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Hello, I'm Matt Pelton, and I'm glad to have a chance to talk to you today about some work that we've been doing over the past several years, to measure new properties of fluids at the nanometer scale by monitoring the vibrations of metal nanoparticles suspended inside those liquids. And I'm going to do this by kind of telling a story explaining how it is that we got into making these measurements in the first place and what we saw as we went along.

So our original motivation for looking at these vibrations of metal nanoparticles in fluids was the idea that we could use those as a way of measuring, weighing individual molecules, such as biomolecules, at the single molecule level. So for example, if you look at larger resonators such as quartz crystal oscillators, those are regularly used for mass sensing, for example, in deposition systems. So if you have an evaporator where you're depositing materials onto a substrate, you'll often have a quartz crystal oscillator next to it that is also getting that material deposited onto it.

So that oscillator is vibrating, and by monitoring those vibrations electrically, you can see very small changes in the vibrational frequency. Basically, as material deposits onto the oscillator, it gets heavier. Vibrational frequency goes down, and those changes can be used to monitor the amount of material deposited to the sub-modulator level. The idea is if you can make these things smaller and smaller, going down from these microscopic resonators to microscopic microfabricated resonators, down to really nanometer scale resonators, such as metal nanoparticles, the amount of material that you could measure would go down too because the fractional change in mass-- which corresponds to the fractional change in frequency-- would be larger for a small resonator when a single molecule attaches to it.

If we wanted to do biomolecular sensing, in particular, we would want to be able to monitor these vibrations in liquids. But in order to do that, we would need to know how these particles are interacting with the liquids in the first place, and that's how these mechanical vibrations are affected by the surrounding liquid environment, particularly how energy is dissipated between the meta

I nanoparticles and the surrounding environment. Because in order to have a precise measurement of mass, you need a precise measurement of the frequency. In order to be able to measure the frequency precisely, the object has to oscillate many times. You have to have a high mechanical quality factor for the oscillations. There's several oscillations before the energy is dissipated, either in the particle or in the surroundings.

Now, we can't attach electrodes to a single metal nanoparticle or to a collection of metal nanoparticles like we can attach them to a quartz crystal oscillator. So we don't have the same ways of measuring that we have in MEMS systems or quartz crystal oscillator systems. But fortunately, we do have the ability to measure these things optically. So it's really this optical manipulation that gives us a hands-off probe of these vibrations that we need, in order to be able to measure them at a nanometer scale.

So the idea is that if these metal nanoparticles absorb light from the laser pulse, they're going to heat up. That means they're going to expand. The expansion happens very quickly. So it's sort of an impulsive excitation with a mechanical vibration, like hitting a bell with a hammer. It will ring-- the vibrations will ring inside the nanoparticles. Except because they're on the nanometer scale, so on the macroscopic scale, the vibrations are really in the gigahertz frequency range, microwave frequencies.

And then we can monitor those vibrations optically as well because the vibration's coupled to plasmon resonances inside the metal nanoparticles. So plasmons are collective oscillations of the electrons inside the particle. If light is incident on the particle, the electric field, the light will push electrons towards one side of the particle. So that negative charge will be left on one side. Part of the charge is left behind on the other side.

There is a restoring force between the two of those. With the restoring force, there's

an associated resonant frequency. So if the particle is driven at that plasmon resonance frequency, then you have a large oscillation, collective oscillation with the electrons inside the particle. That leads to a large optical response, large scattering and absorption of light by the particle at that resonant frequency.

And that resonant frequency depends on the shape of the particle, depends on the electron density inside the particle because the restoring force is between the electrons on one side the particle and the absence of electrons, so positive ion cores on the other side of the particle. So that electrostatic restoring force depends on how many electrons you have and how they're separated spatially. It also depends on-- less obviously-- on the band structure of the material, what's called the so-called deformation potential.

So if you strain the material, if you compress it or expand it, then you're effectively changing the potential landscape that the electrons are moving inside. So as the particles are oscillating back and forth, all of these are changing. They're getting bigger and smaller. The shape is changing if it's a non-spherical particle. And then you have this local strain that changes the potential energy landscape.

So we did some calculations to relate all of those different factors to the shift in the plasmon frequencies that we could measure experimentally. We see that it's a very complicated relationship in general between the measurable phase shifts, which can be very large or very small, depending on the modes we're looking at. It can be positive or negative depending on the kinds of particles we're looking at. But as a rule of thumb, if we want a large signal, we want a good sort of spatial overlap between the mechanical mode and the electromagnetic or plasmonic mode. That is, we want the deformation of the particle to be largest where the fields are also-- electromagnetic fields are often concentrated in these particles.

And then we can measure these things in the time domain using ultra fast transient-absorption spectroscopy or pump-probe spectroscopy. So there's nothing really special about this measurement.

ent method. It's used quite a bit for all sorts of other kind of measurement. But it might be a little less familiar to people in the optical trapping and optical manipulation community.

So just to go through it very quickly, we have an ultrafast laser system that produces about 100 femtosecond pulses in 8,800 nanometers micro dual pulse energies. We split those into two things that we call the pump and the probe. The pump can go through an optical parametric oscillator, which converts the frequency so that we can tune the wavelength of this pump to match the plasmonic resonance of the particles. The pump comes in, gets absorbed when a particle sees them up. They start vibrating.

The probe gets converted into a white light, so a very broadband spectrum. And then it arrives at the sample some time after the pump, which that time--

controlled basically just by how far the probe has to travel before arriving at the sample. And then we monitor how much of the probe gets transmitted through the sample, as a function of the wavelength through the probe but also as a function of the time delay between the pump and the probe. Just by tuning this mechanical delay line, we can measure on the femtosecond timescale.

So what we see is things that look like this. This is showing the change in wavelength between having the pump there and not having the pump there, how much the absorption of the probe has changed as a function of the wavelength, as a function of the delay between the pump and the probe. So every vertical slice represents a different spectrum between pump on and pump off. We can fit that different spectrum by assuming that the plasmon resonances are Lorentzian.

So for each time point, we can get a shift in the plasmon resonance frequency. We see these damped oscillations of the shift on top of the background. So we can fit those damped oscillations and get the quality factor and frequency of the oscillations. Again, the quality factor being a measure of the lifetime of the vibrations.

And what's really enabled us to get the information that we can out of these things to look at how energy is damped from the metal nanoparticles into the surrounding fluid has been our access to very high quality samples. So really, what made our measurements better than what came before is not our superior measurement ability, but my ability to work with collaborators who can make very uniform either bipyramidal metal nanoparticles or my ability to buy spherical metal nanoparticles. They've recently become available commercially.

The reason it's important to have very uniform particles is to overcome the inhomogeneous dephasing system. So if your particles are all different sizes, they're all going to oscillate at slightly different frequencies. So the initial pump pulse comes in. It sets them all off oscillating at the same time. They're initially going to be oscillating in phase, and you're going to have a large signal.

But some are a little faster. Some are a little slower. They're all going to get out of phase with each other. They're going to cancel each other out, and the signal is going to decay with this inhomogeneous dephasing, at a rate-- if the particles are fully dispersed-- that's faster than the energy exchange in the system. So we do have to take this into account, even for these model disperse samples, measure the size distribution from these transmission electron microscope images, and then subtract that from the measured decay rates to infer these through the energy decay rates in the system.

So if you look at the bipyramids, these things will oscillate longitudinally, like in that cartoon that I showed you before, with lines getting longer and shorter. So the main motion inside the fluid is a shear motion. Surfaces of the bipyramid are moving laterally within the fluid.

And the damping of that shear motion will be viscous due to the shear viscosity of the liquid. It's just like a pendulum oscillating back and forth inside a viscous medium. You'd expect the damping rate to be proportional to the square root of the viscosity of the system.

And so we tested this by taking these bipyramidal samples, putting them into different solvents with different viscosities, from glycerol, down to water, and down to methanol. And we see a good sort of square root of viscosity damping. The lines actually represent a quantitative analytical theory developed by our collaborator, John Sader at the University of Melbourne--

but again, shows that at least up to these moderate viscosities, we can understand this damping very well as shear viscous damping of these oscillations.

But as we go up to higher and higher viscosities, we do see that the agreement between theory and experiment is getting worse. Firstly, our error bars are getting a lot higher too. So we went back to this, improved the measurements, pushed down these error bars. And then John Sader and his postdoc also worked on improving the model, going beyond this simple analytical model that involves approximating the spheres infinitely large and doing fully numerical models that take into account the real size and shape of the particles.

And then we compare our experimental measurements. In this case, we're looking at these oscillations as a function of time as we're increasing the viscosity of the liquid, in this case, mixing together water and glycerol and changing the amount of glycerol in that mixture, so that the liquid becomes more and more viscous. And we see, actually, as we got the measurements better, as we got the theory better, they actually moved further apart from each other. Especially at these high viscosities, the theory predicts that the oscillations would be over-damped.

Now, around 75%, 80% glycerol, you shouldn't even have a single oscillation. But what we see is the oscillations just keep going, even in these extremely viscous liquids. And we realized that this was happening because the liquids were not simply viscous. But at these high frequencies that we're monitoring at, they are viscoelastic. They have the properties not only of a Newtonian viscous liquid, but also of an elastic solid. So instead of simply dissipating energy irreversibly into the liquid, the vibrations are storing energy as it would in elastic solid. The liquid is storing that energy and then restoring it into the particle as it oscillates back and forth.

So this is reflected in both our measurements on the quality factor. Instead of decreasing methodically down to being overdamped, as we'd expect for a Newtonian liquid, are plateauing and even increasing slightly as the liquid becomes more and more elastic. And this is also reflected in the frequency of these oscillations. You would expect, if this was a Newtonian fluid, as you increase the damping, as the viscosity goes up, the frequency should go down because the resonances are just damped more and more. But the frequency actually goes up because the elastic energy is being restored to these vibrations and increasing their oscillation frequency.

And this all happens because we're probing the liquid on its inherent relaxation times. That is, the vibrations of these metal nanoparticles are occurring on periods that are comparable to the molecular relaxation time inside liquids. So basically, the molecules can't get out of the way fast enough as the particle is moving within them, and they just compress and restore like a spring.

So you can see that in our numerical simulation, by looking at where the energy is stored inside this vibrating particle. So in pure water, which is having a fairly viscous effect, almost all of the energy is within the nanoparticle itself. There's very little energy inside liquid because it's just being dissipated irreversibly. But if you go up to high glycerol concentration which is highly viscous and relatively long relaxation times, you see that most of the energy is now being stored in the liquid instead of in the particle. The liquid is restoring that to the particle and is preventing its damping.

Now, when I talked about this about three years ago-- actually, in San Diego, at the same session-- this was as much as we had at the time. Somebody-- I wish I remembered who it was-- asked whether we could use this to measure boundary slip inside the liquids. And I said at the time I thought that would be pretty hard to do because slip lengths are going to be extremely small.

But then fortunately, the D. Chakraborty, collaborator in Melbourne, realized that this remaining discrepancy between the theory and the experiment might actually be because of boundary slip. So for those that don't know what that means, in most of the time with fluid mechanics, you assume what's called the no-slip boundary condition between a solid surface and every liquid. That is, you assume that the velocity of the liquid at the surface-- relative to the surface is zero. So that if, say, the phases of this nanoparticle move back and forth inside the liquid, the liquid immediately adjacent to those phases would move in concert with that vibrating surface.

But we know that this is just an approximation, that there has to be some non-zero slip in real liquids. And most of the time, we don't worry about that because the slip lengths are so small in liquids. So they can be relatively large and noticeable in gases. But in wetting liquids that make good contact with the surfaces, we expect slip length on the order of nanometers.

When I say slip length, it's in this Navier description of the slip. So if you imagine, there's a finite velocity of the liquid relative to the surface which increases in the regular way as you get further away from the surface. So if you extrapolate that back into the solid, you have an effect of no-slip boundary condition again, but it's as if the surface has moved down by the slip length into the solid.

So then we made some more measurements. In this case, we took our 20% glycerol mixture, which is almost entirely Newtonian, and we changed the temperature in order to change the viscosity, measured the quality factors. We compared it to our previous model. We saw that there was a sort of systematic deviation between theory and experiment, regardless of what fitting parameters were used. And again, there's only one fitting parameter we're using here that can tear the theory to experiment. That's how much energy is being dissipated within the particles themselves. We're calling it the intrinsic quality factor.

I'll explain that a little bit more. As the particles are going back and forth, we're measuring how quickly the energy is being dissipated from the particles, and there's two places they can be dissipated. Could be dissipated to the surrounding liquid or could be dissipated internally within the particle itself. And so assuming that that internal dissipation process is always the same, we used that as a single number to describe it under all these different conditions. And we see that no matter how hard we try, we don't get a good fit between theory and experiment.

But

now, if we allow slip to come into the models, we can get remarkably good agreement between our experiments and our fit theory. There's only one additional fitting parameter in this case, which is the slip length. And so we got a slip place of about 3 and 1/2 nanometers for the best fit between these.

Now, I realize this is a fairly small discrepancy, so maybe we're making a lot out of something that's really just at the edge of these error bars. But my student did a whole lot of measurements. This took a very long time. So in a whole series of different glycerol mixtures, at a whole series of different temperatures, we took the values of this fit, and we put them into these graphs without changing anything else.

So for comparison between this data and the experiment, there are no free parameters. We see remarkably good agreement. That is clearly better than the agreement that we get if we don't include the effects of slip. This is really showing that there is a single slip length, about 3 and 1/2 nanometers, that describes the motion of these gold surfaces within these water-glycerol mixtures.

Apart from being a way of measuring slip quantitatively at these various small length scales--

which has been a real challenge and I'd say a subject of some controversy --

we also realized in doing this that the viscoelasticity that we had measured

before was enabling this to happen. So normally, in these highly visible liquids, the effects of slip would be unnoticeable because the damping would be so strong. But if you now have viscoelasticity going on, the effects of slip could become important where it otherwise wouldn't be.

We can quantify this just to see what's going on in terms of a sensitivity parameter, which is basically the difference in the quality factor as the slip length changes. This is plotted in this graph here as a function of the mass polar fraction of glycerol. You can see-- [COUGH] and the dotted dash line is what would happen in the absence of viscoelasticity. The slip would just become unimportant as the viscosity of this liquid increased.

But what happens instead is eventually, it levels off, and the sensitivity remains high, even for a very high viscosity. This is quantified here on the top axis in terms of Deborah number. That's the ratio between the measurement time and the characteristic molecular relaxation time inside the liquid. We see here, the sensitivity increases basically without bound as the Deborah number increases.

Just to show some of the most recent stuff in the way of work in progress, all of the measurements I've showed you so far have been produced by pure metal gold particles in shear motion. So the motion that we've been looking at has been almost entirely shear motion of the phases of the particles sideways, back and forth inside the liquid, as the rods get longer and shorter. But if we use those spherical particles I showed you a while ago instead, there's no shear motion. Instead, there's only radial motion.

And so now, we would have to take into account not the shear viscosity but the bulk viscosity of liquid. That means there's going to be an interaction in terms of the energy dissipation between the liquid viscosity and the compressibility of a liquid, the generation of propagating sound waves inside the liquid. This is something that is quite complicated to treat theoretically, and again, our collaborator John Sader developed models for it

his only in the last few years. There's been very few tests of this interplay between viscosity and compressibility for viscoelasticity liquids.

So again, my student, Brian Uthe has been extremely patient in generating a thorough data set for these vibrating spherical particles in liquids, where you can see, again, as we increase the viscosity, either by increasing the fraction of glycerol or by decreasing the temperature, instead of simply decreasing to zero, as you would expect for a viscous liquid, these plateau, showing clear effects of viscoelasticity. Sorry, this is the temperature one, where we see it going--

viscoelastic effects coming at low temperatures and high mass concentrations of glycerol. A couple of years ago, John Sader's group developed a theory in order to be able to explain this sort of data, and they're hopefully very soon going to be able to compare that to this data set that we have.

So with that, I'd just like to summarize that these measurements, these all-optical measurements, nanoparticle suspended liquids, have given us access to unconventional properties of conventional liquids of the nanoscale. By conventional, I mean simple, like what people call simple liquids, single component molecular liquids with small molecules, water, glycerol, the stuff that makes up most of the world. Viscoelastic effects and boundary slip, viscoelasticity boundary slip, have been seen in so-called complex liquids before, things like fluid suspensions, polymer melts, and so on. But the phenomena there are quite different and occur on very different timescales and length scales to what we're looking at here.

And what this means for us is that we can't use conventional fluid mechanics unthinkingly at the nanometer scale. You have to take into account viscoelasticity, boundary slip, and the interplay between the two of them if we really want to know what's going on. This seems to me to have important implications for anything where you're talking about motions of fluids at the nanometer scale. So the mass-based sensing of molecules that I started with is clearly going to be impacted by this in a positive way because it means that we would be able to measure vibrations in liquids that would otherwise be damped out.

It will be important for a flow of fluids through lab-on-chip systems. Membrane filtration and separation turns out to be extremely sensitive to boundary slip. Fracking, for better or for worse, just is highly affected by the flow of liquids through nanoscale pores. And I'd say, it seems to me, even biomolecular and cellular processes will be affected by liquid flows at the nanometer scale, and the proper models of water will be essential to really understanding biomechanics.

And an important future goal for us is to take these measurements where we're seeing viscoelasticity effects, boundary slip in water-glycerol mixtures, even move to the higher frequencies that would allow us to measure them in pure water. And ultimately, understanding not just what phenomena occur at the diameter scale, the picosecond timescale, the characteristic of nanoscale motion in simple liquids but understanding where those come from, making a connection between these sort of bulk fluid mechanic models here and the underlying microscopic mechanisms that give us the parameters that we have.

So I'd like to finish there. I'm sorry that I can't actually be there with you in person in San Diego to answer questions, but I'd be very happy to have any questions or comments that you have by email. I look forward to hearing from anybody that would like to get in touch with me. Thank you.