

Acoustic vibration of metal nanoparticles: a local probe of their environment

C. Voisin^a, D. Christofilos^b, N. Del Fatti^{a,c} and F. Vallée^{a,c}

^aLaboratoire d'Optique Quantique du CNRS, Ecole Polytechnique, 91128 Palaiseau, France

^bSchool of Technology, Aristotle Univ. of Thessaloniki, 54006 Thessaloniki, Greece

^cC.P.M.O.H., Université Bordeaux I, 351 cours de la libération, 33405 Talence, France

The reduction of the size of a material to a nanometric scale leads to drastic modification of its vibrational properties. For acoustic modes, the low frequency phonon spectrum is first altered with the appearance of discrete vibrations. Their frequency and damping reflect not only the size and shape of the nanoobjects but also the properties of their environment. In particular, in the case of nanoparticles in a matrix, the damping is due to acoustic energy transfer at the interface and spherical acoustic wave expansion in the surrounding medium. The quantized mode properties thus contain information on the material characteristics, such as the particle-matrix coupling, interface quality or matrix response, making them sensitive probe of their local environment and of its acoustic properties.

It has been shown that the breathing acoustic mode of metal nanoparticles can be coherently excited and probed using time-resolved pump-probe optical techniques, permitting precise determination of its frequency and, for the first time, its damping [1,2]. In these experiments a nonequilibrium electron distribution is first created by absorption of a femtosecond pulse by the metal nanoparticle conduction electrons. The absorbed energy is quickly damped to the lattice which impulsively launches the nanoparticle breathing mode [2]. The coherent (in phase) vibration of the excited particles is subsequently detected by measuring the induced transmission change of a time delayed femtosecond probe pulse. Using this technique, we have investigated the breathing mode frequency and damping as a function of the nature of the surrounding material and of the particle-matrix interface in silver nanospheres in solution or in a glass matrix. In the latter case, the nanoparticle-matrix interface has also been modified by applying high pressure to the composite material.

The frequency and damping rate of the breathing mode were found to be smaller in solution than in a glass matrix, demonstrating their large sensitivity to the particle environment. The reduced damping is consistent with the higher metal-solution than metal-glass acoustic mismatch, i.e., weaker particle-matrix coupling. The frequency decrease can be ascribed to the presence of the stabilizing thiols at the interface that follow the nanoparticle surface oscillation, in quantitative agreement with our simple modeling.

The impact of the interface quality has been tested by performing pressure dependent measurements in glass embedded nanoparticles. A weak dependence of the mode frequency on pressure (up to 60 kbar) has been observed, consistent with the material elastic property changes. In contrast, the damping time exhibits a fast decay, up to 10 kbar, followed by a slow one. This low pressure behavior indicates a pressure induced rearrangement at the particle-matrix interface level improving the energy transfer. The measured decay times stay however significantly longer than the theoretical ones, calculated for elastic media and a perfect metal-glass contact, suggesting the existence of an interface layer and/or modified glass elastic properties at the breathing mode frequency.

[1] N. Del Fatti, C. Voisin, F. Chevy, F. Vallée, C. Flytzanis, *J. Chem. Phys.*, **110**, 11484 (1999).

[2] C. Voisin, N. Del Fatti, D. Christofilos, and F. Vallée, *Appl. Surface Science*, **164**, 131 (2000).