Fundamentals of Atomic Force Microscopy
Part 2: Dynamic AFM Methods

Week 4, Lecture 1
Relationship between Frequency Shift and Potential Energy

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From the last lecture

- VEDA simulations for approach and scanning using FM-AFM
Force spectroscopy

• Extracting $F_{ts}$ as a function of ‘d’ on a surface
• Quantifying properties such as local Hamaker constant, chemical forces, elastic modulus etc.

Static force-distance curves (Part 1)

Dynamic AFM methods

FM-AFM* approach/retraction curves
AM-AFM approach/retraction curves

* There are two ways to implement FM-AFM - one the way we have discussed in the class, but another method that of self-excitation is also used sometimes
Recall that tip amplitude and phase remain fixed!

- Excitation magnitude $F_0$ increases to keep tip amplitude fixed
- Drive frequency $f$ tracks $f'_0$

$$f'_0 = f_0 - f_0 \frac{V_{ts}(Z,A)}{kA^2}$$

$$F_0 = \frac{kAf}{Qf_0} + \frac{E_{ts}}{\pi A}$$

- How to convert $f = f'_0$ vs $Z$ into $F_{ts}^{CONS}$ vs $d$?
- How to convert $F_0$ vs $Z$ into $F_{ts}^{DISS}$ vs $d$?
Understanding $f_0$ and $f_0'$ in terms of potential energy

- $f_0'$ depends on conservative forces, so let's consider a model without any dissipation or excitation.

\[
mq + kq = F_{ts}^{\text{CONS}}(d), \quad d = Z + q(t) \quad (1)
\]

with \[\omega_0 = \sqrt{\frac{k}{m}}\]

But \[F_{ts}^{\text{CONS}}(d) = -\frac{\partial U_{ts}(d)}{\partial d}\] \[\quad (2)\]

$U_{ts}$ is the potential energy associated with conservative tip-sample interaction forces.

\[
\therefore U_{ts}(\infty) - U_{ts}(d) = -\int_{d}^{\infty} F_{ts}^{\text{CONS}}(\xi)d\xi
\]

or, defining $U_{ts}(\infty)=0$, we have

\[
U_{ts}(d) = \int_{d}^{\infty} F_{ts}^{\text{CONS}}(\xi)d\xi \quad (3)
\]
Understanding $f_0$ and $f_0'$ in terms of potential energy

It can be shown (See Appendix) that (1) is simply a restatement of the conservation of total energy

$$E_{\text{total}} = T + U_{\text{total}}, \quad U_{\text{total}} = U_{\text{cant}} + U_{\text{ts}}$$

where $$T = \frac{1}{2} m \dot{q}^2$$ is the kinetic energy of the point mass oscillator

$$U_{\text{total}}(q) = \frac{1}{2} k q^2 + U_{\text{ts}}(Z + q)$$

Or

$$U_{\text{total}}(d) = \frac{1}{2} k (d - Z)^2 + U_{\text{ts}}(d)$$

and the equation of motion (1) can be rewritten as

$$m \ddot{q} = \frac{\partial U_{\text{ts}}(q)}{\partial q}$$

(4)

Thus Eq(1) can be understood in the context of a point mass oscillator in a potential energy well
As an example, consider a probe with $k=15 \text{ N/m}$ and tip-sample potential energy of the form

$$U_{\text{tot}}(eV) = \left(10^{-5} / d^5 - 0.8 / d\right) / 0.1602 \quad (\text{where } d \text{ is in nm})$$

$$U_{\text{tot}}(eV) = \left(U_{\text{ts}}(d) + \frac{1}{2} k(Z - d)^2\right) / 0.1602 \quad (\text{where } Z, d \text{ are in nm})$$

Note: $1 \text{ eV} = 0.1602 \text{ attoJoules}$

Potential well becomes asymmetric and changes curvature as $Z$ is decreased.
\( f_0' \) in a quadratic potential

\[ U_{\text{tot}} = \frac{1}{2} kq^2, U_{\text{ts}} = 0 \]

\[ m\ddot{q} + \frac{\partial U_{\text{tot}}(q)}{\partial q} = m\ddot{q} + kq = 0 \]

Solution has a frequency

\[ f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \]

- Frequency does not depend on initial \( q \)!
- Max potential energy is quadratic with initial \( q \)

![Graph showing the potential energy as a function of initial \( q \)]
\[ U_{\text{tot}} = \frac{1}{2} kq^2 + \frac{1}{4} \alpha_3 q^4 \]

\[ m\ddot{q} + \frac{\partial U_{\text{tot}}(q)}{\partial q} = m\ddot{q} + kq + \alpha_3 q^3 = 0 \]

\[ q(t) = a_0 + \sum_{n=1}^{\infty} \left( a_n \sin(n\omega_0 t) + b_n \cos(n\omega_0 t) \right) \]

\( a_0 = 0; \quad a_n = 0; \quad b_2 = b_4 = b_6 = \ldots = 0 \) from symmetry

Leading non-zero term is \( b_1 \)

\[ f'_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m} + \frac{3}{4m} b_1^2 + \frac{3}{128m} k_3^4 b_1^4 + \ldots} = f_0 + \Delta f(b_1) \]

- Natural frequency now depends on oscillation amplitude!
$f'_0$ in perturbed potentials

\[ U_{\text{tot}} = \frac{1}{2} kq^2 - \frac{1}{3} \alpha_2 q^3 + \frac{1}{4} \alpha_3 q^4 \]

\[ m\ddot{q} + \frac{\partial U_{\text{tot}}(q)}{\partial q} = m\ddot{q} + kq - \alpha_2 q^2 + \alpha_3 q^3 = 0 \]

\[ q(t) = a_0 + \sum_{n=1}^{\infty} \left( a_n \sin(n\omega_0 t) + b_n \cos(n\omega_0 t) \right) \]

solution now contains BOTH even and odd harmonics and $a_0 \neq 0$

\[ f'_0 \simeq \frac{1}{2\pi} \sqrt{\frac{k}{m} + \frac{3}{4} \frac{\alpha_3}{m} b_1^2 - \frac{5}{6} \frac{\alpha_2}{m} \frac{\alpha_2}{\alpha_1} b_1^2 + \ldots} = f_0 + \Delta f(b_1) \]

- Natural frequency now depends on oscillation amplitude!
- Going back to potential earlier in the class
- The following freq shift vs $Z$ (and amplitude is expected)