08

Coupled Oscillators Model and Wandering Optical Modes in Nanostructured Media

© *A.G. Yashenkin*[1,2], *S.V. Koniakhin*[3,4], *O.I. Utesov*[3]

[1] St. Petersburg State University,
St. Petersburg, Russia
[2] St. Petersburg Nuclear Physics Institute, National Research Center „Kurchatov Institute“,
Gatchina, Russia
[3] Institute of Fundamental Science,
Daejeon, Republic of Korea
[4] Fundamental Science Program, Korean Science and Engineering University,
Daejeon, Republic of Korea

E-mail: ayash@mail.ru

Received April 30, 2024
Revised October 28, 2024
Accepted October 30, 2024

With the use of Coupled Oscillators Model we develop and utilize an approach allowing to model the propagation of collective optical excitations within the wide range of nanostructured media as well as to extract the information about the structure of these media from corresponding Raman spectra.

Keywords: optical modes, porous media, agglomerates and aggregates, Raman scattering.

DOI: 10.61011/PSS.2024.12.60178.6553PA

1. Introduction

These days a true science and technology breakthrough is happening, which is related to the opening opportunities for the controlled manufacturing, research and further practical use of various nanoobjects, including two-, one- and zero-dimensional systems of all kinds. The latter (nanoparticles) are of special interest due to substantial difference of their properties from the properties of macroobjects arising first of all (but not only) due to the finite-size quantization effect and its consequences. Quite often the nanoparticles are organized in ensembles of various degrees of density and orderliness, which also contributes to the diversity of the observed phenomena. Therefore, searching for the methods of non-destructive, precise and cheap detection and specification of nanoobjects and their arrays is a rather important objective of the modern physics and physical chemistry.

One of such methods is Raman effect in nanoparticles (e.g. see paper [1] and references therein). Previously our group developed a microscopic approach [2,3], making it possible to rather precisely describe the Raman spectra of non-polar nanocrystals. The approach is based on a combination of atomistic dynamic matrix method (DMM) (or, for relatively large particles, solution to the continuous Klein-Gordon-Fock equation in Euclidean space (EKFG)) with the polarized bond model (BPM); broadening of phonon lines happening due to the presence of the internal disorder in the particles, is determined within the diagram technique and/or using computational modeling. The description of real experimental data obtained as a result of such procedure, first of all, contains no adjustment parameters, second, substantially exceeds in quality the previous methods (for example, PCM — phonon confinement model [4,5]), and third, makes it possible with the good precision to extract from the experiment such important parameters of nanopowder as the average nanoparticle size, particle size variance in the powder, degree of particle contamination and even their shape parametrized by the effective number of facets.

Besides, the described approach and the existing alternatives thereto currently handle only the ensembles of independent and non-interacting nanoparticles, fully ignoring the capability of hybridizing the states in various particles, and as a result — occurrence of collective effects. The present paper is dedicated to studying this particular phenomenon.

2. Method development

Developing this approach, we came across the fact that for description of collective modes of the array and distribution of optical excitations therein at the distances substantially exceeding the nanoparticle dimensions, neither the atomistic method of internal mode calculation DMM, nor the more cost-effective continuous method EKFG allow handling somewhat large arrays of nanoparticles, especially when it is about disordered arrays. Therefore, we suggested an alternative method — a coupled oscillator model (COM), which consists in replacement of each pair of hybridizing optical modes of various particles in a contact with a pair of coupled oscillators, see Figure 1. From the physical point of view such replacement may be justified by mutual orthogonality of eigenfunctions of vibration modes

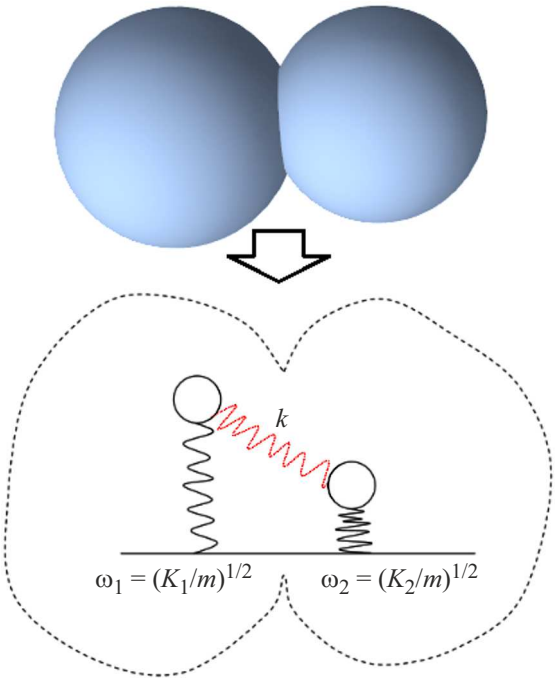

Figure 1. Replacement of hybridized optical modes in contacting nanoparticles with coupled oscillators.

in each particle and is described by effective Hamiltonian of COM [6]. Replacement of the solution to the DMM system of equations or EKFG equation with the boundary Dirichlet conditions for a single „superparticle“ of complex shape, including the entire ensemble of the primary nanoparticles with account of their overlapping, or at least for the set of particles with account of their paired overlapping — „dimers“ (which is already approximation) on the system of COM-equations would be a tremendous progress from the point of view of saving the used computer time. To justify this transition, we attempted the comparative analysis of the results of DMM- and EKFG-descriptions of the optical spectra of dimers consisting of two overlapping primary nanoparticles, and the results of the COM-approach to this objective, studying the dependence of the observables on the difference in the dimensions of these particles, and on the degree of their mutual overlapping. Note that the objective on the spectra of dimers (colloidal quantum dot molecules) is of independent interest in connection with the recent practical realization of the latter [7].

As a result of the completed analysis it was demonstrated that the COM approach could serve as a good approximation for the task on the distribution of optical modes in the system of nanoparticles, where the individual modes of certain particles turned out to be collectivized as a result of their hybridization in the areas of contact/overlapping, and could further spread in the entire array. The comparison of the microscopic and COM-approaches typical for this analysis is given in Figure 2, where the dots of different colors indicate the values of the highest phonon frequencies for six optical modes in a dimer with fixed size of the „right“ spherical particle and area of particle overlapping as the function of the size of the „left“ spherical particle, and the dotted line shows the results of the coupled oscillator model. The similar data were obtained for the faceted (cubic) particles in the contact.

In particular, we studied in detail the following models:

– regular 3D array of the identical spherical overlapping nanoparticles (nanocrystal solid);

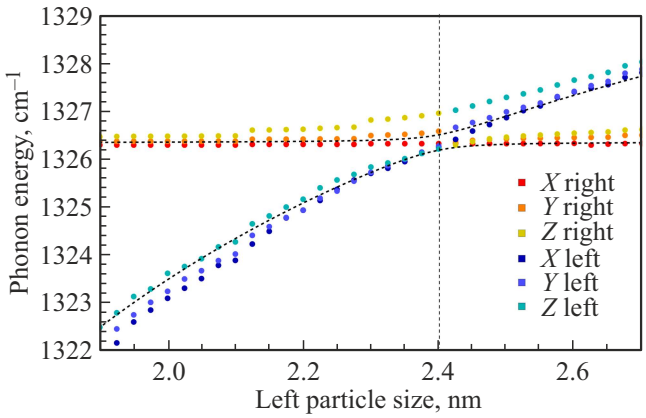

Figure 2. Frequencies of six largest phonon modes in dimer as function of dimensions of the left particle (dot). Dotted lines show the results of COM-approximation.

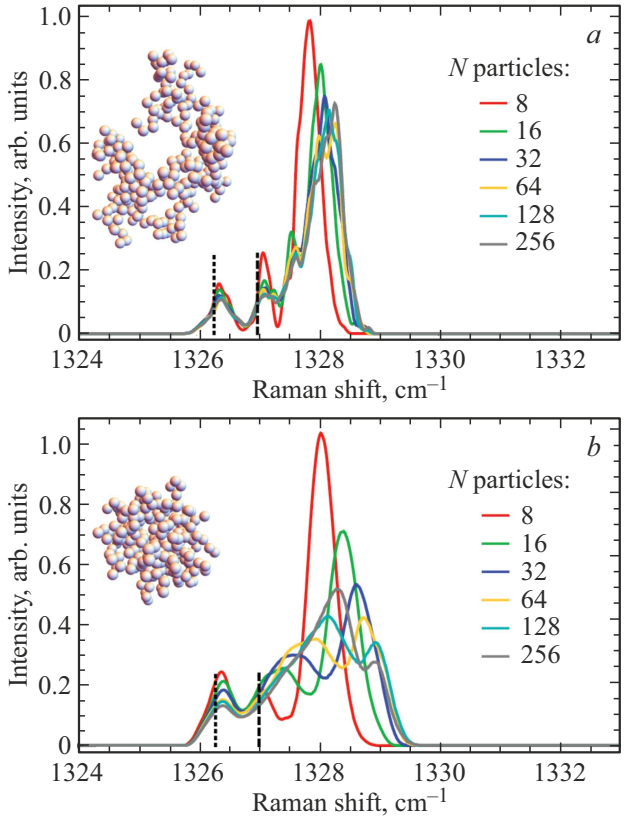

Figure 3. Transformation of Raman peak in agglomerates $c-c$ (a) and $p-c$ (b), with the growth of the number of nanoparticles in agglomerate.

– regular 3D array of spherical overlapping nanoparticles, where the disorder is introduced via the variable size of nanoparticles (and, accordingly, the size of the overlapping areas) — porous media model, similar two-dimensional and unidimensional structures;

– tight agglomerates of nanoparticles of various degree of cohesion built in the models of cluster-cluster and particle-cluster aggregation [8,9] — highly disordered irregular objects, having fractal structure.

The detailed description of the work will be published in the large article; to save the space, here we will only demonstrate (Figure 3) transformation of the Raman peak with the change in the number of particles that form agglomerates $c-c$ (a) and $p-c$ (b). The positions of the Raman peak for individual particles and dimers are marked on the left on the curves.

3. Conclusion

A relatively simple method has been developed and tested for modeling and numerical study of a rather wide class of nanostructured media (arbitrary arrays of nanoparticles, ordered and disordered, with various types of disorder, including those that are as close to the real ones as possible, where optical excitations spread that „escaped“ from the individual nanoparticles, and now collectivized), collective optical excitations arising therein, and also for detection of the specified phenomena in the Raman effect experiments. For optical excitations, the issues may be raised on the mean free path of excitation in the medium, and also on the radius of its localization (in case of the latter). With the help of the previously developed BPM method, using the obtained optical spectrum, a Raman peak is built, from the shift, shape and width of which the information is now extracted not only on the properties of individual nanoparticles, from which the nanostructured medium is designed, but on the properties of the medium itself.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.K. Arora, M. Rajalakshmi, T. Ravindran, V. Sivasubraminian. J. Raman Spectrosc. **38**, *6*, 604 (2007). https://doi.org/10.1002/jrs.1684
[2] S.V. Koniakhin, O.I. Utesov, I.N. Terterov, A.V. Siklitskaya, A.G. Yashenkin, D. Solnyshkov. J. Phys. Chem. C **122**, *33*, 19219 (2018). https://doi.org/10.1021/acs.jpcc.8b05415
[3] O.I. Utesov, A.G. Yashenkin, S.V. Koniakhin. J. Phys. Chem. C **122**, *39*, 22738 (2018). https://doi.org/10.1021/acs.jpcc.8b07061
[4] H. Richter, Z. Wang, L. Ley. Solid State Commun. **39**, *5*, 625 (1981).
[5] I. Campbell, P.M. Fauchet. Solid State Commun. **58**, *10*, 739 (1986).
[6] S.V. Koniakhin, O.I. Utesov, A.G. Yashenkin. Phys. Rev. Research **5**, *1*, 013153 (2023). https://doi.org/10.1103/PhysRevResearch.5.013153
[7] Y.E. Panfil, D. Shamalia, J. Cui, S. Koley, U. Banin. J. Chem. Phys. **151**, *22*, 224501 (2019). https://doi.org/10.1063/1.5128086
[8] M. Avdeev, N. Rozhkova, V. Aksenov, V. Garamus, R. Willumeit, E. Osawa. J. Phys. Chem C **113**, *22*, 9473 (2009). https://doi.org/10.1021/jp900424p
[9] A. Brasil, T.L. Farias, D.G. Carvalho, U.O. Koylu. J. Aerosol Sc. **32**, *4*, 489 (2001).

Translated by M.Verenikina