Solitonic mechanisms of dissipation in adsorbed atomic mono-layers

Relatore: Dott. Nicola Manini
Correlatore: Prof. Giuseppe Santoro

Carlotta Negri
Matricola n° 672584
A.A. 2006/2007

Codice PACS: 62.25.g
Solitonic mechanisms of dissipation in adsorbed atomic mono-layers

Carlotta Negri
Dipartimento di Fisica, Università degli Studi di Milano,
Via Celoria 16, 20133 Milano, Italia

October 25, 2007

Abstract

In this work we investigate the possibility of a dissipation topography sensitive to local bonding defects (solitons or kinks) of adatoms monolayers. We carry out this study in a very idealized scheme: the standard Frenkel-Kontorova model, with a harmonic chain representing the layer of atoms adsorbed on a crystalline surface, interacting with a periodic potential representing the solid substrate. In experiments dissipation is mapped through the tip of an Atomic Force Microscope (AFM), which we simulate by means of a Gaussian-shaped oscillating potential. We find evidence of two distinct dissipative regimes, low and a high tip frequency, both showing a pronounced dissipation contrast for the kinks with respect to in-register adatoms. The high visibility of the kinks is explained by the resonant behavior of the power dissipated by the tip as a function of the local atomic vibration frequency, which is strongly sensitive to the rigidity of the local bonding. For weak adatom-adatom interaction, kinks are strongly localized and pinned to the substrate; under these conditions we obtain stationary reproducible dissipation maps. In contrast, when the adatom-adatom interaction exceeds the corrugation of the adatom-substrate interaction, kinks become extended weakly pinned objects which can be dragged along by the tip: correspondingly the dissipation maps acquire a history-dependent quality.

Advisor: Dr. Nicola Manini
Co-Advisor: Prof. Giuseppe Santoro
Contents

1 Introduction 5

2 The model 6

3 Numerical Method 9
   3.1 Periodic boundary conditions 9
   3.2 Boundary condition for the tip potential 9
   3.3 Dissipative dynamics 10

4 The linear-response regime 10

5 Results 18
   5.1 Soft kinks 22
      5.1.1 Underdamped regime 22
      5.1.2 Overdamped regime 25
   5.2 Hard kinks 25
      5.2.1 Dragging 25
      5.2.2 Fixed Boundary Conditions 30
      5.2.3 Peyrard-Remoissenet substrate potential 32
   5.3 Anti-kinks 39

6 Conclusions 39

Bibliography 41
1 Introduction

Adatoms deposited on flat crystalline surfaces tend to enforce different lattice periodicities compared to that of the surface itself. This general tendency produces a great variety of geometrical arrangements of monolayers of adatoms, including all sorts of reconstructions. Among these, when the periods of the substrate and the adlayer are close, large-cell Moiré patterns often develop, see Fig. 1. These patterns are formed by the regular alternations of regions of adatoms sitting almost at register with the substrate, at energetically favorable highly coordinated (e.g. hollow) sites, and regions where the adatoms are pushed to less favorable configurations (e.g. near top sites) by geometric size constraints. The latter regions are sometimes viewed as topological defects of an otherwise perfect lattice of adatoms, and are often referred to as 'solitons', 'solitonic waves', or 'kinks'. The solitonic atoms are less pinned to their equilibrium position than their in-register counterpart, thus one can expect different response properties when stimulated dynamically, e.g. via an Atomic-Force Microscope (AFM) tip. In particular the AFM can be used in a dynamical mode (DFM) to map the covered surface local dissipation properties [1, 2, 3]. We expect that solitons should provide well-distinct dissipation signals compared to perfect in-register regions. To investigate this expectation, we resort to a simple, strongly idealized and widely studied model, the one-dimensional Frenkel-Kontorova (FK) model [4], using it to represent the monolayer of atoms adsorbed on a crystal surface. We then add a Gaussian-shaped oscillating potential to represent the AFM tip. The one-dimensional FK model, as exhaustively reported in Ref. [4], describes the dynamics of an adsorbate monolayer, idealized as interacting with a crystalline surface and represented by a simple harmonic chain of particles in a sinusoidal...
external potential. In the continuum-limit approximation, the FK model maps to a non-linear differential equation (the sine-Gordon equation) showing solitonic solutions which describe transitions between equivalent ‘vacuum’ states, representing the kinks. This feature is visible also in the original discrete model, where the ‘vacuum’ corresponds to all atoms sitting at substrate potential minima, with a kink representing an extra particle with the induced local distortion of the otherwise regular lattice. The proposal of the present work is precisely to investigate the different response of the solitons and of the in-register particles to the AFM tip perturbation. The simple one-dimensional model used here permits us to understand and illustrate the basic physical properties underlying the dissipation-contrast mechanism, avoiding the complications and details of a fully realistic treatment. That would be object of further future investigations.

2 The model

We represent the AFM tip as a repulsive Gaussian-shaped oscillating potential. The Lagrangian for the model dynamics is

$$\mathcal{L} = T - U,$$

where $T$ and $U$ are the kinetic and potential energies respectively. The kinetic term is

$$T = \sum_i \frac{1}{2} m \dot{x}_i^2,$$

with $m$ and $\dot{x}_i$ mass and velocity of $i$-th particle. The potential energy includes three contributions:

$$U = U_{\text{sub}} + U_{\text{spring}} + U_T.$$
Figure 3: The tip potential \( u_T \) with the relevant physical parameters outlined.

The first term accounts for the interaction between adatoms and the surface periodic potential:

\[
U_{\text{sub}} = \sum_i u(x_i) \quad \text{with} \quad u(x_i) = -\frac{1}{2} u_{\text{sub}} \cos(k_{\text{sub}} x_i),
\]

and with \( k_{\text{sub}} = \frac{2\pi}{a_{\text{sub}}} \), where \( a_{\text{sub}} \) is the period of the substrate potential, and the amplitude \( u_{\text{sub}} = \frac{F_{\text{sub}}}{2\pi} a_{\text{sub}} \). The second term, representing the potential energy of the springs, takes into account only interactions between nearest neighbors at a harmonic level:

\[
U_{\text{spring}} = K \sum_i (x_{i+1} - x_i - a_0)^2,
\]

\( a_0 \) being the relaxed length of the springs, with restoring constant \( K \). The last term is the tip potential:

\[
U_T = \sum_i u_T(x_i),
\]

with:

\[
u_T(x_i) = \begin{cases} 0 & \text{if} \quad \left( \frac{x_i - x_T - \Delta_T \sin(\omega_T t)}{\sigma_T} \right)^2 \geq 100 \\ A_T \exp \left[ - \left( \frac{x_i - x_T - \Delta_T \sin(\omega_T t)}{\sigma_T} \right)^2 \right] & \text{otherwise} \end{cases}
\]

where \( A_T \) is the amplitude (proportional to the intensity of the tip force), \( \sigma_T \) the spatial tip width, \( \Delta_T \) the oscillation amplitude around the central position \( x_T \) and \( \omega_T \) the angular frequency of the tip oscillation, see Fig. 3. The Gaussian is cut-off deep into the tail region, in order not to waste calculation time in the regions
Table 1: Natural units for several mechanical quantities in a system where lengths, forces and masses are expressed in units of \( a_{\text{sub}} \), \( F_{\text{sub}} \) and \( m \) respectively.

where the potential is negligible. A friction force term \(-\gamma \sum_i \dot{x}_i\) accounts for all sorts of dissipative phenomena which cause losses of energy into the substrate.

The equation of motion for the \( i \)-th particle is then

\[
m \ddot{x}_i = -\frac{1}{2} F_{\text{sub}} \sin(k_{\text{sub}} x_i) + K(x_{i+1} + x_{i-1} - 2x_i) - \gamma \dot{x}_i + 2 \frac{A_T}{\sigma_T^2} (x_i - \bar{x}_T - \Delta_T \sin(\omega_T t)) \exp \left[ -\left( \frac{x_i - \bar{x}_T - \Delta_T \sin(\omega_T t)}{\sigma_T} \right)^2 \right],
\]

where \( F_{\text{sub}} = k_{\text{sub}} u_{\text{sub}} \) is the amplitude of the substrate corrugation force. The two periodicities \( a_0 \) and \( a_{\text{sub}} \) define the coverage ratio

\[
\theta = \frac{a_{\text{sub}}}{a_0}.
\]

For convenience we take \( a_{\text{sub}} \) as unit length, \( F_{\text{sub}} \) as unit force, the mass \( m \) of the particles as unit mass and choose to define all other physical quantities in terms of these units, so that they are expressed as dimensionless numbers. The explicit dimensional form can be obtained by simply multiplying the numerical value of one physical quantity by the corresponding unit shown in Table 1.
3 Numerical Method

To solve the differential equation of motion (8), a standard adaptive fourth-order Runge-Kutta algorithm is used [5]. The model of Sec. 2 could be applied to a chain of infinite length, but to perform a practical numerical calculation, a finite number $N$ of particles must be considered: finite-size effects are minimized by applying periodic boundary condition (PBC), in particular to the spring term. We consequently need also to make the tip potential fit into the PBC.

3.1 Periodic boundary conditions

For PBC to be perfectly implemented the $(N + 1)$-th particle replica is to be found at the same static position relative to the substrate potential $u(x)$ as the first one, which is obtained by choosing $N$ so that $L = Na_0$ is a multiple of $a_{\text{sub}}$, i.e. $N$ is a multiple of $\theta = \frac{a_{\text{sub}}}{a_0}$. This is possible only for rational values of $\theta$. In the irrational case PBC could be implemented by taking suitable rational approximants of $\theta$, e.g. the first convergents of its continued fraction expansion. For example, good rational approximants of the Golden Mean $\phi = \frac{1 + \sqrt{5}}{2}$ are given by the Fibonacci Sequence ($F_{n+1} = F_n + F_{n-1}$, $F_0 = F_1 = 1$), Fibonacci Numbers occurring as the ratio of successive convergents of the continued fraction for $\phi$; so approximating $\theta = \frac{F_{n+1}}{F_n}$ produces a system with $N = F_{n+1}$ particles placed in a ring of length $L = Na_0 = F_n a_{\text{sub}}$ and subjected to a substrate potential with $F_n$ minima. In practice, to check the role of kinks in the dissipation mechanism, a commensurate situation is perfectly adequate: we will then stick to rational $\theta$ in all calculations of the present work.

3.2 Boundary condition for the tip potential

To implement the tip Gaussian potential in a periodic framework, assuming $\sigma_T \ll L$, we approximate the particles to interact with one single replica of the tip, periodically repeated every $L$ length units. To specify the closest one among the infinitely many tip replicas that a given particle should interact with, we add a shift $\Phi \cdot L$ to the argument of the Gaussian, for a suitably chosen integer $\Phi$. We take $\Phi$ such that:

$$-\frac{1}{2} < \frac{x_i - \bar{x}_T - \Delta_T \sin(\omega_T t) + \Phi L}{L} \leq \frac{1}{2},$$

(10)
thus

\[ \Phi = -\text{int}\left( \frac{x_i - \bar{x}_T - \Delta_T \sin(\omega_T t)}{L} \right), \tag{11} \]

where \( \text{int}(\ ) \) means the nearest integer to its argument. The tip force, representing the interaction with the tip potential, in the equation of motion (8) is therefore to be replaced by

\[ F_T(x_i) = 2 \frac{A_T}{\sigma_T^2} (x_i - \bar{x}_T - \Delta_T \sin(\omega_T t) + \Phi L) \cdot \exp \left[ - \left( \frac{x_i - \bar{x}_T - \Delta_T \sin(\omega_T t) + \Phi L \sigma_T}{\sigma_T} \right)^2 \right]. \tag{12} \]

The so-modified equation of motion is then integrated in our computations, starting from fully relaxed springs, i.e. starting off with stationary particles at positions \( x_i = i \cdot a_0 \).

### 3.3 Dissipative dynamics

The instantaneous total power dissipated by the viscous friction term amounts to

\[ P_{\text{diss}} = \sum_i \dot{x}_i \cdot (\gamma \dot{x}_i) = \gamma \sum_i \dot{x}_i^2 = \frac{2 \gamma}{m} T, \tag{13} \]

thus it is proportional to the total kinetic energy. By our numerical simulations, we also compute the instantaneous power dissipated by the tip as

\[ P_T = \sum_i F_T^i \cdot \dot{x}_i. \tag{14} \]

These two quantities fluctuate but, on average, in the stationary dynamical state, must be equal,

\[ \frac{1}{T} \int_T dt P_T(t) = \frac{1}{T} \int_T dt P_{\text{diss}}(t) = \langle P \rangle, \tag{15} \]

meaning that the work supplied by the tip oscillation is eventually, on average, lost entirely through the viscous-friction term.

### 4 The linear-response regime

The nature of the dissipative mechanism at play in the model at hand is identified most clearly within the simplest, single-particle case, when no complications are
introduced by the interparticle harmonic couplings. In this basic configuration, if the tip amplitude of vibration is so small that it can be neglected, we are in the presence of a stationary time-independent 1-particle dynamics. The particle reaches rapidly equilibrium at a point \( x_{eq} \) when the condition \( F_T + F_{sub} = 0 \) is satisfied, which means:

\[
- \frac{\partial}{\partial x} [\tilde{u}_T(x) + u(x)] \bigg|_{x_{eq}} = 0,
\]

(16)

where \( \tilde{u}_T(x) = A_T \exp \left[ - \frac{(x - \bar{x}_T)^2}{\sigma_T^2} \right] \) is the stationary tip term. Of course, for a weak tip, \( x_{eq} \) sits close to one of the minima of the substrate potential \( u(x) \). We determine \( x_{eq} \) by solving numerically equation (16). We then restore the time dependence in the tip potential and consider the dynamics in a neighborhood of \( x_{eq} \) by expanding \( u_{tot} = u_T + u \) in Taylor series and neglecting all terms beyond the quadratic one. We assume that the oscillatory term \( \Delta_T \sin(\omega_T t) \) in the tip potential is of the same order as \( x - x_{eq} \). We thus obtain the following expression for the leading force term:

\[
-F_{tot} \simeq \frac{\partial}{\partial x} u(x) \bigg|_{x_{eq}} + \frac{\partial}{\partial x} u_T(x, t) \bigg|_{x_{eq}} + \frac{\partial^2}{\partial x^2} u(x) \bigg|_{x_{eq}} (x - x_{eq}) + \frac{\partial^2}{\partial x^2} u_T(x, t) \bigg|_{x_{eq}} (x - x_{eq}) - \frac{\partial^2}{\partial x^2} \tilde{u}_T(x) \bigg|_{x_{eq}} \Delta_T \sin(\omega_T t) .
\]

(17)

We find two linear restoring terms \( \propto (x - x_{eq}) \) and a further oscillating term, showing explicit linearity in \( \Delta_T \). Equation (17) is of the form \( F_{tot} \simeq -\alpha \xi - B \sin(\omega_T t) \), with

\[
\xi = x - x_{eq} \quad \alpha = \frac{\partial^2}{\partial x^2} u(x) \bigg|_{x_{eq}} + \frac{\partial^2}{\partial x^2} \tilde{u}_T(x) \bigg|_{x_{eq}} \quad B = - \frac{\partial^2}{\partial x^2} \tilde{u}_T(x) \bigg|_{x_{eq}} \Delta_T .
\]

(18)

The ensuing linearized equation of motion is then exactly the one of a driven damped harmonic oscillator:

\[
m \ddot{\xi} + \gamma \dot{\xi} + \alpha \xi = -B \sin(\omega_T t) .
\]

(19)
The well-known stationary solution which survives after an initial transient is:

\[ \xi(t) = \frac{B}{m \sqrt{\left(\frac{\alpha}{m} - \omega_0^2\right)^2 + \frac{\gamma^2 \omega_T^2}{m^2}}} \cos(\omega_T t + \phi). \]  

(20)

The total power dissipated by the tip can be obtained based on relation (14) or equivalently (15). The average over a period \( T = \frac{2\pi}{\omega_T} \) evaluates to

\[ \langle P \rangle = \frac{B^2}{m^2} \frac{\gamma \omega_T^2}{(\omega_0^2 - \omega_T^2)^2 + \frac{\gamma^2 \omega_T^2}{m^2}} \frac{1}{T} \int_T \sin^2(\omega_T t + \phi) dt = \]

\[ = \frac{B^2}{2m^2} \frac{\gamma \omega_T^2}{(\omega_0^2 - \omega_T^2)^2 + \frac{\gamma^2 \omega_T^2}{m^2}}. \]  

(21)

Notice that the mean power dissipated in a period is quadratic in \( B \), thus in \( \Delta_T \).

The parameter \( \omega_0 = \sqrt{\frac{\alpha}{m}} \) is the natural frequency of the oscillator and sets the resonance frequency. Indeed the mean power shows a typical resonant behavior and reaches a maximum when \( \omega_T \) equals \( \omega_0 \). It is then natural to express the dissipated power as a function of the ratio \( \Omega = \frac{\omega_T}{\omega_0} \), as follows:

\[ \langle P \rangle = \frac{\gamma B^2}{2m^2 \omega_0^2} \left( \frac{\Omega^2}{(1 - \Omega^2)^2 + \frac{\gamma^2}{m^2} \Omega^2} \right). \]  

(22)

The resulting curve is depicted in Fig. 4 for several values of dissipation.

We compare the power dissipated according to Eq. (21) to the actual result of a simulation carried out at finite oscillation amplitude \( \Delta_T \): Fig. 5 shows an excellent agreement within the chosen range of \( \Delta_T \), which remains in the linear regime. As the amplitude of the oscillation increases, the linear approximation is no longer valid and we see that the simulation data deviate from the linear curves, Fig. 6. All these calculations are carried out with a choice of parameters which represents a fairly gentle \( (A_T = 0.01) \) tip slightly oscillating close to the particle \( (x - \bar{x}_T \simeq 0.1) \). The tip is sharp, of width \( \sigma_T = 0.1 \). We check that for a fairly wide range of values of \( A_T \) the simulations data deviate from the analytical expression (21) by less than 20%, with \( \Delta_T \lesssim 0.01 \). We have tested and found the same essentially linear behavior both in the overdamped \((\frac{\gamma^2}{m^2} \gg 1)\) and the underdamped \((\frac{\gamma^2}{m^2} \ll 1)\) regime, which we analyzed by using \( \gamma = 20 \) and \( \gamma = 0.2 \) respectively. We also checked that the linear-response regime holds for slightly different choices of tip width, \( \sigma_T = 0.05 \div 0.5 \).

The resonant behavior illustrated in Fig. 4 is the key of the high visibility that kinks can produce when explored in a dissipation scan. This provides a powerful way to detect local variations of adatoms bonding, through the mechanism
\( \Omega = \frac{\omega_T}{\omega_0} = \frac{\omega_T}{\sqrt{\alpha/m}} \) for several values of the dimensionless dissipation parameter \( \gamma^2/(m\alpha) \). The power values are consistent with \( \frac{P^2}{2m\gamma^2} \approx 9.84 \times 10^{-6} \) and \( \alpha = 4.008 \), which correspond for example to a tip of amplitude \( A_T = 0.01 \) and width \( \sigma_T = 0.1 \) placed at a distance \( \bar{x}_T = 0.1 \) away from the \( u(x) \) potential minimum (at \( x = 0 \)) near which the adatom is sitting. These conditions lead to \( x_{eq} = -0.0185 \).
Figure 5: Comparison of the mean power dissipated by the oscillating tip, coupled to a single adatom, according to the linear-response formula (21) (lines) and the numerical calculations (points), as a function of the squared amplitude of oscillation $\Delta^2_T$. A small damping $\gamma = 0.2$ is taken here. The comparisons are carried out for different values of the tip potential amplitude $A_T$, and at a fixed distance $\tilde{x}_T = 0.1$ from the nearest minimum of $u(x)$, which is $x = 0$. The tip width is $\sigma_T = 0.1$. The oscillation frequency is $\omega_T = 0.1\pi < \omega_0$. 

$A_T = 0.05$

$A_T = 0.03$

$A_T = 0.02$

$A_T = 0.015$

$A_T = 0.01$

$A_T = 0.005$
Figure 6: Comparison of the mean power dissipated by the oscillating tip, coupled to a single adatom, according to the linear-response formula (21) (lines) and the numerical calculations (points), as a function of the squared amplitude of oscillation $\Delta_T^2$. The tip width, the oscillation frequency and the viscous friction coefficient $\gamma$ are the same as in Fig. 5. The range of variation of $\Delta_T^2$ is extended here enough to show clearly the deviation of the numerical simulations from the analytical expression (21). Again the comparisons are carried out for different values of the tip potential amplitude $A_T$, and at a fixed distance $\bar{x}_T = 0.1$ from the nearest minimum of $u(x)$, which is $x = 0$. 
Indeed, if the restoring coefficient $\alpha$ in the linearized equation of motion (19) varies from one particle to another, the present theory shows that the dissipation should also change in correspondence, due to changes of $\Omega = \frac{\omega_T}{\sqrt{\alpha/m}}$. This should occur especially for suitable values of $\omega_T$ putting $\Omega$ in a region around the resonance, where, for fixed $\omega_T$, dissipation can vary quite substantially when varying $\alpha$ only by a little. In particular, we distinguish two different regimes: a low-frequency one, $\Omega < 1$, and a high-frequency one $\Omega > 1$. As illustrated in Fig. 7, a decreased $\alpha$ produces an increased or decreased dissipation depending on being, on average, at the left or at the right of the peak, respectively. In practice the high-frequency regime is not accessible experimentally, since the natural tip frequency is many orders of magnitude smaller than typical adatom vibration frequencies. We investigate the high-frequency regime mostly for its conceptual interest.

Importantly, as illustrated in Fig. 4, the visibility of the solitons is strongly enhanced in the underdamped regime, while it is strongly suppressed for large damping $\gamma$. Notice also that, due to the tip contribution in Eq. (18), even in a single-particle calculation, $\alpha$ is not a constant but varies as function of the tip-particle distance $x_{eq} - \bar{x}_T$ resulting in the curve of Fig. 8 (with tip parameters $A_T = 0.01$ and $\sigma_T = 0.1$). The two contributions from the substrate potential
Figure 8: The total potential curvature $\alpha$ as a function of $|x_{eq} - \bar{x}_T|$, for a stationary tip defined by $A_T = 0.01$ and $\sigma_T = 0.1$. The large-distance value $\alpha = \pi$ is the pure $u(x)$ contribution, while at shorter distance also the tip Gaussian potential contributes, initially increasing $\alpha$ and then eventually reducing it by $\frac{A_T}{\sigma_T^2}$. 
and the tip potential,
\[ \alpha = \alpha_{\text{sub}} + \alpha_T, \]
\[ \alpha_{\text{sub}} = \frac{\partial^2}{\partial x^2} u(x) \bigg|_{x_{eq}} = \pi \cos \left( \frac{2\pi x_{eq}}{a_{\text{sub}}} \right), \]
\[ \alpha_T = \frac{\partial^2}{\partial x^2} \tilde{u}_T(x) \bigg|_{x_{eq}} = 2 \frac{A_T}{\sigma_T^2} \left[ 2(x_{eq} - \bar{x}_T)^2 - \sigma_T^2 \right] \exp \left[ - \left( \frac{x_{eq} - \bar{x}_T}{\sigma_T} \right)^2 \right]. \]

When the distance of \( \bar{x}_T \) from the equilibrium value \( x_{eq} \) is infinitely large, the particle is undisturbed by the tip, \( x_{eq} = 0 \), and only the contribution \( \alpha = \pi \) by the substrate remains. When the tip is brought exactly on the top of the adatom, \( x_{eq} = \bar{x}_T = 0 \), so that \( \alpha = \alpha_{\text{sub}} + \alpha_T = \pi - 2 \frac{A_T}{\sigma_T^2} = 1.14 \) with the parameters of Fig. 8. For these parameters the maximum value \( \alpha_{\text{max}} = 4.0156 \) is reached at \( |x_{eq} - \bar{x}_T| \approx 0.123 \). In the following we only consider tip parameters for which, at \( \bar{x}_T = x_{eq} = 0, \alpha > 0 \) so that the adatom rest position is not destabilized.

\[ \textbf{5 Results} \]

We explore the dissipation mechanisms of the tip interacting with the adatoms chain. The choice of the tip parameters is made such as to remain close to the linear regime: in most simulations \( A_T = 0.01, \sigma_T = 0.1 \) and \( \Delta_T = 0.001 \) are used, resulting in a sharp and rather gentle tip, oscillating at an amplitude much smaller than periodicity of the substrate potential. In this condition we expect that most of the power is supplied by the tip to the nearest adatom, so that, by varying the center of oscillation \( \bar{x}_T \) along the chain and computing the corresponding mean dissipated power based on an integer number of oscillation periods, we observe dissipation peaks near each particle equilibrium position, with little or no dissipation between them. In the following, we present the results of simulations with a commensurate choice of the length ratio of Eq. (25): \( \theta = 1.16 = \frac{29}{25} \). We realize this with a chain of \( N = 29 \) particles initially separated by \( a_0 = \frac{a_{\text{sub}}}{\theta} \) along a periodic domain of length \( L = 25 \), fitting in the 25 minima of \( u(x) \). This mismatch produces local compressions of the chain due to four substrate potential minima needing to hold two particles rather than just one: these topological coverage defects represent the so-called kinks or solitons, well known and studied in the FK model. As outlined in previous works, the
Peculiar to a discrete model like the FK model here considered is the existence of the so-called Peierls-Nabarro (PN) periodic potential which opposes to the kinks motion. The PN barrier $E_{PN}$ represents the smallest energy required for a kink to move through a lattice and is given by the difference between the kink’s potential energy in two states corresponding to a stable and unstable stationary configuration, with a kink placed at the minimum of the PN potential and a kink situated at the top respectively [4]. Approximate expressions for the PN barrier have been calculated in a number of papers for several different conditions. In the case of strong coupling between particles, $\tilde{g} \gg 1$, where $\tilde{g} = \frac{a_{sub}}{\frac{F_{sub}}{a_{sub}} K \pi}$, with $K$ the spring constant of Eq. 5, the energy $E_{PN}$ for a static kink, expressed in the natural units of our model, was estimated as follows [4]:

$$E_{PN} = \frac{F_{sub} a_{sub}}{4\pi} 32\pi^2 \frac{\tilde{g}}{\sinh(\frac{\pi^2}{2} \sqrt{\tilde{g}})} \left(1 + \frac{1}{2\pi^2 \tilde{g}}\right).$$

The corresponding curve, as a function of $K$ is displayed in Fig 9.

We plan to exploit for the FK chain the resonant behavior of the mean power dissipated by the tip as a function of the oscillation frequency $\omega_T$ demonstrated
within the single-adatom linearized model, Sec. 4. When we consider the dynamics of the whole chain, the springs contribution to the local curvature must be included. From Eq. (5) we have:

\[ \frac{\partial^2}{\partial x_i^2} U_{\text{springs}} \bigg|_{x_i = x_{\text{eq}}} = 2K. \]

If the response of \( x_{i-1} \) and \( x_{i+1} \) could be neglected, a further term of the order \( 2K \) must then be added to \( \alpha \) in order to estimate the effective value \( \alpha_{i,\text{eff}} \) relevant for adatom \( i \). The range of variability of this parameter is not evaluated so simply as for the single-adatom molecule: we just estimate that \( \alpha_{i,\text{eff}} \) should vary between a maximum and a minimum value given by:

\[
\begin{align*}
\alpha_{\text{eff}}^{\text{max}} &\simeq \alpha_{\text{max}} + 2K \\
\alpha_{\text{eff}}^{\text{min}} &\simeq 2K - \alpha_{\text{sub}} + \alpha_T,
\end{align*}
\]

where \( \alpha_{\text{max}} \) is the single-particle one calculated in Sec. 4 and \( \alpha_{\text{sub}} \) is the curvature at the minimum of \( u(x) \). The curvature \( \alpha_{\text{eff}} \) of the total potential at the stable equilibrium point \( x_{\text{eq}} \) must be positive, and this restricts the validity of the former hypothesis about \( \alpha_{\text{eff}}^{\text{min}} \) to a range of sufficiently large \( K \). For smaller values (e.g. \( K = 1 \)) there is no simple immediate analytical expression: we imagine the adatoms to climb only partly the substrate potential wells where they are placed and do not go beyond the inflection points of each well, so that the minimum curvature is reached exactly at these points, where the curvature of the substrate potential vanishes and only a term \( 2K \) and a term due to the tip contribute.

To test the efficiency of our method to compute the system dissipation we initially explore briefly the small-\( K \) limit, that is we select a very small value of the spring constant, for example \( K = 0.001 \). In this condition the particles interact weakly and the system does not show special dissipative behavior: we expect to find the same amount of dissipation for each particle. Varying the tip position along the chain should be pretty much the same as ‘counting’ the particles. This prediction is verified in Fig. 10. The doubling of the dissipated power near \( \bar{x}_T = 3, 9, 16, 22 \) is explained by the presence of the four small solitons at those points: when the tip encounters each soliton, it dissipates twice as much, as it interacts with two very close particles near that minimum of \( u(x) \) rather than just one. In this test \( \alpha_{\text{eff}} \) is the same for all particles, thus no visibility effect is produced by shifts in \( \Omega = \frac{\omega_T}{\sqrt{\alpha_{\text{eff}}/m}} \) and the dissipation is trivially proportional to the local particles density.
Figure 10: Total mean power dissipated by the tip as a function of its position $\bar{x}_T$ for $\gamma = 0.2$ and $K = 0.001$. Here $\sigma_T = 0.1$, $A_T = 0.01$, $\omega_T = 0.1\pi$ and $\Delta_T = 0.001$. The final adatoms positions for $\bar{x}_T = 6$ are represented by circles; open circles represent pairs of particles localized in the same well (small kinks). The substrate potential $u(x)$ is drawn below the chain (with an arbitrary energy scale). The four higher peaks correspond to the four solitons produced by the coverage $\theta = \frac{29}{25}$. We have checked that for this tiny $K$ the mean adatom position (after a transient) is affected very little by the mean position $\bar{x}_T$ of the tip, so that, in particular, the position of the solitons remains the same for all $\bar{x}_T$. 
Figure 11: Total mean power dissipated by the tip as a function of its position $\bar{x}_T$ for $\gamma = 0.2$, $K = 1$, in the low-frequency regime $\omega_T = \pi/4 = 0.785$. Here $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$. The final adatoms positions for $\bar{x}_T = 6$ are represented by circles. The substrate potential is drawn below the chain. We have checked that, for this value of $K$, the final particles position is practically independent of the mean position of the tip $\bar{x}_T$. Sharp peaks of dissipation are visible corresponding to kink-adatoms. Elsewhere the dissipation does not exceed 2% of the kink-related maxima.

5.1 Soft kinks

5.1.1 Underdamped regime

Consider again the underdamped regime $\gamma = 0.2$. We take $K = 1$, to investigate a system of rather loosely interacting adatoms, producing 'soft' and fairly localized kinks. According to considerations above, for such an intermediate-small value of the spring constant we lack an explicit expression for $\alpha_{\text{eff}}^{\text{min}}$ but we can expect it to be near to unity (due to the contribution of the tip potential to the curvature), so that a frequency $\omega_T < 1$ should put all values of the local ratio $\Omega = \frac{\omega_T}{\sqrt{\alpha_{\text{eff}}/m}}$ in the
Figure 12: Total mean power dissipated by the tip as a function of its position $\bar{x}_T$ for $\gamma = 0.2$ and $K = 1$, in the high-frequency regime $\Omega > 1$, $\omega_T = 3\pi/2$. Here $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$. The final adatoms positions are represented by circles. The substrate potential is drawn below the chain. Kinks are characterized by a drop in dissipation. We checked by integration that the dissipation near an isolated adatom at a minimum of $u(x)$ is similar to the one produced by the two particles composing each kink.

region before the resonance of Fig. 4. In this region smaller values of $\alpha_{\text{eff}}$ produce higher dissipation, that is we expect higher peaks of dissipation at the kinks and smaller ones at isolated particles near the $u(x)$ minima (where the curvature of $u(x)$ is maximum). This shows in the calculation, as illustrated in Fig. 11.

An opposite behavior is obtained in the high-frequency regime $\Omega > 1$, obtained by selecting $\omega_T^2 > \alpha_{\text{eff}}^{\text{max}}$: here we find the lowest dissipation at kink positions, while dissipation peaks at adatoms fully pinned at the minima of $u(x)$, as reported in Fig. 12. For an intermediate frequency $\omega_T$, $\alpha_{\text{eff}}$ changes so that $\Omega$ can sit before, precisely at, or after resonance. Dissipation peaks occur for those adatoms which happen to be nearest to resonance. As reported in Fig. 13, the resonances can occur for atoms sitting at the sides of kinks.
Figure 13: Total mean power dissipated by the tip as a function of its position $\bar{x}_T$ for $\gamma = 0.2$, $K = 1$, at an intermediate $\omega_T = 6\pi/15$, such that $\Omega \simeq 1$. The tip is defined by $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$. The final adatom positions are represented by circles. The peaks on particles sitting next to solitons display resonance occurring for $\alpha_{\text{eff}}$ very close to the corresponding one.
5.1.2 Overdamped regime

We carried out simulations in the overdamped regime, choosing a large value of the viscous friction coefficient $\gamma$. In this dynamical framework we do not expect interesting dependencies of the power dissipation on the frequency of tip oscillations to be particularly visible, since the curve of Fig. 4 in Sec. 4 becomes rather flat in the overdamped regime of large $\gamma$. Results of simulations with several values of $\gamma$ are reported in Fig. 14 showing the relative difference of the dissipation on the kinks respect to the rest of the chain diminishing as $\gamma$ is increased. For $\gamma = 200$ we see practically the same dissipation for all particles.

5.2 Hard kinks

5.2.1 Dragging

If the value of the spring constant $K$ is increased, the pinning of kinks becomes weaker and weaker: the dynamically stable position of the solitons is not independent of $\bar{x}_T$, but it is pushed forward as the tip advances. Note that the simulations involve tiny stepwise advancements of the tip, with the adatom configuration at the beginning of the simulation after the tip advances starting off at the final positions of the previous step. For $K = 2$ this is depicted in Fig. 15, where the final adatoms positions are reported for different values of $\bar{x}_T$. The chosen frequencies are representative of the low and high-frequency regime respectively: although the soliton dragging makes the dissipation curves a little confused, the two-fold dissipative behavior (strong dissipation at kinks at low-frequency, weak at high frequency) previously illustrated is still recognizable. The novelty here is that the kink closest to the tip is made advance for a few lattice spacings, until it eventually stops, due to the increasing repulsion of the next stationary kink. At this point the tip advances through a pinned region, and finally reaches the next kink, and drags that one along for a while, and so on.

For even larger $K$ full chain dragging occurs, regardless of the tip initial position. As the tip advances, we find all particles correspondingly shifting ahead by roughly the same amount. We report here three simulations for $K = 5, 6, 7$ resulting in the curves of Fig. 16 and Fig. 17. The spiky appearance of the $K = 5$ dissipation curve is explained as follows: the Peierls-Nabarro barrier (Fig. 9) is still sizable, thus it produces a significant resistance to the dragging, so that the tip action is not uniform along the chain: we find an increasing dissipa-
Figure 14: Total mean power dissipated by the tip as a function of its position $\bar{x}_T$ for $K = 1$ and $\gamma = 2, 10, 20, 200$, from bottom to top panel. Here $\sigma_T = 0.1$, $A_T = 0.01$, $\omega_T = 0.1\pi$ and $\Delta_T = 0.001$. The final positions of the particles are represented by circles. Even in this low-frequency regime the dissipation tends to become the same for all particles as $\gamma$ increases: the increased dissipation at kinks associated to their lower value of $\alpha_{\text{eff}}$ is here progressively washed away by the increasing $\gamma$, which corresponds to a flatter and flatter curve in Fig. 4.
Figure 15: Total mean power dissipated by the tip as a function of its mean position $\bar{x}_T$, for $\gamma = 0.2$ and $K = 2$. Tip parameters are $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$. We carried out calculations for each new value of $\bar{x}_T$ restarting from the final chain configuration of the previous $\bar{x}_T$. Frequencies $\omega_T = \pi/3$ and $\omega_T = 2\pi/3$ characterize the low-frequency and the high-frequency regime respectively. The chain positions, as $\bar{x}_T$ moves from 0 to 12 are represented by points under the two dissipation plots. The first kink is dragged by approximately one lattice spring as the tip passes along, but is rapidly released due to the repulsion of the second one. This remains pinned for some more because the next kink (not displayed) is more far away in the chain and the repulsion is less.
Figure 16: Total mean power dissipated by the tip as a function of its position $\bar{x}_T$, for $\gamma = 0.2$, $\omega_T = 4\pi/3$ and a rather stiff chain, $K = 5$. Tip parameters are $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$. The adatom positions $x_i$ for $\bar{x}_T$ advancing from 5 to 9 are represented by chains of successive points. Every calculation for a new value of $\bar{x}_T$ starts from the final adatom positions obtained by the previous one, so that as $\bar{x}_T$ proceeds along the $x$ axis we see the whole chain dragged along correspondingly.
Figure 17: Total mean power dissipated by the tip as a function of $\bar{x}_T$ for $\gamma = 0.2$, $K = 6$ at the top and $K = 7$ at the bottom. Tip parameters are $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$. Here $\omega_T = 4\pi/3$. The adatom positions for $\bar{x}_T$ going from 0 to 6 with unit steps are represented by chains of points. The dragging phenomenon of Fig. 16 is even clearer here.
Figure 18: Total mean power dissipated by the tip as a function of $\bar{x}_T$ for the same conditions as Fig. 16 except for the tip strength, here reduced to $A_T = 0.0001$ only. Also, the amplitude of oscillation is increased to $\Delta_T = 0.01$ in order to restore a measurable dissipation. No dragging is observed for this ‘soft’ tip.

5.2.2 Fixed Boundary Conditions

The kinks mobility somewhat disturbs the mapping of the solitonic dissipation mechanisms. In principle we could work around this phenomenon by employing a suitably ‘soft’ tip: indeed we expect that a tip whose potential-energy profile is small with respect to the Peierls-Nabarro potential barrier for a given value of the springs constant $K$ should be unable to drag kinks forward. According
Figure 19: Total mean power dissipated by the tip as a function of its position $\bar{x}_T$ for the $K=7$ chain stopped with FBC, and using the usual parameters $\gamma=0.2$, $\sigma_T=0.1$, $A_T=0.01$ and $\Delta_T=0.001$. The final adatom positions for $\bar{x}_T$ going from 0 to 25 with unit steps are represented by successive rows of circles. The substrate potential is drawn below the chain. Here $\omega_T=\pi/4$ (top) and $\omega_T=7\pi/4$ (bottom) represent the low-frequency and the high-frequency regimes respectively. Kinks are recognizable as particles away from minima of the substrate potential. Boundary effects due to FBC are visible.
to the estimation for $E_{PN}$ of Eq. (27), for $K = 5$ the barrier to overcome for a kink to move amounts to $E_{PN} \simeq 0.0003$, Fig. 9. This suggests that a tip unable to produce dragging should be defined by an amplitude $A_T < E_{PN}$. We tested this prediction with a few simulations: Fig. 18 reports results for exactly the same parameters as in Fig. 16 except for the tip being ‘softened’, that is with $A_T = 0.0001$ and $\Delta_T = 0.01$ instead of $A_T = 0.01$ and $\Delta_T = 0.001$. No dragging is observed. The problem with this approach is that, according to formulas, the amount of dissipated power is proportional to the squared amplitude of the tip potential $A_T^2$ as well: when reducing $A_T$ we also need to increase the amplitude of oscillation $\Delta_T$, to compensate for the $A_T$ reduction and maintain the signal at the same order of magnitude. Of course we must keep the amplitude of oscillation below the tip width, $\Delta_T < \sigma_T$, in order to remain in the linear-response regime and retain the spatial resolution, thus we select $\Delta_T = 0.01$. We see in Fig. 9 that the PN barrier decreases rapidly as the springs constant increases, so that for $K = 7$ the required tip amplitude is already too small to be easily compensated by a larger $\Delta_T$. The tip softening therefore allows to leave the adatoms undisplaced only within a limited range of $K$.

A more radical method to kill particle dragging even for very rigid chains is simply removing the PBC and replacing them with fixed extremes, imposing null velocities to the first and the last particle:

$$\dot{x}_1(t) = 0 \quad \dot{x}_N(t) = 0.$$ 

This choice introduces small boundary effects (which anyway could easily be minimized by choosing longer chains) but we checked with $K = 1$ that in the central region of the chain the results are the same as with PBC. Even with fixed boundary conditions (FBC) some degree of adatom mobility remains for intermediate $K \approx 4$, but it decreases with increasing $K$. Of course no complete chain dragging is observed with FBC, Fig. 19. The two dissipative regimes remain as clear as for $K = 1$. Similar results are found for $K = 10$, but with even smaller adatom displacements, see Fig. 20.

### 5.2.3 Peyrard-Remoinesset substrate potential

The strong dependence of the dissipated power on the curvature of the potential suggests that a different solitonic dissipation would show up more in the presence of substrate potentials with a marked curvature difference in different regions. This seems also to fit better our proposal to address a chain of adsorbate atoms. The sinusoidal potential of the standard FK model represents in fact only the
Figure 20: Total mean power as in Fig. 19 but with $K = 10$. The substrate potential is drawn in both frames under the chain. The upper frame is representative of the low-frequency regime, with $\omega_T = \pi/4$. The lower frame shows the smaller kink dissipation characteristic of the high-frequency regime, $\omega_T = 2\pi$. 
Figure 21: The PR potential $u^{PR}(x)$ for a few values of the shape parameter: as $s$ increases between 0 and 1 we have a periodic potential with sharper bottoms and flatter barriers, as suitable to represent the interaction of a surface with a chain of adsorbate atoms.

Figure 22: The curvature $\frac{\partial^2}{\partial x^2} u^{PR}(x)$ for the same values of $s$ of Fig. 21.
first harmonic in the Fourier expansion of the effective potential resulting from
the chain-substrate interaction, and is the lowest possible approximation. As it
has been shown, for real adsorption systems interaction between particles is more
complicated, and for example atoms adsorbed on a metal surface, are better ad-
dressed as interacting with a substrate potential deviating from the sinusoidal
form and presenting sharp bottoms and flat barriers [4, 8, 9]. We therefore sub-
stitute \( u(x) \) in Eq. (4) with the following non-sinusoidal profile, first introduced
by M. Peyrard and M. Remoinesset (PR) in Ref. [10] (in that work the parameter
\( r = -s \) was used):

\[
U_{PR}(x) = \frac{u_{sub} (1 + s)^2 [1 - \cos(2\pi x)]}{2 \left[1 + s^2 - 2s \cos(2\pi x)\right]},
\]

(29)

with \(|s| < 1\). The parameter \( s \) determines the shape: \( s > 0 \) produces a potential
with sharp bottoms and flat barriers, Fig. 21 while \( s < 0 \) leads to flat bottoms
and thin barriers (not shown). Note that the periodicity \( a_{sub} \) is kept unchanged
from \( u(x) \), and also the peak-to-peak amplitude \( u_{sub} \) is the same. With \( s = 0 \),
\( U_{PR}(x) \) reduces exactly to the sinusoidal potential of Eq. (4) (apart from an
irrelevant constant). This potential is displayed in Fig. 21 for a few positive
values of \( s \). Figure 22 reports its second derivative. Note that the difference of
curvature seen by particles sitting at minima or barrier regions of the potential is
much enhanced with respect to the case of the sinusoidal potential (whose second
derivative has again a sinusoidal form). In order to show the different dissipative
behavior between high- and low-frequency regime, these new curvatures must be
taken into account in evaluating \( \alpha_{eff} \), and thus the values of \( \omega_T \) leading to low-
or high-frequency regimes for each choice of \( s \).

In addition, for large \( s \) approaching unity, as the potential wells become
steeper and steeper to climb up, we expect the dragging phenomenon found in
the sinusoidal case to be depressed, for \( K \) not too large. This allows us to restore
PBC and get rid of undesired boundary effects. We report for example simulations
for \( s = 0.9 \), \( K = 5 \) and \( K = 10 \) in Fig. 23 the dragging of solitons previously
found (Fig. 10) for the same value \( K = 5 \), is not showing here, even with PBC:
we find a clean illustration of the low-frequency dissipation regime, with lowest
values corresponding to particles sitting at minima of the substrate potential and
highest one for solitons. A dissipative profile not unlike that of Fig. 12 is observed
in the high-frequency regime.
Figure 23: Total mean power dissipated by the tip as a function of $\bar{x}_T$ for $\gamma = 0.2$. Tip parameters are $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$. The PR potential $u^{PR}(x)$, here with the shape parameter $s = 0.9$, is drawn below the chain and the final adatom positions are reported as circles. Upper frame: $K = 5$, $\omega_T = \pi/6$, in the low-frequency regime, with enhanced dissipation for kinks. Lower frame: $K = 10$, again in the low-frequency regime despite the larger value $\omega_T = 2\pi$, due to $\omega_0 \simeq 33.7$ at the minima of $u^{PR}(x)$. 
Figure 24: Total mean power dissipated in a period as a function of $\bar{x}_T$ in the antikink case $\theta = 0.84$, with $N = 21$ particles, in the low-frequency regime $\omega_T = \pi/4$ ($\gamma = 0.2$, $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$). Upper panel: $K = 1$, sinusoidal substrate potential. Lower panel: $K = 5$, PR non-sinusoidal potential of Eq. (24) with $s = 0.5$. The potentials are drawn under the chain. Increased dissipation peaks mark the four anti-kinks.
Figure 25: Total mean power dissipated in a period as a function of $\bar{x}_T$ for antikinks ($\theta = 0.84$), with $N = 21$ particles ($\gamma = 0.2$, $\sigma_T = 0.1$, $A_T = 0.01$ and $\Delta_T = 0.001$). Upper panel: $K = 1$, $\omega_T = 11\pi/12 \simeq 2.879$ and sinusoidal substrate potential. Lower panel: $K = 2$, $\omega_T = 2\pi$, PR non-sinusoidal potential with $s = 0.5$. Both panels show the high-frequency regime, with a decreased dissipation corresponding to anti-kinks.
5.3 Anti-kinks

As a conclusion, we report results for a system showing anti-kinks instead of kinks. Antikinks are topological objects representing local stretching in the otherwise perfectly commensurate lattice structure of adatoms, with some substrate potential minima showing vacancies of particles. Describing kinks as effective particles, antikinks would be the correspondent anti-particles, with opposite ’topological charge’. Antikinks are favored when the ratio $\theta$ of Eq. (9) is $\theta < 1$, so that for a given length of the chain there are more substrate potential minima than particles: we choose $\theta = \frac{21}{25} = 0.84$ with $N = 21$ particles, distributed along a chain of length $L = 25a_{\text{sub}}$. Similarly to Eq. (26), we now have $\rho_{ak} = (1 - \theta)/a_{\text{sub}}$ and four antikinks are therefore to be found in the chain.

Being antikink-adatoms as softly bound as kinks atoms, we expect the dissipation to show exactly the same features found for kinks, with similar high/low-frequency regimes, irrespective of the topological charge. This is confirmed in Figs. 24 and 25, representing the high-frequency and the low-frequency characteristic behaviors respectively. Note that in the low-frequency regime anti-kinks produce the highest dissipation, despite corresponding to local adatom density minima.

6 Conclusions

All calculations within the present simple model are consistent with the following conclusions:

- Adatoms covering a surface sit at more or less rigidly pinned positions, depending on whether they belong to a highly coordinated site or they are pushed by geometric constraints to less weakly bonded transition regions; this latter case is sometimes referred to as a solitonic wave.

- Soliton adatoms show modified local vibrational properties, and, as long as their dynamics is underdamped, they can couple differently to an approaching AFM tip, thus producing sensibly different dissipation, with a visibility contrast which can easily reach two orders of magnitude.

- A similar dissipation imaging is already an established technique for the investigation of local bonding properties of adatoms layers on surfaces, but
the present work suggests that such kind of dissipation topography can be tuned to be especially sensitive to solitonic waves.

- Of the two frequency regimes, showing opposite visibility contrast, only the low-frequency regime applies to concrete experimental AFM/DFM setups.

- Under suitable conditions (adatom-adatom interaction strength dominating over the surface period corrugation) AFM tips could be used to manipulate kinks (rather than single atoms), or even whole adatom layers.
References


