for σ, W, and x_0 with those from a Kohn-Sham calculation for a planar surface;[22] the difference reflects the error of the gradient expansion (21). The TFDGW4 Euler equation for a planar surface has been solved by Tarazona and Chacón,[28] and our results for σ and W agree with theirs

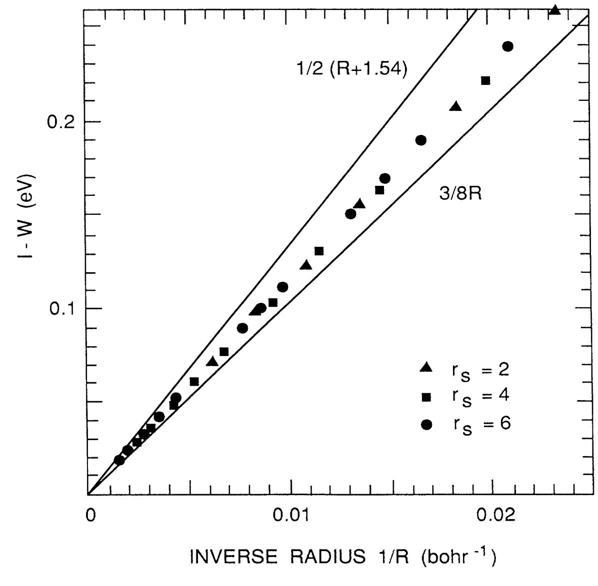

FIG. 2. Analysis of TFDGW4 first ionization energies I for jellium spheres of large radius R.

TABLE I. Bulk energy per electron $\varepsilon=\alpha 4\pi r_s^3/3$ (hartree), and quantities extracted from the TFDGW4 calculations for jellium spheres with density parameters r_s: the surface energy σ (hartree/bohr^2), the curvature energy γ (hartree/bohr), the work function W (hartree), the constant c of Eq. (2) (hartree bohr), and the distance x_0 from a planar Gibbs surface to the centroid of infinitesimal excess charge (bohr). Values in parentheses are from a Kohn-Sham orbital calculation for the planar surface (Ref. 22).

r_s	ε	σ	γ	W	c	x_0
2	0.002 372	-6.079×10^{-4}	1.64×10^{-3}	0.125 50	-0.0723	1.63
		(-5.533×10^{-4})		(0.138 9)		(1.58)
4	$-0.077\,266$	8.759×10^{-5}	2.60×10^{-4}	0.099 38	-0.0825	1.02
		(10.50×10^{-5})		(0.106 6)		(1.23)
6	$-0.071\,021$	3.1210×10^{-5}	6.82×10^{-5}	0.078 71	-0.0750	0.79
		(3.82×10^{-5})		(0.082 7)		(1.11)

after account is taken of the difference[29] between the Wigner correlation they use and our Vosko-Wilk-Nusair[21] correlation.

Table II presents a subset of our calculated values for E, μ, and I (with fewer significant figures than we calculate), and compares them with the asymptotic forms (1), (2), and (5). (Note that E includes the background electrostatic self-energy, $3e^2N^2/5R$.) The numbers show that taking d of Eq. (2) equal to x_0 yields the correct ionization energy to order R^{-2}. [In fact, $(\mu-\mu_+)^{-1}-R$ tends to x_0 as R tends to ∞.]

In the absence of shell-structure oscillations, the asymptotic forms provide an accurate account of the size dependence, even for very small particles. In particular, the error of Eq. (1) for the energy per electron E/N is no more than 1 (m hartree), even for $N=1$. This fact suggests a way to extract the unknown curvature energies of real metals from experimental data, which we now describe.

The shell-structure oscillations in small clusters make it difficult to extract the curvature energies, as in the work of Utreras-Díaz and Shore.[30] (See also Fig. 1.) But these oscillations are absent for vacancies in bulk metals, since the one-electron levels then form a continuum. The formation energy ε_{vac} of a monovacancy[13] is defined as the energy required to remove one atom from the bulk of a macroscopic metal, and place it on the surface. This process creates a "hole" of area $4\pi r_0^2$ and *negative* curva-

TABLE II. Total energy E, chemical potential μ, and first ionization energy I (hartree) from TFDGW4 calculations for neutral jellium spheres with N electrons, compared with asymptotic forms of Eqs. (1), (2), and (5).

r_s	N	E/N	$\varepsilon+(\sigma 4\pi R^2+\gamma 2\pi R)/N$	$-\mu$	$W+c/R$	I	$-\mu+1/2(R+x_0)$
2	1	$-0.006\,317$	$-0.007\,576$	0.0971	0.0894	0.3063	0.2348
	10	$-0.007\,152$	$-0.007\,371$	0.1112	0.1087	0.2048	0.1954
	10^2	$-0.003\,231$	$-0.003\,254$	0.1183	0.1177	0.1653	0.1641
	10^3	$-0.000\,476$	$-0.000\,477$	0.1220	0.1219	0.1453	0.1451
	10^4	0.000 998	0.000 998	0.1238	0.1238	0.1350	0.1350
	10^5	0.001 723	0.001 723	0.1247	0.1247	0.1300	0.1300
	5×10^5	0.001 990	0.001 990	0.1250	0.1250	0.1282	0.1282
4	1	$-0.053\,633$	$-0.053\,120$	0.0805	0.0788	0.2036	0.1801
	10	$-0.067\,760$	$-0.067\,684$	0.0902	0.0898	0.1442	0.1420
	10^2	$-0.073\,176$	$-0.073\,169$	0.0950	0.0949	0.1208	0.1205
	10^3	$-0.075\,440$	$-0.075\,440$	0.0973	0.0973	0.1095	0.1095
	10^4	$-0.076\,435$	$-0.076\,435$	0.0984	0.0984	0.1042	0.1042
	10^5	$-0.076\,884$	$-0.076\,884$	0.0989	0.0989	0.1016	0.1016
	10^6	$-0.077\,089$	$-0.077\,089$	0.0992	0.0992	0.1004	0.1004
6	1	$-0.054\,301$	$-0.054\,331$	0.0668	0.0662	0.1543	0.1405
	10	$-0.063\,925$	$-0.063\,914$	0.0730	0.0729	0.1104	0.1095
	10^2	$-0.067\,862$	$-0.067\,860$	0.0760	0.0760	0.0936	0.0935
	10^3	$-0.069\,584$	$-0.069\,584$	0.0775	0.0775	0.0857	0.0857
	10^4	$-0.070\,361$	$-0.070\,360$	0.0781	0.0781	0.0820	0.0820
	10^5	$-0.070\,716$	$-0.070\,716$	0.0784	0.0784	0.0802	0.0802
	10^6	$-0.070\,879$	$-0.070\,880$	0.0786	0.0786	0.0794	0.0794

ture radius $-r_0$, where $r_0=z^{1/3}r_s$ is the radius of the Wigner-Seitz spherical cell containing one atom, so

$$\varepsilon_{\text{vac}} \approx \sigma 4\pi r_0^2 - \gamma 2\pi r_0 \ . \tag{34}$$

From measured surface energies and vacancy-formation energies, one may estimate the curvature energy γ.[31] More generally, a "liquid drop model for crystalline metals" has been developed in Ref. 31.

V. ORIGIN OF THE ASYMPTOTIC SIZE DEPENDENCE OF THE CHEMICAL POTENTIAL

As argued near the end of Sec. III, nonzero c in Eq. (2) arises within the TFDGW4 approximation from the gradient terms T_2 and T_4 of Eq. (21). Here we will describe an explicit mechanism by which this happens.

The chemical potential μ satisfies the Euler equation (26). Equations (30) and (31) show that the functional derivatives of T_2 and T_4 involve Laplacians such as

$$\nabla^2 n(r) = \frac{d^2 n}{dr^2} + \frac{2}{r}\frac{dn}{dr} \ . \tag{35}$$

The second term on the right-hand side of Eq. (35) arises *explicitly* from curvature. For a jellium sphere of large radius R, this term may be replaced by $(2/R)\,dn/dr$, since dn/dr vanishes away from the surface. In this limit, the terms of this form can be treated as a weak perturbation on the planar surface problem.

For a planar surface with electron density profile $\rho(x)$, we multiply both sides of Eq. (26) by $-\rho'(x)/\bar{n}$ and integrate over $x=r-R$, the distance from the surface plane $x=0$, obtaining

$$\mu = \int_{-\infty}^{\infty} dx \frac{\delta E}{\delta \rho(x)} \left[\frac{-1}{\bar{n}}\right] \frac{d\rho}{dx} \ . \tag{36}$$

Now the perturbation theory described in the previous paragraph contributes c_2/R from $\delta T_2/\delta\rho(x)$ and c_4/R from $\delta T_4/\delta\rho(x)$, where

$$c_2 = \frac{-1}{18\bar{n}} \int_{-\infty}^{\infty} dx \frac{1}{\rho} \left[\frac{d\rho}{dx}\right]^2 , \tag{37}$$

$$c_4 = \frac{(3\pi^2)^{-2/3}}{540\bar{n}} \int_{-\infty}^{\infty} dx \left[8\rho^{-5/3}\frac{d^3\rho}{dx^3} - \frac{73}{3}\rho^{-8/3}\left[\frac{d\rho}{dx}\right]\left[\frac{d^2\rho}{dx^2}\right] + \frac{136}{9}\rho^{-11/3}\left[\frac{d\rho}{dx}\right]^3 \right] \frac{d\rho}{dx} \ . \tag{38}$$

The third derivative in Eq. (38) may be eliminated via integration by parts.

Table III shows c_2 and c_4, obtained from our TFDGW4 electron density profiles in the limit $R\rightarrow\infty$. Together, c_2 and c_4 account for most but not all of c. As discussed in the Appendix, the electron density profile and electrostatic potential near the surface have asymptotic R^{-1} corrections. These contributions add up to $c=0$ in the TF and TFDG approximations, but not in TFDGW2 and TFDGW4.

TABLE III. The constants c_2 and c_4 of Eqs. (37) and (38), explicit contributions to c of Eq. (2) from the second- and fourth-order gradient terms of the kinetic energy, for jellium spheres in the TFDGW4 approximation. (hartree bohr).

r_s	c_2	c_2+c_4	c
2	-0.044	-0.059	-0.0723
4	-0.036	-0.064	-0.0825
6	-0.032	-0.068	-0.0750

Two neglected effects could increase the magnitude of c_2+c_4. (1) Errors in the surface energy arising from the fourth-order gradient expansion of the kinetic energy (Table I) could be reduced by scaling T_4 by a factor of about 1.34,[32] and c_4 would then be scaled by about the same factor. (2) Even in the simple metals, the planar-averaged valence-electron density profile $\rho(x)$ can be rather different[33,34] from that for the jellium surface, because of the ionic pseudopotential. Within the simple "structureless pseudopotential model[34]," these effects enhance c_2+c_4 by as much as 40% for the high-density metals ($r_s=2$). Thus it is not hard to accept that $c=-0.12\pm0.06$ for large Ag clusters, as reported in Ref. 9.

Finally, we note that nonlocal contributions to the exchange-correlation energy could also contribute to c of Eqs. (2), (7), and (8). Accurate determination of c for any given metal awaits the development of more accurate continuum approximations to the kinetic and exchange-correlation energies (perhaps along the lines of Refs. 35 and 36), or more accurate measurements for very large clusters. [By applying the conclusions of Ref. 20 to Eqs. (5) and (6), we find that the optimum continuum approximation to $E_{\text{XC}}[n]$ makes $\lim_{r\rightarrow\infty}\delta E_{\text{XC}}/\delta n(\mathbf{r}) = 1/2(R+d)$ for large R, and not 0 as in the local-density approximation of Eq. (13)].

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APPENDIX: ASYMPTOTIC SIZE DEPENDENCE OF THE DENSITY PROFILE AND ELECTROSTATIC POTENTIAL

Consider a jellium sphere of *large* radius R, and let $x=r-R$ represent distance from the surface. Let

$$\rho_R(x)=n(R+x) \tag{A1}$$

be the electron density profile. The charge neutrality condition is

$$\int_{-R}^{\infty} dx\, 4\pi(R+x)^2[\rho_R(x)-\bar{n}\Theta(-x)]=0\ , \tag{A2}$$

where $\Theta(-x)$ is a step function which vanishes for $x>0$. Equation (A2) must be satisfied to all orders in R, so (to order R^{-1}) the profile near the surface is

$$\rho_R(x)=\rho(x)+\frac{f(x)}{R}\ , \tag{A3}$$

where $\rho(x)$ is the profile for a planar surface and $f(x)$ vanishes away from the surface:

$$\int_{-\infty}^{\infty} dx[\rho(x)-\bar{n}\Theta(-x)]=0\ , \tag{A4}$$

$$\int_{-\infty}^{\infty} dx f(x)=-2\int_{-\infty}^{\infty} x[\rho(x)-\bar{n}\Theta(-x)] = -\frac{1}{2\pi}[\phi(\infty)-\phi(-\infty)]\ . \tag{A5}$$

The right-hand side of (A5) involves the surface dipole barrier of the planar surface, which is clearly not zero.

The electrostatic potential $\phi_R(x)$ satisfies Poisson's equation

$$\nabla^2\phi_R=\frac{d^2}{dx^2}\phi_R+\frac{2}{R}\frac{d\phi_R}{dx} = -4\pi\left[\rho(x)+\frac{f(x)}{R}-\bar{n}\Theta(-x)\right]\ . \tag{A6}$$

Expand

$$\phi_R(x)=\phi(x)+\frac{h(x)}{R}\ , \tag{A7}$$

where

$$\frac{d^2}{dx^2}\phi=-4\pi[\rho(x)-\bar{n}\Theta(-x)]\ , \tag{A8}$$

and find

$$h(x)=-\int_{x}^{\infty} dx_1 \int_{x_1}^{\infty} dx_2 \left[2\frac{d\phi}{dx_2}+4\pi f(x_2)\right]\ . \tag{A9}$$

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