PHYSICAL REVIEW B VOLUME 56, NUMBER 3 15 JULY 1997-I

Stress sum rules for the flat surface of stabilized jellium

A. Kiejna
Institute of Experimental Physics, University of Wrocław, Plac M. Borna 9, PL-50-204 Wrocław, Poland

P. Ziesche
c/o Max-Planck-Institut für Physik komplexer Systeme, Bayreuther Strasse 40, D-01187 Dresden, Germany

(Received 19 February 1997)

The surface virial theorem and a sum rule for the planar surface of simple metals modeled by a semi-infinite stabilized jellium are derived and tested numerically. They follow from the surface stress theorem and relate surface energy components to the number of electrons spilled out into the vacuum region. [S0163-1829(97)08028-4]

I. INTRODUCTION

The jellium model describes well basic properties of the inhomogeneous electron gas near the surface of s-p-bonded (simple) metals.[1,2] However, ordinary jellium is stable only for the electron density corresponding roughly to sodium, which is a consequence of the complete neglect of the effects of crystallinity. To remedy this drawback of jellium, Perdew, Tran, and Smith[3] have proposed a structureless pseudopotential model that retains the simplicity of jellium and stabilizes it for any (e.g., experimentally given) valence electron density (compare also Ref. 4). The model called *stabilized jellium* takes into account the discrete lattice effects in an averaged way and equilibrates the forces at the jellium surface. The calculated surface characteristic quantities (surface energy, work function) show better agreement with the experimental data than for ordinary jellium.[5,6] Another static quantity, surface stress, was calculated in Ref. 7. By modifying the electronic density profile the stabilization has an important effect on the response properties of simple metal surfaces (cf. Ref. 8).

The wide applicability of the stabilized jellium explains current interest in exact relations or sum rules, which allows one to control the accuracy of the model[9] and are useful checks of the self-consistency of calculations of the electronic properties.[1] For ordinary jellium there exist several exact relations[2,10–14] involving bulk and surface quantities. In Ref. 14 a theorem has been derived that relates mutually different contributions to the surface energy of jellium. In this paper we present the derivation and the results for numerical checks of the stabilized-jellium counterpart of this sum rule as well as of the related surface virial theorem.

II. HALF-SPACE STABILIZED JELLIUM

In the stabilized jellium model, the total energy of a system of N electrons as a functional of the electron density $n(\mathbf{r})$ and the positive background density $n_+(\mathbf{r})=\overline{n}\,\Theta_{\mathcal{V}}(\mathbf{r})$ is given by

$$E[n,n_+]=E_{\rm jell}[n,n_+]+(\varepsilon_M+\overline{w_{\mathcal{R}}})\int d^3r\,n_+(\mathbf{r})+\langle\delta v\rangle_{\rm WS}\int d^3r\,\Theta_{\mathcal{V}}(\mathbf{r})[n(\mathbf{r})-n_+(\mathbf{r})],\qquad(1)$$

where $\Theta_{\mathcal{V}}(\mathbf{r})$ is a step function equal to 1 inside the background region $\mathcal{V}$ and 0 outside. $E_{\rm jell}$ is the standard jellium energy with the kinetic, electrostatic, and exchange-correlation energy contributions. The last two terms in Eq. (1) originate from the corrections that are needed to transform ordinary jellium into stabilized jellium as a more realistic model of a real metal:[3] (i) the average Madelung energy $\varepsilon_M(\overline{n})$ of point ions embedded in a uniform negative background, (ii) the Ashcroft pseudopotential contribution $\overline{w_{\mathcal{R}}}$, averaged over the Wigner-Seitz cell, and (iii) a ''difference potential'' being the average over the Wigner-Seitz sphere of the difference $\delta v(\mathbf{r})$ between the pseudopotential of the ions and the electrostatic potential of the uniform positive background.

Making use of the metal bulk stability condition, $\langle\delta v\rangle_{\rm WS}$ and consequently the prefactors of the two integrals in Eq. (1), can be expressed[3] as the structureless averages

$$\langle\delta v\rangle_{\rm WS}=-\overline{n}\frac{d\varepsilon(\overline{n})}{d\overline{n}},\qquad(2)$$

where $\varepsilon(\overline{n})$ is the total energy per particle of the uniform electron gas. Note that $\langle\delta v\rangle_{\rm WS}$ vanishes for the Wigner-Seitz density parameter $r_s=4.2$, when ordinary jellium is stable.

Now, consider a flat surface of semi-infinite metal represented by uniform positive background of density $\overline{n}=3/4\pi r_s^3$ occupying the half-space $z\leqslant 0$. The ground-state electron density $n(z)$ is constructed from the solution of the Kohn-Sham equations with the effective potential

$$v_{\rm eff}(z)=\phi(z)+v_{\rm xc}(z)+\langle\delta v\rangle_{\rm WS}\Theta(-z),\qquad(3)$$

where the electrostatic potential $\phi(z)$, experienced by electrons, is obtained from the Poisson equation

$$\phi(z)=-4\pi\int_{-\infty}^{z}dz'(z-z')[n(z')-n_{+}(z')] \tag{4}$$

and the exchange-correlation potential $v_{\mathrm{xc}}[n(z)]$ is evaluated in the local density approximation (LDA):

$$v_{\mathrm{xc}}(z)=\left.\frac{d(n\varepsilon_{\mathrm{xc}})}{dn}\right|_{n(z)}. \tag{5}$$

(Hartree atomic units are used throughout.) The effective one-particle potential for the Kohn-Sham equation differs from the one for ordinary jellium by the third term on the right-hand side of Eq. (3), producing a discontinuity in the effective potential that stabilizes the jellium.[3]

The surface energy of stabilized jellium can be decomposed into kinetic, electrostatic, exchange-correlation and structureless pseudopotential energy terms, which follow from Eq. (1) [note that the second term in Eq. (1) is purely a bulk term and does not contribute to surface energy]:

$$\sigma=\sigma_{s}+\sigma_{\mathrm{es}}+\sigma_{\mathrm{xc}}+\sigma_{\mathrm{ps}} \tag{6}$$

with

$$\sigma_{s}=\sigma_{\mathrm{bs}}-\sigma_{v}=\frac{1}{2\pi^{2}}\int_{0}^{k_F}dk\,k^{3}\left(\eta_{k}-\frac{\pi}{4}\right)-\int_{-\infty}^{\infty}dz\,n(z)\times[v_{\mathrm{eff}}(z)-v_{\mathrm{eff}}(-\infty)], \tag{7}$$

where η_k is the phase shift. It describes the asymptotic behavior of the wave function for $z\to-\infty$ (deep in the bulk). The phase shifts obey the Sugiyama-Langreth neutrality sum rule.[1,2] In the above expression, following the notation of Ref. 14, the kinetic surface energy σ_s is decomposed into the band-structure and potential surface energies, respectively. The other terms appearing in Eq. (6) are given by standard expressions:[1,2]

$$\sigma_{\mathrm{es}}=\frac{1}{2}\int_{-\infty}^{\infty}dz[n(z)-n_{+}(z)]\phi(z), \tag{8}$$

$$\sigma_{\mathrm{xc}}=\int_{-\infty}^{\infty}dz\,n(z)\{\varepsilon_{\mathrm{xc}}[n(z)]-\varepsilon_{\mathrm{xc}}[\bar{n}]\}, \tag{9}$$

$$\sigma_{\mathrm{ps}}=\langle\delta v\rangle_{\mathrm{WS}}\int_{-\infty}^{0}dz[n(z)-n_{+}(z)]. \tag{10}$$

The jellium terms σ_{bs}, σ_{es}, and σ_{xc} are influenced by stabilization only indirectly through a different density profile, while σ_v and σ_{ps} depend directly on it.

III. SURFACE STRESS AND VIRIAL THEOREMS

The Nielsen-Martin stress theorem[15] proves to be a dyadically generalized virial theorem. It has been derived from the many-body Schrödinger equation as well as within the one-particle Kohn-Sham description.[16] Later, it was generalized beyond LDA (Refs. 17 and 18) and in Ref. 14 it has been applied to semi-infinite jellium.

Proceeding similarly as in the derivation of the surface stress theorem for ordinary jellium,[14] we obtain the following for stabilized jellium:

$$\left(\bar{n}\frac{d}{d\bar{n}}-1\right)\sigma=-\sigma_{\mathrm{bs}}+\sigma_{\mathrm{es}}-g_{\mathrm{xc}}+\left(\bar{n}\frac{d}{d\bar{n}}\bar{n}\frac{d\bar{\varepsilon}}{d\bar{n}}\right)\nu, \tag{11}$$

$$\bar{n}\frac{d}{d\bar{n}}\sigma=4\sigma_{\mathrm{bs}}-2\sigma_{v}-\sigma_{\mathrm{es}}-g_{\mathrm{xc}}+\left(\bar{n}\frac{d}{d\bar{n}}\frac{d\bar{\varepsilon}}{d\bar{n}}\right)\nu, \tag{12}$$

where

$$-g_{\mathrm{xc}}=\int dz\left[n^{2}\left.\frac{d\varepsilon_{\mathrm{xc}}}{dn}\right|_{n(z)}-\Theta(-z)\bar{n}^{2}\frac{d\bar{\varepsilon}_{\mathrm{xc}}}{d\bar{n}}\right] \tag{13}$$

is the exchange-correlation component of the surface stress[19] and

$$\nu=\int_{0}^{\infty}dz\,n(z) \tag{14}$$

gives the number of electrons (per unit area) spilled out into the vacuum region. Note that the stress arises generally from the change of the total energy E, when scaling the background density $\bar{n}$ via $\bar{n}(d/d\bar{n})$. Because E contains the additional (stabilization) term $\bar{n}(d\bar{\varepsilon}/d\bar{n})N_{\mathrm{vac}}$ (the last term in Eq. (1), where $N_{\mathrm{vac}}=-\int d^{3}r\,\Theta_{\mathcal{V}}(\mathbf{r})[n(\mathbf{r})-n_{+}(\mathbf{r})]$ is the number of electrons outside the region $\mathcal{V}$ occupied by the metal) in the stress expression the additional term, $[\bar{n}(d/d\bar{n})\bar{n}(d\bar{\varepsilon}/d\bar{n})]N_{\mathrm{vac}}$, describes the stabilization. The left-hand sides of Eqs. (11) and (12) are the negative of the components of the surface stress parallel and perpendicular to the surface, respectively.

TABLE I. The numerical values for different surface energy and surface stress components (in erg/cm^2) of the virial theorem (15) for a flat surface of stabilized jellium. The last column displays the sum of the terms appearing on the right-hand side of Eq. (15). lhs and rhs denote left- and right-hand side.

r_s	lhs	$2\sigma_s$	σ_{es}	$-3g_{\mathrm{xc}}$	$3\bar{n}(d/d\bar{n})\bar{n}(d\bar{\varepsilon}/d\bar{n})\nu$	Σ (rhs)
2	−266	−8362	718	2564	4813	−267
3	267	−1182	129	633	686	266
4	164	−270	41	233	159	163
5	94	−76	18	105	46	94
6	57	−22	9	55	15	57

TABLE II. The same as in Table I for the sum rule (16).

r_s	$4\sigma_{\rm bs}$	σ_v	$3\sigma_{\rm es}$	$\sigma_{\rm xc}$	$\bar{n}(d\varepsilon/d\bar{n})\nu$	Σ (rhs)
2	14376	7775	2154	2775	1672	14376
3	2436	1200	387	695	153	2435
4	696	309	123	258	6	696
5	264	104	54	118	−11	265
6	120	41	27	62	−11	119

The sum of twice of Eq. (11) and of (12) gives the surface virial theorem

$$\left(3\bar{n}\frac{d}{d\bar{n}}-2\right)\sigma=2\sigma_s+\sigma_{\rm es}-3g_{\rm xc}+3\left(\bar{n}\frac{d}{d\bar{n}}\bar{n}\frac{d\varepsilon}{d\bar{n}}\right)\nu, \tag{15}$$

while the difference of Eqs. (11) and (12) eliminates the (xc component of the) surface stress and so yields the new sum rule holding for stabilized jellium

$$4\sigma_{\rm bs}=\sigma_v+3\sigma_{\rm es}+\sigma_{\rm xc}+\bar{n}\frac{d\varepsilon}{d\bar{n}}\nu. \tag{16}$$

Equation (16) relates the components of the surface energy and unlike Eq. (15) it does not involve $g_{\rm xc}$. Note that these equations differ from the corresponding surface virial theorem[12–14,19] and sum rule[14] for ordinary jellium by the appearance of the last (stabilization) term.[20] Similar to the case of ordinary jellium[14] the existence of the additional sum rule (16) is because the jellium, in distinction to a crystal, has only one geometry parameter, viz., $\bar{n}$ or r_s. Scaling the background charge parallel and perpendicular to the surface thus results in the same kind of change, and instead of relations for two different stress components, one gets two different equations for the same quantity $d\sigma/d\bar{n}$.

Combining Eq. (16) with Eqs. (6) and (7), the total surface energy of stabilized jellium can be written in the form

$$\sigma=\frac{1}{4}\left[-3\sigma_v+5\left(\sigma_{\rm xc}+\bar{n}\frac{d\varepsilon}{d\bar{n}}\nu\right)+7\sigma_{\rm es}\right], \tag{17}$$

which is an explicit functional of the density and does not involve the phase shifts η_k. Other (Hellmann-Feynman force) sum rules holding for the flat surface of stabilized jellium are[9]

$$[\bar{n}-n(0)]\frac{d\varepsilon}{d\bar{n}}=\int_{-\infty}^{0}dz\mathcal{E}(z), \tag{18}$$

$$4\sigma_{\rm bs}-2\sigma_v-\sigma_{\rm es}-g_{\rm xc}=\bar{n}\int_{-\infty}^{0}dz\,z\mathcal{E}(z), \tag{19}$$

with $\mathcal{E}(z)=d\phi(z)/dz$ being the electric field. Note that the left-hand side of Eq. (19) appears on the right-hand side of Eq. (12). While in Eq. (19)—apart from $\bar{n}$—only surface properties appear, in the surface stress theorem (11), (12), in the surface virial theorem (15), in the new sum rule (16), and in the Monnier-Perdew theorem (18) surface properties are related to the bulk property $\varepsilon(\bar{n})$. For ordinary jellium Eq. (18) is to be replaced by the Theophilou (Budd-Vannimenus) theorem,[10] which does not contain the term $n(0)$; this term is a result of the stabilization.[9,22]

IV. NUMERICAL VERIFICATION

The validity of the surface virial theorem and the sum rule (16) has been tested numerically for the r_s values covering the whole range of metallic densities. The Kohn-Sham equations have been solved self-consistently with the effective potential including the stabilizing term $-\bar{n}[d\varepsilon(\bar{n})/d\bar{n}]$ on the metal side. The calculated surface energy components of stabilized jellium (kinetic, electrostatic, and exchange-correlation terms plus the structureless pseudopotential contribution) are given in Tables I and II. The exchange and correlation energy was evaluated using the parametrized values of Ceperley-Alder for the correlation energy.[21]

The comparison of the numerical values of the first column of Table I, giving the numbers for the left-hand side of Eq. (15) with the sum of the other columns representing components of the right-hand side, shows excellent fulfillment of the surface virial theorem. The same is observed for the sum rule (16), whose components are given in Table II. In both cases, in the whole range of electron densities $\bar{n}$, the deviations are less than 1%.

Summarizing, in this paper we have derived the surface virial theorem (15) and the new sum rule (16) for the surface energy of stabilized jellium. They follow from the surface stress theorem and, compared to the similar theorems for ordinary jellium, each of them contains an extra term proportional to the number of electrons spilled out into the vacuum region, which results from the stabilization procedure. The numerical tests show that the surface virial theorem and the new sum rule (16) are very well satisfied. Hence, these sum rules, similar to the Vannimenus-Budd sum rule[11] or the surface virial theorem[12,13] for ordinary jellium, can be applied [together with other sum rules, (18) and (19), for stabilized jellium[9]] for checking the consistency of numerical calculations for the flat surface of stabilized jellium.

ACKNOWLEDGMENTS

A.K. was supported by the University of Wrocław under the Grant No. 2016/W/IFD/97. P.Z. thanks P. Fulde for supporting this work.

[1] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).

[2] A. Kiejna and K. F. Wojciechowski, *Metal Surface Electron Physics* (Pergamon, Oxford, 1996).

[3] J. P. Perdew, H. Q. Tran, and E. D. Smith, Phys. Rev. B **42**, 11 627 (1990).

[4] H. B. Shore and J. H. Rose, Phys. Rev. Lett. **66**, 2519 (1991).

[5] C. Fiolhais and J. P. Perdew, Phys. Rev. B **45**, 6207 (1992).

[6] A. Kiejna, Phys. Rev. B **47**, 7361 (1993).

[7] A. Kiejna and P. Ziesche, Solid State Commun. **88**, 143 (1993).

[8] A. Liebsch, *Electronic Excitation at Metal Surfaces* (Plenum, New York, 1997).

[9] A. Kiejna, P. Ziesche, and R. Kaschner, Phys. Rev. B **48**, 4811 (1993).

[10] A. Theophilou, J. Phys. F **2**, 1124 (1972); H. F. Budd and J. Vannimenus, Phys. Rev. Lett. **31**, 1218 (1973); **31**, 1430(E) (1973).

[11] J. Vannimenus and H. F. Budd, Solid State Commun. **15**, 1739 (1974).

[12] J. Vannimenus and H. F. Budd, Phys. Rev. B **15**, 502 (1977).

[13] P. Ziesche and D. Lehmann, J. Phys. C **15**, 4807 (1982); **16**, 879 (1983); D. Lehmann and P. Ziesche, Helv. Phys. Acta **57**, 621 (1984); Solid State Commun. **56**, 847 (1985).

[14] P. Ziesche and J. Gräfenstein, Phys. Rev. B **46**, 1715 (1992).

[15] O. H. Nielsen and R. M. Martin, Phys. Rev. Lett. **50**, 697 (1983); Phys. Rev. B **32**, 3780 (1985); **35**, 9308(E) (1987).

[16] P. Ziesche, J. Gräfenstein, and O. H. Nielsen, Phys. Rev. B **37**, 8167 (1988).

[17] Yu. A. Uspenski, P. Ziesche, and J. Gräfenstein, Z. Phys. B **76**, 193 (1989).

[18] A. Dal Corso and R. Resta, Phys. Rev. B **50**, 4327 (1994).

[19] R. J. Needs and M. J. Godfrey, Phys. Rev. B **42**, 10 933 (1990).

[20] The new sum rule (16) has been mentioned, but erroneously with a prefactor 4 at the stabilization term, by P. Ziesche in *Density Functional Theory,* edited by E.K.U. Gross and R.M. Dreizler (Plenum, New York, 1995).

[21] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[22] R. Monnier and J. P. Perdew, Phys. Rev. B **17**, 2595 (1978); **22**, 1124(E) (1980).