Unidimensional model of adatom diffusion on a substrate submitted to a standing acoustic wave. I. Derivation of the adatom motion equation

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The effect of a standing acoustic wave on the diffusion of an adatom on a crystalline surface is theoretically studied. We used an unidimensional space model to study the adatom + substrate system. The dynamic equation of the adatom, a generalized Langevin equation, is analytically derived from the full Hamiltonian of the adatom + substrate system submitted to the acoustic wave. A detailed analysis of each term of this equation as well as of their properties is presented. Special attention is devoted to the expression of the effective force induced by the wave on the adatom. It has essentially the same spatial and time dependencies as its parent standing acoustic wave.

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I. INTRODUCTION

While the semiconductors industry extensively uses the lithography process to stamp the microdevices at the nanoscale, research centers and laboratories have investigated the self-assembling properties of materials to avoid this expensive and time consuming process. Most strategies to self-assemble materials at the nanoscale, especially during the atomic deposition process of semiconductor benefit from the elastic properties or from the structure of the substrate: the Stranski-Krastanov growth mode relies on the competition between the surface and elastic energies to organize the 3D growth,[1,2] buried dislocations networks in the substrate induce a periodic strain field at the substrate surface that drives the diffusion of adatoms,[3,4] and, finally, the use of patterned substrates (vicinal surfaces, holes, or mesas) can create some preferential nucleation sites.[5–8]

An alternative approach to self-assemble materials at the nanoscale, *the dynamic substrate structuring effect* has been recently proposed.[9] At the macroscopic scale, a sand bunch on a drum membrane excited at one of its eigenfrequencies self-structures by accumulating around the nodes or antinodes displacements of the membrane.[10] Transposing this concept at the nanoscale, we investigate the diffusion of an adatom on a crystalline substrate submitted to a standing acoustic wave (StAW).[11] Molecular dynamic simulations have evidenced that the StAW structures the diffusion of the adatom by encouraging its presence in the vicinity of the maximum displacements of the substrate.[9] These simulations have evidenced that the effect of the StAW is strong enough to have measurable effects. The typical and relevant StAW wavelengths vary from a few to hundreds of nanometers. Experimentally, the production of standing surface acoustic waves of a few hundred nanometers to micrometers wavelengths are nowadays available through the use of interdigital transducer[12,13] or optically excited nanopatterned surfaces,[14] whereas one does not know yet how to efficiently generate smaller wavelengths (few to tens nanometers) phonons.

In this study, we propose to analytically study the diffusion of a single adatom on a crystalline surface submitted to a StAW. The goal of this study is to establish the formalism and the dynamic equation that describes the diffusion of an adatom on a crystalline substrate submitted to a StAW. In Sec. II, a generalized Langevin equation governing the adatom diffusion on a one-dimensional substrate is analytically derived from the Hamiltonian of the system (adatom + substrate). Sections III, IV, V, and VI detail the different terms involved in this generalized Langevin equation as well as their properties.

II. ADATOM MOTION EQUATION

We consider the diffusion of an adatom on a crystalline substrate submitted to a StAW with a wave vector in the x direction. Since the adatom diffusion is expected to be mainly affected in the x direction, we specialize to a system with one degree of freedom. The extension to a 2D system to model a more complex StAW system (for instance, two StAWs with wave vectors in the x and y directions form a square lattice of nodes and antinodes) is straightforward, though analytical calculations may become tedious.

Figure 1 reports a sketch of the model under study. x and $x_{-N},\ldots,x_N$, respectively, design the positions of the adatom and of the $2N+1$ substrate atoms in the reference frame of the center of mass of the substrate. Following the work of Zwanzig[15] and related works,[16–18] we start with the Hamiltonian of the isolated system (adatom + substrate):

$$H_0 = \frac{p^2}{2m} + \Phi(x, x_{-N}, \ldots, x_N) + \sum_{j=-N}^{N} \frac{p_j^2}{2m_j} + V_{\text{sub}}(x_{-N}, \ldots, x_N), \tag{1}$$

where m, p and m_j, p_j are, respectively, the masses and momenta of the adatom and of the substrate atoms, $V_{\text{sub}}(x_{-N}, \ldots, x_N)$ and $\Phi(x, x_{-N}, \ldots, x_N)$ the potential energies of the substrate-substrate and adatom-substrate interactions. At this point, the generation process of the StAW has not been yet introduced, this will be done later on.

The motion of the substrate atoms will be described in the harmonic approximation[19] with the associated phonons of eigenvibration frequencies ω_n, normal coordinates Q_n, and

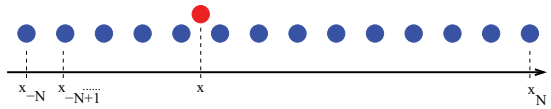

FIG. 1. (Color online) Schematic representation of the model under study. The adatom (red) and substrate atoms (blue) are characterized by their coordinates x and x_j ($j \in \{-N..N\}$) in the reference frame of the center of mass of the substrate. Note that, for clarity reasons, the adatom is not reported on the same horizontal line as the substrate atoms, but the model is unidimensional.

momenta Π_n:

$$\sum_j \frac{p_j^2}{2m_j} + V_{\text{sub}}(x_{-N},\ldots,x_N) \simeq \frac{1}{2}\sum_n \left(\Pi_n\bar{\Pi}_n + \omega_n^2 Q_n \bar{Q}_n\right), \tag{2}$$

where over-bar quantities are complex conjugate quantities and where the potential origin has been fixed at the equilibrium positions, $V_{\text{sub}}(x_{-N}^0,\ldots,x_N^0) = 0$. In this and in all the following equations, unless otherwise stated, the summations over the substrate atoms j are from $-N$ to N and those over the normal modes n are from $-N$ to N excluding $n = 0$. Note that, within the harmonic approximation, for an isolated substrate, there is no substrate dilation with temperature nor energy exchanges between the phonons.

The substrate atom displacements, $u_j = x_j - x_j^0$, around their equilibrium positions x_j^0 are thus given by

$$u_j = \frac{1}{\sqrt{m_j}}\sum_n e^{ik_n x_j^0} Q_n, \tag{3}$$

where k_n is the wave vector of the n normal mode. In Eqs. (2) and (3), we have

$$k_{-n} = -k_n,\ \omega_{-n} = \omega_n,\ \bar{Q}_n = Q_{-n}, \text{ and } \bar{\Pi}_n = \Pi_{-n}. \tag{4}$$

From Eqs. (2) and (3) and performing a development of the potential Φ to first order in the u_j's,

$$\begin{aligned}\Phi(x,x_{-N},\ldots,x_N) &= \Phi\left(x,x_{-N}^0,\ldots,x_N^0\right) \\ &\quad + \sum_j u_j \frac{\partial\Phi}{\partial x_j}\left(x,x_{-N}^0,\ldots,x_N^0\right) \\ &= \Phi_0(x) \\ &\quad + \frac{1}{2}\sum_n [Q_n\,\Psi_n(x) + \bar{Q}_n\,\bar{\Psi}_n(x)],\end{aligned} \tag{5}$$

where

$$\Phi_0(x) = \Phi\left(x,x_{-N}^0,\ldots,x_N^0\right), \tag{6}$$

$$\Psi_n(x) = \sum_j \frac{1}{\sqrt{m_j}} e^{ik_n x_j^0}\frac{\partial\Phi}{\partial x_j}\left(x,x_{-N}^0,\ldots,x_N^0\right). \tag{7}$$

The interaction of the adatom with the substrate has been separated into two contributions. $\Phi_0(x)$, the first one, appears as an external static force field. It is due to the frozen equilibrated substrate interatomic periodic potential. The second one, represents the interaction of the adatom with the phonons Q_n, i.e., with the moving substrate atoms around their equilibrium positions.

Equation (1) hence reads

$$\begin{aligned}H_0 &= \frac{p^2}{2m} + \Phi_0(x) \\ &\quad + \frac{1}{2}\sum_n [Q_n\,\Psi_n(x) + \bar{Q}_n\,\bar{\Psi}_n(x)] \\ &\quad + \frac{1}{2}\sum_n \left(\Pi_n\bar{\Pi}_n + \omega_n^2 Q_n\bar{Q}_n\right).\end{aligned} \tag{8}$$

Note that the coupling between the substrate and the adatom is linear in the phonon variables and nonlinear in the adatom variable, i.e., the reverse situation of the one studied by Cortes *et al.*[17]

To model the presence of a StAW in Eq. (8), we add a forcing term with the same F amplitude on two specific normal variables of opposite wave vectors $Q_{n_{\text{ex}}}$ and $\bar{Q}_{n_{\text{ex}}}(= Q_{-n_{\text{ex}}})$. However, since our model does not consider any dissipation of the substrate vibration modes, we slightly detune the forcing frequency $\Omega_{n_{\text{ex}}} = \omega_{n_{\text{ex}}} + \delta\omega_{n_{\text{ex}}}$ from the eigenfrequency $\omega_{n_{\text{ex}}}$ to avoid any resonance and subsequent divergence of the amplitude of the mode $Q_{n_{\text{ex}}}$. These two modes will be equally excited and thus, from basic forced oscillation theory,[20] one expects a forced oscillation substrate displacement field proportional to that of the parent standing wave:

$$u(x,t) = -\frac{2F}{M\Delta^2}\cos(\Omega_{n_{\text{ex}}}t)\cos(k_{n_{\text{ex}}}x + \eta), \tag{9}$$

where M is the mass of the oscillator, η a phase depending on the initial conditions and with

$$\Delta^2 = \Omega_{n_{\text{ex}}}^2 - \omega_{n_{\text{ex}}}^2 = (\omega_{n_{\text{ex}}} + \delta\omega_{n_{\text{ex}}})^2 - \omega_{n_{\text{ex}}}^2. \tag{10}$$

We thus consider the following Hamiltonian for the system (adatom + substrate submitted to a StAW):

$$\begin{aligned}H &= \frac{p^2}{2m} + \Phi_0(x) + \frac{1}{2}\sum_n [Q_n\,\Psi_n(x) + \bar{Q}_n\,\bar{\Psi}_n(x)] \\ &\quad + \frac{1}{2}\sum_n \left(\Pi_n\bar{\Pi}_n + \omega_n^2 Q_n\bar{Q}_n\right) \\ &\quad - (Q_{n_{\text{ex}}} + \bar{Q}_{n_{\text{ex}}})F\cos(\Omega_{n_{\text{ex}}}t).\end{aligned} \tag{11}$$

Note that, in Eq. (11), the addition of the StAW term makes the Hamiltonian time dependent. In addition, the work of the operator to induce the StAW [the last term of Eq. (11)] is not null on average and leads to a monotonous increase of the average energy of the system (adatom + substrate). This would be the case even taking into account all the nonlinear terms we have omitted in Eq. (11).

We, however, assume that despite this monotonous increase of the energy, the temperature of the system remains constant, either by considering that the substrate is infinite and has the behavior of a thermostat, or by considering that the system is not totally isolated and coupled to an external thermostat.

The dynamic equations derived from Eq. (11) read[21]

$$\frac{dQ_n}{dt} = \Pi_n, \tag{12a}$$

$$\frac{d\Pi_n}{dt} = -\omega_n^2 Q_n - \bar{\Psi}_n(x) + \Lambda_{n,n_{\text{ex}}} F\cos\left(\Omega_{n_{\text{ex}}}t\right), \tag{12b}$$

$$\frac{dx}{dt} = \frac{p}{m}, \tag{12c}$$

$$\frac{dp}{dt} = -\frac{d\Phi_0}{dx}(x) - \frac{1}{2}\sum_n \left[Q_n \frac{d\Psi_n}{dx}(x) + \bar{Q}_n \frac{d\bar{\Psi}_n}{dx}(x) \right], \tag{12d}$$

where $\Lambda_{i,j} = \delta_{i,j} + \delta_{i,-j}$ with $\delta_{i,j}$ the Kronecker symbol.[22] In Eq. (12b), $-\bar{\Psi}_n(x)$ is the force on the substrate normal mode n, induced by the adatom at position x. Solving Eqs. (12a) and (12b) between t_0 and t, the normal substrate coordinates read

$$\begin{aligned} Q_n(t) = {} & Q_n(t_0)\cos[\omega_n(t-t_0)] + \frac{\Pi_n(t_0)}{\omega_n}\sin[\omega_n(t-t_0)] \\ & - \int_{t_0}^{t} \bar{\Psi}_n(x(t'))\frac{\sin[\omega_n(t-t')]}{\omega_n}dt' \\ & + \int_{t_0}^{t} \Lambda_{n,n_{\rm ex}} F \cos\left(\Omega_{n_{\rm ex}} t'\right)\frac{\sin[\omega_n(t-t')]}{\omega_n}dt', \end{aligned} \tag{13}$$

where $Q_n(t_0)$ and $\Pi_n(t_0)$ are fixed by the initial conditions. An integration of the second integral and an integration by parts of the first one gives

$$\begin{aligned} Q_n(t) = {} & C_n(t_0)\cos[\omega_n(t-t_0)] + D_n(t_0)\sin[\omega_n(t-t_0)] \\ & - \frac{\bar{\Psi}_n[x(t)]}{\omega_n^2} \\ & + \int_{t_0}^{t} \frac{\cos[\omega_n(t-t')]}{\omega_n^2}\frac{dx}{dt}(t')\frac{d\bar{\Psi}_n}{dx}[x(t')]dt' \\ & - \Lambda_{n,n_{\rm ex}}\frac{F}{\Delta^2}\cos\left(\Omega_{n_{\rm ex}} t\right), \end{aligned} \tag{14}$$

with

$$C_n(t_0) = Q_n(t_0) + \Lambda_{n,n_{\rm ex}}\frac{F}{\Delta^2}\cos\left(\Omega_{n_{\rm ex}} t_0\right) + \frac{\bar{\Psi}_n[x(t_0)]}{\omega_n^2}, \tag{15a}$$

$$D_n(t_0) = \frac{\Pi_n(t_0)}{\omega_n} - \Lambda_{n,n_{\rm ex}}\frac{F}{\Delta^2}\frac{\Omega_{n_{\rm ex}}}{\omega_n}\sin\left(\Omega_{n_{\rm ex}} t_0\right). \tag{15b}$$

From Eqs. (4) and (7), we have

$$\bar{C}_n = C_{-n} \quad \text{and} \quad \bar{D}_n = D_{-n}. \tag{16}$$

Using Eqs. (12c), (12d), and (14), we derive the generalized Langevin equation governing the adatom diffusion:

$$\begin{aligned} m\frac{d^2x}{dt^2} = {} & -\frac{d\Phi_{\rm eff}}{dx}(x) - \int_{t_0}^{t}\gamma[x(t),x(t'),t-t']\frac{dx}{dt}(t')dt' \\ & + \xi(t) + F_{\rm SAW}(x,t). \end{aligned} \tag{17}$$

The left-hand side term of Eq. (17) is the usual inertial term. On the right-hand side, we distinguish four terms, which are successively:

(1) The force induced by the effective crystalline potential $\Phi_{\rm eff}(x)$, defined by

$$\Phi_{\rm eff}(x) = \Phi_0(x) - \frac{1}{2}\sum_n \frac{1}{\omega_n^2}\Psi_n(x)\bar{\Psi}_n(x). \tag{18}$$

The properties of this potential will be studied in Set. VI.

(2) The friction term $-\int_{t_0}^{t}\gamma[x(t),x(t'),t-t']\frac{dx}{dt}(t')dt'$ that depends on the adatom velocity and on the memory kernel $\gamma(x,x',t-t')$ which reads

$$\gamma(x,x',t-t') = \sum_n \frac{\cos[\omega_n(t-t')]}{\omega_n^2}\frac{d\Psi_n}{dx}(x)\frac{d\bar{\Psi}_n}{dx}(x'). \tag{19}$$

The properties of $\gamma(x,x',t-t')$ will be studied in Set. IV.

(3) The stochastic force[17,18] $\xi(t)$ is

$$\begin{aligned} \xi(t) = {} & -\sum_n \{C_n(t_0)\cos[\omega_n(t-t_0)] \\ & + D_n(t_0)\sin[\omega_n(t-t_0)]\}\frac{d\Psi_n}{dx}[x(t)]. \end{aligned} \tag{20}$$

This term depends on the initial conditions and adatom position and is a quickly varying force generated by the substrate. The properties of this force will be described in Sec. V.

(4) The last term $F_{\rm SAW}(x,t)$ is the effective force due to the applied forcing term at $\Omega_{n_{\rm ex}}$, i.e., the force $F_{\rm SAW}(x,t)$ induced by the StAW on the adatom through the substrate:

$$F_{\rm SAW}(x,t) = \frac{F}{\Delta^2}\left[\frac{d\Psi_{n_{\rm ex}}}{dx}(x) + \frac{d\bar{\Psi}_{n_{\rm ex}}}{dx}(x)\right]\cos\left(\Omega_{n_{\rm ex}} t\right). \tag{21}$$

This force will be detailed in Sec. III. The three first forces, crystalline, friction and stochastic, exist even in the absence of the StAW excitation. They are the usual forces describing the dynamics of the atoms in a crystalline material.

We have chosen to keep in $F_{\rm SAW}(x,t)$ only the forced oscillation term at the angular frequency $\Omega_{n_{\rm ex}}$. All the other terms depending on F have been included in the stochastic force $\xi(t)$. They correspond to the responses of the oscillators $Q_{n_{\rm ex}}$ and $\bar{Q}_{n_{\rm ex}}$ to the initial conditions at $t = t_0$. Since the normal modes of the substrate are undamped, these last terms are periodic and do not cancel. For damped oscillators, the terms depending on F in the stochastic force would correspond to a transient regime and would thus cancel, contrary to the forced oscillation term at the angular frequency $\Omega_{n_{\rm ex}}$.

III. THE STAW FORCE

To derive the expression of the force $F_{\rm SAW}(x,t)$ induced by the StAW, we need to explicit the expression of $\Psi_{n_{\rm ex}}(x)$ in Eq. (21). Since interaction potentials depend only on the relative position of the interacting particles, so do Φ_0 and Ψ_n. Ψ_n then reads

$$\begin{aligned} \Psi_n(x) = {} & \sum_j \frac{1}{\sqrt{m_j}} e^{ik_n x_j^0}\frac{\partial\Phi}{\partial x_j}\left(x - x_{-N}^0, \ldots, x - x_N^0\right) \\ = {} & \alpha_n(x)e^{ik_n x}, \end{aligned} \tag{22}$$

with $\alpha_n(x)$ defined as

$$\alpha_n(x) = \sum_j \frac{1}{\sqrt{m_j}} e^{-ik_n(x-x_j^0)}\frac{\partial\Phi}{\partial x_j}\left(x - x_{-N}^0, \ldots, x - x_N^0\right). \tag{23}$$

Note that for an infinite crystal, the $\alpha_n(x)$ functions have the lattice periodicity.[23] In addition, $\bar{\alpha}_n(x) = \alpha_{-n}(x)$ so that introducing the real $\alpha_n^r(x) = \Re[\alpha_n(x)]$ and imaginary $\alpha_n^i(x) = \Im[\alpha_n(x)]$ parts of $\alpha_n(x)$, we have

$$\alpha_n^r(x) = \alpha_{-n}^r(x) \quad \text{and} \quad \alpha_n^i(x) = -\alpha_{-n}^i(x), \tag{24}$$

which leads to

$$\frac{d\Psi_n}{dx} + \frac{d\bar{\Psi}_n}{dx} = 2[g_n(x)\cos(k_n x) + h_n(x)\sin(k_n x)], \tag{25}$$

with

$$g_n = \frac{d\alpha_n^r}{dx} - k_n\alpha_n^i \qquad h_n = -\left(k_n\alpha_n^r + \frac{d\alpha_n^i}{dx}\right), \tag{26}$$

where $g_n(x)$ and $h_n(x)$ have the lattice substrate periodicity. The $F_{\mathrm{SAW}}(x,t)$ force then reads

$$F_{\mathrm{SAW}}(x,t) = \frac{2F}{\Delta^2}\cos\left(\Omega_{n_{\mathrm{ex}}}t\right)\left[g_{n_{\mathrm{ex}}}(x)\cos\left(k_{n_{\mathrm{ex}}}x\right) + h_{n_{\mathrm{ex}}}(x)\sin\left(k_{n_{\mathrm{ex}}}x\right)\right]. \tag{27}$$

The comparison of Eqs. (27) and (9) shows that, as expected, the SAW force on the adatom, induced by the standing surface acoustic wave through the substrate, has the large scale spatial and time dependence of the corresponding standing wave. This dependence at spatial length scales $2\pi/k_{n_{\mathrm{ex}}}$ has been exhibited in molecular dynamic simulations[9] of adatom diffusing on a substrate submitted to a standing surface acoustic wave. However, at a finer scale, x smaller than the lattice parameter, this force experiences an amplitude and a phase modulation due to the presence of the crystalline potential through the functions $g_{n_{\mathrm{ex}}}(x)$ and $h_{n_{\mathrm{ex}}}(x)$.

At this point, it is instructive to turn to a particular case by specifying the substrate and the interaction potential between the adatom and the substrate atoms, especially in order to get an explicit expression of the functions $\alpha_n(x)$ and thus of $g_n(x)$ and $h_n(x)$. We assume that the substrate atoms have the same mass M and that the adatom interacts with each substrate atom through an attracting pair potential $V_{\mathrm{pair}}(x - x_i)$ that cancels at infinity. We choose for V_{pair} an exponential curve of extension σ (roughly the pair interaction range), i.e., a potential expression, that is physically meaningful and that allows the derivation of analytical calculations:

$$\Phi\left(x,x^0_{-N},\ldots,x^0_N\right) = \sum_j V_{\mathrm{pair}}\left(x - x^0_j\right) = -\sum_j V_0 e^{\frac{-|x-x^0_j|}{\sigma}}, \tag{28}$$

where V_0 is the bonding energy. Note that minima of Φ correspond to atoms substrate positions. We have $x^0_j = ja$ where a is the lattice spacing and $j \in [-N,N]$. $\alpha_n(x)$ then reads

$$\begin{aligned}\alpha_n(x) &= \frac{1}{\sqrt{M}}\sum_j e^{-ik_n(x-x^0_j)}\frac{\partial\Phi}{\partial x_j}\left(x - x^0_{-N},\ldots,x - x^0_N\right)\\ &= -\frac{1}{\sqrt{M}}\sum_j e^{-ik_n(x-x^0_j)}\frac{dV_{\mathrm{pair}}}{dx}\left(x - x^0_j\right)\\ &= \frac{V_0}{\sqrt{M}}\sum_j e^{-ik_n(x-ja)}\frac{d}{dx}\left[e^{\frac{-|x-ja|}{\sigma}}\right].\end{aligned} \tag{29}$$

To take into account the discontinuities of the derivative of V_{pair} at its minima, we define $m_0(x)$ and $r(x)$, respectively, the quotient and the rest of the Euclidian division of x by a: $x = m_0 a + r$, with $m_0 \in [-N,+N]$ and $0 \leqslant r(x) < a$. $m_0(x)$ is related to the potential well $[m_0 a,(m_0+1)a]$ in between which the adatom is and $r(x)$ where it is exactly in between. Extending the size of the substrate to infinity ($N \to \infty$) in Eq. (29), we obtain

$$\alpha_n(x) = \frac{V_0}{\sigma\sqrt{M}}\left[\sum_{j=m_0+1}^{\infty} e^{-ik_n(x-ja)}e^{\frac{x-ja}{\sigma}} - \sum_{j=-\infty}^{m_0} e^{-ik_n(x-ja)}e^{-\frac{(x-ja)}{\sigma}}\right] \tag{30}$$

$$= \frac{V_0}{\sigma\sqrt{M}}\left(\frac{e^{-ik_n r+\frac{r}{\sigma}}}{e^{\frac{a}{\sigma}-ik_n a}-1} - \frac{e^{-ik_n r-\frac{r}{\sigma}}}{1-e^{-ik_n a-\frac{a}{\sigma}}}\right). \tag{31}$$

$\alpha_n(x)$ appears then as a function of $r(x)$ only, which reads

$$\alpha_n[r(x)] = \frac{V_0}{\sigma\sqrt{M}}\frac{e^{ik_n a}\cosh\left(\frac{r}{\sigma}\right) - \cosh\left(\frac{r-a}{\sigma}\right)}{\cosh\left(\frac{a}{\sigma}\right) - \cos(k_n a)}e^{-ik_n r}. \tag{32}$$

From this expression of α_n, we deduce the following expressions for Ψ_n, g_n, and h_n:

$$\Psi_n(x) = \frac{V_0}{\sigma\sqrt{M}}\frac{e^{ik_n a}\cosh\left(\frac{r}{\sigma}\right) - \cosh\left(\frac{r-a}{\sigma}\right)}{\cosh\left(\frac{a}{\sigma}\right) - \cos(k_n a)}e^{ik_n m_0 a}, \tag{33}$$

$$g_n(r) = \frac{V_0}{\sigma^2\sqrt{M}\left[\cosh\left(\frac{a}{\sigma}\right) - \cos(k_n a)\right]}\left\{\cos[k_n(r-a)]\sinh\left(\frac{r}{\sigma}\right) - \cos(k_n r)\sinh\left(\frac{r-a}{\sigma}\right)\right\}, \tag{34}$$

$$h_n(r) = \frac{V_0}{\sigma^2\sqrt{M}\left[\cosh\left(\frac{a}{\sigma}\right) - \cos(k_n a)\right]}\left\{\sin[k_n(r-a)]\sinh\left(\frac{r}{\sigma}\right) - \sin(k_n r)\sinh\left(\frac{r-a}{\sigma}\right)\right\}. \tag{35}$$

Note that, since $g_n(x)$ and $h_n(x)$ in Eq. (26) have the lattice periodicity, we have $g_n(x) = g_n(m_0 a + r) = g_n(r)$ and $h_n(x) = h_n(m_0 a + r) = h_n(r)$. One can easily verify that F_{SAW} [see Eq. (27)] is a continuous function of x, despite the discontinuity of the derivative of V_{pair}. A more symetric expression can be obtained through the $r = r' + a/2$ translation, with now $-a/2 \leqslant r' \leqslant a/2$ ($r' = 0$ corresponds to the midposition between two successive potential wells, located at $r' = \pm a/2$):

$$F_{\mathrm{SAW}}[x,r'(x),t] = F_{\mathrm{saw}}(r')\cos\left(\Omega_{n_{\mathrm{ex}}}t\right)\cos\left[k_{n_{\mathrm{ex}}}(x-r') + \varphi_0(r')\right] = F_{\mathrm{saw}}(r')\cos\left(\Omega_{n_{\mathrm{ex}}}t\right)\cos\left[k_{n_{\mathrm{ex}}}x + \varphi(r')\right], \tag{36}$$

with

$$F_{\rm saw}(r') = 2F_0\left[\cos^2\frac{k_{n_{\rm ex}}a}{2}\sinh^2\frac{a}{2\sigma}\cosh^2\frac{r'}{\sigma} + \sin^2\frac{k_{n_{\rm ex}}a}{2}\cosh^2\frac{a}{2\sigma}\sinh^2\frac{r'}{\sigma}\right]^{1/2},$$
$$= 2F_0\cos\left(\frac{k_{n_{\rm ex}}a}{2}\right)\sinh\left(\frac{a}{2\sigma}\right)\left[1+\left(1+\tan^2\frac{k_{n_{\rm ex}}a}{2}\coth^2\frac{a}{2\sigma}\right)\sinh^2\frac{r'}{\sigma}\right]^{1/2}, \quad (37)$$

$$\tan[\varphi_0(r')] = \tan\frac{k_{n_{\rm ex}}a}{2}\coth\frac{a}{2\sigma}\tanh\frac{r'}{\sigma}, \quad (38)$$

$$F_0 = \frac{2V_0F}{\Delta^2\sigma^2\sqrt{M}\left[\cosh\left(\frac{a}{\sigma}\right)-\cos\left(k_{n_{\rm ex}}a\right)\right]}, \quad (39)$$

where $F_{\rm saw}(r')$ and $\varphi(r') = \varphi_0(r') - k_{n_{\rm ex}}r'$ are, respectively, the amplitude and the phase of the large scale spatial dependence of $F_{\rm SAW}[x,r'(x),t]$. Equation (36) again evidences the large scale spatial and time dependence of the SAW. This point is also evidenced by evaluating the force at the substrate atoms positions, $r' = \pm a/2$, and at the midway position between two successive potential wells, $r' = 0$:

$$F_{\rm SAW}(x,r' = \pm a/2,t) = F_0\sinh\left(\frac{a}{\sigma}\right)\cos\left(k_{n_{\rm ex}}x\right)\cos\left(\Omega_{n_{\rm ex}}t\right), \quad (40)$$

$$F_{\rm SAW}(x,r' = 0,t) = 2F_0\cos\left(\frac{k_{n_{\rm ex}}a}{2}\right)\sinh\left(\frac{a}{2\sigma}\right) \times \cos\left(k_{n_{\rm ex}}x\right)\cos\left(\Omega_{n_{\rm ex}}t\right). \quad (41)$$

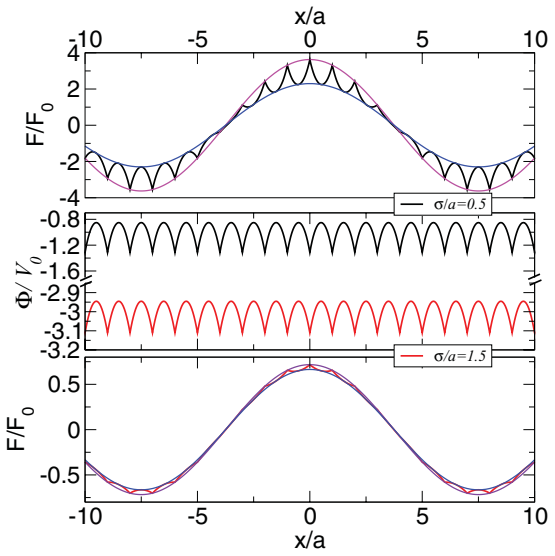

FIG. 2. (Color online) Top and bottom: maximum force induced by the StAW [$t = 0[2\pi/\Omega_{n_{\rm ex}}]$ in Eq. (36)] and middle: interatomic potential [see Eq. (28)] as a function of x/a, for $k_{n_{\rm ex}}a = 2\pi/15$ and two values of σ/a: 0.5 (black) and 1.5 (red). Top and bottom: envelop curve at the substrate atom positions [blue, Eq. (41)] and midway in between [magenta, Eq. (40)].

Figure 2 reports both the maximum force [$t = 0[2\pi/\Omega_{n_{\rm ex}}]$ in Eq. (36)] induced by the StAW and the interatomic potential [see Eq. (28)] as a function of x/a for $k_{n_{\rm ex}}a = 2\pi/15$ and two values of σ/a: 0.5 and 1.5. The large scale spatial dependence in $\cos(k_{n_{\rm ex}}x)$ of the force $F_{\rm SAW}[x,r'(x),t]$ is clearly evidenced, whereas the finer scale, between two successive potential wells exhibits the sinus hyperbolic-based dependence of the force evidenced in Eq. (37). As σ increases, the amplitude of the wells of the adatom-substrate potential [see Eq. (28)] and the amplitude of the variations of the force at both the large scale $2\pi/k_{n_{\rm ex}}$ and at the fine scale a decrease: indeed, if the interaction between the adatom and the substrate is less pronounced, the force induced by the wave on the adatom will also be reduced on both fine and large spatial scales.

IV. THE MEMORY KERNEL

Let's now study the memory kernel $\gamma(x,x',t-t')$ of the friction force [see Eq. (19)] that depends on the α_n functions through $\Psi_n(x)$ [see Eq. (22)]:

$$\gamma(x,x',t-t') = \sum_n \frac{\cos[\omega_n(t-t')]}{\omega_n^2}\frac{d\Psi_n}{dx}(x)\frac{d\bar{\Psi}_n}{dx}(x').$$

Note that this memory kernel depends on the adatom position so that the dissipation term in Eq. (17) is nonlinear in the adatom variables.[15,24] An explicit expression of γ is out of scope. However, since the α_n functions are periodic functions of period the lattice parameter a, we can make an evaluation of the kernel without taking into account their spatial variations. They are then replaced in Eq. (19) by their mean value over the period a. This is equivalent to take into account only the first term, $\tilde{\alpha}_n(0)$, of their Fourrier expansion:

$$\gamma(x,x',t-t') \approx \sum_n \frac{\cos[\omega_n(t-t')]e^{ik_n(x-x')}}{\omega_n^2}k_n^2\tilde{\alpha}_n(0)\overline{\tilde{\alpha}_n(0)}, \quad (42)$$

with

$$\tilde{\alpha}_n(0) = \frac{1}{a}\int_0^a \alpha_n(x)dx. \quad (43)$$

Again using the particular interatomic potential [see Eq. (28)] with Eqs. (31) or (32), one gets

$$\tilde{\alpha}_n(0) = \frac{2ik_nV_0}{a\sigma\sqrt{M}\left(k_n^2+1/\sigma^2\right)}. \tag{44}$$

Within this approximation, the memory kernel reads

$$\gamma(x-x',t-t') \approx \frac{4V_0^2}{a^2M}\sum_n \frac{k_n^4\cos[\omega_n(t-t')]}{\omega_n^2} \times \left(\frac{\sigma}{1+k_n^2\sigma^2}\right)^2 e^{ik_n(x-x')}. \tag{45}$$

In the same spirit, we will use the Debye model,[25] which is well adapted for simple monoatomic lattices at intermediate temperatures, to describe the phonon dispersion relation, $\omega_n = c_sk_n$, where c_s is the speed of sound of the substrate, and change the discrete summation to an integral:

$$\gamma(x-x',t-t') \approx \frac{4V_0^2\sigma^2}{a^2Mc_s^2} \times \int_{-k_D}^{k_D} \frac{k^2\cos[c_sk(t-t')]e^{ik(x-x')}}{(1+k^2\sigma^2)^2} g(k)dk, \tag{46}$$

where $k_D = \pi/a$ is the Debye wave number and $g(k) = L/(2\pi)$ the density of states in the reciprocal space, with $L = 2Na$ the size of the substrate. Moreover, since the function $k^2/(1+k^2\sigma^2)^2$ is a peaked function centered at $k = 0$ of extension $1/\sigma$, and considering that σ is generally larger than a, the limits of integration are extended to ∞. An integration by parts leads to the calculation of Fourier transform of Lorentzians and to the following approximated γ expression:

$$\gamma(x-x',t-t') = \frac{LV_0^2}{2c_s^2a^2M\sigma}\left\{H\left[\frac{|x-x'+c_s(t-t')|}{\sigma}\right] + H\left[\frac{|x-x'-c_s(t-t')|}{\sigma}\right]\right\} \quad \text{with} \quad H(x) = (1-x)e^{-x}. \tag{47}$$

The expression of the memory kernel in Eq. (47) is an even function of $x-x'$ and $t-t'$. The dependence on $x-x'$ is a direct consequence of the elusion of the dependence of $\alpha_n(x)$ on x (at the scale a) (see Sec. VI). We do not find for $\gamma(x,x',t-t')$ a simple exponentially decreasing function of $|t-t'|$ as usually assumed in most textbooks.[26–28] However, we emphasize that the γ expression in Eq. (47) crucially depends on the interaction potential chosen [see Eq. (28)] and that Eq. (47) provides a rather crude estimation of $\gamma(x,x',t-t')$: we have ignored the dependence of Ψ_n on the length scale a and the extension of the integral Eq. (46) to infinity is a rough assumption (σ/a is not, in general, very large compared to one).

In addition, from Eq. (47), the correlation time appears to be of the order of σ/c_s. Knowing that σ is of the order of magnitude of the lattice paramater, this correlation time is of the order of the inverse of the Debye frequency.

V. THE STOCHASTIC FORCE

In this section, we describe the properties of $\xi(t)$, the stochastic force [see Eq. (20)]. Since this force depends on the adatom position through the coupling term $\frac{d\Psi_n}{dx}[x(t)]$, it represents multiplicative fluctuations.[24] Using Eqs. (15a) and (15b), it reads

$$\xi(t) = -\sum_n \left(\left\{Q_n(t_0) + \Lambda_{n,n_{\rm ex}}\frac{F}{\Delta^2}\cos\left(\Omega_{n_{\rm ex}}t_0\right) + \frac{\bar{\Psi}_n[x(t_0)]}{\omega_n^2}\right\}\cos[\omega_n(t-t_0)] + \left[\frac{\Pi_n(t_0)}{\omega_n} - \Lambda_{n,n_{\rm ex}}\frac{F}{\Delta^2}\frac{\Omega_{n_{\rm ex}}}{\omega_n}\sin\left(\Omega_{n_{\rm ex}}t_0\right)\right] \times \sin[\omega_n(t-t_0)]\right)\frac{d\Psi_n}{dx}[x(t)]. \tag{48}$$

This force partially results from the initial state of the substrate. In that sense, our system is completely deterministic. However, we have considered a quadratic approximation in Eq. (2) and a linear development of Φ in Eq. (5). In a real substrate, the nonlinear terms can hold and/or exchange some energy with the normal substrate modes and in addition the substrate is never completely uncoupled to the experimental setup. To take into account these exchanges of energy without explicitly describing them, we characterize the state of the substrate $(\vec{Q},\vec{\Pi})$ at t_0 using a probability distribution $p[\vec{Q}(t_0),\vec{\Pi}(t_0)]$, where $\vec{Q}$ and $\vec{\Pi}$ are vectors whose coordinates are the variables Q_n and Π_n. We suppose that the StAW forcing terms in Eq. (11) initially switched off are switched on at t_0: the Hamiltonian describing our system at $t < t_0$ is thus given by Eq. (8).

Besides, if we want Eq. (17) to be regarded as a conventional generalized Langevin equation, the quantity $\xi(t)$ ought to have the properties that are expected for Langevin noise. Especially, its average is expected to cancel with respect to the probability distribution $p[\vec{Q}(t_0),\vec{\Pi}(t_0)]$.[27] In order to satisfy this last requirement, we choose the following expression for $p[\vec{Q}(t_0),\vec{\Pi}(t_0)]$:

$$p[\vec{Q}(t_0),\vec{\Pi}(t_0)] = Z^{-1}e^{-\beta H_s}, \tag{49}$$

where $\beta = 1/(k_BT)$, k_B the Boltzmann constant, T is the temperature of a surrounding thermostat that mimics the coupling of the system with the experimental setup, and H_s given by

$$H_s(\vec{Q},\vec{\Pi}) = \frac{1}{2}\sum_n\left(\Pi_n\bar{\Pi}_n + \omega_n^2Q_n\bar{Q}_n\right) + \frac{1}{2}\sum_n\{Q_n\,\Psi_n[x(t_0)] + \bar{Q}_n\,\bar{\Psi}_n[x(t_0)]\} + \frac{1}{2}\left(Q_{n_{\rm ex}} + \bar{Q}_{n_{\rm ex}}\right)\frac{F\omega_{n_{\rm ex}}^2}{\Delta^2}\cos\left(\Omega_{n_{\rm ex}}t_0\right). \tag{50}$$

H_s describes the coupling between the substrate and the adatom at position $x(t_0)$ and contains a term derived from the StAW force to take into account the initial conditions imposed by the StAW on the Q_n variables at $t = t_0$. The Hamiltonian H_s is hence different from the H_0 one [see Eq. (8)] of the system

for $t < t_0$, i.e., the probability distribution $p[\vec{Q}(t_0),\vec{\Pi}(t_0)]$ corresponds to a nonequilibrium (macro-)state of the system described by H_0 coupled to a thermostat at temperature T. We will now establish the properties of the fluctuating force $\xi(t)$ for the probability distribution (49).

The examination of Eqs. (48) and (50) reveals that the appropriate variables are

$$R_n = Q_n + \frac{\bar{\Psi}_n}{\omega_n^2} + \Lambda_{n,n_{\rm ex}} \frac{F}{\Delta^2} \cos\left(\Omega_{n_{\rm ex}} t_0\right). \tag{51}$$

With these variables, H_s and $\xi(t)$ read

$$H_s(\vec{Q},\vec{\Pi}) = \frac{1}{2}\sum_n \left[\Pi_n \bar{\Pi}_n + \omega_n^2 R_n \bar{R}_n - \left| \frac{\bar{\Psi}_n}{\omega_n^2} + \Lambda_{n,n_{\rm ex}} \frac{F}{\Delta^2} \cos\left(\Omega_{n_{\rm ex}} t_0\right) \right|^2 \right], \tag{52}$$

$$\xi(t) = -\sum_n \frac{d\Psi_n}{dx}[x(t)] \left\{ R_n(t_0)\cos[\omega_n(t-t_0)] + \left[\frac{\Pi_n(t_0)}{\omega_n} - \Lambda_{n,n_{\rm ex}} \frac{F}{\Delta^2} \frac{\Omega_{n_{\rm ex}}}{\omega_n} \sin\left(\Omega_{n_{\rm ex}} t_0\right) \right] \times \sin[\omega_n(t-t_0)] \right\}. \tag{53}$$

From Eqs. (49) and (52), variables Π_n and R_n appear as complex variables with centered Gaussian distributions of variance β^{-1}. Note, however, that since $\bar{\Pi}_n = \Pi_{-n}$ and $\bar{R}_n = R_{-n}$, all these variables are not independent. One can easily rewrite Eq. (52) using a set of $2N$ independent variables (R_n,Π_n) with $n > 0$:

$$H_s(\vec{Q},\vec{\Pi}) = \sum_{n>0} \left[\Pi_n \bar{\Pi}_n + \omega_n^2 R_n \bar{R}_n - \left| \frac{\bar{\Psi}_n}{\omega_n^2} + \Lambda_{n,n_{\rm ex}} \frac{F}{\Delta^2} \cos\left(\Omega_{n_{\rm ex}} t_0\right) \right|^2 \right]. \tag{54}$$

So that, for any two variables X and $Y \in \{\omega_n R_n, \Pi_n\}$ $(n > 0)$, their mean values $\langle X\rangle$ are 0 and their covariances $\langle [X - \langle X\rangle][\bar{Y} - \langle \bar{Y}\rangle]\rangle$ are $(2/\beta)\delta_{XY}$.

From which we deduce the stochastic properties of $\xi(t)$:

$$\langle \xi(t)\rangle = \frac{F}{\Delta^2} \left\{ \frac{d\Psi_{n_{\rm ex}}}{dx}[x(t)] + \frac{d\bar{\Psi}_{n_{\rm ex}}}{dx}[x(t)] \right\} \times \left\{ \frac{\Omega_{n_{\rm ex}}}{\omega_{n_{\rm ex}}} \sin\left(\Omega_{n_{\rm ex}} t_0\right) \sin[\omega_{n_{\rm ex}}(t-t_0)] \right\}, \tag{55}$$

$$C(t,t') = \langle [\xi(t) - <\xi(t)>]\,[\xi(t') - <\xi(t')>] \rangle = \frac{1}{\beta}\sum_n \frac{\cos[\omega_n(t-t')]}{\omega_n^2} \left\{ \frac{d\Psi_n}{dx}[x(t)] \frac{d\bar{\Psi}_n}{dx}[x(t')] \right\} = \frac{1}{\beta}\gamma[x(t),x(t'),t-t']. \tag{56}$$

We recover in this last equation the fluctuation-dissipation theorem: this result is especially independent of the precise expression of the potentials Φ and $V_{\rm sub}$ in Eq. (1) as soon as this later can be approximated by Eq. (8). The same result has been demonstrated in a general frame by Zwanzig.[15] The non-null value of $\langle \xi(t)\rangle$ is related to the time-dependent Hamiltonian (11) and, more precisely, to the initial conditions that are imposed by abruptly switching on the StAW term at t_0. The Hamiltonian H_s, see Eq. (52), actually takes into account the initial conditions imposed by the StAW on the Q_n variables but not on the Π_n variables. As a consequence, the non-null value of $\langle \xi(t)\rangle$ is directly correlated to the initial conditions imposed on the Π_n variables.

To recover that the average value of the stochastic force cancels, we impose that $\Omega_{n_{\rm ex}} t_0 = 0[\pi]$: this corresponds to switching on the StAW force at an extremum of the force.

VI. THE EFFECTIVE CRYSTALLINE POTENTIAL

The effective crystalline potential $\Phi_{\rm eff}(x)$ reads

$$\Phi_{\rm eff}(x) = \Phi_0(x) + \Delta\Phi_0(x), \tag{57}$$

$$\text{with } \Delta\Phi_0(x) = -\sum_n \frac{1}{2\omega_n^2} \Psi_n(x)\bar{\Psi}_n(x). \tag{58}$$

Using Eq. (22), $\Delta\Phi_0(x)$ reads

$$\Delta\Phi_0(x) = -\sum_n \frac{1}{2\omega_n^2} \alpha_n(x)\bar{\alpha}_n(x). \tag{59}$$

$\Delta\Phi_0(x)$ is then a periodic function of the lattice. $\Delta\Phi_0(x)$ physically corresponds to the potential seen by the adatom induced by the modifications of substrate atoms positions due to the adatom at position x. Such interaction also appears in the memory kernel. Actually, both terms $\Delta\Phi_0(x)$ and the memory kernel derive from the integration by parts of the third term of Eq. (13) leading to Eq. (14). The term $\Delta\Phi_0(x)$ derived from the third term of Eq. (14), corresponds to the static and instantaneous modification of the substrate variables due to the presence of the adatom at position x, while the memory kernel derived from the fourth term of Eq. (14), corresponds to the retarded effects, i.e., how the past positions of the adatom influence the substrate positions at present. Both quantities $\Delta\Phi_0(x)$ and $\gamma(x,x',t-t')$ can be related by introducing the function $\Theta(x,x',t-t')$:

$$\Theta(x,x',t-t') = \sum_n \frac{\cos[\omega_n(t-t')]}{\omega_n^2} \bar{\Psi}_n(x') \frac{d\Psi_n}{dx}(x),$$

$$\frac{d\Delta\Phi_0(x)}{dx} = -\frac{1}{2}\left[\Theta(x,x,0) + \bar{\Theta}(x,x,0)\right],$$

$$\gamma(x,x',t-t') = \frac{\partial\Theta}{\partial x'}(x,x',t-t').$$

An explicit expression of the spatial dependence of $\Delta\Phi_0(x)$ can be obtained using the particular interatomic potential [see

Eq. (28)], and the Ψ_n expression of Eq. (33), in Eq. (58):

$$\Delta\Phi_0(x) = -\frac{V_0^2}{2\sigma^2 M}\left\{\left[\cosh^2\left(\frac{r}{\sigma}\right)+\cosh^2\left(\frac{r-a}{\sigma}\right)\right]\times\sum_n\frac{1}{\omega_n^2\left[\cosh\left(\frac{a}{\sigma}\right)-\cos(k_n a)\right]^2}-2\cosh\left(\frac{r}{\sigma}\right)\cosh\left(\frac{r-a}{\sigma}\right)\times\sum_n\frac{\cos(k_n a)}{\omega_n^2\left[\cosh\left(\frac{a}{\sigma}\right)-\cos(k_n a)\right]^2}\right\}, \quad (60)$$

where the two sums are only numerical factors independent of x. We recover in Eq. (60) that $\Delta\Phi_0(x)$ is a periodic function of the lattice.

VII. CONCLUSION

We have studied the diffusion of an adatom on a substrate submitted to a StAW. We found that the adatom motion is governed by a generalized Langevin equation:

$$m\frac{d^2x}{dt^2} = -\frac{d\Phi_{\text{eff}}}{dx}(x)+\xi(t)-\int_{t_0}^{t}\gamma(x,x',t-t')\frac{dx}{dt}(t')dt' + F_{\text{SAW}}(x,t). \quad (61)$$

We have characterized each of the terms involved in this equation and have given them their analytical expression and most of the time, an explicit expression. A key result is the expression of the force F_{SAW} induced by the StAW as a function of x and t. F_{SAW} essentially varies as $\cos(k_{n_{\text{ex}}}x)\cos(\Omega_{n_{\text{ex}}}t)$, where $k_{n_{\text{ex}}}$ and $\Omega_{n_{\text{ex}}}$ are the spatial and angular frequencies of the StAW. However, a deeper analysis reveals that this force also varies on the crystalline substrate lattice scale. The next paper of this series is devoted to the study of the solutions of Eq. (61).

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