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Ab-initio step- and kink-formation energies on Pb(111)

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Ab-initio formation energies for (100)- and (111)-microfacet steps on Pb(111) are in satisfactory agreement with measured values, given that these values are known only as well as the Pb(111) surface energy; the calculated step-energy ratio, 1.29, is within ~8% of experiment. In contrast, calculated kink-formation energies, 41 and 60 meV for the two step types, are 40-50% below published experimental values derived from STM images. The discrepancy results from interpreting the images with a step-stiffness vs. kink-energy relation appropriate to (100) but not (111) surfaces. Good agreement is found when the step-stiffness data are reinterpreted, taking proper account of the trigonal symmetry of Pb(111).

I) Introduction - The energies needed to form steps and kinks are fundamental parameters in the quasi-continuum description of surface morphology, and key to predicting how surfaces evolve in time.[1] Step wandering, for example, is governed by kink-formation energies, while the orientation-dependence of step-formation cost determines equilibrium island shapes.

Because of these connections, "experimental" step- and kink-formation energies tend to be best-fit parameters that emerge from a comparison between a contin-

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uum surface model and high-resolution surface microscopic data.[2-4] To test the reliability of such fits, one ought to seek independent confirmation of the results.[5] In this spirit, I compare Arenhold, et al.'s recent determination[2] of step- and kink-formation energies on Pb(111) to *ab-initio* Density Functional Theory (DFT)[6] total-energy calculations.

Several DFT results build confidence in the theory at the level of ~10% accuracy. The computed Pb(111) surface energy, 35 meV/Å^2, is ~10% smaller than the rough value obtained by extrapolating liquid Pb measurements to 0K.[7] The average of *ab-initio* formation energies for (100)- and (111)-microfacet (or "A-type" and "B-type") steps on Pb(111) is within ~15% of Arenhold, et al.'s result, satisfactory agreement given that the latter is scaled to the rough experimental surface energy.[2] Finally, if the interaction between the convex and concave corners that delimit a kink can be neglected, then the ratio of A- to B-step formation energies agrees with Ref. 2 to ~8%.

Given this record, it is a surprise that forming kinks on A- and B-type steps costs about 41 and 60 meV according to DFT, but 61 and 87 meV in Arenhold, et al.'s analysis. In what follows, after discussing the *ab initio* method and results in detail, I show that this substantial discrepancy results from the tacit assumption in Ref. 2 that step stiffness and kink-formation energy obey the same relation on the (100) and (111) faces of a Lead crystallite -- they do not. Reasonable agreement is found between DFT and experimental kink energies only when the latter are re-evaluated using a step-stiffness formula appropriate to a (111) surface.

The remainder of this article is organized as follows: In Sec. II, I review specifics of the DFT implementation behind the present results. Sec. III concerns the surface energy and outer layer relaxations of perfect Pb(111) in comparison with what is known experimentally. In the three parts of Sec. IV, I develop formalism later used to extract step and kink-formation energies from total energy calculations of Pb(111) slabs with monolayer high "stripe-islands" on them. Sec. V is devoted to results, both theoretical and experimental, for step- and kink-formation energies on Pb(111), including a detailed critique of energies extracted from Pb crystallite shapes in Ref. 2. Finally, in Sec. VI, I consider the significance of the level of agreement between theoretical and experimental step- and kink-energies for Pb(111).

II) DFT method - Formation-energies reported here were obtained with the *VASP*[8-10] total-energy code, its ultrasoft pseudopotentials (USP's),[11] and the Perdew-Wang '91 version of the Generalized Gradient Approximation (PW'91-GGA).[12] Using the Ceperley-Alder local exchange-correlation potential[13] in place of the PW'91-GGA produces surface and step-formation energies ~50% larger and in significantly worse agreement with experiment.

USP's yield converged total-energy differences with modest basis size. For Pb, a 6.5 Ry plane-wave cutoff is sufficient. I compute surface-, step- and kink-formation energies starting with 7-layer slabs to represent Pb(111), then removing atoms in the uppermost layer to create monolayer-high islands bounded by straight and kinked edges. In all cases I fix the atoms of lowermost three slab layers at bulk relative positions and relax the rest till forces are <0.01 eV/Å. I set the slab lattice parameter to 5.05 Å, the bulk GGA value for a 60 point sample of the irreducible 48th of the Brillouin Zone (exp't. = 4.95 Å). To accelerate electronic relaxation, I use Methfessel and Paxton's Fermi-level smearing method (width = 0.2 eV).[14]

III) Surface energy and structure of Pb(111) - To evaluate the surface energy of Pb(111), I compare the energy of an L-layer slab with L times that of a (111)-layer in bulk Pb. To allow a convergence assessment, I report results in Table I for several values of L and three Surface Brillouin Zone (SBZ) samples. For the sake of error cancellation in later step and kink energy calculations the results reported there were obtained using a large, $1 \times 4\sqrt{3}$, rectangular unit cell.

Note that the fluctuation of the computed surface energy vs. slab thickness is <10% for 5-7 layer films and that SBZ convergence already appears good with an 8×1 **k**-sample. On the other hand, finite-size fluctuations are minimized when using the finest sample of the SBZ, an incentive for using more **k**-points.

The best surface energy value, corresponding to the thickest slab and finest SBZ mesh is 35 meV/Å^2, in comparison with experimental values[6] of 37-38 meV/Å^2. This is reasonable agreement, given that the measurements were on liquid drops rather than crystalline Pb, then extrapolated to T=0K.[6]

The comparison of GGA and measured layer separations is less satisfying, though theory and experiment do agree that the outer-layer spacing of Pb(111) undergoes an unusually large contraction for a close-packed metal surface. To obtain accurate theoretical results, I relax the slab till forces on the atoms of its upper four layers are less than 0.01 eV/Å. This high level of convergence is needed because the distances atoms must be moved to reduce a small force to zero are larger for a soft metal like Pb, than for a harder one. The computed relaxations for the 7-layer slab are then Δd_{12}= -6.9%, Δd_{23}= +0.6% and Δd_{34}= -0.7%, referencing to the bulk, GGA layer spacing, 2.917Å. By contrast, the percent relaxations of the first three layer-spacings, according to the Low Energy Electron Diffraction

(LEED) analysis of Li, Jona and Marcus, are Δd_{12}= -(3.5±1)%, Δd_{23}= +(0.5±1.4)% and Δd_{34}= +(1.6±1.8)%.[15] It is hard to say why quantitative agreement between the DFT and LEED values of Δd_{12} is not better.

IV) Methods for computing step and kink formation energies -

A) The average formation energy of straight steps - The arrangement of atoms on a close-packed surface dictates that a stripe island is bounded by an A-type step on one side and a B-type on the other. Thus, $\bar{E}_{form}$, the average of A and B-type step formation energies, is given by,[16]

$$2\bar{E}_{form} = E(s, v) - \frac{[sE(N+1) + vE(N)]}{s+v}. \qquad (1)$$

Here E(s,v) is the energy of a striped slab N+1 layers thick in cross-sections through the stripe islands and N-layers thick through the inter-island valleys, with stripes and valleys s and v atomic rows across. E(N) is the energy of a perfect N-layer slab. To minimize finite-size effects, one must choose sufficiently large s and v.

B) The straight step formation energy difference - To obtain the *difference* between A- and B-step formation energies, ΔE_{form}(step), one must perform DFT calculations for slabs that support islands with different A- and B-edge lengths, for example, Refs. 16's slabs, which support triangular islands whose edges are purely A- or purely B-type. Alternately, one can obtain the A- vs. B-step formation-energy difference from calculations involving kinked stripe-islands, the same ones used to compute kink energies, as described in the section following this one. This is possible because forming a kink in either type of step amounts to creating a microfacet of the other type.

More precisely, because the A- and B-steps of a (111) surface intersect at 120° angles (see Fig. 1), creating a kink in an A-type step: *a)* adds a B-type microfacet one inter-atomic spacing long, *b)* eliminates one-half that length of the original A-type step, and *c)* adds two 120° corners, one convex, the other concave. To form a kink in an A-type step thus requires energy,

$$E_{\mathrm{form}}(\text{A-kink; 1}) = E_{\mathrm{form}}(\text{B-step}) - E_{\mathrm{form}}(\text{A-step})/2 + E_C(\text{A-kink}) \quad , \qquad (2)$$

where the last term is a "corner-formation" energy.[17] If the B-step created is extended from one to n_k Pb-Pb spacings (see Fig. 2), then the formation-energy cost becomes

$$E_{\mathrm{form}}(\text{A-kink; } n_k) = n_k[E_{\mathrm{form}}(\text{B-step}) - E_{\mathrm{form}}(\text{A-step})/2] + E_C(\text{A-kink}) \quad , \qquad (3)$$

where in principle E_C(A-kink) depends on n_k, approaching a constant as n_k becomes sufficiently large. The same, of course, applies for a B-step of length n_k, whose formation-energy is,

$$E_{\mathrm{form}}(\text{B-kink; } n_k) = n_k[E_{\mathrm{form}}(\text{A-step}) - E_{\mathrm{form}}(\text{B-step})/2] + E_C(\text{B-kink}) \quad , \qquad (4)$$

Eqs. 3 and 4 combine to allow evaluation of the step-formation energy difference in terms of kink- and corner-formation energy differences. This approach maximizes the cancellation of finite-size error.

Assuming for simplicity that the E_C are independent of n_k already for $n_k \leq 2$, one may subtract Eq. 4 from Eq. 3, with $n_k=1$ and then with $n_k=2$, to obtain,

$$E_{form}(\text{A-kink};1)-E_{form}(\text{B-kink};1)=3[E_{form}(\text{B-step})-E_{form}(\text{A-step})]/2+E_C(\text{A-kink})-E_C(\text{B-kink}) , \quad (5)$$

and,

$$E_{form}(\text{A-kink};2)-E_{form}(\text{B-kink};2)=3[E_{form}(\text{B-step})-E_{form}(\text{A-step})]+E_C(\text{A-kink})-E_C(\text{B-kink}) . \quad (6)$$

Combining Eqs. 5 and 6, one obtains an estimate of the step energy difference,

$$E_{form}(\text{B-step})-E_{form}(\text{A-step})=2[E_{form}(\text{A-kink};2)-E_{form}(\text{B-kink};2)-E_{form}(\text{A-kink};1)-E_{form}(\text{B-kink};1)]/3 \quad (7)$$

and also of the difference between the corner-formation energies, in the form,

$$E_C(\text{A-kink})-E_C(\text{B-kink})=2[E_{form}(\text{A-kink};1)-E_{form}(\text{B-kink};1)]-[E_{form}(\text{A-kink};2)-E_{form}(\text{B-kink};2)] . \quad (8)$$

For completeness, note that adding Eqs. 3 and 4, with $n_k=1$, yields,

$$E_C(\text{A-kink}) + E_C(\text{B-kink}) = E_{form}(\text{A-kink}; 1) + E_{form}(\text{B-kink}; 1) - [E_{form}(\text{A-step}) + E_{form}(\text{B-step})]/2 . \quad (9)$$

Eqs. 8 and 9 combined to yield E_C(A-kink) and E_C(B-kink) separately, just as Eqs. 1 and 7 allow separate evaluation of E_{form}(A-step) and E_{form}(B-step). Below it is found that E_C(A-kink) and E_C(B-kink) are relatively small for Pb(111). Thus the assumption that these corner energies are independent of n_k is essentially harmless.

C) Kink formation energies - To this point, I have presented formulas for step-formation energies in terms of energies of kink-formation, but have not indicated how the latter may actually be calculated. For this purpose, imagine two stripe-islanded slabs. On the first, the stripes and valleys are *s* and *v* rows wide, on the other, they are *s-1* and *v+1* rows across. To proceed, in a supercell *2r* atoms long, parallel to the stripes and valleys, remove a block of *r* atoms from either the A- or the B-type island edge of the first slab and attach it to the step of the same character on the second (See Fig. 3). This forms four kinks, two per supercell on each of two slabs with identical kinked-stripe islands. Thus, if *r* is big enough that kink-kink interaction can be neglected, the kink-formation energy, E_{form}(kink), is given by

$$4E_{form}(\mathrm{kink}) = 2E_{kinked}(r,s,v) - 2r[E(s,v) + E(s-1,v+1)]\,, \qquad (10)$$

where $E_{kinked}(r,s,v)$ is the energy of one kinked, striped slab and $E(s,v)$ is the energy of a striped slab with unkinked stripe islands and valleys *s* and *v* rows wide. The factor, *2r*, on the right-hand side of Eq. 10, accounts for the supercell length.

V) Results -

A) Average step-formation energy - In Table II, I show GGA values of $\overline{E}_{form}$(step) for stripe islands on a 6-layer slab, and different SBZ samples. The calculations were performed using a rectangular $1 \times 4\sqrt{3}$ supercell containing 8 Pb atoms per layer (except in the uppermost one, of course), and for a $1 \times 5\sqrt{3}$ supercell with 10 Pb atoms per layer.

Note that a reasonably fine SBZ sample is required to obtain converged step-formation energies, and also that stripe-islands should be 4 or 5 atomic rows across to produce formation energies reliable to 10 meV/atom. From the information in Table II, one can conclude that the GGA value of $\overline{E}_{form}$(step) is 88 meV/atom, to within a percent or two.

To assess how well this T=0K result agrees with Arenhold, et al.'s STM-based formation *free energy,*[2] 86 meV/atom at T=440K, one needs to estimate the step-formation *entropies* that result from step wandering. Since, however, it is by forming kinks that steps wander, this estimate requires a knowledge of kink-formation energies. These are discussed in the following section.

B) Experimental kink formation energies[18] - By comparison to a lattice-gas result relating entropic step-wandering to kink-formation probability,[19] Arenhold, et al.[2] determine that 61 meV is needed to create a kink in an A-type step on Pb(111). B-steps are straighter, on average, in the STM images. Thus they are stiffer and must require a higher investment of energy per kink. Accordingly, Arenhold, et al. find a formation energy of 87 meV for a kink in a B-type step.

Though this qualitative inference is incontestable, i.e., that kink formation on B-steps is the more costly, Ref. 2's absolute kink-formation energies are not correct. The reason is that they are obtained by applying a relation between step stiffness and kink energy (cf. Eqs. 5 and 6 of Ref. 2) derived specifically for a square array of atoms, which Pb(111) is not. Use of the stiffness formula for square lattices underestimates the step stiffness for a given E_{form}(kink), by a factor of ~2, for example, when E_{form}(kink)=T, the temperature. Since stiffer steps correspond to larger values of E_{form}(kink), this means that Ref. 2's values of the A- and B-step kink-formation energies are deduced to be too large.

To obtain correct experimental kink-formation energies for Pb(111), one must apply a formula appropriate to a hexagonal lattice, e.g., that derived by Akutsu and Akutsu (AA).[20] One may translate the step stiffnesses measured by Arenhold *et al.*[2] into approximately correct experimental kink energies, still more simply by assuming the quench temperature, 440K, according to Ref. 2, to be low enough that only single kink excitations in the step edge are important. The step stiffness $\tilde{\beta}$ is then given by,[19]

$$\tilde{\beta} = \frac{2}{3}\left(\frac{k_B T}{a}\right) e^{\varepsilon / k_B T} , \qquad (11)$$

where the factor 2/3 embodies the effect of the hexagonal geometry of the outer atomic layer, a is the nearest-neighbor atomic spacing and $\varepsilon \equiv E_{\mathrm{form}}$(kink).

Comparing with the temperature dependence of the step stiffness in AA's triangular Ising model,[20] we expect this approximation to be accurate to approximately 25% for $k_B T < \varepsilon$, to 10% for $k_B T < 0.8\varepsilon$ and to 1% for $k_B T < 0.5\varepsilon$. Substituting Arenhold *et al.*'s measured stiffnesses for A and B-type steps, $\tilde{\beta}_A / h = 6.11 meV/$ Å^2 and $\tilde{\beta}_B / h = 15.25 meV$ into Eq. 11, using a=3.5Å, h=2.9Å [h is the ideal outer layer spacing of Pb(111)] and $k_B T$=*38 meV*, yields ε_A = 34 meV and ε_B = 69 meV. The deduced A-step kink energy is low enough – approximately equal to $k_B T$ – that the single kink approximation Eq. 11 is a concern. Indeed AA's results suggest that Eq. 11 overestimates $\tilde{\beta}$ by about 25% when $k_BT=\varepsilon$. Applying this 25% correction to Eq. 11, we arrive at the revised experimental estimate, $\varepsilon_A = 42$ meV.

C) Digression: Internal inconsistency of Ref. 2's kink formation energies - It is worth noting that even without realizing that an inappropriate stiffness formula was being used, the existence of an error in the kink energies of Ref. 2 could have been deduced from an internal inconsistency. Arenhold, et al. extracted the A- and B-step kink formation energies 61 and 87 meV from their step-stiffness observations *under the assumption that the corner energies,* E_C*(A-kink) and* E_C*(B-kink) are equal to 0.* But substituting these values into Eq. 9, together with their A- and B-step formation energies, 90.7 meV/atom and 81.9 meV/atom, one finds that E_C(A-kink)+E_C(B-kink)=62 meV, not 0. Thus, assuming that the corner energies vanish leads to a contradiction, namely that they do not.

D) Experimental step-formation energies[18] - To convert Arenhold *et al.*'s step free energies per length, f, into T=0K step formation energies, $e \equiv E_{\text{form}}$(step), one may again use a single-kink-excitation approximation, which in this case takes the form,

$$f(T) = e - \frac{k_B T}{a} \ln(1 + 2e^{-\varepsilon/k_B T}) \quad . \qquad (12)$$

Comparing this approximation to AA's results for the triangular lattice, one concludes that it is accurate to better than 10% for $k_BT < \varepsilon$. Substituting ε_A=42meV and ε_B=69 meV into Eq. 12, as well as the measured step free energies, f_A=91 meV/

atom and f_B = 82 meV/atom, yields the T=0K step formation energies, E_{form}(A-step) = 110 meV/atom and E_{form}(B-step) = 93 meV/atom. These are the experimental values that should be compared to the DFT results. Note that the T=0K ratio E_{form}(A-step)/E_{form}(B-step) = 1.19. This is appreciably larger than the 440K ratio of free energies, 1.11 because of the relative ease of A-step wandering.

E) GGA step and kink formation energies for Pb(111) - The challenge in computing surface, step- and kink-formation energies is to arrive at results relatively free of finite-size error, whether quantum or strain-field induced. In the case of surface energies, the model slab must be thick enough. For average step-formation energies, the stripe islands on the slabs must be sufficiently wide, as must the valleys between them. To obtain kink-formation energies, additionally, the distance between neighboring kinks must be adequately large.

Ideally, one would know the asymptotic behavior of the inter-surface interaction across a slab, of the inter-step interaction across stripes and valleys, and of the kink-kink interaction. That would allow subtraction of the leading finite-size errors. Without such knowledge, but with access to ever-increasing computer power, the alternative of choice is the "brute-force" approach, increasing all size parameters until finite-size errors in the energies of interest are acceptable. The worst case is the computation of kink energies, because it requires the unit cell to be big in all three dimensions. I report kink-formation energies here based on total energies of >500-atom unit cells, and at that the results (see Table III) are not converged with respect to stripe-island-width to better than ~5 meV, or ~10% of the absolute kink-formation energies. On the other hand -- and this result is representative -- the computed *difference* between kink-formation energies for A- and B-steps is converged to better than 1 meV. This reflects a very desirable error cancellation, and suggests the greater reliability of any result that can be represented as a difference between quantities computed for A- and B-type steps.

That said, in what follows I discuss GGA results for step- and kink-formation energies uniquely drawn from calculations for stripe islands 6 rows across separated by valleys 4 atomic rows wide. The use of the wider islands is preferred for the sake of deriving corner formation energies from kinks with n_k=2, as in Fig. 2.

As reported in Table III, the values of E_{form}(A-kink;1) and E_{form}(B-kink;1) computed via Eq. 10 with s=6 and v=4 are 41 and 60 meV. To compute E_{form}(A-kink;1) – E_{form}(B-kink;1), I evaluate the energy needed to remove four atoms from the first row and then three more from the second row of the A- as against the B-type edge of a 6-row stripe island in an $8 \times 5\sqrt{3}$ supercell (cf. Fig. 2).

The result is that

$$E_{form}(\text{A-kink};2) - E_{form}(\text{B-kink};2) = -52 \text{ meV} \quad , \tag{13}$$

while,

$$2[E_{form}(\text{A-kink};1) - E_{form}(\text{B-kink};1)] = -39 \text{ meV} \quad . \tag{14}$$

According to Eq. 8, this means that

$$E_C(\text{A-kink}) - E_C(\text{B-kink}) = 13 \text{ meV} \quad , \tag{15}$$

while Eq. 7 implies that

$$E_{form}(\text{A-step}) - E_{form}(\text{B-step}) = 22 \text{ meV/atom} \quad . \tag{16}$$

To proceed, recall (cf. Table II) that the average of A- and B-step formation energies is 86 meV for the *s*=6, *v*=4 stripe island. Thus Eq. 16 implies E_{form}(A-step) = 97 meV/atom, while E_{form}(B-step) = 75 meV/atom.

VI) Comparison of theory and experiment -

A) Theoretical vs. experimental step-formation energies - These *ab-initio* step-formation energies appear to be quite a bit smaller than the corresponding experimental results (extrapolated to T=0K), 110 and 93 meV/atom. On the other hand, the experimental step-formation energies are determined in Ref. 2 only to within a factor of the rather poorly known Pb(111) surface energy. If the surface energy is, e.g., assumed to take the GGA value of 35 meV/Å^2 instead of the 38 meV/Å^2 that Arenhold, et al. draw from early, sessile-drop measurements, then the experimental step-formation energies would be 101 and 86 meV/atom for A- and B-type steps, in better agreement with the present calculations.

A less ambiguous test of the *ab-initio* results is to compare calculated and experimental step-formation energy *ratios*, since the Pb(111) surface energy then factors out. The GGA result for E_{form}(A-step)/E_{form}(B-step) is 1.29, is in fair agreement with the experimental T=0K ratio of 1.19. The comparison might be better if the calculations were redone using larger unit cells, so that kinks with n_k >2 could be used to compute corner formation energies more accurately.

B) Theoretical vs. experimental kink-formation energies - In Sec. VB, reexamination of the relation between step stiffness and kink-formation energies led to revised experimental kink-formation energies, namely, E_{form}(A-kink) = 42 meV and E_{form}(B-kink) = 69 meV. As in the case of step-formation energies, these results are known only as well as the Pb(111) surface energy, to which they are scaled.

Thus if the surface energy were 35 instead of 38 meV, the formation of kinks on A- and B-steps would instead cost 39 and 64 meV. These results are in rather good agreement with the kink formation energies computed for a stripe island 6 rows across (cf. Table III), 41 and 60 meV.

C) Should one assume that corner formation energies vanish? - Finally, it should be recalled that the formulas used above as a standard for deriving kink-formation energies from stiffness data, those of Akutsu and Akutsu, Ref. 20, are based on the assumption of vanishing corner-formation energies. Whether this assumption is a good one, for Pb(111), is tested by Eqs. 9 and 15.

Substituting the average step formation energy, 86 meV, and the calculated n_k=1 kink formation energies into Eq. 9, one obtains

$$E_C(\text{A-kink}) + E_C(\text{B-kink}) = 15 \text{ meV} . \tag{17}$$

Combining Eqs. 15 and 17, then yields E_C(A-kink) = 14 meV and E_C(B-kink) = 1 meV. For the B-type step, the assumption of vanishing corner formation energy is evidently very good. But for the A-type step, corner-formation accounts for about 1/3 the energy cost of forming a kink of length n_k=1. This suggests that elaborating on Ref. 20 to include a corner-energy contribution would provide an improved estimate of the A-step-stiffness as a function of kink-formation energy.

VII) Lessons drawn from the present work - Important lessons should be drawn from this study of step- and kink-formation on Pb(111):

a) Because steps and kinks are geometrically related, it is a mistake to view step- and kink-formation energies in isolation. The two types of formation energy are related, and their inter-comparison can signal error in the analysis of experimental information.

b) Care is essential in assuming that formulae valid for one surface symmetry extend to another.

c) GGA provides a reasonably accurate description of the defect energetics of Pb. This result, together with similar conclusions[16] for Cu suggest that GGA studies of Pb wetting of Cu, i.e., in solder joint formation, are likely to produce information of value.

d) Information on the asymptotics of kinks and step interactions would be of considerable value in eliminating leading finite-size effects in the computation of formation energetics, thereby allowing the calculations to become smaller and more efficient.

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droplet might be expected to move to the interior if they are of an active species or to desorb if they are not. A direct test of this idea would be welcome.

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Table Captions -

I) GGA surface energy (in meV/Å^2) of Pb(111) vs. SBZ sample and number of slab layers. The SBZ sample corresponds to a $1 \times 4\sqrt{3}$ supercell, and is specified as $n_x \times n_y$, referring to the number of equally spaced points in the x- and y-directions.

II) GGA average step-formation energy, $\overline{E}_{form}$(step), in meV/atom, on 6-layer Pb(111) slabs, for stripe islands *s* atomic rows across and valleys between them *v* rows wide. The SBZ sample used is specified by $n_x \times n_y$, referring to the number of equally spaced points in the x- and y-directions.

III) Formation energies for kinks in A- and B-type stripe-island edges, tabulated in meV, in the columns headed "A" and "B," for various supercells, island widths, *s*, valley widths *v*, and SBZ samples. In each case atoms are *removed* from the stripe island of width s to form a kink pair, so at its narrowest the kinked island is only *s*-1 atomic rows across.

Figure Captions -

1. A stripe island, s=6 atom-rows wide, with kinks on its A-type edge. Upper-layer Pb atoms are darkened for clarity.

2. A stripe island, s=6 atom-rows wide, with n_k=2 kinks on its A-type edge. The island is separated by a valley v=4 rows wide from the next one, as indicated. If the atoms labelled b are removed and used to fill in the indentation on the A-step, then one has created an analogous double kink pair and indentation on the B-step side of the island. The energy cost of this operation per repeated cell is $2[E_{\text{form}}(\text{A-kink};2)-E_{\text{form}}(\text{B-kink};2)]$. The $8 \times 5\sqrt{3}$ supercell used in the kink-formation energy computation is indicated by the dotted rectangle. Upper-layer Pb atoms are darkened for clarity.

3. Illustration (with s=4 and v=4) of the method by which kink energies are calculated. Removing the atoms labeled "R" from the 4-row-wide stripe-island in panel a) and adding them as atoms "A" to the 3-row stripe island in panel b) creates two identical kinked stripe islands, each of which has two kinks per unit cell. Upper-layer Pb atoms are darkened for clarity.

Table I:

	4-lyrs	5-lyrs	6-lyrs	7-lyrs	8-lyrs
8×1	29	36	33	38	35
18×3	32	39	35	38	35
24×4	31	38	34	36	35

Table II:

supercell	s	v	**k**-sample	$\overline{E}_{form}$
$1\times4\sqrt{3}$	4	4	18x3	76
$1\times4\sqrt{3}$	4	4	24x4	88
$1\times4\sqrt{3}$	4	4	36x6	88
$1\times4\sqrt{3}$	3	5	24x4	103
$1\times4\sqrt{3}$	5	3	24x4	90
$1\times5\sqrt{3}$	4	6	32x4	87
$1\times5\sqrt{3}$	5	5	32x4	89
$1\times5\sqrt{3}$	6	4	32x4	86

Table III:

supercell	s	v	**k**-sample	A	B
$8\times 5\sqrt{3}$	5	5	4×4	46	65
$8\times 5\sqrt{3}$	6	4	4×4	41	60

Fig. 1

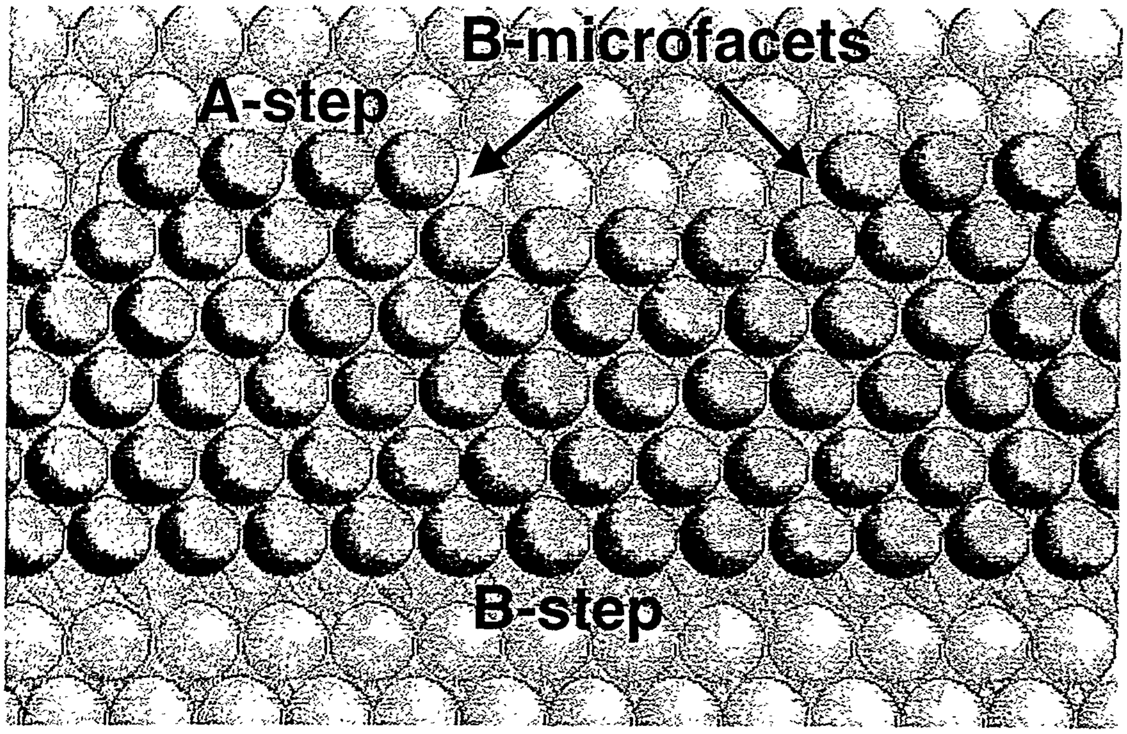
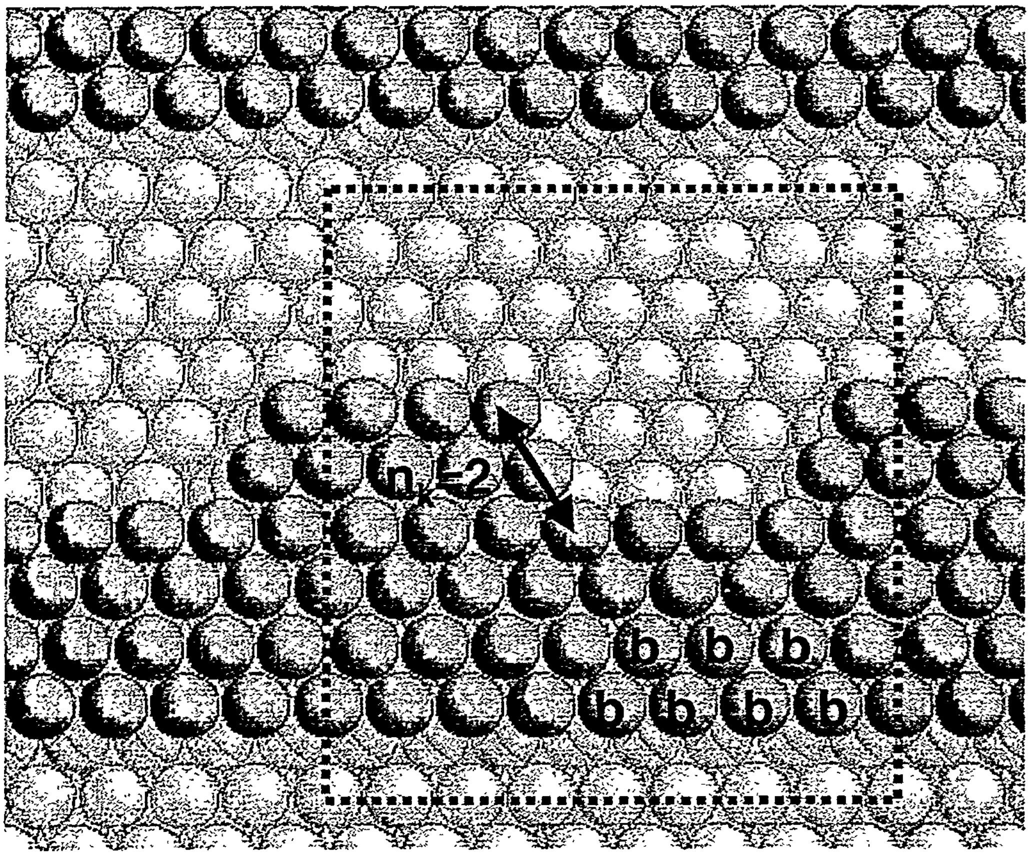


Fig. 2



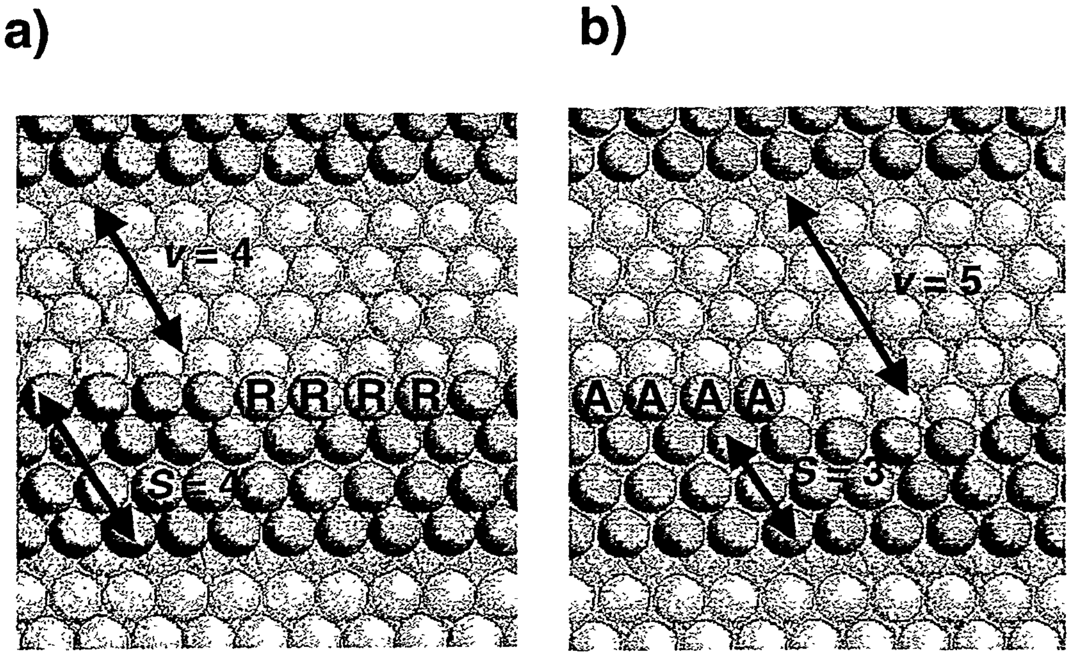


Fig. 3