

## COMMENT

## Extracting convergent surface formation energies from slab calculations

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**Abstract.** It is known that surface formation energies obtained as differences between slab energies and an independently determined bulk energy will diverge linearly with the slab thickness. A recent paper by Fiorentini and Methfessel presented ‘a solution to this problem that eliminates the divergence and leads to rapidly convergent and accurate surface energies’. Although their work is correct, the solution they propose is not new. In this comment, we provide some of the historical background neglected by Fiorentini and Methfessel.

A recent paper by Fiorentini and Methfessel [1] discussed two important aspects of the determination of surface energies  $E_s$  from slab (or more precisely, ordered film) calculations. Unfortunately, all of the conceptual and procedural issues discussed in [1] had been treated previously [2–7] in work ignored in [1]. The only original physics in [1] is the finding that the linear divergence in calculated  $E_s$  values discussed originally by Boettger [3] becomes significant for very thick slabs even after taking care to obviate potential inconsistencies between the calculated bulk and film total energies per cell. (While the numerical example given in [1] is new in the literal sense of being for a different material and more precise, it does however repeat several already published illustrations.)

The central issue addressed by [1] is that the use of the sequence of incremental film energies (per surface unit cell)  $\Delta E$  as an estimator of the bulk crystalline energy per unit cell as suggested in [3] may result in a substantial imprecision in the resulting calculated surface energy  $E_s$  because of quantum size effects. This potential difficulty and its cause were already recognized explicitly by Boettger and coworkers [4], a study of quantum size effects in Al films. The discussion of those effects specifically mentioned that the results for  $E_s$  are especially sensitive to the behaviour of  $\Delta E$  for  $N_{max} = 6$  versus 7 ( $N_{max}$  = number of atomic layers used to estimate the bulk energy). Since there was only one experimental value, from liquid Al, with which to compare, Boettger’s group [4] did not pursue stabilization of the calculated  $E_s$  beyond an imprecision of 0.08 eV. At that point the calculated values (a) bracketed the liquid drop datum and (b) were both relatively flat as a function of thickness.

The solution recommended by [1] is to use a linear fit in  $N$  to the calculated film energies per cell. Precisely this procedure was used in a calculation of  $E_s$  for Cu(100) by Gay and coworkers [2] in 1983. That is the earliest reference of which we are aware, though there seems to have been common awareness in surface science of at least the rough validity of the idea prior to then.

The same procedure was utilized more recently by Birkenheuer and coworkers [5] to calculate the surface and bulk energies of MgO in 1994 and Li a year later [6]. Shortly after, Apell's group [7] showed that the linear fitting procedure worked extremely well for the Al results of [4]. They also confirmed the linear behaviour for Li films, and added graphite and diamond films as further examples. The linear fitting idea was also extended [7] to the  $N$ -dependence of proton-stopping powers in films and was used to extract the bulk value of the proton-stopping power.

These data and citations are sufficient to demonstrate that most of what [1] reports is actually a simple confirmation of effects already well known to be important and equally well-known procedures for dealing with those effects.

## References

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