Oscillations

Nonlinear theory and applications in AFM

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Glossary

m	mass
z	position of the tip relative to the cantilever
d	tip-sample distance
t	time
Q	Q factor
ω_0	natural frequency
k	spring constant
F_0	magnitude of drive force
ϕ	phase shift
F_{ts}	tip-sample (surface) force
$\ddot{z}$	acceleration
$\dot{z}$	velocity
T	period
W	work
U	potential energy
KE	kinetic energy
E_T	total energy
E_{avg}	average energy
<E>	average energy
δ	deformation
P_{dis}	power dissipation
A	amplitude
A_0	free amplitude
W_D	work done by the drive
V	virial
E_{dis}	energy dissipation
ω_r	resonance frequency
ω_{eff}	effective resonance frequency
ω_0'	effective resonance frequency

Introduction

The theory of oscillations can be studied from a mathematical point of view in terms of differential equations. The differential equation is written and then the solution or solutions worked out and mathematically analysed. Provided physical, economic, social, or other phenomena can be modelled in terms of equivalent differential equations, the solutions and results are applicable to all phenomena all the same. On the other hand, it is sometimes easier to learn a topic by having an experimental topic in mind. It is otherwise maybe surprising that a large body of phenomena in many fields of application will be easily understood if the equations are understood for a given case. The experimental analysis that forms the basis of this book is cantilever dynamics in dynamic atomic force microscopy (AFM). In a nutshell, the motion of the cantilever in dynamic AFM can be approximated to a perturbed driven oscillator. The generality of the analysis presented here can be confirmed by noting that much of what is covered in this book, particularly when dealing with the linear equation in section 1, is similar to what is covered in generic expositions such as that by Tipler and Mosca[1] or the Feynman's lectures on physics[2]. Maybe the main advantage of this exposition is that the linear and nonlinear theories of oscillators, particularly phenomena that can be reduced to the analysis of a point-mass on a spring, are discussed in detail and differences in terminology that could lead to doubt, clarified. This means that this book can be used as a textbook to teach oscillation theory with a focus on applications. This is possible because oscillations are present generally in physics, engineering, biology, economics, sociology and so on. In summary, all phenomena dealing with oscillations can be reduced, to a first approximation, to a restoring parameter, i.e., force in mechanics, following Hooke's law.

Since the AFM field is a niche in science, the general theory of oscillation does not cover the particularities of the field. This book covers such particularities. Thus, the book can be used as an introduction to dynamic AFM and oscillation theory that covers the terminology required to understand dynamic AFM. On the other hand, the ubiquity and generality of oscillation theory ensures that the book can also be used as a general introduction to oscillation theory at an undergraduate level. There is also advanced material, particularly in the second section of the book where nonlinearities are covered.

For the sake of transnationality, standard terminology is employed throughout when possible, especially in the first section (Book 1). The first section is based on the standard linear differential equations. The second section is based on non-linear theory and covers advancements in dynamic FM over the past three decades (1990s – 2022). Both sections are complimentary and exploit standard terminology in oscillation theory when possible.

The first section can be supplemented with the chapter on oscillations by Tipler and Mosca[1] and with Feynman's lectures on physics, volume 1, chapters 21 to 23. These two textbooks use standard terminology, even if not necessarily the same. Examples are drawn here from both texts and analogies also exploited.

The second section is mathematically more advanced since it discusses nonlinear theory. The second section is highly geared towards applications in AFM, but this does not mean that the discussion lacks generality. Rather, the nonlinear theory presented here is highly general and translational. The second section can be supplemented by following Raman's course on dynamic AFM. His course is available online[3]. There are another two important resources to supplement the second section. First, the thesis of Carlos Álvarez Amo, also available online[4]. Second, a varied set of papers that are referenced throughout the text.

2.1. Nonlinearities and the driven oscillator

2.1.1 Linear differential equations

This is the second part of the book on oscillations and the aim is to expand the linear theory of oscillations, in particular of the theory of the point mass model. The point mass model is an ideal system, but it has many applications in science since many systems can be expressed as a point mass attached to a spring. For example, Wilhelm H. Westphal writes that "[A] point mass is an idealization of a real solid body. It possesses mass, but its dimensions are assumed to be so small that its location can be sufficiently accurately defined by the position of a point."[5]

For nonlinearity we understand the standard mathematical definition, namely, a system for which the output is not proportional to its input. The Wikipedia entry[6] on nonlinear systems opens with two interesting statements. First

1) "In mathematics and science, a nonlinear system is a system in which the change of the output is not proportional to the change of the input."

It is typical for people to think in linear terms, that is, proportionally. For example, if you work twice the hours it could be expected that you make twice the money. If something has twice the mass, it should weigh twice, etc. Many times however, whatever multiplies a variable does not do so proportionally to the variable.

The second statement in the Wikipedia entry reads,

2) "Nonlinear problems are of interest to engineers, biologists, physicists, mathematicians, and many other scientists because most systems are inherently nonlinear in nature."

This second statement in the entry shows that, while linearity is relevant and important, the nonlinear analysis is many times more accurate in its representation of reality.

While the above definitions are useful, it is important to give a strict definition of nonlinearity since, here, the theme will be discussed both theoretically and practically. The theme of oscillations is further discussed in this text by working on the equations of motion. These are differential equations. In this respect, Feynman more precisely defines what a linear differential equation is, namely, "[A] linear differential equation is a differential equation consisting of a sum of several terms, each term being a derivative of the dependent variable with respect to the independent variable, and multiplied by some constant". The above statement is translated into a linear differential equation with constant coefficients as follows

$$c_k \frac{d^k x}{dt^k} + c_{k-1} \frac{d^{k-1} x}{dt^{k-1}} + \cdots + c_1 \frac{dx}{dt} + c_o x = \mathrm{f(t)} \qquad \text{Eq. 2.1}$$

The dependent variable in Eq. 1 is x and the independent variable is t. The coefficients c_k are constants. Physically the independent variable t might stand for time, but it does not have to. Furthermore, the function f(t) might have any functional relationship with t with the only limitation being, for linearity to apply, that x is not involved. If x was involved in a way that the function f(t) can be assimilated as one of the linear terms on the left of Eq. 1, the equation is still linear. The coefficients however might not be constant if they depend on t. If x appears in ways different to those of the linear terms on the left of Eq. 2.1, the equation is non-linear. The tip-sample force in AFM is typically non-linear implying that the term on the right of Eq. 1 is non-linear. It is not coincidental that Richard Feynman starts his discussion on oscillations with a chapter on linear differential equations and the methods to solve these equations.

Everything said about the linear system in section 1 (Chapters 1.1 to 1.10) will be assumed here. The results from those chapters will be explored here for the analysis of the non-linear system when possible.

The linear system is expressed in Eq. 2.2 while the non-linear system is expressed in Eq. 2.3. F_{ts} means tip-sample force and it is typical terminology in AFM, but the term stands for any non-linear force in general. If the term represents other than force, the solution of the equations is equivalent, only the physical interpretation chances according to the phenomena represented.

$$m\frac{d^2 z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz = F_0 \cos\ \omega t \qquad \text{Eq. 2.2}$$

$$m\frac{d^2 z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz = F_{ts} + F_0 \cos\ \omega t \qquad \text{Eq. 2.3}$$

where all the terms in the equations are defined in the glossary and in chapters 1.1 to 1.10. Eq. 2.2 has been extensively explored in section 1. The objective of this section is the analysis of Eq. 2.3. The rheological models for both equations are shown in Fig. 2.1. As stated, the linear model can be directly applied to many systems of interest. For example, it turns out that the linear model for the oscillator, the phenomena related to “an electron orbiting a massive, stationary nucleus”[7] can be modelled as a point mass model on spring with a driven sinusoid. This model is termed “the Lorentz oscillator model”. For example, Colton says that “[T]he Lorentz oscillator model, also known as the Drude-Lorentz oscillator model, involves modelling an electron as a driven damped harmonic oscillator”.[8] Levi says “[T]he Lorentz oscillator model applies the classical concepts of a driven damped mechanical oscillator to the problem of an electromagnetic field interacting with a dielectric material".[9] I.F. Almog, M.S. Bradley, and V. Bulović have a great document on the applications of this model[10]. Since the Lorentz oscillator model is based on phenomena that can be represented by a differential equation that is equivalent to the one discussed here (chapters 1.1 to 1.10) for the AFM system, the resulting solutions and interpretations are also the same.

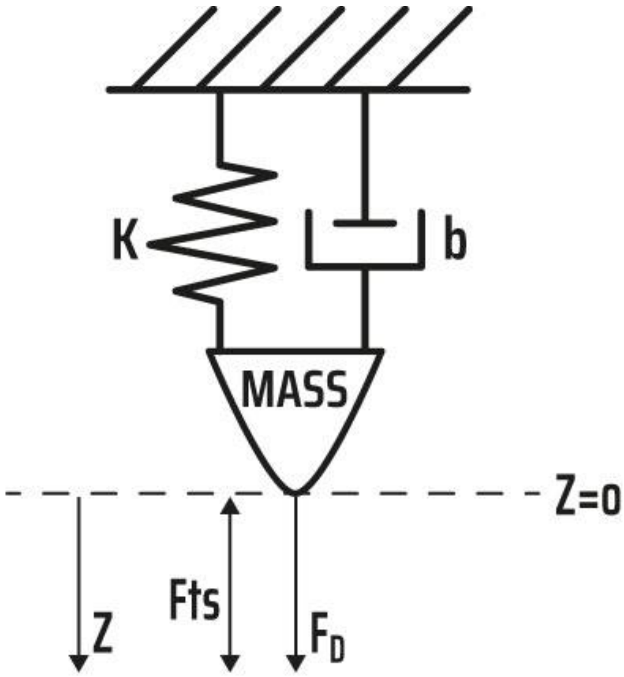

Figure 2.1. Rheological model representing the tip's motion and forces in the equation of motion in Eq. 2.3.

The nonlinear formalism results from the addition of the tip-sample force F_{ts} in Eq. 2.3 as shown in the rheological model in Fig. 2.1. F0 is the magnitude of the driving force F_{DRIVE} or F_D.

2.1.2 Non-linear differential equation of motion for the driven oscillator

It is important to recognize from the beginning that the nonlinear results can be derived from the linear ones by considering "effective" parameters. This concept is not new or unique to the non-linear analysis. For example, when the mass m is considered in the harmonic oscillator, the value of m is "effective" in that it is the value m necessary for the model to adjust to, or better represent, the real system. The implication is that the actual mass m of the system does not need to coincide with the effective mass m. Many times when speaking of effective values people use the prime notation, i.e., m', or simply write as a subscript eff for effective, i.e., m_{eff}.

The concept "effective" will be exploited here to derive an "effective" Q factor and an "effective" resonance frequency ω_r when dealing with the nonlinear system. Effective will mean that were we use effective values for Q and ω_r, the interpretation of the non-linear system is reduced to the interpretation and terminology used in the linear analysis. Of course the interpretation and discussion must be considered with care. To provide such a discussion is also the focus of this book. I summary, most of the linear results can be extrapolated or transformed so they can be adapted to the analysis of the nonlinear system.

If F_{ts} is negligible compared to every other term in Eq. 2.3, F_{ts} has no significant effect in the response. In such case, the system can be analysed using the linear theory derived from the analysis of Eq. 2.2 only (section 1 and chapters 1.1 to 1.10). However, as F_{ts} becomes comparable to the other terms, the non-linear phenomena must be considered.

To begin, the comparison between the following equations can be considered,

$$m\frac{d^2z}{dt^2}+\frac{m\omega_0}{Q}\frac{dz}{dt}+kz=F_0\cos\omega t \qquad \text{linear} \qquad \text{Eq. 2.4}$$

$$m\frac{d^2z}{dt^2}+\frac{m\omega_0}{Q}\frac{dz}{dt}+kz=F_0\cos\omega t-\frac{\alpha}{z^2} \qquad z>B\text{ }, nonlinear\ attrative \qquad \text{Eq. 2.5}$$

$$m\frac{d^2z}{dt^2}+\frac{m\omega_0}{Q}\frac{dz}{dt}+kz=F_0\cos\omega t+\beta z^{3/2} \qquad z<\text{C, nonlinear repulsive} \qquad \text{Eq. 2.6}$$

$$m\frac{d^2z}{dt^2}+\frac{m\omega_0}{Q}\frac{dz}{dt}+kz=F_0\cos\omega t-\frac{\alpha}{z^2}+\beta|z|^{3/2} \qquad \text{nonlinear attractive-repulsive} \qquad \text{Eq. 2.7}$$

Figs. 2.2-2.5 show the difference between the linear and the nonlinear response in terms of the presence or absence of a nonlinear force. The response is typically represented by the amplitude and phase shift ϕ as a function of drive frequency in Eq. 2.4 to 2.7 as prescribed by $F_0\cos\omega t$. Four cases will be discussed next from the linear response to cases where the nonlinear term is "attractive", "repulsive", and a combination of both. These cases are important in AFM because atomic forces behave in a similar way. Arvind Raman has a similar discussion in "nanoHUB-U Fundamentals of AFM L2.3: Analytical Theory - Nonlinearity, Virial, and Dissipation."[3]

2.1.2.a The linear response

The response of the linear expression is given by the expression for the amplitude A and the phase shift ϕ. The phase shift is the difference in phase between the amplitude response and the drive force $F_0 \cos\ \omega t$. The position z is parametrized as

$$z(\omega) = Acos(\omega - \phi)$$

where (see Eq. 95 in chapter 1.8)

$$A(\omega) = \frac{F_0}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + b^2\omega^2}} \qquad \text{Eq. 2.8}$$

and (see Eq. 96 in chapter 1.8)

$$\tan\ \phi(\omega) = \frac{b\omega}{m(\omega_0^2 - \omega^2)} \qquad \text{Eq. 2.8(2)}$$

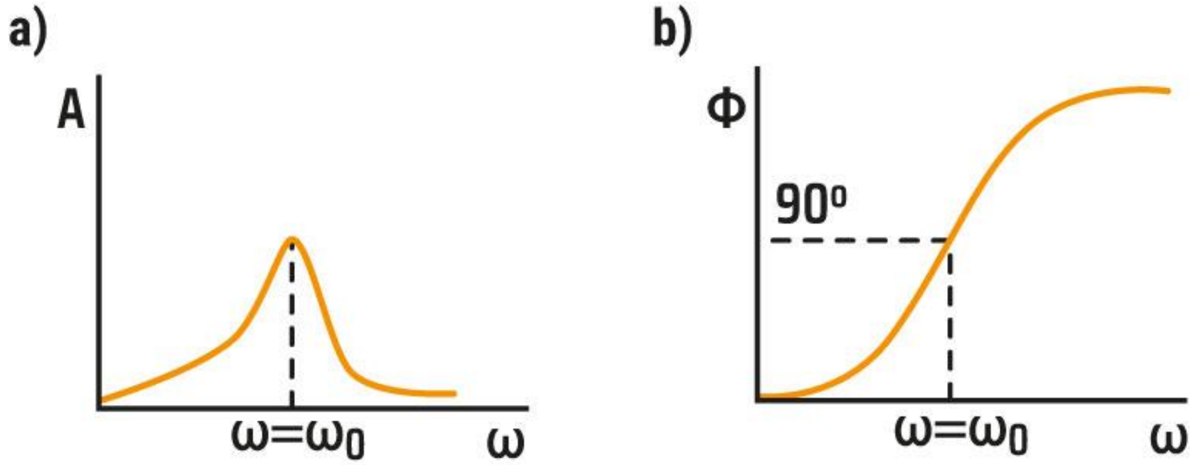

Figure 2.2. LINEAR CASE. Illustration of a standard frequency sweep showing the a) amplitude A and b) phase ϕ response where the resonance curve is seen to peak at $\omega_r \approx \omega_0$. The finite width of the curve indicates that there is dissipation meaning that Q takes on a finite value. The shapes in a) and b) are standard for a driven oscillator and are well represented by a linear model as that in Eq. 2.2. The equations for A and ϕ (Eqs. 2.8 and 2.8(2)) are solved analytically from 2.2.

The reader should note that the amplitude and phase versus frequency ω curves shown in Figs. 2.2-2.7 are only sketches and "real" curves are typically found by numerically solving the equation of motion[11]. This point will be further discussed in the next chapter when discussion the derivation of the virial of interaction V. While the linear response has been discussed analytically in chapters 1.1 to 1.10, the amplitude and phase response as a function of drive frequency, i.e., ω, had not been shown before. Some notes are relevant in order to later interpret the non-linear response. First, in AFM the drive frequency can be set by the user. In other systems ω is given by other phenomena which is not controlled in the experiment.

1) If $\omega < \omega_0$, then $\phi < 90°$,

2) If $\omega = \omega_0$, then $\phi = 90°$,

3) If $\omega > \omega_0$, then $\phi > 90°$.

For the linear equation in Eq. 2.4 there is no constraint in the above results. This means that the results are true independently of Q, F_0, k, b, ω_0 and m. The same is true for ϕ. Namely, ϕ is determined by ω alone for a given set of parameters Q, F_0, k, b, ω_0 and m. The same holds for the amplitude A, namely, for a given set of parameters Q, F_0, k, b, ω_0 and m, the maximum amplitude occurs at (Eq. 102)

$$\omega_r|_{A=A_{\max}} = \omega_0\left[1-\frac{1}{2Q^2}\right]^{1/2} \qquad \text{Eq. 2.9}$$

The maximum amplitude A_{max} is usually also termed A_0 in AFM. The amplitude behaves as follow

1) If $\omega < \omega_r$, then $A < A_0$ and A monotonically decreases with decreasing ω,

2) If $\omega = \omega_r$, then $A = A_0$,

3) If $\omega > \omega_r$, then $A < A_0$ and A monotonically decreases with increasing ω.

The amplitude A further takes on a single value at each ω. We recall that "[I]n mathematics, a function from a set X to a set Y assigns to each element of X exactly one element of Y". In terms of Eqs. 2.8 and 2.8(2) for the linear equation this means that each value of ω maps exactly to one value of A and ϕ respectively. We will see that this is not the case in the non-linear case.

2.1.2.b The nonlinear response and the coexistence of several stable states of oscillation

Already in 1991[12] it was reported that a tip vibrating near a surface would lead to bi-stable behaviour. Here, bi-stability means that for a set of parameters, the oscillation will stabilize, i.e., the steady state of oscillation might be reached, at two different values of A[13-17]. In the linear case, for a given ω the response z is

$$z(\omega) = Acos(\omega t - \phi) \qquad \text{Eq. 2.10}$$

The expression in Eq. 2.10 satisfies the definition of mathematical function as each ω maps to a unique z. Namely, the definition "[I]n mathematics, a function from a set X to a set Y assigns to each element of X exactly one element of Y" is satisfied between ω and z in Eq. 2.10.

The presence of bi-stability, or several oscillation states, means that for a given ω there will be at least two stable solutions. For example, a low L and high H branch for z can be written as follows for a given ω

$$z_L(\omega) = A_L cos(\omega t - \phi_L)$$

$$z_H(\omega) = A_H cos(\omega t - \phi_H) \qquad \text{Eq. 2.11}$$

The above expressions, i.e., Eqs. 2. 11, show that the mapping from ω to z does not satisfy the definition of a mathematical function expressed above. The implication is that the coexistence of several oscillation states leads to a mapping of ω to z that cannot be represented as a single function (Fig. 2.3). It will be later shown that analytical expressions for A in terms of ω are no longer of the form given by Eq. 7 where a single A results for every ω. These expressions are thus consistent with the existence of 2 stable oscillation states. In Fig. 2.3 three values of A and ϕ can be observed for some values of ω but, in such cases, the middle one is not physically accessible[11]. Such phenomena was reported by numerically solving the equation of motion instead[11]. In Fig. 2.3 the amplitude A and phase ϕ are distorted versions of the linear response shown in Fig. 2.2.

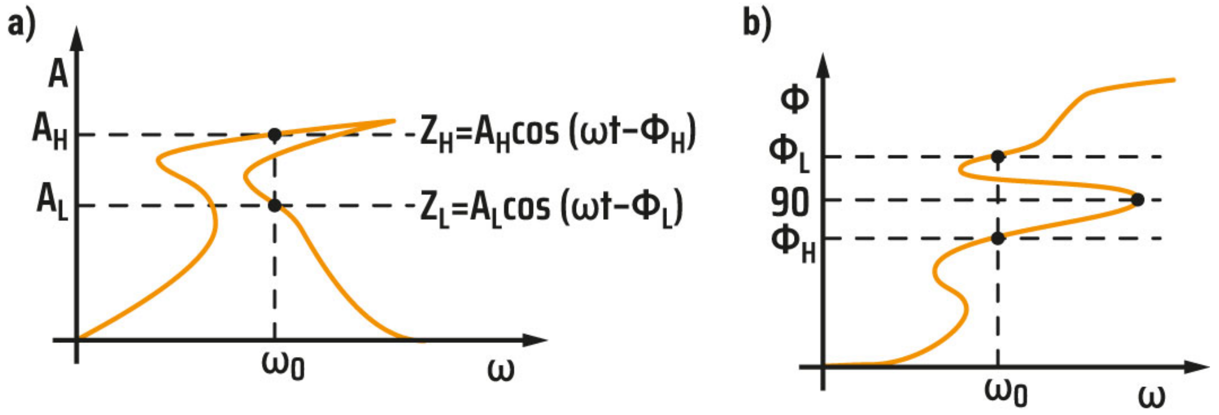

Figure 2.3. NONLINEAR CASE. Illustration of a standard frequency sweep showing the a) amplitude A and b) phase ϕ response. The curves show distortions due to the presence of nonlinear attractive and repulsive forces. The distortions are large at and near ω_0 where two stables branches are available, i.e. H and L (high and low state). Far from ω_0 the oscillator behaves as in the linear case.

Attractive and repulsive forces are responsible for distorting the amplitude A and phase ϕ versus ω curves to lower and higher values of ω respectively as shown schematically in Fig. 2.4. When only attractive forces distort the curves toward lower frequencies only an oscillation branch, where F_{ts} is not negligible, is accessible a range of values of ω. There might be another oscillation branch for which F_{ts} is negligible at the same range of ω. This other branch coincides with the branch produced by the linear response. When repulsive forces distort the curve, the phenomenon is mirrored toward higher values of ω. When there are attractive and repulsive forces present there are two distortions that contribute to the total distortion and the accessible branches of z are accessible for which Fts is not negligible. These are represented by Eq. 2.11.

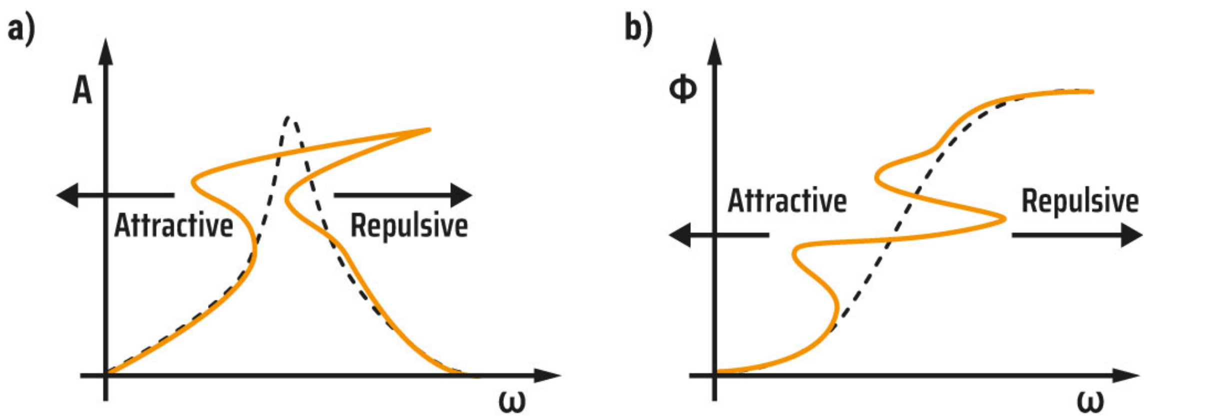

Figure 2.4. NONLINEAR CASE. Illustration of a standard frequency sweep showing the a) amplitude A and b) phase ϕ response where the origin of the distortions is shown in terms of whether nonlinear forces are attractive or repulsive. Attractive forces pull the curves to lower frequencies while repulsive forces pull them towards higher frequencies.

2.1.2.c The nonlinear response (attractive case)

The first type of nonlinearity to discuss is that shown in Figure. 2.5 as expressed by Eq. 2.5. Here, the force is attractive as expressed by the negative sign in the equation, i.e., $F_{ts} \propto -\alpha z^{-2}$. If the force varied linearly with z it could be absorbed by the kz term and the solution would reduce to the case discussed in chapter 1.6. Nevertheless, here the differential equation is nonlinear because one of the terms, i.e., F_{ts}, is expressed in terms of z, the dependent variable, as a power. It is assumed that α is a positive constant (Eq. 2.5).

Several points are worth mentioning

1) The oscillation amplitude A depends on ω (Fig. 2.3) but also on the equilibrium position. This is because if the force is proportional to $\propto z^{-2}$, the way in which the force affects the amplitude depends on the actual values of z^{-2}. See Chapter 1.6 when discussing distance independent forces to see that linearity implies that only the reference point for which kz=0 varies in these cases. For example, a linear term such as kz produces a differential of force that is independent of the actual value of z

$$F = kz \; => \; dF = \mathrm{kdz} \qquad \text{Eq. 2.12}$$

The above equation expressed proportionality with dz. The magnitude of the differential of the force depends on k, i.e., a constant only. For the nonlinear case, i.e., $-\alpha z^{-2}$, the differential of F gives

$$F = -\frac{\alpha}{z^2} \; => dF = \; 2\frac{\alpha}{z^3}\mathrm{dz} \qquad \text{Eq. 2.13}$$

Eq. 2.13 shows that the differential dF depends on z and on the reference value of z. This means that if a new reference value for which kz=0 is considered, the net force in Eq. 2.13 will also vary. For this reason the integral over an oscillation cycle for a given A depends on the equilibrium position z_0, that is, on the absolute values of z that the mass covers in its motion. For the linear case the total range covered by the point-mass system is 2A, i.e., peak to peak. This is clear from the fact that $z = A\cos(\omega t - \phi)$. In the linear case the absolute values of z are irrelevant and only relative values matter since the instantaneous (conservative) net force is always kz as measured from the reference point kz=0 (see chapter 1.6). For the non-linear case the range covered is also 2A but the instantaneous net (conservative) force depends on the actual values of z. This means that if the equilibrium position is displaced the forces acting on the mass for the range of motion under consideration also change (Fig. 2.5)

2) Neither the amplitude curve A, nor the phase curve ϕ, are a mathematical function any longer since the amplitude A no longer takes on a single value at each ω. Rather the curve deforms towards lower values of ω (Figs. 2.3 to 2.5).

3) The phase = 90° for values of $\omega < \omega_0$. This is due to the deformation of the curve. In particular, a new "natural" frequency of resonance ω_0' can be defined where $\omega_0' = \omega_0 - \Delta\omega_0$. The fact that the force is attractive accounts for the deformation toward lower values of ω as discussed when interpreting Fig. 2.4.

4) The shape of the curve, and therefore the value of ω_0' depends on the equilibrium position. Because of what has been said in point 1, the deformation of the curve also depends on the actual values of force and on the equilibrium position.

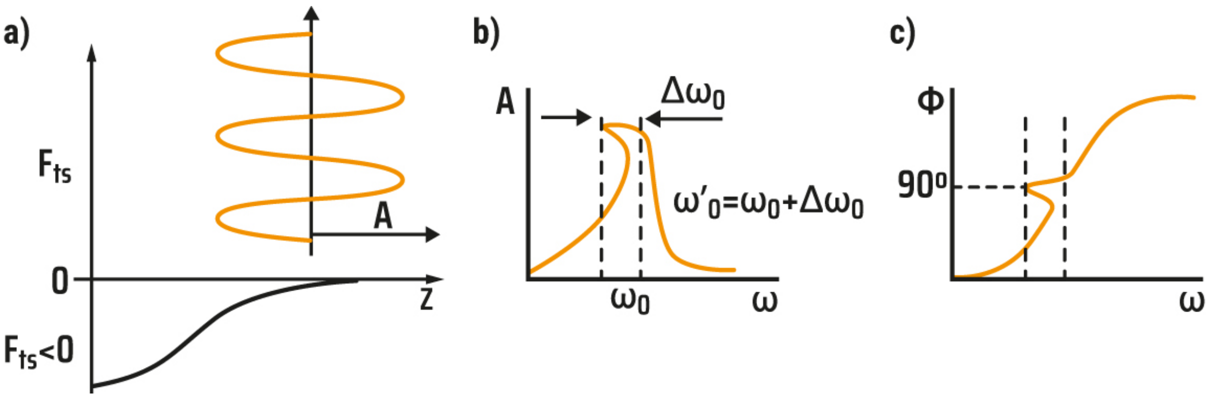

Figure 2.5. NONLINEAR CASE. a) Illustration of a nonlinear (attractive) force showcasing how a sinusoidal wave, i.e., the motion of the oscillator, would be affected by it. Corresponding illustration of a standard frequency sweep showing the b) amplitude A and c) phase ϕ response where the origin of the distortions is shown in terms of nonlinear attractive forces only.

2.1.2.d The nonlinear response (repulsive case)

The second type of nonlinearity to discuss is that shown in Figure. 2.6 and expressed by Eq. 2.6. The force is repulsive, i.e., always pushes the mass toward higher values of z. Again, the differential equation is nonlinear because z, the dependent variable, is expressed as a power, i.e., $\propto z^{3/2}$, in one of its terms. Here (Eq. 2.6) β is a constant. Again, if the force varied linearly with z it could be absorbed by the kz term.

Several points are worth mentioning for the repulsive case

1) The oscillation amplitude A depends on ω (Fig. 2.6) but also on the equilibrium position. This is because if the force is proportional to $\propto z^{-2}$, the way in which the force affects the amplitude depends on the actual values of z and the equilibrium position. See Chapter 1.6 when discussing distance independent forces. The interpretation is similar to that give in point one above for the attractive case.

2) The amplitude A and phase ϕ curves are not a mathematical function any longer (Figs. 2.3-2.4 and 2.6) since the amplitude A no longer takes on a single value at each ω. Rather the curve deforms towards higher values of ω (Fig. 2.6).

3) The phase = 90° for values of $\omega > \omega_0$. This is due to the deformation of the curve. In particular, a new "natural" frequency of resonance ω_0' can be defined where $\omega_0' = \omega_0 + \Delta\omega_0$.

4) The shape of the curve, and therefore the value of ω_0' depends on the equilibrium position. The deformation of the curve also depends on the force and the equilibrium position as in the attractive nonlinear case.

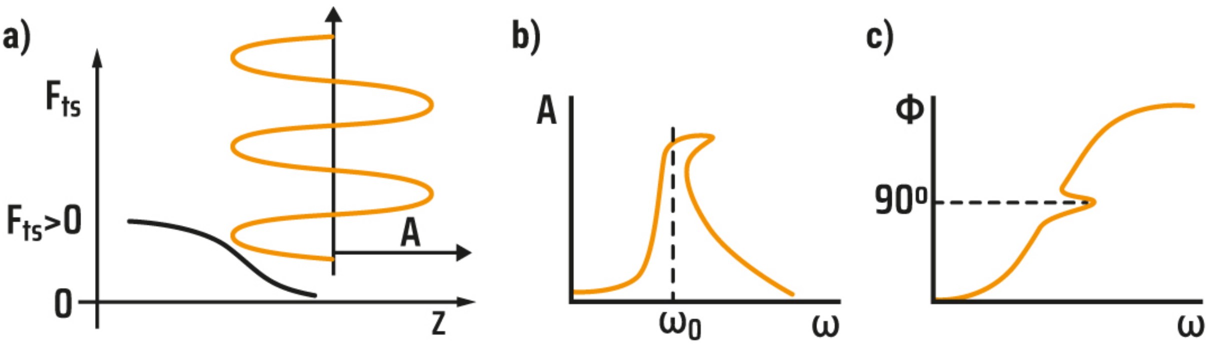

Figure 2.6. NONLINEAR CASE. a) Illustration of a nonlinear (repulsive) force showcasing how a sinusoidal wave, i.e., the motion of the oscillator, would be affected by it. Corresponding illustration of a standard frequency sweep showing the b) amplitude A and c) phase ϕ response where the origin of the distortions is shown in terms of nonlinear repulsive forces only.

2.1.2.e The nonlinear response (attractive/repulsive case)

This case is expressed by Eq. 2.7. The behaviour of the amplitude A and the phase ϕ are shown in Fig. 2.7. The force has an attractive and a repulsive term. The force combines the expressions in Eqs. 2.5 and 2.6 as illustrated in Fig. 2.7.

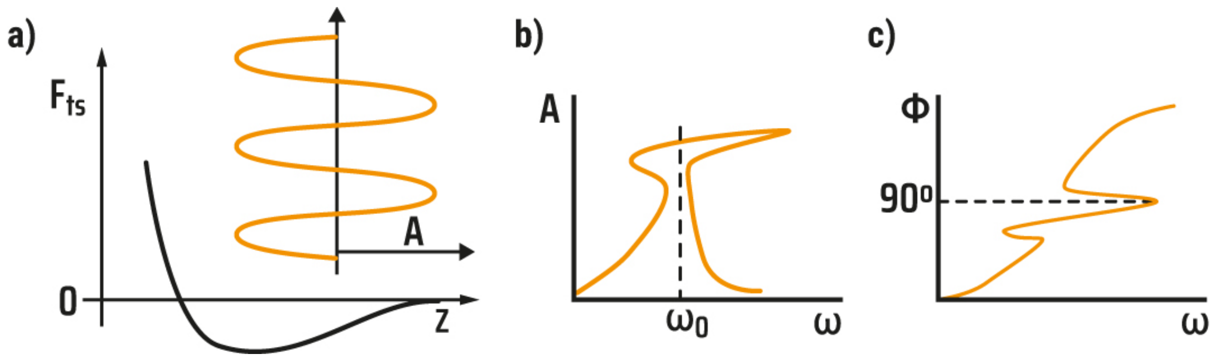

Figure 2.7. NONLINEAR CASE. a) Illustration of a nonlinear force with attractive and repulsive components showcasing how a sinusoidal wave, i.e., the motion of the oscillator, would be affected by it. Corresponding illustration of a standard frequency sweep showing the b) amplitude A and c) phase ϕ response where the origin of the distortions is shown in terms of the presence of nonlinear attractive and repulsive forces.

2.1.3 Summary

The above figures (2.3 to 2.7) and the respective nonlinear equations of motion, i.e., Eq. 2.5-2.7, have been descriptively discussed only since the nonlinear terms must be well parametrized in order to avoid divergence and to determine their value as a function of z to avoid other similar problems. Typically, the parametrization or determination will be established from the phenomena being modelled. Note for example that Eqs. 2.5 and 2.7 are not well defined for z=0 because there is a term that divides by zero. In AFM the physical interpretation to avoid this problem is that there cannot be matter interpenetration. That is, two bodies cannot occupy the same space. The distance from the tip to the sample will determine the actual values of z. Otherwise the discussion above is general.

Equations Eq. 2.5-2.7 will be parametrized below in order to better analyse such phenomenon and understand the models and the physical system in AFM.

Finally, it is worth remembering that the physical representation of the variables in the equations of motion (Eq. 2.5-2.7) do not have to be position or time. The implication is that any phenomena that can be represented by a model mathematically equivalent to the above can also be analysed via the discussion provided here and extended below.

2.2 The cantilever and tip-sample system in AFM: forces

The discussion above and the interpretation of Figs. 2.3 to 2.7 is general but the nonlinear terms in Eq. 2.5 to 2.7 have not been well defined yet. The definition or determination of these terms depends on the experimental set-up or, theoretically, on the parameters of the model being considered.

Here we proceed to constrain the parameters of the nonlinear terms in order to understand more clearly how the amplitude and phase response vary as a function of ω. For this purpose we use a typical model for the tip-sample force employed in AFM. In AFM the distance d is measured from the surface of the sample to the tip. The schematic of the geometry of the cantilever-tip-sample system is shown in Fig. 2.8. A main constrain worth mentioning is that d = zc +z.

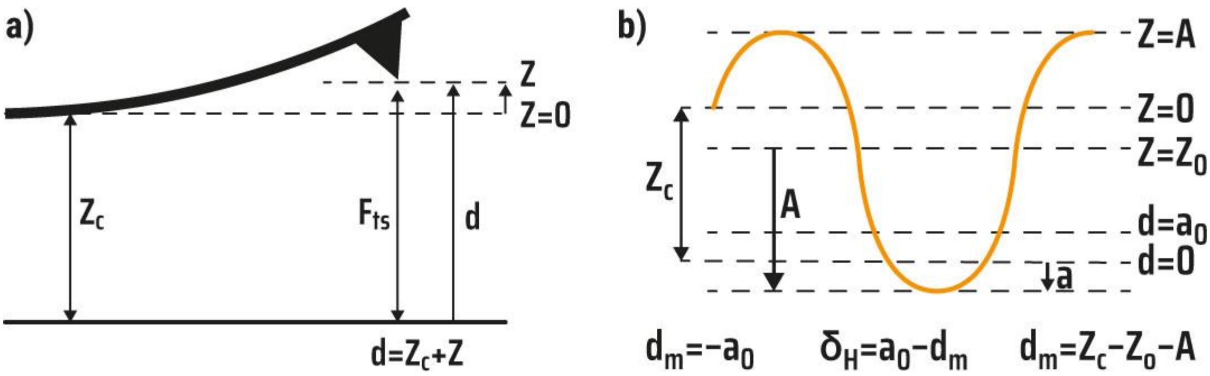

Figure 2.8. a) Schematic of an AFM cantilever from which geometrical constraints can be derived. b) Illustration of the tip' motion showcasing the geometric parametrization.

2.2.1 The attractive force

The attractive force is typically modelled by invoking the van der Waals force considering an approach first developed by Hamaker[18-19]. This is a force of attraction since it tends to pull surfaces towards each other (Fig. 2.7). The surface here provides the constraint that determines a zero distance d. In this model, the tip is modelled a sphere of radius R where R parametrizes the geometry of the tip. The force is proportional to H (Hamaker) where H depends on the properties of the tip and the sample. Then the attractive force is

$$d = z_c + z$$

$$\alpha = \frac{RH}{6}$$

$$F_{ts} = -\frac{\alpha}{d^2} \qquad\qquad d > a_0$$

$$F_{ts} = -\frac{\alpha}{a_0^2} = F_{AD} \qquad\qquad d \leq a_0 \qquad\qquad \text{Eq. 2.14}$$

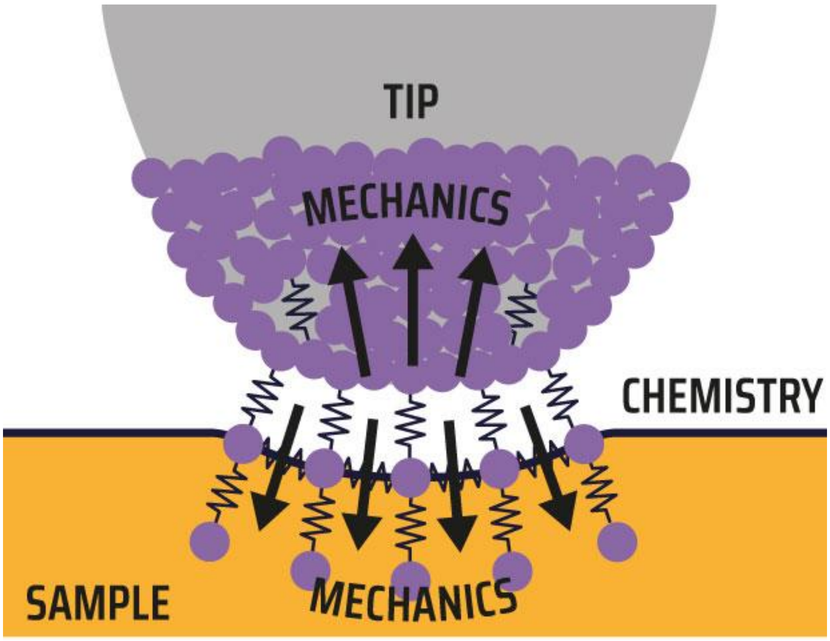

Figure 2.9. Illustration showcasing the interaction between an AFM tip and a surface where attractive and repulsive forces result from chemical and mechanical interactions. See a detailed discussion in the literature. [20]

Eq. 2.14 has a parameter a_0 which physically represents an intermolecular distance that impedes matter interpretation[21], i.e., the tip's and the sample's atoms cannot occupy the same distance (Fig. 2.7). At $d=a_0$ we have minima for F_{ts}, or the force of adhesion F_{AD}. Beyond a_0 the surfaces cannot physically come any closer so mechanical deformation occurs. An illustration of such phenomenon is shown in Fig. 2.9. This implies that negative values of d are possible but physically these correspond to sample deformation δ[20]. The force profile (or nonlinear term) resulting from Eq. 1.14 is illustrated in Fig. 2.10.

The parameter a_0 in Eq. 2.14 solves the problem of divergence since the nonlinear term in Eq. 2.5 never divides by zero because d is never zero.

If there was no other force and if the tip oscillated only at distances $d < a_0$, the attractive force would only shift the equilibrium position and the equation would reduce to a linear equation of motion (see chapter 1. 6).

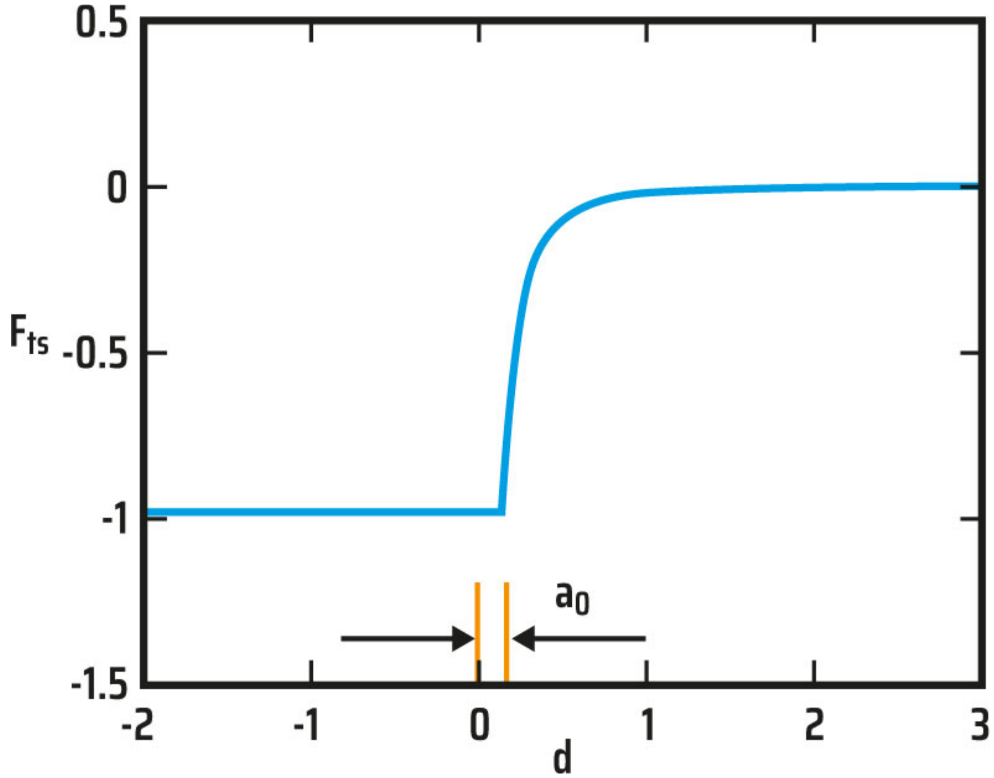

Figure 2.10. Example of an attractive force F_{ts} shown as a function of distance d and representing the force in Eq. 2.14. a_0 is an intermolecular distance that ensures that d is never zero, i.e., two bodies never occupy the same space.

2.2.2 The repulsive force

From the schematic in Fig. 2.6 the general equation for the tip-sample instantaneous distance d (ignoring higher harmonics and modes) can be written as

$$z = z_0 + Acos(\omega t - \phi)$$

$$d = z_c + z_0 + Acos(\omega t - \phi) \quad \text{Eq. 2.15}$$

where z_0 is the mean deflection and negative if the mean force $<F_{ts}>$ is negative and positive otherwise. From the schematic in Fig. 2.7 the minimum distance of approach is given when $z = -A$, then

$$d_m = z_c + z_0 - A \qquad \text{Eq. 2.16}$$

Typically the mean deflection z_0 is much smaller than A so that

$$d_m \approx z_c - A \qquad \text{Eq. 2.17}$$

The cantilever-sample separation z_c can be written in terms of physically meaningful parameters from Eqs. 2.16-2.17

$$z_c = d_m - z_0 + A \qquad \text{Eq. 2.18}$$

Assume now that $z_c + a_0 < A + |z_0|$ where $z=A\cos(\omega t-\phi)$. Then there are values of d during an oscillation for which $d < a_0$. At this point mechanical contact occurs, that is, there is mechanical deformation $\delta > 0$. The deformation can be written as

$$\delta = a_0 - d \qquad d \leq a_0 \qquad \text{Eq. 2.19}$$

The maximum of deformation δ_M can be written as

$$\delta_M = a_0 - d_m \qquad \text{Eq. 2.20}$$

In terms of observables A and z_0,

$$d = d_m + A + A\cos(\omega t - \phi) \qquad \text{Eq. 2.21}$$

$$\delta = a_0 - d \qquad d \leq a_0 \qquad \text{Eq. 2.22}$$

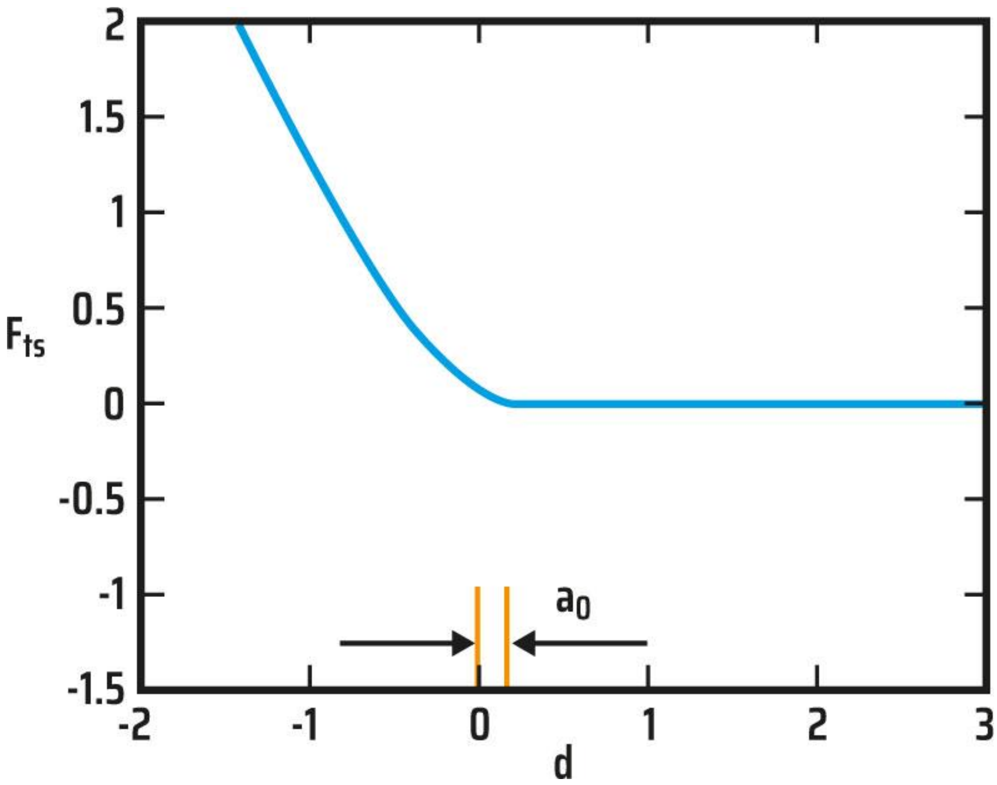

Figure 2.11. Example of a repulsive force F_{ts} shown as a function of distance d and representing the force in Eq. 2.23. a_0 is an intermolecular distance that ensures that d is never zero, i.e., two bodies never occupy the same space.

The repulsive force in Eqs. 2.6 and 2.7 is typically expressed in AFM as follows[11, 18, 22-23]

$$d = z_c + z$$

$$\beta = \frac{4}{3}E'\sqrt{R}$$

$$\delta = a_0 - d \qquad d \leq a_0$$

$$\beta\delta^{3/2} \qquad \text{Eq. 2.23}$$

where E' is the reduced elastic modulus of tip and sample pair and R is the effective radius of the tip. With the above set of expression the repulsive term is parametrized and physically determined in AFM. Namely, the term is non zero and positive only where there is sample deformation, .i.e., $\delta \geq 0$ (Figs. 2.8 and 2.9).

2.2.3 The tip-sample interaction: attractive-repulsive components

The expressions in Eq. 2.14 and 2.23 can be added to give a force profile (Fig. 2.10) identified with the Dejarguin-Muller-Toporov (DMT) theory of contact mechanics[14, 24] where

$$F_{ts} = -\frac{RH}{6d^2} \qquad d > a_0$$

$$F_{ts} = -F_{AD} + \frac{4}{3}E'\sqrt{R}\delta^{3/2} \qquad d \leq a_0 \qquad \text{Eq. 2.24}$$

The profile shown in Fig. 2.12 displays both attractive and repulsive nonlinearities. This agrees with the claim that, in AFM, the amplitude and phase curves expressed in terms of ω may present distortions as those shown in Figs. 2.3-2.7. More complex models are sometimes discussed in the literature. In particular, dissipative forces may also distort the curves. The analytical expressions leading to such distortions in terms of conservative and dissipative contributions will be the object of the next chapters.

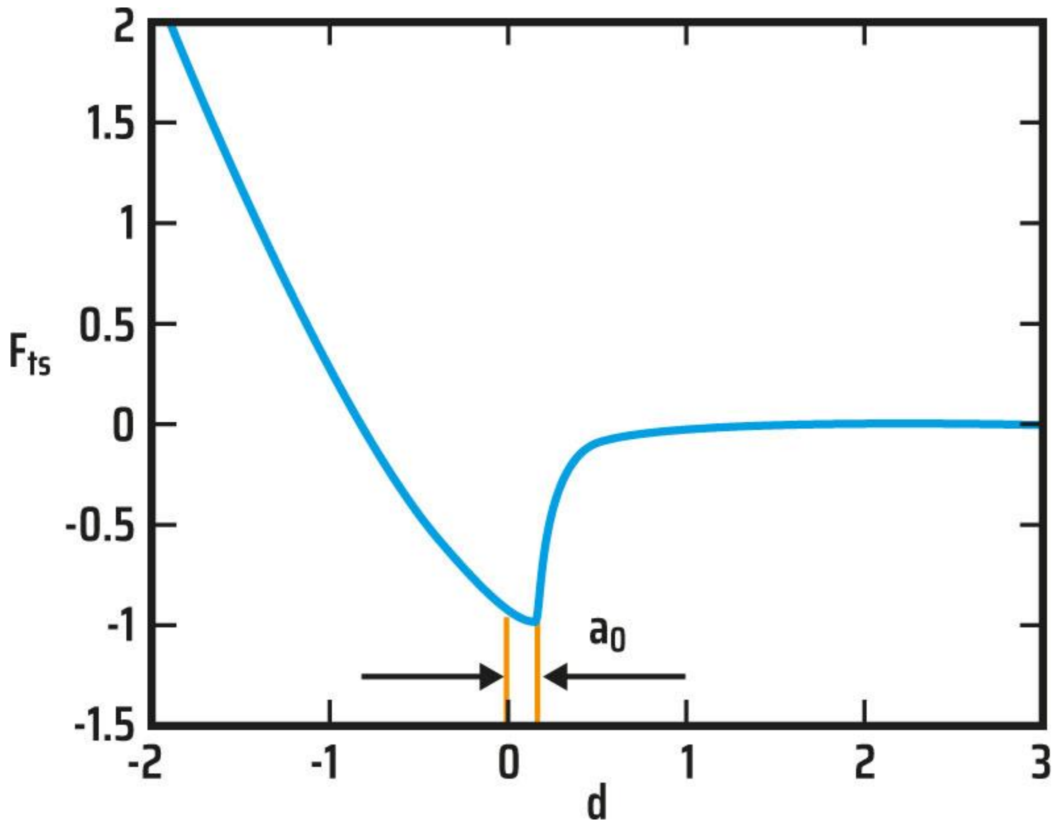

Figure 2.12. Example of attractive and repulsive forces F_{ts} shown as a function of distance d and representing the force in Eqs. 2.24. a_0 is an intermolecular distance that ensures that d is never zero, i.e., two bodies never occupy the same space.

2.3 Conservative and dissipative terms: the virial and energy dissipation

Here the theory of nonlinear interactions is developed by solving the equation of motion in Eq. 2.3. The equation is reproduced here to examine the terms

$$m\frac{d^2z}{dt^2}+\frac{m\omega_0}{Q}\frac{dz}{dt}+kz=F_{ts}+F_0\cos\ \omega t \qquad \text{Eq. 2.25}$$

2.3.1 Energy dissipation

In 1998 Tamayo and García[25-26] and Cleveland, Anczykowski, Schmid, and Elings[27-28] independently developed a formalism based on Eq. 225 to compute an expression to for the energy dissipated in the tip-sample interaction. This energy is dissipated because of the dissipative component of F_{ts} and is to be distinguished from the dissipation due to the linear term $\frac{m\omega_0}{Q}\frac{dz}{dt}$. Cleveland et al. focused on the average power dissipated per cycle while Tamayo and García focused on the average energy dissipated per cycle. Physically, it is arguably more relevant to speak of average power, that is, of energy per second but energy dissipation is meaningful when one speaks of physical processes. For example, atomic phenomena is typically considered in eV units and the energy dissipate per cycle in dynamic AFM is also expressed in these units, i.e. $<E_{dis}>$ ~ 1-100 eV[29]. In any case moving from energy to power is straight forward

$$<P_{dis}>_{cycle}=\frac{<E_{dis}>_{cycle}}{T} \qquad \text{Eq. 2.26}$$

Here we will simplify the notation by writing

$$<E_{dis}>_{cycle}\equiv\ E_{dis} \qquad \text{Eq. 2.27}$$

The energy dissipated per cycle can be obtained directly by considering that this is the work done by the force F_{ts} per cycle. The period T determines the length of a cycle in terms of time. Then

$$E_{dis}=-\int_0^T\ F_{ts}\dot{z}dt \qquad \text{Eq. 2.28}$$

where it is assumed that (compare with Eq. 98) the response is harmonic

$$z = z_0 + A\cos(\omega t - \phi)$$

$$z \approx A\cos(\omega t - \phi) \qquad \text{Eq. 2. 29}$$

Derivatives over time produce

$$\dot{z} = -\omega A\sin(\omega t - \phi) \qquad \text{Eq. 2.30}$$

$$\ddot{z} = -\omega^2 A\cos(\omega t - \phi) \qquad \text{Eq. 2.31}$$

Note that while φ < 0, we have taken the convention of assigning the sign already in Eq. 2.29. Then the angle, i.e., the phase shift between the drive and the response will be taken as an absolute value. Eq. 2.28 can be derived from unknowns by rearranging Eq. 2.3 (2.25)

$$m\frac{d^2z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz = F_0\cos\omega t + F_{ts}$$

$$-F_{ts} = F_0\cos\omega t - m\frac{d^2z}{dt^2} - \frac{m\omega_0}{Q}\frac{dz}{dt} - kz$$

$$E_{dis} = -\int_0^T F_{ts}\dot{z}dt$$

$$E_{dis} = \int_0^T \left[F_0\cos\omega t - m\frac{d^2\dot{z}}{dt^2} - \frac{m\omega_0}{Q}\frac{dz}{dt} - kz\right]\dot{z}dt \qquad \text{Eq. 2.32}$$

The term z only appears as kz. The other terms only contain $\dot{z}$ or $\ddot{z}$. Note that all the terms on the right are identical to the terms of the linear theory. Compare for example Eq. 2.2 with Eq. 2.33 below

$$m\frac{d^2z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz = F_0\cos\omega t + F_{ts}$$

$$0 = F_0\cos\omega t - \left[m\frac{d^2z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz\right] \qquad F_{ts}=0 \qquad \text{Eq. 2.33}$$

Then, E_{dis} is found by solving the integrals of the 4 linear terms (the knowns) as follows

$$E_{dis} = -\int_0^T F_{ts}\dot{z}dt$$

$$E_{dis} = \int_0^T \left[F_0 \cos \omega t - m\frac{d^2\dot{z}}{dt^2} - \frac{m\omega_0}{Q}\frac{dz}{dt} - kz\right]\dot{z}dt$$

$$E_{dis} = I_1 + I_2 + I_3 + I_4 \qquad \text{Eq. 2.34}$$

Note that if the integrals of the 4 terms on the right cancel out E_{dis}=0. Each of the integrals can be easily solved by considering orthogonality

$$I_1 = \int_0^T F_0 \cos \omega t \, \dot{z}dt$$

$$I_1 = -\omega F_0 A \int_0^T \sin(\omega t - \phi) \cos \omega t \, dt$$

$$I_1 = -\omega F_0 A \int_0^T [\sin(\omega t) cos\phi - \cos(\omega t) sin\phi] \cos \omega t \, dt$$

$$I_1 = \omega F_0 A \int_0^T cos^2(\omega t) sin\phi dt$$

$$I_1 = \omega F_0 A sin\phi \frac{T}{2}$$

$$I_1 = \pi F_0 A sin\phi \qquad \text{Eq. 2.35}$$

$$I_2 = -\int_0^T m\frac{d^2 z}{dt^2}\dot{z}dt$$

$$I_2 = \omega^3 A^2 m \int_0^T \cos(\omega t - \phi)\sin(\omega t - \phi)dt$$

$$I_2 = \omega^3 A^2 m \int_0^T [-\cos^2(\omega t)\cos\phi sin\phi + \sin^2(\omega t)\cos\phi sin\phi]dt$$

$$I_2 = \omega^3 A^2 m\cos\phi sin\phi \int_0^T [\sin^2(\omega t) - \cos^2(\omega t)]dt$$

$$I_2 = \omega^3 A^2 m\cos\phi sin\phi [\tfrac{T}{2} - \tfrac{T}{2}]$$

$$I_2 = 0 \qquad \text{Eq. 2.36}$$

$$I_3 = -\int_0^T \frac{m\omega_0}{Q} \dot{z}^2 dt$$

$$I_3 = -\frac{m\omega_0}{Q} A^2\omega^2 \int_0^T \sin^2(\omega t - \phi) dt$$

$$I_3 = -\frac{m\omega_0}{Q} A^2\omega^2 \left[\frac{T}{2}[\sin^2\ \phi + \cos^2\ \phi]\right]$$

$$I_3 = -\frac{m\omega_0}{Q} \omega\pi A^2 \qquad \text{Eq. 2.37}$$

$$I_4 = -k \int_0^T z\dot{z} dt$$

$$I_4 = -k \int_0^T [z_0 + A\cos(\omega t - \phi)]\dot{z} dt$$

$$I_4 = \mathrm{k}A^2\omega \int_0^T \cos(\omega t - \phi)\sin(\omega t - \phi) dt - kz_0 \int_0^T \dot{z} dt$$

$$I_4 = 0 \qquad \text{Eq. 2.38}$$

We note from the above result that z_0 does not add to E_{dis}. Finally, combining Eqs. 2.34-2.38

$$E_{dis} = \pi F_0 A sin\phi - \frac{m\omega_0}{Q} \omega\pi A^2 \qquad \text{Eq. 2.39}$$

Where the term containing the sign is always positive or zero since $0° \leq \varphi \leq 180°$. The last term is always negative because there is a minus sign and all the terms involved are positive. Note that F_0 depends on ω amongst other and it can be experimentally found by considering the expression for A from the linear results (Eq. 2.8). The above expression already gives us a condition for $E_{dis}=0$

$$0 = \pi F_0 A sin\phi - \frac{m\omega_0}{Q} \omega\pi A^2$$

$$sin\phi = \omega \frac{m\omega_0}{Q} \frac{A}{F_0}$$

$$sin\phi = \omega b \frac{A}{F_0} \qquad \text{Eq. 2.40}$$

When $\omega=\omega_0$

$$sin\phi = \frac{m\omega_0^2}{Q}\frac{A}{F_0}$$

$$sin\phi = \frac{k}{Q}\frac{A}{F_0}$$

$$sin\phi = \frac{A}{A_0}$$

$$\phi = sin^{-1}(\frac{A}{A_0}) \qquad \text{Eq. 2.41}$$

The only non-zero terms are the one related to viscosity, i.e., Q, and the one derived from the drive. This is because in the steady state the kz term and the inertia terms remain constant and neither add not subtract from the energy delivered by the driving force. In the steady state the drive is the only term delivering energy to the system and the only terms dissipating are the linear viscosity and the nonlinear part of F_{ts} provided there are dissipative forces introduced by F_{ts}. This is intuitive and Eq. 2.39 simply confirms this.

The above expression provides two branches for $E_{dis}=0$ since sinφ is symmetric around φ=90°. The phase shift is thus prescribed from A and A_0 alone if $E_{dis}=0$. This is shown Fig. 2.13. In particular, in dynamic AFM A_0 is the free amplitude obtained when there is no tip-sample interaction. In AM AFM A can be set as a target by the user. The amplitude A is reduced when there is interaction.

The following equation also applies because of the phenomenon being analysed cannot act as a drive, i.e., can never make the amplitude larger than the amplitude when $F_{ts}=0$. Then,

$$0 \leq \frac{A}{A_0} \leq 1 \qquad \text{Eq. 2.42}$$

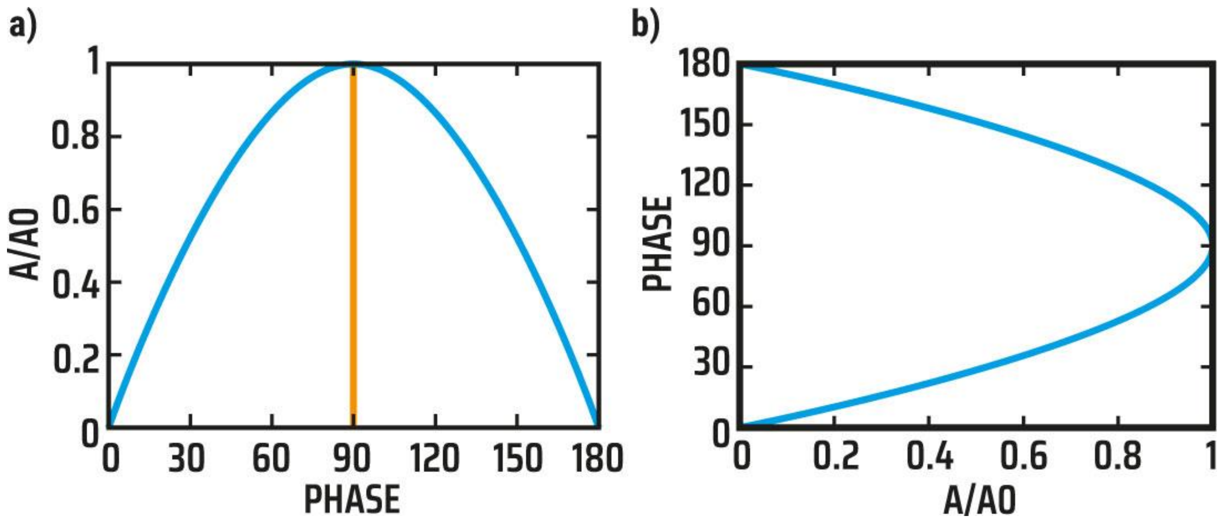

Figure 2.13. NONLINEAR RESPONSE. a) Graph displaying the behaviour of the amplitude A normalized in terms of the unperturbed or free amplitude A_0 as a function of phase ϕ. The graph shows the behaviour when only conservative nonlinear terms are present. Two branches can be observed. In AFM these are called attractive and regime regimes, but they can be identified with the available states, H and L, in Fig. 2.3. b) The same graph plotted in terms of A/A_0 in the x-axis. See the literature for more details[30].

In 2012 Gadelrab et al.[30] discussed that only values of phase shift φ lying within the function in Fig. 2.13 are physically possible. This is because values of φ lying above the curve would imply that the system is generating energy. This is against energy conservation and thus impossible. For example, since the forces in Eq. 2.24 are conservative, for a given amplitude A and a given drive force producing A_0 the constraints in phase φ in Eqs. 2.41 and 2.42 must apply. This means that any contrast in phase φ images when maintaining A, A_0 and ω constant must be due to dissipative interactions. The constraint can be written as follows:

There will be dissipation as indirectly observed from phase shifts φ whenever

$$\frac{A}{A_0} < sin\phi \qquad \text{Eq. 2.43}$$

This is interesting since it provides a means to interpret phase contrast in AM AFM and also in frequency modulation FM AFM. In AM AFM A is constant while imaging while in FM AFM it might vary. From the above discussion it follows that

1) In AM AFM, heterogeneity in dissipative interactions will be observed as phase contrast maps.

2) Whenever $A/A_0 < \sin\varphi$, it can be concluded that there is dissipation in the tip-sample interaction. Mechanisms of dissipation can thus be investigated.

3) Furthermore, for a given set of driving parameters A, A_0 and ω, a difference of phae shift can be defined Δφ where

$$\Delta\phi = \phi - sin^{-1}(\frac{A}{A_0}) \qquad \text{Eq. 2.44}$$

The larger the above in a phase contrast map the more dissipation. This provides an indirect method to visually interpret energy dissipation in phase contrast images. For example, in Fig. 2.14 (adapted from reference 30) below a phase contrast image obtained in AM AFM was investigated[30] where the system was a carbon nanotube (CNT) on a quartz surface. By plotting Δφ instead of φ the data clearly shows that more energy is dissipate on the CNT than on the quartz surface.

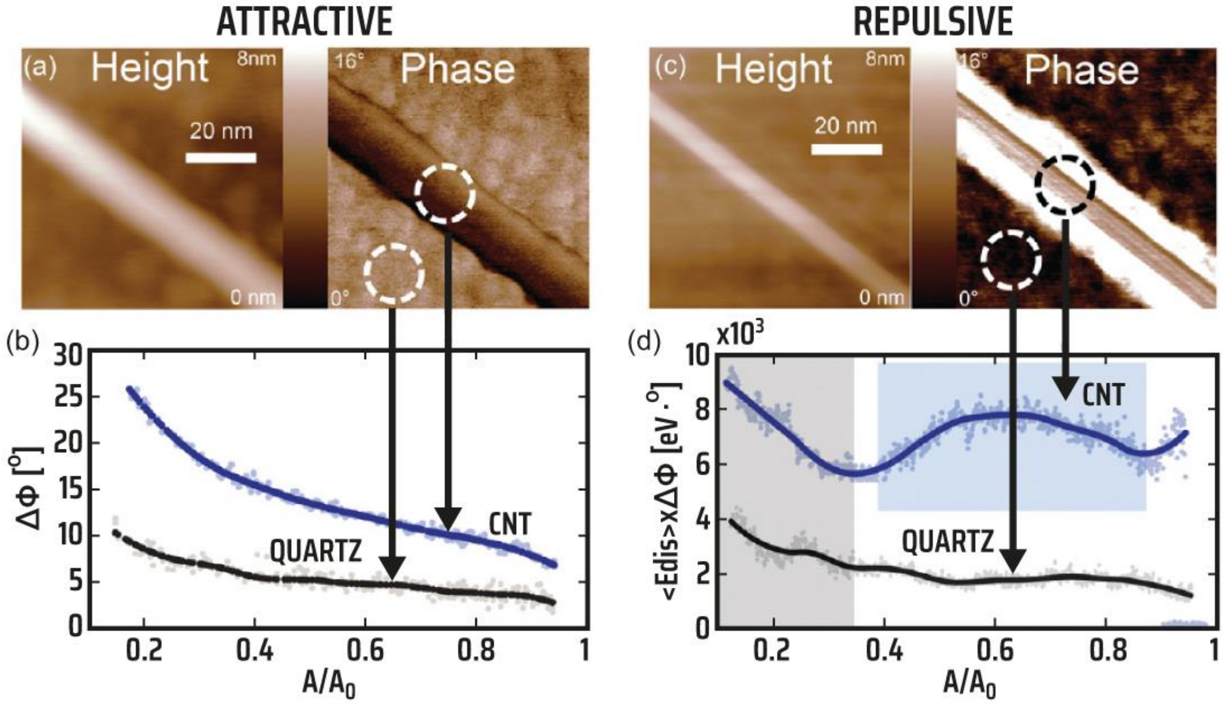

Figure 2.14. a) Height and phase contrast for a CNT on a quartz surface obtained in the attractive regime. b) The phase difference Δϕ from Eq. 2.44 is plotted as a function of A/A_0. c) Height and phase contrast for the same CNT and quartz system obtained in the repulsive regime. d) The product $E_{dis}\Delta\varphi$ is shown to lead to distinctive maxima at intermediate A/A_0 values for viscous and hysteretic dissipation. See the literature for details[30]. Journal of Physics D: Applied Physics 45, 1 (2011). Copyright 2011 IPO Publishing.

Finally, the energy dissipation expression in Eq. 2.39 can be written more compactly for $\omega=\omega_0$ as

$$E_{dis}(d) = \frac{\pi k A_0 A(d)}{Q}\left[\sin(\Phi(d)) - \frac{A(d)}{A_0}\right] \qquad \text{Eq. 2.45}$$

where the expression emphasizes that both A and φ are a function of d or d_m (see schematic in Fig. 2.8). The energy dissipation expression can also be interpreted as the F_{ts} term doing work on the mass-spring system does reducing its energy. From this interpretation it follows that the work done should be written in terms of a negative sign

$$E_{dis} = \int_0^T F_{ts}\dot{z}dt \qquad \text{Eq.2.46}$$

Here E_{dis} would be negative, but the interpretation clarifies that it is the work done by the force on the system, i.e., the work done would be less than zero because Fts can only remove energy from the system.

2.3.2 The virial of the interaction

In 2001 San Paulo and García exploited the virial theorem[31] to find a transfer function from Eq. 2.3. The virial theorem was introduced for the first time in 1870 by Rudolf Clausius[32] but San Paulo and García referred to a classical book in classical mechanics[33]. The theorem "provides a general equation that relates the average over time of the total kinetic energy of a stable system of discrete particles, bound by potential forces, with that of the total potential energy of the system."[34] Mathematically and in relation to Eq. 2.3 San Paulo and García used the fact that "the time averaged kinetic energy of the tip is equal to its virial"[31]. Then

$$< KE > = \frac{1}{2} m < \dot{z}^2 > = -\frac{1}{2}\langle F_{ts} z\rangle$$

$$V = \langle F_{ts} z\rangle = \frac{1}{T}\int_0^T F_{ts} z dt \qquad \text{Eq. 2.47}$$

Here V is the virial of F_{ts}. The average kinetic energy <KE> was already computed Eq. 39 in chapter 1.5, and the method to compute it is equivalent to that obtained when considering the linear system

$$< KE >= \frac{1}{T}\int_0^t \frac{1}{2} m\dot{z}^2 dt$$

$$< KE >= \frac{1}{2}\mathrm{m} < \dot{z}^2 > \qquad \text{Eq. 2.48}$$

The method to compute the virial if the same as that used in the previous section. Namely, from the equation of motion Eq. 2.3

$$m\frac{d^2z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz = F_0 \cos\omega t + F_{ts}$$

$$0 = -F_0 \cos \omega t + \left[m \frac{d^2 z}{dt^2} + \frac{m\omega_0}{Q} \frac{dz}{dt} + kz \right] \qquad F_{ts}=0 \qquad \text{Eq. 2.49}$$

Then, V is found by solving the integrals of the 4 linear terms as follows

$$V = < F_{ts} z > = \frac{1}{T} \int_0^T \left[-F_0 \cos \omega t + m \frac{d^2 z}{dt^2} + \frac{m\omega_0}{Q} \frac{dz}{dt} + kz \right] zdt$$

$$V = I_1 + I_2 + I_3 + I_4 \qquad \text{Eq. 2.50}$$

Note that if the integrals of the 4 terms on the right cancel out V=0. Each of the integrals can be easily solved by considering orthogonality. The term z_0 will only be considered in the integral that contains the kz terms since it can be easily shown from orthogonality that the product of a constant, i.e., z_0, and a sine or cosine integrated over a cycle is 0.

$$I_1 = -\frac{1}{T} \int_0^T F_0 \cos \omega t \, zdt$$

$$I_1 = -\frac{1}{T} \int_0^T F_0 \cos \omega t \, [z_0 + \mathrm{A}\cos(\omega t - \phi)] dt$$

$$I_1 = -\frac{1}{T} z_0 \int_0^T F_0 \cos \omega t \, dt - \frac{1}{T} z_0 \int_0^T F_0 \cos \omega t \, \mathrm{A}\cos(\omega t - \phi) dt$$

$$I_1 = -F_0 A \frac{1}{T} \int_0^T \cos(\omega t - \phi) \cos \omega t \, dt$$

$$I_1 = -F_0 A \frac{1}{T} \int_0^T [\cos(\omega t) cos\phi + \sin(\omega t) sin\phi] \cos \omega t \, dt$$

$$I_1 = -F_0 A \frac{1}{T} \int_0^T cos^2(\omega t) cos\phi dt$$

$$I_1 = -F_0 A \frac{1}{T} cos\phi \frac{T}{2}$$

$$I_1 = -\frac{1}{2} F_0 A cos\phi \qquad \text{Eq. 2.51}$$

$$I_2 = \frac{1}{T}\int_0^T m\frac{d^2z}{dt^2}zdt$$

$$I_2 = \frac{1}{T}\int_0^T m\frac{d^2z}{dt^2}[z_0 + \mathrm{A}\cos(\omega t - \phi)]\,dt$$

$$I_2 = -\frac{1}{T}\omega^2 Amz_0\int_0^T \cos(\omega t - \phi)dt - \frac{1}{T}\omega^2 A^2 m\int_0^T \cos(\omega t - \phi)\cos(\omega t - \phi)dt$$

$$I_2 = -\frac{1}{T}\omega^2 A^2 m\int_0^T \cos(\omega t - \phi)\cos(\omega t - \phi)dt$$

$$I_2 = -\frac{1}{T}\omega^2 A^2 m\int_0^T [\cos(\omega t)cos\phi + \sin(\omega t)sin\phi]^2 dt$$

$$I_2 = -\frac{1}{T}\omega^2 A^2 m\int_0^T [\cos^2(\omega t)\cos^2\phi\ + \sin^2(\omega t)\sin^2\phi\ ]^2 dt$$

$$I_2 = -\frac{1}{T}\omega^2 A^2 m\left[\frac{T}{2}\cos^2\phi + \frac{T}{2}\sin^2\phi\right]$$

$$I_2 = -\tfrac{1}{2}\omega^2 A^2 m \qquad \text{Eq. 2.52}$$

$$I_3 = \frac{1}{T}\int_0^T \frac{m\omega_0}{Q}\dot{z}zdt$$

$$I_3 = \frac{1}{T}\int_0^T \frac{m\omega_0}{Q}\dot{z}[z_0 + \mathrm{A}\dot{\cos}(\omega t - \phi)]dt$$

$$I_3 = -\frac{1}{T}\frac{m\omega_0}{Q}Az_0\omega\int_0^T \sin(\omega t - \phi)dt - \frac{1}{T}\frac{m\omega_0}{Q}\omega A^2\int_0^T \sin(\omega t - \phi)\cos(\omega t - \phi)dt$$

$$I_3 = -\frac{1}{T}\frac{m\omega_0}{Q}\omega A^2\int_0^T \sin(\omega t - \phi)\cos(\omega t - \phi)dt$$

$$I_3 = \frac{1}{T}\frac{m\omega_0}{Q}\omega A^2 \cos\phi sin\phi[\frac{T}{2} - \frac{T}{2}]$$

$$I_3 = 0 \qquad \text{Eq. 2.53}$$

$$I_4 = \frac{1}{T}k\int_0^T z^2 dt$$

$$I_4 = \frac{1}{T}k\int_0^T [z_0 + Acos(\omega t - \phi)]^2 dt$$

$$I_4 = \frac{1}{T}k\int_0^T [z_0^2 + 2z_0 A(\omega t - \phi) + A^2\cos^2(\omega t - \phi)\ ]dt$$

$$I_4 = \frac{1}{T}k\int_0^T z_0^2\ dt + \frac{1}{T}k\int_0^T A^2\cos^2(\omega t - \phi)\ dt$$

$$I_4 = \mathrm{k}z_0^2 + \frac{1}{T}kA^2\int_0^T \cos^2(\omega t - \phi)\ dt$$

$$I_4 = \frac{1}{T}kA^2\left[\frac{T}{2}[\sin^2\ \phi + \cos^2\ \phi]\right]$$

$$I_4 = \mathrm{k}z_0^2 + \tfrac{1}{2}kA^2 \qquad \text{Eq. 2.54}$$

We note from the above result that z_0 does not add to the dynamic part of V. This can be shown as follows

$$V\ = \frac{1}{T}\int_0^T F_{ts} z dt$$

$$V\ = \frac{1}{T}\int_0^T F_{ts}[z_0 + Acos(\omega t - \phi)]dt$$

$$V\ = \frac{1}{T}\left[z_0\int_0^T F_{ts}dt + \int_0^T F_{ts}Acos(\omega t - \phi)dt\right]$$

$$V\ = z_0 \frac{1}{T}\int_0^T F_{ts}dt + \frac{1}{T}\int_0^T F_{ts}Acos(\omega t - \phi)dt$$

$$V\ = z_0 < F_{ts} > + \frac{1}{T}\int_0^T F_{ts}Acos(\omega t - \phi)dt \qquad \text{Eq. 2.55}$$

But $<F_{ts}> = kz_0$ as the reader can confirm by averaging all the terms of Eq. 2.3 (the equation of motion) over a cycle. Then

$$V\ = kz_0^2 + \frac{1}{T}\int_0^T F_{ts}Acos(\omega t - \phi)dt \qquad \text{Eq. 2.56}$$

Combining Eqs. 2.51-2.54 with Eq. 2.56

$$kz_0^2 + \frac{1}{T}\int_0^T F_{ts}Acos(\omega t - \phi)dt = -\frac{1}{2}F_0Acos\phi - \frac{1}{2}\omega^2A^2m + \mathrm{k}z_0^2 + \frac{1}{2}kA^2 \qquad \text{Eq. 2.57}$$

The terms multiplying z_0 cancel out. Thus

$$\frac{1}{T}\int_0^T F_{ts}Acos(\omega t - \phi)dt = -\frac{1}{2}F_0Acos\phi + \frac{1}{2}A^2[k - \omega^2m] \qquad \text{Eq. 2.58}$$

Typically it is only the term on the left hand side of Eq. 2.58 that is termed V for virial in AFM. That is, the mean deflection z_0 does and the respective average force do not count as virial. Then

$$V\ = \frac{1}{T}\int_0^T F_{ts}Acos(\omega t - \phi)dt$$

$$V = -\frac{1}{2}F_0Acos\phi + \frac{1}{2}A^2[k - \omega^2m] \qquad \text{Eq. 2.59}$$

When $\omega=\omega_0$

$$V = -\frac{1}{2}F_0 A cos\phi + \frac{1}{2}A^2[k - \omega_0^2 m] \qquad \text{any arbitrary } \omega$$

$$V = -\frac{1}{2}F_0 A cos\phi \qquad \omega=\omega_0 \qquad \text{Eq. 2.60}$$

Already in 2001 when San Paulo and García[23] described the relationship between the virial V and the cosine of the phase shift φ recognized the relationship between this relation (Eq. 2.60) and the expression for the frequency shift in FM AFM. In particular, in 1997 Giessibl[35] showed for the first time that the natural frequency ω_0 of a weakly perturbed oscillator shifts according to

$$\frac{\Delta f_0}{f_0} \approx -\frac{1}{kA^2}\langle F_{ts}z\rangle$$

$$\frac{\Delta\omega_0}{\omega_0} \approx -\frac{1}{kA^2}\langle F_{ts}z\rangle$$

$$\frac{\Delta\omega_0}{\omega_0} \approx -\frac{1}{kA^2}V \qquad \text{Eq. 2.61}$$

The derivation of Eq. 261 exploits the Hamilton-Jacobi formalism, and the reader can refer to the paper by Giessibl to find the details. The expression in Eq. 261 is in agreement with results also reported by San Paulo and García in 2002 in a paper[11] that discussed the distortion of the amplitude A versus ω curves. The authors showed the shape of the curves resulting from numerical integration of the equation of motion. The shapes of the curves produced by numerical integration are similar to the ones illustrated in Figs. 2.2-2.7. Several points are worth noting.

1) z, d, and F_{ts} are defined as positive in the direction normal and away from the surface (see Fig. 2.8). If the force is repulsive i.e., $F_{ts} > 0$, and largest when the tip is close to the surface, the largest values of $F_{ts}z$ are to be obtained for negative values of cantilever deflection z. In such cases the virial is negative, i.e., $<F_{ts}z> < 0$. The implication is that the frequency shift $\Delta\omega_0/\omega_0$ is positive, i.e., $\Delta\omega_0/\omega_0 > 0$. Namely, the curve should shift toward larger values of ω.

2) If the force is attractive instead, i.e., $F_{ts} < 0$, and largest when the tip is close to the surface, the largest values of $F_{ts}z$ are to be obtained for negative values of cantilever deflection z, i.e., z <0. In such cases the virial is positive, i.e., $\langle F_{ts}z \rangle > 0$. The implication is that the frequency shift $\Delta\omega_0/\ \omega_0$ is negative, i.e., $\Delta\omega_0/\omega_0 < 0$. Namely, the curve should shift toward larger values of ω.

3) From Eq. 2.61, the effective natural frequency of the oscillator is found to be

$$\omega_0 + \Delta\omega_0 = \omega_0 - \omega_0 \frac{1}{kA^2} V$$

$$\omega_0' = \omega_0 - \omega_0 \frac{1}{kA^2} V$$

$$\omega_0' = \omega_0 \left[1 - \frac{1}{kA^2} V\right] \qquad \text{Eq. 2.62}$$

Since φ=90 when $\omega = \omega_0'$, the phase shift φ should follow the same distortions as the amplitude.

4) When there are attractive and repulsive forces contained in Fts, the distortions should be double. Namely, and as discussed when interpreting the Figs. 2.2-2.7, attractive forces pull the curve to lower values of ω and repulsive forces pull it to higher values.

The reader can follow the interpretation of Eq. 2.61 given in the above four points by inspecting Fig. 2.4 (reproduced below as Fig. 2.15).

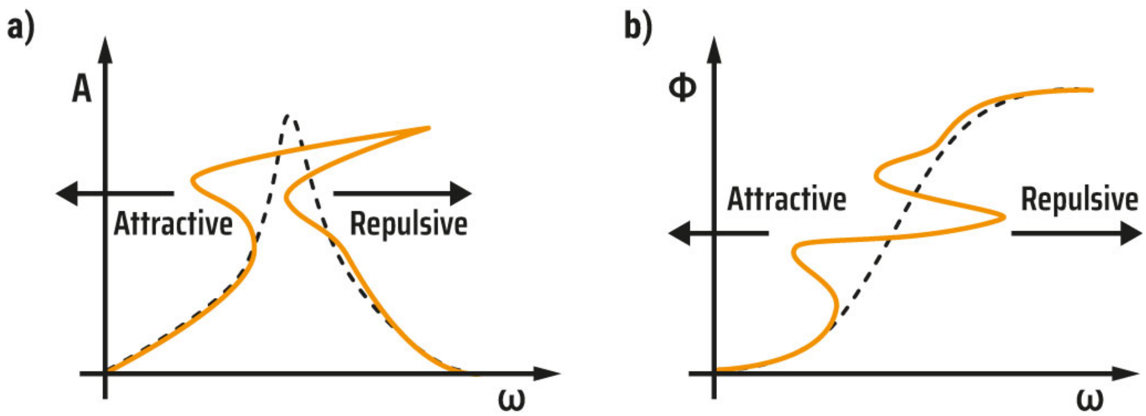

Figure 2.15. NONLINEAR CASE. Illustration of a standard frequency sweep showing the a) amplitude A and b) phase ϕ response where the origin of the distortions is shown in terms of whether nonlinear forces are attractive or repulsive. Attractive forces pull the curves to lower frequencies while repulsive forces pull them towards higher frequencies (reproduced from Fig. 2.4).

Giessibl already provided the first hint that only conservative forces affect the effective natural frequency ω_0' when he showed that Eq. 2.61 could be derived from the Hamilton-Jacobi formalism. Such formalism accounts for conservative forces. San Paulo and García derived the virial expression in 2001 and showed that the amplitude and phase curves distort in a way that agrees with Eq. 2. 61 but they felt short of writing down the relation explicitly. This relationship can be found by combining 2.60 and 2.61. To our knowledge the first to exploit this relationship were Katan et al. in 2008[36-37]. The authors showed that a general expression for force reconstruction employed in FM AFM, since Sader and Jarvis first presented them in 2004[38-39], could be employed in AM AFM by obtaining the frequency shift from the cosine of the angle.

The combination of Eqs. 2.60 and 2.61 gives ($\omega=\omega_0$)

$$\frac{\Delta\omega_0}{\omega_0} = -\frac{1}{kA^2}V$$

$$V = -\frac{1}{2}F_0 A cos\phi$$

$$\frac{\Delta\omega_0}{\omega_0} = -\frac{1}{kA^2}\left[-\frac{1}{2}F_0 A cos\phi\right]$$

$$F_0 = \frac{kA_0}{Q} = kA_D$$

$$\frac{\Delta\omega_0}{\omega_0} = \frac{1}{2}\frac{A_0}{AQ}cos\phi$$

$$\frac{\Delta\omega_0}{\omega_0} = \frac{1}{2}\frac{A_D}{A}cos\phi \qquad \text{Eq. 2.63}$$

An expression for any ω will be given in the next chapter.

2.3.3 Amplitude Modulation (AM) AFM

In AM AFM A_D, A and φ are experimentally found. More thoroughly A_D is set by the user, for a given Q, by setting a drive force that produces the required A_0. Then A must be set as a target amplitude to track the surface. The phase shift φ results from the interaction and is a "free" parameter that provides information about the tip-sample force F_{ts}. In particular, in AM AFM the frequency shift $\Delta\omega_0/\omega_0$ is responsible for the information provided by the phase shift. This is because in order to reach a given amplitude A in AM AFM while driving at a constant ω (this is typical operation in AM AFM), $\Delta\omega_0/\omega_0$ must vary, i.e., the A(ω) curve must distort.

2.3.4 Frequency Modulation (FM) AFM

In FM AFM A_D, and φ are set as a target by the user. In particular φ is set by tracking ω_0'. Here, a frequency shift is set as a target, if the amplitude A is also set to be constant, the system is then tracking a constant virial. This can be shown by referring to Eq. 2.61. In FM AFM a constant A can be targeted by tracking ω_0' and simultaneously varying the drive, i.e., F_0, to reach a target A. The distortion of the curve is the same in AM and FM since the phenomenon explored is exactly the same, i.e., a cantilever with a sharp tip vibrating near a surface. It is only the parameters being tracked tat vary from one method to another.

For more information on AM and FM AFM we refer the reader to the literature[37, 40-41].

2.4 Expanding the expressions of energy dissipation and virial

2.4.1 Virial, energy dissipation, and harmonics

In this chapter several concepts already developed will be discussed in detail to clarify some technical aspects of the formalism so far.

The derivation of the virial V and the energy dissipation terms E_{dis} has been discussed so far from a point of view of physical phenomena. The virial V has been computed by invoking the virial theorem typically exploited in statistical and classical mechanics[33]. In short the virial theorem claims that the virial of the force is

$$V = \langle F_{ts} z \rangle = \frac{1}{T}\int_0^T F_{ts} z dt \qquad \text{Eq.2.64}$$

where only the first harmonic of z is considered when computing V. This can be shown by writing z as a Fourier series expansion in its amplitude-phase form. Namely,

$$z = z_0 + A_1 cos(\omega t - \phi_1) + A_2 cos(\omega t - \phi_2) + \cdots \qquad \text{Eq. 2. 65}$$

So far we have identified A_1 with A and ϕ_1 with ϕ. Then, the virial has been computed so far as follows

$$V = \langle F_{ts} z \rangle \equiv \frac{1}{T}\int_0^T F_{ts} A_1 cos(\omega t - \phi_1) dt \qquad \text{Eq. 2. 66}$$

Strictly speaking this (Eq. 2.66) would be the virial of the fundamental harmonic A_1. This point is particularly relevant in multifrequency AFM, a technique whereby multiple drive forces, at different frequencies, are employed to excite the microcantilever[42-44]. In particular, the equation of motion of higher modes must be employed[42] when driving at higher frequencies implying that Eqs. 1-3 in chapter 1 must be considered[45].

2.4.2 Dissipative forces

The energy dissipation expression has been defined as the negative of the work done by the force F_{ts} per cycle (Eq. 2. 28)

$$E_{dis} = -\int_0^T F_{ts}\dot{z}dt \qquad \text{Eq. 2. 67}$$

Again, the derivative of Eq. 2.65 shows that, strictly speaking, E_{dis} (Eq. 2. 67) has been computed so far in terms of the first harmonic only. Then

$$E_{dis} = \int_0^T F_{ts}\omega A_1 sin(\omega t - \phi_1)dt \qquad \text{Eq. 2.68}$$

Expressions Eq. 2.66 and 2.68 show that these terms can be more or less identified with the first Fourier coefficients. In 1999, Dürig[46] used the least-action principle to derive an expression equivalent to that of Giessibl (1997, Eq. 2.61) by also developing a Fourier series expansion. Giessibl's expression was shown to be derivable by considering the lowest order harmonic approximation. In 2004, Sader et al. further proposed to expand F_{ts} in terms of its odd and even components to show that Eq. 261 for the frequency shift (FM AFM), or equivalently, the expression for the virial V by San Paulo and García in AM AFM (Eq. 2.60), contains only the odd component of F_{ts} to its first harmonic term. The "damping" was shown to contain an integral expression with the odd terms only. In 2008 Hu and Raman also made the connection between the viral and energy dissipation and Fourier series by proceeding to expand F_{ts} in terms of the Fourier coefficients. In his PhD thesis, Álvarez Amo computed (Eqs. 2.10 and 2.11 in the thesis[4]) the Fourier coefficients of F_{ts} directly from the equation of motion to then show how these, but for a factor, correspond to the typical Fourier coefficients of a_n (virial or conservative interactions) and b_n (energy dissipation or dissipative interactions).

It is important to note that both the cosine and the sine terms exploited to derive the virial V (Eq. 2.47) and E_{dis} (Eq. 2.28) contain ωt but also the angle ϕ. This is because the physical interpretation to derive these expressions is based on the work done which contains $\dot{z}$ and the virial which contains z. Hu and Raman expanded on this problem by also claiming that the nonlinear force F_{ts} can be written in terms of even and odd terms as follows[47]

$$F_{ts}(d, \dot{d}) = F_{ts}(odd) + F_{ts}(even) \qquad \text{Eq. 2.69}$$

where the expression emphasizes that forces are a function of distance d and velocity $\dot{d}$. The odd term is identified with dissipative forces as follows

$$F_{ts}(d,\dot{d})\big]_{odd} = \frac{F_{ts}(d,\dot{d}) - F_{ts}(d,-\,\dot{d})}{2} \qquad \text{Eq. 2.70}$$

The expression shows that the odd term of the force is identified with forces that are not identical independently of the sense of motion, i.e., the force depends on whether the tip moves to the surface or away from the surface. Clearly, if the force depends on the sense of motion, energy will be dissipated during each cycle. Eq. 2.71 was defined by Hu and Raman in a way that odd (dissipative) forces had to meet the condition in Eq. 2. 71[47],

$$F_{ts}(d,\dot{d}) = -F_{ts}(d,-\,\dot{d}) \;\; for\ odd/dissipative\ forces) \qquad \text{Eq. 2.71}$$

Eq. 271 would imply that the odd term contains the part of the force which depends on the sense of motion but is otherwise symmetrical. This is not strictly true. For example, Santos et al.[48] showed that the formalism in Eq. 2.70 is general enough to successfully decouple forces that are not identical independently of the sense of motion (Eq. 2.72). The following relation thus applies

$$F_{ts}(d,\dot{d}) \neq -F_{ts}(d,-\,\dot{d})\ for\ odd/dissipative\ forces) \qquad \text{Eq. 2.72}$$

The results predicted by the expression in Eq. 2.72 was confirmed by Santos et al.[48] by numerically solving the equation of motion and showing that the formalism that divides the force between odd and even components, can effectively be used to decouple hysteretic and viscous effects. In short while both hysteretic and viscous forces dissipate, hysteretic forces do not necessarily depend on $\dot{d}$ but on the sense of motion and history alone. Viscous forces on the other hand depend on the absolute value of the velocity and might or might not be symmetrical as Eq. 2.70 assumes. The description of hysteresis and viscosity given here is illustrated in Fig. 2.16. The figure shows that there might by hysteretic forces in the region of non-contact, i.e., $d > a_0$, and the region of mechanical contact, i.e., $d \leq a_0$. The same is true for viscous forces. Viscous forces are typically modelled in AFM by exploiting a Voigt model[22, 30, 49]. Then

$$F_{ts}\left(d,\dot{d}\right) = -\eta(d)(R\delta)^{1/2}\dot{d} \qquad \delta \geq 0 \qquad \text{Eq. 2.73}$$

where the viscous term might or might not depend on d, η is the viscosity of the tip-sample interaction, R is the tip radius, δ is the deformation and $\dot{d}$ is the velocity. There is a minus sign to indicate that the force opposes the motion. A hysteretic force indicates that there is force depending on the sense of motion and possibly history. For example, capillary interactions are history dependent[50]. A simply hysteretic force can be modelled in AFM as follows

$$F_{ts}\left(d,\dot{d}\right) = -\alpha F_{AD} \qquad \delta \geq 0 \text{ and } \dot{d} > 0 \qquad \text{Eq. 2.73(2)}$$

where α is a coefficient proportional to the force of adhesion F_{AD}. The condition for the even part of the force F_{ts}(even) defined by Hu and Raman (Eq. 2.74) was also put to the test by Santos et al.[48].

$$F_{ts}\left(d,\dot{d}\right)\Big]_{even} = \frac{F_{ts}(d,\dot{d})+F_{ts}(d,-\dot{d})}{2} \qquad \text{Eq. 2.74}$$

It was shown that in the presence of hysteretic components, the condition in Eq. 2.74 cannot be identified with the conservative force. Rather, the condition gives the average of the force where hysteresis is present. The implication is that Eq. 2. 74, i.e., the even components of the force, cannot be identified at once with conservative forces when hysteretic forces are present. For the same reason Eq. 2.70 cannot be identified at once with dissipative forces. Rather, if hysteretic forces are present, the force will be contained in both the even and odd components. This is also the case for the equations for the energy dissipation E_{dis}, the virial V and the frequency shift. Eqs. 2.28, 2.47 and 2.51 respectively. Some evidence of this was given by Santos et al. in 2014[51]. The dissipative and conservative components can be recovered however components if different velocities are probed to recover the force and the dissipative and conservative parts are compared for the two different tip velocities. Such a formalism was presented exploiting numerical integration by Santos et al. in 2012 but it is experimentally challenging and cumbersome[48].

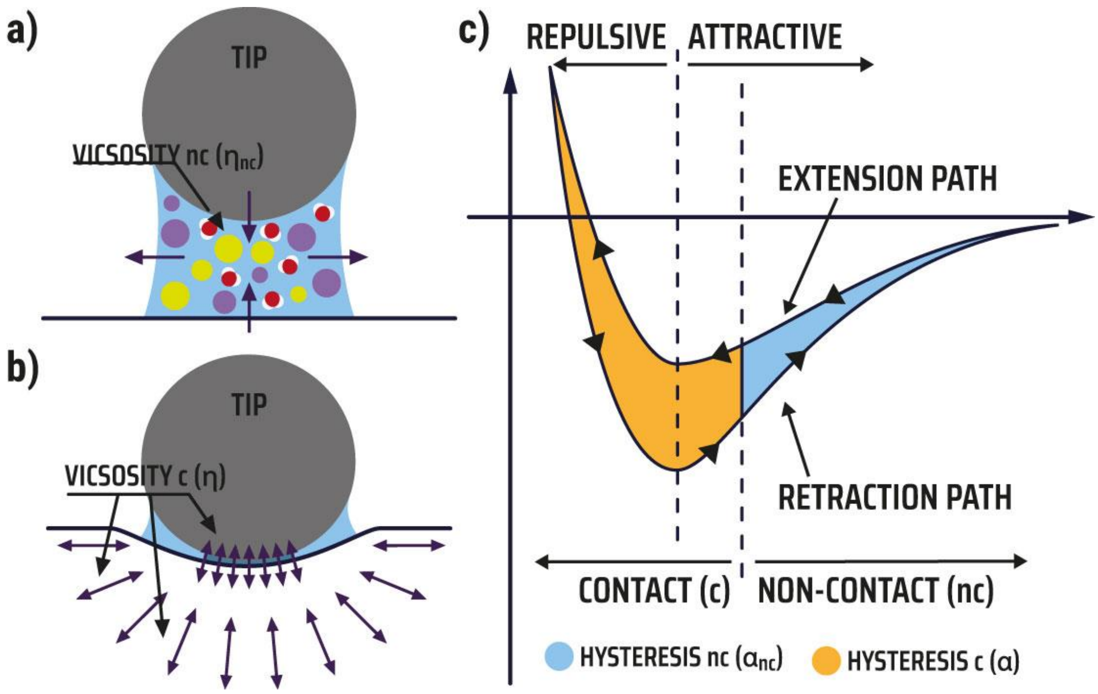

Figure 2.16. Illustrations depicting the mechanisms of viscosity in a) the nc region and b) the c region (Eq. 2.73). See the literature for details on modelling viscosity in the different regions[49]. c) Hysteretic processes (Eq. 2.73(2)) can be characterized by an increment in force depending on the sense of motion. Adapted with permission from Nanotechnology 22, 34 (2011). Copyright 2011 IPO Publishing.

In summary, strictly speaking it is best using expressions 2.70 and 2.74 to refer to even and odd forces and only roughly identify these terms with conservative and dissipative forces. This point was already emphasized by Sader et al.[39] in 2005 but it is not a well-known fact. We reproduce the discussion of this point given in 2005 by Sader et al. in full:

"However, we emphasize that such connections to 'conservative' and 'dissipative' forces, although common and appealing, can be misleading and ambiguous since the origin of the forces cannot be determined solely by analysing the harmonic motion of the tip in isolation. Indeed, it is entirely possible that the 'conservative' force results from a combination of conservative, dissipative and energy gaining processes over different parts of the oscillation cycle, even though the net energy lost or gained is zero over a complete cycle. Importantly, a formal connection to conservative and dissipative forces can only be made if the precise nature and origin of the forces involved is known. Therefore, contrary to convention, it is preferable to refer to these forces simply as 'even' and 'odd' in general, which shall henceforth be adopted."[39]

Sader et al. correctly pointe d out that the even component simply requires that "the net energy lost or gained is zero over a complete cycle." For example, as corroborated by Santos et al.[48], in the presence of hysteretic forces (Eq. 2.73) the even components produce a "mean" path, i.e., a zero net energy loss/gain over a cycle, between the approach and retract paths. In terms of the illustration of Fig. 2.16, this would mean that the average between the approach and retract paths would contribute to the frequency shit/virial in Eqs.

2.4.3 Sign conventions

The signs in the expressions are defined when the physical phenomenon is modelled. For example, the equation of motion in Eq. 2.3 can be defined in terms of z, as position (ignoring mean deflection and higher harmonics), as

$$z = A\cos\,(\omega t - \phi) \qquad \text{Eq. 2.75}$$

The virial V and energy dissipation E_{dis} expressions Eqs. 228 and 2. 64, can then be defined

$$V = \langle F_{ts} \cdot z \rangle = \frac{1}{T}\int_0^T F_{ts} A\cos\,(\omega t - \phi)dt \qquad \text{Eq. 2.76}$$

$$E_{dis} = -\int_0^T F_{ts}\dot{z}dt \qquad \text{Eq.2.77}$$

1) Since ϕ has physical significance in the driven oscillator, the minus sign in Eq. 2.75 implies that the angle obtained as the difference in phase from the response and the drive will be taken in absolute terms. Physically, the response z lags in relation to the drive $F_0\cos(\omega t)$ (see Fig. 15).

2) While sin(-ϕ) = - sinϕ, the minus sign is already considered in Eq. 275. Thus, with the above convention, sinϕ ≥ 0 always since 0 ≤ ϕ ≤ 180°.

3) The solution of the equation of motion is equivalent when defining z as

$$z = A\sin\,(\omega t - \phi) \qquad \text{Eq. 2.78}$$

Differences again arise in terms of signs since $\dot{z}$ is negative when the cosine is used instead for z. Arvind Raman[3] defines z as q and develops his theory starting from the sine as in Eq. 2.78. Still his results are equivalent as expected.

With Eq. 2.75 and using the convention in 2.77

$$z = A\cos\,(\omega t - \phi)$$

$$E_{dis} = -\int_0^T F_{ts}\dot{z}dt$$

$$E_{dis} \; = -\int_0^T F_{ts}(-\omega)A\sin\,(\omega t - \phi)dt$$

$$E_{dis} \; = \omega A \int_0^T \; F_{ts}\sin\,(\omega t - \phi)dt \qquad \text{Eq. 2.79}$$

Using the convention of Álvarez Amo[4]

$$z = A\cos\,(\omega t + \phi) \qquad \text{Eq. 2.80}$$

$$E_{dis} = \int_0^T \; F_{ts}\dot{z}dt \qquad \text{Eq.2.81}$$

$$E_{dis} \; = \int_0^T F_{ts}(-\omega)A\sin\,(\omega t + \phi)dt$$

$$E_{dis} \; = -\omega A \int_0^T \; F_{ts}\sin\,(\omega t + \phi)dt \qquad \text{Eq. 2.82}$$

where it is to be noted that ϕ is negative, i.e., $\phi \; \leq 0$, because of the definition of z in Eq. 280. The derivation is the same as that leading to Eq. 2.39

$$E_{dis} = \int_0^T F_{ts}\dot{z}dt$$

$$E_{dis} = \int_0^T \left[-F_0\cos\omega t + m\frac{d^2 z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz\right]\dot{z}dt$$

$$E_{dis} = I_1 + I_2 + I_3 + I_4 \quad \text{Eq. 2.83}$$

Note that if the integrals of the 4 terms on the right cancel out E_{dis}=0 as before. Each of the integrals can be easily solved by considering orthogonality

$$I_2 = I_4 = 0 \quad \text{Eq. 2.84}$$

$$I_1 = -\int_0^T F_0 \cos\omega t\, \dot{z} dt$$

$$I_1 = \omega F_0 A \int_0^T \sin(\omega t + \phi)\cos\omega t\, dt$$

$$I_1 = \omega F_0 A \int_0^T [\sin(\omega t) cos\phi + \cos(\omega t) sin\phi] \cos\omega t\, dt$$

$$I_1 = \omega F_0 A \int_0^T cos^2(\omega t) sin\phi dt$$

$$I_1 = \omega F_0 A sin\phi \frac{T}{2}$$

$$I_1 = \pi F_0 A sin\phi \quad \text{Eq. 2.85}$$

$$I_3 = \int_0^T \frac{m\omega_0}{Q} \dot{z}^2 dt$$

$$I_3 = \frac{m\omega_0}{Q} A^2 \omega^2 \int_0^T \sin^2(\omega t + \phi) dt$$

$$I_3 = \frac{m\omega_0}{Q} A^2 \omega^2 \left[\frac{T}{2}[\sin^2 \phi + \cos^2 \phi]\right]$$

$$I_3 = \frac{m\omega_0}{Q} \omega \pi A^2 \quad \text{Eq. 2.86}$$

Finally, combining Eqs. 2.83 to 2.86, Eq. 287 follows

$$E_{dis} = \pi F_0 A sin\phi + \frac{m\omega_0}{Q} \omega \pi A^2, \quad z = A\cos(\omega t + \phi), \; E_{dis} = \int_0^T F_{ts} \dot{z} dt \quad \text{Eq. 2.87}$$

$$E_{dis} = \pi F_0 A sin\phi + \frac{m\omega_0}{Q} \omega \pi A^2, \quad z = A\cos(\omega t + \phi), \; E_{dis} = -\int_0^T F_{ts} \dot{z} dt \quad \text{Eq. 2.88}$$

Eqs. 2.87 and 2.88 are equivalent and only the definitions change. The sign convention however needs to be taken into account. Comparing 2.87 with Eq. 2.39 (rewritten here as Eq. 2.88), obtained from the convention in 2.79, shows several issues with signs.

First, the second term on the right of Eq. 287 adds to the first term on the right.

Second sinϕ ≤ 0 in Eq. 287 since ϕ ≤ 0. This is because the response lags the drive.

Third, the first term on the right in Eq. 287 must be, from considerations of energy conservation, larger in absolute terms than the second term on the right (see discussion of Eq. 2.40 to 2.44). The result is that

$$E_{dis} = \pi F_0 A sin\phi + \frac{m\omega_0}{Q}\omega\pi A^2 < 0 \qquad \text{Eq. 2.89}$$

The interpretation of 2.89 is that the work done by dissipative forces is negative. In the definition of Eq. 228 leading to Eq. 2.39 (also 2.88), the energy dissipated is positive since the definition was for the negative of the work done, i.e., energy dissipated, rather than for the work done. While this discussion on signs leads to equivalent results, it is important to maintain the signs consistent when developing the equations in the next chapters.

At $\omega=\omega_0$, Eq. 2.89 gives

$$E_{dis}(d) = \frac{\pi k A_0 A(d)}{Q}\left[\sin\big(\phi(d)\big) + \frac{A(d)}{A_0}\right] \qquad \text{Eq. 2.90}$$

where it is explicitly stated that E_{dis}, ϕ, and A depend on d. Strictly speaking Eq. 2.90 should be defined as word done per cycle. Again Eqs. 2.45 and 2.90 are equivalent but the signs are inverted because of the definition of E_{dis}.

Finally, note that Arvind Raman, in his course, obtains an expression like that in Eq. 2.88 for E_{dis} and an expression like that in Eq. 2.59 for V when defining

$$z = A\sin(\omega t - \phi) \qquad \text{Eq. 2.91}$$

This is because Raman defines E_{dis} as the negative of the work done in agreement with the definition in Eq. 2. 28 leading to 2.39 (2.88). See nanoHUB-U Fundamentals of AFM L2.4 by Arvind Raman[3] (see Eqs. 1 and 2 there).

2.5 The virial and energy dissipation and the frequency shift

2.5.1 The tangent of the phase shift ϕ in the nonlinear theory

The nonlinear theory will be further developed in this chapter in order to derive expressions for the frequency shift of the "natural" resonant frequency, to find the transfer function of the nonlinear system to express the perturbed amplitude A in terms of E_{dis} and V.

Using Eq. 2. 59 for V (here 2.92) and Eq. 2.87 for E_{dis} (here 2.92)

$$z = A\cos(\omega t + \phi)$$

$$V = -\frac{1}{2}F_0 A cos\phi + \frac{1}{2}A^2[k - \omega^2 m] \quad \text{Eq. 2.92}$$

$$E_{dis} = \frac{m\omega_0}{Q}\omega\,\pi A^2 + F_0 A\pi \sin\phi \quad \text{Eq. 2.92(2)}$$

Since the virial V is a function of the cosine of the phase shift ϕ (-180° ≤ ϕ ≤ 0), the virial can be both positive and negative. The sine is always negative for this range (-180° ≤ ϕ ≤ 0). The energy dissipation expression must always be positive by definition. Nevertheless we have used the convention of Álvarez Amo (see the chapter on sign convention in 2.3) to express E_{dis} in terms of the work done by the Fts force (Eq. 2.92). Next an expression for tanϕ based on the thesis of Álvarez Amo[4] is developed.

Rearranging Eq. 2.92

$$2V = A^2 m(\omega_0^2 - \omega^2) - F_0\,A\cos\phi$$

$$2V = A^2 k\left(1 - \left[\frac{\omega}{\omega_0}\right]^2\right) - F_0\,A\cos\phi \quad \text{Eq. 2.93}$$

An approximation for F_0 is now employed to simplify Eq. 293

$$F_0 = \frac{kA_0}{Q} \quad \text{Eq. 2.94}$$

Eq. 2.94 assumes that $\omega=\omega_0$. See for example the linear expression for A in Eq. 2.7. Dividing Eq. 293 by 2.94

$$V\,\frac{2Q}{kA_0} = \frac{Q}{A_0}\left[1-\left(\frac{\omega}{\omega_0}\right)^2\right]A^2 - \mathrm{A}\cos\phi \qquad \text{Eq. 2.95}$$

Rearranging the expression for E_{dis} in Eq. 2.92 (again following Álvarez Amo's development)

$$E_{dis} = \frac{m\omega_0}{Q}\,\omega\,\pi A^2 + F_0 A\pi\sin\phi$$

$$E_{dis} = \frac{k}{Q}\frac{\omega}{\omega_0}\pi A^2 + F_0 A\pi\sin\phi \qquad \text{Eq. 2.96}$$

Finally, dividing by F_0 with the same assumption of Eq. 2.94

$$E_{dis}\,\frac{Q}{\pi k A_0} = \frac{1}{A_0}\left(\frac{\omega}{\omega_0}\right)A^2 + A\sin\,\phi \qquad \text{Eq. 2.97}$$

Eqs. in 2.95 and 2.97 can be rearranged to give

$$\mathrm{A}\cos\phi = \frac{Q}{A_0}\left[1-\left(\frac{\omega}{\omega_0}\right)^2\right]A^2 - \frac{2Q}{kA_0}V$$

$$A\sin\phi = E_{\mathrm{dis}}\frac{Q}{\pi k A_0} - \frac{\mu}{A_0}A^2 \qquad \text{where} \qquad \mu = \frac{\omega}{\omega_0} \qquad \text{Eq. 2.98}$$

Maintaining the cosine and the sine on the left hand side of the expressions is useful to compute tanφ but the expressions can also be rearranged with the terms V and E_{dis} on the left hand side. Then

$$V\,\frac{2Q}{kA_0} = \frac{Q}{A_0}\left[1-\left(\frac{\omega}{\omega_0}\right)^2\right]A^2 - \mathrm{A}\cos\phi \qquad \text{Eq. 2.99}$$

$$E_{\mathrm{dis}}\frac{Q}{\pi k A_0} = \frac{\mu}{A_0}A^2 + A\sin\phi \qquad \text{Eq. 2.100}$$

The following definitions are then proposed by Álvarez Amo[4]

$$\varepsilon = -E_{dis}\ \frac{Q}{\pi K A_0} \qquad \text{Eq. 2.101}$$

$$\nu = V\frac{2Q}{kA_0} \qquad \text{Eq. 2.102}$$

The negative sign in the expression in Eq. 2.201 by Álvarez Amo effectively redefines E_{dis} as the energy dissipation. That is, the integral is redefined as Eq. 2.79 reproduced here to support this discussion

$$E_{dis} = -\int_0^T\ F_{ts}\dot{z}dt$$

$$\varepsilon = E_{dis}\frac{Q}{\pi K A_0} = -\frac{Q}{\pi K A_0}\int_0^T\ F_{ts}\dot{z}dt \qquad \text{Eq. 2.103}$$

Combing Eq. 2.100 and 2.101

$$\varepsilon = -\left(\frac{\mu}{A_0}A^2 + \mathrm{Asin}\,\phi\right) \qquad \phi \leq 0 \qquad \text{Eq. 2.104}$$

In summary, since the assumptions leading to Eq. 2.104 are that $\phi\ \leq 0$ and that $F_0 = \frac{kA_0}{Q}$ (this is an approximation that assumes $\omega=\omega_0$), and since in absolute terms $\mathrm{Asin}\,\phi > \frac{\mu}{A_0}A^2$, using ε rather than E_{dis} effectively leads to talking about E_{dis} as a positive term. Then

$$E_{dis} = -\frac{\pi k A_0 A}{Q}\left[\sin\ \phi + \mu\frac{A}{A_0}\right] \qquad \text{Eq. 2.105}$$

The above expression still assumes that z=Acos(ωt+φ) but now we are speaking of energy dissipated rather than work done by the force F_{ts}. The development of the formalism continues by defining, from the combination of Eqs. 2.98 and 2.101

$$A\sin\phi = -\varepsilon - \mu\frac{A^2}{A_0} \qquad \text{Eq. 2.106}$$

Combining Eqs. 2.98 and 2.102

$$A\cos\ \phi = \frac{Q}{A_0}[1-\mu^2]A^2 - \nu \qquad \text{Eq. 2.107}$$

The discussion continues by assuming that $\omega=\omega_0$. This assumption implies that $F_0=kA_0/Q$ and thus the assumption in Eq. 2.95 and 2.97 hold. Then ($\omega=\omega_0$)

$$A\cos\ \phi = -\nu \qquad \text{Eq. 2.108}$$

$$A\sin\phi = -\varepsilon - \frac{A^2}{A_0} \qquad \text{Eq. 2.109}$$

Eqs. 2.108 and 2.109 can now be used to compute $\tan\phi$ following the convention of Álvarez Amo[4]

$$\tan\ \phi = \frac{-\varepsilon - \frac{A^2}{A_0}}{-\nu} \qquad \text{Eq. 2.110}$$

From the discussion of dissipative forces in chapter 2.4 it follows that E_{dis} ($\varepsilon=0$) does not contribute to the frequency shift, then (from the discussion on dissipation the expression below considers only even forces)

$$\tan\phi = \frac{A^2}{A_0\nu} \qquad \text{Eq. 2.111}$$

Writing Eq. 2.111 in terms of V ($\omega=\omega_0$)

$$\tan\ \phi = \frac{\frac{A^2}{A_0}}{V\frac{2Q}{kA_0}}$$

$$\tan\phi = \frac{kA^2}{2Q}\frac{1}{V} \qquad \text{Eq. 2.112}$$

The virial V can be written in terms of the cosine of the phase shift (Eq. 2.60). Then ($\omega=\omega_0$)

$$\tan\ \phi = \frac{kA^2}{2Q}\cdot\frac{1}{-\frac{1}{2}F_0A\cos\ \phi}$$

$$\tan\ \phi = \frac{kA^2}{2Q} \cdot \frac{-1}{\frac{kA_0}{2Q} A\cos\ \phi}$$

$$\tan\ \phi = \frac{-A}{A_0 \cos\ \phi} \qquad \text{Eq. 2.113}$$

It is trivial to show that Eq. 113 holds for (Eqs. 280 and 2.81) Álvarez Amo´s convention where -180° ≤ φ ≤ 0

$$z = A\cos\,(\omega t + \phi) \qquad \text{Eq. 2.114}$$

$$E_{dis} = \int_0^T F_{ts} \dot{z} dt \qquad \text{Eq. 2.115}$$

Eq. 2.113 simply expresses that E_{dis}=0. This can be shown by writing (from Eq. 2.113)

$$\tan\phi \cos\phi = -\frac{A}{A_0}$$

$$\sin\phi = -\frac{A}{A_0} \qquad \text{Eq. 2.116}$$

Eqs. 2.113 and 2.116 result from the consideration of the same phenomenon, namely, tracking a shift in natural frequency ω_0 due to conservative, i.e., or strictly speaking, even, forces. This can be shown by considering the energy dissipation equation at $\omega=\omega_0$, from Álvarez Amo´s convention

$$E_{dis} = -\frac{\pi k A_0 A}{Q}\left[\sin\ \phi + \mu \frac{A}{A_0}\right] \qquad \text{(Eq. 2.105)}$$

Combining Eqs. 2.105 and Eq. 2.116 at $\omega=\omega_0$ (μ=1)

$$E_{dis} = -\frac{\pi k A_0 A}{Q}\left[-\frac{A}{A_0} + \frac{A}{A_0}\right] = 0 \qquad \text{Eq. 2.117}$$

2.5.2 The solution for tanϕ for any ω

The expression tanϕ for any ω can be found directly from Eq. 2.92 and 2.92(2) without invoking the assumption that $F_0=kA_0/Q$ that holds only for $\omega=\omega_0$. Rearranging the equations

$$Acos\phi = \frac{A^2}{F_0}[k-\omega^2 m] - \frac{2}{F_0}V \qquad \text{Eq. 2.118}$$

$$A\sin\phi = \frac{1}{\pi F_0}E_{dis} - \frac{k}{QF_0}\mu A^2 \qquad \mu = \frac{\omega}{\omega_0} \qquad \text{Eq. 2.119}$$

Then,

$$tan\phi = \frac{\frac{1}{\pi F_0}E_{dis} - \frac{k}{QF_0}\mu A^2}{\frac{A^2}{F_0}[k-\omega^2 m] - \frac{2}{F_0}V} \qquad \text{Eq. 2.120}$$

The result in Eq. 2.112 by Álvarez Amo can be found by setting $\omega=\omega_0$, for which $F_0=kA_0/Q$, and the condition that $E_{dis}=0$ in Eq. 2.120. Then

$$tan\phi = \frac{kA^2}{2Q}\frac{1}{V} \qquad \text{Eq. 2.121}$$

The above expression is the same as that in Eq. 2.112. Nevertheless this is because $\omega=\omega_0$. Strictly speaking, the correct results for any ω are those in Eqs. 2.118-2.121 since Álvarez Amos's approximation for F0, i.e., F0=kA0/Q, is valid only at $\omega=\omega_0$.

2.5.3 Comparison between sign conventions for tanφ

The convention established by Eqs. 2.39, 2.59 and 2.77-2.79 can be shown to lead to the same results as those by Álvarez Amo's convention (Eq. 2.121). The derivation is carried out here in detail. From the alternative definition

$$z = A\cos(\omega t - \phi) \qquad \text{(Eq. 2.75)}$$

$$E_{dis} = -\int_0^T F_{ts}\dot{z}dt \qquad \text{(Eq. 2.77)}$$

$$E_{dis} = \pi F_0 A sin\phi - \frac{m\omega_0}{Q}\omega\pi A^2 \quad \text{(Eq. 2.39)}$$

$$V = \frac{1}{2}A^2[k - \omega^2 m] - \frac{1}{2}F_0 A cos\phi \quad \text{(Eq. 2.59)}$$

The sine and cosine functions can now be expressed as

$$Acos\phi = \frac{A^2}{F_0}[k - \omega^2 m] - \frac{2}{F_0}V \quad \text{Eq. 2.122}$$

$$Asin\phi = \frac{1}{\pi F_0}E_{dis} + \frac{m\omega_0}{QF_0}\omega A^2 \quad \text{Eq. 2.123}$$

The expression for tanϕ gives

$$tan\phi = \frac{\frac{1}{\pi F_0}E_{dis} + \frac{k}{QF_0}\mu A^2}{\frac{A^2}{F_0}[k-\omega^2 m] - \frac{2}{F_0}V} \quad \text{where } z = A\cos(\omega t - \phi),\ E_{dis} = -\int_0^T F_{ts}\dot{z}dt$$

Eq. 2.124

The expression in Eq. 2.124 is equivalent to that in 2.120 (Álvarez Amo) since cosϕ is an even function and symmetrical around ϕ=0. Compare 2.124 with 2.120 below

$$tan\phi = \frac{\frac{1}{\pi F_0}E_{dis} - \frac{k}{QF_0}\mu A^2}{\frac{A^2}{F_0}[k-\omega^2 m] - \frac{2}{F_0}V} \quad \text{where } z = A\cos(\omega t + \phi),\ E_{dis} = \int_0^T F_{ts}\dot{z}dt \quad \text{(Eq. 2.120)}$$

In summary,

1) In Eq. 2.120 the term containing E_{dis} <0 because of the definition given to compute E_{dis}.

2) In Eq. 2.120 the two terms on the numeration are negative and the numerator is positive in both Eqs. 2.120 and 2.124.

3) Because of the above two points the phase shift in Eq. 2.120 is negative and since the tan function is odd, -tan(ϕ)=tan(-ϕ).

4) By definition, the term in the numerator in 2.124 is positive and the term in the denominator is the same as in 2.120 because cosϕ is an even function, cos(-ϕ)= cosϕ.

Finally, either Eq. 2.120 or Eq. 1.24 can be used to compute the tangent of ϕ or E_{dis} provided

1) The term E_{dis} is interpreted as energy dissipation in Eq. 2.124 and as work done W by F_{ts} in Eq. 2.120. Then

$$E_{dis} = -W \qquad \text{Eq. 2.125}$$

2) The sign of the phase shift ϕ in 2.124 is considered as negative, i.e., the response lags the drive, and the phase shift in 2.120 is consider as positive and the sign is defined already when defining z.

For the condition $\omega=\omega_0$ and $E_{dis}=0$, Eq. 2.124 gives

$$tan\phi = -\frac{\mathrm{k}A^2}{2Q}\frac{1}{V} \qquad \text{where } z = A\cos(\omega t - \phi),\ E_{dis} = -\int_0^T F_{ts}\dot{z}dt \qquad \text{Eq. 2.126}$$

Again, Eq. 2.121 and 2.126 only differ in terms of a negative sign because the negative sign is already accounted for when defining z in Eq. 2.126. Writing $\tan\phi$ in terms of the cosine function

$$tan\phi = -\frac{\mathrm{k}A^2}{2Q}\frac{1}{\left[-\frac{1}{2}AF_0cos\phi\right]}$$

$$tan\phi = \frac{\mathrm{A}}{A_0cos\phi} \qquad \text{if } \omega=\omega_0,\ F_0=\mathrm{k}A_0/Q \qquad \text{Eq. 2.127}$$

The difference in sign is encountered again in Eq. 2.127 as compared with Eq. 2.113.

The (natural) frequency shift in the nonlinear theory

The natural frequency of the linear oscillator ω_0 does not coincide with the resonant frequency ω_r (chapter 1.9 and Eq. 102). The resonant frequency, sometimes called effective frequency in nonlinear theory, is the sum of both ω_0 and $\Delta\omega_0$ as shown in Equation 102.

$$\omega_r = \omega_{eff} = \omega_0' = \omega_0 + \Delta\omega_0 \qquad \text{Eq 2.128}$$

2.5.4 Deriving the "natural" frequency shift from the assumption of a weakly perturbed oscillator

The derivation first presented by Giessibl in 1997 can be derived directly from the results of the linear theory. A similar derivation is provided by Álvarez Amo in his thesis[4]. Here some details will be given regarding the sign convention and solutions.

Using Eq. 2.8 (Eq. 92 in chapter 1.8) from the driven oscillator, one can deduce that,

$$\tan\phi = \frac{\frac{\omega\omega_0}{Q}}{\omega_0^2 - \omega^2}$$

$$\tan\phi = \frac{1}{Q\left[\frac{\omega_0}{\omega} - \frac{\omega}{\omega_0}\right]} \qquad \text{(Eq. 2.8)}$$

Eq. 2.129 is a main source of issues when it comes to signs. In principle, the phase shift is negative implying that either

$$\tan\phi = \frac{1}{Q\left[\frac{\omega_0}{\omega} - \frac{\omega}{\omega_0}\right]} \qquad \text{linear theory} \qquad z = A\cos(\omega t - \phi) \qquad \text{Eq. 2.129}$$

or,

$$\tan\phi = -\frac{1}{Q\left[\frac{\omega_0}{\omega} - \frac{\omega}{\omega_0}\right]} \qquad \text{linear theory} \qquad z = A\cos(\omega t + \phi) \qquad \text{Eq. 2.130}$$

In Eq. 2.130 the sign is defined in terms of z whereas the sign is conserved in φ in Eq. 2.131. We recall that the term tanφ in the nonlinear theory results in (nonlinear theory, $\omega=\omega_0$)

$$tan\phi = \frac{kA^2}{2Q}\frac{1}{V} \qquad \text{where } \ z = A\cos\left(\omega t + \phi\right), E_{dis} = \int_0^T F_{ts}\dot{z}dt \qquad \text{(Eq. 2.121)}$$

$$tan\phi = -\frac{kA^2}{2Q}\frac{1}{V} \qquad \text{where } \ z = A\cos\left(\omega t - \phi\right), E_{dis} = -\int_0^T F_{ts}\dot{z}dt \qquad \text{(Eq. 2.126)}$$

The weakly perturbed resonant frequency shift ω_0' can be derived from Eq. 2.129 or Eq. 2.130.

Solving Eq. 2.129 for ω_0,

$$\omega_0 = \frac{\omega}{2Q\tan\phi}\left[\sqrt{1+4Q^2\tan^2\ \phi}+1\right] \qquad \text{linear theory} \qquad \text{Eq. 2.131}$$

Solving Eq. 2.130 for ω_0,

$$\omega_0 = \frac{\omega}{2Q\tan\phi}\left[\sqrt{1+4Q^2\tan^2\ \phi}-1\right] \qquad \text{linear theory} \qquad \text{Eq. 2.132}$$

The solution of 2.129 and 2.130 can be easily found (Eqs. 2.131 and 2.132) by exploiting software such as Matlab. For example,

Matlab script to solve 2.129

```
syms theta w w0 Q

F=tan(theta)+(-w*w0/Q)/(w0^2 -w^2);

Sol = solve(F,w0)
```

Matlab script to solve 2.130

```
syms theta w w0 Q

F=tan(theta)+(w*w0/Q)/(w0^2 -w^2);

Sol = solve(F,w0)
```

The new natural frequency can be defined by using Eq. 2.131 (or 2.132) but replacing tanϕ as defined by Eqs. 2.121 (or 2.126)

$$\omega_0' = \frac{\omega}{2Q[\tan\phi]_{\text{nonlinear}}}\left[\sqrt{1+4Q^2\,[\tan^2\,\phi]_{\text{nonlinear}}} - 1\right]$$ nonlinear theory Eq. 2.133

$$\omega_0' = \frac{\omega}{2Q[\tan\phi]_{\text{nonlinear}}}\left[\sqrt{1+4Q^2\,[\tan^2\,\phi]_{\text{nonlinear}}} + 1\right]$$ nonlinear theory Eq. 2.134

From now on the subscript nonlinear is dropped since it is cumbersome.

Eq. 2.133 with 2.126 and 2.134 can be rewritten as

$$\omega_0' = \omega\left[\sqrt{1+\frac{1}{4Q^2\tan^2\,\phi}} - \frac{1}{2Q\tan\phi}\right]$$ nonlinear theory Eq. 2.135

$$\omega_0' = \omega\left[\sqrt{1+\frac{1}{4Q^2\tan^2\,\phi}} + \frac{1}{2Q\tan\phi}\right]$$ nonlinear theory Eq. 2.136

The expressions in Eqs. 2.135 and 2.136 can be simplified by writing

$$x = 2Q\tan\phi$$ Eq. 2.137

A Taylor expansion that ignores higher terms produces, from Eq. 2.135

$$\omega_0' = \omega\left[\sqrt{1+\frac{1}{x^2}} - \frac{1}{x}\right]$$

$$\omega_0' \approx \omega\left[1+\frac{1}{2x^2} - \frac{1}{x}\right]$$ Eq. 2.138

Since in both (equivalent) expressions for tanϕ in the nonlinear theory, i.e., Eqs. 2.121 and 2.126, the virial V is in the denominator and kA^2 is in the numerator, it follows that

$$\omega_0' \approx \omega\left[1 - \frac{1}{x}\right] \qquad \text{where} \qquad kA^2 \gg V \qquad \text{Eq. 2.139}$$

Combining Eq. 2.139 with 2.121 and 2.137, implying that $\omega = \omega_0$,

$$\omega_0' \approx \omega_0\left[1 - \frac{1}{2Q\tan\phi}\right] \quad \text{where} \qquad tan\phi = \frac{kA^2}{2Q}\frac{1}{V} \qquad \text{Eq. 2.140}$$

$$\omega_0' \approx \omega_0\left[1 - \frac{V}{kA^2}\right] \qquad \text{Eq. 2.141}$$

Finally,

$$\frac{\omega_0'}{\omega_0} \approx 1 - \frac{V}{kA^2}$$

$$\frac{\omega_0 + \Delta\omega_0}{\omega_0} \approx 1 - \frac{V}{kA^2}$$

$$\frac{\Delta\omega_0}{\omega_0} \approx -\frac{V}{kA^2} \qquad \text{Eq. 2.142}$$

Eq. 2.142 is equivalent to that provided in Eq. 2.61 by Giessibl in 1997 when exploiting the Hamilton Jacobi formalism.

The reader can confirm that a similar derivation leads to Eq. 2.142 with the correct sign by combining Eqs. 2.136 and 2.126.

Finally, the virial V at $\omega = \omega_0$ is given in AM AFM by

$$V = -\frac{1}{2}F_0 Acos\phi \qquad \text{(Eq. 2.60)}$$

Then, combining Eq. 2.142 and Eq. 2.60

$$\frac{\Delta\omega_0}{\omega_0} \approx \frac{1}{2}\frac{F_0}{kA}cos\phi \qquad \text{Eq. 2.143}$$

But $F_0=kA_0/Q$ (at $\omega=\omega_0$). Then

$$\frac{\Delta\omega_0}{\omega_0} \approx \frac{1}{2}\frac{A_0}{QA}cos\phi$$

$$\frac{\Delta\omega_0}{\omega_0} \approx \frac{1}{2}\frac{A_D}{A}cos\phi \qquad \text{Eq. 2.144}$$

The result is equivalent to that given in Eq. 2.63

2.5.5 Frequency shift and virial

The first derivation of the frequency shift in 1997 by Giessibl[35] was presented as follows (chapter 2.3 under "the virial of the interaction")

$$\frac{\Delta f_0}{f_0} = -\frac{1}{kA^2}\langle F_{ts}z\rangle \qquad \text{(Eq. 2.61)}$$

$$z = Acos\,(\omega t + \phi) \qquad \text{(Eq. 2.114)}$$

where

$$\langle F_{ts}z\rangle = \frac{1}{T}\int_0^T F_{ts}zdt \qquad \text{(Eq. 2.47)}$$

The expressions in Eqs. 2.47, 2.61 and 2.114 was derived to compute the frequency shift in FM AFM in 1997. Eq. 247 is equivalent to the virial V first invoked[31] to derive an expression for the amplitude reduction in AM AFM.

Here we explore alternative methods to write down Eqs. 247 and 2.61. For example, Sader and Jarvis[52] write

$$\frac{\Delta\omega_0}{\omega_0} = -\frac{1}{\pi kA}\int_{-1}^{1} F_{ts}\frac{u}{\sqrt{1-u^2}}du \qquad \text{Eq. 2.145}$$

The expression in Eq. 2.145 is found by applying a change of variable in Eq. 261 as follows

$$\langle F_{ts}z\rangle = \frac{1}{T}\int_0^T F_{ts}zdt$$

$$\langle F_{ts}z\rangle = \frac{1}{T}\int_0^T F_{ts}Acos(\omega t+\phi)dt$$

$$\langle F_{ts}z\rangle = \frac{A}{T}\frac{1}{\omega}\int_0^{2\pi} F_{ts}cos\varphi d\varphi$$

$$\langle F_{ts}z\rangle = \frac{A}{2\pi}\int_0^{2\pi} F_{ts}cos\varphi d\varphi \qquad \text{Eq. 2.146}$$

where

$$\omega = \frac{2\pi}{T},\ \ \varphi = \omega t+\phi\ \ and\ \ d\varphi = \omega dt \qquad \text{Eq. 2.147}$$

Another change of varible is typically applied

$$\langle F_{ts}z\rangle = \frac{A}{2\pi}\int_0^{2\pi} F_{ts}cos\varphi d\varphi$$

$$\langle F_{ts}z\rangle = \frac{A}{2\pi}\oint F_{ts}\frac{u}{\pm\sqrt{1-u^2}}du \qquad \text{Eq. 2.148}$$

where

$$cos\varphi = u$$

$$-sin\varphi d\varphi = du$$

$$sin\varphi = \sqrt{1-u^2} \qquad \text{Eq. 2.149}$$

For the sake of easing the computation of Eq. 2.148

$$\langle F_{ts}z\rangle = \frac{A}{2\pi}\oint F_{ts}\frac{u}{\pm\sqrt{1-u^2}}du \equiv \frac{A}{\pi}\int_{u=-1}^{u=1} F_{ts}\frac{u}{\sqrt{1-u^2}}du \qquad \text{Eq. 2.150}$$

Where Eq. 2.150 exploits the fact that 1/2 the period should be identical to the other half provided the motion of the tip is sufficientlt sinusoidal, i.e., z ∝ cos(ωt+ϕ).

Finlly, combining Eqs. 2.61 and 2.150

$$\frac{\Delta\omega_0}{\omega_0} = -\frac{1}{kA^2}\left[\frac{A}{\pi}\int_{u=-1}^{u=1} F_{ts}\frac{u}{\sqrt{1-u^2}}du\right]$$

$$\frac{\Delta\omega_0}{\omega_0} = -\frac{1}{\pi k A}\int_{u=-1}^{u=1} F_{ts}\frac{u}{\sqrt{1-u^2}}du \qquad \text{Eq. 2.151}$$

where starting from the standard form of the virial V in Eq. 2.146 the integral in Eq. 2.151 is found. Eq. 2.151 is the expression used by Sader et al. in Eq. 2.145.

2.6 Nonlinear amplitude decay, frequency shift and transfer function

2.6.1 Frequency shift and virial at arbitrary drive frequencies

This section discusses the expression for the frequency shift $\Delta\omega_0/\omega_0$ at any drive frequency ω, i.e., when it is possible that $\omega \neq \omega_0$. The general expression for tanϕ in terms of E_{dis} and V

Has

$$tan\phi = \frac{\frac{1}{\pi F_0}E_{dis} - \frac{k}{QF_0}\mu A^2}{\frac{A^2}{F_0}[k-\omega^2 m] - \frac{2}{F_0}V} \quad \text{where } z = A\cos(\omega t + \phi),\ E_{dis} = \int_0^T F_{ts}\dot{z}dt \qquad \text{(Eq. 2.120)}$$

$$tan\phi = \frac{\frac{1}{\pi F_0}E_{dis} + \frac{k}{QF_0}\mu A^2}{\frac{A^2}{F_0}[k-\omega^2 m] - \frac{2}{F_0}V} \quad \text{where } z = A\cos(\omega t - \phi),\ E_{dis} = -\int_0^T F_{ts}\dot{z}dt \qquad \text{(Eq. 2.124)}$$

As an exercise, the reader can compare the above expressions with Eqs. 19 and 20 provided in 2021 by Bahram et al.[53] It has already been shown that for $\omega = \omega_0$ $(\mu = 1)$, E_{dis}=0 and $F_0 = kA_0/Q$, and $V = -\frac{1}{2}AF_0\cos(\phi)$, Eqs. 2.120 and 2.124 reduce to

$$\tan\phi = \frac{-A}{A_0\cos\phi} \qquad z = A\cos(\omega t + \phi) \qquad \text{(Eq. 2.113)}$$

$$tan\phi = \frac{A}{A_0 cos\phi} \qquad z = A\cos(\omega t - \phi) \qquad \text{(Eq. 2.127)}$$

The general expression for the virial V is the same independently of the definition oz z, then

$$V = -\frac{1}{2}F_0 A cos\phi + \frac{1}{2}A^2[k - \omega^2 m] \qquad \text{(Eq. 2.59)}$$

From the weakly perturbed oscillator formalism developed above (combination of Eq. 2.137 and Eq. 2.139), the general expression for ω_0' at any ω can be written as

$$\omega_0' \approx \omega\left[1-\frac{1}{2Q\tan\phi}\right] \quad \text{where} \quad kA^2 \gg V \quad z = A\cos(\omega t+\phi) \qquad \text{Eq. 2.152}$$

$$\omega_0' \approx \omega\left[1+\frac{1}{2Q\tan\phi}\right] \quad \text{where} \quad kA^2 \gg V \quad z = A\cos(\omega t-\phi) \qquad \text{Eq. 2.153}$$

Again, the two expressions above are equivalent by the signs must be considered depending on the definition of z.

The theory is next elaborated for the convention in Eq. 2.153.

Combining Eq. 2.124 and 2.153, the general natural (resonant) frequency is found

$$\omega_0' \approx \omega\left[1+\frac{1}{2}\frac{A^2[k-\omega^2 m]-2V}{\frac{Q}{\pi}E_{dis}+k\mu A^2}\right] \qquad \text{Eq. 2.154}$$

The expression in Eq. 2.61 can be recovered from the general Eq. 1.154 when $\omega = \omega_0$ ($\mu = 1$) and E_{dis}=0

$$1+\frac{\Delta\omega_0}{\omega_0} \approx 1+\frac{1}{2}\frac{(-2V)}{kA^2}$$

$$\frac{\Delta\omega_0}{\omega_0} \approx -\frac{V}{kA^2} \qquad \text{Eq. 2.155}$$

2.6.2 The nonlinear transfer function

In this section, we look at the nonlinear resonant frequency and dissipation by exploring the linear theory from another point of view. This alternative approach is explored by Arvind Raman in his course ("nanoHUB-U Fundamentals of AFM L2.4: Analytical Theory - Amplitude, Phase, Frequency Shift, Excitation."[3]). The reader can also refer to a recent paper (2021), where Arvind Raman appears as corresponding author[53], that employs the concepts of virial and E_{dis}, transfer function and tanϕ, as will be developed here, to extract mechanical properties from the sample.

The analysis starts from E_{dis} and V in terms of the since and cosine functions

$$Acos\phi = \frac{A^2}{F_0}[k - \omega^2 m] - \frac{2}{F_0}V \qquad \text{(Eq. 2.122)}$$

$$Asin\phi = \frac{1}{\pi F_0}E_{dis} + \frac{m\omega_0}{QF_0}\omega A^2 \qquad \text{(Eq. 2.123)}$$

Pythagoras theorem provides the mean to relate the sine and cosine function above

$$1 = \sin^2\ \phi + \cos^2\ \phi \qquad \text{Eq. 2.156}$$

Combining Eqs. 2.122, 2.123 and 2.156

$$\frac{kA}{F_0} = \frac{1}{\sqrt{\left(\frac{\omega_0'^2 - \omega^2}{\omega_0^2}\right)^2 + \left(\frac{\omega}{\omega_0 Q'}\right)^2}} \qquad \text{Eq. 2.157}$$

where

$$\omega_0' = \omega_0 - \omega_0 \frac{V}{kA^2} \qquad \text{Eq. 2.158}$$

and

$$\frac{1}{Q'} = \frac{1}{Q} + \frac{\omega_0 E_{dis}}{\omega \pi k A^2} \qquad \text{Eq. 2.159}$$

Eq. 2.158 is equivalent to Eq. 2.61. Eq. 2.159 is the effective Q factor. The advantage of writing a transfer function such as that in Eq. 2.157 is that it is analogous to the linear transfer function in Eq. 95 in chapter 1.8.

$$A = \frac{F_0}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + b^2\omega^2}}$$

$$\frac{kA}{F_0} = \frac{1}{\sqrt{\left(\frac{\omega_0^2 - \omega^2}{\omega_0^2}\right)^2 + \left[\frac{\omega}{\omega_0 Q}\right]^2}} \qquad \text{(Eq. 2.8)}$$

Indeed the whole point of rearranging the expressions in Eqs. 2.122 and 2.123 to get to 2.157 is that the term ω_0' seems to be playing the role of ω_0 in the linear theory and Q' that of Q. For this reason the expressions for ω_0' and Q' can be called "effective", i.e., they take values that make the system behave "as if" the linear system has such natural frequency and Q values. Compare, for example, the positions in the equations in Eq. Eq. 2.157 and Eq. 2.8 above.

Eq. 2.160 is simplified at $\omega=\omega_0$

$$\frac{kA}{\frac{kA_0}{Q}} = \frac{1}{\sqrt{\left(1-\left[\frac{\omega_0'}{\omega_0}\right]^2\right)^2+\left(\frac{1}{Q'}\right)^2}} \qquad where \qquad \frac{\omega_0'}{\omega_0} = 1-\frac{V}{kA^2} \;\; and \;\; F_0 = \frac{kA_0}{Q} \qquad \text{Eq. 2.160}$$

Combining Eq. 2.158-2.159 and 2.160

$$\frac{A}{A_D} = \frac{1}{\sqrt{\left(1-\left[1-\frac{V}{kA^2}\right]^2\right)^2+\left(\frac{1}{Q}+\frac{E_{dis}}{\pi kA^2}\right)^2}}$$

$$\frac{A}{A_D} = \frac{1}{\sqrt{\left(1-\left[1+\left[\frac{V}{kA^2}\right]^2-2\frac{V}{kA^2}\right]\right)^2+\left(\frac{1}{Q}+\frac{E_{dis}}{\pi kA^2}\right)^2}}$$

$$\frac{A}{A_D} = \frac{1}{\sqrt{\left(\left[\frac{V}{kA^2}\right]^2-2\frac{V}{kA^2}\right)^2+\left(\frac{1}{Q}+\frac{E_{dis}}{\pi kA^2}\right)^2}} \qquad \text{Eq. 2.161}$$

Considering the case of a weakly perturbed oscillator $V \ll kA^2$ (see Eqs. 2.152-2.153)

$$\frac{A}{A_D} \approx \frac{1}{\sqrt{\left(-2\frac{V}{kA^2}\right)^2+\left(\frac{1}{Q}+\frac{E_{dis}}{\pi kA^2}\right)^2}} \qquad \text{where} \qquad V \ll kA^2 \; and \; \omega=\omega_0 \qquad \text{Eq. 2.162}$$

Arvind Raman also provides[3] the "linear equivalent" expression for tanϕ

$$\tan(\phi) = \frac{\left(\frac{\omega}{\omega_0 Q'}\right)}{\left(\frac{\omega_0'^2-\omega^2}{\omega_0^2}\right)} \qquad \text{Eq. 2.163}$$

Again, Eq. 2.163 is simplified at $\omega=\omega_0$

$$\tan(\phi) = \frac{\frac{1}{Q'}}{\left[\frac{\omega_0'}{\omega_0}\right]^2 - 1} \qquad \text{Eq. 2.164}$$

Combining Eq. 2.158-2.159 and 2.164

$$\tan(\phi) = \frac{\frac{1}{Q}+\frac{E_{dis}}{\pi k A^2}}{\left[1-\frac{V}{kA^2}\right]^2 - 1} \quad \text{where} \quad \frac{\omega_0'}{\omega_0} = 1 - \frac{V}{kA^2} \qquad \text{Eq. 2.165}$$

Eq. 2.165 can be simplified for the weakly perturbed oscillator as follows

$$\tan(\phi) = \frac{\frac{1}{Q}+\frac{E_{dis}}{\pi k A^2}}{\left[1+\left[\frac{V}{kA^2}\right]^2 - 2\frac{V}{kA^2}\right] - 1}$$

$$\tan(\phi) \approx \frac{\frac{1}{Q}+\frac{E_{dis}}{\pi k A^2}}{-2\frac{V}{kA^2}} \qquad \text{where} \qquad V \ll kA^2 \ and \ \omega = \omega_0 \qquad \text{Eq. 2.166}$$

To obtain the term $\tan\phi$ where $E_{dis}=0$ is relevant since this allows determining the frequency shift (see Eqs. Eq. 2.152-2.153) . Then,

$$\tan(\phi) \approx \frac{1}{-2Q\frac{V}{kA^2}} \qquad \text{where} \qquad V = -\frac{1}{2}F_0 A\cos\phi \quad \text{and} \quad F_0 = \frac{kA_0}{Q} \qquad \text{Eq. 2.167}$$

Finally, simplifying Eq. 2.167

$$\tan(\phi) \approx \frac{A}{A_0\cos\phi} \qquad \text{Eq. 2.168}$$

2.6.3 The transfer function and amplitude decay

The general transfer function results can be written in terms of V and E_{dis} by combining Eq. 2.157-2.159

$$\frac{kA}{F_0} = \frac{1}{\sqrt{\left(\left[1-\frac{V}{kA^2}\right]^2-\frac{\omega^2}{\omega_0^2}\right)^2+\left(\frac{\omega}{\omega_0}\left[\frac{1}{Q}+\frac{\omega_0 E_{dis}}{\omega\pi kA^2}\right]\right)^2}}$$

$$\frac{kA}{F_0} \approx \frac{1}{\sqrt{\left(1-2\frac{V}{kA^2}-\frac{\omega^2}{\omega_0^2}\right)^2+\left(\frac{\omega}{\omega_0}\left[\frac{1}{Q}+\frac{\omega_0 E_{dis}}{\omega\pi kA^2}\right]\right)^2}} \qquad \mathrm{V} \ll kA^2 \qquad \text{Eq. 2.169}$$

Eq. 2.169 says that the virial V and E_{dis} control the amplitude decay together with the Q factor and the ratio ω/ω_0. For example, if $\omega/\omega_0=1$, and $V=E_{dis}=0$, Eq. 2.169 reduces to the well-known expression for F_0 at $\omega/\omega_0=1$ in the linear case

$$\frac{kA}{F_0} = \frac{1}{\frac{1}{Q}}$$

$$F_0 = \frac{kA}{\mathrm{Q}} \qquad \text{Eq. 2.170}$$

There is a case that was not discussed in the linear theory and is useful in the analysis of amplitude decay in the nonlinear theory. This is the case where there is drive but there is no viscosity, namely

$$m\ddot{z} + kz = F_0 \cos\ \omega t \qquad \text{Eq. 2.171}$$

As an exercise, the reader can use the methods detailed in chapters 1.4 and 1.8 to find that, in the steady state, the solution to Eq. 2.171 is

$$z = A\cos\left(\omega t\right) \quad \text{where} \quad A = \frac{F_0}{m[\omega_0^2-\omega^2]} \qquad \text{Eq. 2.172}$$

According to 2.172, the amplitude A will be maximum when $\omega=\omega_0$. The drive will pump energy into the system at the frequency ω. Note that there is no mechanism for dissipation in Eq. 2.171. The first implication is that $\omega_r = \omega_0$. That is, if there is no mechanism for dissipation the resonant frequency is identical to the natural frequency. Second, at $\omega=\omega_0$ the amplitude A tends to infinity with time since, as energy is delivered into the system, it all adds to A. A third implication is that, even in the absence of dissipation, the amplitude A will be finite outside $\omega=\omega_0$. This is because, in such cases, the drive eventually adds nothing to the oscillation. This can happen when the power delivered by the drive with time tends to zero. Practically, such phenomenon can be experienced when pushing someone in a swing and the pushing happens at the "wrong" time or the "wrong" frequency. Pushing in such cases damps the oscillation. More on Eq. 2.171 can be found in chapter 21 of the Feynman's lectures on physics.

San Paulo and Garcia[31] explored the amplitude decay in AM AFM (nonlinear case) as early as 2001. From the discussion of Eq. 2.171- Eq. 2.172, it is clear that variations in the effective value of ω_0, i.e., ω'_0, can change A. In chapters 1.4 and 1.8, it was also shown that dissipation adds to amplitude decay in the linear case. In summary, the linear theory teaches us that the amplitude A is controlled by ω_0 and energy dissipation, i.e., Q (see chapter 1.9 and Figs. 16-18).

Arguably, when invoking the virial theorem, San Paulo and Garcia had in mind finding the mechanism for amplitude decay in AM AFM. They also indirectly found the relationship between AM and FM AFM since they found a relationship between the virial V and the cosine of the angle and recalled that Giessibl had already found in 1997 that the virial is proportional to a frequency (natural) shift. In short, the authors found that the expression controlling E_{dis} was related to the sine of the phase shift while the virial V was related to the cosine (Eqs. 2.122-2.123). These two expressions in combination with Pythagoras (Eq. 2.156) theorem can be used to find the relationship between A, E_{dis} and V as follows

$$1 = \sin^2\ \phi + \cos^2\ \phi \qquad \text{(Eq. 2.156)}$$

The cosine and the sine of the phase shift are given by the expressions containing the virial V and E_{dis} respectively

$$cos\phi = \frac{A}{F_0}[k - \omega^2 m] - \frac{2}{AF_0}V \qquad \text{(Eq. 2.122)}$$

$$sin\phi = \frac{1}{\pi A F_0}E_{dis} + \frac{m\omega_0}{QF_0}\omega A \qquad \text{(Eq. 2.123)}$$

Combining Eqs. 2.122-2.123 and 2.56

$$1 = \left[\frac{1}{\pi A F_0} E_{dis} + \frac{m\omega_0}{Q F_0}\omega A\right]^2 + \left[\frac{A}{F_0}[k - \omega^2 m] - \frac{2}{A F_0} V\right]^2 \qquad \text{Eq. 2.173}$$

The drive in Eq. 2.173 can be factorized in terms of F_0. From F_0 an amplitude A_0 can be defined, i.e., the unperturbed amplitude, which differs from the perturbed amplitude A. It is useful to define the drive in terms of A_0 because it can be experimentally measured. In dynamic AFM A0 is the value of oscillation amplitude A obtained in the absence of tip-sample interaction. Then, the system behaves like the driven oscillator. Thus, A_0 can be identified with the amplitude A obtained when E_{dis}=V=0, i.e., for the conditions of the linear theory or driven oscillator. Then, Eq. 2.173 reduces to

$$\frac{F_0^2}{A^2} = [k - \omega^2 m]^2 + \left[\frac{m\omega_0}{Q}\omega\right]^2$$

$$F_0^2 = A^2\left[[k - \omega^2 m]^2 + \left[\frac{m\omega_0}{Q}\omega\right]^2\right] \qquad \text{Eq. 2.174}$$

Writing Eq. 2.174 terms of A

$$A^2 = \frac{F_0^2}{[k - \omega^2 m]^2 + \left[\frac{m\omega_0}{Q}\omega\right]^2}$$

$$A = \frac{F_0}{\sqrt{[k-\omega^2 m]^2 + \left[\frac{m\omega_0}{Q}\omega\right]^2}} \qquad \text{Eq. 2.175}$$

Or equivalently,

$$A = \frac{F_0}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + b^2\omega^2}}$$

$$F_0 = A\sqrt{m^2(\omega_0^2 - \omega^2)^2 + b^2\omega^2} \qquad \text{(Eq. 2.8)}$$

The free amplitude A_0 and the drive force F_0 are simultaneously defined from Eq. 2.8, then (A_0 defined)

$$A_0 = \frac{F_0}{\sqrt{m^2\left(\omega_0^2-\omega^2\right)^2+b^2\omega^2}} \qquad \text{Eq. 2.176}$$

The expression above is the standard result that relates the amplitude with the drive (Eq. 2.8) but it is useful to define A_0 a shown in Eq. 2176 since it is a way to distinguish the unperturbed amplitude A_0 (E_{dis}=V=0) with the perturbed amplitude, i.e., nonlinear.

Having clarified the difference between A_0 and A, the relation between F_0 and A_0, and that the standard expression relating A and F_0 can be recovered from the nonlinear expression in Eq. 2.173 (Eq. 2.174- Eq. 2.176 and Eq. 2.8), the objective is to find the roots of A in the nonlinear expression (Eq. 2.173) and to express them in terms of E_{dis} and V.

First, F_0 can be factorized from Eq. 2.173

$$F_0^2 = \left[\frac{1}{\pi A}E_{dis} + \frac{m\omega_0}{Q}\omega A\right]^2 + \left[A[k-\omega^2 m] - \frac{2}{A}V\right]^2 \qquad \text{Eq. 2.177}$$

Second, Eq. 2.177 can be factorized as follows

$$F_0^2 = \left[\frac{1}{\pi A}E_{dis}\right]^2 + \left[\frac{m\omega_0}{Q}\omega A\right]^2 + 2\left[\frac{1}{\pi A}E_{dis}\frac{m\omega_0}{Q}\omega A\right] + \left[A[k-\omega^2 m]\right]^2 + \left[\frac{2}{A}V\right]^2 - 2\left[A[k-\omega^2 m]\frac{2}{A}V\right] \qquad \text{Eq. 2.178}$$

Factorizing in terms of A and simplifying

$$F_0^2 = \frac{1}{A^2}\left[\frac{1}{\pi}E_{dis}\right]^2 + A^2\left[\frac{m\omega_0}{Q}\omega\right]^2 + \left[\frac{2}{\pi}E_{dis}\frac{m\omega_0}{Q}\omega\right] + A^2[k-\omega^2 m]^2 + \frac{1}{A^2}[2V]^2 - \left[[k-\omega^2 m]4V\right] \qquad \text{Eq. 2.179}$$

Multiplying all terms by A^2 and collecting terms

$$A^4\left[\left[\frac{m\omega_0}{Q}\omega\right]^2 + [k-\omega^2 m]^2\right] + A^2\left[\frac{2}{\pi}E_{dis}\frac{m\omega_0}{Q}\omega - 4[k-\omega^2 m]V - F_0^2\right] +$$

$$+\left[\left[\frac{1}{\pi}E_{dis}\right]^2+[2V]^2\right]=0 \qquad \text{Eq. 2.180}$$

The expression in Eq. 2.180 is a quadratic equation in terms of A^2. This is true because the term A_0 is not the same as the perturbed amplitude A. Note that while Eq. 2.180 produces an explicit solution for A for arbitrary values of ω, F_0, E_{dis}, V, Q and ω_0, Eq. 2.169 does not. An explicit solution for A was found by Álvarez Amo[4] (Eqs. 2.20 to 2.25 in the thesis) assuming that $F_0=kA_0/Q$. This is approximately true provided $\omega\approx\omega_0$. The advantage of Eq. 2.180 is that there is no assumption about F_0, or, equivalently, it is valid for any drive frequency ω and drive force F_0.

Simplifying Eq. 2.180 by driving at $\omega=\omega_0$

$$A^4+A^2\left[\frac{2Q}{\pi k}E_{dis}-\left[\frac{QF_0}{k}\right]^2\right]+\left[\left[\frac{Q}{\pi k}E_{dis}\right]^2+\left[\frac{2Q}{k}V\right]^2\right]=0 \qquad \text{Eq. 2.181}$$

Eq. 2.180 is general for any ω and does not assume $F_0=kA_0/Q$. Nevertheless, in Eq. 2.181 the expression $F_0=kA_0/Q$ is valid since $\omega=\omega_0$. Then, Eq. 2.181 can be further reduced to give

$$A^4+A^2\left[\frac{2Q}{\pi k}E_{dis}-A_0^2\right]+\left[\left[\frac{Q}{\pi k}E_{dis}\right]^2+\left[\frac{2Q}{k}V\right]^2\right]=0 \qquad \omega=\omega_0 \qquad \text{Eq. 2.182}$$

The expression in Eq. 2.182 is equivalent to the result of Álvarez Amo[4] in his equation 2.26 and the solution was first reported in 2001 by San Paulo and García[31] in their Eq. 9. The solution can be easily found using software like Matlab. A script to solve Eq. 2.182 is

Matlab script to solve 2.182

```
syms A a b c

F=A^4 + A^2*(2*a - b) + a^2+c;

Sa = solve(F, A)
```

The expression in Eq. 2.182 has been simplified in order to solve it in Matlab by defining

$$a = \frac{Q}{\pi k} E_{dis}$$

$$b = A_0^2$$

$$c = \left[\frac{2Q}{k} V\right]^2 \qquad \text{Eq. 2.183}$$

Of the 4 solutions only two are valid since, from energy conservation, $A \leq A_0$. The two valid solutions are

$$A = \left[\frac{b}{2} - a \pm \frac{1}{2}\sqrt{b^2 - 4ab - 4c}\right]^{1/2} \qquad \text{Eq. 2.184}$$

Combining Eqs. 2.183 and Eq. 284 and arranging the terms

$$A = \frac{A_0}{\sqrt{2}}\left[1 - \frac{2Q}{\pi k A_0^2} E_{dis} \pm \sqrt{1 - \frac{4\frac{QA_0^2}{\pi k}E_{dis} - 4\left[\frac{2Q}{k}V\right]^2}{A_0^4}}\right]^{1/2} \quad \omega=\omega_0 \qquad \text{Eq. 2.185}$$

Eq. 2.185 is valid for interactions with dissipation and with conservative terms, i.e., any nonlinear interaction. The equation shows that both E_{dis} and V contribute to the amplitude decay. If we allow E_{dis}=V=0, Eq. 2.185 is undetermined, i.e., A=0 is the only solution. But San Paulo and García[31] showed by numerical integration of the equation of motion that Eq. 2.185 is valid for any interaction provided $\omega=\omega_0$.

Eq. 2.182 can be written for the case for conservative interactions only, i.e., E_{dis}=0. The expression shows that A depends on A_0, V, Q and k ($\omega=\omega_0$)

$$A^4 - A^2A_0^2 + \left[\frac{2Q}{k}V\right]^2 = 0 \quad \text{where} \quad E_{dis}=0 \quad \text{and} \quad \omega=\omega_0 \qquad \text{Eq. 2.186}$$

Matlab script to solve 2.182

```
syms theta a b

F=A^4 -(A^2)a + b;

Sa = solve(F,A)
```

The two valid solutions of Eq. 2.186 are given by the script above

$$A = \frac{A_0}{\sqrt{2}}\left[1 \pm \sqrt{1 - \frac{16Q^2}{k^2A_0^4}V^2}\right]^{1/2} \quad \text{where} \quad E_{dis}=0 \quad \text{and} \quad \omega=\omega_0 \qquad \text{Eq. 2.187}$$

The expression in Eq. 2.187 is equivalent to Eq. 11 presented in 2001 by San Paulo and García[31]. It can also be found as Eq. 2.28 in the thesis of Álvarez Amo[4]. In their, paper San Paulo and García solve the equation of motion (Eq. 2.3) numerically to show that Eq. 2.184 is exact when only conservative forces are present in the nonlinear term. Eq. 2.187 can be combined with Eq. 2.60 to express the amplitude decay in term of the cosine of the phase shift

$$A = \frac{A_0}{\sqrt{2}}\left[1 \pm \sqrt{1 - \frac{16Q^2}{k^2A_0^4}\left[\frac{1}{2}F_0Acos\phi\right]^2}\right]^{\frac{1}{2}} \qquad \text{Eq.2.188}$$

$$where\ \ V = -\frac{1}{2}F_0Acos\phi \ \ and\ \ F_0 = \frac{kA_0}{Q}$$

Simplifying

$$A = \frac{A_0}{\sqrt{2}}\left[1 \pm \sqrt{1 - 4\frac{A^2}{A_0^2}cos^2(\phi)}\right]^{1/2} \quad \text{where} \quad E_{dis}=0 \quad \text{and} \quad \omega=\omega_0 \qquad \text{Eq. 2.189}$$

Eq. 2.189 shows that by expressing V in terms of F_0 and the cosine of the phase shift ϕ (Eq. 2.60), the equations expressing the amplitude decay A are shown to express implicit relations. The same is true for E_{dis} since E_{dis} depends on A (2.39). On the other hand, one can argue that E_{dis} and V can be taken as experimentally computable quantities directly extracted from physical phenomena and inputted into expressions such as that in Eq. 2.189.

Finally, factorizing A in Eq. 2.189 produces a true expression for the amplitude decay without implicit relationships with A. The steps for factorization are shown below

$$\frac{2A^2}{A_0^2} = 1 - \sqrt{1 - 4\frac{A^2}{A_0^2}cos^2(\phi)}$$

$$\left[\frac{2A^2}{A_0^2} - 1\right]^2 = 1 - 4\frac{A^2}{A_0^2}cos^2(\phi)$$

$$\left[\frac{2A^2}{A_0^2}\right]^2 - \frac{4A^2}{A_0^2} + 1 = 1 - 4\frac{A^2}{A_0^2}cos^2(\phi)$$

$$\frac{4}{A_0^4}A^4 + \frac{4}{A_0^2}[cos^2(\phi) - 1]A^2 = 0$$

$$\frac{4}{A_0^2}\left[\frac{1}{A_0^2}A^4 + [cos^2(\phi) - 1]A^2\right] = 0$$

$$\frac{1}{A_0^2}A^2 + cos^2(\phi) - 1 = 0$$

where $cos^2(\phi) - 1 = sin^2(\phi)$

$$\frac{A^2}{A_0^2} = -sin^2(\phi)$$

$$sin(\phi) = \frac{A}{A_0}$$

$A = A_0 sin(\phi)$ where $E_{dis}=0$ and $\omega=\omega_0$ Eq. 2.190

Eq. 2.190 shows that when only the virial V, i.e., a conservative force, is responsible for the decay of the perturbed amplitude A, i.e., $A \leq A_0$, the amplitude A can be found directly from A_0 and the sine of the phase shift alone. This is consistent with Eq. 2.44 and the relations shown in Fig. 2.13. In summary, setting $E_{dis}=0$ in 2.39 provides an expression for the amplitude decay A when $E_{dis}=0$ and $\omega=\omega_0$.

2.6.4 The limit of small amplitudes

If the amplitude of oscillation A is small compared to the variations of the nonlinear term the linear approximation can be exploited. It is important to note that the unperturbed, or linear, amplitude A_0 can take on any value, that is, the derivation involves A not the drive F_0.

When the oscillation A is small compared to the variations in the nonlinear term F_{ts} (see Fig. 16), the curve of F_{ts} can be approximated to a straight line. This is why transforming Fts to a straight line is termed "linearizing" the equation.

The tangent to a curve in a point gives the slope of the curve at that point. For an arbitrary point at d_0, the tangent of F_{ts} is

$$\frac{\partial F_{ts}}{\partial d}(d_0) = -k_{ts}(d_0) \qquad \text{Eq. 2.191}$$

where k_{ts} is the tangent or slope at a point d_0. If the value of k_{ts} is approximately constant in a neighbourhood of points around d_0, i.e., $d_0 - A < d < d_0 + A$, the nonlinear term F_{ts} can be approximated as

$$\frac{\partial F_{ts}}{\partial d}(d) \approx \frac{\partial F_{ts}}{\partial d}(d_0) \quad for\ d_0 - A \le d \le d_0 + A \qquad \text{Eq. 2.192}$$

$$F_{ts}(d) \approx -k_{ts}(d_0)Acos(\omega t - \phi) \qquad \text{Eqs. 2.193}$$

where the negative sign in 2.193 implies that the gradient should be positive for repulsive forces and negative for attractive forces. This sign is thus related the physics of the phenomena under consideration. In AFM it must be negative. Fig. 2 has been reproduced here as Fig. 2.17 to support the exposition since the geometry of the problem can be used to derive the expressions.

Only the dynamic part of z is used here since, as shown in chapter 2.3 when deriving the virial, the equilibrium position z_0 does not add to the virial V.

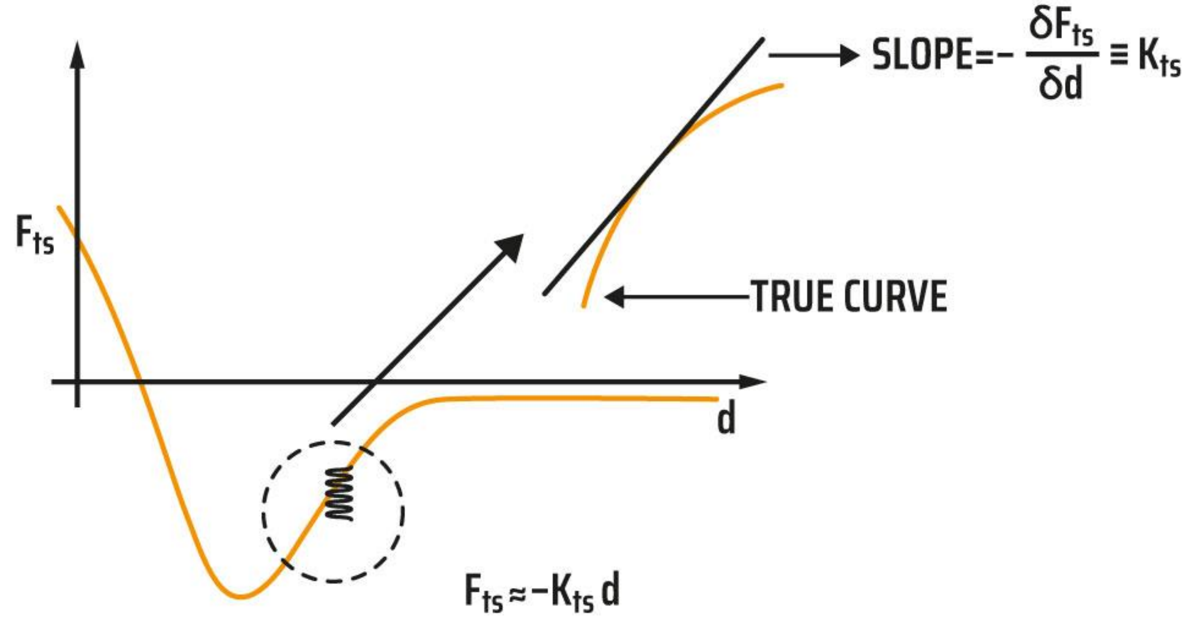

Figure 2.17. Illustrations depicting of nonlinear force F_{ts} in terms of distance d where, as indicated, if the oscillation amplitude A is small enough, the equation of motion can be linearized. The slope, gradient or tangent at the position of equilibrium z_0.

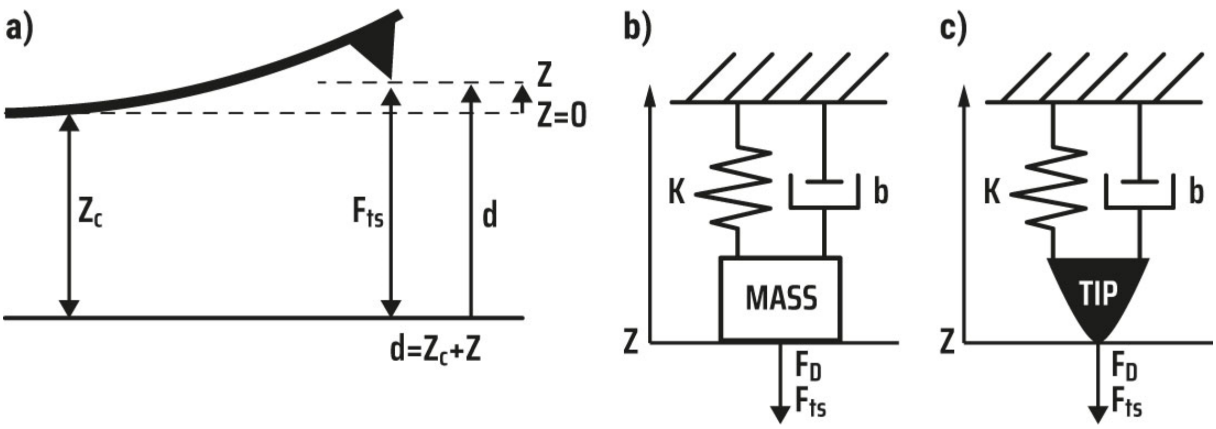

Figure 2.18. a) Schematic of an AFM cantilever from which geometrical constraints can be derived. b) and c) Rheological models of the tip' motion. Both models are mathematically equivalent but the illustration in c) showcases that the motion is discussed in terms of the tip.

In summary, d_0 is identified with the equilibrium position of oscillation, that is, with the neutral position of equilibrium, i.e., $z=z_0$ or mean deflection. The mean deflection is given by the average force per cycle (Eq. 255) and there is oscillation around this neutral position. For this reason, in the limit of small oscillations, the tangent, or derivative of F_{ts} is taken in the neutral position of oscillation and assumed to be approximately constant for the range of d covered (Eq. 2.192). The linear approximation is thus constrained by Eq. 2.192, i.e., the better 2.192 holds the better the linear approximation. Physically, the tangent of the curve depends on the physical phenomena by the AFM user can improve the approximating by reducing the oscillation amplitude A (see Fig. 2.16).

The general expression for the virial V is

$$V \equiv \langle Fz \rangle = \frac{1}{T}\int_0^T Fzdt \qquad \text{(Eq. 2.47)}$$

where

$$z = A\cos(\omega t - \phi)$$

The virial V for a force based on the derivative or slope at d can be written by Combining Eqs. 2.192 and 2.193

$$V = -\frac{1}{T}\int_0^T k_{ts}(d)z^2dt \qquad \text{Eq. 2.194}$$

In the limit of small oscillations A the slope (also termed gradient or tangent) is approximately constant (Fig. 2.16), then

$$V \approx -\frac{1}{T}k_{ts}(d_0)\int_0^T z^2dt \quad \text{where} \quad \frac{\partial F_{ts}}{\partial d}(d) \approx \frac{\partial F_{ts}(d)}{\partial d}(d_0) \qquad \text{Eq. 2.195}$$

A change of variable is then applied as shown bellow

$$\mathrm{z} = \mathrm{A}\cos\varphi \quad \text{where } \varphi = \omega \mathrm{t} - \phi \text{ and } d\varphi = \omega dt$$

Combining 2.194 and 2.195

$$V \approx -\frac{1}{2\pi}k_{ts}(d_0)A^2\int_{\varphi=0}^{\varphi=2\pi} cos^2(\varphi)d\varphi \qquad \text{Eq. 2.196}$$

Since the integral in Eq. 2.196 is π, the virial for small oscillation amplitudes is

$$V \approx -\frac{1}{2}k_{ts}A^2 \qquad \frac{\partial F_{ts}}{\partial d}(d) \approx \frac{\partial F_{ts}(d)}{\partial d}(d_0) \equiv k_{ts} \qquad \text{Eq. 2.197}$$

where k_{ts} is the effective spring constant resulting from the nonlinear term F_{ts} and computed as its gradient.

Combining Eq. 2.197 with Eq. 2.61 gives the frequency shift for a weakly perturbed oscillator and the small amplitude, i.e., linear, approximation. Then

$$\frac{\Delta\omega_0}{\omega_0} = -\frac{1}{kA^2}V \qquad \text{(Eq. 2.61)}$$

$$\frac{\Delta\omega_0}{\omega_0} \approx -\frac{1}{k}\left[\frac{1}{2}k_{ts}A^2\right]$$

$$\frac{\Delta\omega_0}{\omega_0} \approx -\frac{1}{2}\frac{k_{ts}}{k} \quad \text{where} \quad k_{ts} \equiv \frac{\partial F_{ts}}{\partial d}(d) \qquad \text{Eq. 2.198}$$

In Eq. 2.198 the sign is negative because the negative in Eq. 1.61 already contained the negative of the gradient. The result in Eq. 2.198 was already reported[54] in 1991 one FM AFM was first introduced. Giessibl also acknowledged[35] that his equation (Eq. 2.61) gave the right solution in the limit of small amplitudes.

The frequency shift for the small amplitude A limit can also be computed directly via the linear equation of motion (Eq. 2.2). A main result from the linear theory is that m, k and ω_0 are related (Eq. 13)

$$\omega_0^2 = \frac{k}{m} \qquad \text{(Eq. 13)}$$

For small perturbations, i.e., $\Delta\omega_0 << \omega_0$

$$[\omega_0 + \Delta\omega_0]^2 = \frac{k'}{m} \qquad \Delta\omega_0 << \omega_0 \quad \text{and} \quad k' = k - k_{ts} \qquad \text{Eq. 2.199}$$

where k' is the effective spring constant and where k_{ts} has the minus sign to indicate that repulsive forces produce negative sloped. Factorizing

$$\omega_0^2 + \Delta\omega_0^2 + 2\omega_0\Delta\omega_0 = \frac{k - k_{ts}}{m}$$

The simplification for weakly perturbed oscillators, i.e., $\Delta\omega_0 << \omega_0$, produces

$$\omega_0^2 + 2\omega_0\Delta\omega_0 \approx \frac{k}{m} - \frac{k_{ts}}{m} \qquad \text{Eq. 2.200}$$

Finally, simplifying Eq. 2.200

$$\omega_0\Delta\omega_0 m \approx -\frac{1}{2}k_{ts}$$

$$\omega_0\Delta\omega_0\left[\frac{k}{\omega_0^2}\right] \approx -\frac{1}{2}k_{ts}$$

$$\frac{\Delta\omega_0}{\omega_0} \approx -\frac{1}{2}\frac{k_{ts}}{k} \qquad \text{Eq. 2.201}$$

Eq. 2.201 coincides with Eq. 1.198 and it is thus in agreement with the weakly perturbation theory presented here.

For large amplitudes, other than the problem of linearity, i.e., the gradient is not constant during the oscillations, higher harmonics are excited and cannot be neglected[55-57]. Oscillating in highly damped medium might also distort the harmonicity of the motion[58-60]. In short, the small amplitude approximation requires that A is much smaller than the features being probed. The attractive forces probed in AFM are ~ 1nm[41]. Thus the amplitude to probe nanoscale forces much be A<< 1 nm. This is a typical characteristic of microscopy.

2.6.5 Thermal energy, energy dissipation and virial

The smallest virial V that can be detected in an oscillator above thermal noise can be computed from the equipartition theorem[33]

$$\frac{1}{2}k < \dot{z}^2 > = \frac{1}{2}k_B T \qquad \omega=\omega_0 \qquad \text{Eq. 2.202}$$

where k_B is Boltzmann's constant and T is the temperature in Kelvin.

From Eq. 2.48

$$< KE > = \frac{1}{2} \mathrm{m} < \dot{z}^2 >$$

$$< KE > = \frac{1}{2} E_T = \frac{1}{2} \left[\frac{1}{2} k A^2 \right] \qquad \text{(Eq. 2.48)}$$

Combining Eqs. 2.202 and 2.48 provides the condition for the minimum amplitude A to be detected at temperature T (in Kelvin) is

$$\frac{1}{4} k A^2 = \frac{1}{2} k_B T$$

$$A^2 = 2 \frac{k_B}{k} T \qquad \text{Eq. 2.203}$$

From Eq. 2.185, the amplitude A is found for any energy dissipation E_{dis} and virial V at $\omega=\omega_0$. Combining Eq. 2.203 and Eq. 2.185

$$\frac{A_0^2}{2} \left[1 - \frac{2Q}{\pi k A_0^2} E_{dis} \pm \sqrt{1 - \frac{4 \frac{Q A_0^2}{\pi k} E_{dis} - 4 \left[\frac{2Q}{k} V \right]^2}{A_0^4}} \right] = 2 \frac{k_B}{k} T \qquad \omega=\omega_0 \qquad \text{Eq. 2.204}$$

The minimum detectable E_{dis} and V follow from Eq. 2.204. We leave this problem unresolved here but suffice it to say that it requires that E_{dis} and V are explicitly written in term of T. The equation can be simplified if either E_{dis} or V are zero. For example, if E_{dis}=0, the amplitude A in terms of V is simplified to Eq. 2.187. Combining Eq. 2.187 and 2.203

$$\frac{A_0^2}{2} \left[1 \pm \sqrt{1 - \frac{16 Q^2}{k^2 A_0^4} V^2} \right] = 2 \frac{k_B}{k} T \qquad \text{where} \quad E_{dis}=0 \quad \text{and} \quad \omega=\omega_0 \qquad \text{Eq. 2.205}$$

$$\sqrt{1-\frac{16Q^2}{k^2A_0^4}V^2}=4\frac{1}{A_0^2}\frac{k_B}{k}T-1$$

$$1-\frac{16Q^2}{k^2A_0^4}V^2=\left[4\frac{1}{A_0^2}\frac{k_B}{k}T-1\right]^2$$

$V^2=\frac{k^2A_0^4}{16Q^2}\left[1-\left[4\frac{1}{A_0^2}\frac{k_B}{k}T-1\right]^2\right]$ minimum V at T where E_{dis}=0 and $\omega=\omega_0$ Eq. 2.206

From Eq. 2.206 it follows that when T=1, the minimum detectable virial V is zero as required. This assumes however that no other sources of noise, i.e., electric, etc., are present. For this reason Eq. 2.206 is a limiting case, i.e., the physically minimum detectable V at temperature T. A similar relationship can be found for the phase shift from Eq. 2.190 in combination with Eq. 2.203. We also leave the problem unresolved.

2. 7 Bimodal

In the first chapter, the first equation discussed in the analysis of oscillations was that of a cantilever parametrized in terms of beam theory[61] (Eq. 1 in chapter 1 on linear theory)

$$EI\frac{\partial}{\partial x^4}\left[w(x,t)+a_1\frac{\partial w(x,t)}{\partial t}\right]+\rho bh\frac{\partial^2 w(x,t)}{\partial t^2} = -a_0\frac{\partial w(x,t)}{\partial t}+\delta(x-L)[F_{\mathrm{exc}}(t)+F_{ts}(d)] \qquad \text{(Eq. 1)}$$

where all the parameters are defined there. Eqs. 2-3 showed that Eq. 1 can be reduced to a set of equations that represent the vertical motion of the beam at x=L, i.e., at the edge of the cantilever (see the schematic in Fig. 2.17). In short, Eq. 1 is equivalent to a set of anharmonic differential equations[43, 62] (Eq. 3 in chapter 1 on linear theory)

$$\ddot{z}_m(t)+\frac{\omega_m}{Q_m}\dot{z}_m(t)+\omega_m^2 z_m(t)=\frac{F_{\mathrm{exc}}(t)+F_{ts}(d)}{\mathrm{m}}, m(subscript)=1,2,\ldots \qquad \text{(Eq. 3)}$$

where z(t) is the modal projection of the tip motion (Fig. 2.17). All the other parameters are defined in chapter 1 when discussing Eqs. 1-3. In Eq. 3 all the parameters are equivalent to those appearing in the equation of motion analysed in chapters 2.1-2.7 so far (Eq. 2.3) with the only difference being the appearance of a subscript m in Eq. 3. This subscript stands for mode m. The subscript m should not be confused with the mass m. Using m rather than n for mode is useful because Fourier series are typically developed using n for harmonic. It is now more or less standard terminology in AFM to use n for harmonics and m[63] or i [44]for mode.

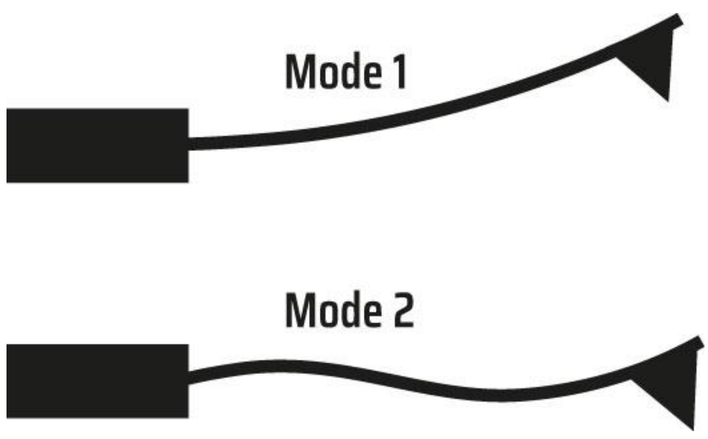

Figure 2.19 Illustration of the first two modes of a cantilever. See literature for details[64].

While all modes have a finite response at all frequencies ω, the signal for each mode m is significant mostly near the resonance of each mode m. The response of the first two modes is illustrated in Fig. 6 - reproduced here as Fig. 2.18.

In short, the equations of motion for the first two modes are

$$m\ddot{z}_1 = -k_1 z_1 - \frac{m\omega_{01}}{Q_1}\dot{z}_1 + F_{01}\cos\ \omega_1 t + F_{02}\cos\omega_2 t + F_{\mathrm{ts}}(z_1 + z_2) \qquad \text{Eq. 2.207}$$

$$m\ddot{z}_2 = -k_2 z_2 - \frac{m\omega_{02}}{Q_2}\dot{z}_2 + F_{01}\cos\ \omega_1 t + F_{02}\cos\omega_2 t + F_{\mathrm{ts}}(z_1 + z_2) \qquad \text{Eq. 2.208}$$

where the subscripts 1 and 2 stand for mode 1 and 2 respectively. The subscripts 01 and 02 stand for natural frequency of mode 1 and 2 respectively. In terms of the drive force they stand for the drive F_0 at mode 1 and 2 respectively. Here higher modes will be ignored in order to develop a theory based on the virial V and the energy dissipation E_{dis} for each mode. This theory is will be briefly discussed in the remainder of this book[64-65]. Lozano and García provided a general theory in 2008 [44] in terms of the virial theorem and supplemented their results and interpretation via numerical integration of the equations of motion. Experimental "amplitude" (power density) versus frequency ω curves, are shown in Fig. 5 – reproduced here as Fig. 2.19.

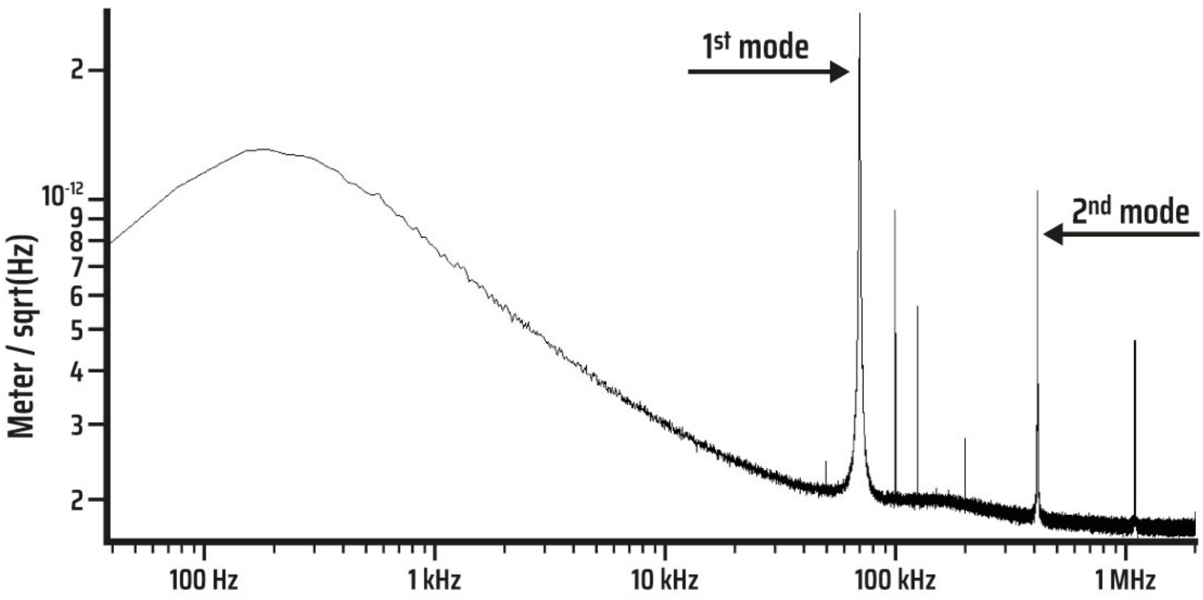

Figure 2.20. Standard frequency sweep for an AFM cantilever showing the response of modes 1 and 2. The response of the 3rd mode can also be seen near 1MHz. The other peaks are noise, i.e., electronic or other.

Key phenomena from Eqs. 2.207-2.208 relate to the presence of two drives, one exciting at or near the natural frequency of mode 1 (m=1) ω_{01}, and the other at or near the natural frequency of mode 2 (m=2) ω_{01}. The position z is further expressed as the sum of z_1 and z_2

$$z(t) = z_1(t) + z_2(t) + O(\varepsilon) \approx A_1\cos(\omega_1 t - \phi_1) + A_2\cos(\omega_2 t - \phi_2) \quad \text{Eq. 2.209}$$

where $O(\varepsilon)$ is the term carrying the contributions of higher harmonics and higher modes, i.e., it is the error not accounted for by the first two terms. The force F_{ts}, i.e., the nonlinear term, is also, and approximately, determined by z_1 and z_2

$$F_{\text{ts}}(\text{z}) \approx F_{\text{ts}}(z_1 + z_2) \quad \text{Eq. 2.210}$$

we emphasize $z_1(t)$ and $z_2(t)$ are the positions of modes 1 and two. Another approximation can be applied here by assuming that the responses for each mode coincide with the frequencies of excitation at each mode. This is a good approximation if the first drive acts at a frequency near the natural frequency of the first mode, and the second near that of the second mode. Then the subscripts in Eqs. 2.209 and 2.210 can be taken to represent the harmonics at the drive frequencies ω_1 and ω_1 respectively. It turns out that the virial V and energy dissipation expressions for each mode are identical to those already discussed. This is because the equations of motion (Eqs. 2.207-2.208) are identical to Eq. 3 (provided the approximations in Eq. 2.209 are assumed and the interpretation given for z is considered, namely, each drive only excites one mode because each drive drives near the resonance of each mode). The virials V_1 and V_2 stand for the virials of mode 1 and 2 respectively and can be written as (from 2.60)

$$V_1 = \langle F_{ts} z_1 \rangle = \frac{1}{T}\int_0^T F_{ts} z_1 dt$$

$V_1 = -\frac{1}{2}F_{01}A_1 cos\phi_1 + \frac{1}{2}A_1^2[k_1 - \omega_{01}^2 m]$ an arbitrary ω

$V_1 = -\frac{1}{2}F_{01}A_1 cos\phi_1$ $\omega=\omega_0$ Eq. 2.211

$$V_2 = \langle F_{ts} z_2 \rangle = \frac{1}{T}\int_0^T F_{ts} z_2 dt$$

$V_2 = -\frac{1}{2}F_{02}A_2 cos\phi_2 + \frac{1}{2}A_2^2[k_2 - \omega_{02}^2 m]$ an arbitrary ω

$V_2 = -\frac{1}{2}F_{02}A_2 cos\phi_2$ $\omega=\omega_0$ Eq. 2.212

Note that for both modes the fundamental period T is used to derive the expressions. This means that V_2 is an average for a fundamental cycle of oscillation. For the energy dissipation we have (from Eq. 2.39)[66]

$$E_{dis(1)} = -\int_0^T F_{ts} \dot{z}_1 dt$$

$E_{dis(1)} = \pi F_{01} A_1 sin\phi_1 - \frac{m\omega_{01}}{Q_1}\omega_1 \pi A_1^2$ an arbitrary ω

$$E_{dis(1)} = \frac{\pi k_1 A_{01} A_1}{Q_1}\left[sin\phi_1 - \frac{A_1}{A_{01}}\right] \qquad \omega_1=\omega_{01} \qquad \text{Eq. 2.213}$$

$$E_{dis(2)} = -\int_0^T F_{ts}\dot{z}_2 dt$$

$$E_{dis(2)} = \pi F_{02} A_2 sin\phi_2 - \frac{m\omega_{02}}{Q_2}\omega_2 \pi A_2^2 \qquad \text{an arbitrary } \omega$$

$$E_{dis(2)} = \frac{\pi k_2 A_{02} A_2}{Q_2}\left[sin\phi_2 - \frac{A_2}{A_{02}}\right] \qquad \omega_2=\omega_{02} \qquad \text{Eq. 2.214}$$

As a note, it should be emphasized that it is clear that the drives will affect both modes. In the expressions above the approximation is that the displacement z near the drives ω_1 and ω_1 can be accounted for by the response at each mode only. The numerical integration of the equation of motion however shows that this is a good approximation, particularly in air and vacuum where the Q factor is high[43-44, 63, 66].

The frequency shift of the second mode

For the frequency shift of the second mode, the derivation does not fully follow from the analysis of the first mode. The analysis of Giessibl however still holds for the higher modes. Then,

$$\frac{\Delta f_{02}}{f_{02}} \approx -\frac{1}{k_2 A_2^2}\langle F_{ts} z_2 \rangle \qquad \text{Eq. 2.215}$$

where the virial is obtained from Eq. 2.21. It turns out that solving Eq. 2.215 is very difficult because typically $A_1 >> A_2$. Instead of solving it directly, Kawai at al.[67] proposed that the general linear result in Eqs. 2.198 or 2.201 apply to the second mode provided the oscillation of the second mode A_2 is much smaller than that of the first mode A_1 and that the time averaged derivative of F_{ts} is used instead of the derivative at z_0. The proposed approximation is

$$k_2 \frac{\Delta f_2}{f_2} \cong -\frac{1}{4\pi} \int_0^{2\pi} \frac{\partial F_{ts}(d)}{\partial d} (z_0 + A_1 \cos\ \theta_1) d\theta_1 \qquad A_1 >> A_2 \qquad \text{Eq. 2.216}$$

The above expressions can be combined as follows

$$\frac{1}{T} \oint \frac{\partial F_{ts}}{\partial \mathrm{d}} dt \approx -2k_2 \frac{\Delta f_{02}}{f_{02}} \qquad \text{Eq. 2.217}$$

$$V_2 \approx -k_2 A_2^2 \frac{\Delta f_{02}}{f_{02}} \qquad \text{Eq. 2.218}$$

$$V_2 = -\frac{1}{2} F_{02} A_2 cos\phi_2 \qquad \omega=\omega_0 \qquad \text{(Eq. 2.211)}$$

Combining the three equations above

$$\frac{\Delta f_{02}}{f_{02}} \approx -V_2 \frac{1}{k_2 A_2^2}$$

$$\frac{\Delta f_{02}}{f_{02}} \approx \frac{1}{2} \frac{F_{02}}{k_2 A_2} cos\phi_2$$

$$\frac{1}{T} \oint \frac{\partial F_{ts}}{\partial \mathrm{d}} dt \approx -\frac{F_{02}}{A_2} cos\phi_2 \quad \omega=\omega_0 \text{ and } A_2 << A_1 \qquad \text{Eq. 2.219}$$

Eq. 2.2189 provides the means to compute the average of the gradient of the nonlinear term F_{ts} via the drive force, amplitude, and phase of the second mode. Importantly Eq. 2.219 , is fully general for any oscillator where the conditions expressed there are shown. Expressions similar to the one in Eq. 2.219 have been simultaneous exploited[68] with the terms for the virials and energy dissipation (Eqs. 2.211-2.214)[69-71] to extract material properties from models such as those shown in Eq. 2.24.

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