Restored quantum size effects of Pb overlayers at high coverages.

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Abstract

Abnormally large stability of Pb nanostructures grown on metallic or semiconductor substrates has been observed even for heights of about 30 monolayers. Using both density functional theory calculations and analytical models, we demonstrate that the stability at even higher coverages ($N > 30$ MLs) is supported by an extra second quantum beat pattern in the energetics of the metal film as a function of the number of atomic layers. This pattern is triggered by the butterfly-like shape of the Fermi surface of lead in the (111) direction and supports the detection of stable magic islands of higher heights than measured up to now.

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The literature of the last twenty years presents many examples of new structures of nanometer scale, showing a different behaviour from the bulk due to quantum size effects (QSE's). Oscillations of quantum origin have been observed in the stability of atomic clusters [1] and later in nanowires [2–4]. As a result of the electronic confinement perpendicular to the substrate, QSE's show up during the growth of metallic thin films [5–10], when the thickness is comparable with the Fermi wavelength λ_F. Pb nanoislands over Cu(111) [11] or Si(111) [12] have revealed their preference for bi-layer growth in the [1 1 1] orientation. The origin of the "magic" height selection is easy to understand qualitatively with a simple picture of electrons confined in a potential well [13, 14]. When the energy of the films is displayed in terms of the number of MLs a modulated pattern or quantum beat structure is obtained, as the interlayer spacing is approximately $3/4\lambda_F$. Nevertheless, a quantitative agreement with the measured magic heights requires more sophisticated models.[15, 16] In these works a single value of the Fermi wave vector of Pb is considered.

The quantum oscillations of the physical properties of nanostructures decay in amplitude as their size increases, but an open general question is the convergence of this behavior towards the bulk. Pb is certainly a suitable candidate to check this point. In this paper we explore larger sizes (up to 60 MLs) of Pb thin films than usually considered in the literature by using the Density Functional Theory (DFT) and including the atomic structure. To study the stability of the films we have calculated the energy as a function of the number of Pb MLs. Our main ab-initio result is displayed in Fig. 2. We find that the oscillatory part of the energy as a function of the number of ML's has a second quantum beat structure that emerges from the nesting of two Pb Fermi wave vectors, as we will explain later. This second pattern affects considerabily the amplitude of these oscillations and explains the stability up to the calculated thickness of 60 MLs. We have been able to fit recent measurements up to 35 MLs [10] with a more sophisticated model that assumes two k_F values. Nevertheless, the effects of this second beat pattern emerge clearly just close to this thickness, so for a more extensive comparison, experiments for even higher coverages would be helpful.

Extra modulations or quantum beats given by extra nestings of the Fermi surface have been shown in other context, such as sandwiched Co magnetic layers with a nonmagnetic Cu spacer [17–20]. Both theoretical and experimental works, discussed at length the role of the second Cu wave vector nesting on the magnetic coupling between the sandwiched magnetic layers. However, the role of a second wave vector nesting on the stability during the growth

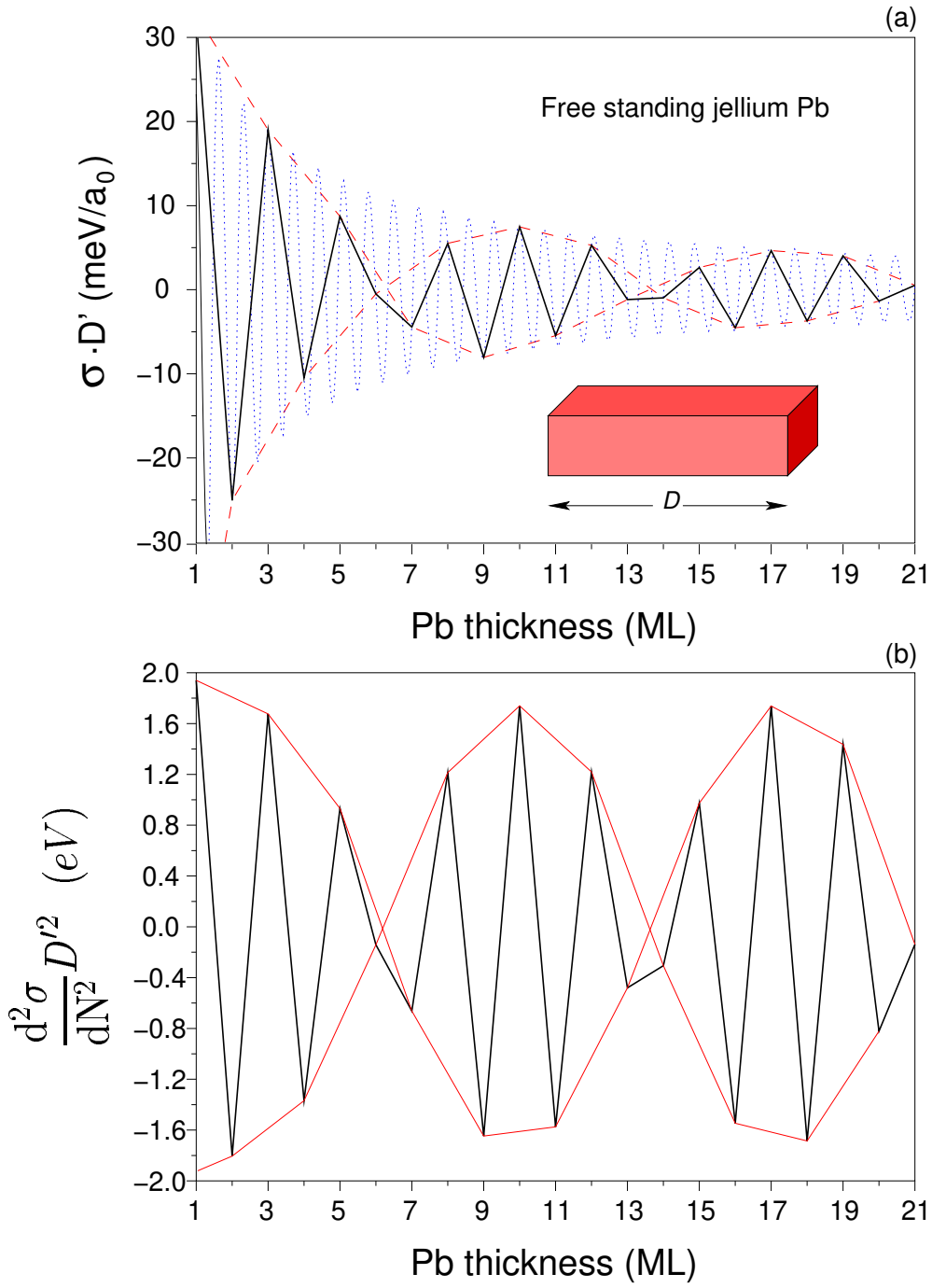

FIG. 1: (*color on line)* (a) Oscillating part of the total energy per surface area(σ) multiplied by the Pb slab effective thickness D' for a free standing Pb, and calculated by means of self-consistent jellium calculations [15]. The dotted line is a function of the continuous thickness, and the full line connects the values of completed MLs. The dashed lines guide the eye to show the (first) beat pattern. (b) Second derivative of σ multiplied by the square of the effective thickness (black line) and its envelope function (blue line).

of layers has not been addressed yet.

Let us first summarise the main features for Pb islands, successfully modeled with the uniform jellium model in previous works [15, 16]. The oscillating part of the energy as a function of the Pb thickness is given in Fig. 1(a) with full line. The minima of the curve correspond to the theoretically stable islands. Alternatively, one can look at (minus) the second derivative of the energy versus the thickness, in terms of number of ML's, N, as shown in Fig. 1(b). The valleys are associated with the most stable sizes [9, 10], as also studied in wires and clusters [21]. The second derivative has been multiplied by the square of the effective thickness [16] (D'^2) to show the damping factor of the amplitude.

These oscillations and their decay using the jellium model assume implicitly only one Fermi wavelength, i.e. the Fermi surface is a circle in the directions perpendicular to the surface film. In this work we address the question concerning stability at larger thicknesses ($N > 30$ MLs) of the Pb slabs, when we allow for a second critical spanning vector of the Fermi surface. In the context of the present investigation, the second Fermi wavelength arises because the Fermi surface in the (111) direction is not perfectly circular but has a butterfly shape [11, 22], as sketched in the inset of Fig. 3.

Jellium calculations describe the amplitude of the oscillations and their phase for a spherical Fermi surface. Therefore, in order to analyse the effect of the crystal structure with a realistic Fermi surface we have calculated with DFT ab-initio methods, the energy as a function of thickness for the free standing Pb slabs grown in the (111) direction. The calculations have been done with the VASP code [23] by using the generalized gradient approximation (GGA) [24] for the exchange-correlation potential and the projector augmented-wave method (PAW) [25]. Details on our calculation are given in Ref. [26]. We have assumed bulk distances between atoms [27]. For our purpose, it is unnecesary to relax the atomic positions because self-compression effects at the surface produce negligible changes in the energy [28]. Stress at the interface or interaction with the substrate produce a shift on the oscillating structure or slight differences afecting only very few ML thickness, but they do not change the qualitative behaviour of the oscillations, therefore we neglet the substrate in this study [15]. As we are interested in the stability of the slabs, we have calculated first the total energy as a function of the number of atomic layers N up to $N = 60$, and then we have evaluated the second derivatives of the energy versus the thickness as done before in Fig. 1 (b). The result is displayed in Fig. 2.

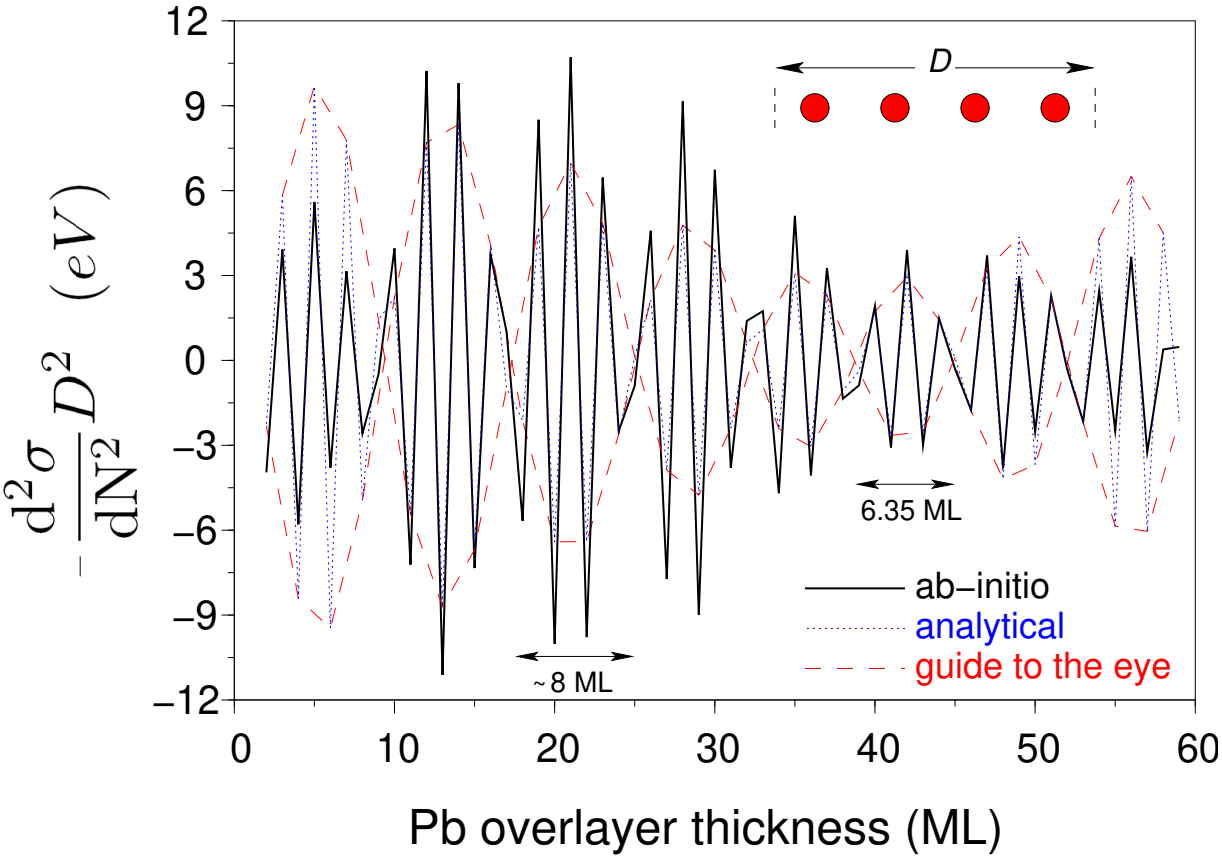

FIG. 2: *(Color on line)* Second derivative of the energy per surface atom times the square of the Pb slab thickness versus the number of ML's (continuous line). The dotted blue line is the analytical curve obtained with two values of the Fermi wavelength $\lambda_1 = 7.472a_0$ and $\lambda_2 = 7.538a_0$ with weights 0.72 and 1.28 respectively. The dashed line is its envelope function.

For small thickness ($N < 30$) the structure is similar to Fig. 1, so there is no contradiction with previous simple models. However, our central predictions are obtained when looking at the periods and decay of the oscillations at larger thickness. The amplitude of the oscillations in the $N = 1 - 40$ range decay, while for the jellium data it remains constant, i.e., the ab-initio results have stronger damping than the jellium results. Nevertheless, for sizes larger than 40 ML the amplitude remains constant. To our knowledge, experiments have not explored distances beyond this thickness, bur our results indicate that oscillations would survive for larger sizes than explored currently up to now.

In addition, a progressive shortening of the beat periods for large thicknesses ($N > 30$) is observed, with a non-negligible period change between N=33 and N=39 with a value of 6.35 ML.

This behaviour is reproduced analitically with a simple description as the interference of two sinusoidal functions

$$\sigma_{osc} * D'^2(N) = A_1 \sin(2k_1(dN + \delta_0)) + A_2 \sin(2k_2(dN + \delta_0)) \quad (1)$$

where k_1 and k_2 are the two nesting Fermi wave vectors in the [111] direction (see sketch in Fig. 3), A_1 and A_2 are their corresponding weights, δ_0 is a surface shift that accounts for the wavefunction spill out at the slab walls, N is the number of atomic layers and d is the interlayer spacing in the (111) direction. The agreement between the ab-initio calculation and the analytical model (dotted line in Fig. 2) is excellent. In fact, the key point is that the calculations can not be fitted by using only one Fermi wave vector. On the contrary, one is enough to fit the results of Fig. 1(b). In summary, an extra nesting of the Fermi vectors provides clearly the mechanism that stabilises the Pb slab.

To analyse this mechanism we plot Eq. 1 for $A_1 = A_2 = 0.5$ in Fig 3. The energy oscillations have beats every ≈ 8 ML's, as it is known, but with a new modulation and the second quantum beat at 29 ML's. The absence of a clear second quantum beat in Fig. 2 is because $A_1 \neq A_2$. It must be noticed that the position of the second quantum beat is inversely proportional to the difference of the wavelengths, so its determination is very sensitive to the input parameters.[29] The Fermi wave length of the vectors used in the Fig. 3 are very close to the free electron λ_F and to the values found in the literature for Pb ($\lambda_1 = 7.50\ au$ and $\lambda_2 = 7.59\ au$ with an experimental error around $0.1\ au$ [11]). Nevertheless, these values fit the experimental results of Pb/Si(111) [10]. Although in the experiments the largest thickness measured hardly reaches to the second quantum beat position, our fitting reproduces completely the measuered features. Again, by using only one Fermi wave vector the agreement is worse. An additional hint of the double quantum beat comes out by the even-even successive regions intercalated in the even-odd alternation pattern of Fig. 3. This even-even characteristic appears about $N = 29$. It seems to go unnoticed in the already published experimental paper [10], where they have measured with X-ray diffraction up to $N \approx 35$ MLs, and therefore with lower resolution this even-even pattern emerges just in the borderline. Further experimental work is encouraged in order to look for such a second quantum beat pattern.

The decay of the amplitude of the energy smear out the energy oscillations at large thickness, so the size selection should disappear in experiments. Nevertheless, if this is

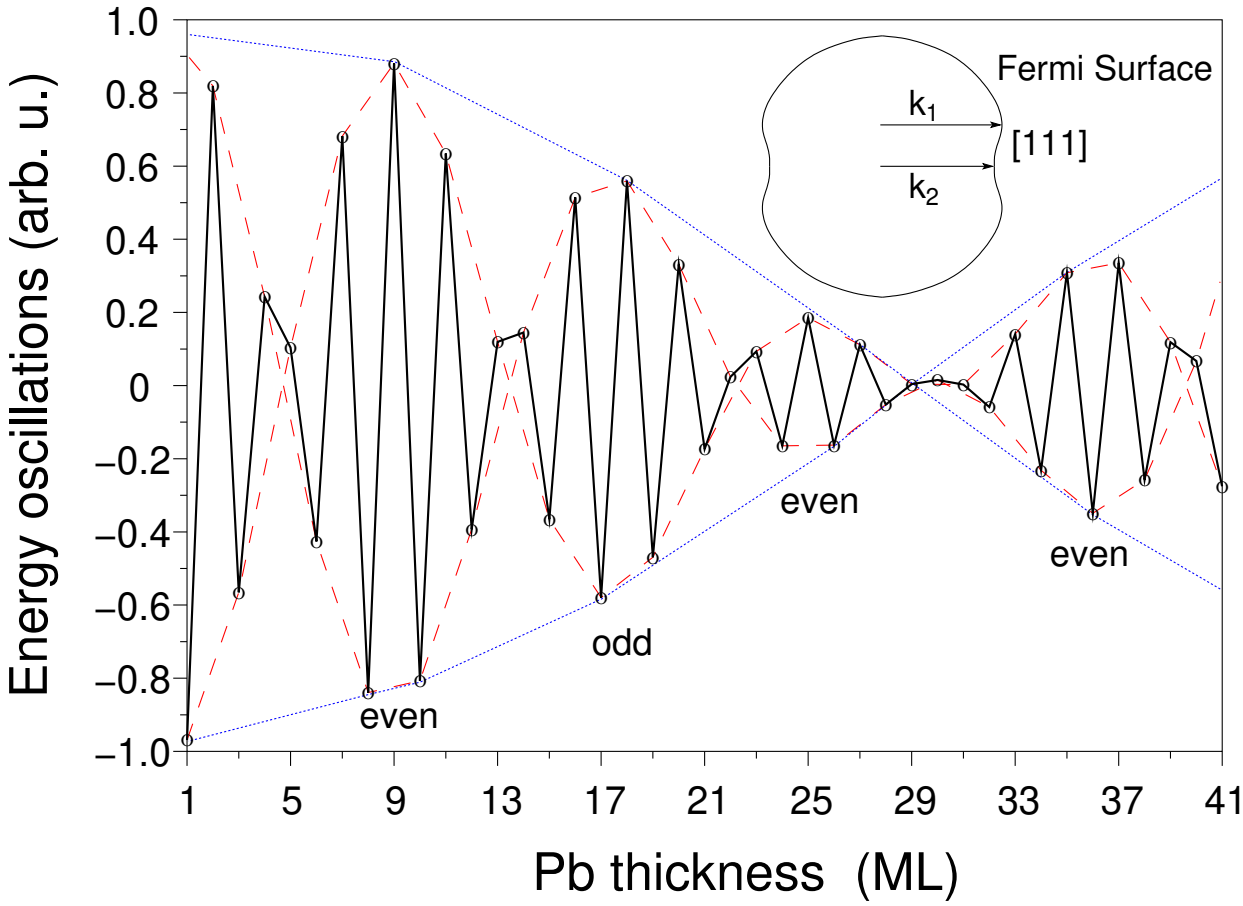

FIG. 3: Modulated oscillatory pattern of the energy obtained by superposition of two oscillations following Eq. (1) and using the Fermi wavelength values $\lambda_1 = 7.40$ *a.u.* and $\lambda_2 = 7.48$ *a.u.*, that are obtained by fitting the experimental curve [10, 29]. The dashed line is the envelope of the first beat pattern and the dotted line is the envelope of the second modulation, the so-called second beat pattern. The inset is a sketch of the cross-section of the Fermi surface of Pb, showing both nesting vectors in (111) direction.

accompanied by the second quantum modulation we predict that they must emerge again at larger sizes. The observation of this effect in the stability is still an open question because the experiments did not go beyond that size. For example, the same effect of the non-spherical shape of the Fermi surface has been also pointed out to influence the magnetic interlayer coupling in multilayers, being important upto distances as long as 100 ML's [30, 31]. This indicates that the detection of high stability with larger sizes is possible in experiments.

In conclusion, both model and density functional calculations show that there is a reentrance of QSE's and ensuing new features in the stability patterns at sizes substantially

larger than the sizes studied up to now (or in the borderline). This suggests that the nesting with a second wave vector of the Fermi surface provides a mechanism to understand the stability at the large sizes in the growth of Pb layers. This second quantum beat claims for a new interpretation of experiments, as well as for new measurements at higher Pb coverages to shed light about the existence of the second quantum modulation and its role in the self-selection and self-assembly processes.

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