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Nonconvergence of surface energies obtained from thin-film calculations

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It is demonstrated that one of the most common methods used to determine surface energies from thin-film total-energy calculations introduces a computational error that increases linearly with the thickness of the film. This linear divergence is shown to have had a major impact on a recent calculation of the Li(111) surface energy, using one- to five-layer-thick films.

For many years, thin-film electronic-structure calculations have been an important tool for investigating the properties of surfaces including the surface energy (E_s).[1-11] In this approach, the surface in question is modeled by an ultrathin film (UTF) that is periodic in two dimensions and is only a few atomic distances thick. For this approximation to be useful, the model UTF must be thick enough that its two surfaces are decoupled, but thin enough to make a high-precision electronic-structure calculation affordable. It has been generally assumed that the precision of the calculated surface properties always can be improved by increasing the thickness of the model UTF. Unfortunately, it will be shown here that the validity of this assumption with regards to the surface energy (E_s) depends on the method used to extract E_s from the total energy of the film.

In most UTF calculations, E_s is determined from the basic relationship

$$E_s(n)=\tfrac{1}{2}(E_n-nE_b) , \tag{1}$$

where E_n is the energy per unit cell of the n-layer film and E_b is the bulk energy of the infinite solid per unit cell in a monatomic system (and the cellular equivalent per plane for more complex systems).[1-11] The factor of $\frac{1}{2}$ takes into account the two surfaces of the film. In principle, for a sufficiently large value of n, $E_s(n)$ will converge to the surface energy of the semi-infinite solid.

There are two methods typically used to determine E_s from Eq. (1) using UTF calculations. In the first, E_n is calculated for one reasonably large value of n, and E_b is obtained from an independent bulk calculation.[1-6] This method has the advantage of requiring only one UTF calculation and using the "best" available bulk energy. However, it will be shown here that, in practice, this method is computationally divergent as n increases. In the second method, E_n is calculated for at least two values of n and then, E_s and E_b are both determined from Eq. (1).[7-11] This technique has the disadvantage of requiring multiple UTF calculations and, for small n, may produce a rather imprecise estimate of E_b. However, this second method should converge quite rapidly with increasing n (see below).

In the simplest version of the latter method for calculating $E_s(n)$, UTF calculations are carried out for two adjacent values of n. Then the bulk energy in Eq. (1) is approximated by the incremental energy

$$\Delta E(n)=E_n-E_{n-1} , \tag{2}$$

to get

$$E_s'(n)=\tfrac{1}{2}[E_n-n\Delta E(n)] . \tag{3}$$

For clarity, a prime will be used to distinguish surface energies determined with method two from those obtained with method one. In addition, henceforward, E_b will only be used to denote the independently determined bulk energy used in method one.

For either method to converge, a bulklike interior must be obtained for a reasonable value of n. Hence, the incremental energy must converge rapidly for large n, i.e., it must be possible to find an integer N such that $\Delta E(n)=\Delta E(N)$, to any desired level of precision, for all $n>N$. (This restriction should be satisfied for any UTF electronic-structure code that treats all interior layers equivalently.) This converged incremental energy represents the best approximation to the bulk energy that can be obtained from the UTF code being used. Then, for $n>N$, the energy of the n layer can be written as

$$E_{n>N}=E_N+(n-N)\Delta E(N) . \tag{4}$$

Combining Eqs. (3) and (4) gives

$$E_s'(n>N)=\tfrac{1}{2}[E_N-N\Delta E(N)]=E_s'(N) . \tag{5}$$

Thus, $E_s'(n)$ will always converge if $\Delta E(n)$ is rapidly convergent.

Now, consider the convergence properties of the first method for determining the surface energy. Combining Eqs. (1) and (4) gives

$$E_s(n>N)=\tfrac{1}{2}[E_N-N\Delta E(N)]+\tfrac{1}{2}n[\Delta E(N)-E_b] \tag{6}$$

or

$$E_s(n>N)=E_s'(N)+\tfrac{1}{2}n[\Delta E(N)-E_b] . \tag{7}$$

It is clear from Eq. (7) that the surface energy obtained from the first method will diverge linearly with increasing n unless the independently calculated bulk energy E_b is precisely equal to the converged incremental energy $\Delta E(N)$. Since the direction perpendicular to the plane of the film is treated differently by film and bulk codes, any such cancellation would be largely fortuitous. In general, the surface energy determined from Eq. (1) will either diverge linearly for large n or, at best, will converge to the same result as Eq. (3). Thus, Eq. (3) should be preferred to Eq. (1) in virtually all cases.

A recent UTF calculation[4] of the Li(111) surface ener-

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gy provides a dramatic example of the impact of the linear divergence just discussed. In that work, the linear combinations of Gaussian-type orbitals–fitting-function (LCGTO-FF) technique was used to calculate the properties of Li(111) n layers with $n=1-5$. Surface energies were calculated for all five of the films using Eq. (1) in conjunction with a bulk energy for Li calculated with the full-potential linearized augmented-plane-wave (FLAPW) technique.[12] The surface energies calculated in Ref. 4 increase steadily with n for all of the films considered, exhibiting no signs of convergence. Since Ref. 4 also listed incremental energies for the Li films, it is easy to reanalyze the LCGTO-FF results using Eq. (3). For this purpose, the surface energy of each film was recalculated here using the incremental energy for the five layers as the reference energy.

Figure 1 compares the Li(111) surface energies reported in Ref. 4 with those obtained here using the incremental energy of the five-layer film. An empirical value for the Li surface energy, deduced from the surface energy of the liquid metal,[13] is also shown in Fig. 1. The surface energies determined here via Eq. (3) converge rapidly to 0.20 eV/atom, in reasonable agreement with the empirical estimate of 0.26 eV/atom.[13] In contrast, the E_s vs n curve obtained with Eq. (1) obviously is diverging linearly with n and, for $n=5$, has already reached 0.50 eV/atom,[4] nearly double the empirical estimate. Thus, by $n=5$, the linear divergence has already produced a 100% error in E_s. Although this error is exceptionally large due to the major inconsistency between the LCGTO-FF film energies and the FLAPW bulk energy, the linear divergence seen in Fig. 1 will exist to some degree in any surface-energy calculation that uses an independently determined E_b in Eq. (1).

For an example of how the linear divergence in Eq. (7) might affect a surface-energy calculation that uses the same electronic-structure technique, but different codes, to determine E_n and E_b, consider the W(001) and V(001) surface energies calculated by Fu *et al.*[2] using the FLAPW method. In that work, E_s was obtained from Eq. (1) by combining the total energy of a seven-layer film with an independently determined FLAPW bulk energy. For the largest FLAPW basis sets used, the calculated surface energies of the unrelaxed W(001) and V(001) surfaces were 237 and 154 mRy/atom, respectively.

Fu *et al.*[2] tested the convergence of their results by calculating total energies for five-layer films of W and V, and then estimating the incremental energies for both systems as half the energy difference between the five-layer and the seven-layer. For the W(001) and V(001) films, the incremental energies were smaller than the calculated bulk energies by 6 and 5 mRy, respectively. Fu *et al.*[2] cited these small differences as evidence that the interiors of the seven-layer films were nearly converged to the bulk; i.e., it was implicitly assumed that the incremental energy would eventually converge to the independent bulk value.

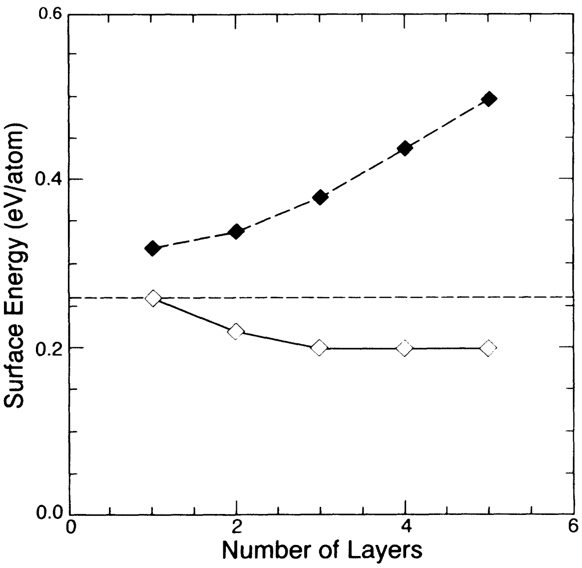

FIG. 1. Surface enerigies for Li n layers obtained using the five-layer incremental energy as a reference (solid line) compared with those obtained in Ref. 4 using an independently determined bulk energy as the reference (dashed line); in eV/atom. Also shown is the empirical estimate of the Li surface energy from Ref. 13; horizontal line.

However, it may be that the small differences between the incremental film energies and the bulk energies were actually due to small inconsistencies between the bulk and film calculations. In that case, more precise surface energies could be obtained from Eq. (3) using the incremental energies reported in Ref. 2. Following that procedure gives $E_s=216$ and 136 mRy for the W(001) and V(001) surfaces. In each case, the surface energy obtained from Eq. (3) is roughly 10% smaller than the result originally reported and is closer to the appropriate empirical estimate from Ref. 13; 166 mRy/atom for W and 109 mRy/atom for V.

Based on the preceding analysis and examples, it is clear that the incremental energy approach to extracting surface energies from UTF calculations generally should be prefered to the independent bulk-energy approach. Ideally, a series of n-layer calculations should be carried out for increasing values of n until the incremental energy has converged to the desired level of precision. Then the surface energies of all of the films can be calculated from Eq. (3) using the converged incremental energy. If convergence of the incremental energy proves intractable, it will at least be possible to assess realistically the uncertainty in the surface energy.

If, for some reason, the independent bulk-energy approach is used to determine the surface energy, every effort should be made to ensure consistency between the film and bulk calculations. For example, the bulk calculation ideally should treat the solid as a repeated slab with the same unit cell as the film. In addition, the Brillouin zone (BZ) scan used in the bulk calculation should be identical to the film BZ scan for the in-plane directions. Finally, it should be recognized that, if a separate E_b is used, the accuracy of the calculated surface energy may actually deteriorate if the film thickness is increased.

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[1] P. J. Feibelman, Phys. Rev. B **27**, 1991 (1983).

[2] C. L. Fu, S. Ohnishi, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **31**, 1168 (1985).

[3] I. P. Batra, S. Ciraci, G. P. Srivastava, J. S. Nelson, and C. Y. Fong, Phys. Rev. B **34**, 8246 (1986).

[4] J. C. Boettger and S. B. Trickey, Phys. Rev. B **45**, 1363 (1992).

[5] H. M. Polatoglou, M. Methfessel, and M. Scheffler, Phys. Rev. B **48**, 1877 (1993).

[6] V. Fiorentini, M. Methfessel, and M. Scheffler, Phys. Rev. Lett. **71**, 1051 (1993).

[7] J. A. Appelbaum and D. R. Hamann, Solid State Commun. **27**, 881 (1978).

[8] J. G. Gay, J. R. Smith, R. Richter, F. J. Arlinghaus, and R. H. Wagoner, J. Vac. Sci. Technol. A **2**, 931 (1983).

[9] T. Hong, J. R. Smith, D. J. Srolovitz, J. G. Gay, and R. Richter, Phys. Rev. B **45**, 8775 (1992).

[10] R. Wu and A. J. Freeman, Phys. Rev. B **47**, 3904 (1993).

[11] J. C. Boettger, U. Birkenheuer, N. Rösch, and S. B. Trickey, Int. J. Quantum Chem. Symp. (to be published).

[12] J. A. Nobel, S. B. Trickey, P. Blaha, and K. Schwarz, Phys. Rev. B **45**, 5012 (1992).

[13] F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals* (North-Holland, Amsterdam, 1988).