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Application of the non-equilibrium statistical operator method (NESOM) to dissipation atomic force microscopy

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Abstract

We apply the non-equilibrium statistical operator method to non-contact atomic force microscopy, considering explicitly the statistical effects of (classical) vibrations of surface atoms and associated energy transfer from the tip to the surface. We derive several, physically and mathematically equivalent, forms of the equation of motion for the tip, each containing a friction term due to the so-called *intrinsic* mechanism of energy dissipation first suggested by Gauthier and Tsukada. Our exact treatment supports the results of some earlier work which were all approximate. We also demonstrate, using the same theory, that the distribution function of the tip in the coordinate–momentum phase subspace is governed by the Fokker–Planck equation and should be considered as strongly peaked around the exact values $\langle P \rangle_t$ and $\langle Q \rangle_t$ of the momentum and the position of the tip, respectively.

1. Introduction

Non-contact atomic force microscopy (NC-AFM) [1–10] is becoming a powerful tool in the study of the atomistic structure of the surfaces of real systems. 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 provided by maintaining a constant frequency shift in the cantilever oscillations which is achieved by adjusting the equilibrium position of the cantilever in the vertical direction for every lateral position of the tip above the surface.

It is well known that the cantilever oscillations are damped and, in order to keep the oscillation amplitude constant, one has to apply an additional driving signal, usually of sinusoidal form, $F_d(t) = A_d \sin(\omega t)$, to the oscillating cantilever system, $\omega = 2\pi/T_0$ being the oscillation frequency and T_0 the oscillation period. The driving signal is changed during the scan and recently [11] atomic resolution has been achieved in this, so-called dissipation (or damping) signal.

Several models have been suggested to explain the damping in the NC-AFM system. In reference [12] it is suggested that the damping may not be related to the energy dissipation, but could be a consequence of a complex behaviour of the solution for the forced oscillations

of the cantilever. However, this becomes unimportant if, when analysing the experimental data, the actual equation of motion for the tip is considered as e.g. in references [13, 14]. Other authors [14–20] suggest various dissipation mechanisms, e.g. that there is some energy transfer from the tip system to the surface leading to the damping of the cantilever oscillations. In particular, the adhesion hysteresis mechanism, based on the assumption that the force field is different on the approach and the retraction of the tip, is invoked in references [14–19]. In references [20–22] an intrinsic dissipation mechanism has been considered whereby there is energy transfer from the tip to the vibrating surface atoms due to non-equilibrium effects, resulting in the appearance of a friction force in the cantilever equation of motion. The Langevin equation method has been used in references [20, 21], whereas in reference [22] a Langevin-type equation for the tip has been derived from the Fokker–Planck equation for the tip distribution function, $f^{(T)}(t)$, which has been obtained by integrating the corresponding Liouville equation for the whole system (tip + surface). The coarse-graining approach [23, 24] has been used in references [20–22] to account for the non-equilibrium effects. Note that the vibrating lattice has been treated classically in references [20–22].

The main objective of the present paper is to confirm the results of the previous study [22] of the dissipation effects in the NC-AFM, using an *exact* non-equilibrium method not based on such an artificial tool as the coarse graining. Indeed, instead of considering a distribution function which satisfies the Liouville equation, in the coarse-graining approach one considers its average taken over a time τ . This time is assumed to be much longer than any process to be sampled over (e.g. atomic vibrations) and, at the same time, to be microscopic, i.e. very small on the macroscopic scale (e.g. $\tau \ll T_0$). This time is not specified explicitly though, as only terms which do not depend on τ are kept; terms proportional to τ are assumed to be small and are dropped. As the result of this approach, there is always a certain amount of freedom in keeping or dropping any terms which are e.g. linear with the coarse-graining time τ in any final expression, so care is needed to obtain correct results.

We shall illustrate this point with an example from reference [22]. When deriving the equation of motion for the tip [22], one finds the friction coefficient γ given as a time integral of the autocorrelation function

$$\gamma(Q) = \int_0^\tau \langle \Delta X(t) \Delta X(t+s) \rangle_{eq} ds$$

with τ as the upper limit, where $\Delta X = X - \langle X \rangle_{eq}$ is the fluctuating part of the tip–surface force, $\langle \dots \rangle_{eq}$ being an equilibrium average when the tip is *fixed* at some Q above the surface. Now, we note that this expression can also be written in the following equivalent form: $\gamma(Q) = \gamma_1(Q) - \tau \langle X \rangle_{eq}^2$, where

$$\gamma_1(Q) = \int_0^\tau \langle X(t)X(t+s) \rangle_{eq} ds$$

is the time integral of the correlation function of the force X itself. Within the coarse-graining method, either expression, $\gamma(Q)$ or $\gamma_1(Q)$, can be used for the friction, as they differ only by a term linear in τ . However, the correlation function $\langle X(t)X(t+s) \rangle_{eq}$ tends to a *finite* limit $\langle X \rangle_{eq}^2$ as $s \rightarrow \infty$, whereas

$$\lim_{s \rightarrow \infty} \langle \Delta X(t) \Delta X(t+s) \rangle_{eq} = 0.$$

Therefore, if one wants to extend the upper limit in the time integrals in the transport coefficient to infinity as is usually done, only correlation functions of *fluctuations* of the dynamical variables are to be used: ΔX in the NC-AFM case. This may require adding certain terms linear in τ in the final expression within the coarse-graining method to ensure the proper behaviour of the corresponding correlation functions.

In the non-equilibrium statistical operator method (NESOM) developed originally by Zubarev (see references [24, 25]) no artificial parameters are involved and this method is considered to be *the exact* formulation of irreducible processes in many-body classical or quantum systems which are arbitrarily far away from equilibrium. Therefore, it is of great importance to consider the NC-AFM system using this method and to confirm the results of the earlier treatments [20–22].

We note that our consideration here will also be entirely classical, i.e. we ignore quantum effects while considering *atomic vibrations* of the surface. We note that classical treatment of surface atoms is justified at temperatures which are around or higher than the corresponding Debye temperature of the crystal. In the case of room temperature NC-AFM experiments there are many crystals (e.g. RbF, RbCl, RbBr, NaBr, NaI, KCl, KBr, BaO) which satisfy this condition. In other cases including the low-temperature AFM experiments [26, 27] a quantum treatment is necessary. However, the entirely quantum description of the NC-AFM system appears to be rather complicated. That is why we decided that it would be appropriate to consider the classical problem first. After all, the previous work [20–22] was also done within this approximation. We are working on the quantum analysis at the moment and it will be published separately. Note that electrons enter the theory indirectly via the atomic potential energy surface that they produce within the Born–Oppenheimer approximation and can be assumed to be entirely quantum objects. This means that potential energies for atoms entering the Hamiltonian in our model (see below) are assumed to be calculated using a quantum mechanical description for the electrons.

The plan of the paper is as follows. In section 2 we present the main ideas of the NESOM to facilitate the reading of the further sections and also to introduce our notation. In section 3 we *derive* the generalized Langevin equation (with memory effects) for the tip with the friction term built in. The latter term is given in accordance with the fluctuation-dissipation theorem [28–30] as the time integral of the autocorrelation function of the fluctuating part ΔX of the tip–surface force, X . The time integration is carried out from zero to infinity with the proper factor ensuring the convergence of the integral at the upper limit. No artificial coarse-graining time is introduced. Note that the equation derived is highly non-linear. However, within the same approximation, it can be linearized (section 3.4) and then, in the Markovian approximation, appears to be identical to the Langevin equation derived previously [21, 22]. In section 4 the Fokker–Planck equation for the tip is then *derived*, which, in the Markovian approximation, is shown to be identical to that derived previously in reference [22] using the coarse-graining approach. Two methods are used to derive the Fokker–Planck equation in section 4. It is also shown in section 4 that a somewhat different form of the Langevin equation follows from the Fokker–Planck equation. Finally, in section 5 we discuss all forms of the Langevin equation obtained and their relation to each other and show that, from the physical and also mathematical points of view, they are all equivalent.

2. The NESOM

The NESOM can be considered as a direct extension of the Gibbsian ensembles from equilibrium to non-equilibrium many-body systems. As in the coarse-graining approach, in the NESOM one has to decide what timescale is of interest so that all degrees of freedom of the given system can be divided into fast (to be sampled or averaged over) and slow (to be considered explicitly) components. However, the further analysis does not rely on any specific time τ and, at least in principle, is exact. A *reduced* description of the system is used in which a certain *incomplete* level of consideration is chosen. Then, only such solutions $\rho(t)$ of the Liouville equation are considered (the *true* non-equilibrium distribution) as originate from some specific

initial (at $t = -\infty$) distribution function, called the *relevant* distribution, ρ_{rel} , based upon a set of so-called *relevant dynamical variables*, $\{\wp_m\}$, specific for the chosen *level* of the reduced description. The relevant variables are some functions of the coordinates and momenta of all or some particles of the whole system. The relevant distribution describes generalized Gibbsian ensembles, called relevant statistical ensembles, which are characterized by a set of exact statistical averages $\langle \wp_m \rangle_t$ calculated using the true distribution $\rho(t)$, i.e. $\langle \wp_m \rangle_t = \text{Tr}\{\rho(t)\wp_m\}$. Here and in the following we use the trace symbol Tr to indicate the integration over the entire phase space Γ (all coordinates and momenta).

The relevant distribution is obtained by maximizing the information entropy $S_{inf}[\rho_{rel}] = -\text{Tr}(\rho_{rel} \ln \rho_{rel})$ of the system under the auxiliary conditions that the averages $\langle \wp_m \rangle_{rel} = \text{Tr}\{\rho_{rel}\wp_m\}$ of the relevant variables calculated using ρ_{rel} coincide exactly with the exact averages $\langle \wp_m \rangle_t$ (the so-called self-consistency conditions). This is achieved by using a set of Lagrange multipliers which enter the expression for the relevant distribution. The exact averages depend on time (as does the true distribution, $\rho(t)$), so the Lagrange multipliers and, therefore, the relevant distribution also implicitly depend on time.

It should be noted [24] that the Liouville equation alone does not give a unique solution and is very sensitive to any additional even infinitesimally small terms which can break the time-reversal symmetry inherent to the equation. Mathematically, the desired solution in the NESOM is obtained by solving the following Liouville equation with broken time-reversal symmetry:

$$\left(\frac{\partial}{\partial t} + i\widehat{L}\right)\rho(t) = -\epsilon\{\rho(t) - \rho_{rel}(t)\} \quad (1)$$

where \widehat{L} is the Liouville operator of the whole system (for any dynamical variable Θ of the system, $i\widehat{L}\Theta = \{\Theta, \widehat{H}\}$, where $\{\dots, \dots\}$ is the Poisson bracket and \widehat{H} the total Hamiltonian), and the limit $\epsilon \rightarrow +0$ is implied in all averages calculated with $\rho(t)$ *after* taking the thermodynamic limit. Equation (1), which will be referred to in the following as the broken-symmetry Liouville equation for brevity, differs from the ordinary Liouville equation by an extra infinitesimal (source) term in the right-hand side. Its purpose is to pick up the proper solution $\rho(t)$ evolved from $\rho_{rel}(t)$ at $t = -\infty$. The source term is equivalent to introducing *boundary conditions* for the Liouville equation at $t = -\infty$, so that the correct *retarded* solution bounded by $\rho_{rel}(t)$ at $t = -\infty$ is obtained. This is also similar to the well known prescription in the scattering theory [24, 31] whereby a particular retarded solution (the outgoing wave) is selected for the given incoming (initial) wave at $t = -\infty$ by adding an extra source term to the Schrödinger equation which is then set to zero at the end of the calculation. Equation (1) is the basis of the NESOM and allows for the exact consideration of any irreversible processes in many-body non-equilibrium statistical mechanics.

The choice of the proper set of the relevant variables $\{\wp_m\}$ is of principal importance for any problem under study. The particular choice is dictated by the corresponding level of the reduced description required and by the desired set of evolution (kinetic) equations to be derived. Thus, $\{\wp_m\}$ should contain as a subset such variables as correspond to the desired set of the observables, $\langle \wp_m \rangle_t$. Once the true non-equilibrium distribution $\rho(t)$ is calculated from equation (1), the kinetic equations for the observables $\langle \wp_m \rangle_t$ are obtained from the relations [24]

$$\frac{\partial \langle \wp_m \rangle_t}{\partial t} = \text{Tr}\left\{\frac{\partial \rho(t)}{\partial t}\wp_m\right\} = \text{Tr}\{\dot{\wp}_m \rho(t)\} \quad (2)$$

where the broken-symmetry Liouville equation (1) has been used in the derivation of the last expression, followed by the self-consistency conditions and integration by parts. The dynamical variable $\dot{\wp}_m = i\widehat{L}\wp_m = \{\wp_m, \widehat{H}\}$ is called the generalized flux associated with

\wp_m . Since the relevant distribution $\rho_{rel}(t)$ depends implicitly on the observables $\langle \wp_m \rangle_t$ (recall that the Lagrange multipliers are some functions of these because of the self-consistency conditions), the true distribution $\rho(t)$ will also be some non-linear function of them. As a result, equations (2) (for $\forall m$) become a closed set of generalized *transport equations* for the chosen set of observables which could be, however, of an extremely formidable form.

Several choices of the relevant variables will be discussed in the present paper for the problem that we are interested in, namely of forced oscillations of the cantilever in the NC-AFM system. We shall show that one choice leads to the Langevin equation for the tip, whereas another leads to the corresponding Fokker–Planck equation which, upon integration, results in a slightly different type of Langevin equation. We will demonstrate, however, that from the physical point of view either equation describes correctly the NC-AFM system and corresponds to the same reduced level of system consideration.

3. Derivation of the Langevin equation for the tip

3.1. Relevant variables and the relevant distribution

We start from the microscopic classical Hamiltonian \widehat{H} for the whole system consisting of the tip and surface atoms connected to a heat bath kept at the constant temperature T :

$$\widehat{H}(pqPQ) = H_s + H_T = (H_{pq} + \Phi_{Qq}) + \left(\frac{P^2}{2M} + U_Q \right). \quad (3)$$

The tip is described by its vertical coordinate, Q , and the conjugate momentum, P , while the surface is described by the coordinates q and momenta p of all of its atoms. In equation (3) H_{pq} is the Hamiltonian of the surface atoms, Φ_{Qq} their interaction with the tip, $P^2/2M$ the kinetic energy and U_Q the potential energy of the tip (the elastic energy, $\frac{1}{2}k(Q - Q_{eq})^2$, and the energy associated with the driving signal, $-F_d(t)Q$). Here M is the tip effective mass, k the elastic constant and Q_{eq} the equilibrium position of the tip. Because of the q -dependence, the force acting on the tip, $X(Qq) = -\partial\Phi_{Qq}/\partial Q$, fluctuates rapidly around its average value. The potential energy, U_Q , in equation (3) gives rise to some external force $Y(Q)$ (elastic and driving forces) acting on the tip which is changing with time on a much longer timescale than atomic vibrations. For convenience, we shall call $H_s = H_{pq} + \Phi_{Qq}$ the surface Hamiltonian and $H_T = P^2/2M + U_Q$ the tip Hamiltonian as indicated in equation (3).

We are interested here in the oscillations of the macroscopic tip representing a very slow subsystem, atomic vibrations being a very fast one. Therefore, in the present problem the desired level of reduced description is achieved by considering any functions of the tip coordinate and momentum, Q and P , as the relevant variables. As in this section we would like to derive the Langevin equation for the tip which is of the general form of the equation of motion, i.e. the derivative $\partial\langle P \rangle_t / \partial t$ equal to the total force, it is reasonable to choose Q and P in the set of relevant variables.

This is somewhat similar to the Brownian motion, as has already been suggested in references [20–22], since we are dealing here with a single slow and massive particle (the tip) interacting with light atoms performing very fast movements (vibrations). In the case of the Brownian motion with no external field applied, all positions in space are equivalent and just two dynamical variables, namely the total Hamiltonian of the system, \widehat{H} , and the particle momentum, P , are sufficient for the derivation of its equation of motion (the Langevin equation) [24]. In the case of the NC-AFM, however, such description is insufficient as there is a Q -dependent force applied to the tip (both the elastic force and the tip–surface interaction); the translational symmetry is broken and so the coordinate Q of the tip has to be also considered

alongside P and \widehat{H} as another relevant variable. Note that the Hamiltonian \widehat{H} is to be included in the list of relevant variables, since in our treatment the total energy of the *whole* system (surface + tip) is conserved and has a certain value.

The relevant distribution is obtained in the standard way [24] by maximizing the information entropy subject to the auxiliary self-consistency conditions

$$\langle P \rangle_t = \text{Tr}\{\rho_{rel}(t)P\} \quad (4)$$

$$\langle Q \rangle_t = \text{Tr}\{\rho_{rel}(t)Q\} \quad (5)$$

and is given by

$$\rho_{rel}(t) = \frac{1}{Z(t)} \exp\{-\beta[\widehat{H} - V(t)P - F(t)Q]\} \quad (6)$$

where β and the functions $V(t)$ and $F(t)$ play the role of Lagrange multipliers. Since we assume that the temperature is constant anywhere in the system and is set to T (the macroscopically large surface performs as a heat bath), the Lagrange multiplier β can be simply chosen as $\beta = 1/k_B T$. The other two Lagrange multipliers, $V(t)$ and $F(t)$, are found from the self-consistency conditions (4) and (5), whereas the normalization factor is given as

$$Z(t) = \text{Tr} \exp\{-\beta[\widehat{H} - V(t)P - F(t)Q]\}. \quad (7)$$

The integration in the right-hand side of equation (4) is easily performed using the substitution $P' = P - MV$, and we get the same expression for the Lagrange multiplier $V(t)$ as for the Brownian motion [24]:

$$V(t) = \frac{\langle P \rangle_t}{M} \equiv \frac{P_t}{M}. \quad (8)$$

This has the physical meaning of the tip velocity. Note that the shortened notation Q_t and P_t will often be used hereafter for the exact averages $\langle Q \rangle_t$ and $\langle P \rangle_t$, respectively.

Unfortunately, it is not possible to obtain an explicit expression for the other Lagrange multiplier, $F(t)$, as an explicit function of the observables Q_t and P_t because the integration over q and Q in the right-hand side of equation (5) cannot be performed analytically in the general case. One can easily recognize, however, that a contribution due to the integration over the momenta p and P cancels out exactly with the corresponding contribution in $Z(t)$, equation (7). We conclude, therefore, that $F(t)$ depends only on Q_t , not on P_t . Several useful exact identities can also be derived as shown in appendix 1. We will be using them later on in our further analysis.

To understand the physical meaning of $F(t)$, we consider the average $\langle \dot{P} \rangle_{rel}$ of the generalized flux $\dot{P} = i\widehat{L}P = \{P, \widehat{H}\} = -\partial(\Phi_{Qq} + U_Q)/\partial Q$. This is a dynamical variable—the force acting on the tip. Since $\dot{P} = -\partial\widehat{H}/\partial Q$, one can perform the Q -integral in equation (5) by parts. The calculation is straightforward and gives immediately

$$F(t) = -\langle \dot{P} \rangle_{rel} \quad (9)$$

where

$$\langle \dot{P} \rangle_{rel} = -k(Q_t - Q_{eq}) + \langle X(Qq) \rangle_{rel} + F_d(t) \quad (10)$$

can be considered as an average force (see the end of this subsection). Note that the self-consistency condition (5) for the tip coordinate has been used here. Thus, the Lagrange multiplier $F(t)$ corresponds to the minus force acting on the tip which is calculated using the relevant distribution. Equation (9) can be considered as an algebraic equation for the Lagrange multiplier $F(t)$ as a function of Q_t (note that the average $\langle X(Qq) \rangle_{rel}$ does not depend on P_t since the P -integration can be performed explicitly there, giving a factor which cancels out with the corresponding term in $Z(t)$, equation (7)).

In order to clarify the physical meaning of $F(t)$ even further, let us consider the relevant distribution (6) in more detail. Using explicit expressions for the Lagrange multipliers (8), (9) and (10), one can rewrite the relevant distribution in the following equivalent form:

$$\rho_{rel}(t) = \rho_{eq}(pq|Q) \Psi(PQ, t) \quad (11)$$

where

$$\rho_{eq}(pq|Q) = \frac{1}{Z_s(Q)} e^{-\beta H_s} \quad (12)$$

is the *equilibrium distribution* of the surface atoms calculated for the tip *fixed* at Q , and

$$Z_{eq}(Q) = \text{tr} \exp(-\beta H_s) \quad (13)$$

is the corresponding Q -dependent surface partition function. Note that the equilibrium distribution weakly depends on Q as is indicated above. Here and in the following, the symbol $\text{tr} \dots = \int dp dq \dots$ means the trace calculated with respect to the surface variables only (i.e. the integration with respect to p, q). The function

$$\Psi(PQ, t) = \frac{1}{Z_1(t)} \exp \left\{ \Omega(Q) - \frac{\beta}{2M} (P - P_t)^2 - \frac{\beta k}{2} (Q - Q_t)^2 \right\} \quad (14)$$

in equation (11) serves as an *envelope* function. Indeed, the function

$$\Omega(Q) = -\beta(\langle X \rangle_{rel} + F_d)(Q - Q_{eq}) + \ln Z_{eq}(Q)$$

is some function changing relatively weakly with the tip position, Q , and $Z_1(t)$ is the corresponding normalization factor. One can see that the relevant distribution is given as a product of the surface equilibrium distribution, ρ_{eq} , and two Gaussians, one centred at Q_t and another at P_t , which are the exact average position and momentum of the tip at time t . Note that the elastic constant $k = \omega_0^2 M$ is very large owing to the large effective mass of the tip M and, therefore, the quadratic term proportional to k in the exponential dominates the Q -dependence. Thus, the relevant distribution is strongly (in fact, in a δ -like fashion in the $M \rightarrow \infty$ limit) *peaked* around the exact position of the tip Q_t at any time t , and is Maxwellian with respect to its momentum with the average value equal to the exact momentum P_t . This property of the relevant distribution will be used later on in section 3.4 to shed more light on the kinetic equation that we derive in section 3.3.

It follows from the form of the relevant distribution just discussed that for any dynamical variable $\Theta(Qq)$ not depending on momenta one has

$$\langle \Theta(Qq) \rangle_{rel} \simeq \langle \Theta(Q_t q) \rangle_{eq}. \quad (15)$$

Note that the equilibrium average above is calculated at the exact position of the tip, Q_t . Therefore, we can approximately substitute for $\langle X(Qq) \rangle_{rel}$ in equation (10) the equilibrium force $\langle X(Q_t q) \rangle_{eq}$. This means that the Lagrange multiplier $F(t)$ is approximately equal to the minus force acting on the tip in *equilibrium* when the tip is *fixed* at Q_t above the surface. We shall demonstrate in section 3.4 that the result in equation (15) is correct up to the order of $1/M$.

3.2. Solution of the Liouville equation

To derive the kinetic (transport) equation for P_t (the equation of motion for the tip or the Langevin equation), we first have to solve the broken-symmetry Liouville equation (1). First of all, we note that the solution of the Liouville equation (1) can be formally written as follows:

$$\rho(t) = \rho_{rel}(t) + \Delta\rho(t) \quad (16)$$

$$\Delta\rho(t) = - \int_{-\infty}^t e^{-\epsilon(t-t')} e^{-i(t-t')\widehat{L}} \left\{ \frac{\partial}{\partial t'} + i\widehat{L} \right\} \rho_{rel}(t') dt' \quad (17)$$

where \widehat{L} is the total Liouville operator of the whole system. The Langevin equation is then obtained by calculating the derivative $\partial P_t / \partial t$. Substituting equation (16) into equation (2) which is written for the relevant variable P , we have

$$\frac{\partial P_t}{\partial t} = \langle \dot{P} \rangle_{rel} + \text{Tr}\{\dot{P} \Delta\rho(t)\}. \quad (18)$$

Therefore, formally the Langevin equation sought for is obtained by substituting $\Delta\rho(t)$ from equation (17) into the right-hand side of equation (18). Although this result is exact, we note that it is very difficult to calculate $\Delta\rho(t)$ in practice because of the exponential operator in equation (17) containing the Liouville operator. Before we introduce certain approximations, some simplifications are necessary.

Our further treatment is in parts similar to that presented in reference [22]. We split the Liouville operator \widehat{L} into two contributions: \widehat{L}_0 and \widehat{L}_T . The operator \widehat{L}_0 is associated with the surface atoms only and is related to the surface Hamiltonian, \widehat{H}_s (i.e. for any dynamical variable A we have $i\widehat{L}_0 A = \{A, \widehat{H}_s\}$). The other component of \widehat{L} is the Liouville operator of the tip:

$$\widehat{L}_T = \frac{P}{M} \frac{\partial}{\partial Q} - \{-k(Q - Q_{eq}) + X(Qq) + F_d(t)\} \frac{\partial}{\partial P} \quad (19)$$

where the expression in the curly brackets is the total force, $\dot{P} = -\partial\widehat{H}/\partial Q$, acting on the tip; see equation (3).

In order to calculate $\rho(t)$ according to equations (16) and (17), we should first calculate $(\partial/\partial t)\rho_{rel}(t)$ and $i\widehat{L}\rho_{rel}(t)$. Let us start from the latter term: $i\widehat{L}\rho_{rel} = i\widehat{L}_0\rho_{rel} + i\widehat{L}_T\rho_{rel}$. The first term is zero since the operator $i\widehat{L}_0$ (associated with the surface Hamiltonian H_s) acts only on the surface variables p, q and the relevant distribution $\rho_{rel} \sim \exp(-\beta H_s)$ with respect to these variables:

$$i\widehat{L}_0\rho_{rel}(t) = 0. \quad (20)$$

This is easily checked by inspection. Then, using equations (19) and (6), one can calculate $i\widehat{L}_T\rho_{rel}$ and get

$$i\widehat{L}_T\rho_{rel}(t) = \frac{\beta}{M}\rho_{rel}(t)(\dot{P}P_t - \langle \dot{P} \rangle_{rel}P). \quad (21)$$

To calculate $(\partial/\partial t)\rho_{rel}(t)$ we note that the time dependence of the relevant distribution originates exclusively from that of the Lagrange multipliers $V(t)$ and $F(t)$. Using the explicit expression for the relevant distribution, equations (6) and (7), the derivatives $\delta\rho_{rel}/\delta V(t)$ and $\delta\rho_{rel}/\delta F(t)$ are easily calculated to give

$$\frac{\partial\rho_{rel}(t)}{\partial t} = \beta\rho_{rel}(t) \left[(Q - Q_t) \frac{\partial F}{\partial t} + \frac{1}{M}(P - P_t) \frac{\partial P_t}{\partial t} \right] \quad (22)$$

where we also used equation (8). The derivative $\partial F/\partial t$ is calculated in appendix 1. To calculate the derivative $\partial P_t/\partial t$, we make use of equation (18). Collecting all terms together, we arrive at the following expression for the term immediately after the exponential operator in the expression for $\Delta\rho(t)$ in equation (17):

$$\left\{ \frac{\partial}{\partial t} + i\widehat{L} \right\} \rho_{rel}(t) = \frac{\beta}{M}\rho_{rel}(t) \left[(\dot{P} - \langle \dot{P} \rangle_{rel}) + \frac{1}{\beta} \frac{Q - Q_t}{\langle Q^2 \rangle_{rel} - Q_t^2} P_t + (P - P_t) \text{Tr}\{\dot{P} \Delta\rho(t)\} \right]. \quad (23)$$

This expression is still exact. Substituting it into equation (17), we obtain a very complicated equation for $\Delta\rho(t)$. It can be solved, however, approximately if a small parameter is introduced into the theory.

Since in equilibrium $\langle P^2 \rangle = M/\beta$ and, therefore, $P \sim \sqrt{M}$, we notice that the operator $\widehat{L}_T \sim M^{-1/2}$. Similarly, the surface Liouville operator $\widehat{L}_0 \sim m^{-1/2}$ where m is the characteristic mass of a surface atom. Since $m \ll M$, the Liouville operator of the tip is much smaller than that of the surface. This allows us to use a kind of perturbation theory to solve the equation for $\Delta\rho(t)$. This method is equivalent to that used in the theory of the Brownian motion [24, 28, 29]. Employing $\eta = (m/M)^{-1/2}$ as the small parameter, we see that the first term in equation (23) is of the order of η ; the second term there contains a factor which is also of the order of η . By solving the equation for $\Delta\rho(t)$ iteratively, we can keep only the first term which is, in fact, equivalent to dropping the second term in equation (23) which contains $\Delta\rho(t)$. Thus, to the first order in η , the exponential operator in equation (17) acts only on the first term in equation (23).

Our next step will be simplifying the exponential operator. It can also be expanded in a series with respect to the small parameter η . As the expression which the exponential operator in equation (17) is acting upon is already of the order of η , it is sufficient to keep only the very first term in the expansion. Thus, it is sufficient to substitute for \widehat{L} in the exponential operator in equation (17) the Liouville operator of the surface, \widehat{L}_0 :

$$\Delta\rho(t) \simeq - \int_{-\infty}^t e^{-\epsilon(t-t')} \widehat{S} \left\{ \frac{\partial}{\partial t'} + i\widehat{L} \right\} \rho_{rel}(t') dt' \quad (24)$$

where

$$\widehat{S} = e^{-i(t-t')\widehat{L}_0}. \quad (25)$$

Before we apply the operator \widehat{S} to the first term in the right-hand side of equation (23), we first note that this operator commutes with the relevant distribution because of equation (20). Secondly, the operator \widehat{L}_0 (and, therefore, \widehat{S}) acts only on the surface variables, p and q , and there is only one dynamical variable in equation (23), namely \dot{P} , which depends on q . Therefore, we get

$$\Delta\rho(t) \simeq - \frac{\beta}{M} \int_{-\infty}^t e^{-\epsilon(t-t')} \rho_{rel}(t') \left\{ \widehat{S} \dot{P} - \langle \dot{P} \rangle_{rel} + \frac{1}{\beta} \frac{Q - Q_{t'}}{\langle Q^2 \rangle_{rel} - Q_{t'}^2} \right\} P_{t'} dt'. \quad (26)$$

3.3. The kinetic equation for the tip

The desired kinetic equation for the dynamical variable P is now obtained by substituting $\Delta\rho(t)$ from equation (26) into the right-hand side of equation (18) and using the identity (A1.5):

$$\frac{\partial P_t}{\partial t} = \langle \dot{P} \rangle_{rel} - \frac{\beta}{M} \int_{-\infty}^t e^{-\epsilon(t-t')} \left\{ \langle \dot{P} \widehat{S} \dot{P} \rangle_{rel} - \langle \dot{P} \rangle_{rel}^2 - \frac{1}{\beta^2} \frac{1}{\langle Q^2 \rangle_{rel} - Q_{t'}^2} \right\} \langle P \rangle_{t'} dt'. \quad (27)$$

Note that in all of the averages in the curly brackets the relevant distribution is taken at time t' and the operator \widehat{S} depends on the time difference $t - t' > 0$.

This result can be further simplified if we use the explicit expression for the force:

$$\dot{P} = \Delta X(Qq) + \langle X(Qq) \rangle_{rel} - k(Q - Q_{eq}) + F_d(t). \quad (28)$$

Here ΔX represents a *fluctuating* part of the tip–surface force, $\Delta X = X - \langle X \rangle_{rel}$, since according to equation (15), $\langle X(Qq) \rangle_{rel}$ is the average force acting on the tip fixed at its exact position Q_t at time t . Then, the surface Liouville operator \widehat{L}_0 acts only on the surface variables, so the \widehat{S} -operator in $\langle \dot{P} \widehat{S} \dot{P} \rangle_{rel}$ (see equation (27)) acts only on the fluctuating part of the tip–surface force leaving the other components in the total force (28) intact. Note that the average

force $\langle X(Qq) \rangle_{rel}$ depends only on time via the time dependence of the Lagrange multipliers in the relevant distribution. Then a somewhat lengthy though straightforward manipulation yields

$$\langle \dot{P} \widehat{S} \dot{P} \rangle_{rel} - \langle \dot{P} \rangle_{rel}^2 = \langle \Delta X \widehat{S} \Delta X \rangle_{rel} + k^2 (\langle Q^2 \rangle_{rel} - Q_t^2) - 2k (\langle QX \rangle_{rel} - Q_t \langle X \rangle_{rel}). \quad (29)$$

Two identities have been used: $\langle X \widehat{S} \Theta \rangle_{rel} = \langle \Theta X \rangle_{rel}$ and $\langle \Theta \widehat{S} X \rangle_{rel} = \langle \Theta X \rangle_{rel}$. These are valid for any dynamical variable $\Theta = \Theta(P, Q, t)$ not depending on the variables p, q of the surface atoms. The first identity follows from the fact that the operator \widehat{S} acts only on dynamical variables which depend explicitly on the surface variables p, q ; therefore $\widehat{S} \Theta = \Theta$. To prove the second identity, we note that $\widehat{S} X(Qq) = X(Qq')$, where q' is the column vector of atomic coordinates evolved from q during the time $t' - t$ when the tip is *fixed* at Q ¹. The integration with respect to p, q in the average $\langle \Theta(P, Q, t) X(Qq) \rangle_{rel}$ is then performed by transforming to the variables p', q' (associated with time t') and using the fact that a volume of the phase space associated with the surface variables (the Hamiltonian H_s , the Liouville operator L_0) does not change during the evolution when the tip is fixed: $dp dq = dp' dq'$.

Using equation (29) in equation (27) and also substituting for $1/\beta$ there using equation (A1.6), we obtain

$$\frac{\partial P_t}{\partial t} = \langle \dot{P} \rangle_{rel} - \frac{\beta}{M} \int_{-\infty}^t e^{-\epsilon(t-t')} \langle \Delta X \widehat{S} \Delta X \rangle_{rel} P_{t'} dt' + \delta \langle \dot{P} \rangle \quad (30)$$

where

$$\delta \langle \dot{P} \rangle = \frac{\beta}{M} \int_{-\infty}^t e^{-\epsilon(t-t')} (\langle QX \rangle_{rel} - Q_{t'} \langle X \rangle_{rel}) \frac{\partial \langle X(Qq) \rangle_{rel}}{\partial Q_{t'}} P_{t'} dt' \quad (31)$$

is a correction term. In order to write it down in this form, equation (A1.4) has also been used.

3.4. Linearization

The transport (kinetic) equation (30) obtained above is highly non-linear. Indeed, the averages there are calculated with respect to the relevant distribution which depends, in a rather complicated way, on the quantities P_t and Q_t (see section 3.1). It can, however, be linearized owing to the large elastic constant $k = \omega_0^2 M$ of the tip (cf. the end of section 3.1).

First of all, let us calculate the normalization constant $Z(t)$, equation (7). The integration with respect to P is straightforward:

$$Z(t) = Z_P \int dQ e^{-\beta \Sigma(Q)} \quad (32)$$

where

$$Z_P = \sqrt{\frac{2\pi M}{\beta}} \exp\left[\frac{\beta P_t^2}{2M}\right]$$

and we have introduced a Q -dependent function

$$\Sigma(Q) = \frac{1}{2} k (Q - Q_{eq})^2 - [F(t) + F_d(t)] Q - \frac{1}{\beta} \ln Z_{eq}(Q) \quad (33)$$

where $Z_{eq}(Q)$, the surface partition function (13), results from the integration with respect to the surface variables. The first term in equation (33) dominates, so the main contribution to the integral will be due to some vicinity of $\Sigma(Q)$ around its minimum at $Q = Q_0$, $\Sigma'(Q_0) = 0$. Therefore, the Q -integration in equation (32) can be performed asymptotically for large k

¹ Since $t' - t < 0$, the coordinates q' correspond to the evolution *reversed* in time.

using the steepest-descent method [32,33]. First, we calculate the tip coordinate, Q_0 , at which the function $\Sigma(Q)$ is minimum. Using the fact that

$$\frac{d}{dQ} \ln Z_{eq}(Q) = \frac{1}{Z_{eq}(Q)} \frac{dZ_{eq}(Q)}{dQ} = \beta \left\langle -\frac{\partial \Phi_{Qq}}{\partial Q} \right\rangle_{eq} = \beta \langle X(Qq) \rangle_{eq} \quad (34)$$

where equation (13) has been used, and setting the derivative $\Sigma'(Q)$ to zero, one finds

$$-F(t) = -k(Q_0 - Q_{eq}) + \langle X(Q_0q) \rangle_{eq} + F_d(t). \quad (35)$$

That is, the Lagrange multiplier is equal to the minus force acting on the tip at $Q = Q_0$. Then, expanding the function $\Sigma(Q)$ around Q_0 and dropping all terms beyond the square one, we have

$$Z(t) = Z_P \sqrt{\frac{2\pi}{\beta \Sigma''(Q_0)}} e^{-\beta \Sigma(Q_0)} + O\left(\frac{1}{M}\right) \quad (36)$$

where

$$\Sigma''(Q_0) = k - \frac{d}{dQ_0} \langle X(Q_0q) \rangle_{eq} \quad (37)$$

is the second derivative of the function $\Sigma(Q)$. Note that $\Sigma''(Q_0) > 0$ which is the necessary condition for the stability of the NC-AFM system: the elastic force should be greater than the tip-surface force in order to prevent the tip from 'jumping to contact'; see equation (35).

Similarly one can calculate $\langle Q \rangle_{rel}$ using the steepest-descent method and the result will be simply Q_0 . Using the self-consistency condition (5), we therefore find

$$Q_0 \simeq Q_t \equiv \langle Q \rangle_t. \quad (38)$$

Comparing this formula with equation (35), we obtain

$$-F(t) = -k(Q_t - Q_{eq}) + \langle X(Q_tq) \rangle_{eq} + F_d(t) \equiv \langle \dot{P} \rangle_{eq} \quad (39)$$

so, asymptotically, the Lagrange multiplier $F(t)$ is equal to the minus force acting on the tip in *equilibrium* when the tip is *fixed* at Q_t at every time instant t . We have already mentioned this (without a rigorous proof though) at the end of section 3.1.

Now we consider an average with respect to the relevant distribution of an arbitrary function $\Theta(Qq)$ which changes with the distance Q from the surface not faster than an exponential function. Again, we use the method of steepest descent to calculate the average:

$$\langle \Theta(Qq) \rangle_{rel} = \frac{Z_P}{Z(t)} \int dQ e^{-\beta \Sigma(Q)} \langle \Theta(Qq) \rangle_{eq}.$$

Expanding $\Sigma(Q)$ up to the square term around Q_t as above and using equation (36) for the normalization constant, we obtain equation (15) since $k \sim M$. Note that this equation has been given before in section 3.1 without proof, using a sort of intuitive argument.

The general expression just derived can be used to linearize our transport equation (30) for the tip oscillations. Indeed, first of all, all averages there with respect to the relevant distribution can be substituted for with the corresponding equilibrium averages calculated at the exact position Q_t of the tip at time t . In addition, within the same approximation, $\langle QX \rangle_{rel} \simeq \langle Q_t X(Q_tq) \rangle_{eq} = Q_t \langle X(Q_tq) \rangle_{eq}$ and $Q_t \langle X(Qq) \rangle_{rel} \simeq Q_t \langle X(Q_tq) \rangle_{eq}$, so the correction term, equation (31), can be dropped. Therefore, we obtain the following *linearized transport equation* for the tip:

$$\frac{\partial P_t}{\partial t} = \langle \dot{P} \rangle_{eq} - \frac{\beta}{M} \int_{-\infty}^t e^{-\epsilon(t-t')} \langle \Delta X \widehat{S} \Delta X \rangle_{eq} P_{t'} dt' \quad (40)$$

where $\langle \dot{P} \rangle_{eq}$ is calculated at Q_t and is given by equation (39). The correlation function

$$\langle \Delta X \widehat{S} \Delta X \rangle_{eq} = \text{tr} \{ \rho_{eq} \Delta X(Q_t, q) e^{-i(t-t')\widehat{L}_0} \Delta X(Q_t', q) \} = \text{tr} \{ \rho_{eq} \Delta X(Q_t', q) \Delta X(Q_t', q') \} \quad (41)$$

is also calculated in equilibrium for the same position of the tip (fixed at Q_t'); the atomic coordinates q' are calculated from their initial coordinates and momenta, q and p , using classical mechanics (the Hamiltonian H_s) after the time lapse $t - t'$. Note that, within the same approximation, the fluctuation of the tip–surface force, $\Delta X = X - \langle X \rangle_{rel}$, is calculated here with respect to the force $\langle X(Qq) \rangle_{rel} \simeq \langle X(Q_t', q) \rangle_{eq}$ in equilibrium. The transport equation obtained is the central result of this section.

The transport equation (40) describes the tip oscillations taking into account the fact that, because of the constant movement, the tip never allows the surface atoms to reach full equilibrium. As a result of this completely non-equilibrium phenomenon, the tip experiences a certain response linear in the tip velocity which is described by the second term in the right-hand side of equation (40).

Note that the equation that we just obtained is more general than the one derived previously [20–22] as it contains non-Markovian *memory* effects as well. In fact, this is a *generalized Langevin equation* [28, 29, 34, 35]. If one assumes, however, that the correlation function (41), which depends on the time difference $|t - t'|$, decays much faster than the characteristic time associated with the tip, i.e. that the tip velocity does not change appreciably during the relaxation time (and this can indeed be verified only by an explicit calculation yet to be done), then one can use the Markovian approximation. Indeed, only the times t' close to t at the upper limit in the integral in equation (40) contribute, so one can take the tip momentum $P_{t'}$ out of the integral and calculate it at time t . Then essentially the same Langevin equation for the tip as in references [20–22] is finally obtained:

$$\frac{\partial P_t}{\partial t} = -k(Q_t - Q_{eq}) + \langle X(Q_t q) \rangle_{eq} + F_d(t) - \frac{\beta}{M} \gamma(Q_t) P_t. \quad (42)$$

Here

$$\gamma(Q) = \int_0^\infty e^{-\epsilon s} \langle \Delta X(Qq) e^{is\widehat{L}_0} \Delta X(Qq) \rangle_{eq} ds \quad (43)$$

is the friction coefficient and, in order to write it in this form, we have used the substitution $s = t - t'$ as well as the fact that the correlation function in the integrand is an even function of time. Note that the exponential factor $e^{-\epsilon s}$ in equation (43), which ensures convergence of the integral at the upper limit, appears automatically in the expression for the friction coefficient $\gamma(Q_t)$ above. We recall that it has been introduced in reference [22] somewhat artificially when the coarse-graining time τ at the upper limit in the time integral was extended to infinity. One can appreciate that the NESOM leads to this result automatically without using any tricks.

One important remark is now in order. The kinetic (transport) equation for the tip (40) has been derived in this section by calculating the corresponding averages in the exact equation (30) asymptotically up to the first order. In fact, the same result, equation (40), can be obtained directly by using the steepest-descent method consistently from the very beginning. This calculation is somewhat simpler and some details of it can be found in appendix 2.

4. The Fokker–Planck equation for the tip

The kinetic (transport) equation derived in the previous section gives useful but rather limited information about the tip: for every t , only the average position and momentum of the tip can be calculated. If one is interested in calculating other quantities which are functions of the

variables P and Q , one needs to know the tip *distribution function*, $f^{(T)}(PQ, t)$, at every time moment t . In this case a somewhat different analysis may be necessary.

4.1. The Fokker–Planck equation: the ‘natural’ choice of relevant variables

Since the tip distribution function can be obtained from the true distribution function $\rho(t) \equiv \rho(pqPQ, t)$ of the whole system upon reduction with respect to the surface variables (i.e. by integrating with respect to p, q):

$$f^{(T)}(P_0Q_0, t) = \text{tr}\{\rho(pqP_0Q_0, t)\} \equiv \text{Tr}\{\delta(P - P_0)\delta(Q - Q_0)\rho(pqPQ, t)\} \quad (44)$$

it is natural (cf. reference [25]) to consider a continuous set of dynamical variables

$$\{\mathcal{P}_m\} \Rightarrow \{\delta(P - P_0)\delta(Q - Q_0)\}$$

(alongside the total Hamiltonian of the whole system, \widehat{H} , equation (3)), as a set of relevant variables in this case. Note that the set $\{\delta(P - P_0)\delta(Q - Q_0)\}$ is continuous since we are interested in the tip distribution function in the whole phase space, $\Gamma_T = (P_0Q_0)$, associated with the tip.

The corresponding relevant distribution in this case is given by

$$\begin{aligned} \rho_{rel}(pqPQ, t) &= \frac{1}{Z(t)} \exp\left\{-\beta\widehat{H} - \int \Lambda(P_0Q_0t)\delta(P - P_0)\delta(Q - Q_0) dP_0 dQ_0\right\} \\ &= \frac{1}{Z(t)} \exp\{-\beta\widehat{H} - \Lambda(PQ, t)\} \end{aligned} \quad (45)$$

where β and $\Lambda(PQ, t)$ are the corresponding Lagrange multipliers. As in our previous treatment, we fix $\beta = 1/k_B T$ as the inverse temperature. The functions $\Lambda(PQ, t)$ are to be calculated from the corresponding self-consistency conditions:

$$\langle \delta(P - P_0)\delta(Q - Q_0) \rangle_{rel} = \langle \delta(P - P_0)\delta(Q - Q_0) \rangle_t \equiv f^{(T)}(P_0Q_0, t). \quad (46)$$

Using the explicit expression for the system Hamiltonian, equation (3), which we split into two parts, H_s and H_T , and calculating the integral in the left-hand side of equation (46) using the current choice of the relevant distribution, equation (45), one gets

$$f^{(T)}(P_0Q_0, t) = \frac{Z_{eq}(Q_0)}{Z(t)} \exp\{-\beta H_T(P_0Q_0) - \Lambda(P_0Q_0t)\}$$

where $Z_{eq}(Q)$ is the surface partition function in equilibrium, equation (13). This expression shows that the self-consistency condition (46) can be solved with respect to the Lagrange multipliers $\Lambda(P_0Q_0t)$ explicitly. Comparing the last expression with equation (45) for the relevant distribution, we find

$$\rho_{rel}(pqPQ, t) = \frac{e^{-\beta H_s}}{Z_{eq}(Q)} f^{(T)}(PQ, t) = \rho_{eq}(pq|Q) f^{(T)}(PQ, t). \quad (47)$$

Thus, for this particular choice of the relevant variables, the relevant distribution takes an especially simple form and is given as a product of the equilibrium distribution ρ_{eq} of surface atoms, equation (12), and of the true tip distribution. Note that the equilibrium distribution, $\rho_{eq} \equiv \rho_{eq}(pq|Q)$, depends parametrically on the tip position Q .

A standard method of deriving the Fokker–Planck equation for the tip consists of the integration of the both sides of the Liouville equation with respect to the surface variables p, q [22]. This is exactly the same method as is used for the Brownian particle in the kinetic theory of liquids [23, 35, 36]. We shall use the same approach, but the starting point for us in the NESOM should be the broken-symmetry Liouville equation (1). Therefore, taking the

trace $\text{tr}\{\cdot\cdot\cdot\} = \int dp dq \dots$ from both sides of equation (1) and making use of the fact that, according to equations (44) and (47),

$$\text{tr}\{\rho\} = \text{tr}\{\rho_{rel}\} \quad (48)$$

we get

$$\frac{\partial}{\partial t} f^{(T)}(PQ, t) = -\text{tr}\{i\widehat{L}\rho(t)\} \equiv \Omega. \quad (49)$$

Splitting the Liouville operator into two parts, the surface part, \widehat{L}_0 , and the tip part, \widehat{L}_T , we first notice (using integration by parts and assuming that $\rho \equiv 0$ at the boundaries of the surface phase space $\Gamma_s = (pq)$) that $\text{tr}\{i\widehat{L}_0\rho(t)\} = 0$, so only the operator \widehat{L}_T contributes to Ω . Using the explicit expression (19) for \widehat{L}_T , one finds

$$\Omega = -\frac{P}{M} \frac{\partial f^{(T)}}{\partial Q} - (\langle X(Qq) \rangle_{eq} + Y(Q, t)) \frac{\partial f^{(T)}}{\partial P} - \frac{\partial}{\partial P} \text{tr}\{(X(Qq) + Y(Q, t)) \Delta\rho\} \quad (50)$$

where $Y(Q, t) = -k(Q - Q_{eq}) + F_d(t)$ is the sum of the elastic and driving forces, and we have split the true distribution ρ into two parts, ρ_{rel} and $\Delta\rho$; see equation (16).

In order to calculate the last term here, we have to calculate $\Delta\rho$ for the present choice of the relevant variables. For that, we use expression (24), valid in the present case as well. First, we notice, using the explicit expression (47) for the relevant distribution, that

$$\frac{\partial \rho_{rel}}{\partial t'} = \rho_{eq} \frac{\partial f^{(T)}(PQ, t')}{\partial t'}$$

and $i\widehat{L}_0\rho_{rel} = 0$. Then, by means of equation (34) the calculation of $i\widehat{L}_T\rho_{rel}$ becomes straightforward and we obtain

$$\begin{aligned} \Delta\rho(t) = & - \int_{-\infty}^t dt' e^{-\epsilon(t-t')} \rho_{eq} \left\{ \frac{\partial f^{(T)}(t')}{\partial t'} + \frac{P}{M} \frac{\partial f^{(T)}(t')}{\partial Q} \right. \\ & \left. + \beta \frac{P}{M} (\widehat{S}X(Qq) - \langle X(Qq) \rangle_{eq}) f^{(T)}(t') + (\widehat{S}X(Qq) + Y(Q, t')) \frac{\partial f^{(T)}(t')}{\partial P} \right\} \end{aligned} \quad (51)$$

where the operator \widehat{S} is given by equation (25). Now we are in a position to calculate the trace with $\Delta\rho$ in the right-hand side of equation (50). After some rather lengthy but simple algebra, we get

$$\begin{aligned} \text{tr}\{(X(Qq) + Y(Q, t)) \Delta\rho\} = & (\langle X(Qq) \rangle_{eq} + Y(Q, t)) A \\ & - \int_{-\infty}^t dt' e^{-\epsilon(t-t')} \langle \Delta X \widehat{S} \Delta X \rangle_{eq} \left(\beta \frac{P}{M} + \frac{\partial}{\partial P} \right) f^{(T)}(t') \end{aligned} \quad (52)$$

where $\Delta X = X(Qq) - \langle X(Qq) \rangle_{eq}$ is the fluctuation of the tip–surface force and

$$A = - \int_{-\infty}^t dt' e^{-\epsilon(t-t')} \left\{ \frac{\partial f^{(T)}(t')}{\partial t'} + \frac{P}{M} \frac{\partial f^{(T)}(t')}{\partial Q} + (\langle X(Qq) \rangle_{eq} + Y(Q, t')) \frac{\partial f^{(T)}(t')}{\partial P} \right\}.$$

Using now the explicit expression for $\Delta\rho$ given above, equation (51), we notice that A appears to be exactly equal to $\text{tr}\{\Delta\rho\}$ which is equal to zero because of equation (48). Therefore, the first term in the right-hand side of equation (52) is identically equal to zero.

Finally, substituting Ω from equation (50) into equation (49) and making use of equation (52) for the trace with $A = 0$, we arrive at the following integro-differential equation for the tip distribution function that was sought for:

$$\begin{aligned} \left[\frac{\partial}{\partial t} + \frac{P}{M} \frac{\partial}{\partial Q} + (\langle X(Qq) \rangle_{eq} + Y(Q, t)) \frac{\partial}{\partial P} \right] f^{(T)}(PQ, t) \\ = \frac{\partial}{\partial P} \left(\beta \frac{P}{M} + \frac{\partial}{\partial P} \right) \int_{-\infty}^t dt' e^{-\epsilon(t-t')} \langle \Delta X \widehat{S} \Delta X \rangle_{eq} f^{(T)}(PQ, t'). \end{aligned} \quad (53)$$

Note that the operator

$$\frac{\partial}{\partial P} \left(\beta \frac{P}{M} + \frac{\partial}{\partial P} \right)$$

has been taken out of the integral since the correlation function $\langle \Delta X \widehat{S} \Delta X \rangle_{eq}$ does not depend on the tip momentum P . This is because the evolution operator \widehat{S} containing the Liouville operator of the surface \widehat{L}_0 does not depend on P .

This equation is very general. Note that it also contains *memory* effects due to the time integral in the right-hand side. Again, assuming that the correlation function $\langle \Delta X \widehat{S} \Delta X \rangle_{eq}$ (which depends on the time difference $s = |t - t'|$) decays much faster with time than the distribution function $f^{(T)}(t')$ of the tip, we arrive at the Markovian description. Thus, only times t' near t contribute and we can take the whole term containing $f^{(T)}(t')$ out of the integral and calculate it at t . In this way we get a Fokker–Planck equation for the tip identical to that obtained earlier in reference [22]:

$$\left[\frac{\partial}{\partial t} + \frac{P}{M} \frac{\partial}{\partial Q} + (\langle X(Qq) \rangle_{eq} + Y(Q, t)) \frac{\partial}{\partial P} \right] f^{(T)} = \gamma(Q) \frac{\partial}{\partial P} \left(\beta \frac{P}{M} + \frac{\partial}{\partial P} \right) f^{(T)} \quad (54)$$

where $\gamma(Q)$ is the friction coefficient given by equation (43).

As one of the possible applications of the Fokker–Planck equation, one can consider the equation of motion for the tip, i.e. the equation for the tip position and momentum:

$$\begin{aligned} Q_t &= \int Q f^{(T)}(PQ, t) dP dQ \equiv (Q)_t \\ P_t &= \int P f^{(T)}(PQ, t) dP dQ \equiv (P)_t \end{aligned}$$

where the notation $(\cdot \cdot)_t$ has been used to indicate the average with respect to the tip distribution function, $f^{(T)}(PQ, t)$, calculated at time t . The derivation of the equation of motion can be carried out in exactly the same way as in reference [22] and the result is as follows:

$$\frac{d(P)_t}{dt} \equiv M \frac{d^2(Q)_t}{dt^2} = -k[(Q)_t - Q_{eq}] + (\langle X(Qq) \rangle_{eq})_t + F_d(t) - \frac{\beta}{M} (P\gamma(Q))_t. \quad (55)$$

Note that this equation, although very similar to that derived in the previous section, equation (42), is not exactly the same. One can verify, however, that this equation becomes identical to equation (42) if we assume that the tip distribution function is *strongly peaked* around its average values Q_t and P_t (cf. reference [22]). However, before going into a detailed comparison of various forms of the kinetic (transport) equations for the tip (which will be made in section 5), it is instructive to give yet another possible derivation of the Fokker–Planck equation.

4.2. The Fokker–Planck equation: variables P and Q

The derivation of the previous subsection was based on a specific ‘natural’ choice of the relevant variables, such that the Fokker–Planck equation followed as a transport equation for these variables. Then, the equation of motion for the tip, equation (55), also follows as in reference [22]. However, we know from section 3 that the equation of motion for the tip can be derived avoiding a rather complicated step of deriving the Fokker–Planck equation. In order to do that, we have used another set of relevant variables, namely P and Q (alongside the system Hamiltonian). It would be instructive to see whether the Fokker–Planck equation can be derived using the same set of the relevant variables as in section 3. After all, we have given in this section an expression for the true distribution function of the whole system, $\rho(t) = \rho_{rel}(t) + \Delta\rho(t)$, where $\rho_{rel}(t)$ and $\Delta\rho(t)$ are given by equations (6) and (26), respectively. Therefore, the tip

distribution function, $f^{(T)}(PQ, t)$, can be obtained, at least in principle, from the true $\rho(t)$ by integrating with respect to the surface variables according to equation (44).

However, the actual calculation is more easily accomplished if, as in the previous subsection, we simply integrate the corresponding broken-symmetry Liouville equation with respect to the surface variables. We will not reproduce the derivation here since the calculation is actually very similar to that of the previous subsection (the difference is only in the expressions for the relevant distributions used in the two cases). The result, however, seems to be slightly different from equation (53) as there is an extra contribution, $-\epsilon \text{tr}\{\rho - \rho_{rel}\} = -\epsilon \text{tr}\{\Delta\rho\}$, in the right-hand side of it arising from the source term in the Liouville equation (1). Using equation (26), we find that, oppositely to the case for the previous choice of the relevant variables in section 4.1, $\text{tr}\{\Delta\rho\} \neq 0$ in this case:

$$\text{tr}\{\Delta\rho\} = -\frac{\beta}{M} \int_{-\infty}^t e^{-\epsilon(t-t')} \Psi(t') \left\{ \langle \dot{P} \rangle_{eq} - \langle \dot{P} \rangle_{rel} + \frac{1}{\beta} \frac{Q - Q_{t'}}{\langle Q^2 \rangle_{rel} - Q_{t'}^2} \right\} P_{t'} dt' \quad (56)$$

where the function $\Psi(t')$ is given by equation (14). The question that we ask is whether the solution $f_\epsilon^{(T)}(PQ, t)$ of the modified Fokker–Planck equation (with the source term) tends to that of the Fokker–Planck equation without this extra term, $f^{(T)}(PQ, t)$, in the $\epsilon \rightarrow +0$ limit. It is not easy to answer that question. However, we believe there are at least two reasons for which this extra term can be dropped.

First of all, one can demonstrate, applying consistently the steepest-descent method of section 3.4, that this term is probably small. Indeed, using the exact expression for the force, equation (28), and the steepest-descent approximation, equation (15), we get

$$\begin{aligned} \langle \dot{P} \rangle_{eq} - \langle \dot{P} \rangle_{rel} &\simeq -k(Q - Q_{t'}) + (\langle X(Qq) \rangle_{eq} - \langle X(Q_{t'}q) \rangle_{eq}) \\ &\simeq (Q - Q_{t'}) \left\{ -k + \frac{d}{dQ_{t'}} \langle X(Q_{t'}q) \rangle_{eq} \right\} \end{aligned}$$

where only the first non-vanishing term has been left in the expansion of the average force $\langle X(Qq) \rangle_{eq}$ around $Q_{t'}$. One then notices that the expression in the curly brackets above is the same as in equation (A1.7) within the steepest-descent method. Therefore, if we replace this expression with the right-hand side of equation (A1.7), then we find that it cancels out exactly with the last term in the curly brackets in equation (56).

The second argument is based on the underlying idea of introducing the source term to the Liouville equation [24]. Its purpose is to pick out the proper solution corresponding to the assumed boundary conditions. Alternatively, one can drop this term in the equation and constrain the solution by applying the boundary conditions. The two methods should give identical results. Therefore, if we drop this term from the very beginning, we would arrive at the Fokker–Planck equation (53) and the corresponding boundary conditions associated with it as in the previous subsection.

That means that the extra source term in the Fokker–Planck equation can be dropped. Thus, we conclude that the choice of the relevant variables as used in section 3 to derive the Langevin equation for the tip results in exactly the same Fokker–Planck equation for the tip as that of section 4.1 where the ‘natural’ choice of relevant variables was made.

5. Summary

In this paper we have considered the interaction between the tip and surface in the NC-AFM system. Our treatment is based on the (entirely classical) model already used in the previous work [21, 22]. A coarse-graining method has been used in references [21, 22] to account for the non-equilibrium effects in the tip–surface system. In this paper, the *exact* non-equilibrium

formalism based on the non-equilibrium statistical operator method (NESOM) [24] has been applied. As in the coarse-graining method, the NESOM assumes a certain timescale with respect to which the system characteristic times are considered. However, one neither needs to know this time explicitly nor needs to assume its order of magnitude, since the timescale of interest is implied in the particular choice of the relevant variables used.

Two sets of relevant variables have been considered. Using the first set, we have derived the equation of motion for the tip (the Langevin equation). It has been formulated as an integro-differential equation for the exact averages $\langle Q \rangle_t$ and $\langle P \rangle_t$ of the tip position and momentum calculated using the true non-equilibrium distribution function $\rho(t)$ of the system. We stress that the equation derived is quite general since it also contains memory effects. We have also found that the equation obtained, equation (30), appears to be rather non-linear with respect to the averages $\langle Q \rangle_t$ and $\langle P \rangle_t$. However, we have shown in section 3.4, that, to the same level of approximation with respect to the small parameter $\eta \sim M^{-1/2}$, this equation can be linearized and brought into a simpler form (40). In the Markovian approximation (no memory), the linearized equation of motion becomes simply a differential equation for the averages and contains a familiar friction term. The latter is given as a time integral of the autocorrelation function of the fluctuation of the tip–surface force. Therefore, we have reproduced the main result of the earlier treatments of references [20–22], where a much simpler coarse-graining method was used.

Then, using a second, quite different, set of relevant variables, we have derived the Fokker–Planck equation for the tip distribution function $f^{(T)}(PQ, t)$. This result is also quite general and goes beyond the Markovian approximation (i.e. contains memory effects). Similarly to the equation of motion for the tip, derived using the first set of the relevant variables, there is also a friction term in the Fokker–Planck equation due to the stochastic nature of the tip–surface interaction. It is worth mentioning here that the Fokker–Planck equation obtained appears already in a linear form with respect to the distribution function and no additional linearization has been necessary. However, one has to bear in mind that the Fokker–Planck equation obtained is also valid in the first order with respect to the small parameter $\eta \sim M^{-1/2}$. In the Markovian approximation the Fokker–Planck equation derived coincides with that obtained in reference [22] where the coarse-graining method was used.

The approach based on the Fokker–Planck equation has an advantage as it allows one to consider the time evolution

$$\langle \Theta \rangle_t = \int dP dQ f^{(T)}(PQ, t) \Theta(PQ)$$

of *any* dynamical variable $\Theta(PQ)$ which is an arbitrary function of the tip position and momentum. In particular, we have derived another form of the equation of motion for the tip starting from the Fokker–Planck equation which, again, in the Markovian approximation, has been found identical to that derived in reference [22]. However, this equation of motion appeared to be somewhat different to that derived directly in section 3 (avoiding the step involving the Fokker–Planck equation), i.e. when using the first choice of relevant variables.

The two equations would coincide, however, if the tip distribution function (the solution of the Fokker–Planck equation, $f^{(T)}(PQ, t)$) is strongly peaked around the exact averages $\langle P \rangle_t$ and $\langle Q \rangle_t$ [22]. As has been explained in reference [22], this is not easy to demonstrate using a direct calculation (i.e. by solving the Fokker–Planck equation). However, our assertion concerning the peaked structure of the tip distribution function seems to be reasonable owing to the fact that the tip is a macroscopic object with well defined position and momentum at every time t . However, there is also another, more fundamental, reason for that.

Indeed, the Hamiltonian of the system, used for both sets of relevant variables, is needed to fix the temperature of the heat bath. The other variables in the first set are the tip position

Q and momentum P . These variables are used to set up the *timescale* of interest (i.e. the level of reduced description of the system)—the characteristic time which is much larger than the phonon time and much smaller than the macroscopic time of the tip oscillations. Therefore, using this set of relevant variables, all atomic vibrations are sampled over.

Then, in the second set of relevant variables we have used a continuous set of functions $\delta(P - P_0)\delta(Q - Q_0)$ in place of P and Q . As this set is based on the same information about the system (only the same variables P and Q are involved), it corresponds to the *same* timescale and, therefore, should be considered as *physically equivalent*. The difference between different descriptions (different choices of the relevant variables) will be of the next order with respect to the small parameter of the theory being chosen, $\eta \sim M^{-1/2}$. This conclusion is also supported by the fact that, if the steepest-descent method is used consistently throughout, the Fokker–Planck equation can also be derived using the first set of relevant variables (see section 4.2). An immediate consequence of this is that the tip distribution function, $f^{(T)}(P, Q, t)$, will be strongly peaked around the averages $\langle P \rangle_t$ and $\langle Q \rangle_t$ for every t , so, within the same approximation with respect to the small parameter $\eta \sim M^{-1/2}$, one has

$$\langle \Theta \rangle_t = \int dP dQ f^{(T)}(P, Q, t) \Theta(P, Q) = \Theta(\langle P \rangle_t, \langle Q \rangle_t) + \mathcal{O}\left(\frac{1}{M}\right)$$

for any dynamical variable $\Theta(P, Q)$.

Thus, all equations of motion derived in this paper using various means are equivalent from both physical and mathematical points of view as, on one hand, they correspond to the same timescale and also, on the other, they are valid in the first order with respect to the small parameter $\eta \sim M^{-1/2}$.

We note that the method used here is rather formal. However, we believe that it should provide a good starting point for future developments. In particular, using an explicit microscopic model for the surface and the tip, it is important to calculate the correlation functions entering the theory. This is needed not only for the calculation of the dissipation energy involved in this particular mechanism (which can be checked experimentally), but also to validate the Markovian approximation used in the previous publications [20–22]. However, this kind of calculation goes far beyond the scope of this paper and will be provided elsewhere. We also mention the adhesion hysteresis mechanism [14–19, 21] as another interesting and important application of the NESOM. Finally, as has already been mentioned in the introduction, a completely quantum description of the surface within the NESOM would also be highly desirable. This is not straightforward, however, as one has to combine a classical treatment of the tip with a quantum mechanical consideration of the surface. Work on these developments is in progress in our laboratory.

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Appendix 1

A number of useful identities will be derived here. Differentiating both sides of equation (5) with respect to $Q_t = \langle Q \rangle_t$ and taking into account that $F(t)$ depends on it (note that $Z(t)$ is a function of $F(t)$ as well), we find after a straightforward calculation

$$\frac{dF(t)}{dQ_t} = \frac{1}{\beta} (\langle Q^2 \rangle_{rel} - Q_t^2)^{-1} \quad (\text{A1.1})$$

where here and in the following the notation $\langle \dots \rangle_{rel}$ is equivalent to the average $\text{Tr}\{\rho_{rel}(t) \dots\}$ calculated using the relevant distribution. Using this identity, one can calculate the time derivative of $F(t)$ as

$$\frac{dF(t)}{dt} = \frac{dF(t)}{dQ_t} \frac{\partial Q_t}{\partial t} = \frac{P_t}{M\beta} (\langle Q^2 \rangle_{rel} - Q_t^2)^{-1} \quad (\text{A1.2})$$

where $P_t = \langle P \rangle_t$ and use has been made here of the fact [22,24] that according to equation (2)

$$\frac{\partial Q_t}{\partial t} = \text{Tr}\{\dot{Q}\rho(t)\} = \text{Tr}\left\{\frac{P}{M}\rho(t)\right\} = \frac{P_t}{M}. \quad (\text{A1.3})$$

We will also find useful in the following yet another identity which is derived similarly by differentiating the average tip–surface force

$$\langle X(Qq) \rangle_{rel} = -\text{Tr}\left\{\rho_{rel}(t) \frac{\partial \Phi_{Qq}}{\partial Q}\right\}$$

with respect to Q_t :

$$\frac{\partial \langle X(Qq) \rangle_{rel}}{\partial Q_t} = \frac{\langle XQ \rangle_{rel} - \langle X \rangle_{rel} Q_t}{\langle Q^2 \rangle_{rel} - Q_t^2}. \quad (\text{A1.4})$$

Note that $\langle Q \rangle_{rel} = Q_t$ because of the self-consistency condition (5). We also consider the average

$$\langle \dot{P}Q \rangle_{rel} = -\text{Tr}\left\{\rho_{rel}(t) \frac{\partial \hat{H}}{\partial Q} Q\right\}.$$

Performing the integral $\int dQ$ by parts and using the identity (9), we get

$$\langle \dot{P}Q \rangle_{rel} - \langle \dot{P} \rangle_{rel} Q_t = -\frac{1}{\beta} \quad (\text{A1.5})$$

where again we have used the self-consistency condition (5). In particular, since the force \dot{P} contains the tip–surface, $X(Qq)$, the elastic, $-k(Q - Q_{eq})$, and the driving, $F_d(t)$, forces, this expression can also be rewritten as follows:

$$(\langle QX \rangle_{rel} - Q_t \langle X \rangle_{rel}) - k(\langle Q^2 \rangle_{rel} - Q_t^2) = -\frac{1}{\beta}. \quad (\text{A1.6})$$

Combining equations (A1.4) and (A1.6), one also has

$$-k + \frac{\partial \langle X(Qq) \rangle_{rel}}{\partial Q_t} = -\frac{1}{\beta} \frac{1}{\langle Q^2 \rangle_{rel} - Q_t^2}. \quad (\text{A1.7})$$

Appendix 2

In this appendix we will derive the linearized form of the transport equation (40) directly by solving the broken-symmetry Liouville equation (1) within the steepest-descent approximation, the main ideas of which have been considered in section 3.4.

We first note that the Lagrange multipliers, $V(t)$ and $F(t)$, are given by the exact expression (8) and the asymptotic one (39), respectively. Therefore, within the steepest-descent approximation, the function $F(t)$ can be expressed explicitly via $Q_t = \langle Q \rangle_t$. Our next step is to calculate $\Delta\rho$ from equation (17). The calculation essentially repeats the one made in section 3.2. The only difference now is that the derivative $dF(t)/dt$ in equation (22) can be calculated explicitly owing to the known dependence of $F(t)$ on Q_t :

$$\frac{dF(t)}{dt} = \frac{dF(t)}{dQ_t} \frac{P_t}{M} = \left[k - \frac{\partial \langle X(Q_t q) \rangle_{eq}}{\partial Q_t} \right] \frac{P_t}{M}$$

(note that a relatively small derivative dF_d/dt can be neglected in the calculation of $\partial\rho/\partial t$). One then obtains

$$\left\{ \frac{\partial}{\partial t} + i\widehat{L} \right\} \rho_{rel}(t) = \frac{\beta}{M} \rho_{rel}(t) P_t \left(X(Qq) - \langle X(Q_tq) \rangle_{eq} - (Q - Q_t) \frac{\partial \langle X(Q_tq) \rangle_{eq}}{\partial Q_t} \right) + \frac{\beta}{M} \rho_{rel}(t) (P - P_t) \text{Tr}\{\dot{P} \Delta\rho(t)\}$$

which can be compared with equation (23) for the exact calculation. This expression is then used in equation (17) to the first order, and, after that, in the kinetic equation (18), resulting in

$$\frac{\partial P_t}{\partial t} = \langle \dot{P} \rangle - \frac{\beta}{M} \int_{-\infty}^t dt' e^{-\epsilon(t-t')} P_{t'} \left\{ \langle \dot{P} \widehat{S} X \rangle - \langle X \rangle \langle \dot{P} \rangle - (\langle Q \dot{P} \rangle - Q_t \langle \dot{P} \rangle) \frac{\partial \langle X(Q_tq) \rangle_{eq}}{\partial Q_t} \right\} \quad (\text{A2.1})$$

where by $\langle \cdot \cdot \cdot \rangle$ the averages with respect to the relevant distribution are implied. Using the explicit expression for the force, \dot{P} (see equation (28)), and the fact that

$$k \gg \frac{\partial \langle X(Q_tq) \rangle_{eq}}{\partial Q_t} \quad (\text{A2.2})$$

(the necessary condition for the NC-AFM system stability), the expression in the curly brackets in equation (A2.1) reads

$$\langle \Delta X \widehat{S} \Delta X \rangle + k \left[-(\langle QX \rangle - Q_t \langle X \rangle) + (\langle Q^2 \rangle - Q_t^2) \frac{\partial \langle X(Q_tq) \rangle_{eq}}{\partial Q_t} \right]. \quad (\text{A2.3})$$

Then, we replace the first term in the square brackets using equation (A1.4) and the difference $\langle Q^2 \rangle - Q_t^2$ using equation (A1.7). Then the second term in the right-hand side of equation (A2.3) becomes

$$\frac{1}{\beta} \frac{k(\partial \langle X(Q_tq) \rangle_{eq} / \partial Q_t - \partial \langle X(Qq) \rangle_{rel} / \partial Q_t)}{k - \partial \langle X(Q_tq) \rangle_{eq} / \partial Q_t}$$

which is zero up to terms $O(1/k) \sim O(1/M)$, and we are just left with the correlation function term, $\langle \Delta X \widehat{S} \Delta X \rangle$, in the curly brackets in equation (A2.1). Since, in the same approximation, averages with respect to the relevant distribution are equivalent to those calculated with respect to the equilibrium distribution when Q is set equal to Q_t , we arrive at the same transport equation (40) as in section 3.4.

References

- [1] Fukui K, Onishi H and Iwasawa Y 1997 *Phys. Rev. Lett.* **79** 4202
- [2] Guggisberg M, Bammerlin M, Lüthi R, Loppacher Ch, Battiston F, Lü J, Baratoff A, Meyer E and Güntherodt H-J 1998 *Appl. Phys. A* **66** S245
- [3] Meyer E 1992 *Prog. Surf. Sci.* **41** 3
- [4] Giessibl F J 1995 *Science* **267** 68
- [5] Giessibl F J 1994 *Japan. J. Appl. Phys.* **33** 3726
- [6] Lüthi R, Meyer E, Bammerlin M, Baratoff A, Lehman T, Howard L, Gerber C and Güntherodt H-J 1996 *Z. Phys. B* **100** 165
- [7] Güntherodt H-J, Anselmetti D and Meyer E (ed) 1995 *Forces in Scanning Probe Methods (NATO Advanced Study Institute Series E: Applied Sciences, vol 286)* (Dordrecht: Kluwer)
- [8] Sugawara Y, Ohta M, Ueyama H, Morita S, Osaka F, Ochkouchi S, Suzuki M and Mishima S 1996 *J. Vac. Sci. Technol.* **14** 953
- [9] Erlandsson R, Olsson L and Mårtensson P 1996 *Phys. Rev. B* **54** R8309
- [10] Bammerlin M, Lüthi R, Meyer E, Baratoff A, Guggisberg M, Gerber C, Howard L and Güntherodt H-J 1997 *Probe Microsc.* **1** 3

- [11] Bennewitz R, Foster A S, Kantorovich L N, Bammerlin M, Loppacher Ch, Schar S, Guggisberg M, Meyer E and Shluger A L 2000 *Phys. Rev. B* **62** 2074
- [12] Gauthier M and Tsukada M 2001 *Phys. Rev. Lett* **85** 5348
- [13] Dürig U 1999 *Appl. Phys. Lett.* **75** 433
- [14] Gotsmann B, Seidel C, Anczykowski B and Fuchs H 1999 *Phys. Rev. B* **60** 11 051
- [15] Dürig U 1999 *Surf. Interface Anal.* **27** 467
- [16] Wang L 1999 *Surf. Sci.* **429** 178
- [17] Tamayo J and García R 1997 *Appl. Phys. Lett.* **71** 2394
- [18] García R, Tamayo J and San Paulo A 1999 *Surf. Interface Anal.* **27** 312
- [19] Sasaki N and Tsukada M 2001 *Phys. Rev. Lett.* submitted
- [20] Gauthier M and Tsukada M 1999 *Phys. Rev. B* **60** 11 716
- [21] Kantorovich L N 2001 *J. Phys.: Condens. Matter* **13** 945
- [22] Kantorovich L N 2001 *Phys. Rev. B* submitted
- [23] Rice S A and Gray P 1965 *The Statistical Mechanics of Simple Liquids* (New York: Interscience)
- [24] Zubarev D, Morozov V and Röpke G 1996 *Basic Concepts, Kinetic Theory (Statistical Mechanics of Nonequilibrium Processes vol 1)* (Berlin: Akademie)
- [25] Zubarev D, Morozov V and Röpke G 1996 *Relaxation and Hydrodynamic Processes (Statistical Mechanics of Nonequilibrium Processes vol 2)* (Berlin: Akademie)
- [26] Lantz M A, Hug H J, van Schendel P J A, Hoffmann R, Martin S, Baratoff A, Abdurixit A, Güntherodt H-J and Gerber Ch 2000 *Phys. Rev. Lett.* **84** 2642
- [27] Schwarz A, Allers W, Schwarz U D and Wiesendanger R 2000 *Phys. Rev. B* **61** 2837
- [28] Boon J P and Yip S 1980 *Molecular Hydrodynamics* (New York: Dover)
- [29] Forster D 1975 *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (London: Benjamin)
- [30] Martin P C 1968 *Measurements and Correlation Functions* (New York: Gordon and Breach)
- [31] Gell-Mann M and Goldberger M L 1953 *Phys. Rev.* **91** 398
- [32] Erdélyi A 1956 *Asymptotic Expansions* (New York: Dover)
- [33] Jeffreys H and Swirles B 1956 *Methods of Mathematical Physics* (Cambridge: Cambridge University Press)
- [34] Kubo R, Toda M and Hashitsume N 1995 *Nonequilibrium Statistical Mechanics (Statistical Physics vol 2)* (Berlin: Springer)
- [35] Risken H 1989 *The Fokker-Planck Equation. Methods of Solution and Applications* 2nd edn (Berlin: Springer)
- [36] Ishihara A 1971 *Statistical Physics* (New York: Academic)