Accurate formulas for interaction force and energy in frequency modulation force spectroscopy

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Frequency modulation atomic force microscopy utilizes the change in resonant frequency of a cantilever to detect variations in the interaction force between cantilever tip and sample. While a simple relation exists enabling the frequency shift to be determined for a given force law, the required complementary inverse relation does not exist for arbitrary oscillation amplitudes of the cantilever. In this letter we address this problem and present simple yet accurate formulas that enable the interaction force and energy to be determined directly from the measured frequency shift. These formulas are valid for any oscillation amplitude and interaction force, and are therefore of widespread applicability in frequency modulation dynamic force spectroscopy. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1667267]

The extreme sensitivity of the atomic force microscope (AFM) has led to its development and use in numerous applications. While the most familiar of these is imaging, considerable effort has also been expended in making use of its capabilities in quantitative measurement of forces on the nanometer and atomic scale.[1,2] If performed with sufficient sensitivity, such measurements can even distinguish variations in potential energy with interatomic spacing. This in turn can provide additional chemical sensitivity to topographic lateral characterization of a surface on the atomic scale.

The use of AFM in such force measurements is commonly referred to as *force spectroscopy*. These studies inherently require a relation connecting the observed deflection properties of the cantilever to the interaction force. Initially, such measurements monitored the static deflection of the cantilever as a function of tip–sample separation. The interaction force between tip and sample was subsequently determined using the spring constant of the cantilever.[3] However, when the interaction force gradient exceeds the cantilever spring constant during the measurement of an attractive interaction, a jump-into-contact instability occurs, often rendering the most scientifically interesting part of the interaction curve inaccessible experimentally. While use of stiffer cantilevers can eliminate this problem, they have the undesirable effect of reducing measurement sensitivity.

This sensitivity issue can be resolved using dynamic methods, which facilitate highly sensitive force measurements with stiff cantilevers. In dynamic force microscopy, a vibrating cantilever is used to sense forces between the cantilever tip and sample. In one mode of operation, commonly termed frequency modulation atomic force microscopy (FMAFM),[4] a feedback circuit self-excites the cantilever at its resonant frequency. In this manner, minute changes in the resonant frequency are easily detected with high sensitivity. Since the resonant frequency of the cantilever is modified by changes in the force interaction between cantilever tip and sample, this then enables use of the technique in a range of applications, which include high resolution imaging[5] and force spectroscopy.[6]

In contrast to the simple relation connecting the static deflection of a cantilever to the interaction force, the corresponding relation for FMAFM is significantly more complex and depends on both the spring constant and amplitude of oscillation. This relation was first derived by Giessibl,[7] and is valid for any amplitude of oscillation:

$$\frac{\Delta\omega}{\omega_{\mathrm{res}}}=-\frac{1}{\pi a k}\int_{-1}^{1}F(z+a(1+u))\frac{u}{\sqrt{1-u^2}}du, \tag{1}$$

where k is the spring constant of the cantilever, F is the interaction force between tip and sample, ω_{res} is its unperturbed resonant frequency, $\Delta\omega$ is the change in resonant frequency, a is the amplitude of oscillation, and z is the distance of closest approach between tip and sample.

To determine the interaction force from the observed frequency shift, Eq. (1) must be inverted. While inversion of Eq. (1) for arbitrary amplitudes has proven elusive, it has been performed analytically for cases where the amplitude of oscillation is far smaller or greater than all characteristic length scales of the interaction force.[4,8] However, use of these limiting formulas in practice can potentially lead to significant errors, unless the precise nature of the force is known. This is particularly problematic if the interaction force contains a spectrum of length scales, encompassing short to long-range components, as is often the case. In such situations, it is possible that the oscillation amplitude may be considered small with respect to long-range components, but large for short-range components. Accurate determination of the interaction force may therefore not be possible using these limiting formulas. Consequently, inversion formulas or techniques that are valid for all oscillation amplitudes are highly desirable, since they permit unequivocal determination of the force, regardless of its nature.

At this stage, we note that various numerical schemes have been formulated to invert Eq. (1) for arbitrary ampli-

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tudes of oscillation. Specifically, one technique[9] iterates on the large amplitude solution until convergence is obtained, while another[10] numerically inverts Eq. (1) using a quadrature scheme. While both methods are mathematically straightforward, they exhibit significant complexity and require specialized computational skills for their implementation, which limits their utility. The aim of this letter is therefore to address this issue by presenting simple yet accurate analytical formulas that enable direct determination of the interaction force and energy from the measured frequency shift. These formulas are valid for any amplitude of oscillation, exhibit similar complexity to the small and large amplitude formulas, and are applicable to any force law. Importantly, we only consider the case where the amplitude of oscillation is kept constant and independent of the tip–sample separation z.

To begin, we formally express the interaction force $F(z)$ as

$$F(z)=\int_0^\infty A(\lambda)\exp(-\lambda z)\,d\lambda, \tag{2}$$

where $A(\lambda)$ is the inverse Laplace transform of $F(z)$. Substituting Eq. (2) into Eq. (1), we then obtain

$$\frac{\Delta\omega}{\omega_{\mathrm{res}}}=\frac{1}{ak}\int_0^\infty A(\lambda)T(\lambda a)\exp(-\lambda z)\,d\lambda, \tag{3}$$

where $T(x)=I_1(x)\exp(-x)$, and $I_n(x)$ is the modified Bessel function of the first kind of order n.[11] Therefore, in Laplace space the force and frequency shift only differ by the function $T(x)$. This finding enables Eq. (1) to be inverted exactly, thus defining the force explicitly in terms of the inverse Laplace transform of the frequency shift:

$$F(z)=L\left\{\frac{ka}{T(\lambda a)}L^{-1}\left\{\frac{\Delta\omega(z)}{\omega_{\mathrm{res}}}\right\}\right\}, \tag{4}$$

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

$$L\{Y(\lambda)\}=\int_0^\infty Y(\lambda)\exp(-\lambda z)\,d\lambda, \tag{5a}$$

$$L^{-1}\{Y(z)\}=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} Y(z)\exp(\lambda z)\,dz, \tag{5b}$$

where c is a real constant. While Eq. (4) rigorously inverts Eq. (1), it is of limited practical value due to difficulties in computing the inverse Laplace transform numerically.

To overcome this problem, we replace $T(x)$ by an equivalent approximate formula which facilitates evaluation of Eq. (4). Noting that $T(x)$ has the asymptotic properties, $T(x)=x/2,\ x\ll 1$ and $T(x)=1/\sqrt{2\pi x},\ x\gg 1$, then enables the construction of a Pade approximant representation for $T(x)$

$$T(x)=\frac{x}{2}\left(1+\frac{1}{8}\sqrt{x}+\sqrt{\frac{\pi}{2}}x^{3/2}\right)^{-1}, \tag{6}$$

which satisfies the above asymptotic behavior exactly, and gives an excellent representation of $T(x)$ for all other values of x; the error exhibited by Eq. (6) is less than 5% for all values of x. The second term in the denominator of Eq. (6) is a higher order correction which is obtained empirically using a least-squares fitting procedure, and is used to improve the accuracy of the approximation.

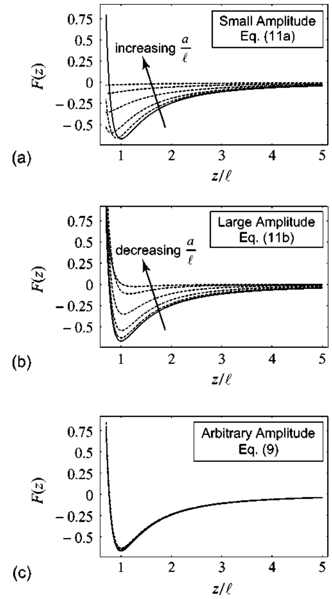

FIG. 1. Actual (solid line) and recovered (dashed line) Lennard-Jones force laws using (a) small amplitude formula [Eq. (11a)]; (b) large amplitude formula [Eq. (11b)]; (c) arbitrary amplitude formula [Eq. (9)]. Amplitudes of oscillation used $a/\ell=0.1$, 0.3, 1, 3, and 10.

Next, we invoke the properties of the Riemann–Liouville fractional integral[12] of order α of a function $\varphi(\lambda)$,

$$I_-^\alpha\varphi(\lambda)=\frac{1}{\Gamma(\alpha)}\int_\lambda^\infty\frac{\varphi(t)}{(t-\lambda)^{1-\alpha}}\,dt, \tag{7a}$$

and the corresponding fractional derivative

$$D_-^\alpha\varphi(\lambda)=\frac{(-1)^n}{\Gamma(n-\alpha)}\frac{d^n}{d\lambda^n}\int_\lambda^\infty\frac{\varphi(t)}{(t-\lambda)^{\alpha-n+1}}\,dt, \tag{7b}$$

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 α.

From Eqs. (5) and (7) it is then easy to prove that

$$L\{\lambda^\alpha Y(\lambda)\}=D_-^\alpha L\{Y(\lambda)\},$$

$$L\{\lambda^{-\alpha}Y(\lambda)\}=I_-^\alpha L\{Y(\lambda)\}. \tag{8}$$

Substituting Eq. (6) into Eq. (4) and using Eq. (8), we then obtain the required explicit expression for the force in terms of the frequency shift

$$F(z)=2k\int_z^\infty\left(1+\frac{a^{1/2}}{8\sqrt{\pi(t-z)}}\right)\Omega(t)-\frac{a^{3/2}}{\sqrt{2(t-z)}}\frac{d\Omega(t)}{dt}\,dt, \tag{9}$$

where $\Omega(z)=\Delta\omega(z)/\omega_{\mathrm{res}}$.

Integrating Eq. (9), and using the definitions in Eq. (7), then gives the corresponding expression for the interaction energy $U(z)$ between tip and sample

$$U(z)=2k\int_z^\infty \Omega(t)\left((t-z)+\frac{a^{1/2}}{4}\sqrt{\frac{t-z}{\pi}}+\frac{a^{3/2}}{\sqrt{2(t-z)}}\right)dt \tag{10}$$

Equations (9) and (10) are the formulas which enable the interaction force and energy to be determined explicitly from the measured frequency shift, irrespective of the amplitude of oscillation. We emphasize that the accuracy of these formulas is dictated only by that of Eq. (6), and is therefore expected to be excellent.

To assess the accuracy and validity of these formulas, we present a simulated experiment for a specified force law. Namely, we use Eq. (1) to determine the frequency shift versus distance curve for a range of different oscillation amplitudes. We then use Eqs. (9) and (10) to recover the force (energy) law from the specified frequency shift. The validity of the formulas can then be directly assessed by comparing the actual and recovered force laws. For completeness, we also present a comparison with the limiting expressions for small and large amplitudes, which are given by the following respective formulas:[4,8]

$$F_{\text{small}}(z)=2k\int_z^\infty \Omega(t)\,dt, \tag{11a}$$

$$F_{\text{large}}(z)=-\sqrt{2}ka^{3/2}\int_z^\infty \frac{d\Omega(t)}{dt}\frac{1}{\sqrt{t-z}}\,dt. \tag{11b}$$

It is important to note that in the limiting cases of small and large amplitude, Eq. (9) yields the exact solution, cf. Eqs. (9) and (11); this is expected since the approximation to $T(x)$ is exact in these limits. From this observation it also follows that an excellent approximation for all amplitudes is obtained by summing the above small and large amplitude solutions, since the term of $O(a^{1/2})$ in Eq. (9) is a higher order correction; it results from the second term in the denominator of Eq. (6). We note, however, that little additional effort is required to implement Eq. (9) in full. The same discussion also applies to the expression for the interaction energy, [Eq. (10)].

To perform the required comparison, a Lennard-Jones force law, consisting of short-range repulsive and long-range attractive interaction, is chosen[9]

$$F(z)=F_0\left(\frac{\ell^4}{3z^6}-\frac{1}{z^2}\right), \tag{12}$$

where F_0 is a constant, and ℓ is the separation where the attractive force is maximum. This separation therefore sets a natural length scale for the interaction.

We now present a comparison of the specified and recovered force laws using Eqs. (9) and (11), for a spectrum of oscillation amplitudes ranging from $a/\ell=0.1$ to $a/\ell=10$, which encompass the small and large amplitude regimes. In Fig. 1(a), a comparison is given of the recovered and actual force curves using the small amplitude formula [Eq. (11a)]. From Fig. 1(a) it is clear that the small amplitude formula yields significant inaccuracies, even for the case of $a/\ell=0.1$, while the results obtained using this formula for intermediate to large amplitudes are not even in qualitative agreement with the actual force law. This demonstrates that even for small amplitudes, Eq. (11a) must be used with care since it can lead to significant inaccuracies. In Fig. 1(b) we present a complementary comparison using the large amplitude formula [Eq. (11b)]. For the case of $a/\ell=10$, good agreement is found between the recovered and actual force laws. As expected, however, this agreement deteriorates with decreasing amplitude and for intermediate to small amplitudes qualitative discrepancies exist. Consequently, these results verify that the small and large amplitude formulas give poor agreement for intermediate amplitudes, and can exhibit qualitative discrepancies when used outside their respective regimes of validity.

The results in Figs. 1(a) and 1(b) are to be compared to the results obtained using Eq. (9), which is derived explicitly for arbitrary amplitudes, the results of which are given in Fig. 1(c). From Fig. 1(c), it is evident that the recovered force laws are virtually independent of the oscillation amplitude, with all force curves almost coinciding with the actual force law. The only discrepancies visible are for the midrange oscillation amplitudes of $a/\ell\sim0.3$, particularly near the minimum in the force law. At this point the error is less than 5%, which is in line with the accuracy of the approximate expression for $T(x)$. We note that similar results are obtained for the interaction energy, and hence not reproduced here. Consequently, these results verify the accuracy of Eqs. (9) and (10), and establish their global validity for arbitrary oscillation amplitudes.

In summary, we have presented simple yet accurate formulas [Eqs. (9) and (10)], for determining the interaction force and energy in dynamic force spectroscopy. These formulas are valid irrespective of the amplitude of oscillation used, and the nature of the force measured. Consequently, they allow for easy and unequivocal determination of force and energy curves from measured frequency shift data using FMAFM.

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