Unravelling Heterodyne Force Microscopy

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Summary

Heterodyne Force Microscopy has shown remarkable subsurface contrast and resolution, which is hard to understand from a physical point of view. This thesis addresses the poorly understood aspects in Heterodyne Force Microscopy. The new insight we gained allowed us to perform a quantitative analysis of a carefully designed Heterodyne Force Microscope (HFM) experiment such that we could determine the physical origin of the contrast formation in this particular experiment.

First, we needed to develop our own Atomic Force Microscope (AFM) add-on such that we could perform HFM experiments in our lab. In a first attempt we used a commercially available cantilever holder of an existing AFM, but it quickly proved not possible to excite the cantilever at MHz frequencies using this device. The reason for this was twofold. Firstly, the resonance frequency of the mounted piezo element is much lower than the ultrasonic frequency, at which we intended to excite the cantilever. As this implies that the response of this piezo element is significantly reduced at frequencies well above its own resonance frequency, the resulting cantilever excitation is negligible. Secondly, the electronic drive signal of this piezo element that ultrasonically excites the cantilever, is sent through one cable, which is part of a bundle of cables. The problem lies in the fact that the signal of the photodetector that measures the motion of the cantilever via a laser beam, is also fed through one of the cables of this same bundle of cables. This creates a severe electronic crosstalk, such that the signal of the photodetector indicates a motion of the cantilever, even if there is no cantilever placed at all in the holder. The solution, described in Section 1.3, was to use a piezo element with a resonance frequency high enough to ultrasonically excite the cantilever and to realize its own electronic connection and shielding such that it is completely separated from the bundle of cables. We also found a solution to ultrasonically excite the sample, as is described in Section 1.3.2.

We then took off on our journey and studied both analytically and numerically the ultrasonic vibration of a polymer sample containing a spherical nanoparticle, as is described in Chapter 2. We studied the propagation of the ultrasound wave for nanoparticles with different mass densities as well as polymers with different elasticities. Using both an analytical model and a finite element analysis, we showed that Rayleigh scattering of the ultrasonic wave that propagates through the sample, indeed generates a contrast in the amplitude as well as in the phase of the ultrasound that arrives at the surface. As the contrast in phase turned out to be in the order of a few millidegrees, we

thought it to be detectable. For comparison, both models revealed that the contrast in the amplitude is undetectably small. This implies that the phase of the difference frequency in HFM is more sensitive to Rayleigh scattering than the amplitude. We verified the typical Rayleigh dependencies on the magnitudes of the contrasts, like the squared dependence of the ultrasonic excitation frequency. It turned out that the region on the surface that is affected by Rayleigh scattering, is at least four times larger in diameter than the nanoparticle. This clearly contradicts many reported HFM experiments on embedded nanoparticles inside a polymer. In these experiments, the lateral resolution on the surface has been observed to be almost equal to the size of the nanoparticles. There exists even one publication, which reports that the observed size of the nanoparticles on the surface decreases with increasing depth of the buried nanoparticles.

We found that both the geometry of the sample and the attenuation length of the ultrasound, which describes the typical absorption length in the sample, is crucial for and, in fact, determines the dependence of the contrasts on the depth. In both models, we applied a lateral sample size significantly larger than the ultrasound attenuation length. Therefore, a scattered wave that propagates from the nanoparticle to the side, is never reflected back to the nanoparticle. This is completely different for the thickness of the sample, as it is usually much smaller than the attenuation length. The two models treat the boundaries at the top and bottom interface of the sample differently. In the analytical model, the scattered wave is not reflected at the top and bottom interface of the sample, whereas in the finite element analysis all waves are fully reflected. Moreover, in the analytical model, the nonscattered wave is partly reflected and partly transmitted at the top and bottom interface of the sample according to the acoustical impedances involved. As a consequence, in the finite element analysis, any depth dependence of the contrasts is averaged out by the hundreds of reflections of the Rayleigh scattered wave between the top and the bottom interface of the sample. Without these reflections, we do observe a 1/depth dependence of the contrasts in the analytical model. We expect the reality to be somewhere in between, since the boundaries will be neither completely transparent nor fully reflective. A possible depth dependence is particulary interesting, as it might provide a mechanism to determine the depth of subsurface features quantitatively.

In order to gain insight in the mechanical response of the cantilever and to enable studies on possible contrast formation mechanisms, we decided to set up a simulation that calculates the forces on the cantilever and its response in finite, very small time-steps, for an ultrasonically excited cantilever that, in addition, is in the vicinity of an ultrasonically vibrating sample. As described in Chapter 3, we determined, on the basis of this simulation, both the amplitude and the phase of the cantilever not only at the (heterodyne) difference frequency but also at the two ultrasonic excitation frequencies. In addition, we also simultaneously determined the static deflection of the cantilever. To our surprise, the results of these simulations showed that the ultrasonic amplitude of the cantilever motion remains almost constant, even if the tip is fully in contact with the sample. The reason for this counterintuitive result is the extremely high bending stiffness of the cantilever at ultrasonic frequencies. The stiffness of the tip-sample contact is unable to reach comparable values, even if the cantilever is pushed ~ 6 nm deep into the sample. The simulations also revealed that the amplitude of the difference frequency has a local maximum in the attractive part of the tip-sample interaction, before it reaches a second maximum in the repulsive part, when evaluated as a function of the tip-sample distance. The height of this second maximum could, surprisingly, be determined simply by beating, although beating should be completely unimportant in nonlinear (heterodyne) measurements, since it is a purely linear effect.

As described in Chapter 4, we experimentally confirmed the (partially surprising) results of the simulations. Although many different models exist in the literature that analytically describe the tip-sample interaction depending on both the elasticity of the tip and the sample as well as on the contact force, we showed that it does not matter at all for the results of the numerical simulations which of the models one uses, as long as the fit to a model perfectly matches the experimentally obtained tip-sample interaction. We demonstrated that only the particular shape (form) of the tip-sample interaction is important. Similar to the numerical simulations, also the experiments showed that the amplitude of the difference frequency has a local maximum in the attractive part of the tip-sample interaction, before it reaches a second maximum in the repulsive part. Surprisingly, the experiment also confirmed the counterintuitive prediction that the ultrasonic cantilever excitation remains almost constant when pushing deep into the sample: at a deflection of 10 nm, which is approximately equal to a contact force of 20 nN, the amplitude is reduced by a mere 0.3%.

This left us with the question how beating, a purely linear effect, is able to describe the generation of a nonlinear signal at its difference frequency. To address this question, we analytically derived a solution for mixing for any type of mixer, independently of its order, such that we could study the effect of beating on nonlinear frequency mixing. In this derivation we used only *linear* expansions and made no restrictions at all on the exact form of the tip-sample interaction, as is described in Chapter 5. We showed how beating completely describes the generation of the heterodyne signal. Our equations are a generalization of the typical expressions found in standard textbooks for nonlinear mixing, as these equations are all an approximation. The standard textbook equations are based on a second-order approximation and only a few publications exist that include approximations to a higher order. Strictly speaking, our completely analytical solution is valid up to infinite order. On the example of HFM, we demonstrated that the contribution of beating is significant in real experiments. In fact, it dominates the generation of the heterodyne signal. Since heterodyne detection schemes are widely applied, many heterodyne measurements may need to be reconsidered.

The new insight we gained concerning the ultrasonic wave propagation in the sample, the ultrasonically excited cantilever and its dynamics in the vicinity of a vibrating sample, and the generation of the heterodyne signal, brought us in the unique position to perform a quantitative analysis of a well-defined HFM measurement, which is described in Chapter 6. We designed a sample with spherical gold nanoparticles with a radius of only 10 nm. We developed a recipe such that these nanoparticles were randomly distributed on a polymer layer and buried by a second polymer layer. This sample represents a model system for "nanoparticles embedded in a polymer". In the experiment, we measured, for different contact forces, the height variations on the surface as well as the amplitude and the phase of the heterodyne signal. Only for high contact forces, i.e. when the tip was pressed deeply into the top polymer ($\sim$ 6 nm), we were able to visualize the gold nanoparticles. Strangely enough, the nanoparticles not only appeared in the amplitude and the phase of the heterodyne signal as expected, but also in the height variations of the surface. This is rather remarkable, as the gold nanoparticles were buried 82 nm under a polymer and we poked only $\sim$6 nm into the sample. Concerning the contrast mechanism in this experiment, we noticed that the magnitude of the contrast in these images were orders of magnitude larger than expected based on Rayleigh scattering. Therefore, we could exclude Rayleigh scattering as the most dominant contrast mechanism. A second observation was that the amplitude of the heterodyne signal was reduced above a gold nanoparticle. This stands in contradiction with elasticity variations of the sample induced by the nanoparticles, as it would result in an opposite contrast (contrast inversion). These elasticity variations can be compared with probing a pea underneath a pillow: the surface above the pea appears harder when pressing on it with your fist. Such an increase in elasticity would actually result in an increase in amplitude of the heterodyne signal above the nanoparticle (pea). We were left with the reduction of the amplitude of the difference frequency above the nanoparticle and had to conclude that either a decrease in ultrasonic vibration amplitude of the tip or the sample must be responsible for this. As we already had shown that the ultrasonic amplitude of the tip remains almost constant, the only remaining possibility was a decrease in amplitude of the ultrasonic sample vibration. In principle, there are only two explanations for such a decrease of the amplitude of the ultrasonic sample motion above the nanoparticle. The first is based on ultrasonic attenuation in the sample realizing that it is material dependent. However, as the ultrasonic attenuation is smaller inside a gold nanoparticle than in the surrounding polymer, the amplitude of the ultrasonic vibration above the nanoparticle should be larger than next to the nanoparticle contradicting the experiments. Therefore, energy dissipation in the form of friction at shaking nanoparticles was the only possible remaining physical mechanism that could explain the reduction in the ultrasonic vibration amplitude of the sample above the nanoparticle. We found additional evidence for this from an estimation of the involved energy dissipation. The value, determined from our experiments, matched the typical energy dissipation in reported friction experiments performed with an AFM, in which the tip of the cantilever has an apex as large as the nanoparticles used in our experiment.

In short, we conclude that the most important physical contrast mechanism of HFM measurements performed on the system "nanoparticles in a polymer" is given by *friction at shaking nanoparticles*. We came to this conclusion after considering each individual aspect in Heterodyne Force Microsocpy.

To conclude our journey, we would like to point out that the physical contrast mechanism on the system "nanoparticles in a polymer" must be different from the system "(gas) voids in a metal". In the latter, friction cannot be the dominating physical contrast mechanism, as the dissipated energy on the interface between a (gas) void and a metal is orders of magnitude lower than on the interface between a metal and a polymer. Therefore, we rather expect elasticity variations in these samples to dominate the contrast.

Our conclusion that different types of samples might have a different physical contrast mechanism complicates a quantitative analysis of measurements obtained by a microscope that is capable of nondestructively measuring subsurface structures with nanometer resolution. In principle, one should perform a full quantitative comparison between the experimentally observed contrast and the numerically calculated contrast in order to elucidate the physical contrast mechanism of each individual sample. This problem might be circumvented by increasing the ultrasonic excitation frequencies from a few MHz to frequencies in the order of a GHz. At these high frequencies, (Rayleigh) scattering of the ultrasonic wave that propagates through the sample, should be the dominating contrast mechanism in any type of sample.