Accurate formula for conversion of tunneling current in dynamic atomic force spectroscopy

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Recent developments in frequency modulation atomic force microscopy enable simultaneous measurement of frequency shift and time-averaged tunneling current. Determination of the interaction force is facilitated using an analytical formula, valid for arbitrary oscillation amplitudes [Sader and Jarvis, Appl. Phys. Lett. 84, 1801 (2004)]. Here we present the complementary formula for evaluation of the instantaneous tunneling current from the time-averaged tunneling current. This simple and accurate formula is valid for any oscillation amplitude and current law. The resulting theoretical framework allows for simultaneous measurement of the instantaneous tunneling current and interaction force in dynamic atomic force microscopy. © 2010 American Institute of Physics. [doi:10.1063/1.3464165]

Since its invention, the atomic force microscope (AFM) has become an indispensable tool for characterization at the nanometer and atomic scales. Its extreme sensitivity has enabled imaging to be performed at unprecedented levels, which include observation of individual atoms in single molecules in ultrahigh vacuum$^1$ and elucidation of the three dimensional solvation shell structure of liquids with atomic resolution.$^2$ In addition, the force measurement capabilities of the AFM have been explored widely, and a host of static and dynamic methods are now used routinely to provide complementary data.$^3,4$ By combining the capacity of the AFM to yield both image and force information, atomically resolved force measurement with chemical specificity has also been achieved.$^5$

In contrast to the AFM, the scanning tunneling microscope (STM) utilizes the short-range nature of the tunneling current between its tip and surface to perform imaging with atomic resolution. The STM has also been extensively utilized in electronic spectroscopy studies.$^6$ However, force information is not easily extracted in such STM studies, which has led to the proposition of combined AFM/STM measurements.$^3,4,7–11$ Such a mode of operation opens the door to imaging using either tunneling current or force feedback, which may be advantageous in various circumstances.

Frequency modulation atomic force microscopy (FM-AFM) is a dynamic mode of operation that uses a vibrating cantilever sensor to measure the interaction force between its tip and sample.$^4$ By employing a feedback circuit, FM-AFM drives its force-sensing cantilever at resonance. A second feedback circuit is also often used to maintain constant tip amplitude. The presence of an interaction force modifies the effective cantilever stiffness, which is detected with high sensitivity using the shift in resonant frequency.

Simultaneously, the tunneling current through the tip can also be monitored. Since the cantilever oscillates at high frequency, the time-averaged value of the instantaneous current is typically probed;$^{11–13}$ recent advances in detector technology ensure the true time-averaged current can now be measured.$^4,11$ Such combined measurements thus enable both the frequency shift and time-averaged tunneling current to be monitored as a function of tip-sample distance—these AFM/STM spectroscopy studies have been widely reported.$^3,4,11$ However, their interpretation in terms of an instantaneous current and interaction force requires theoretical analysis, due to the nondirect nature of the measured signals. For tunneling currents that exhibit exponential distance dependence, an analytical formula can be derived connecting the instantaneous tunneling current to the average value.$^5,12,13$ However, due to nonideal effects such as atomic relaxation effects or the tip-induced modification of the local density of states, an exponential law does not hold universally.$^{10,11}$

The interaction force in AFM/STM experiments can be easily extracted from the measured frequency shift using a recently presented simple and accurate analytical formula, which is valid for any force law and arbitrary oscillation amplitude.$^{14}$ In contrast, no such formula currently exists for determination of the instantaneous tunneling current from the measured time-averaged value for an arbitrary current law.$^{12}$—available formulas are restricted to the small or large amplitude regimes only.$^{11}$ Here, we overcome this impediment by deriving a simple and accurate formula for the tunneling current that is valid for any current law, which provides the complementary result to the force formula of Ref. 14.

To begin, we consider the relationship between the time-averaged tunneling current, $i_{av}$, and its instantaneous value, $i$: $i_{av} = \frac{1}{T} \int_{0}^{T} i dt$, where $T$ is the oscillation period and $t$ is time. Noting that the motion is (approximately) harmonic, this equation can then be easily transformed into

$$i_{av}(z) = \frac{1}{\pi} \int_{-1}^{1} \frac{i(z + a(1 + u))}{\sqrt{1 - u^2}} du. \quad (1)$$

This expression differs markedly from the corresponding result for the frequency shift, in that a factor proportional to $u$ is not present in the integrand, cf. Eq. (1) of Ref. 14. In Eq. (1), $z$ is the distance of closest approach to the surface, and $a$ is the tip oscillation amplitude. As above, we consider the case where the tip oscillates at constant amplitude as the

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cantilever approaches the surface. We then formally express the instantaneous current $i(z)$ as

$$i(z) = \int_0^\infty A(\lambda) \exp(-\lambda z) d\lambda,$$

(2)

where $A(\lambda)$ is the inverse Laplace transform of the tunneling current, $i(z)$. Substituting Eq. (2) into Eq. (1) gives

$$i_m(z) = \int_0^\infty A(\lambda) T(\lambda a) \exp(-\lambda z) d\lambda,$$

(3)

where $T(x) = I_0(x) \exp(-x)$, and $I_0(x)$ is the modified Bessel function of the first kind, zeroth order. From Eqs. (2) and (3), an explicit expression for the instantaneous current $i(z)$ in terms of the average current $i_m(z)$ is easily obtained,

$$i(z) = L \left\{ \frac{1}{T(\lambda a)} L^{-1}\{i_m(z)\} \right\},$$

(4)

where the operators $L\{\}$ and $L^{-1}\{\}$ refer to the Laplace and inverse Laplace transforms, respectively.

While Eq. (4) is the exact inverse of Eq. (1), it is of little value in practice due to the requirement for numerical computation of the inverse Laplace transform. An approximation to $1/T(\lambda a)$ is thus desirable to enable explicit evaluation of the Laplace and inverse Laplace transforms in Eq. (4). We note the following exact asymptotic forms for $1/T(x)$,

$$\frac{1}{T(x)} = \begin{cases} 1 + O(x): & x \ll 1 \\ \sqrt{2 \pi x} + O(1/\sqrt{x}): & x \gg 1. \end{cases}$$

(5)

This suggests approximating $1/T(x)$ as a sum over powers of $x$, while satisfying these asymptotic limits. The simplest approach would be to add the leading order asymptotic terms for small and large $x$ in Eq. (5).\textsuperscript{14} However, since the powers of these terms are not significantly different, this approximation results in large ($\sim 80\%$) error at intermediate $x$. As such, we use an alternate approach whereby a shift in Laplace space is introduced to separate these functional forms. This enhances decay of the small $x$ asymptotic form at large $x$, and minimizes the effect of the large $x$ term at small $x$. A least-squares fit then yields the required expression

$$\frac{1}{T(x)} = \exp(-x) + \sqrt{2 \pi x} \left[ 1 - \sqrt{\frac{2}{\pi}} \exp(-x) \right].$$

(6)

Importantly, Eq. (6) possesses the exact asymptotic forms in the limits of small and large $x$, and exhibits an error of less than 3.7% for all $x$; see Fig. 1. The expression in Eq. (6) also permits direct evaluation of the Laplace and inverse Laplace transforms in Eq. (4), through use of fractional calculus and the properties of the Laplace transform.

We note the following definition for the Riemann–Liouville fractional derivative\textsuperscript{14} of order $\alpha$ of a function $\varphi(\lambda)$,

$$D^\alpha \varphi(\lambda) = \frac{(-1)^n}{\Gamma(n-\alpha)} \frac{d^n}{d\lambda^n} \int_\lambda^\infty \varphi(\tau) (\tau-\lambda)^{\alpha-n+1} d\tau,$$

(7)

where $\Gamma(\alpha)$ is the gamma function, $\alpha > 0$ is any real positive number, and $n = [\alpha]+1$, where $[\alpha]$ is the integer component of $\alpha$. Substituting Eq. (6) into Eq. (4) and using Eq. (7) and $L\{\lambda^a \varphi(\lambda)\} = D^\alpha L(\varphi(\lambda))$ then yields the required result

$$i(z) = i_m(z + a) - \int_z^\infty \frac{2a}{\sqrt{\tau-z}} \frac{d i_m(\tau)}{d\tau} - \sqrt{\frac{2}{\pi}} \frac{d i_m(\tau + a)}{d\tau} \, d\tau.$$

(8)

The first term in Eq. (8) corresponds to the small amplitude solution in the limit as $a \to 0$, whereas the second term is the well-known large amplitude solution.\textsuperscript{11} The third term provides a correction that captures behavior at intermediate amplitude. Note that the first and third terms in Eq. (8) possess arguments that are shifted to larger separations by a factor equal to the oscillation amplitude. Consequently, in the limit of large amplitude, these terms do not contribute to the overall result and we recover the usual large amplitude solution, i.e., the second term.

Equation (8) is the result we seek that allows the instantaneous current to be evaluated from the measured average current, regardless of the oscillation amplitude. Since the approximation Eq. (6) used in deriving Eq. (8) exhibits good accuracy, Eq. (8) is also expected to exhibit similar accuracy. This will be examined in the following discussion.

For completeness, we also provide an assessment of the accuracy of the well-known formulas for small and large amplitude. In the asymptotic limit of small amplitude,

$$i(\text{small}) = i_m(z),$$

(9a)

whereas for large amplitude\textsuperscript{11}

$$i(\text{large}) = -\int_z^\infty \frac{2a}{\sqrt{\tau-z}} \frac{d i_m(\tau)}{d\tau} \, d\tau.$$  

(9b)

To perform this assessment, we present results of a simulated experiment for a specified tunneling current law. Namely, we use Eq. (1) to determine the average current versus distance curve for a range of different oscillation amplitudes. We then use Eqs. (8) and (9) to recover the instantaneous current law from the calculated average current. Validity of the above formulas can be directly examined by comparing the original and recovered instantaneous currents.

The instantaneous current law chosen is a Morse potential type function, which displays similar behavior to recent studies,\textsuperscript{10,11} i.e., the current drops at small separation,

$$i(z) = i_0 (e^{-\kappa z} - e^{-2\kappa z}),$$

(10)

where $i_0$ is a constant, and $\kappa$ is the inverse decay length scale. This current law possesses a maximum at a separation of $z_{\text{max}} = \kappa^{-1}$ In 2, and $\kappa^{-1}$ sets a natural length scale.

We now present a comparison of the original and recovered current laws using Eqs. (8) and (9), for different ampli-
tudes of oscillation. We cover a spectrum of oscillation amplitudes ranging from $\kappa \alpha = 0.1$ to $\kappa \alpha = 10$, which encompasses the small and large amplitude regimes. Figure 2(a) presents results for the small amplitude solution, Eq. (9a). As expected, this formula gives poor accuracy for intermediate to high amplitudes but is quite accurate for small amplitude. Analogous results for the large amplitude solution, Eq. (9b), are presented in Fig. 2(b). It is interesting to note that the large amplitude solution yields somewhat reasonable accuracy for intermediate to large amplitudes $\kappa \alpha \simeq 0.5$. This is not entirely unexpected, since the large amplitude asymptotic behavior of $T(x)$ extends to relatively small normalized amplitude $x$; see Fig. 1. Results for Eq. (8), which is valid for arbitrary amplitude, are given in Fig. 2(c). Note the excellent accuracy exhibited by this formula in comparison to both the small and large amplitude formulas, regardless of oscillation amplitude; see Fig. 2(c). Discrepancies are visible but the error is in line with the accuracy of the approximate expression for $T(x)$. This formula thus exhibits similar accuracy to the complementary force conversion formula in Ref. 14.

We emphasize that while an exact solution exists connecting the average current to the instantaneous current for Eq. (10), it is not used in this assessment. Similar accuracy to that exhibited in Fig. 2(c) is also achieved for other current laws, including $i(z) = i_0 \beta^2 [1 / (\kappa \alpha)^2 - 1 / (\kappa \alpha)]^3$ and $i(z) = i_0 \kappa \alpha \exp(\kappa \alpha)$, providing further evidence for the universal validity of Eq. (8).

From a practical perspective, it is important to assess the robustness of the derived formula in the presence of measurement noise. From Eqs. (7) and (9), it is evident that the instantaneous current is given by the measured average current itself at small amplitude; whereas in the limit of large amplitude it is related to the half fractional derivative of the average current. As such, measurement noise is only weakly enhanced in going from small to large amplitudes. Importantly, the arbitrary amplitude formula, Eq. (8), does not possess any terms of order higher than the half fractional derivative, and thus noise effects are also only weakly enhanced in going from small to large amplitude. As such, the performance of Eq. (8) in the presence of measurement noise is no worse than that of the commonly used large amplitude solution, Eq. (9b).

We have presented a simple and accurate formula, Eq. (8), for determining the instantaneous current in dynamic atomic force spectroscopy that is valid for arbitrary amplitudes of oscillation. This provides a result complementary to the formula for determining the interaction force from the measured frequency shift in FM-AFM; Eq. (9) of Ref. 14. These two formulas for the interaction force and tunneling current exhibit similar accuracy. Their combined use thus yields a robust theoretical framework for conducting quantitative and simultaneous AFM/STM measurements.

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