Atomic-Scale Wear in UHV: Connection Between AFM Induced-Abrasion and Debris Recrystallization

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Abstract Recent Ultrahigh Vacuum (UHV) scratching Atomic Force Microscopy (AFM) experiments showed the formation of regular patterns composed by small atomic clusters or mounds located around the surfaces being scanned. The formation of such structures has been theoretically reproduced and explained as, mainly produced by the flux of adatoms generated by the AFM tip stripping off adatoms during the continuous passage of the probe tip on the analysed surface. The homoepitaxy growth process on Aluminium was used for the identification of the direct connection between the adatoms flux due to wear mechanisms and the self-assembled growth processes. Such theoretical results were based on the general assumption that surface diffusion is the dominant transport mechanism of mass, and a nonequilibrium thermodynamics framework for the self-organized growth process has been developed showing evidence of the direct connection between the growth structures due to atomic debris formation and the flux of the atomic debris due to the activated wear mechanisms. In this article, we revisit the preview model giving new contributions to it and, in turn, we suggest that the improved model as proposed in this article can be supported with a new class of experiments for the quantification of the wear rates occurring for AFM probe tips in UHV conditions. In turn, a general review on activated wear mechanisms is briefly discussed.

Keywords Abrasive wear · AFM · Aluminium · Contact mechanics · Wear mechanisms

1 Introduction

On macroscale, wear is usually measured either by removing the specimen at intervals and weighing or measuring it, or by continuously measuring its position with an electrical or mechanical transducer and deducing the wear from its changes in dimensions [1, 2]. In traditional force-based models, under sliding conditions wear depends principally on the distance slid, normal load, real area of contact, real contact pressure, sliding speed and testing time. In addition, some other variables must be considered and monitored in wear testing, such as temperature, thermally activated chemical processes, and in lubricated systems, lubricant viscosity. All such variables affect the wear mechanism that can be mainly quantified measuring the mean wear *observable*: the wear volume. For example, abrasive wear volume is quantified using the Archard formula [3] (later extended by Bhushan to adhesive wear, [4]), or the formula Khrushchev–Babichev formula [5], or the Rabinowitz formula [6, 7]. For their simplicity, such formulas highlight the main variables influencing sliding wear. In addition, they yield a method for describing the severity of wear, by means of a wear coefficient, which is valuable. Generally, such formulas can be used for a wide range of materials and the quantification of wear mechanisms measuring wear volume has become the *paradigm* of wear measurements. The common assumption of such formulas is based on the normal load, i.e. that contact between the two surfaces will occur where asperities touch, and that the true area of contact will be equal to the sum of the individual asperity contact areas. This area will be closely proportional to the normal load, and under most conditions, the local deformation of the asperities will be plastic. For eg., Archard describes the wear volume V of macroscopic plastic contact with multiple asperities to be

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proportional to the load force F_N and sliding distance L and inversely proportional to hardness H in the following manner:

$$V = k_w \frac{F_N L}{H} \quad (1)$$

where k_w is an adimensional wear coefficient. An alternative assumption has been made recently revealing the connection between wear and energy dissipation, in this case the friction energy is dissipated mainly in three mechanisms that correspond to three different observables: rise temperature, entropy change associated with material transformation located at the surface region and wear particles generation [8]. At the nanoscale, where wear mechanisms can be studied limited to single-asperity nanoscale contacts using Scanning Probe Microscopy (SPM) family techniques [9–11], careful studies have theoretically predicted, [12–15], and experimentally shown, [16–18], that wear can occur in a smooth and gradual manner. In such experiments, the wear tests are made as follows: a probe tip scans repeatedly a small area of the surface of interest. As in the macroscale, in a common sample-tip configuration, the wear is generally addressed to the material with a lower hardness coefficient. For simplicity, here we consider the sample wear, whilst tip wearing is briefly discussed in the Sect. 4. An alternative formula has been introduced on nanoscale, where the wear volume can be quantified using the following Arrhenius-like formula [12, 14]:

$$V = \Omega n_w \quad \text{or} \quad V = \Omega n \Gamma t \quad \text{where} \quad \Gamma = \nu \exp \left[-\frac{\varepsilon_{\text{eff}}}{k_B T} \right] \quad (2)$$

where Ω is the mean debris volume, n is the total number of surface atoms involved in the stressing passage of the Atomic Force Microscopy (AFM) tip during the scratch test, n_w is the effective number of stripped off atoms, t is the total residence time of contact between the sample atoms and the tip during the scratching test (see Appendix), Γ is the wear rate where ε_{eff} is the activation energy for stripping off an atom from its primitive location, ν is an attempt frequency, generally falling in the phononic vibration range, k_B is the Boltzmann constant and T the temperature. It must be noted that Eq. 2 is a multiscale expression depending on the mean dimension of the debris size, where the mean debris volume must be intended in statistical sense as the distribution function of the 3D spatial dimension of debris produced during the interface contact, therefore, Eq. 2 can be generalized as $V = n_w \int \Omega p(\Omega) d\Omega$, where $p(\Omega)$ is the distribution density of debris size volume. For simplicity, on atomic scale Ω can be identified with the atomic volume. One experimental problem in low wear regime is the exact definition of n , in the Eq. 2, i.e. the dimension of the sample atoms directly

interested to possible wearing due to the stressing passage of the probe tip. This quantity also defines the percentage portion of worn material with respect to the entire undamaged sample. On nanoscale, n can be located to the tip-sample contact, but on a meso- and macroscale the reasonable identification of such value could be quite different generating possible ambiguity due to large range propagation of surface damages through bulk due, for example, to fracture dynamics. Wear volume calculated using Eq. 2 resumes a fundamental statement of a recent model based on the Kramers picture of the transition rate theory introduced to describe atomic wear mechanisms [12, 14, 15]. In this theory, the basic wear mechanisms are described in terms of activation energies due to stressing contact between the two surfaces in an analogous manner to chemical–mechanical reactions between solids. The decoupling of normal force from shearing force on the abrasive or adhesive-wear mechanism has also been proposed and actually waiting for an experimental validation. Single-asperity nanoscale contacts give the possibility to observe new processes dominating the occurrence of basic wear mechanisms such as atom-by-atom processes [16–18]. An activated-like expression has been used by Gostmann and Lantz to describe the atom-by-atom wear process generated by a conical tip during the sliding motion [16]. Gostmann and Lantz also found that the classical wear law of Archard does not hold on nanoscale being unable to correctly quantify wear rates and volumes. In both the Archard formula and the activated volume formula, wear volume is still the main observable to be measured, and the quantification of the mass loss is the main effort to address the quantification of the occurrence of wear. Nevertheless, a new observable for the investigation of wear could be introduced if the recent results obtained in Recent Ultra-high Vacuum (UHV) conditions are confirmed by new similar experiments. Nanowear experiments performed in UHV conditions showed that in scratching AFM-based tests the areas surrounding the scratched area present the formation of regular atomic clusters (ripples) or coarse-grained mounds structures composed of atomic debris produced by the scanning AFM tip [19, 20]. Such experiments were performed on ionic crystals (NaCl or KBr) and Aluminium (Al). Two different theoretical explanations of such ripple structures have been recently proposed [21, 22]. Following what was presented in the Ref. [21], in this article, we enforce the thermodynamics approach previously suggested for the comprehension of some basic wear mechanisms looking at the surface growth patterns induced by the abrasive wearing AFM scratching tests for Al/Al(111) homoepitaxy, although our approach is rather general and it can be applied to the widest class of solid materials making few and appropriate modifications. We describe the time evolution of the portion of the sample surface $z = h_w(x, y, t)$ undergoing wear abrasion, and the portion of the sample surface $z = h_g(x, y, t)$ that

experiences the growth process, where the final pattern of h_g obeys the relation $V = \Omega n_w = \int_0^{L_x} \int_0^{L_y} h_g(x, y) dx dy$, where the integral is calculated on an area $[0, L_x] \times [0, L_y]$ surrounding the scratched worn area. The abrasion-growth process can be described as follows: the growing structures on h_g are formed via surface diffusion by the adatoms stripped off by the AFM tip, which are an indirect measure of the basic wear mechanisms, described by h_w . The adatoms are the debris produced during the tip-sample stressing contact and their ability to re-organize around the surrounding surface being worn is strongly dependent by their rate production, i.e. ultimately, by the rapidity of the activated wear mechanisms. The self-organised ordered growth structures described by the time evolution of h_g are a secondary effect of the wear processes described by the time evolution of h_w . In this article, further physical motivations for the connection between the damaging stressing wear process and the growth phenomena will be presented. This is particularly important because the quantification of wear volume is generally made at the end of the scratching test, on the contrary, a model suggesting appropriate rates for the occurrence of wear can help the interpretation of the experimentally measured direct time evolution of a wear abrasion process as it happens. One main implication of the direct connection between the rate of atomic debris production and the growth processes is that the wear volume, that corresponds to the scratched volume, is not the main observable identifying the wear processes. The new main *observable* in the UHV experiments is the specific growth process that in an indirect way gives the rate of debris production.

2 Surface Wear Rates in an AFM Scratching Test, Multistability and Activation Energy

In this section, some basic concepts involved in the ongoing description of activated wear mechanisms such as interface multistability, activation energy or activation

wear rate will be briefly introduced. Multistability could become a key for understanding the basic wear mechanisms on nanoscale. During the relative contact between two surfaces, at the atomic scale, the system is multistable: for example, a single atom is confined in a potential energy basin (interatomic potential) separated by large energy barriers, the atom stays in this basin for a very long time compared to a typical vibrational period before hopping to other basins. If the potential energy has multiple minima, that represent the metastable states, the atom can evolve through infrequent transitions from one metastable state to another (up to be stripped off). In addition, multistable systems aid describing physical systems dominated by infrequent events, where information about the waiting times at each state, the transition mechanism leading to other states, and their relative probabilities are essential for understanding and predicting their behaviour. Analogically, the description of basic wear mechanisms with a multistable system implies the knowledge of the rate of transition of barriers amongst the multistable states; this is equivalent to knowing the threshold conditions for the onset wear. A double-well potential system is a bistable system, which is also the easiest multistable system, where the crossing barrier is only one. In the last decade, a double-well potential has been used to describe the transition rates for atomic onset basic wear mechanisms where an atom is captured by a surface with respect to the other one [12], Fig. 1.

One legacy of double well is that the basic wear mechanisms on atomic scale can be described by a solid state rate reaction formalism between the atoms involved in the mechanical contact. Analogously to a chemical reaction, some bonds are broken in the reactants surfaces freeing some atoms forming new bonds in the product surfaces, we simply define the products as debris. Generally, reverse reactions can be denied. The rate of product formations depends on the stressing contact forces, and mechanical properties of the reactants surfaces, as Young

Fig. 1 Example of the double-well model involved in the wear process during the contact between a tip and aluminium sample surfaces. The tip approaches the sample surface, on the left, when the distance between the atoms of the two sharing surfaces is close to

intermolecular distance, on the right, the potential well is reduced by the stressing contact, $\delta\epsilon$, making it possible to drop the energy barrier, ϵ_{eff} , bonding the atom in the primitive potential basin

moduli, hardness, energy bond strength etc. Since, breaking bonds require energy and forming bonds release energy, the net energy of a chemical reaction will depend on the sum of energy absorbed and generated. A measure of the potential energy of a reaction is the Gibbs free energy $\Delta G = \Delta H - T\Delta S$, where G is the Gibbs free energy, H is the enthalpy, T is the temperature (here supposed constant) and S the entropy. Reaction environment plays a key role for the reactions, and generally complicate the reaction rates. It has been shown that in the case of reactions generated in UHV environments, the reduced mobility of the debris products makes it possible to study the eventual reorganization of debris in regular growth structure, giving an indirect measure of the rates of the debris formation during the wear process [21].

Let us consider two surfaces, S(ample) and T(ip), contacting each other as in Fig. 1, the two surfaces are characterized by some mechanical properties, such as Hardness, Young elastic modulus, that can be substantially different from the bulk values. Once on contact, the two surfaces share a common surface where friction and wear can take place. As an example, let us consider an abrasion mechanism, two surfaces characterized by different relative hardness $H_T \gg H_S$, so that the wear can be addressed only to the S surface, onset wear or low wear processes before gross wear take place can be described as a chemo-like process, where an activation energy must be reached by the atoms in the reactant with lower surface hardness therefore the following reaction could be written:

where n_w represents the atom number stripped off from one surface (generally the surface with the lower hardness value) and Γ is the reaction rate constant. The reactants S and T are specified by a certain atomic density, interatomic potentials, the temperature and the surface mechanical properties, including the load and shearing forces. The final state of S^* after the wearing contact also includes surface atoms mismatched by their stable positions. Such mismatching could involve wear rates for succeeding tip-sample contacts. The final state of the atom number n_w also describes the specific type of wear mechanism. On atomic scale, the distinction of the wear mechanisms that on macroscale are commonly recognized as abrasive- or adhesive-wear mechanisms, could be not so drastic. In the adhesive basic wear, described by the second expression in Eq. 3, the final state of the atom number can be localized on the wearing surface, for example, if the wearing surface is a T surface, the whole reaction described within the double-well potential, the n_w atoms move through the double-well potential dropping the energy

barrier, Fig. 1, and relocating themselves in a stable state, i.e. the second well. It is also assumed that Γ is expressed as Eq. 2, where Ω is an attempt frequency constant and ε_{eff} is an activation energy of the reaction which is equivalent to the potential barrier from the lower well. In agreement with Arrhenius-like thermally activated processes, included the Kramers rate, the activated wear rate, i.e. the probability that an atom is stripped off during the passage of a probe tip, is given by [13, 15]:

$$\Gamma_{i,j,k} = v(F) \exp\left\{-\left[\varepsilon_{i,j,k}^b - \delta\varepsilon^s\right]/k_B T\right\} \quad (4)$$

where $\Gamma_{i,j,k}$ is the single atomic probability to be stripped off during the contact with the AFM tip, the integers i,j,k denote the sites of the cubic lattices, ε^b its binding energy, $\delta\varepsilon^s$ represents the stress-induced deviation which is a function of the applied load and lateral force, Fig. 1, $v(F)$ is the attempt frequency, eventually dependent by the forces acting at the interface contact, k_B is Boltzmann's constant and T is the temperature. The stress-induced deviation is a combined effect of the compression and shear stresses and it lowers the energy barrier allowing the atoms to be stripped off from the substrates.

Alternatively, the Zhurkov–Arrhenius theory provides that the stress-induced deviation contains a volume activation term defined as the derivation of Gibbs free energy as a function of shear stress [16]. The volume activation term is derived using a thermodynamics rigorous definition, but, its functional dependence on the characteristic time scales involved during the tip-sample sliding contact still has not been outlined. However, both the approaches were able to quantify the threshold value for an onset atomic wearing around ~ 1 eV a front of a thermal energy of $\sim 10^{-2}$ eV [15], and confirmed by experiments on silicon tips wearing [17].

Such results can be rather surprising because the thermally activated processes play a key role for the rupture of atomic bonds. Although, tensile rupture of atomic bonds require a stress comparable to the Young's modulus, solids commonly present fracture ruptures at a much lower applied stress, approximately three order of magnitude lower. A somewhat similar and quite striking effect is the occurrence of failure even through the solid stressed below its experimental breaking threshold. A possible driving mechanism for this subcritical damaging process is thermal activation as supported by the idea that time of rupture follows an Arrhenius law with an energy barrier decreasing with increasing stress [12–17].

The role of thermally activated wear mechanisms could be clarified conducting specific experiments on the temperature dependence of wear rates, at the moment, this temperature dependence has not yet been demonstrated for atomic-scale wear. The wear mechanisms based on single

atom transition rates are very close to dissolution or low rate erosion of atoms from a surface. This is reasonable because dissolution or desorption are generally modelled as thermally activated processes. Another important role must be assigned to surface forces, first, the van der Waals forces. It must be noted that such forces have the effect of fluctuation noise on breaking atomic bonds. In the diffusion model proposed by the present author, van der Waals forces act analogously to thermal fluctuations as a noise, being approximately two orders of magnitude greater than thermal energy and strongly dependent on the tip-sample distance, van der Waals force should play a key role for the activation of wear rates. Future experiments may show the leading role of such fluctuations.

Since, knowing the Γ rate is impossible during the measurement of the wear-activated mechanisms when the scratch test takes place, the alternative proposed is to look at the fluxes of adatoms stripped off during the stressing passage of the probe tip [20]. It has been shown that such fluxes are deeply connected to growth structures generated by the adatoms moving along the sample surface. The growth of structures induced by the formation of debris in an UHV AFM scratching test can be schematized in the following steps: 1, formation of debris (atoms) induced by the AFM tip scratching the substrates; 2, the debris jump and diffuse around the worn area, this process depends on the environmental conditions; 3, the diffusion process induces nucleation of adatoms and 4, depending on the intensity and time function of the flux of adatoms, the nucleation process can lead to the formation of self-organized array of dots or mounds [21] (Fig. 2).

The AFM imaging recorded at the end of the scratching process suggests considering the whole process wear and growth as an *inverse problem*, i.e. it is more useful to look at the recording data of the surface growth process taking information from the abrasive wear process whilst studying the growing structures. Consequently, it could be possible to describe wear mechanisms (onset wear conditions, gross wear threshold transition, etc.) considering the growth

phenomena. We will try to demonstrate that such processes are essentially conditioned by the rate of production of the adatoms made available by the abrasive wear process for the nucleation and subsequent growth of regular patterns.

During the scratching test, the area stressed by the probe tip changes due to the abrasive test. For simplicity, we will consider that the probe tip is significantly harder than the sample, so that tip wearing can be neglected. As matter is removed, the z-component of the worn surface area can be expressed using the following relation:

$$\frac{\partial h_w(x, y, t)}{\partial t} = -\Omega \nabla j(x, y) = \Omega F_{\text{outgoing}}(x, y, t) \quad (5)$$

where the time evolution of the surface $h_w(x, y, t)$ is calculated on the scratched area, the debris current j is due to the stressing role of the probe tip and Ω is the atomic debris volume, and F_{outgoing} is the flux of the adatoms stripped off by the probe tip, diffusing along the sample surface. The evaluation of the surface abrasion, the current of adatoms, or the effective free energy change due to abrasion can be complicated and experimentally difficult to test. This is because the imaging of the scratched area and its surroundings are made immediately after the test, as a result, it is difficult to control in real time the time evolution of the abrasion previously produced. In [21], a derivation of the effective free energy as a function of the number of stripped off atoms during the scratch test has been performed.

The study of the surface growth processes of the atomic debris produced during the abrasion is an indirect method for the analysis of the basic wear mechanisms during the scratching. We shall show that the growth processes depend essentially on the adatom fluxes, and the different possible fluxes are directly connected to the activated wear mechanisms. All the quantities such as the surface current density j , the free energy, the chemical potential μ are unknown quantities, and it is practically impossible to determine them during the scratch test. On the contrary, it is possible to quantify the progressive incidence of the activated wear mechanisms by acquiring

Fig. 2 A schematic sketch of the specular abrasion-growth process occurring for Al substrates. I, the AFM tip scratches the sample surface during the contact, the debris is removed atom-by-atom, and hence, II, the atom stripped off diffuses on the surface growing in clustering structures or coarse-graining in mounds. The growing

structures observed depend on the surface energy landscapes that the atoms meet during the surface diffusion. The dimension of such structures depends on the diffusion constant D and the flux rate F (where F is an indirect measurement of the rate and efficiency of the activated wear mechanisms)

the image of a region surrounding the scratched area with the same scratching unworn AFM tip. As we will demonstrate, this is because the growth structures (small clusters or large mounds) are strongly dependent on the incidence of the adatomic debris flux induced by the scratching probe tip.

The functional form of the fluxes that will be presented below need to be commented. The flux as expressed by Eq. 5 is essentially identified by the gradient current, ∇j , nevertheless, the change of surface due to a net flux of adatoms should be in principle composed by two terms, one is the gradient current and a noise source, $\nabla j + \text{noise}$. In our case, where the net flux is small due to the stripped off processes triggered by the wear mechanisms, the two terms, the gradient current and the flux overlap, therefore the gradient current can be modelled by a noise-like function.

The flux of debris (adatoms) is a direct measurement of the efficiency of the wear process, and therefore, the structures that we observe at the end of the scratching test are an indirect measurement of the efficiency of the wear process. When the number of atoms stripped off during the scratch test, n_w , is known, the wear volume can be forwardly calculated as $V = \Omega n_w$. The flux is also a discontinuous function for low wear rate, mainly zero with the exception of stripping off events, with an order of magnitude of a single atom per i th contact point per residence time. In general, such function can be gathered by Eq. 5, once the wear rate via Γ and diffusion constant D are defined, which for surface diffusion at atomic scale is approximately 10^{-11} (m^2/s). We noted that for a range $F \approx 10^{-17} \div 10^{-12}$ (adatoms $\text{m}^{-2} \text{s}^{-1}$) the results of recrystallization growth described within the mean field nucleation theory do not change significantly. Amongst the possible noise-like functions for the adatom flux, two possible time functions have been suggested [21]. The choice is between a Poissonian-like production of independent pulse of adatoms (adatom-by-adatom) or a sigma function flux that considers the progressive nucleation of worn areas inside the scratched

volume. In the Poissonian case, the probability of stripping off an atom does not depend on by the previous stripped off atom, and such stripping events occur with an average rate, consequently, one possible functional form for the rate flux, $F_1(t)$ (expressed for unity of lattice cell), can be the shot-noise-like form as:

$$F_1(t) = \eta \sum_{m=\bar{m}}^M \delta(t - mt_{\text{res}}) \quad (6)$$

where $\eta \sim \Gamma A_p/a^2$ denotes the numerical density of adatoms produced during the AFM scratching, a is the lattice constant, $\bar{m}$ is a threshold value above which the wear process starts, M is the ratio between the total time of the scratch test and the residence time taken as an entire number, Mt_{res} is the duration of the scratching test. At any pulse, a number of η adatoms start to diffuse along the sample surface. Analogously, to Eq. 6 for the flux rate, it is possible to have a continuous flux rate given by the nucleation of wear domains during the progressive AFM scratching [23]:

$$F_2(t) = \eta(1 - \exp(-\Gamma t)) \text{ or } F_3(t) = \frac{\eta}{1 + \exp(-\Gamma t)} \quad (7)$$

where Γ and η are the same as in Eq. 7. A time function flux, as described in Eq. 7, is a typical example of a nucleation mechanism for progressive wear domains where the occurrence of progressive defects take place. It has been previously demonstrated that nucleation of defects provides a realistic mechanism for the growing of worn domains during gross wear when a critical threshold is reached, Fig. 3 [23]. It is interesting to note that the second expression in Eq. 7 is the well-known simple logistic map, that is a S-shaped curve strongly used for the study of growth of populations, as well as in a myriad of different fields [24].

In the next section, the surface growth induced by abrasive adatoms will be calculated using the mean field

Fig. 3 Example of nucleation of wear domain on the surface being worn by a stressing contact with harder tip. From left to right, once the first atom is stripped off, the surrounding atoms reorganize themselves reducing bonding strength due to the vacancy (as denoted

by the arrows), making possible further simultaneous debonding events due to tip stress with a progression that follows the flux as described by Eq. 7

nucleation Theory and with continuum methods in Sect. 4. The flux of adatoms generated during the probe tip scratch will be included in the equations expressing the surface growth and calculating the number cluster density

3 Debris Recrystallization Process Described by Mean Field Nucleation Theory

The recrystallization of adatom debris leads to two classes of growth structures, self-organized dots clusters (sometimes ripples structures) or mounds induced by coarse graining. Both such structures are conditioned by the surface diffusion constant and flux rate of arriving adatoms produced during the scratching test. The quantification of the number of the structures crystallizing on the surface is performed in this section using a simple model, depending on the surface diffusion constant and flux time function [25, 26]. Once the atoms are stripped off during the wearing, in the course of deposition, the atoms arriving from the gas phase with a rate F diffuse with rate D until they meet a second adatom and create a dimer. The Mean field nucleation theory (MFNT) and nonlocal MFNT are a powerful tool for extracting fundamental microscopic parameters such as diffusion barriers and adsorbate–adsorbate binding energies from island density data [26–29].

Let us consider the numerical density of the surface structures formed via surface diffusion by the adatom flux produced during the scratching test. We like to follow the nucleation process for a cluster structure with an average cluster–cluster distance l on a flat substrate in a stationary state. All clusters are assumed to be stable, i.e. neither dissociating nor diffusing. If the capture numbers can be calculated, the cluster density can be predicted with D as the only parameter. Conversely, D and thereby the adatom diffusion barrier, E_d , can be extracted from experimental cluster-density data. For freshly deposited adatoms, it takes about a time $t = l^2/D$ to migrate in a region of a linear dimension l . During this time interval, other adatoms are deposited to a density $n = Ft$, and the initial adatom has a probability nl^2 to meet another adatom during its migration. By assuming that the encounter causes the instantaneous nucleation, the encounter probability is the same as the nucleation probability per site. The latter is given by $(al^2)^2$ with a being the lattice constant, since there is a nucleus within a region of l^2 . The time evolution density quantification for such surface structures in the presence of a time-dependent rate flux can be written using a system of two relatively simple equations: the total number of growing clusters, $x(t)$ and the density of clusters of size 1 adatoms, $y(t)$. The time-dependent equations for the $x(t)$ (that can be considered the nucleation density, the aggregation of more

than two clusters is excluded) and $y(t)$, the system equations in dimensionless form are written as follows [21, 30]:

$$\dot{y}(t) = F(t) - Dx(t)y(t)(x(t) + 2y(t)) \quad (8)$$

$$\dot{x}(t) = Dy^2(t)[x(t) + y(t)] \quad (9)$$

where the rate flux of adatoms, $F(t)$, can assume the functional form as given by a shot-noise-like flux, Eq. 6 or by a sigma-like function, Eqs. 7, 8 and 9 are justified within a Smoluchowski model, i.e. assuming 1) a Brownian motion for the cluster of size 1 with diffusion constant D , whilst the mass > 1 are static and 2) irreversible aggregation, i.e. when an adatom contacts a cluster thus aggregates irreversibly to it forming a cluster with a larger mass $+1$. In addition, the capture numbers are considered equal to unity, and the capture number is defined as the probability per time and diffusivity unit for a random walker to be captured by a certain island. The fluxes depend on the activated wear processes, therefore, the formation of surface structures due to adatom debris is an indirect measure of the fundamental wear-activated mechanisms. The Eqs. 8 and 9 have been integrated using the two different fluxes, Eqs. 6 and 7, respectively, and the results are illustrated in Fig. 4.

Figure 4 illustrates the two possible regimes that occur in the surface growing structures and depending on the flux-type produced during the wear abrasion process. The two regimes differ because they are characterized by different surface morphologies (that will be displayed in Fig. 5), that is, the number and size of islands are distributed differently. In addition, the islands should remind us of fractal objects in both cases and their fractal dimension can be approximately calculated within the diffusion limited aggregation (DLA) model [30]. The system equations as Eqs. 12 and 13 derived by the nonlocal MFNT theory define the growing structures that will also be described by a nonequilibrium thermodynamics continuum approach condensed by a PDE in the next section. The adatoms generated by a Poissonian shot-noise-like flux lead to a population of dots, undergoing coalescence at a time ~ 300 . On the contrary, the S-shaped flux generates a sudden saturating curve with a production of few islands due to Ostwald ripening. This implies that the few islands give coarse graining producing mounds rather than clusters. Practically, the growth surface regime depends on the nature of the flux and ultimately, on the type of wear process. Obviously, such behaviours cannot minimally be represented by the Archard law, provided that a volume of the removed material should be proportional to the sliding length and normal load. It is interesting to note that in the dots regime, i.e. in the Poissonian shot-noise-like flux, where the number density of dots can be calculated as $n_{\text{dot}} \sim (A/Dt)^{1/2}$, where A is the total deposition area taken in

Fig. 4 The numerical density of growing structures, $x(t)$, as a function of asymptotic time using two types of adatoms fluxes in Eqs. 12 and 13, integrated with a Runge–Kutta 4th order routine. On the left, the number cluster density is calculated using the Poissonian shot-noise-like flux function as given in Eq. 8, with $\bar{m}=0$, $\eta = 1$, $t_{\text{res}} = 10^{-3}$ s. The number density reproduces the growing clusters as in Fig. 5a (see the next section). Fixing the time of the scratching test and knowing the diffusion constant and flux rate we obtain the number of islands growth with the debris adatoms. On the right, the number density of growing structures, $x(t)$, showing coalescent

consideration. We can obtain some characteristic system quantities, such as the dot–dot distance, l , and the migration time from the stripped off site to the deposition dot, t . Taking $n_{\text{dot}} \sim 130$, and a reasonable diffusion constant as $D \cong 1.8 \times 10^{-11}$ m²/s [31], we obtain a migration time of $\sim 10^{-6}$ s a dot–dot length as $\sim 10^{-9} \div 10^{-8}$ m. In the next section, we will confirm to the results obtained here, using a continuous nonequilibrium thermodynamics approach, where the growth processes are leaded by the components of the chemical potential. All the considerations made on the growth mechanisms (dots density, Ostwald ripening, nucleation, etc.) will be further described in the next section, where the nonequilibrium thermodynamics continuum approach will be described in detail.

4 Thermodynamical Nonequilibrium Treatment of The Debris Recrystallization

In this section, we show how the growth of regular patterns induced by a mature wear process can be described by a continuous height function $h_g(x, y, t)$, where x, y are the surface coordinates. On the average, the surface receives a flux of adatoms, F , produced by the stressing probe tip making the scratch. Such flux depends on the incidence of the activated wear production of single adatoms or small clusters of adatoms debris. The various processes by which matter is redistributed along the surface are represented by functions of the derivatives of h with respect to space coordinates [32]. Under UHV conditions, it is reasonable to suppose that the whole stripped off mass goes in the growth process and a mass-conservation condition will be fulfilled:

mounds, correspondent to Fig. 5b. Such mounds are obtained integrating Eqs. 8 and 9 using the first sigma-like form for the adatom flux, as given in Eq. 7, and the continuous line, and the second sigma-like form in Eq. 7, dashed line. When the arrival of adatoms is given by a sigma-like function, the mound structures tend to grow driven by instability as in an Ostwald ripening process. The growing process tends to reduce the ratio surface/volume, and a coalescent process suddenly gives growing structures around the scratched area. Number density of growing clusters dependence on the normal load was demonstrated elsewhere [21]

$$\frac{\partial h_g(x, y, t)}{\partial t} = \Omega \nabla j(x, y) = \Omega F_{\text{incoming}}(x, y, t) \quad (10)$$

where similarly to Eq. 5, Ω is the atomic volume, j is the adatom (debris) number current density within the surface and $F_{\text{incoming}} (=F_{\text{outgoing}})$ is the total adatom flux produced during the wear process, growing in mounds or clusters. Equation 10 connects the time-dependent growth process to the wear production of the debris adatoms. In fact, the current density is referred to the surface diffusion current of adatoms produced during the stressing passage of the AFM probe tip.

Surface diffusion is supposed to be the unique mass transport mechanisms, this is reasonable in UHV conditions. The surface flux of atoms j can be considered to be proportional to the surface gradient of a chemical potential, μ , [32, 33]:

$$j = -\frac{D\rho}{k_B T} \nabla_s \mu \quad \text{on} \quad z = h_g(x, y, t) \quad (11)$$

where D is the diffusion constant, ρ is the surface density of the lattice sites, $\nabla_s \mu$, is the surface gradient of the chemical potential and $k_B T$ is the thermal energy. The similarity of Eq. 10 with Eq. 5 is a consequence of the specularity of the two main processes, i.e. wearing and growing, that may be seen as mirror processes. We will demonstrate that the relative specular affinity between the two processes gives the possibility of studying the basic wear mechanisms reproducing the growth structures and to address the specific growing structures (their self-assembly, structure number density, etc.) as a product of the wear fluxes of adatoms moving from the worn sites during the scratching.

Fig. 5 AFM simulated images as observed at the end of the wear test integrating Eq. 15, to areas ($20L \times 20L$, corresponding to nearly $100 \text{ nm} \times 100 \text{ nm}$ real area) around the scratched regions. The abrasive wear process leads to the formation of regular clusters or

coarse-graining mounds due to surface diffusion of adatoms debris. (The parameters used are, respectively: $\alpha = 0.2$, $\chi = 1.4$, $\varphi = 1.0$ in the image A; $\alpha = 0.23$, $\chi = 1.2$, $\varphi = -2.0$, in the image b). In the insets, the correspondent distribution density as in Fig. 4 is shown

One main problem in Eq. 11 is the specification of the chemical potential, and one possible choice is given manipulating such equation by using the thermodynamics of stressed solids with a reference state for the film of zero strain, and under the additional assumptions of isotropic surface energy, the gradient of the chemical potential can be written as [34–36]

$$\nabla_s \mu = \Omega \nabla_s (U_e + k\gamma(h) + \Phi) \quad (12)$$

where $U_e = E(a_g - a_s)^2 / a_s^2 (1 - \nu_g)$ (where E , a_g , ν_g are the Young modulus, lattice parameter and Poisson ratio, respectively, of the growth structure and a_s is the lattice parameter of the substrate, and $(a_g - a_s)/a_s$ is the possible misfit at the interface) is the elastic energy density, k is the free surface mean curvature, $\gamma(h)$ is the isotropic surface energy and $\Phi(h, |\nabla h|^2) = (d\gamma/dh) (1 + |\nabla h|^2)^{-1/2}$ is the surface chemical potential related to wetting interactions with the substrate (wetting chemical potential), and it is a function of the height and slope [36, 37]. The morphology of a surface, where a scratch test takes place, needs to be described with an abrasion process and a localised accumulations of atoms due to surface diffusion, therefore combining Eq. 12 with Eq. 11 [36, 37] can be described as follows:

$$\frac{\partial h_g}{\partial t} = -\frac{\partial h_w}{\partial t} \text{ on the scratched area} \quad (13.a)$$

$$\frac{\partial h_g}{\partial t} = D \sqrt{1 + |\nabla h|^2} \nabla_s^2 (U_e + k\gamma + \Phi) \text{ outside the scratched area} \quad (13.b)$$

Eq. 13.b describes the time evolution of a surface where a localised scratched area produces adatomic debris, via surface diffusion growth in regular clusters or mounds. This equation has revealed rich dynamics of surface evolution such as self-assembly of quantum dots. The large impact of this equation for describing the nonlinear evolution of epitaxially strained thin solid film subjected to

surface diffusion on solid substrate is due to its completeness to capture many physical properties connected to the linear instability of a planar surface of a stressed solid to small perturbations, finding that the planar surface is unstable for wave numbers less than a critical value. This instability is generally manifested by a mass transport via surface diffusion, where wetting potential plays a key role in the competition between the elastic energy and the surface energy, because the elastic energy in the solid is a destabilizing factor, whilst the surface energy is a stabilizing one for the surface growing structures.

In a nanoscale AFM-induced wear process, the adatom density is generally poor, therefore, the film only changes its thickness weakly and locally relating to specific sites that remain under a threshold value, above which the film becomes unstable. Also if the fluxes in our physical situation are very different with respect to ones expected in an epitaxially growing experiment, it has been shown that Eq. 13.b is able to capture the basic physics of the surface growing properties [20].

The surface being worn and undergoing growth process can be divided in three distinct regions, I, II and III. The first one, I, is the area where the scratching test is located: the AFM probe tip scratches a limited region, where abrasion process is totally predominant and the abraded surface is described by Eq. 13.a. The second region is conditioned by the mismatch lattice due to the stressing around the scratched area and the third region is the surface area far from the scratched area, this area can be considered as unaffected by the scratching test. The last two regions, II and III, can be described in a unique form using the Eq. 13.b, but the growth processes that should take place can be characterized by a different morphology due the different mismatch gradients and, therefore, the different elastic energy densities. Otherwise, in the first region, where we can consider only the abrasion term, the impossibility of measuring the abrasive mechanisms, implies that we can focus the attention totally on the

growth process. Being interested in having a representation of the growth process at the end of the scratch test, we can set the worn region as $h = -h_0$ in Eq. 13.a.

There is another reason for splitting of Eq. 13. Equation 13.a and b are expressions that consider both the slow abrasion dynamics driven by the AFM tip scanning velocity and the fast time growth process dominated by the surface diffusion. The process of abrasion and the process of growing surface structures have different scale times. Slow time is for the abrasion process that depends on the scanning velocity of the probe tip, and fast time is for the growing structures that depend on the surface diffusion. The different time scales are a further reason obliging us to focus the attention on the growth process, which is the target of this section, looking at the growth structures at the end of the scratch test, i.e. when the wear volume has been eroded by the AFM tip.

One basic assumption is that the mass is conserved, i.e. all the mass produced during the scratch needs to be found in the growth structures, therefore, we can write the wear volume as $\Omega n_w = \int_0^{L_x} \int_0^{L_y} h_g(x, y) dx dy$. In our simulation, this means recording a surface where the volumetric dimensions of the hole produced during the scratch is equal to the volume of the growth structures, when the volume is calculated with respect to the planar surface not involved in the scratch or the growth debris deposition. In addition, it is necessary to manage Eq. 13.b to simplify it and to draw a numerical quantification. We introduce the ratio length as (L/Λ) , with $\Lambda = 1/20$, and the time scale, τ . The time scale represents how fast the surface perturbations grow on the scale length L . The new set of rescaled variables is selected to have $\nabla \sim \Lambda$, $\partial_t \sim \Lambda^2$. Making the due changes, the length scale and the characteristic time scale become, respectively, [21]:

$$L = \frac{\gamma(1-\nu)}{4\mu\epsilon_z^2(1+\nu)} \text{ and } \tau = \frac{L^2}{D} \quad (14)$$

where $\gamma = 1,070 \text{ mJ/m}^2$ is the Al surface energy [38], $\mu = 26 \text{ GPa}$ its shear elastic modulus [38], ν is the Al Poisson ratio (0.33), $\epsilon_z \cong 3 \times 10^{-2}$ is a lattice misfit value (the lattice misfit can be generated at the Al/Al interface due to different local strains between the substrate and the growth structure in condition of uniform equibiaxial stress). The diffusion constant is $D = a^2 \nu_0 \exp[-E_d/k_B T]$, using $E_d = 25 \text{ meV}$ as a suitable barrier height (i.e. the activation energy for diffusion) [31], $a^2 = 4 \times 10^{-20} \text{ m}^2$ as the Al lattice constant and $\nu = 10^{13} \text{ Hz}$ as the attempt frequency, we obtain the diffusion constant $D = 1.8 \times 10^{-11} \text{ m}^2/\text{s}$, already used in the previous section. Making use of such parameters, the two new variables are $L \cong 5 \text{ nm}$ and $\tau \cong 10^{-6} \text{ s}$, that are the quantities identifying the characteristics length and time of

our growing dynamics, and they are in optimal agreement with the correspondent quantities obtained in the previous section, when the density number of dots produced by a Poissonian shot-noise-like flux was taken in consideration. After appropriate rescaling the following dimensionless equation for h is obtained (details for the derivation can be found in [39]):

$$\partial_t h = \nabla^2 \left[\alpha h + \nabla^2 h + \nabla^4 h + \left(h \nabla^2 h + \chi |\nabla h|^2 + \phi h^2 \right) \right] \quad (15)$$

where α is a slope parameter, and the parameters $\chi/\alpha \sim \partial\Phi(L,0)/\partial|\nabla h|^2$ and $\phi/\alpha \sim \partial\Phi(L,0)/\partial h$ are connected to the derivative dependence of the wetting potential with respect to the slope or the height of the surface, in particular, χ , ϕ drives the nonlinear contributions in the Eq. 15 that are considered in a perturbative way. Since, Eq. 15 must describe a conserved quantity (in this case h), any term in the right-hand side may be written in the form of a divergence.

Let us assume the planar surface has a small perturbation $h \sim e^{\lambda t + i k r}$. Inserting this expression for h into Eq. 15, we obtain the dispersion relation $\lambda = -\alpha k^2 + k^4 - k^6$. Therefore, the instability occurs for $\alpha < \alpha_c = 1/4$ at a wave number $k_c = \sqrt{2}/2$, which corresponds to stationary, spatial periodic patterns. The presence of the wetting potential in Eq. 15 changes significantly the dispersion relation modifying the linear instability range [37]. Consider the 2 + 1 case of 2D surface whose time evolution is described with Eq. 15, using a weakly nonlinear analysis of stationary solutions near the instability threshold it is possible to show that the growth process is bifurcated in two different regimes: dots or mounds. Details on such derivation on different solutions correspondent to dots or mounds can be found in [21]. Here, we are interested in describing the basic growth mechanisms and how such mechanisms are connected to the adatom fluxes that keep memory of the wear rate.

We have performed the numerical simulations of Eq. 15 by means of a pseudopotential code with boundary conditions [35, 39]. The computational cell of size $20L$ by $20L$ is discretized into a 256 by 256 grid, and the normalised time step $\Delta t = 0.1$ for a total time scale $t = 10^4 \Delta t$. Refining the computational grid and the time step leads to no difference in the simulation results. Results of the numerical simulations are shown in Fig. 5. It is possible to observe the formation of regular arrays of dots or mounds for suitable parameters, α , χ , ϕ .

In Fig. 5a, the wear volume produced in the scratched area is $20 \times 20 \times 1 \text{ nm}^3$, using a 0.2-nm lattice constant and an atomic volume $\Omega \cong 1.5 \times 10^{-29} \text{ m}^3$ for the Al sample, the number of growth clusters is nearly 150 with a narrow size distribution. With such dimensions, a cluster is

composed by nearly 300 Al atoms, for an average volume of $3 \div 4 \text{ nm}^3$. The clusters can be represented as pyramids with a squared base, as in the zoom set in Fig. 5a, side $\approx 2.5 \div 3 \text{ nm}$, with a height of approximately $1 \div 1.5 \text{ nm}$. It must be noted that in the numerical simulation, the wear volume is *manually* added, and the images reproduce the state of the surface at the end of the scratching test, where the mass conservation is imposed, i.e. the wear volume is equal to the summarised cluster volumes. Figure 5b shows the formation of large mounds surrounding the scratched area. Such structures can be imputed to Oswald ripening and coarse graining.

Self-assembled structures can be determined using parameters obtained looking at steady state solutions [37, 39]. Self-organized growth of such nanostructures is based on a detailed understanding of the microscopic pathways of diffusion, nucleation and aggregation. On surfaces, the hierarchy in the migration barriers as well as the non-uniform strain fields induced by mismatched lattice parameters can be translated into geometric order and well-defined shapes and length scales of the resulting aggregates. Nevertheless, mismatching decreases moving from the scratched area, and observing Fig. 5a, we can note that some zones take place to growth structures only randomly. This can be due to the fact that the stability conditions determining regions in the (χ, φ) plane where self-organization of hexagonal arrangements of clusters can be observed are strongly unstable and critical thresholds are still not well defined [21, 37]. Inside these regions, self-organised surface structures with hexagonal symmetry can be stable in a certain range of the α parameter. But an accurate definition of such parameters is beyond the scope of this article. We limited our research to find the parameter regions in the (χ, φ) plane leading to self-organized array of clusters or coarse-graining mounds, where the parameter regions in the (χ, φ) plane corresponding to the different surface morphologies can be obtained slightly increasing parameter α . This is because the dispersion curve has a larger range of k values which provide a mound solution for Eq. 15.

The morphology obtained after a scratch test results by minimizing the total free energy or the chemical potential. It has been previously demonstrated that the total free energy depends on the flux of adatoms, because it depends on the number of adatoms and chemical potential [40, 41]. Analogously, since it is difficult to find an analytical expression connecting the parameters used in Eq. 15 and the flux forms as given in Eqs. 6 and 7, we used an alternative approach. The growth structures and their morphology can be found using suitable parameters falling in different regions of the instability range (identified by the linear analysis) for the energetic balance in Eq. 15 or using the mean field nucleation theory that connects the growth

structures to the diffusion constant, D , and the flux, F as made in the previous section.

In the first case, we have to find the conditions and the corresponding parameters that minimize the chemical potential with the presence of a growing volume V that yield the equilibrium morphology. In a general point of view, first we have to quantify the free energy gain of the system during the growth process due to the adatom debris. This requires knowing the free energy gain at any passage of adatom debris from a primitive solid location to the final collocation on a dot or a mound and which of the two final states minimize the surface free energy. The chemical potential, Eq. 12, is composed of three terms, the elastic energy density (connected to the strain energy), the surface energy and the wetting potential. For small volumes V , the elastic energy (proportional to V), is small and the surface free energy ($k\gamma$), is mainly due to the size of the clusters. The area of these clusters is proportional to $\sqrt{Vh}$, therefore the clusters should be as small as possible. If the wetting potential dominates in the chemical potential, then the wetting interaction between the film and the substrate can lead to the self-organization of dots with uniform sizes only if the wetting potential is strongly dependent on the surface slope [37].

For larger cluster sizes, the elastic energy dominates with respect to the other two terms. Since, in a homoepitaxy process, the form of U_e , dominated by the ratio of the different mismatched lattice parameters, the larger cluster size can be found near the worn surface, because its edge presents a more marked mismatch due to the wearing effect of the AFM tip. This is the reason why we found the larger cluster size in the region II. The energy of a cluster can be written as $\mathfrak{S}(r) \approx -V(r)\Delta\rho\Delta\mu + \gamma k(r) + \Phi(r)$, where $V(r)$ is the cluster volume as a function of the radius, $\Delta\rho$ is the adatom number density, $\Delta\mu$ is the variation of the chemical potential for the formation of clusters, $k(r)$ is the surface curvature induced by the cluster and $\Phi(r)$ is the wetting potential connected to the clusters. The first volume term in the total energy decreases with cluster size, whilst the second surface term increases with cluster size due to the increase of surface area, the wetting potential that is strictly connected to the slope therefore leading to the growth on the lateral surface of the clusters. The balance condition requires $d\mathfrak{S}(r)/dr = 0$ which estimates the stable cluster size. The derivative, with respect to surface height of the wetting potential, directly gives the ratio φ/α , with which a positive or a negative value can make the cluster size stable or unstable. When a condition such as $d\mathfrak{S}(r)/dr = 0$ is approached, the new arriving adatoms prefer to grow in new clusters, favourable in an energetic point of view, leaving the old structures stable. The wetting potential drives the self-organization that gives the narrow

shape and the regular array of the cluster structures. The wetting interaction between the growth structure and the substrate also depends on the derivative of the surface energy $\gamma(h)$ addressing the new arriving adatoms on the structures that present a more marked change of $\gamma(h)$ with their radius. The dependence of the free energy on the wear rate can be explained as follows: the energy of a cluster can be written as $n_c \cong n \exp(-\mathfrak{Z}(n_c)/k_B T)$, where n_c is the number of adatoms forming the cluster. Using Eq. 2, the cluster energy can be written as $\mathfrak{Z}(n_c) \cong k_B T \ln(\Gamma_{\text{res}} N)$, where N is the total number of periodic contact during the scratching test. We have not yet explicated a form for the surface energy; nevertheless, at the cluster-surface boundary the surface energy generally has a drastic variation that implies a severe change in wetting potential, this can lead to the self-organization of dots with almost uniform sizes if the wetting potential is strongly dependent on the surface slope. Many authors have investigated the stability of regular dot patterns with respect to patterns having other symmetries [35–37]. It is shown that, with the increase of the parameter α , a regular dot pattern can become unstable leading to stripe patterns. Nevertheless, it could be difficult to observe experimentally stripe patterns because their mean size is less the mounds dimension as due to Ostwald ripening [42], because both the morphologies (stripe patterns or mounds) should be located in the region II, dominated by a more marked elastic energy density due to mismatched lattice parameters.

Mound structures surrounding the scratched area are located in region II, see Fig. 5b, and they can be obtained by choosing a suitable choice of parameters in Eq. 15. The reduced incidence of the role of the wetting potential determines the coarse-grained mechanism that can be identified as an activated Ostwald ripening. Ostwald ripening is a process where large clusters grow at the expense of small clusters through an exchange of monomers. The process is governed by the inverse dependence of the chemical potential on the cluster size that should induce coalescence between the dots more than the formation of new dots. For a system containing both large and small clusters, the chemical potential difference causes material to be transferred from small to large clusters. The reduction of the effects of the wetting potential implies that in case of homoepitaxy Al/Al the elastic energy tends to remain rather limited, and in the absence of the wetting potential, only the surface energy should be considered as the leading term inducing the final morphology. The evolution growth tends to reduce the surface energy, and therefore, the total surface of the clusters. Since, the adsorbate volume practically does not change in time, and the incoming flux of adatoms is extremely low with a slow time scale, the ratio surface/volume decreases, and therefore the average cluster size increases. Adatoms can eventually escape from

smaller clusters and diffuse on the surface to bigger clusters where the free energy per atom, which is the chemical potential, is lower in smaller clusters. Therefore, the coarse graining of the few mounds is strongly favoured as shown in Fig. 5b. Equation 15 is a powerful tool to capture the physical behaviour. As demonstrated, there are different classes of parameters in such equation that lead to self-organized regular cluster arrays or coarse-graining mounds. Since, intermediate regime with a mixing of mounds and dots has not been observed in our simulation, also for a wide range of parameter values, this could imply that wear-activated mechanisms for the creation of the debris adatoms correspond to the two different classes of fluxes, Eq 6 or Eq. 7 and one is dominant with respect to the other. In accordance to experimental observations [19], a mound morphology, as obtained in Fig. 5b, and is the common morphology experienced in UHV scratch tests, this is also confirmed by the wide range of parameters (χ , φ) by which such typical morphology is obtained in our simulation.

Another interesting result is obtained when the geometry of a worn area, region I, is changed. On the contrary to Fig. 5, where a square region was considered, if we split the worn region to a linear area, as Socoliuc et al. [20], we observe a revealing difference of morphology between the regions II and III, Fig. 6. The misfit around the scratched area is now taken as 0.5%, and the morphology of growth dots is modified producing the well-known pattern commonly called ripples. The origin of such ripples morphology can be addressed to different misfits between the region surrounding the scratched area and the region III,

Fig. 6 AFM simulated image of ripples as observed at the end of the wear test integrating Eq. 15, to areas (corresponding to nearly 100 nm × 100 nm real area) around the scratched regions. The scratched region I is a line. The different growth between the regions II and III is evident. The abrasive wear process leads to the formation of two different dot morphologies. The first one, periodic ripples-pit located near the *scratching edges* is conditioned by the elastic energy density, whilst the second one, is given by the *conical dots* as observed in Fig. 5A. (The parameters used are $\alpha = 0.2$, $\chi = -0.78$, $\varphi = 1.41$, the lattice parameters a_g is taken for giving a misfit of 0.5% in region II surrounding the scratched line)

due to an asymmetrical distribution of strain and stress due to the passage of the AFM tip. The misfit will be higher around the region surrounding the scratched area. An increasing of the misfit implies a leading role for the elastic energy in the chemical potential, Eq. 12, and the nucleation process starting around the scratched line will have a reduced barrier energy favouring a rapid growth mechanism. Nevertheless, the adatoms that are not captured by the growth dots surrounding the scratched area can freely self-assemble far from the scratched area (with distances ranging from few nanometres to some tens, Fig. 6). It must be noted that we obtain a ripple-pit structure, where the pits unobserved in the experiment limited by tip-resolution, on the contrary, such structures can be revealed in the simulation. Refinements on the simulation routine could improve the ripple periodicity in order a closer agreement with experimental results.

The framework of the UHV wear scratches described above can help the comprehension of AFM tip wearing. The knowledge of the progressive tip degradation due to wear is fundamentally practical in all the scanning probe applications. The tip degradation introduces artefacts in imaging, which lead to errors and low image resolution. In addition, tip wearing also affects nanopatterning techniques as the size of patterned features depends on the radius of the tip. Tip wearing is important in nanoindentation tests and in many other applications where the tip radius plays a fundamental role for the final measurements [43–45]. Recently, Gotsmann and Lantz measured the wear of AFM tip indirectly via the detection of the adhesion force between a silicon tip and a polymer surface [17]. This indirect link between adhesion and wear, however, was based on the fact that the tip had a perfect flat punch geometry and the polymer sample was extremely flat. This is an instance that cannot be generalized to all tip-sample configurations, especially when surface roughness becomes important. Recently, Schmutz et al. proposed a technique based on the combination of friction force with dynamic force microscopy [45]. The basic idea is to record the mass change of the probe through the detection of the resonance frequency of the cantilever after scratching the sample surface. Using this method it has been possible to measure tip mass change down to picograms. The method is promising for all possible tip-sample configurations, as well as long sliding distances, nevertheless, the resolution is still too high for studying the onset wear.

In the case of tip wear, the main difference with respect to sample wear is that the tip is continuously in contact with the sample, whilst, on the contrary, for a sample surface the time of contact with the stressing tip is periodic, because determined by the tip passage. Another important difference is the tip possesses a well-defined geometry, whilst we have systematically defined the sample surface as flat

also at the atomic scale. The approach used in the previous section is not applicable in the case of tip wear. In the case of a tip material characterized by lower hardness with respect to sample hardness, the wear processes during the scanning can be decoupled and we can observe the wearing of the tip. Producing a scratch test in UHV conditions and looking at the patterning of the self-organized re-crystallization debris we should have an indirect measurement of the wear mechanism activated during the scratch. Therefore, all the theory developed for the identification on what structures can be observed after a scratch test made in UHV, the self-organized dots structures or mounds, could be experimentally validated and directly used to study tip wearing. A scratching experiment made under UHV conditions between a tip characterized by a material with a lower hardness with respect to sample hardness, could help to identify in a direct manner the role of activated processes [46], the time stochastic nature of the generated fluxes and the correspondent growth structure emerging on the sample surface.

5 Conclusions

Recent UHV scratching AFM experiments showed the formation of small clusters, larger aggregates or regular patterns on the surface being scanned. In this article, we have improved a former theory that identified a nonequilibrium thermodynamics framework able to capture the basic mechanisms producing the formation of such self-assembled structures and showing their direct connection with the activated mechanisms for wearing. In an AFM scratching experiment, a probe tip continuously scratches a small-localised area. If at the end of the scratch test, a larger surface surrounding the worn area is recorded with the same tip, than a surface presenting both the scratched area and growth structures can be observed. Such growth structures are built by the adatoms produced by the abrasive wear process activated during the scratching, and, therefore, studying the nature of the growth structures it is possible to collect knowledge on the basic wear process producing the adatoms. In this article, we have shown that self-organised regular arrays of clusters or coarse-grained mounds can be obtained as a function of the adatoms flux produced during the wearing test. This implies that wear basic mechanisms can be indirectly studied looking at such growth structures. Aluminium, Al (111), has been identified as the sample material test because of its specific homoepitaxy properties. In turn, a direct experiment on tip wearing to be performed in UHV conditions has been suggested to highlight the reported results. Such experiments should further improve knowledge and control on the basic wear mechanisms on nanoscale.

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Appendix A. Tip-Sample Contact Data

We simulate the contact area using Hertz theory within continuum mechanics that could give a good approximate value for the real area of contact even if the contact is composed by discrete atoms. For a paraboloid shape of the probe tip in non-adhesive contact with a flat surface, the real area of contact and penetration depth are, respectively,

$$A_r = \pi \left(\frac{3F_N R}{4E^*} \right)^{2/3} \quad \text{and} \quad z_d = \frac{1}{2} \left(\frac{3F_N}{4E^* \sqrt{R}} \right)^{2/3} \quad (\text{A.1})$$

where F_N is the applied load, $R = 15$ nm is the tip radius and $E^* = [(1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2]^{-1}$ is the reduced elastic modulus, $E_{1,2}$ are the Young moduli and $\nu_{1,2}$ is the Poisson's ratios for the Al sample ($E_l \cong 70$ GPa, $\nu_l = 0.33$) and the tip. We consider two materials with different hardness, so that the wearing can be essentially addressed to the material with the lower hardness value. For this reason, a diamond probe tip is taken in consideration ($E_2 = 1220$ GPa, $\nu_2 = 0.2$), respectively. Making use of a value $a \cong 0.2$ nm for the Al lattice period and for an applied load of 50 nN in Eq. A.1 a real area of contact $A_r \cong 12.4$ nm², and a penetration depth of 0.15 nm, respectively, are obtained. The volume contact is made approximately $300 \times$ atoms are estimated to be simultaneously in contact with the probe tip at any point of contact. For an applied load of 25 nN, we obtain a real area of contact of 7.8 nm² and a penetration depth of 0.1 nm.

Another important quantity is the residence time, that is the duration of the contact for any single contact point during the sliding passage of the tip. The residence time is given by the ratio of contact area and image area multiplied by the time required for an image, i.e. $t_{\text{res}} = t_{\text{image}} \cdot [A_r/A_{\text{image}}]$, [13].

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