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Review of the Doctoral Thesis "Evaluation of elastic properties of nanomaterials by Brillouin light scattering" elaborated by Višnja Babačić, MSc, at the Faculty of Physics of the Adam Mickiewicz University in Poznan under the supervision of dr hab. Bartłomiej Graczykowski, prof. UAM

The thesis of Višnja Babačić presents a fascinating and relevant topic related to the mechanical properties of various nanomaterials. Different types of 1D, 2D and 3D nanomaterials play an important role for the development of advanced technologies, especially as thin coating layers. During confinement at the nanoscale, these materials can show changed properties in comparison to the bulk state. This behavior makes them especially attractive for sophisticated applications with advanced requirements in mechanical properties. However, the changes in elastic properties at nanoconfinement still are not well understood and even contradicting results have been published for different nanomaterials. The reason is that the description of their elastic properties is not straight forward due to their complex composition. Furthermore, the morphological features can influence the elastic properties in different degrees. Another problem is the precise evaluation of the elastic properties of nanoconfined nanomaterials. Methods described in literature are based on different principles and can provide dissimilar results.

In her doctoral work, Višnja Babačić applied Brillouin light scattering (BLS) to study the elastic properties of three different nanomaterials representing classes of 1D, 2D and 3D systems. The advantage of BLS is the contactless, non-destructive probing of the elastic properties. This method is based on inelastic scattering of monochromatic laser light by thermally populated elastic waves/phonons in the material.

The thesis of Višnja Babačić was prepared at the Faculty of Physics of the Adam Mickiewicz University in Poznan under the supervision of dr hab. Bartłomiej Graczykowski, prof. UAM. The thesis contains 133 pages, is well structured and well written in clear English language. The figures, tables and equations have been prepared with care. There are no formal mistakes which could be criticized. After acknowledgments, the thesis begins with the abstract written in both Polish and English followed by the table of contents. After the list of publications on which the thesis is based on, a preface provides a general introduction to the topic, the methodology, motivation and aim of the thesis. Thereafter, the thesis outline is presented including a detailed contribution listing of each of the publications on which the thesis is based on. The main core of the thesis is divided in 5 chapters. Chapter 1 provides basics of elastodynamic theory with two subchapters about theory of elasticity and elastic waves in solids. BLS theory together with the description of the used experiment setup are introduced in Chapter 2. The experimental results of the three different nanomaterials are discussed separately in Chapters 3, 4, and 5. The effect of tantalum content on the Young modulus of tantalum hafnium carbide (Ta-Hf-C) is evaluated in Chapter 3. The role of composite thickness on elastic properties is discussed for molybdenum diselenide in Chapter 4. Mechanical reinforcement via cold soldering of polystyrene colloid crystals (PS CC) by using supercritical nitrogen and argon is presented in Chapter 5. Finally, concluding remarks, future perspectives and a reference list close the thesis.

The author has chosen three important nanomaterials as representative examples to discuss prominent effects on elastic properties. The discussions in the three experimental chapters can be regarded separately from each other and are based mainly on the published papers. In Chapter 3, a typical slow-on-fast system behavior is proven for Ta-Hf-C nanocomposites containing different Ta% contents on Si (001) substrate, as the velocities of surface acoustic waves (SAWs) were observed to be lower than of the transverse bulk acoustic wave in the [110] direction of Si. The Young modulus of the Ta-Hf-C/Si system was determined from dispersion relations of these waves supported by a finite element method (FEM) model. It was found that the Young modulus of (TaC)x(HfC)y composites is higher in comparison to neat TaC and HfC. These results from BLS combined with FEM are in good agreement with data obtained by nanoindentation that have been reported in literature. The analysis and discussion of the results have been performed with much care, however, there are few points that need further clarification.

- For better understand for the reader, it would be helpful to provide the chemical structure of the (TaC)x(HfC)y nanomaterials.
- Another point is the film morphology of the nanomaterial. Does the crystal size play a role on the Young modulus and is it controlled during sample preparation for all compositions?
- A further question is related to the substrate material. Does the substrate influence the results on the Young modulus? Can residual stress occur after the sample preparation and does the stress depend on the substrate surface. Is it necessary to take the residual stress into consideration?

- In Figure 3.3c the velocity is plotted as a function of wave number. However, it is not clear to the reader which type velocity is considered.
- In Figure 3.7. some of the experimental data show a rather less precise fit, e.g. 3rd WS for (TaC)0.7(HfC)0.3. What can be the reason for this discrepancy?
- The data points in Figure 3.8. for the Young modulus obtained by nanoindentation contain error bars. Is it possible to add error bars to the BLS data points for a fair comparison of both methods? Which factors should be then considered to describe the deviation?
- Minor typos are found on page 55 for ° (degrees) and on pages 53 and 55 for “X-ray”.

In Chapter 4, the author used μBLS to determine dispersion relations of acoustic waves in the single-crystal bulk and few-layer MoSe2 membranes. For bulk MoSe2, the results for elastic constants $C11$, $C66$ and $C44$ show good agreement with literature, although the literature values were obtained from theoretical calculations or Raman studies. Interestingly, the BLS results show for MoSe2 an elastic softening when the thickness decreased from bulk to two layers. This is a surprising observation and would benefit from a further discussion together with other clarifications as following.

- As shown in Figure 4.1. the MoSe2 membranes contain a biaxial residual stress. Is this residual stress controlled and on which factors does it depend on? Does the residual stress have an influence on elastic properties? In Table 4.5. the residual stress shows a high variation between different sample thicknesses. What is the reason for this variation?
- As shown Figure 4.16. the Young modulus decreases with the MoSe2 membrane thickness. What is the physical reason for this surprising relation? Is it possible for the author to establish a theory to explain this phenomenon?

In Chapter 5, cold soldering effects on PS CC were investigated by in-situ BLS using a dedicated chamber where the processing took place. This experimental setup is unique and allows to closely monitor the soldering process that takes place during increase of temperature and pressure, respectively. As shown by the BLS results and confirmed by scanning electron microscopy images, after exposure to supercritical N2 or Ar the physical bonding between the PS nanoparticles is significantly enhanced, while maintaining their sphericity and colloidal lattice. This effect is explained by a combination of compressive hydrostatic pressure and plasticization due to gas diffusion into PS particles leading to a decrease of both temperatures for the glass transition and softening of the nanoparticle surface. The in-situ BLS measurements allowed to establish $T(p)$ phase diagrams for N2 or Ar gases in which the soldering region was assigned. It is shown that at high gas pressures the soldering can occur even near room temperature. These insights on cold soldering are very valuable opening the doors towards an efficient method for increasing the toughness of polymer colloidal crystals. There are two points for would need further explanation.

- As presented in Figure 5.9. the as-prepared sample shows a certain frequency $f_{1,1}$ (indicated as point P) that is even higher in comparison to the samples treated at 348 K and 1 bar. What is the reason for this phenomenon and which model can be used for its description?
- The images in Figure 5.12. show drop-cast PS CC films before and after the resilience test. What is the reason for the formation of cracks visible for the soldered samples?

In summary, Ms. Babačić has confirmed her competency on the field of BLS for a wide range of various nanomaterials taking into consideration their different behaviors. Her research methodology has been prepared in a senseful and clear manner and the research as well as analysis of the results has been performed with high competence and care leading to comprehensive interpretations and conclusions without leaving doubts.

The publication record of Ms. Babačić in the frame of her thesis is impressive. She is (co-)author of six papers published in high-ranking international journals, with two of them as first author. This confirms her intensive involvement in her research.

Therefore, in my opinion the reviewed thesis fulfills the statutory criteria set for the doctoral dissertations in Article 13, Paragraph 1 of the Act of 14 March 2003 and I ask for admission of Višnja Babačić to the public defense of the dissertation.

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