Vibrational symmetry breaking of supported nanospheres

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Coherent particle vibrations of gold nanospheres on a solid surface are detected by optical spectroscopy and time-resolved x-ray scattering. A new dominant mode arises, which is described by the monopolar mode symmetry forbidden of free spheres. Molecular dynamics studies of single-crystalline and polycrystalline particles confirm the assignment of these modes.

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The elastic properties of nanoscale particles have been a matter of intense investigations in the recent past. On the one hand, noble metal nanoparticles can serve as model systems for accessing electron-phonon interactions.^{1–3} On the other hand, nanoscale dynamics and structure are accessible via macroscopic optical tools to investigate size-dependent phenomena such as vibrations,^{4,5} vibrational damping, or melting.^{6,7} Nanoparticle vibrations play an interesting role in determining particle interaction with adsorbing species or surfaces^{8,9} or can be used as resonances for coherent control,^{10,11} laser cleaning,¹² or determination of adhesion forces.¹³

The goal of the present study is to understand the vibrational symmetry breaking of a particle attached on a surface, which represents the generalization of different aspects of adhesion.^{5,8} By comparing the results from femtosecond spectroscopy, time-resolved x-ray scattering, and molecular dynamics (MD) simulations, the assignment of the modes of adsorbed gold particles on a surface is clarified. The observed vibrations consist of a long-period translational mode, which is forbidden for a free particle. It adds to the uncoupled modes of spherical and spheroidal symmetry.

Time-resolved x-ray scattering has been performed by exciting gold particles with sub-monolayer coverage on a surface of silicon with pulses of an amplified femtosecond laser (frequency-doubled Ti:Sa radiation at 400 nm) and probing the lattice dynamics by synchronized pulses of monochromatic x rays at the storage ring of the European Synchrotron Radiation Facility (ESRF).^{14–16} Synchronization is achieved by an absorptive x-ray chopper at 1 kHz, whereafter the powder scattering is recorded by means of a charge-coupled device detector (CCD) and used to determine lattice expansion from the angular peak shift.^{16,17} Time resolution is determined by the x-ray pulse length, which, depending on electron pulse charge, ranges from 90 to 120 ps in 16-bunch mode. A further reduction of pulse length can be observed in reduced charge modes, one of which occurs during hybrid pulse patterns.¹⁵

Thus the pulse length reduces down to 55 ps (full width at half maximum).

Femtosecond optical spectroscopy was performed in the so-called asynchronous optical sampling (ASOPS) scheme. Two slightly frequency-wise detuned Ti:Sa femtosecond oscillators (800 nm, 1 GHz repetition rate) act as pump and probe sources, thereby allowing one to rapidly scan the mutual delay without moving parts to achieve high signal-to-noise ratio.^{6,18} The probe beam was detected at a reflection angle of about 45°.

To model a realistic situation of adsorbed nanoparticles, a molecular dynamics (MD) simulation was set up including both the forces to a substrate and effects from polycrystallinity. Spherical gold particles were first defined by using the glue model of Ercolessi *et al.*^{19–21} In a second optional step a series of “Rubik” transformations were applied to create a polycrystalline particle. During such a transformation a specific part of the nanoparticle is being separated by a plane, rotated, and fused again with the main particle body (see Fig. 1). A ninefold repetition of this transformation using different parts subjected to rotation angles with equal probability between –90° and 90° is performed. Subsequent equilibration at elevated temperatures leads to polycrystalline particles. In the final step the particles are “landed” on a surface by a slow movement against a plane which provides short-range attraction energy ϵ in the range of 2–10 eV per atom. Stronger attraction and higher approach speed lead to a large contact area.

Parameters extracted here were two scalar components of the symmetric tensor of second moments

$$S = m \sum_i \vec{r}_i \otimes \vec{r}_i = m \sum_i \begin{pmatrix} x_i^2 & x_i y_i & x_i z_i \\ y_i x_i & y_i^2 & y_i z_i \\ z_i x_i & z_i y_i & z_i^2 \end{pmatrix} \quad (1)$$

$$= \begin{pmatrix} S_x & S_{xy} & S_{xz} \\ S_{yx} & S_y & S_{yz} \\ S_{zx} & S_{zy} & S_z \end{pmatrix} \quad \forall \text{ atoms } i. \quad (2)$$

FIG. 1. (Color online) MD results for a 14.6 nm sphere on a surface ($\epsilon = 4$ eV). (a) Temporal evolution of $S_{\parallel}$ and $S_{\perp}$ as function of the delay; (b) evolution of C_z , and (c) Fourier transform power FT of $S_{\perp}$ and C_z from polycrystalline particles with dots and single-crystalline particles as bold lines; the lower curves stand for FT(C_z). An inset on top displays the procedure of Rubik transform and a rendered nanoparticle of 10 nm diameter on a surface.

The first scalar component chosen is taken along the z axis, i.e., perpendicular to the surface:

$$S_{\perp} = \vec{e}_z^T \cdot \mathbf{S} \cdot \vec{e}_z = S_z,$$

and the second scalar component is taken along the axis $\vec{\omega} = \frac{1}{\sqrt{2}}(\vec{e}_x + \vec{e}_y)$, i.e., parallel to the surface:

$$S_{\parallel} = \vec{\omega}^T \cdot \mathbf{S} \cdot \vec{\omega} = \frac{1}{2}(S_x + 2S_{xy} + S_y).$$

They serve as proportional measures for the uniaxial elongation. The radius of gyration is mainly sensitive on the fundamental mode, while motion relative to the surface is visualized by the height of the center of mass C_z .

Nanoparticles are adsorbed on a silicon (100) surface by aid of electrostatic assembly or by layer transfer²² to yield a low-density coverage in the former and a dense monolayer assembly in the latter case. Results are not affected by the coverage. Single-crystalline (BBInternational) as well as polycrystalline particles^{23,24} showed similar lattice response both in amplitude and temporal behavior.

Polycrystallinity mainly affects the lifetime of vibrations²⁵ as seen in the MD simulations. Figure 1 displays $S_{\perp}$ and $S_{\parallel}$ for a polycrystalline particle of 14.6 nm diameter and surface contact of 0.31 expressed by the ratio of contact diameter versus particle diameter s/D . After sudden heating to 700 °C the $S_{\perp,\parallel}$ increase by about 1% in average, which is comparable to linear expansion at this temperature.²⁶ Several modes of oscillation are seen, with Fourier transform power

TABLE I. Lowest normalized eigenfrequencies of free gold spheres as calculated by the Lamb model.

Mode	(0,0)	(0,1)	(0,2)	(0,3)
$f \times D$ (THz nm)	3.11	1.52	1.06	1.58

FT at frequencies of 11 [label 1 in Fig. 1(c)], 43–73 (2), and 218 GHz (3), corresponding to size-normalized values of 0.16, 0.63–1.07, and 3.18 THz nm. $S_{\perp}$ and $S_{\parallel}$ are very similar in FT. The analytic calculation of eigenfrequencies of elastic spheres has been given by Lamb²⁷ according to an oscillation frequency f of

$$f = \frac{c_l \chi_{n,\ell}}{\pi D}, \quad (3)$$

where $\chi_{n,\ell}$ is an eigenvalue characteristic for a mode with radial quantum number n and angular number ℓ (torsional modes neglected) and c_l (c_t) is the longitudinal (transversal) speed of sound, respectively. The eigenvalues are solutions of the following equations:

$$\chi_n \cot(\chi_n) = 1 - \left(\frac{\chi_n c_l}{2 c_t} \right)^2, \quad \text{only for } \ell = 0; \quad (4)$$

$$0 = 2 \left[\eta^2 + (\ell - 1)(\ell + 2) \left(\frac{\eta j_{\ell+1}(\eta)}{j_{\ell}(\eta)} - (\ell + 1) \right) \right] \frac{\chi j_{\ell+1}(\chi)}{j_{\ell}(\chi)} - \frac{\eta^4}{2} + (\ell - 1)(2\ell + 1)\eta^2 + [\eta^2 - 2\ell(\ell - 1)(\ell + 2)] \frac{\eta j_{\ell+1}(\eta)}{j_{\ell}(\eta)}, \quad \ell > 0, \quad (5)$$

with $\eta = c_l/c_t \chi$, and j_n the Bessel functions of the first kind. The lowest modes of a free gold sphere are listed in Table I, with the notation (n, ℓ) , n being the radial and ℓ the angular quantum number.

Indeed, the fundamental mode (0,0) is well reproduced by the simulations, as well as FT signal in the range of the modes with angular momenta (0,1), (0,2), and (0,3). The clarity of the FT around the (0,2) mode varies with MD run, because interference of the different vibrations and the pre-existing vibrations prior to sudden heating affect the visibility in an arbitrary way. There exists, however, a mode of extremely low frequency at 0.16 THz nm, which is not predicted by elasticity theory. In particular the movement of the center of mass [Fig. 1(b)] identifies this mode as an elongation perpendicular to the surface. Optical spectroscopy on different sizes of supported nanoparticles, as seen in Fig. 2, generally reproduces well the fundamental mode, but is almost insensitive to the angular modes. This has been explained earlier by a low probe sensitivity on these modes as well as a possible inefficient excitation mechanism.^{4,10} The 60 nm particles, which show the clearest probe response, reveal some FT amplitude at the angular modes (inset in Fig. 2), but not at the lowest frequency.

In contrast to that, it is possible to observe this low frequency by time-resolved x-ray scattering (see Fig. 3). In fact, with x-ray scattering one can discern between the lattice vibration perpendicular to the surface and parallel to the surface by choice of the scattering direction. A slow mode is seen for the vertical lattice vibration but hardly for the parallel motion. Comparison between the change of $S_{\perp}$ and $S_{\parallel}$ with

FIG. 2. (Color online) ASOPS traces from different sized gold particles ($\square, \diamond, \circ$ for 20, 60, 152 nm particles, respectively). The inset displays the FT of the trace from 60 nm particles.

vertical and horizontal lattice expansion, respectively, show a good agreement and an antipodal movement. The fundamental mode in the experiment is barely visible, just because of the low time resolution of the experiment, which is about 90 ps in the standard 16-bunch mode. The inset in Fig. 3 plots a kinetic trace from an experiment with reduced pulse length, which enhances the visibility of the fundamental mode at the expected 3.11 THz nm (47 ps for 146 nm particles).

Both from the MD simulations and x-ray scattering, the low-frequency mode is identified as a vertical movement and extension of the particle relative to the surface. The translational mode is forbidden in an isolated particle, as the energy is not conserved. This is no longer true for a bound particle, whose center of mass can very well move along the vertical direction, because the bond to the surface provides a spring force which keeps the total (kinetic plus potential) energy constant. The same odd symmetry is expected for (0,1) and (1,1) modes which couple to the directional movement. The lowest order of the uncoupled modes is, however, expected at 1.52 versus 0.16 THz nm for the observed mode. Therefore

FIG. 3. (Color online) Time-resolved lattice expansion of 146 nm gold particles determined in vertical (full symbols) and in-plane (open symbols) directions together with the temporal evolution of S_{xy} and S_z after a convolution with the temporal x-ray profile. The inset shows the vertical lattice expansion within an experiment with higher time resolution together with the trace of S_z .

FIG. 4. (Color online) Frequencies as derived from MD simulations ($\star, \circ, \square, \blacksquare$) as functions of the ratio of contact diameter s over D together with the values of the elastic vibrations from continuum theory. ASOPS data are added independently from the x axis ($\square, \diamond, \circ$). The lowest bold line represents the prediction for a bound mode according to Ref. 8.

we conclude that the extensional mode couples to the lowest order modes with angular momentum l and quantum number $m = 0$.²⁸ The degeneracy of the modes is lost between $m = 0$ and $|m| > 0$.

A similar situation has been treated earlier, when trying to explain the vibration of coupled particles. Different models have been developed which start from the assumption of a two-mass system bound by a spring force⁵ or dumbbell-like particle.^{8,9} The latter has the advantage that the contact area enters as a coupling constant. In both cases frequencies similar to the presently observed ones are reproduced.

When analyzing MD results one can directly deduce the contact diameter s from the particle shape as a flat part at the bottom. The frequencies as function of s/D are displayed in Fig. 4. It is clearly seen that the fundamental mode is almost unaffected by the contact with the surface. Even polycrystallinity does not change its frequency. The angular modes for a free particle are seen in all footprint ranges, but cannot be distinguished one from the other due to the phase interference, as explained below. Instead we plotted all peaks in the FT, which group around the expected (0,2) and (0,3) modes. Additionally the low frequency mode shows a distinct stiffening with larger footprint. It should be noted that s/D ratios below 0.2 are not accessible, because the particle would detach intermittently from the surface at the applied excitation strength. The stiffening is rationalized by an increased spring force between particle and surface with increasing footprint. Consequently the dumbbell model by Tchegbotareva *et al.*⁸ predicts a power-law behavior with contact area and particle size. The corresponding prediction is shown as a bold line in Fig. 4.

The observed frequencies in MD fall partly below the prediction of the dumbbell model. This is mainly caused by the polycrystallinity of the particles. In fact, changing from a polycrystalline to single-crystal structure results in an increase in frequency of all angular modes. Modes from single-crystalline particles are shown as open squares in Fig. 4 compared to polycrystalline ones with full symbols. As compared to the fundamental mode, shear stress plays a larger role for these modes, which will then affect both the

frequency and the damping time. Recently it was pointed out that internal dissipation may play a major role in the damping of gold particles as compared to the external damping by either water medium or a surface.²⁵ The particles in the x-ray experiment are known to rest on a (111) facet, which provides a finite contact area. Inspection of scanning electron microscopy images under low incidence angle gives a rough estimate for s/D of about 0.3. This contact area provides the spring force for the oscillation, rather than a possible substrate elasticity.¹² Note that the MD simulation assumes a flat rigid support.

A closer look at the nature of the slow mode shows that vertical and horizontal motions of the particle possess an antipodal component. This is indicative of a (0,2) mode, which is described by an oblate-prolate transition with two nodal lines ($\ell = 2$) on the surface. Therefore the low-frequency mode has also a character of the higher angular modes and can be regarded as a hybridized mode between (0,1), (0,2), and (0,3) on the surface.

In both x-ray scattering¹⁷ and femtosecond spectroscopy there is high sensitivity on the fundamental mode, whereas the angular modes are barely visible in spectroscopy. It was argued that the homogeneous lattice heating of the (in most cases small) particles does not couple to modes of broken rotational symmetry. This may be the case for free particles, but the surface leads to an immediate coupling between the

modes. The MD results prove that even a highly uniform initial excitation populates the angular modes. These modes were still not clearly detected in the presented spectroscopy data. The reason is that the detection mechanism is a mixture of red shift due to particle elongation²⁹ and periodic changes of electron density.⁴ Angular modes show a smaller change in electron density, thus do not affect the transient optical absorption.

In summary we have observed a low-frequency mode in surface-supported gold nanoparticles by time-resolved x-ray scattering, which allows us to distinguish the modal components relative to the surface. It is identified as a hybridized angular mode and is in good agreement with earlier observations in binary particles. Although not being visible in femtosecond spectroscopy it represents a prominent mode, which should be available for exciting coherently, for instance, for particle removal or transport from the surface.

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²⁰An fcc lattice is occupied by atoms within a spherical region. The temperature is set by a Nosé-Hoover thermostat, the equations of motion are solved by a fourth-order gear-predictor-corrector algorithm. The Nosé mass and time steps were chosen to maintain energy conservation. Equilibration prior to and after landing is allowed for 300 ps. Sudden heating is performed by resampling the Maxwell velocity distribution. 10 MD steps after resampling the partitioning between kinetic and potential energy is achieved and the thermostat is restarted. By using an improved, segmented neighborhood list, particles of up to 100 000 atoms can be simulated on a desktop computer within a few days.

²¹See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.86.100101> for a movie during the heating of a 14 nm particle on a substrate.

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²³Commercial gold particles of 152 nm diameter (BBInternational) are to a large extent single crystalline as proven by single-particle x-ray scattering. Chemically synthesized particles of 146 nm diameter produced by a seeded reduction approach after Ref. 24 are polycrystalline with approx. 10 nm sized domains.

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