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# Non-equilibrium dynamics of a classical tip interacting with a quantum surface

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## Abstract

We apply the non-equilibrium statistical operator method within the mixed quantum–classical representation to the non-contact atomic force microscopy system in which a macroscopic tip is made to oscillate above a sample surface. In our treatment the tip is treated classically, whereas a microscopic system comprising atoms in the surface and in the nano-tip is considered quantum mechanically. Using a very general non-Markovian approach, we obtain both the Fokker–Planck equation for the tip and, independently, its equation of motion with friction terms and memory effects completely accounted for. In the classical limit (high temperatures) our equations turn exactly into the classical counterparts derived previously.

## 1. Introduction

Observed atomic-scale dissipation effects [1–9] in non-contact atomic force microscopy (NC-AFM) (see e.g. [10]) are attracting a lot of attention at present. This is due to an exciting possibility to access vibrational properties of metal and insulating surfaces using the NC-AFM. However, in spite of a growing number of theoretical works on the subject [11–19], our understanding of this physical phenomenon is still far from being complete, the main difficulties being to explain

- (i) relatively large dissipation energies (0.1–2 eV per oscillation cycle) [3, 5, 7, 9] and
- (ii) that the stable atomic-scale dissipation imaging is observed even on plain terraces.

Two main mechanisms are thought to be mainly responsible for the atomic-scale damping observed experimentally. The ‘Brownian motion’ (or *the stochastic friction force*) mechanism [11, 13–15] is based on the idea that due to atomic vibrations there is a stochastic component in the tip–surface force which can be described as a *friction* experienced by the oscillating tip. This latter point can be understood only using non-equilibrium statistical mechanics. Hence, the oscillation signal applied to the cantilever performs work against the friction force observed as a damping. The magnitude of the dissipation due to this mechanism

is still the subject of an ongoing discussion: some earlier estimates [11, 15, 17] suggest that the Brownian motion mechanism is capable of providing just a small fraction of the observed dissipation energies. However, recently it was found [16] that the situation may be very different due to local vibrational modes (LMs), either induced by the tip or already existing on the tip-free surface. Indeed, it appears that, depending on the amount of anharmonic coupling of the LMs with other phonon modes, large dissipation energies can be expected.

The second mechanism, called the *adhesion hysteresis* mechanism [12], is essentially identical to that believed to be responsible for dissipation effects in the tapping mode microscopy [20]. The main idea here is strong atomic reconstruction during the tip approach leading to a different atomic arrangement in the junction when the tip is retracted. As a result, the force exerted on the tip becomes different at the approach and retraction (the so-called force hysteresis), leading to atomic-scale dissipation effects. Although this mechanism can easily explain large dissipation energies observed in experiments, it is still unclear whether a stable dissipation imaging can be explained. Note that in the first approximation this mechanism requires only calculation of the tip–surface potential energy surfaces; however, full treatment would require incorporation of non-equilibrium effects [13].

In this paper we shall consider in more detail the first, stochastic, mechanism. The corresponding non-equilibrium theories existing so far [11, 14, 15] have a fundamental gap, which needs to be filled in: they are all based on a *classical* treatment of both the tip and a microscopic system, the latter comprising atoms in the surface and in the nano-tip. Although the classical consideration of the macroscopic tip is perfectly adequate, the classical treatment of the microscopic system can only be valid at rather high temperatures, well above the surface Debye temperature,  $T_D$ . Therefore, a consistent *quantum theory* for the microscopic system is required. It has been suggested in [17] that the Kubo consideration of a quantum Brownian particle [21] could be the basis for such a generalization. However, in the Kubo linear response theory the environment providing the stochastic force for the Brownian particle is not present explicitly. In the case of the NC-AFM system the role of the environment is played by the surface, while the tip is just a probe. At the same time, we are especially interested in the physical properties of the surface system rather than in those of the tip. Therefore, it is apparent that the Kubo theory is not applicable in our case, and a different method is needed.

Such a method, based on the so-called *mixed quantum–classical representation* for the statistical operator, has been recently suggested in [22], where within the Markovian approximation it has been applied to derive both the Fokker–Planck equation for the tip and its equation of motion. In this paper we suggest a more general *non-Markovian* treatment based on the non-equilibrium statistical operator method (NESOM) [23]. We have already successfully used this method previously for describing the tip oscillations in the NC-AFM system [14]. There we derived an equation of motion for the tip and obtained an expression for the friction force with memory effects completely included. We found that the friction force is expressed via an autocorrelation function of the fluctuation of the tip–surface force. However, our consideration in [14] was entirely classical and so the correlation function for the friction was obtained in the classical form. Here we extend this treatment by considering the microscopic system consistently quantum mechanically. Note that our main concern in this paper is to provide a rigorous theoretical analysis of the non-equilibrium dynamics of the NC-AFM system which would be valid at any temperature. The corresponding numerical estimates can be found elsewhere [22].

The plan of the paper is as follows. First, in section 2 we shall consider using NESOM, an equation of motion for the tip and then the derivation of a more general Fokker–Planck equation. In either case the full non-Markovian treatment will be provided and the classical limit (high temperatures) will also be applied to verify that the equations will turn, as they should, into

the corresponding classical ones obtained previously in [14]. Finally, brief conclusions will be drawn in section 3.

## 2. Theory

### 2.1. The model

We start from the Hamiltonian of the combined system

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

Here the matrix-column  $q = \|q_i\|$  contains coordinates of all atoms in the microscopic system consisting of the surface and the nano-tip, and  $p = \|p_i\|$  is the corresponding quantum operators of their momenta. The vertical position of the macroscopic tip (i.e. the cantilever) with respect to the surface is designated by  $Q$  and its momentum is  $P$ ,  $M$  being the tip effective mass. The latter is related to the elastic constant  $k$  of the oscillating cantilever via  $\omega_0^2 = k/M$ , where  $\omega_0$  is the oscillating frequency without the surface. The first term in the Hamiltonian above,  $H_{pq}$ , corresponds to the microscopic subsystem given as a sum of individual (quantum) Hamiltonians of the surface and the nano-tip. Note that it does not depend on the tip position  $Q$ . The last two terms in equation (1) describe the classical Hamiltonian of the macroscopic tip, which includes its kinetic,  $P^2/2M$ , and potential,  $U_Q$ , energies; the latter incorporates the energy associated with the excitation signal and the elastic energy of the cantilever. The second term in the Hamiltonian,  $\Phi_{Qq}$ , contains all interactions which depend on both  $q$  and  $Q$ . In particular, it includes interaction between atoms in the surface and the nano-tip. Note that the operator  $H_s = H_{pq} + \Phi_{Qq}$  serves as the total Hamiltonian of the microscopic system interacting with the classical counterpart *fixed* at its position  $Q$ .

### 2.2. Mixed quantum–classical representation and NESOM

In treating our combined system consisting of both classical (the tip) and quantum mechanical (surface + nano-tip) parts, we shall use the mixed quantum–classical representation for the statistical operator of the whole system suggested recently [22, 24]. The basic idea is to consider a single statistical operator for the whole system,  $\hat{\rho}(t)$ , to be a *function* of the classical variables  $P$  and  $Q$ , and, at the same time, an *operator* acting on wavefunctions of the quantum system. Consequently, it is normalized in the following sense:

$$\text{Tr}(\hat{\rho}) \equiv \int \text{tr}(\hat{\rho}) d\Gamma = 1 \quad (2)$$

where  $d\Gamma = dQ dP$  is the element of the phase space associated with the classical system, and  $\text{tr}(\dots)$  is the trace taken with respect to the wavefunctions of the quantum system. The notation  $\text{Tr}(\dots)$  will also be used throughout to indicate both operations together. An exact statistical average at time  $t$  of any dynamical variable  $A$  which is an operator with respect to the microscopic system, and may also depend on the classical variables, is defined as

$$A_t = \langle A \rangle_t = \text{Tr}(A \hat{\rho}(t)). \quad (3)$$

If the dynamical variable  $A$  does not depend on the coordinates of the microscopic system, then  $A_t = \int A f_T(PQ, t) d\Gamma$ , where

$$f_T(PQ, t) = \text{tr}(\hat{\rho}(t)) \quad (4)$$

is the distribution function of the tip obtained by the corresponding reduction of the full statistical operator  $\hat{\rho}$ .

In studying a non-equilibrium dynamics of our system, we shall use the NESOM, which is based on the idea of relevant dynamical variables and relevant statistical ensembles [23]. As in our previous classical study [14], we choose  $H$ ,  $P$  and  $Q$  as our relevant variables to derive an equation of motion for the tip. (Note that a different set of variables should be chosen [14] when deriving the Fokker–Planck equation for the tip distribution function  $f_T(P, Q, t)$ , which will be done in a later section.) The corresponding relevant distribution in this case

$$\hat{\rho}_{rel}(t) = \frac{1}{Z(t)} \exp[-\beta(H - V(t)P - F(t)Q)] \quad (5)$$

looks similar to that in the classical case [14]. Remember, however, that the Hamiltonian  $H$  here contains the quantum part  $H_s$ . In equation (5)  $Z(t)$  is the normalization factor, while  $V(t)$  and  $F(t)$  are the Lagrange multipliers, which are found from the self-consistency conditions  $\langle P \rangle_{rel}^t = P_t$  and  $\langle Q \rangle_{rel}^t = Q_t$ , where  $\langle \dots \rangle_{rel}^t = \text{Tr}(\dots \hat{\rho}_{rel}(t))$  is the statistical average (also in the mixed representation) in the relevant ensembles. Note that we do not consider the corresponding self-consistency condition for  $H$ , assuming that the Lagrange multiplier  $\beta$  in equation (5) is fixed to the inverse temperature  $\beta = (k_B T)^{-1}$  of the heat bath.

The exact non-equilibrium statistical operator of the whole system in NESOM within the mixed representation is governed by the Liouville equation with the broken time-reversal symmetry [24]:

$$\left( \frac{\partial}{\partial t} + i\hat{L}_T + i\hat{L}_s \right) \hat{\rho}(t) = -\epsilon(\hat{\rho}(t) - \hat{\rho}_{rel}(t)) \quad (6)$$

where  $\epsilon \rightarrow 0$  at the end of the calculation,  $i\hat{L}_s = [\dots, H_s]/i\hbar$  is the *quantum* Liouville operator of the microscopic system and

$$i\hat{L}_T = \{ \dots, H_T \}_{P.B.} = \frac{P}{M} \frac{\partial}{\partial Q} + [F_c(Q) + \Delta X(Qq)] \frac{\partial}{\partial P} \quad (7)$$

is the *classical* Liouville operator [14, 15] of the tip defined via the classical Poisson brackets and the tip Hamiltonian  $H_T = P^2/2M + U_Q + \Phi_{Qq}$ . The instantaneous tip–surface force defined as  $X(Qq) = -\partial\Phi_{Qq}/\partial Q$  contains both the conservative and the random parts. In the expression above

$$F_c(Q) = -\frac{\partial U_Q}{\partial Q} + \langle X \rangle_{eq} \quad (8)$$

is the total conservative force acting on the tip, while  $\Delta X = X - \langle X \rangle_{eq}$  is the fluctuating part of the force. The notation  $\langle \dots \rangle_{eq} = \text{tr}(\dots \hat{\rho}_{eq}(Q))$  here corresponds to the statistical average with respect to the *equilibrium statistical operator* for the microscopic system when the tip is *fixed* at  $Q$ . It is defined as

$$\hat{\rho}_{eq}(Q) = \frac{1}{Z_{eq}} e^{-\beta H_s} \quad (9)$$

where  $Z_{eq} = \text{tr}[\exp(-\beta H_s)]$  is the equilibrium partition function. Note that due to explicit dependence of  $H_s$  on the classical variable  $Q$ , the operator  $\hat{\rho}_{eq}$  depends on it as well as the tip being *fixed* at  $Q$ ; in the following this dependence will be indicated explicitly where necessary. It is clear that  $\langle X \rangle_{eq}$  depends on the tip position  $Q$  used for  $\hat{\rho}_{eq}$ .

It is worth mentioning that we use here a slightly different definition of  $\Delta X$  than in [14]; our present definition appears to be more natural and convenient. With this definition we also have an identity:

$$\langle \Delta X \rangle_{rel}^t = 0. \quad (10)$$

Indeed, it follows from equation (5) that  $\hat{\rho}_{rel} = \Psi(P, Q, t)\hat{\rho}_{eq}(Q)$ , where  $\Psi(P, Q, t)$  is some well defined function of the classical variables and time (cf [14]) which is peaked at the exact position  $Q_t$  and momentum  $P_t$  of the tip at time  $t$ . Therefore,

$$\text{Tr}(\Delta X \hat{\rho}_{rel}) = \int \text{tr}(\Delta X \hat{\rho}_{rel}) d\Gamma = \int \Psi(P, Q, t) \text{tr}(\Delta X \hat{\rho}_{eq}) d\Gamma = 0$$

since  $\langle \Delta X \rangle_{eq} = 0$  by definition.

Finally, concluding this subsection, we note that the time derivative  $\dot{A}$  of an arbitrary dynamical variable is defined in the mixed representation as  $\dot{A} = (i\hat{L}_s + i\hat{L}_T)A$ , which is a generalization of the usual definition in classical and quantum mechanics [23].

### 2.3. Equation of motion for the tip

Our present consideration is somewhat similar to the classical treatment suggested in [14]. Therefore, we shall give only a brief outline of the main steps used in the derivation, paying special attention to the features which are affected by the quantum consideration of the microscopic system.

First of all, we check using the same reasoning as in [14] that  $V(t) = P_t/M$ . Also,

$$\dot{P} = (i\hat{L}_s + i\hat{L}_T)P = i\hat{L}_T P = F_c + \Delta X \quad (11)$$

is the total tip–surface force as expected. Taking its average with respect to  $\hat{\rho}_{rel}$  and calculating the integral with respect to  $Q$  in  $\text{Tr}(\dots)$  by parts, we again obtain

$$\langle \dot{P} \rangle_{rel}^t = \langle F_c \rangle_{rel}^t = -F(t).$$

Thus, the Lagrange multipliers  $V(t)$  and  $F(t)$  correspond to the tip velocity and the minus conservative force acting on the tip and calculated in the relevant ensembles. The parameter  $F(t)$  depends only on  $Q_t$  since the  $P$ -integration in  $\langle F_c \rangle_{rel}^t$  can be performed exactly and the parameter  $V(t)$  disappears by normalization. Another useful identity is obtained using the Liouville equation (6) and the definition of the Liouville operator of the tip (7) as follows:

$$\dot{Q}_t = \text{Tr}\left(Q \frac{\partial \hat{\rho}}{\partial t}\right) = -\text{Tr}(Q i\hat{L}_T \hat{\rho}(t)) = \frac{P_t}{M} \quad (12)$$

since  $\text{tr}(i\hat{L}_s \hat{\rho}) = \text{tr}([\hat{\rho}, H_s]/i\hbar) = 0$ ; the integration by parts has been used in the third passage in equation (12). The time derivative of  $P_t$  is calculated similarly to equation (12), giving

$$\dot{P}_t = -\text{Tr}(P i\hat{L}_T \hat{\rho}(t)) = \langle \dot{P} \rangle_t = \langle \dot{P} \rangle_{rel}^t + \text{Tr}(\dot{P} \Delta \hat{\rho}(t)) \quad (13)$$

where we have introduced  $\Delta \hat{\rho} = \hat{\rho}(t) - \hat{\rho}_{rel}(t)$ .

Similarly to the classical case [14, 15], on average  $P \propto \sqrt{M}$ , so the Liouville operator of the tip can be considered as being of the order of  $M^{-1/2}$ , i.e. it can be treated as small in comparison with  $i\hat{L}_s$ . Therefore, the Liouville equation (6) can be solved to the first order in  $i\hat{L}_T$ , giving

$$\Delta \hat{\rho}(t) = -\int_{-\infty}^t dt_1 e^{\epsilon(t_1-t)} e^{i(t_1-t)\hat{L}_s} \left[ \left( \frac{\partial}{\partial t_1} + i\hat{L}_s + i\hat{L}_T \right) \hat{\rho}_{rel}(t_1) \right] \quad (14)$$

where we note that the exponential operator acts on the expression in the square brackets; generally, its action on arbitrary operator  $A$  is equivalent to using the Heisenberg picture (denoted by tilde) [23]:

$$e^{is\hat{L}_s} A = e^{isH_s/\hbar} A e^{-isH_s/\hbar} = \tilde{A}(s). \quad (15)$$

In order to calculate the expression in the square brackets in equation (14), we first notice that  $\hat{\rho}_{rel} \propto \hat{\rho}_{eq} \propto \exp(-\beta H_s)$ , so that

$$i\hat{L}_s \hat{\rho}_{rel} = \frac{1}{i\hbar} [\hat{\rho}_{rel}, H_s] = 0 \quad (16)$$

and, therefore,

$$e^{is\hat{L}_s} \hat{\rho}_{rel}(t_1) = \hat{\rho}_{rel}(t_1). \quad (17)$$

Then,  $\hat{\rho}_{rel}(t_1)$  depends explicitly on time  $t_1$  via the Lagrange multipliers  $V(t_1)$  and  $F(t_1)$ . Using equation (5), the self-consistency conditions and the identity  $\dot{V}(t) = \dot{P}_t/M$ , we obtain

$$\frac{\partial}{\partial t_1} \hat{\rho}_{rel}(t_1) = \frac{\beta}{M} \left[ \dot{P}_{t_1} (P - P_{t_1}) + M \frac{\partial F(t_1)}{\partial t_1} (Q - Q_{t_1}) \right] \hat{\rho}_{rel}(t_1). \quad (18)$$

Also,  $i\hat{L}_T \hat{\rho}_{rel}(t_1)$  can be calculated using the explicit expression for the Liouville operator of the tip (7). While the differentiation with respect to  $P$  is straightforward, one has to use the Kubo identity (see e.g. [23]) when differentiating equation (5) with respect to  $Q$ . We obtain

$$\frac{\partial}{\partial Q} \hat{\rho}_{rel}(t_1) = \beta \left( \int_0^1 \widetilde{\Delta X}(i\beta x \hbar) dx + F_c + F(t) \right) \hat{\rho}_{rel}(t_1). \quad (19)$$

When substituting equations (16)–(19) into the right-hand side of  $\Delta \hat{\rho}(t)$  in equation (14) and replacing  $\dot{P}_t$  from equation (13), we shall obtain an integral equation with respect to  $\Delta \hat{\rho}$ . It can be solved iteratively, e.g. by expanding the solution into a power series with respect to the small parameter  $M^{-1/2}$ . To obtain the first-order term, one can effectively put  $\dot{P}_{t_1} \simeq \langle \dot{P} \rangle_{rel}^{t_1}$  inside the time integral in equation (14). Thus, noticing that  $\dot{P} = F_c + \Delta X$ , we obtain

$$i\hat{L}_T \hat{\rho}_{rel}(t_1) = \frac{\beta}{M} \left[ \dot{P} P_{t_1} - P \langle \dot{P} \rangle_{rel}^{t_1} - P \Delta X + P \int_0^1 \widetilde{\Delta X}(i\beta x \hbar) dx \right] \hat{\rho}_{rel}(t_1).$$

Collecting all terms together in equation (14), we have

$$\begin{aligned} \Delta \hat{\rho}(t) = & -\frac{\beta}{M} \int_{-\infty}^0 ds e^{\epsilon s} \left[ P \int_0^1 \widetilde{\Delta X}(i\beta x \hbar + s) dx + \widetilde{\Delta X}(s)(P_{t_1} - P) \right. \\ & \left. + (F_c - \langle F_c \rangle_{rel}^{t_1}) P_{t_1} + M \frac{\partial F(t_1)}{\partial t_1} (Q - Q_{t_1}) \right] \hat{\rho}_{rel}(t_1) \end{aligned} \quad (20)$$

where  $t_1 = t + s$  here. Thus, we have obtained a solution of the Liouville equation which is exact up to the first order in the small parameter  $M^{-1/2}$  of the theory.

Finally, we have to use this solution in equation (13). First, we note that  $\langle \dot{P} \rangle_{rel}^t = \langle F_c \rangle_{rel}^t$  and  $\text{Tr}(\dot{P} \Delta \hat{\rho}(t)) = \text{Tr}(\Delta X \Delta \hat{\rho}(t))$ . Multiplying both sides of equation (20) by  $\Delta X$  and taking the trace, we arrive at four contributions which correspond to the four terms in the integrand in equation (20). However, only the very first term will survive. Indeed, the second term,  $\langle \Delta X \widetilde{\Delta X}(s)(P_{t_1} - P) \rangle_{rel}^{t_1}$ , amounts to zero after integration with respect to  $P$  in the trace; the third,  $\langle \Delta X (F_c - \langle F_c \rangle_{rel}^{t_1}) \rangle_{rel}^{t_1}$  and the fourth,  $\langle \Delta X(s)(Q - Q_{t_1}) \rangle_{rel}^{t_1}$ , terms can be expressed via  $\text{tr}(\Delta X \hat{\rho}_{rel}(t_1)) \propto \text{tr}(\Delta X \hat{\rho}_{eq}) = 0$  and so they are identically zero. Finally, the first term is simplified by first integrating over  $P$ . Thus, we obtain

$$\dot{P}_t = \langle F_c(Q) \rangle_{rel}^t - \frac{\beta}{M} \int_{-\infty}^0 ds e^{\epsilon s} \langle X, X(s) \rangle_{rel}^{t+s} P_{t+s}. \quad (21)$$

This is our main result. The function

$$\langle X, X(s) \rangle_{rel}^{t_1} = \int_0^1 dx \langle \Delta X \widetilde{\Delta X}(i\beta x \hbar + s) \rangle_{rel}^{t_1} \quad (22)$$

represents a *non-equilibrium correlation function* of the fluctuation of the tip–surface force. Note that it is calculated in the relevant ensembles at a different time, so that it depends on *two* times,  $t_1$  (or  $t$ ) and  $s$ . In addition, one can see that the correlation function is some non-linear function of  $P_{t_1}$  and  $Q_{t_1}$  since  $\hat{\rho}_{rel}(t_1)$  depends on them via the Lagrange multipliers. In fact, the dependence over  $P_{t_1}$  can be exactly eliminated by integrating with respect to  $P$  in the trace in the correlation function. Thus, the total force acting on the tip in the right-hand side of equation (21) consists of the conservative contribution  $\langle F_c \rangle_{rel}^t$  and a friction force (which is exactly *linear* in  $P_{t+s}$ ) with complete account of the memory effects. The correlation function  $(X, X(s))_{rel}^{t_1}$  performs as a *memory function* and it depends explicitly on the tip position  $Q_{t_1}$ , which makes the whole equation highly *non-linear*.

The dependence in the correlation function on  $Q_{t_1}$  can be simplified. As was explained in detail in [14], one can make use of the particular form of the relevant distribution in our case which is represented as a product of  $\hat{\rho}_{eq}$  and the envelope function  $\Psi(P, Q, t_1)$  (mentioned earlier), which appears to be strongly peaked at exact  $P_{t_1}$  and  $Q_{t_1}$ . Thus, in all averages  $\langle \dots \rangle_{rel}^{t_1} = \text{Tr}(\dots \hat{\rho}_{rel}(t_1))$  we can approximately substitute  $\hat{\rho}_{rel}(t_1) \rightarrow \hat{\rho}_{eq}$ , the latter calculated at  $Q_{t_1}$ , and thus simplify the equation of motion (21) for the tip:

$$\frac{dP_t}{dt} = \langle F_c(Q_t) \rangle_{eq} - \frac{\beta}{M} \int_{-\infty}^0 ds e^{\epsilon s} (X, X(s))_{eq}^{t+s} P_{t+s} \quad (23)$$

where  $(X, X(s))_{eq}^{t+s}$  is the *equilibrium autocorrelation function* [23] calculated in the same way as in equation (22), but using  $\hat{\rho}_{eq}(Q_{t+s})$  instead of  $\hat{\rho}_{rel}(t+s)$ . Note that it is still a function of two times,  $t+s$  and  $s$ , since  $\hat{\rho}_{eq}$  depends explicitly on  $Q_{t+s}$ .

In the Markovian approximation one assumes that the correlation function  $\langle \Delta X \widetilde{\Delta X}(i\beta x \hbar + s) \rangle_{rel}^{t_1}$  decays over characteristic phonon times, i.e. much faster than any noticeable change in the tip coordinate and momentum. Therefore, only small times  $s$  should contribute significantly in the integral in equation (23). In other words, we set  $P_{t+s} \rightarrow P_t$ , take it out of the integral and also substitute  $Q_{t+s}$  in  $\hat{\rho}_{eq}$  by  $Q_t$ . This way we obtain the Markovian result:

$$\frac{dP_t}{dt} = \langle F_c(Q_t) \rangle_{eq} - \frac{1}{M} \xi(Q_t) P_t \quad (24)$$

where the second term in the right-hand side is the friction force,  $-\xi(Q_t) \dot{Q}_t$ , with a friction coefficient

$$\xi(Q_t) = \beta \int_{-\infty}^0 ds e^{\epsilon s} (X, X(s))_{eq}^t. \quad (25)$$

It is remarkable that exactly the same result has been independently obtained using the coarse-graining method [22].

We would like to stress again that the Markovian approximation is only valid if the correlation function  $\langle \Delta X \widetilde{\Delta X}(i\beta x \hbar + s) \rangle_{rel}^{t_1}$  decays much faster than the characteristic macroscopic time associated with the tip, e.g. the period of tip oscillations. It has been shown in [15] within the Debye model for the classical correlation function that the Markovian approximation should be perfectly adequate for the NC-AFM system. Optical phonons which are not accounted for in this model have even larger oscillation frequencies and their contribution is expected to decay even faster. The situation may change, however, if there are some *soft modes* in the system either existing on the tip-free surface (e.g. a surface defect with a double-well potential), on the nano-tip (a weakly bound atom) or induced at the surface by the approaching tip (e.g. a substantial local reconstruction at the surface in the tip proximity). In these cases the soft mode may have a characteristic time comparable to that of the tip and these should be considered together [13]. It may also be true that the Markovian approximation breaks down for these types of system and further studies are necessary to clarify this issue.



We should expect that at rather high temperatures equations (21) and (22) will transform into their classical counterparts [14]. It can easily be seen that this is indeed the case. First of all, in the classical limit  $\hbar \rightarrow 0$  and we obtain

$$(X, X(s))'_{rel} \rightarrow \langle \Delta X \widetilde{\Delta X}(s) \rangle'_{rel} = \langle \Delta X e^{is\hat{L}_s} \Delta X \rangle'_{rel}. \quad (26)$$

On the other hand, the quantum Liouville operator  $i\hat{L}_s$  turns into the classical one, so the action of the exponential operator  $\exp(is\hat{L}_s)$  on  $\Delta X$  in the correlation function will correspond to the fluctuating force after *classical* evolution of the system over time  $s$ . One can see that the quantum correlation function goes over to the classical one [14], as it should. Then, we recall that in our classical treatment [14] there were some additional (but small) terms in the equation of motion which we have not obtained here. It can be easily checked that these terms originate from a slightly different definition of  $\Delta X$  used in [14]. We have checked that if we used the same definition of  $\Delta X$  as in the present paper, the classical method would have resulted in exactly identical forms of the equation of motion as given above by the present formulae after applying the classical limit.

#### 2.4. Derivation of the Fokker–Planck equation for the tip

The consideration presented above is limited in a sense that other quantities of interest which are some functions of  $P$  and  $Q$  cannot be calculated directly. This can be overcome, at least in principle, if we know the tip distribution function  $f_T(PQ, t)$  introduced earlier in equation (4). In this section we derive a general non-Markovian ‘equation of motion’ for  $f_T(PQ, t)$ . Our consideration here is an extension of the corresponding classical treatment given previously [14]. The corresponding Markovian derivation based on the coarse-grained approach and the mixed quantum–classical representation for the density operator has been published elsewhere [22].

As in the classical treatment, it is convenient to choose a continuous set of the relevant variables  $\mathfrak{S}_{\Gamma_0} \equiv \delta(P - P_0)\delta(Q - Q_0)$ , where  $P_0$  and  $Q_0$  are some fixed classical variables, in place of the  $P$  and  $Q$  of the previous section. The relevant distribution in this case is constructed in the same way as in the classical case:

$$\hat{\rho}_{rel}(t) = \frac{1}{Z(t)} \exp\left[-\beta H - \int \mathfrak{S}_{\Gamma_0} \Lambda(P_0 Q_0 t) d\Gamma_0\right] = \frac{1}{Z(t)} \exp[-\beta H - \Lambda(PQ t)] \quad (27)$$

where  $\Lambda(PQ t)$  are the corresponding Lagrange multipliers. Using the self-consistency conditions,

$$\langle \mathfrak{S}_{\Gamma_0} \rangle'_{rel} = \langle \mathfrak{S}_{\Gamma_0} \rangle_t \equiv f_T(P_0 Q_0, t) \quad (28)$$

the function  $\Lambda(PQ t)$  can be easily expressed via the exact tip distribution function  $f_T$ , and thus we can rewrite the relevant statistical operator in the form

$$\hat{\rho}_{rel}(t) = \hat{\rho}_{eq}(Q) f_T(PQ, t) \quad (29)$$

which looks the same as in the classical case [14]. One should remember, however, that here the equilibrium distribution  $\hat{\rho}_{eq}(Q)$  is quantum.

Our next step is to take a small trace  $\text{tr}(\dots)$  of the both sides of the Liouville equation (6). Taking into account that  $\text{tr}(i\hat{L}_s \hat{\rho}) = \text{tr}([\hat{\rho}, H_s])/i\hbar = 0$ , we obtain an equation

$$\frac{\partial f_T}{\partial t} + \text{tr}(i\hat{L}_T \hat{\rho}) = 0. \quad (30)$$

Using equations (7) and the self-consistency condition (28), we can calculate the trace and obtain

$$\left( \frac{\partial}{\partial t} + \frac{P}{M} \frac{\partial}{\partial Q} + F_c(Q) \frac{\partial}{\partial P} \right) f_T + \frac{\partial}{\partial P} \text{tr}(\Delta X \Delta \hat{\rho}) = 0 \quad (31)$$

where, as before,  $\Delta\hat{\rho} = \hat{\rho} - \hat{\rho}_{rel}$ . To calculate the ‘collision term’  $\Omega = -\text{tr}(\Delta X \Delta\hat{\rho})$ , we shall also use the formal solution (14) of the Liouville equation which is exact to the first order in the small parameter of the theory  $M^{-1/2}$  in a very general case. Therefore, as in the previous section, we shall have to calculate the expression in the square brackets there using this time another expression for the relevant distribution, namely equation (29). Since  $i\hat{L}_s\hat{\rho}_{rel} = f_T i\hat{L}_s\hat{\rho}_{eq} = 0$  and the calculation of  $\partial\hat{\rho}_{rel}(t_1)/\partial t_1 = (\partial f_T/\partial t_1)\hat{\rho}_{eq}(Q)$  is trivial, we have to calculate only  $i\hat{L}_T\hat{\rho}_{rel}$ , which can be done using explicit expression (7) for the Liouville operator for the tip. First, we recall that  $\hat{\rho}_{eq}$  depends only on  $Q$  (not on  $P$ ); then, similarly to the derivation of equation (19), we obtain

$$\frac{\partial}{\partial Q}\hat{\rho}_{eq} = \beta \left( \int_0^1 \widetilde{\Delta X}(i\beta x\hbar) dx + \langle X \rangle_{eq} \right) \hat{\rho}_{eq} \quad (32)$$

which gives

$$\begin{aligned} i\hat{L}_T\hat{\rho}_{rel}(t_1) &= \left\{ \frac{P}{M} \left[ \frac{\partial}{\partial Q} + \beta \left( \int_0^1 \widetilde{\Delta X}(i\beta x\hbar) dx + \langle X \rangle_{eq} \right) \right] f_T(t_1) \right. \\ &\quad \left. + (F_c(Q) + \Delta X) \frac{\partial f_T(t_1)}{\partial P} \right\} \hat{\rho}_{eq}. \end{aligned} \quad (33)$$

Collecting all terms and replacing  $\partial f_T/\partial t_1$  from equation (31), we obtain

$$\begin{aligned} \left( \frac{\partial}{\partial t_1} + i\hat{L}_s + i\hat{L}_T \right) \hat{\rho}_{rel}(t_1) &= \left\{ \beta \frac{P}{M} \left( \int_0^1 \widetilde{\Delta X}(i\beta x\hbar) dx + \langle X \rangle_{eq} \right) f_T(t_1) \right. \\ &\quad \left. + \Delta X \frac{\partial f_T(t_1)}{\partial P} - \frac{\partial}{\partial P} \text{tr}(\Delta X \Delta\hat{\rho}) \right\} \hat{\rho}_{eq}. \end{aligned} \quad (34)$$

Our reasoning here is essentially the same as in the previous section. An important point is that every term on the right-hand side is proportional to the small parameter  $M^{-1/2}$ . On the other hand, we have a term linear in  $\Delta\hat{\rho}$  inside the curly brackets. Therefore, when we use expression (34) in equation (14), we obtain an integral equation with respect to  $\Delta\hat{\rho}$  which can be solved by iterations. The expression of the first order with respect to  $M^{-1/2}$  is obtained by simply dropping the last term inside the curly brackets in equation (34). In addition, an application of the exponential operator  $\exp(is\hat{L}_s)$  is equivalent to transforming to the Heisenberg picture. Therefore, we obtain after some algebra

$$\Delta\hat{\rho}(t) = - \int_{-\infty}^0 ds e^{\epsilon s} \left[ \beta \frac{P}{M} \left( \int_0^1 \widetilde{\Delta X}(i\beta x\hbar + s) dx + \langle X \rangle_{eq} \right) + \widetilde{\Delta X}(s) \frac{\partial}{\partial P} \right] f_T(t_1) \hat{\rho}_{eq} \quad (35)$$

where  $t_1 = t + s$ . Finally, using this expression in the last term in equation (31) and recalling that  $\text{tr}(\Delta X \hat{\rho}_{eq}) = \langle \Delta X \rangle_{eq} = 0$ , we obtain

$$\left[ \frac{\partial}{\partial t} + \frac{P}{M} \frac{\partial}{\partial Q} + F_c(Q) \frac{\partial}{\partial P} - \frac{\partial}{\partial P} \int_{-\infty}^0 ds e^{\epsilon s} \left( \gamma(Q, s) \frac{\partial}{\partial P} + \beta \frac{P}{M} (X, X(s))_{eq} \right) \right] f_T(t_1) = 0 \quad (36)$$

where

$$\gamma(Q, t) = \langle \Delta X \widetilde{\Delta X}(t) \rangle_{eq} \quad (37)$$

and the other equilibrium correlation function,  $(X, X(s))_{eq}$ , has been introduced in the previous section. Note that in the latter correlation function  $\hat{\rho}_{eq} \equiv \hat{\rho}_{eq}(Q)$  and the second time argument (the superscript) in its definition becomes redundant.

The equation we have just derived is very general and has the form of the Fokker–Planck equation for the tip distribution function [25]. It incorporates all the essential features of the

system, such as memory effects and quantum consideration of the microscopic system. In the classical limit it becomes identical to the Fokker–Planck equation obtained previously in [14] since  $\langle X, X(s) \rangle_{eq} \rightarrow \langle \Delta X \Delta \bar{X}(s) \rangle_{eq} \rightarrow \langle \Delta X \Delta X(s) \rangle_{eq}$ , i.e. both correlation functions turn into the single classical correlation function in which  $\Delta X(s)$  is the classical evolution of the fluctuating force during time  $s$ . In the Markovian approximation  $f_T(t_1) = f_T(t+s) \rightarrow f_T(t)$  and can be taken out from the time integral, and we recover our previous Markovian result [22] obtained using the coarse-grained method. Finally, we note that the equation of motion for the tip, i.e. the equation for  $P_t = \int P f_T(PQ, t) d\Gamma$ , can be derived independently from the Fokker–Planck equation in pretty much the same way as in the classical case [14], so this does not need to be repeated here. We only note that the result coincides exactly with the linearized equation of motion (23) given in the previous section.

### 3. Summary

In this paper we have considered non-equilibrium dynamics of the NC-AFM system treating the microscopic system comprising the atoms in the surface and in the nano-tip quantum mechanically. In order to do this we have made use of the mixed quantum–classical representation for the statistical operator  $\hat{\rho}$  of the combined system [22, 24]. Derived equations for the tip distribution function (the Fokker–Planck equation) and for the tip dynamics (an equation of motion) are non-Markovian (contain memory effects) and have been shown to be generalizations of the corresponding classical equations derived previously [14] using the same NESOM method. We have also demonstrated that in the Markovian limit our equations coincide with those derived in [22] using a different non-equilibrium technique based on the time coarse-graining method.

As expected, non-equilibrium consideration leads to a *friction force* acting on the tip due to vibrations of atoms belonging to the surface and the nano-tip. This result is qualitatively the same as in the previous studies [11, 13–17]. An important difference, however, is that in this paper we have not assumed that the temperature of the surface is much larger than the Debye temperature. Since the quantum treatment of the microscopic system has been employed, our present result will generally hold whatever the temperature. In particular, it can be applied to the low-temperature AFM methods [26, 27]. Since it should be easier to excite phonons by increasing temperature, one can expect that generally dissipation effects due to the considered mechanism [11] will increase with  $T$ . On the other hand, especially at low  $T$ , the classical statistics overestimates the phonon population. Therefore, one would expect that the quantum friction derived above should lead to some reduction of the dissipation effects beyond the classical expression, and, indeed, our recent numerical estimates [22] confirm these conclusions.

### References

- [1] Cleveland J P, Anczykowski B, Schmid A E and Elings V B 1998 *Appl. Phys. Lett.* **72** 2613
- [2] Anczykowski B, Gotsmann B, Fuchs H, Cleveland J and Elings V 1999 *Appl. Surf. Sci.* **140** 376
- [3] Gotsmann B and Fuchs H 2001 *Phys. Rev. Lett.* **86** 2597
- [4] Dürig U 1999 *Surf. Interface Anal.* **27** 467
- [5] Gotsmann B, Seidel C, Anczykowski B and Fuchs H 1999 *Phys. Rev. B* **60** 11 051
- [6] Abdurixit A, Baratoff A and Meyer E 2000 *Appl. Surf. Sci.* **157** 355
- [7] Bennewitz R, Foster A, Kantorovich L, Bammerlin M, Loppacher Ch, Schar S, Guggisberg M, Meyer E and Shluger A 2000 *Phys. Rev. B* **62** 2074
- [8] Molitor S, Güther P and Berghaus T 1999 *Appl. Surf. Sci.* **140** 276

- [9] Loppacher C, Bennewitz R, Pfeiffer O, Guggisberg M, Bammerlin M, Schär S, Barwich V, Baratoff A and Meyer E 2000 *Phys. Rev. B* **62** 13 674
- [10] Bennewitz R, Gerber Ch and Meyer E (ed) 2000 *Proc. 2nd Int. Workshop on Noncontact Atomic Force Microscopy Appl. Surf. Sci.* **157**
- [11] Gauthier M and Tsukada M 1999 *Phys. Rev. B* **60** 11 716
- [12] Sasaki M and Tsukada M 2000 *Japan. J. Appl. Phys.* **39** L1334
- [13] Kantorovich L 2001 *J. Phys.: Condens. Matter* **13** 945
- [14] Mo Man Yue and Kantorovich L 2001 *J. Phys.: Condens. Matter* **13** 1439
- [15] Kantorovich L 2001 *Phys. Rev. B* **64** 245409
- [16] Kantorovich L 2002 *J. Phys.: Condens. Matter* **14** 4329
- [17] Gauthier M and Tsukada M 2001 *Surf. Sci.* **495** 204
- [18] Dorofeyev I, Fuchs H, Wenning G and Gotsmann B 1999 *Phys. Rev. Lett.* **83** 2402
- [19] Persson B N J and Volokitin A I 2000 *Phys. Rev. Lett.* **84** 3504
- [20] García R, Tamayo J and San Paulo A 1999 *Surf. Interface Anal.* **27** 312
- [21] Kubo R 1966 *Rep. Prog. Theor. Phys.* **29** 255
- [22] Kantorovich L 2002 *Surf. Sci.* submitted
- [23] Zubarev D, Morozov V and Röpke G 1996 *Statistical mechanics of nonequilibrium processes Basic Concepts, Kinetic Theory* vol 1 (Berlin: Akademie)
- [24] Kantorovich L 2002 *Phys. Rev. Lett.* submitted
- [25] Risken H 1989 *The Fokker–Planck equation Methods of Solution and Applications* 2nd edn (Berlin: Springer)
- [26] Lantz M, Hug H, 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 and Wiesendanger R 2000 *Phys. Rev. B* **61** 2837