Supplementary material for the manuscript "Contact laws between nanoparticles: the elasticity of a nanopowder"

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CONVERTION FROM BRILLOUIN FREQUENCY TO SOUND VELOCITY FOR A COMPACTED POROUS NANOPOWDER

The Brillouin frequency of the nanopowder can be expressed as:

$$\nu_B(\phi, P) = \frac{2V_{\rm L}(\phi, P)n_{\rm eff}(\phi, P)}{\lambda} \tag{1}$$

where λ is the optical wavelength, $n_{\text{eff}}(\phi, P)$ is the effective refractive index of the powder and $V_{\text{L}}(\phi, P)$ is the sound speed. These quantities are mainly dependent on two variables: the applied pressure P and porosity ϕ . Both vary during a compression cycle. We assume in the following that in the GPa pressure range the minimum porosity for a disordered packing $\phi_{\text{min}}=0.36$ is reached. Deducing the longitudinal sound speed from the Brillouin frequency thus requires to know the effective refractive index downshifted due to the amount of air with volume fraction ϕ_{min} in the powder. This can be done thanks to an effective medium theory such as Maxwell-Garnett model for a bi-component medium (m-air) with $m = \text{TiO}_2$ or ZrO_2 :

$$n_{\text{eff}}(\phi, P) = n_{\text{eff}}(\phi_{\min})$$

= $n_m \sqrt{\frac{1 + 2n_m^2 + 2\phi_{\min}(1 - n_m^2)}{1 + 2n_m^2 - \phi_{\min}(1 - n_m^2)}}$ (2)

where n_m is the refractive index of the matrix of bulk TiO₂ or ZrO₂. Using this expression we obtain $n_{\text{eff}}(\phi_{\min}) = 2.1$ for TiO₂ and $n_{\text{eff}}(\phi_{\min}) = 1.8$ for ZrO₂. The Brillouin frequency now writes:

$$\nu_B(P) = \frac{2V_{\rm L}(\phi_{\rm min}, P)n_{\rm eff}(\phi_{\rm min})}{\lambda} \tag{3}$$

and it only depends, for high pressures when ϕ_{\min} is constant, on the pressure dependence of the powder sound speed $V_{\rm L}(\phi_{\min}, {\rm P})$ that can be estimated from the Hertz-Mindlin description of the inter-grain contact.

TIO₂ - COMPARISON WITH THE BULK

 TiO_2 nanopowder Brillouin spectra at various stages of the compression are shown in figure 1.A and data from two distincts runs are compared in figure 1.B with the sound speeds measured from a bulk single crystal of TiO_2 anatase under pressure with our high-P



FIG. 1. A. Brillouin spectra of TiO_2 nanopowder as a function of applied pressure. The spectra are vertically shifted and the Rayleigh line has been omitted for clarity. B. Comparison of anatase nanopowder sound speed with the one measured from a bulk crystal of anatase. Two runs are presented from HT1 and HT7 nanopowders.

Brillouin setup. The longitudinal Brillouin frequencies were measured only below the structural phase transition towards the colombite structure at 5 GPa, and converted to sound speed. The black line is a linear extrapolation of the low pressure points. TiO₂ nanocrystals don't transit to the colombite phase and keep the tetragonal structure even at high pressure, as previously shown by some of us elsewhere [1–3]. The relatively small difference in sound speed between the compacted nanopowder and the single crystal (12 % at 27 GPa) indicates that at high pressures the elastic behavior of the powder becomes very similar to the bulk, due to the high deformation of the NPs shape upon compression in the GPa pressure range. This can be illustrated in the approximation of two interpenetrated spheres[4] by the large change of interpenetration length of the NPs: $\delta = a_{\rm HM}^2/R$ which varies from 0.02 nm to 0.6 nm between 0.2 to 21.5 GPa (R = 1.8 nm).



FIG. 2. Comparison of zirconia nanopowder sound speed with the calculations from Digby model for different ratios a/R, a being the contact radius and R the NP radius.

DIGBY'S APPROACH FOR ADHESIVE CONTACTS

The Digby model gives effective moduli for a dry, random packing of identical elastic spherical particles. Neighboring particles are initially firmly bonded across small, flat, circular regions of radius a. Outside these adhesion surfaces, the shape of each particle is assumed to be ideally smooth. Notice that this condition differs from that of Hertz, where the shape of a particle is not smooth at the intersection of the spherical surface and the plane of contact. Digbys normal and shear stiffnesses under hydrostatic pressure P are :

$$S_n = \frac{4\mu_0 b}{1-\nu_0} \tag{4}$$

$$S_{\tau} = \frac{8\mu_0 a}{2 - \nu_0} \tag{5}$$

where ν_0 and μ_0 are the Poisson ratio and shear modulus of the grain material, respectively. Parameter b can be found from the relation

$$\frac{b}{R} = \left[d^2 + \left(\frac{a}{R}\right)^2\right]^{1/2} \tag{6}$$

where d satisfies the cubic equation

$$d^{3} + \frac{3}{2} \left(\frac{a}{R}\right)^{2} d - \frac{3\pi(1-\nu_{0})P}{2C(1-\phi)\mu_{0}}$$
(7)

The coordination number C=9. Then, one must solve the cubic equation for d and take the real root, neglecting the pair of complex conjugate roots. We obtain the values of a/Rand b/R which are used to compute S_n , S_τ and the sound speed. The results for different values of a/R are summarized in figure 2, see main text for the discussion.

COMPARISON WITH OTHER RESULTS

In most Brillouin experiments on nanocrystallites, particularly under high pressure [5, 6], the description of grain boundaries dynamics and local elasticity is systematically disregarded. Elastic stiffness is rather discussed in terms of grain size and porosity evolution on the elasticity of nanocrystalline materials [7–9], often described within an effective medium approach as the average between an upper (Voigt) and lower (Reuss) bounds. Our results indicate that the static compression of NPs primarily depends on the NPs contact dynamics and is not related to a possible pressure-induced change of NP size. This affirmation is justified by previous low-frequency Raman measurements of the Lamb modes of these $TiO_2[10]$ and $ZrO_2[11]$ nanopowders. The frequencies of the quadrupolar and breathing modes of the NPs barely change with applied pressure up to 20 GPa. These frequencies scale linearly with the inverse NP diameter ($\nu_{\text{Lamb}} \propto V_{L/T}/D$), where $V_{L/T}$ is the longitudinal or transverse sound speed. Low-frequency Raman is therefore a sensitive probe of possible NP size modification as well as small contact changes between interacting NPs as recently evidenced for sintered nanopowders [12]. The absence of Lamb frequency variation with P demonstrates that no NP size variation is involved in the observed non-linear dependence of the sound speed in the nanopowder with P. We argue that it is neither an artifact due to a possible pressure dependent refractive index behavior in the conversion from Brillouin frequency to acoustic speed, as shown by the weak dependence of $n_{\rm ZrO_2}$ with applied pressure in the GPa range [13]. Additionally, we show that the presence of a few monolayers solid ice shell do not change the pressure power law of the effective elastic stiffnesses as predicted by De Gennes's soft shell model [14], initially developped to explain the exponant 1/2 arising from a thin oxyde surface layer. Here we demonstrate that effective medium theories such as HM theory allows to address the intergrain stifnesses of nanometric powders, and we highlight the importance of subtle effects such as the adsorption of water molecules on the NPs surface, and eventually the presence of organics, on their mechanical properties. Brillouin scattering is demonstrated to be a powerfull alternative to conventional nanoindentation [15, 16], acoustic echography and interferometry [17] or ultrasonic techniques [18] to study the elasticity of nanoscale materials.



COMPLEMENTARY BRILLOUIN AND RAMAN RESULTS

FIG. 3. Hysteresis of Brillouin frequency measured for A. TiO_2 and B. ZrO_2 . Black symboles are for upstroke and red for downstroke.



FIG. 4. Raman spectra of TiO₂ HT1 NPs, showing the vibrational signature of the organics at about 3000 cm^{-1} .

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