A simple non-equilibrium theory of non-contact dissipation force microscopy

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Abstract
The tip–surface interaction in the non-contact atomic force microscopy
(NC-AFM) leads to energy dissipation. Recently, this effect has been harnessed
to obtain images with atomic resolution. In an important paper Gauthier and
Tsukada (GT) (1999 *Phys. Rev.* B **60** 11716) suggested a theory of this, so-
called non-contact dissipation force microscopy (NC-DFM) using a stochastic
approach within a simple one-atomic representation of the surface. In this paper
we elaborate on this model further, stressing the importance of a *consistent*
non-equilibrium consideration. Then, using a more general model, we offer
an alternative derivation based on a rather simple approach to non-equilibrium
phenomenon used by Kirkwood for the Brownian motion. We show that our
method leads to the final result similar to that obtained in the GT paper. We
also discuss some other models for the energy dissipation in NC-AFM. In
particular, we emphasise that the 'stick and slip' (or adhesion hysteresis) model
of energy dissipation, although containing a specific element which requires
additional features to be incorporated in our model, is to be considered using
non-equilibrium methods.

1. Introduction

Non-contact atomic force microscopy (NC-AFM) [1–10] has become an invaluable tool in
studying surfaces of real systems since it has become possible to achieve atomic resolution.
In NC-AFM experiments a tip with a nano-asperity is attached to a cantilever which oscillates
above the sample surface. The imaging mechanism is in maintaining a constant frequency
shift, Δf, in the cantilever oscillations which is achieved by adjusting the cantilever in the
vertical direction for every lateral position of the tip.

  It is well known [11–18] that in order to maintain the amplitude of the tip oscillations,
one has to constantly supply additional energy to the system. In the experiment this is done
by applying an additional driving sinusoidal signal to the cantilever. The observed energy
dissipation (or damping) is due to dissipative forces between the tip and the surface. One
would expect that this effect depends on the lateral position of the tip above the surface and,
therefore, can be used (alongside an ordinary NC-AFM image) for obtaining new images.

Recently energy dissipation measurements have been performed and topographic images with atomic resolution have been reported [19]. Following [20], we shall refer to these kinds of images as non-contact dissipation force microscopy (NC-DFM).

Several models have been suggested to explain the energy dissipation [17]. In [11,13,14,17,18,21,22] an adhesion hysteresis mechanism has been used. According to this mechanism, the force fields upon the tip approach, $X^{\downarrow}$, and retraction, $X^{\uparrow}$, are different due to relaxation of surface atoms which leads to an energy (of the atomic scale) loss every oscillation cycle. Note that this mechanism is normally associated with an irreversible atomic relaxation at the surface and is *not* considered to be due to stochastic behaviour of the system [17,20,22].

In an important paper Gauthier and Tsukada (GT) [20], using a simple model in which the surface was modelled by a single atom, for the first time suggested a *stochastic* mechanism for the energy dissipation in the oscillating tip system. The idea is that a relatively slow tip motion (typical oscillation frequencies are around 2×10^5 Hz) samples extremely fast (frequencies 10^{12}–10^{14} Hz) oscillations of surface atoms, so that the force experienced by the tip has to be calculated as an average over atomic vibrations. They found that the force after averaging attains an additional *friction term*, $-\xi P$, proportional to the tip momentum, P. Here the friction constant, ξ, depends on the actual tip position. It was suggested in their paper that the problem is similar to that of a Brownian particle in a solution: fast and random collisions with light molecules of the solution slow down the heavy Brownian particle every time it is accelerated, so that after some (relaxation) time its average kinetic energy becomes consistent again with the given temperature, T. The friction coefficient derived in [20] appeared as proportional to the square of the derivative of the tip–surface force field and to the displacement-displacement correlation function for the surface atom, so that a particular case of the dissipation-fluctuation theorem [23–25] has been recovered. This result is difficult to underestimate since this fact can be employed not only for the calculation of the NC-DFM images theoretically, but also to get insight into the surface *phonon properties* using NC-DFM [20].

It appeared, however, that the consideration presented in [20] contains elements of equilibrium statistical mechanics (a canonical distribution of the surface is used to calculate the force) alongside those of a non-equilibrium one (e.g. coarse graining [26,27]). We explain this point in detail in the appendix. In fact, in the appendix we show that if the force was calculated in [20] consistently using the equilibrium concept, one would not arrive at any friction term at all. Note that the same kind of inconsistency can be found in some other texts (for example, [28]).

In the present paper we stress the importance of a *consistent* non-equilibrium consideration of the energy dissipation in NC-DFM to account for stochastic effects in atomic vibrations, while calculating the force acting on the tip. We use a rather simple method due to Kirkwood [29] originally applied to the Brownian motion (see also [26,30]). We have chosen this method in this paper because, in our opinion, it is closest in spirit to the method in the GT paper and, therefore, an interesting comparison is possible. We have also found it possible to consider the whole surface atomistically from the very beginning, so that the single-atom approach of the GT model will also be generalized here. A more detailed and rigorous study of the problem which is based on the methods of the kinetic theory of liquids will be published elsewhere [31].

The plan of this paper is as follows. A critical analysis of the GT model can be found in the appendix. An alternative approach based on Kirkwood's method is discussed in section 2. In this method an instantaneous (stochastic) equation of motion for the tip (the Langevin equation) is considered, with subsequent statistical averaging over the fluctuating tip–surface interaction. Finally, some general conclusions are drawn in section 3 where other possible mechanisms of the energy dissipation in NC-DFM are also discussed.

2. Non-equilibrium statistical consideration of the NC-AFM system

We use small letters (like p, q) to indicate momenta and conjugated to them coordinates of the surface atoms, while capital letters (like P, Q) are used for those of the tip. There are N atoms in the surface and the total number of particles therefore is $N + 1$. The setup of the system is given in figure 1 and the microscopic classical Hamiltonian for the whole system is:

$$H(pqPQ) = H_{pq} + \Phi_{Qq} + \frac{P^2}{2M} + U_Q. \tag{1}$$

Here $H_{pq} = H_p + H_q$ is the Hamiltonian of the surface atoms, Φ_{Qq} their interaction with the tip, $P^2/2M$ kinetic energy with M being an effective mass of the tip and U_Q its potential energy.
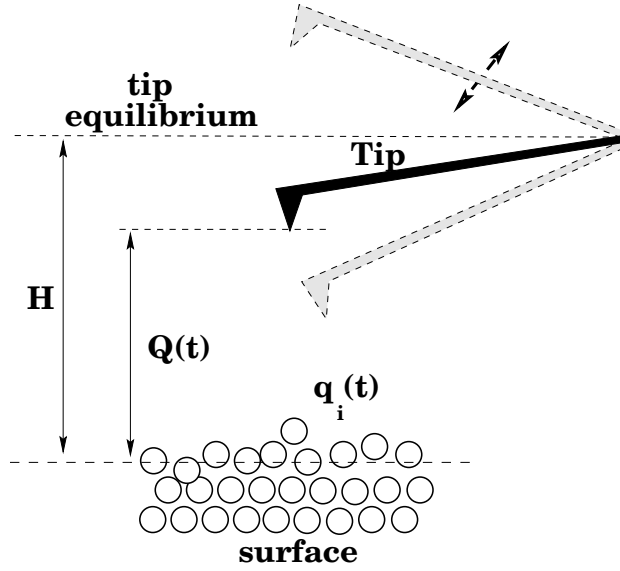

Figure 1. Schematic of the tip–surface system

We start by writing down an *instantaneous* (stochastic) equation of motion for the tip assuming coordinates $P_0 Q_0$ at time t for the tip:

$$\frac{dP_0}{dt} = X(Q_0 q) + F(Q_0) \tag{2}$$

where the force $F(Q_0)$ is associated with the energy U_Q in the Hamiltonian. Here we have indicated explicit dependence of the tip–surface interaction force $X(Q_0 q)$ on the coordinates of surface atoms as well. Because of the q-dependence, the force $X(Q_0 q)$ rapidly fluctuates around its average value defined as an ensemble average over the surface subsystem:

$$\langle X(Q_0 q) \rangle_{eq} = \int dp dq f_0^{(N/1)}(pq|P_0 Q_0) X(Q_0 q) \tag{3}$$

where $f_0^{(N/1)}(pq|P_0 Q_0)$ is the *conditional* probability to find N surface atoms having coordinates p, q when the coordinates of the tip are *fixed* at P_0, Q_0. Note that in this expression $f_0^{(N/1)}$ corresponds to the *equilibrium* distribution of surface atoms and in general should be distinguished from the non-equilibrium conditional distribution, $f^{(N/1)}$ (see below). The force

$F(Q_0)$ (which includes the elastic force and may also include some other externally applied force, F_D) changes very slowly on the scale of atomic oscillations. Therefore, it is sensible to separate out the slowly changing average tip–surface force as well so that the starting Langevin equation becomes:

$$\frac{\mathrm{d}P_0}{\mathrm{d}t} = \Delta X(Q_0 q) + \big(F(Q_0) + \langle X(Q_0 q)\rangle_{eq}\big) \tag{4}$$

where

$$\Delta X(Q_0 q) = X(Q_0 q) - \langle X(Q_0 q)\rangle_{eq} \tag{5}$$

is the fluctuating part of the tip–surface force which will play a central role in the following. The combined force in the round brackets in equation (4) is assumed to be changing very slowly with time.

To derive the Langevin equation in this case, we *first* have to smooth out the fluctuations in the force $\Delta X(Q_0 q)$ due to fast vibrations of the surface atoms. In order to do that we use the time coarse graining approach first suggested by Kirkwood in his seminal paper on Brownian motion [29]. The idea is to average the *instantaneous* equation of motion, equation (4), over a coarse graining time τ [26–28]. The latter is taken to be larger than a characteristic phonon time but much smaller than the macroscopic time characterizing the NC-AFM system (e.g. the period of the tip oscillations). Note that this averaging is introduced as an artificial means to treat the system in a non-equilibrium manner (see corresponding discussions in [26,27]). In what follows, the time average will be denoted $(\ldots)_\tau$ while the ensemble average is denoted by angle brackets, $\langle\ldots\rangle$. Thus, instead of the instantaneous force $\Delta X(Q_0 q)$ in equation (4) one should consider the average force which is obtained from $\Delta X(Q_0 q)$ by taking *first* the time and *then* the ensemble average with respect to positions and momenta of the surface atoms [29]:

$$\langle (\Delta X(Q_0 q))_\tau \rangle = \int \mathrm{d}p\mathrm{d}q f^{(N/1)}(pq|P_0 Q_0)\left[\frac{1}{\tau}\int_0^\tau \Delta X(t+s)\mathrm{d}s\right]. \tag{6}$$

Formally this expression coincides with the one used in [20]; however, the important difference here is that $f^{(N/1)}$ is *not* the canonical distribution. The appropriate comparison of this distribution at two consecutive times will not give unit (as would happen if true canonical distributions are used as explained in the appendix) and, as the result, we will be able to derive a friction force. The notation $\Delta X(t+s)$ corresponds to the force $\Delta X(Q_0 q')$ at the time $t+s$ when all the coordinates evolved to the values $Q_0 q'$ from their values $Q_0 q$ at the time t. Note that here the tip is fixed at Q_0, so that formally these two forces can be related by the Liouville operator $\widehat{L}$ of the surface [26,27] as;

$$\Delta X(t+s) = \Delta X(Q_0 q') = \mathrm{e}^{\mathrm{i}s\widehat{L}}\Delta X(Q_0 q). \tag{7}$$

We will not use properties of the Liouville operator in this paper and will only use the notation above to indicate explicitly the time and the coordinate dependence of the force.

To calculate the average force in equation (6), we first extend the integration over the whole phase space $\Gamma = (pq P Q)$ by introducing delta functions $\delta_Q = \delta(Q_0 - Q)$ and $\delta_P = \delta(P_0 - P)$,

$$\langle (\Delta X(Q_0 q))_\tau \rangle = \frac{1}{\tau}\int_0^\tau \mathrm{d}s \int f^{(N/1)}(pq|P Q)\Delta X(t+s)\delta_P \delta_Q \mathrm{d}\Gamma \tag{8}$$

where $d\Gamma = \mathrm{d}p\mathrm{d}q\mathrm{d}P\mathrm{d}Q$ and $\Delta X(t+s) = \mathrm{e}^{\mathrm{i}s\widehat{L}}\Delta X(Qq)$ here. Then, the total distribution function of the whole system (tip + surface) can be exactly factorized as follows:

$$f^{(N+1)}(pq P Q) = f^{(N/1)}(pq|P Q)f^{(T)}(P Q)$$

where $f^{(T)}(P Q) = \int f^{(N+1)}(pq P Q)\mathrm{d}p\mathrm{d}q$ is the (reduced) distribution function of the tip.

In non-equilibrium the conditional distribution $f^{(N/1)}$ depends on time because the tip is constantly moving thereby effecting the positions and momenta of the surface atoms. In principle, in order to calculate the conditional distribution $f^{(N/1)}$, one has to solve the Liouville equation. In this paper we shall avoid this rather complicated step, however, by using the same trick as Kirkwood used in his study of the Brownian motion [29]. Note that this method can be used only when the system is very close to equilibrium. Due to a very slow (compared with phonon times) motion of the tip, the phonon system should approximately obey this condition.

We start by noting that because the total distribution function $f^{(N+1)}$ satisfies the Liouville equation [26,27], one can exactly relate $f^{(N/1)}$ for the two time instances t and $t + s$ as follows:

$$f^{(N/1)}(pq|PQ) = f^{(N/1)}(p'q'|P'Q')\frac{f^{(T)}(P'Q')}{f^{(T)}(PQ)}. \tag{9}$$

Here primed coordinates correspond to the phase point $\Gamma' = (p'q'P'Q')$ at the time $t + s$ and are the result of the system evolution from the phase point $\Gamma = (pqPQ)$ which the system occupied at the time t. Then, following the method of [29], the evolution of the conditional distribution function from time $t+s$ to t is calculated approximately by replacing the conditional distribution at time $t + s$ with its equilibrium value (indicated with the subscript 0):

$$f^{(N/1)}(pq|PQ) \simeq f_0^{(N/1)}(p'q'|P'Q')\frac{f^{(T)}(P'Q')}{f^{(T)}(PQ)}. \tag{10}$$

This formula is simply saying that the main change in the conditional distribution function of the surface atoms in time is caused by the moving tip and is determined via the ratio of the two tip distributions $f^{(T)}$ taken at the two times. Then, in order to calculate this ratio in equation (10), we note that the equilibrium distribution of the tip,

$$f_0^{(T)}(PQ) \propto \exp\left(-\frac{\beta}{2M}P^2\right)$$

where $\beta = 1/k_BT$ is the inverse temperature. Therefore, the simplest (and successful) approximation to the ratio is in using the exponential Ansatz for $f^{(T)}$ in which the *actual* momentum of the tip at the *given* time is used [29]:

$$\frac{f_0^{(T)}(P'Q')}{f_0^{(T)}(PQ)} \approx \exp\left[-\frac{\beta}{2M}\left(P'^2 - P^2\right)\right] \approx \exp\left(-\frac{\beta}{M}P'\Delta P\right) \approx 1 - \frac{\beta}{M}P'\Delta P. \tag{11}$$

Although this derivation seems to be lacking enough rigour and might be considered as an 'intelligent guess', it does emphasize the point that the time dependence of the conditional distribution for the surface comes from the moving tip interacting with it. It is also well known that it gives the correct description of the Brownian particle [26,27,30].

The difference of the momenta, $\Delta P = P' - P$, is calculated by integrating (from t to $t + s$) the equation of motion (4) (written for P, Q instead of P_0, Q_0) so that we have:

$$\Delta P = \int_0^s \Delta X(t + s')\mathrm{d}s' + \left(F(Q) + \langle X(Qq)\rangle_{eq}\right)s \tag{12}$$

where $\Delta X(t + s') = e^{is'\widehat{L}}\Delta X(t)$. Inserting equations (9)–(12) into equation (8), we get:

$$\langle(\Delta X(Q_0q))_\tau\rangle = \frac{1}{\tau}\int_0^\tau \mathrm{d}s \int \mathrm{d}\Gamma' f_0^{(N/1)}(p'q'|P'Q')\Delta X(t + s)\delta_P\delta_Q\left(1 - \frac{\beta}{M}P'\Delta P\right) \tag{13}$$

While writing this expression down, we have made use of the fact that $\mathrm{d}\Gamma = \mathrm{d}\Gamma'$ since the volume of the phase space is conserved during the time evolution; here $\mathrm{d}\Gamma' = \mathrm{d}p'\mathrm{d}q'\mathrm{d}P'\mathrm{d}Q'$. We can also write:

$$\delta_Q = \delta(Q_0 - Q) \approx \delta(Q_0 - Q') \tag{14}$$

$$\delta_P = \delta(P_0 - P) = \delta(P_0 - P' + \Delta P) \approx \delta(P_0 - P') + \Delta P \frac{\partial}{\partial P_0} \delta(P_0 - P') \tag{15}$$

where ΔP is given by equation (12). After substituting equations (14) and (15) into equation (13) we arrive at a number of contributions to the average force. It is easy to verify that the second term in equation (12) leads to terms which are at least linear in τ. Since τ is meant to be a small parameter, these terms should be neglected in this theory. Therefore, only four terms are left.

Let us consider all four terms in order. The first one, which is due to the first terms both in equation (15) and in the round brackets in equation (13), is simply the equilibrium surface average of the fluctuating force, $\langle \Delta X(Q_0 q) \rangle_{eq}$, calculated for the tip *fixed* at P_0, Q_0. It is equal to zero owing to its definition, equation (5).

The second term arises due to the first term in equation (15) and the second term in the round brackets in equation (13). This contribution contains the product of two forces at two different instances of time, i.e. $\Delta X(t + s) \Delta X(t + s')$, which is an ensemble averaged with respect to the distribution function $f_0^{(N/1)}(p'q'|P_0 Q_0)$ corresponding to the time $t + s$. Therefore, it is convenient to convert the force $\Delta X(t + s')$ also to the same time moment via $\Delta X(t + s') = \Delta X(t + s + (s' - s)) = e^{i(s'-s)\widehat{L}} \Delta X(t + s)$. When the average is calculated, the initial time moment does not matter anymore and can be taken at the time t. This brings about the following contribution:

$$\frac{1}{\tau} \int_0^\tau ds \int_0^s ds' \langle \Delta X e^{i(s'-s)\widehat{L}} \Delta X \rangle_{eq} = \int_0^\tau ds \frac{s + \tau}{\tau} \langle \Delta X e^{is\widehat{L}} \Delta X \rangle_{eq} \tag{16}$$

in which the ensemble average is also taken with respect to the surface subsystem for the fixed position of the tip at Q_0 in the phase space. Here $\Delta X = \Delta X(Q_0 q)$ and we have interchanged the order of integrals while passing to the right hand side. Then for small τ the expression just obtained is transformed into:

$$\gamma(Q_0) = \int_0^\tau ds \langle \Delta X(Q_0 q) e^{is\widehat{L}} \Delta X(Q_0 q) \rangle_{eq}. \tag{17}$$

Note that the correlation function above depends only on the position of the tip, Q_0, but *not* on its momentum, P_0, since the Liouville operator of the surface, $\widehat{L}$, does not depend on the tip momentum.

The third contribution is due to the second term in equation (15) and the first term in the round brackets in equation (13). The derivative $\partial/\partial P_0$ is taken out of the integral and the following consideration nearly repeats the one for the previous term so that the corresponding contribution becomes $\frac{\partial}{\partial P_0} \gamma(Q_0) = 0$. Finally, the last contribution, proportional to $(\Delta P)^2$, is considered along the same lines and is given by a triple correlation function;

$$-\frac{\beta}{M} \frac{\partial}{\partial P_0} \left(P_0 \int_0^\tau ds \int_0^\tau ds' \langle \Delta X(Q_0 q) e^{is\widehat{L}} \Delta X(Q_0 q) e^{is'\widehat{L}} \Delta X(Q_0 q) \rangle_{eq} \right).$$

We assume that ΔP is small and so the contribution above (proportional to the square of it) is negligible and can be omitted. This assumption is also supported by the well-known fact [23,32] that for the Gaussian distribution function any odd-order correlation functions are exactly equal to zero. Therefore, we arrive at the following final expression for the force:

$$\langle X(Q_0 q) \rangle_t = \langle X(Q_0 q) \rangle_{eq} + \langle (\Delta X(Q_0 q))_\tau \rangle \simeq \langle X(Q_0 q) \rangle_{eq} - \frac{\beta P_0}{M} \gamma(Q_0) \tag{18}$$

and the following Langevin equation:

$$\frac{dP_0}{dt} = \langle X(Q_0 q) \rangle_{eq} - \frac{\beta P_0}{M} \gamma(Q_0) + F(Q_0). \tag{19}$$

The second term here is the desired friction force with the friction coefficient $\xi(Q_0) = \beta\gamma(Q_0)/M$. Note that the integration with respect to time in the integral of equation (17) can be extended to infinity (this has to be done with some care: see e.g. a discussion on this, so-called 'plateau problem', in the original Kirkwood paper [29] as well as in [24], section 5.3.1).

3. Discussion

In this paper we have followed up the *intrinsic* mechanism of energy dissipation in NC-DFM suggested in [20] (the GT model) and stressed the importance of using a consistent non-equilibrium theory in order to describe this effect. We indicated a certain inconsistency in the GT method which is to do with a mixture of non-equilibrium and equilibrium methods for treating a fundamentally non-equilibrium phenomenon. Specifically, the main problem was in using a canonical (equilibrium) distribution for the tip while deriving the average tip force. We have used a rather different (although apparently similar in some parts) approach originally due to Kirkwood [29] which is non-equilibrium. Our method is approximate; however, effectively, it is based on a solution of the Liouville equation while considering the Langevin equation for the tip oscillations in NC-DFM, and, therefore, should be more preferable. We have also derived the friction term in the Langevin equation for the tip and found that it is given as a time integral of the fluctuating force autocorrelation function (i.e. a fluctuation-dissipation theorem). We note that the fluctuating force, $\Delta X(Q_0 q)$, responsible for the dissipation, is due to the short-range (chemical) and image interactions which depend explicitly on positions of surface atoms; the Van der Waals and capacitance forces contribute only to the average (conservative) force (see e.g. [33] for the details about the forces in the NC-AFM system).

As has already been mentioned in [20] and several times throughout the text, NC-DFM system is similar to a Brownian particle in a solution. Indeed, the heavy tip behaves as a slow massive subsystem interacting with relatively fast vibrations of surface atoms which, in turn, are analogous to light and fast molecules in the solution colliding with the Brownian particle. If the Brownian particle is accelerated, the molecules of the solution would dissipate its extra energy so that eventually the system recovers its thermal equilibrium. The microscopic mechanism for slowing the Brownian particle down is in the appearance of a friction force due to the random component of the particle–solution interaction. The same is true for the NC-DFM system: the random fluctuating component of the tip–surface interaction causes the tip to slow down which is done by the corresponding friction force. Note that during the course of oscillations the tip moves much faster than its average thermal speed $\sqrt{\langle (P_0/M)^2 \rangle_{eq}} = 1/\sqrt{M\beta} \simeq 0$. This explains why the energy is transferred from the tip to the surface (which is closer to thermal equilibrium), but not in the opposite direction.

The analogy between the NC-DFM system and the Brownian particle is limited, however, and should be used with care. For example, there are different spatial symmetries in these two systems (the surface atoms are positioned only from one side of the tip whereas molecules of the solution surround the Brownian particle from all sides) which results in a non-zero average force, $\langle X(Qq) \rangle_{eq}$, and the friction depending on the tip position Q. Also, the tip oscillates above the surface interacting with the surface atoms only when it comes close enough; in a liquid the Brownian particle performs chaotic movements interacting with the molecules of the solution all the time.

Our result in equation (17) is very similar to that in [20], $\gamma_{GT}(Q_0)$. The only difference is that our expression for the friction coefficient contains the fluctuating force, $\Delta X(Q_0 q)$, rather

than the total force $X(Q_0q)$ as in $\gamma_{GT}(Q_0)$ [20]. It can be easily shown, however, that the difference,

$$\gamma(Q_0) - \gamma_{GT}(Q_0) = \tau\langle X(Q_0q)\rangle_{eq}^2$$

is of the first order in time τ. Therefore, within the coarse graining theory, our result is identical to theirs. There are at least two reasons, however, why the form of equation (17) with the fluctuating force is more preferable. The first reason is physical: the energy dissipation is caused not by the average component of the force (which is conservative) but rather by its fluctuating (random) part. The second reason is technical: if the force in equation (17) contains a non-zero average part (as in $\gamma_{GT}(Q_0)$), then one cannot extend the time integration to infinity as the integral would diverge at the upper limit (at the infinite time).

One has to be absolutely clear about the principal importance of a *stochastic* mechanism in such a phenomenon as energy dissipation. Indeed, let us consider a relatively slow open subsystem (a NC-AFM tip in our case) interacting with a bigger (of the macroscopic size) system (atoms of the surface in our case) connected to a heat bath at a constant temperature. The bigger system and the heat bath are characterized by a much shorter relaxation time. The instantaneous force acting on the tip is shown in figure 2 (dotted line, top panel). It oscillates randomly around the average force, $\langle X(Q_0q)\rangle_{eq}$ (solid line). Note that we assume that the average force is attractive (directed downwards, to the surface) along the whole tip trajectory. Around every position of the tip surface atoms can do very many oscillations so that the tip samples a domain in the phase space (pq) associated with atomic vibrations. However, the surface atoms never come to exact thermal equilibrium with the tip as the tip position *changes* with time. As the result of that, there is an additional friction force acting on the tip which is always directed opposite to the tip velocity so that the final force (dashed line, top panel) is different from the average one. When the tip moves downwards, the friction is directed upwards, resulting in a smaller attractive final force; upon retraction, the friction is directed downwards, increasing the attractive force. Thus, the friction force results in the appearance of a *hysteresis* in the force field: the final forces $\langle X(Q_0q)\rangle_t^{\downarrow}$ and $\langle X(Q_0q)\rangle_t^{\uparrow}$ along the approach and retraction are *different* by the statistical average of the fluctuating force $\langle(\Delta X(Q_0q))_\tau\rangle^{\downarrow}$ and $\langle(\Delta X(Q_0q))_\tau\rangle^{\uparrow}$. As a result, some energy

$$\Delta A = \oint \langle X\rangle_t \mathrm{d}Q_0 = \int_{\downarrow}\langle X\rangle_t^{\downarrow}\mathrm{d}Q_0 - \int_{\uparrow}\langle X\rangle_t^{\uparrow}\mathrm{d}Q_0 = \int_0^{T_0}\frac{\beta P_0^2}{M^2}\gamma(Q_0)\mathrm{d}t\rangle 0$$

will be dissipated by the tip to the surface; the energy will be finally transferred to the heat bath. Note that the integration here is performed over the whole oscillation cycle, T_0 being the oscillation period.

One can also look at the problem from another perspective. We are interested in a *reduced* description of the system [27] when degrees of freedom associated with the surface and the heat bath are not used explicitly. In such a case a *stochastic* description is necessary. This kind of treatment results in the appearance of a friction term serving to restore equilibrium with respect to the open subsystem, the friction constant being given as a time integral of the autocorrelation function of the random 'force' relevant to the given problem [23,25,27,30,32,34]. There are many examples of such a phenomenon which are met in different areas of physics (see e.g. [25,27,32]). It is hoped we have shown in the present paper that the NC-DFM is not an exception.

One remark is now in order. In the intrinsic stochastic mechanism considered in this paper, the energy is dissipated along the whole trajectory when the tip is moving in both directions, up and down (of course, only the part around the turning point near the surface contributes most due to fast decay of the friction coefficient with the distance from the surface). The energy
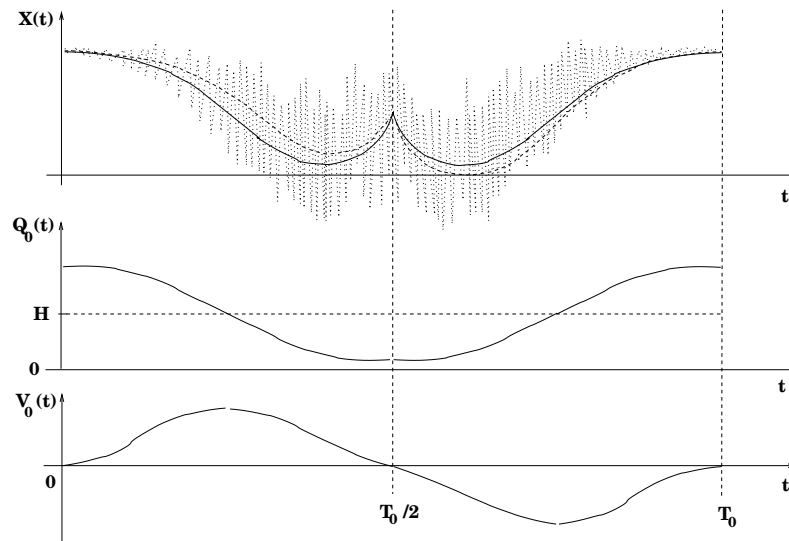
Figure 2. Illustration to the intrinsic dissipation mechanism. Top panel: a qualitative picture of the time dependence of: the instantaneous random force, $X(t)$, acting on the tip (dotted line); the force averaged over atomic vibrations, $\langle X(Q_0 q)\rangle_{eq}$ (solid line) and the exact non-equilibrium force $\langle X(Q_0 q)\rangle_t$, equation (18), containing the friction term (dashed line). Note that the amplitude of the force fluctuations is larger when the tip is closer to the surface. Also shown: the tip coordinate $Q_0(t)$ (middle panel) and the tip velocity $V_0(t) = P_0(t)/M$ (bottom panel) as functions of time t. Here T_0 is the oscillation period.

dissipation is caused by the rapidly fluctuating tip–surface interaction. Therefore, it may seem that the *adhesion hysteresis* mechanism (e.g. stick–slip behaviour) [11,13,14,17,18,21,22] has completely different physics behind it. Indeed, the model considered in this paper does not account for it because the average force acting on the tip, $\langle X(Q_0 q)\rangle_{eq}$, in equation (19) will be the same for the up and down motions. Hence, one has to bring in some additional features to the model to account for this effect. However, it is clear that a *non-equilibrium* (stochastic) behaviour of the system must be an essential necessary ingredient of any adhesion hysteresis model.

We illustrate this point by the following simple observation. Consider some potential energy surface associated with the tip and surface atoms. At the beginning, let us assume an *infinitely slow* (quasi-static) motion of the tip so that at every tip position complete equilibrium is established. Consider, first, the situation when for every position of the tip Q_0 there are two minima in the potential energy surface $U_q = H_q + \Phi_{Q_0 q}$ with respect to the surface atoms (here H_q is the potential energy of the surface atoms, see equation (1)), and one minimum lies deeper than the other. If during approach surface atoms occupied one of the two minima, then upon the retraction they will stay in the same minimum provided that the barrier between them was not eliminated at the tip turning point. However, the situation becomes different if it was eliminated. In this case two situations are possible: (i) the surface atoms will stay in the deeper minimum upon the retraction if they occupied it along the approach, or (ii) they switch to the deeper minimum from the shallow one if the latter was occupied during the approach. Only in the second case the average forces will be different upon the approach and retraction, $\langle X(Q_0 q)\rangle_{eq}^{\uparrow} \neq \langle X(Q_0 q)\rangle_{eq}^{\downarrow}$, which would lead to a hysteresis in the force and energy dissipation.

Now let us consider the situation when the two minima are equivalent. Again, surface atoms will keep staying in the same minimum if the barrier is not eliminated. However, if the barrier is eliminated then it is not clear which minimum will be occupied after the turning point since, according to our initial assumption, at every position of the tip complete equilibrium is established.

This uncertainty can be removed if we consider a real situation when the tip moves with a certain *finite* speed. In addition, it is known [35,36] that surface atoms (ions) may become *unstable* when the tip comes very close to them (about 4 Å in the case of MgO (001) surface). As the result of such instability, the closest surface atom(s) may be displaced considerably towards the tip end and trapped between the tip and the surface experiencing a rather weak energy potential, especially in the lateral direction. Thus, due to atomic (ionic) instability, the tip can activate some *soft* vibrational modes associated with surface atoms at close approach. In this case its trajectory (in the *combined* phase space of the tip *and* the surface atoms) may be quite different on the approach and retraction and the forces will no longer be the same. We stress that this will hold for any case considered above when we assumed a quasi-static motion of the tip. Note that every soft mode corresponds to a *slow* oscillation of the group of surface atoms; the characteristic oscillation time associated with all such modes can be much longer than the usual phonon time. Consequently, the departure from equilibrium for these modes can be greater than for others. This implies that we should assume that at every position Q_0 the tip does not have enough time to sample those modes and the latter should be included explicitly into the consideration. In other words, the soft modes activated by the tip and the tip itself have to be considered on the same footing, so that the reduced description should be used only with respect to the other modes (i.e. for the fast modes which can be sampled over by the tip).

This is illustrated in figure 3: it is assumed that there is at least one *soft* vibrational mode at the surface which has up to two equivalent minima in the potential energy surface. Then, depending on the tip velocity and that of the soft mode(s), one can envisage several possible trajectories of the tip *and* the atoms involved, one of which is shown by the solid arrowed line in either of the panels in figure 3. The trajectory in figure 3(a) leads to the switching of the soft mode to the other minimum, while the trajectory in figure 3(b) leaves the mode in the same minimum. In either case the force acting on the tip will be different for the up and down motions, $\langle X(Qq) \rangle_{eq}^{\uparrow} \neq \langle X(Qq) \rangle_{eq}^{\downarrow}$, which will lead to dissipation of an energy

$$\Delta A = \oint \langle X \rangle_{eq} \mathrm{d}Q = \int_{\downarrow} \langle X \rangle_{eq}^{\downarrow} \mathrm{d}Q - \int_{\uparrow} \langle X \rangle_{eq}^{\uparrow} \mathrm{d}Q \rangle 0$$

[11,14,17,22]. As above, the integration here is performed over the whole oscillation cycle. The dissipated energy in case (a) is expected to be much larger than in case (b). This simple argument shows that, although actual energetics is determined by the particular interactions in a given system, the *finite speed* of the tip plays a very important role in the 'trajectory switching' process. Therefore, a non-equilibrium (stochastic) consideration is important to account for this effect. Work on developing a stochastic model for the adhesion hysteresis mechanism based on the ideas presented here is now in progress and will be published elsewhere.

Another necessary extension of the present theory should be in including relaxation degrees of freedom related to the tip. Presently, the tip is regarded as rigid and is described only by its coordinate and momentum, Q and P. In reality, there is an atomistic nano-tip at the end of the tip which relaxes considerably at close approach and may also participate in the atomic exchange with the surface. These effects can be taken into account by considering the nano-tip on the same footing as the surface and then incorporating its coordinates explicitly to the theory.
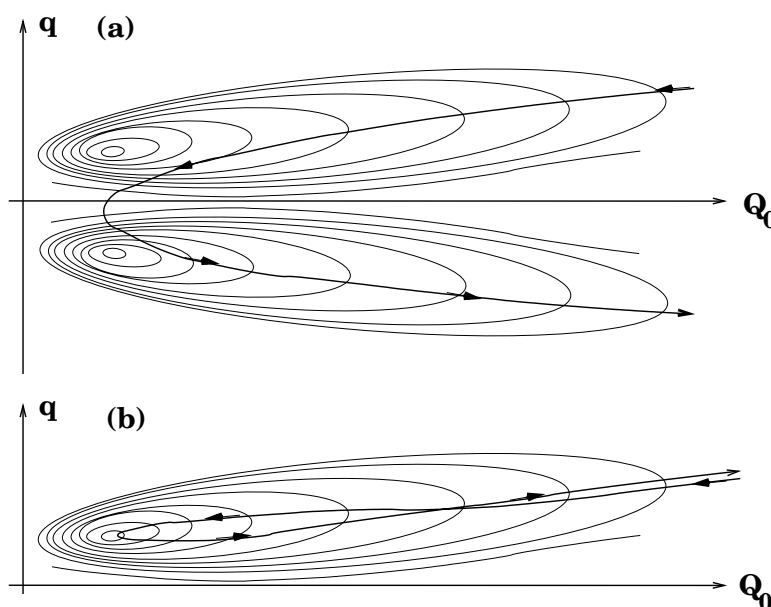
Figure 3. Illustration to the adhesion hysteresis mechanism of dissipation. A qualitative contour plot of the total potential energy of the tip–surface system as a function of the tip coordinate, Q_0, and a generalized coordinate of the soft surface modes, q. The arrowed solid lines show possible trajectories of the system in the $(Q_0 q)$ hyper-surface of the phase space. (a) Stick–slip behaviour: two potential energy minima are assumed for the surface atoms at every position of the tip; upon retraction, the surface atoms switch to another minimum. (b) Adhesion hysteresis: the surface atoms stay in the same minimum, but the trajectory upon retraction is different resulting in a different force field.

Finally, we note that the stochastic nature of the energy dissipation is also confirmed by an experimental observation [37] that the effect is strongly increased as the oscillation frequency is increased. Further experimental evidence is necessary, however, in order to establish other subtle features on the atomic scale of the energy dissipation.

In order to simulate NC-DFM images theoretically, one has to calculate the friction constant, $\gamma(Q)$, for every lateral position of the tip above the surface using the actual force field between the surface and the tip as well as interatomic interactions between surface atoms. This calculation is important in order to assess whether the intrinsic mechanism considered in this paper is sufficient to explain the observed corrugation in NC-DFM images. Note that examples of realistic calculations of the tip–surface force fields can be found e.g. in [19,33]. Note, however, that the calculation of the friction constant is much more difficult as it involves the calculation of the force *fluctuation* due to vibrations of surface atoms as well as atoms of the nano-tip, rather than the average force. We plan to do this work in the near future although some general aspects of the friction constant calculation are addressed elsewhere [31]. Another important application of the NC-DFM, first suggested in [20], is in obtaining information on surface phonons by analysing the friction constants recovered from the experimental NC-DFM images. This question is also addressed in [31]. A more rigorous derivation of the Langevin equation free from all the approximations of the method presented here and based on the Fokker–Planck equation for the tip is also suggested there.

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Appendix

To derive the Langevin equation for the tip, the average force, $\langle X(Q) \rangle$, imposed on the tip due to the fluctuating position of the single surface atom (the primary atom) at two consecutive times t and $t + s$ (where $s \leqslant \tau$) is calculated in [20] (note, however, that the *total* force rather than its *fluctuating* part is considered there). Obviously, the force is determined by the position of the primary atom in every case and is due to different probabilities, $f(x, t)$ and $f(x, t + s)$, for the atom to be at the same position x at these times. In the GT paper, however, $f(x, t)$ and $f(x, t + s)$ are implicitly *canonical* distributions related as:

$$f(x, t + s) \approx f(x, t) e^{\beta \Delta A} \tag{20}$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature and ΔA is the work done on the tip during time s by the surface. Note that ΔA will be the energy transferred to the surface (represented by a single atom in this model) during time s from the tip (the dissipation energy). Using equation (20), the authors of [20] then derived the average force and, after applying coarse graining procedure, they arrived at the correct final force consisting of the average and friction components.

The underlying reasoning for formula (20) is probably borrowed from [28] and is as follows. The surface primary atom (system A) interacting with the heat bath (the rest of the surface, system B) is described approximately using the *equilibrium canonical* distribution as it is assumed that the tip interacts with the atom A only during very short times by transferring energy to it. At all other times the system A+B (the complete surface) can be considered as isolated and, therefore, described using equilibrium statistical mechanics (the micro-canonical distribution). Consequently, the open subsystem A will be described using canonical statistics. We have for the canonical distribution: $f(x, t) \sim \Omega(E_0 - E_x)$, where $\Omega(E_0 - E_x)$ is the total number of microstates available to the reservoir B at the given energy $E_0 - E_x$, E_0 being the total energy of the whole (closed) system A+B while E_x is the energy of the primary atom A. When the amount of energy ΔA is transferred to the *whole* system A+B by external sources (the tip) at time $t + \tau'$, the energy of the system B becomes $E_0 - E_x + \Delta A$, so that the corresponding distribution for the system A changes to $f(x, t + s) \sim \Omega(E_0 - E_x + \Delta A)$. Since Ω is related to the system entropy via $S = k_B \Omega$, one can put $\Omega(E) = \exp(S(E)/k_B)$ and then expand the entropy around E_0 in both $\Omega(E_0 - E_x)$ and $\Omega(E_0 - E_x + \Delta A)$. This standard derivation finally gives:

$$\frac{f(x, t + s)}{f(x, t)} = \frac{\exp(S(E_0 - E_x + \Delta A)/k_B)}{\exp(S(E_0 - E_x)/k_B)} = \exp\left[\frac{\Delta A}{k_B}\left(\frac{\partial S}{\partial E}\right)_{E_0}\right]$$

which is the result quoted above since $(\partial S/\partial E)_{E_0} = T^{-1}$ is the inverse temperature.

It is easy to see, however, where this argument has a problem. Indeed, while comparing the two distribution functions, the *normalization* has not been taken into account: in fact, $f(x, t) = Z^{-1}\Omega(E_0 - E_x)$, where $Z = \sum_x \Omega(E_0 - E_x)$. Obviously, the normalization factors are different for the two time instants, as they also depend on the total energy of the system A+B. Repeating the calculation of the number of microstates via the entropy as we have done above, we arrive at the conclusion that $f(x, t + s) = f(x, t)$, i.e. the two distributions are identical. This is how it should be since the canonical distribution of an open part of a

big isolated system cannot depend on the total energy of the whole system, which is meant to be macroscopic. The distribution $f(x)$ depends only on the temperature of the heat bath T and the energy E_x of the given state x of the open system. The only possible change to the distribution function upon the transfer of some energy ΔA to the whole system can be the change of the heat bath temperature. However, the effect is of the next order and should be neglected.

One can see, therefore, that the motivation for equation (20) implied in [20] is not correct. The important point is that if we used the equilibrium picture correctly as explained above, then two distributions would be the same and there would be no friction term in the Langevin equation at all. One can see, therefore, that the real problem in the GT method is in their main assumption that only during short time intervals when the energy is transferred to the surface from the tip, the surface is away from equilibrium. The equilibrium is, however, quickly restored and, therefore, most of the time the combined system (A+B) can be considered as being at equilibrium. This assumption is wrong. The correct approach should use properly the methods of non-equilibrium statistical mechanics which consider the tip–surface system interacting all the time.

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