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Interpretation of frequency modulation atomic force microscopy in terms of fractional calculus

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It is widely recognized that small amplitude frequency modulation atomic force microscopy probes the derivative of the interaction force between tip and sample. For large amplitudes, however, such a physical connection is currently lacking, although it has been observed that the frequency shift presents a quantity intermediate to the interaction force and energy for certain force laws. Here we prove that these observations are a universal property of large amplitude frequency modulation atomic force microscopy, by establishing that the frequency shift is proportional to the half-fractional integral of the force, regardless of the force law. This finding indicates that frequency modulation atomic force microscopy can be interpreted as a fractional differential operator, where the order of the derivative/integral is dictated by the oscillation amplitude. We also establish that the measured frequency shift varies systematically from a probe of the force gradient for small oscillation amplitudes, through to the measurement of a quantity intermediate to the force and energy (the half-fractional integral of the force) for large oscillation amplitudes. This has significant implications to measurement sensitivity, since integrating the force will smooth its behavior, while differentiating it will enhance variations. This highlights the importance in choice of oscillation amplitude when wishing to optimize the sensitivity of force spectroscopy measurements to short-range interactions and consequently imaging with the highest possible resolution.

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In dynamic mode atomic force microscopy (AFM), the response of an oscillating cantilever to external forces is monitored. This approach has proven useful not only in imaging applications,[1] but also in force spectroscopy.[2] One approach commonly used is to oscillate the cantilever at its resonant frequency and monitor any variation in the resonant frequency resulting from an interaction force. For small oscillation amplitudes,[3] i.e., amplitudes much smaller than the characteristic length scale of the interaction force between tip and sample, it is well established that the change in resonant frequency is proportional to the force gradient of interaction,

$$\frac{\Delta\omega}{\omega_{\mathrm{res}}} = -\frac{1}{2k}\frac{dF}{dz}, \tag{1}$$

where k is the spring constant of the cantilever, ω_{res} is its unperturbed resonant frequency (in the absence of any force), $\Delta\omega$ is the change in resonant frequency, F is the interaction force, and z is the distance of closest approach between tip and sample. Equation (1) is derived under the assumption that the frequency shift $\Delta\omega$ is much smaller than the unperturbed resonant frequency ω_{res}. Recently, Giessibl[4] extended this simple result to the case of arbitrary amplitudes, under the same assumption of $\Delta\omega \ll \omega_{\mathrm{res}}$,

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

where a is the amplitude of oscillation. Importantly, Eq. (1) is recovered from Eq. (2) in the limit of small amplitudes, as required.

While providing a mathematical formalism for quantitative force spectroscopy, Eq. (2) does not provide an intuitive connection between the frequency shift and force, except for the small amplitude limit. Interestingly, a number of workers have observed that in the large amplitude limit, the frequency shift is intermediate between the interaction force and energy.[5–7] Indeed, it has been noted that the frequency shift can be well approximated by a function proportional to the square root of the product of the force and energy, i.e., $\Delta\omega \propto \sqrt{|F(z)E(z)|}$. However, this form is obtained empirically for specific force laws, rather than through rigorous mathematical analysis. We now formally examine the behavior of the frequency shift as a function of oscillation amplitude, and in so doing rigorously establish that, in the large amplitude limit, the frequency shift is proportional to the half-fractional integral of the force. Thus, the observation that frequency shift is intermediate to the force and energy has a simple explanation, and is a universal property of large amplitude frequency modulation AFM.

To begin, we note that the interaction force approaches zero as the separation between the tip and sample approaches infinity. Therefore, we express the interaction force $F(z)$ completely generally as

$$F(z) = \int_0^\infty A(\lambda)\exp(-\lambda z)d\lambda, \tag{3}$$

where $A(\lambda)$ is formally the inverse Laplace transform of $F(z)$. Substituting Eq. (3) into Eq. (2), it can then be easily shown that Eq. (2) becomes

$$\frac{\Delta\omega}{\omega_{\mathrm{res}}} = \frac{1}{ak}\int_0^\infty A(\lambda)T(\lambda a)\exp(-\lambda z)d\lambda, \tag{4}$$

where $T(x) = I_1(x)\exp(-x)$, and $I_n(x)$ is the modified Bessel function of the first kind of order n.[8]

Next, we note that the Riemann-Liouville fractional integral[9] of order α of a function $\varphi(z)$ is given by

$$I_{-}^{\alpha}\varphi(z)=\frac{1}{\Gamma(\alpha)}\int_{z}^{\infty}\frac{\varphi(t)}{(t-z)^{1-\alpha}}dt, \tag{5a}$$

whereas the corresponding fractional derivative is

$$D_{-}^{\alpha}\varphi(z)=\frac{(-1)^{n}}{\Gamma(n-\alpha)}\frac{d^{n}}{dz^{n}}\int_{z}^{\infty}\frac{\varphi(t)}{(t-z)^{\alpha-n+1}}dt, \tag{5b}$$

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. Importantly, fractional derivatives/integrals give functions *intermediate* to the results of full derivatives/integrals.[9]

Consequently, from Eqs. (3) and (5a) we find

$$I_{-}^{1/2}F(z)=\int_{0}^{\infty}A(\lambda)\frac{1}{\sqrt{\lambda}}\exp(-\lambda z)d\lambda. \tag{6}$$

However, in the limiting case where the function $A(\lambda)$ is localized in the region where $\lambda a \gg 1$, which corresponds physically to the situation where the amplitude of oscillation a greatly exceeds the characteristic length scale of the interaction force λ^{-1} [see Eq. (3)], $T(\lambda a)\sim 1/\sqrt{2\pi\lambda a}$. Therefore, Eq. (4) becomes

$$\frac{\Delta\omega}{\omega_{\text{res}}}=\frac{1}{k\sqrt{2\pi a^{3}}}\int_{0}^{\infty}A(\lambda)\frac{1}{\sqrt{\lambda}}\exp(-\lambda z)d\lambda. \tag{7}$$

Comparing Eqs. (6) and (7) then gives the required result

$$\frac{\Delta\omega}{\omega_{\text{res}}}=\frac{1}{k\sqrt{2\pi a^{3}}}I_{-}^{1/2}F(z), \tag{8}$$

thus formally proving that the frequency shift is proportional to the half-fractional integral of the force. Reversing this definition then gives an explicit expression for the force in terms of the half-fractional derivative of the frequency shift

$$F(z)=k\sqrt{2\pi a^{3}}D_{-}^{1/2}\frac{\Delta\omega(z)}{\omega_{\text{res}}}. \tag{9}$$

We note that Eqs. (8) and (9) combined with Eqs. (5a) and (5b) are identical to results obtained previously in the large amplitude limit.[6] Importantly, however, in this paper we make the formal connection to the half-fractional integral of the force, and thus establish an intuitive physical relationship between the frequency shift and the applied force, which is complementary to the result for the small amplitude limit. Namely, in the large amplitude limit, the frequency shift is proportional to the half-fractional integral of the force, or equivalently, the half-fractional derivative of the energy. Since the energy is the full integral of the force, the finding that the frequency shift is proportional to the half-integral of the force then proves that the frequency shift presents a quantity intermediate to the force and energy, regardless of the force law. This therefore explains the previous observation that the frequency shift is intermediate to the force and the energy for specific force laws.[5–7] Furthermore, the findings of this paper establish that for all force laws, the observation that the frequency shift lies intermediate to the force and energy is a universal property of large amplitude frequency modulation AFM.

Finally, we examine the behavior of frequency modulation AFM for intermediate amplitudes. It is important to note that taking the αth fractional derivative of the force law $F(z)$ with respect to separation z is formally equivalent to multiplying the integrand of Eq. (3) by λ^{α}. Since the integrands of Eqs. (3) and (4) only differ by the function $T(x)$, it is then of intrinsic interest to examine the local power law behavior of $T(x)$ in Eq. (4), to determine the nature of the frequency shift. The local power law behavior of the function $T(x)$ around any point $x=\overline{x}$ can be easily evaluated by matching its value and first derivative to the expression $T(x)\sim c\,x^{d}$, where c and d are local constants. This results in a unique expression for the local power law behavior of $T(x)$,

$$d=\frac{\overline{x}(I_{0}(\overline{x})-2I_{1}(\overline{x})+I_{2}(\overline{x}))}{2I_{1}(\overline{x})}, \tag{10}$$

which decreases monotonically from $d=1$ (for small x, or small amplitude limit, corresponding to the full derivative) to $d=-1/2$ (for large x, or large amplitude limit, corresponding to the half-fractional integral). Since $T(x)$, or any function for that matter, can be formally expressed as a piecewise sum of its local power law behavior, it then follows that oscillation amplitudes intermediate to the small and large amplitude limits sample derivatives/integrals of fractional order intermediate to the full derivative and half-fractional integral. Therefore, if $A(\lambda)$ is localized in λ-space, then the frequency shift will be directly proportional to the fractional derivative of the force, whose order is dictated by the local power-law behavior of $T(\lambda a)$ in that region. For example, if $A(\lambda)$ is localized at $a=1.55/\lambda$, then the local power law behavior of $T(\lambda a)$ will be $d=0$ [from Eq. (10), since $\overline{x}=\lambda a=1.55$], and the frequency shift will be directly proportional to the force. This finding is consistent with the observation of Ke *et al.*[5] that the frequency shift is proportional to the force for the intermediate case where the oscillation amplitude is comparable to the characteristic length scale of the force. Consequently, frequency modulation AFM can be interpreted as a fractional differential operator, where the order of differentiation/integration is dictated by the relative difference between the amplitude of oscillation and the length scale of the interaction.

The findings of this study have significant implications for measurements where force laws with different characteristic length scales are measured simultaneously, as we shall now discuss.

Consider the case of an interaction involving both long-range (such as electrostatic) and short-range (such as chemical bonding or solvation) forces. If the oscillation amplitude is intermediate to the characteristic length scales of these two force laws, then the short-range interaction will be half-integrated while the long-range interaction will be differentiated. This will lead to accentuation of variations in the long-range force and smoothing in variations of the short-range force, which in turn can enhance the effect of long-range interactions in the measured frequency shift. Importantly, use of high aspect ratio tips to minimize the effects of long-range forces, which is common in practice, is not immune to this intrinsic property of frequency modulation AFM. The most important physical implication of this finding is that the experimentalist must either remove or significantly reduce long-range interactions by modifying the tip/sample/intervening medium, or must strive towards using oscillation amplitudes which are significantly smaller than the *shortest* interaction length scale of interest.

We also note that this difference in sensitivity of short-range and long-range forces can complicate interpretation of the resulting frequency shift in cases where the oscillation amplitude is intermediate to length scales of short- and long-range forces. This is because the frequency shift will no longer be intermediate to the force and energy, as is the case for pure large amplitudes, nor will it be proportional to the force gradient which corresponds to pure small amplitudes. While this feature presents no conceptual difficulty if Eq. (2) is formally inverted to recover the interaction force,[10–12] it results in ambiguity in interpreting the frequency shift directly in a force measurement. Thus frequency shift measurements made using frequency modulation AFM, where a range of forces with different characteristic length scales are present, as is often encountered in practice, must be interpreted with care.

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