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The virial theorem and the surface energy of an electron gas

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The virial theorem is used to derive an exact relation between the kinetic and interaction parts of the surface energy of an electron gas. A similar result is derived within the framework of the density-functional formalism. These results are generalized to the surface energy of a d-dimensional electron gas. In four dimensions we find that the density dependence of the surface energy is of the form $\sigma = A\rho^{5/4}$.

The calculation of the surface energy of simple metals has attracted much interest in the last few years, and most efforts have focused on the treatment of exchange and correlation effects, for which diverse approximations have been proposed.[1-5] Our approach to this problem has consisted rather in looking for exact relations and sum rules,[6] and using them to discuss the validity of these approximations and the consistency of the numerical results.

In the present work we derive a new exact relation between the kinetic and interaction parts of the surface energy, through the application of the quantum-mechanical virial theorem to the semi-infinite uniform background ("jellium") model of a metal surface. We then consider the virial theorem in the density-functional formalism and derive an analogous relation within this formalism. In the local approximation, this relation is in good agreement with the numerical results of Lang and Kohn.[1]

Finally we present a d-dimensional generalization of the same problem and obtain an exact relation between the surface kinetic and interaction energies. For $d=4$, the result is particularly simple and gives the density dependence of the surface energy. This is another manifestation of the peculiar character of the four-dimensional electron gas, recently pointed out by Toulouse[7] and by Parrinello and March[8] for bulk thermodynamic properties.

DERIVATION OF THE THEOREM

The virial theorem has been invoked to discuss chemical bonding[9] as well as the cohesive energy of solids[10]; in its usual form it gives a relation between the kinetic energy of a quantum-mechanical system, its interaction energy, and the pressure acting on the system. Here we show that a similar relation holds among surface energy contributions, and may be expressed very simply for the model where one replaces the ionic lattice by a uniform positive background. This relation is given in Eq. (9), and we start by presenting its detailed derivation.

Let us consider the Hamiltonian for N electrons in the potential due to a fixed distribution $\rho_+(\vec{r})$ of positive charge such that the global system is neutral. Denoting $\hat{\rho}_-(\vec{r})$ the density operator, $n(\vec{r})$ its expectation value, and writing all quantities in atomic units, we have

$$H = \sum_i \tfrac{1}{2} p_i^2 + \tfrac{1}{2} \iint \{[\rho_+(\vec{r}) - \hat{\rho}_-(\vec{r})][\rho_+(\vec{r}\,') - \hat{\rho}_-(\vec{r}\,')] - \delta(\vec{r}-\vec{r}\,')\hat{\rho}_-(\vec{r})\} |\vec{r}-\vec{r}\,'|^{-1} d\vec{r}\, d\vec{r}\,'. \quad (1)$$

If we now replace the exact ground-state wave function by a scaled trial wave function of the form

$$\psi(\lambda) = \lambda^{3N/2} \psi(\lambda\vec{r}_1, \lambda\vec{r}_2, \ldots, \lambda\vec{r}_N)$$

the energy functional becomes, after a change of variables in the Coulomb term,

$$\begin{aligned} E(\lambda) &= \langle \psi(\lambda) | H | \psi(\lambda) \rangle \\ &= \lambda^2 \langle \psi | T | \psi \rangle \\ &\quad + \tfrac{1}{2}\lambda \iint \langle \psi | [\rho_+(\lambda) - \hat{\rho}_-(\vec{r})][\rho_+'(\lambda) - \hat{\rho}_-(\vec{r}\,')] \\ &\quad - \delta(\vec{r}-\vec{r}\,') | \psi \rangle |\vec{r}-\vec{r}\,'|^{-1} d\vec{r}\, d\vec{r}\,', \end{aligned}$$

where $\langle \psi | T | \psi \rangle$ is the kinetic energy in the ground state and we use the short notation

$$\rho_+(\lambda) = \lambda^{-3} \rho_+(\lambda^{-1}\vec{r}).$$

Since the total energy is minimum for $\lambda = 1$, we obtain by differentiation

$$2\langle \psi | T | \psi \rangle + \langle \psi | V | \psi \rangle = -\frac{\partial}{\partial\lambda} \iint \rho_+(\lambda)[\rho_+(\vec{r}\,') - n(\vec{r}\,')] \frac{d\vec{r}\, d\vec{r}}{|\vec{r}-\vec{r}\,'|}, \quad \lambda = 1, \quad (2)$$

where $\langle\psi|V|\psi\rangle$ is the interaction energy. The expression on the right-hand side of Eq. (2) is related to the pressure exerted on the positive charges and vanishes if the whole system is at equilibrium, leading to the classical relation between the kinetic and interaction energies of a Coulomb system.

A useful model to study the role of conduction electrons in surface phenomena in metals is provided by the jellium model, where the ions are replaced by a uniform positive background maintained in equilibrium by external forces. The right-hand side of Eq. (2) may then be written in useful form, involving bulk and surface properties of direct physical interest.

We note that a dilation by a factor λ of the uniform background at fixed total charge is just equivalent to replacing $\rho_+(\vec{r})$ by $\rho_+(\lambda)$, which yields another uniform background at different volume and density. For a small dilation, $\lambda \approx 1$, first-order perturbation theory yields the following expression for the dilation energy:

$$(\delta E)_{\text{dilat}} = \iint [\rho_+(\lambda) - \rho_+(\vec{r})][\rho_+(\vec{r}\,') - n(\vec{r}\,')] \times |\vec{r} - \vec{r}\,'|^{-1} d\vec{r}\,' d\vec{r}\,' . \tag{3}$$

We now write the total energy of a sufficiently large system in such a way as to separate explicitly a term proportional to the volume Ω, and a term proportional to the surface area S (Ω and S are defined without ambiguity for the jellium):

$$E_{\text{total}} \equiv \Omega\, g(\rho) + S\sigma(\rho) = Nf(\rho) + S\sigma(\rho) . \tag{4}$$

N is the number of electrons, f is the bulk energy per particle, and σ the surface energy for the bulk density ρ. The number of particles is kept constant during the dilation, thus

$$\begin{aligned} \frac{\partial E}{\partial \lambda} &= N\frac{df}{d\lambda} + \frac{d(S\sigma)}{d\lambda} \\ &= -3\rho f' N + (2\sigma - 3\rho\sigma')S \; ; \end{aligned}$$

$$f' = \frac{df}{d\rho}, \quad \sigma' = \frac{d\sigma}{d\rho} . \tag{5}$$

This is the last term of Eq. (2) and we obtain, including surface contributions,

$$2\langle T\rangle + \langle V\rangle = 3N\rho f' + S(3\rho\sigma' - 2\sigma) . \tag{6}$$

To separate bulk and surface properties, we now define the kinetic energy per particle $t(\rho)$ and the interaction energy $v(\rho)$, as well as the kinetic surface energy $\sigma_k(\rho)$ and the interaction surface energy $\sigma_v(\rho)$

$$\langle T\rangle = Nt(\rho) + S\sigma_k(\rho) + \cdots ,$$

$$\langle V\rangle = Nv(\rho) + S\sigma_v(\rho) + \cdots .$$

The bulk properties then obey the relation

$$2t(\rho) + v(\rho) = 3\rho f' .$$

Combining this result with the bulk relation $f = t + v$, and introducing the mean interparticle distance r_s defined by $\frac{4}{3}\pi r_s^3 = \rho^{-1}$, we have

$$t = -\frac{d(r_s f)}{dr_s} , \tag{7a}$$

$$v = r_s^{-1} \frac{d(r_s^2 f)}{dr_s} . \tag{7b}$$

These relations give the possibility of computing the two contributions separately once $f(r_s)$ is known, and a full discussion of their use has been given by March, Young, and Sampanthar.[10] Considering the surface terms in Eq. (6), we obtain

$$2\sigma_k(\rho) + \sigma_v(\rho) = 3\rho\sigma' - 2\sigma \; ; \tag{8}$$

combining this relation with $\sigma = \sigma_k + \sigma_v$, yields

$$\sigma_k = 3(\rho\sigma' - \sigma) = -\frac{1}{r_s^2} \frac{d(\sigma r_s^3)}{dr_s} , \tag{9a}$$

$$\sigma_v = 4\;\; - 3\rho\sigma' = \frac{1}{r_s^3} \frac{d(\sigma r_s^4)}{dr_s} . \tag{9b}$$

Relations (9) constitute our main result; they are exact for the interacting system and enable us to obtain the kinetic contribution to the surface energy once the variation of σ with bulk density is known. The similarity with the bulk relations (7) becomes clearer if one remarks that the energy per surface electron is proportional to σr_s^2 and obeys the same relations as the bulk energy per electron.

As a simple illustration, at very high bulk densities the leading term in the surface energy is given by the Thomas-Fermi expression

$$\sigma_{\text{TF}} = -0.0763\, r_s^{-9/2} ,$$

and Eqs. (9) imply that

$$\sigma_k = -3\sigma_v = \tfrac{3}{2}\sigma ,$$

a result that may be checked directly.[1]

On the other hand, in the very-low-density regime, Wigner crystallization of the surface electrons is expected to occur.[11] The leading term is then of the form $\sigma_W = a r_s^{-3}$ and it is entirely due to the interaction energy, in agreement with Eqs. (9).

In the metallic density regime, we wish to apply our relations to recent numerical studies of the surface energies of metals, keeping in mind that in such calculations one obtains the total energy as the sum of large contributions of opposite sign, and that a small correction to one contribution may result in a sizeable change in σ. For instance, Rose *et al.*[4] have found that a correction of 15% to the exchange and correlation part leads to a 40% variation in σ. Our relations provide a new independent check for these results, but we must first investigate their validity in approximate calculations.

EXTENSION TO THE DENSITY-FUNCTIONAL FORMALISM

Our preceding results concern the true kinetic energy of the system, whereas the quantity usually computed in numerical studies is σ_s, the surface kinetic energy of a noninteracting system with the same density profile $n(r)$ as the interacting system. To investigate whether σ_s satisfies a relation similar to (9a), a convenient framework is provided by the Hohenberg-Kohn-Sham density-functional formalism,[12] which is the basis of these recent studies. In the Hohenberg-Kohn-Sham formalism, the total energy is written in the form

$$E_{\text{total}} = E_{\text{es}}[n(\vec{r}), \rho_+(\vec{r})] + T_s[n] + E_{xc}[n], \tag{10}$$

where $T_s[n]$ is the kinetic energy of a noninteracting system of density $n(r)$; E_{es} is the electrostatic interaction energy between $n(r)$ and the background; and E_{xc}, the exchange and correlation energy, is defined by Eq. (10). The minimization of the energy is equivalent to solving the following system of equations:

$$[-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(\vec{r})]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}), \tag{11a}$$

$$n(\vec{r}) = \sum |\psi_i(\vec{r})|^2, \tag{11b}$$

$$V_{\text{eff}}(\vec{r}) = \int \frac{n(\vec{r}\,') - \rho_+(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, dr' + \frac{\delta E_{xc}}{\delta n(\vec{r})}$$

$$= V_{\text{es}} + V_{xc}, \tag{11c}$$

where the summation is over the N-lowest eigenstates of the Schrödinger equation (11a).

Since the form of the functional $E_{xc}[n]$ is not known, an approximation is necessary to obtain V_{xc}, but we need not specify it at this point. Computing the total energy for a set of trial functions of the form $\{\lambda^{3/2}\psi_i(\lambda\vec{r})\}$, we obtain

$$E_\lambda = \lambda^2 T_s[n] + \lambda E_{\text{es}}[n(\vec{r}), \rho_+(\lambda)] + E_{xc}[\lambda^3 n(\lambda\vec{r})] .$$

The first two terms are similar to the ones obtained in the previous section, but the exchange-correlation term requires special attention. For $\lambda \approx 1$, we have by definition

$$E_{xc}[\lambda^3 n(\lambda\vec{r})] - E_{xc}[n] = \int [\lambda^3 n(\lambda\vec{r}) - n(\vec{r})]\left(\frac{\delta E_{xc}}{\delta n(\vec{r})}\right) d\vec{r}$$

$$= \int n(\vec{r})[V_{xc}(\lambda^{-1}\vec{r}) - V_{xc}(\vec{r})]\, d\vec{r} .$$

Minimizing E then gives the following equation to be compared to Eq. (2):

$$2T_s + E_{\text{es}} - \int n(\vec{r})\vec{r} \circ \nabla V_{xc}\, d\vec{r}$$

$$= -\frac{\partial}{\partial\lambda} \iint \rho_+(\lambda)\, \frac{\rho_+(\vec{r}\,') - n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,', \quad \lambda = 1 . \tag{12}$$

A similar equation has been obtained by Janak,[13] who used it to simplify total-energy and pressure calculations for solids, in the muffin-tin approximation.

We note that Eqs. (2) and (12) can be combined with Eqs. (1) and (10) to yield

$$T - T_s = E_{\text{es}} + E_{xc} - V = -E_{xc} - \int n\vec{r} \circ \nabla V_{xc}\, d\vec{r}$$

which relates the real kinetic and interaction energies to the analogous quantities in the density functional formalism.

Here we restrict our attention to the jellium, and notice that the right-hand side of Eq. (12) may still be interpreted as a dilation energy, as discussed above, as long as the calculations are carried out self-consistently, so that the energy is stationary with respect to variations of $n(r)$ and Eq. (3) remains valid. To separate bulk and surface parts in the exchange and correlation term, we use the expansion of E_{xc} in gradients of the density[12]:

$$E_{xc} = \int d\vec{r}[n\epsilon_{xc}(n) + B_{xc}(n)|\nabla n|^2 + \cdots] ; \tag{13}$$

inserting $n \to \lambda^3 n(\lambda r)$ in Eq. (13) yields

$$\frac{\partial E_{xc}}{\partial\lambda} = \int d\vec{r}[3n^2\epsilon'_{xc}(n) + (5B_{xc} + 3nB'_{xc})|\nabla n|^2],$$

$$\lambda = 1 .$$

The bulk terms reduce to an identity, but the surface terms give an equation corresponding to Eq. (8):

$$2\sigma_s + \sigma_{\text{es}} + 3\int_{-\infty}^{\infty} dx\, n(x)[n\epsilon'_{xc}(n) - \rho\epsilon'_{xc}(\rho)]$$

$$+ \int_{-\infty}^{\infty} dx\, n'^2(x)(5B_{xc} + 3nB'_{xc}) = 3\rho\sigma' - 2\sigma , \tag{14}$$

where the integrals go from deep inside the solid to far out in the vacuum. A simplification occurs because the bulk exchange energy varies as $n^{1/3}$ and drops out of the final result for the surface kinetic energy, that reads

$$\sigma_s = -\frac{1}{r_s^2}\frac{d}{dr_s}(\sigma r_s^3) + \int_{-\infty}^{\infty} dx\left[n\left(\frac{d(\epsilon_c r_s)}{dr_s}\bigg|_n - \frac{d(\epsilon_c r_s)}{dr_s}\bigg|_\rho\right)\right.$$

$$\left. - 3n^{-1/3}\frac{dC}{dn}\left(\frac{dn}{dx}\right)^2\right], \tag{15}$$

where ϵ_c is the bulk correlation energy per particle and $C(n)=n^{4/3}B_{xc}$. The function $C(n)$ has recently been studied by Rasolt and Geldart[14] in the whole metallic range, and varies by less than a factor of 2 from $r_s=2$ to $r_s=6$. Comparing Eqs. (15) and (9a), we see that σ_s does not obey as simple an equation as does the true kinetic energy, and that terms involving the density profile now appear explicitly. In the local approximation ($B_{xc}\equiv 0$) the integral term in Eq. (15) is of the same order of magnitude as the correlation energy, and comparing Eq. (15) with the self-consistent results of Lang and Kohn[1] we find that this term makes a positive contribution to σ_s, and varies from 15% of the first (negative) term for $r_s=2.5$ to as much as 40% for $r_s=5$.

Turning now to the nonlocal approximation ($B_{xc}\neq 0$), we find a second correction and might expect it to be of the same order of magnitude as the nonlocal correction to the total surface energy. However, the coefficient $n^{-1/3}\,dC/dn$ vanishes at high density faster than B_{xc}, so for small r_s the contribution will be relatively small. This conclusion is in agreement with the calculation of Rose *et al.*,[4] who find that the change in surface energy from the local case is substantial but almost completely due to the exchange-correlation part. Such considerations may be made quantitative by explicitly computing the various terms in Eq. (15), and provide an independent self-consistency check for the numerical evaluation of the different contributions to the surface energy.

EXTENSION TO d DIMENSIONS

It has recently become increasingly clear that much insight may be gained by studying the variation of physical properties as a function of space dimensionality, and looking for special dimensions where simple behavior occurs, even if they do not correspond to realizable physical systems. For instance, the properties of the electron gas seem to be very peculiar for $d=4$,[7,8] and it is natural to investigate the surface properties of the d-dimensional electron gas in the same spirit. Among the possible mathematical extensions, it seems physically reasonable to keep as interaction the solution of Laplace's equation in d dimensions:

$$\begin{aligned} V_d(r) &= -e^2 r^{2-d}, \quad d\neq 2 \\ &= -e^2 \ln r, \quad d=2\,. \end{aligned} \tag{16}$$

In writing the total energy we identify a contribution proportional to the number of particles and another proportional to the d-dimensional surface area:

$$E_{\text{total}} = N f_d(\rho) + S_d\,\sigma_d(\rho)\,. \tag{17}$$

We assume that such an expansion exists in d-dimensions and use it to define the surface energy σ_d. This might not be the case at low dimensionalities because of the long range of the interaction, Eq. (16).

As an example of the properties that may easily be generalized, it is straightforward to show that the relation giving the electrostatic potential energy difference ΔV_{es} between the jellium surface and the bulk[6,15] still holds for arbitrary d and may be written

$$\Delta V_{\text{es}} = \rho f_d'(\rho)\,. \tag{18}$$

To obtain scaling relations similar to Eq. (9), we again carry out the calculation of the energy using trial wave functions and the result is the following generalization of Eq. (2):

$$2\langle T\rangle + (d-2)\langle V\rangle = -\frac{\partial}{\partial\lambda}\iint \frac{\rho_+(\lambda^{-1}\vec{r})}{\lambda^d}\,[\rho_+(\vec{r}\,')-n(\vec{r}\,')] \times \frac{d\vec{r}\,d\vec{r}\,'}{|\vec{r}-\vec{r}\,'|^{d-2}}, \quad \lambda=1 \tag{19}$$

The right-hand side of Eq. (19) is related to the dilation energy for the jellium model and, noting that S_d scales with the dilation parameter as λ^{d-1}, we obtain

$$2\langle T\rangle + (d-2)\langle V\rangle = d\rho f_d' N + [\,d\rho\sigma_d' - (d-1)\sigma_d\,]\,S_d\,. \tag{20}$$

One immediately sees, as first pointed out by Toulouse,[7] that for $d=4$ the virial theorem becomes very simple and involves only the total energy. Physically, this is due to the fact that the correlation length and the screening length have the same density dependence, and only one fundamental length enters the problem. From Eq. (20) the bulk energy per particle is then of the form

$$f_4(\rho) = K\rho^{1/2}\,,$$

a result recently obtained by Parrinello and March[8] along similar lines. Collecting now the surface terms in Eq. (20) we find

$$2\sigma_4 = 4\rho\sigma_4' - 3\sigma_4\,.$$

Hence the density dependence of the surface energy is simply

$$\sigma_4 = A\rho^{5/4} = A' r_0^{-5}\,, \tag{21}$$

where r_0 is the radius of the hypersphere occupied by one electron:

$$r_0^d = \tfrac{1}{2}d\pi^{-d/2}\Gamma(\tfrac{1}{2}d)\rho^{-1}\,.$$

The energy per surface electron is proportional to $r_0^3\sigma_4$ and varies as $\rho^{1/2}$, like the bulk energy per electron. This is natural because there is only one energy scale in the problem, and in particular this implies that a Wigner transition cannot occur in four dimensions, whether in the bulk or at the surface. In three dimensions, on the contrary, it has been suggested[11] that a transition might happen near the surface at a higher density than for the bulk, and it would be interesting to see if expansions in $4-d$ can shed light on the problem.

For a general value of the dimensionality, Eq. (20) does not yield a relation for the total energy, but we may still separate a kinetic and an interaction contribution. We obtain for the bulk kinetic energy per particle,

$$t=-\frac{r_0^{3-d}}{4-d}\frac{d}{dr_0}(f_d r_0^{d-2})$$

and for the surface kinetic energy,

$$\sigma_k=-\frac{r_0^{4-2d}}{4-d}\frac{d}{dr_0}(\sigma_d r_0^{2d-3}).$$

The interest of these relations is rather academic for the present time, since surface properties for $d=2$ and $d=1$ have not been examined to our knowledge, but recent work by Sutherland[16] on the one-dimensional Coulomb gas opens the possibility that exact results may be obtained for that case, and we hope our work may stimulate interest in such questions.

CONCLUSION

We have derived new relations for the surface energy of an electron gas from the virial theorem, and discussed their use as checks on the consistency of numerical calculations such as those of Lang and Kohn[1] and of Rose *et al.*[4] These results have been generalized to an arbitrary dimensionality, a domain that has been little explored up to now for surface properties, and where modern methods of statistical mechanics— such as expansions around a critical dimensionality—might provide new insights.

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