Width and Shape of a Raman Peak in Nanopowders of Nonpolar Crystals: I. Analytical Treatment

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Microscopic description of Raman spectra in nanopowders of nonpolar crystals is accomplished by developing the theory of disorder-induced broadening of nanoparticle vibrational eigenmodes. Analytical treatment of this problem is performed, and line shape and width are determined as functions of quantum numbers, nanoparticle shape, size, and the strength of disorder. The results are found to be strongly dependent on either the broadened line is separated or it is overlapped with other lines of the spectrum. Three models of disorder, i.e. weak point-like impurities, weak smooth random potential and strong rare impurities are investigated in details. The possibility to form the phonon-impurity bound state is also studied.

I. INTRODUCTION

The properties of very small particles and their ensembles are a subject of current active scientific investigation, mostly due to their promising applications in material science\textsuperscript{[1]}., quantum computing\textsuperscript{[2,3]}, chemistry\textsuperscript{[4]}, biology and medicine\textsuperscript{[5,6]}, etc. Among others, the disordered arrays (powders and water suspensions) of crystalline nanoparticles of nonpolar crystals, both semiconducting and diamond-like ones, attract very close attention.

Even before being utilized on certain manner, nanopowders need to be attested and certified. In our opinion, for comprehensive certification of a powder such obvious characteristics as chemical formula and crystallographic structure of the material that form the particles of a powder should be supplemented by geometrical parameters of its constituents such as (i) the mean size of a particle, (ii) the particle size distribution function, (iii) the effective faceting number (in case of nontrivial shape of particles), and (iv) the measure of their elongation (if exists), as well as by some characteristics of (v) the nanoparticle intrinsic disorder, surface morphology and phase composition.

In order to examine the nanopowders, several experimental techniques are utilized. The high-resolution transmission electron microscopy (HRTEM\textsuperscript{[7,8]}, atomic force microscopy (AFM)\textsuperscript{[9,10]}, X-ray diffraction\textsuperscript{[11,12]}, X-ray scattering\textsuperscript{[13,14]}, dynamical light scattering\textsuperscript{[15,16]}, Raman spectroscopy (see, e.g., Refs.\textsuperscript{[17,18]} and references therein) are among them. The latter one is of prime importance because it provides unique precise and nondestructive tool for optical investigations of collective excitations in nanoparticles. Examining the shape of a Raman peak and its position one could extract a great deal of information about the nanoparticles including some parameters mentioned above.\textsuperscript{[19,20]}

Indeed, since the momentum in a particle is quantized due to finite size quantization effect, the maximum of the Raman peak for nanoparticles is shifted as compared to the bulk material with the shift value increasing for smaller particles. Furthermore, the entire discrete spectrum of vibrational modes for the particle of a given shape is peculiar and specific for this particular shape.\textsuperscript{[21–24]} This manifests itself in asymmetry of the Raman peak. One can think of restoring (as precisely as possible) the portrait of a particle from the analysis of peak shape and position, thus formulating a sort of “inverse problem”. It makes the Raman data analysis very important and challenging issue.

Recently, we proposed two closely related methods of Raman data evaluation\textsuperscript{[25–27]} which gave much more detailed information about the parameters of a powder than all previously used variations of the phonon confinement model (PCM\textsuperscript{[28–30]} and other models\textsuperscript{[31–35]}). One of these methods (DDM-BPM\textsuperscript{[26]} consists of direct solving the dynamical matrix eigenmodes problem\textsuperscript{[29]} for a particle with further evaluation of its Raman spectrum. The latter procedure utilizes the proportionality between polarization and deformation in nonpolar crystals with the use of the bond polarization model\textsuperscript{[36]}.

After that, the (empirically broadened) individual lines of the spectrum altogether constitute the first (and subsequent) Raman peak\textsuperscript{[20]}. Important observation made in Ref.\textsuperscript{[29]} and related to discrete spectra of nanoparticles before broadening concerns their fine structure shared by all the particle shapes investigated. Namely, the spectrum starts from a threefold degenerate first line which carries the majority (more than 2/3) of the general spectral weight. This triple line is well-separated from the rest of the spectrum that begins effectively with the 13-th line because of dividing the eigenmodes onto “Raman active” and “Raman silent” ones, see Fig. 1. The Raman silent modes...
do not contribute to Raman spectra due to symmetry properties of their eigenfunctions. Furthermore, both Raman silent and Raman active modes form a “quasi-continuum” wherein the energy intervals between the levels are essentially smaller than the first gap. This quasi-continuum is split onto several “bands” by inter band gaps which do not exceed the first one (see Fig. 1a).

Terminologically, we shall distinguish between (i) the phonon lines that form the vibrational spectrum of a nanoparticle (see Fig. 1a), (ii) the Raman spectrum which contains only the Raman active vibrational modes with corresponding weights influenced by the photon-phonon scattering matrix elements (see Fig. 1b), and (iii) the main (and possibly subsequent) Raman peak constituted by broadened Raman spectrum lines (see Fig. 1c) for all particle sizes containing in a powder (Fig. 1d).

Another proposed method (EKFG) replaces original discrete dynamical matrix problem with its long wave length continuous counterpart which is the Euclidian Klein-Fock-Gordon equation under Dirichlet boundary conditions. Being supplemented by continuous version of the bond polarization model and by the phenomenological line broadening procedure this approach generates the Raman spectra hardly distinguishable from those obtained within the DMM-BPM scheme of Ref. 26, although before the line broadening the EKFG spectra look a bit oversimplified as compared to the DMM-BPM ones: they contain one degenerate spectral line in place where the DMM-BPM approach yields a bunch of weakly-splitted levels, etc.

It means that the EKFG correctly captures the spectral weight distribution along the energy axis rather than all rigorous details of the spectra. Therefore, since the spectral line broadening plays the role of an effective energy averaging, the approximate EKFG method appears to be sufficient for reproducing all important features of such integral optical characteristics as the first Raman peak, see Fig. 2.

The imperfection of these theories is the phenomenological character of the line broadening procedure, the line width parameter $\Gamma$ being treated as the
fitting one with no theoretical analysis of its origin and value. To the best of our knowledge, no detailed theory of Raman peak broadening in nanoparticles exists in modern literature, the current attempts are having mostly phenomenological or philological character. (One should mention however the paper by Yoshikawa with co-workers\cite{app1} who extracted $\Gamma \propto \text{const} + 1/L$ dependence, with $L$ being the particle size, from the analysis of experimental data.) The present work aims to accomplish the approach of Refs.\cite{app2,app3}, providing us with the microscopic theory of Raman peaks broadening due to nanoparticle intrinsic disorder and imperfections, as well as with its numerical verification.

In order to get preliminary insight into this theory and to understand better the general picture we propose, let us discuss in details Fig. 3. Panel (a) of this figure represents the typical spectrum of vibrational optical eigenmodes of a nanoparticle. As we have told above, this spectrum consists of three-fold degenerate first line (black) and the sequence of “bands”, the inter level distances between the lines in these bands being essentially smaller than the first gap. Then we introduce disorder into the system. For small amount of disorder this broaden the spectral lines, see Fig. 3b, but the widths of the lines remain narrower than the distances between the levels. It is valid for levels lying inside the bands as well as for the first (triple) line. Therefore, we are in the regime of separated levels now for all parts of the spectrum. With disorder increasing, the levels within the bands start to overlap, while the first line still remain separated from the rest of the spectrum, see Fig. 3c. Hence, for this amount of disorder the band levels crosses over to the continuous regime, while the first triple line remains in the discrete one. We argue that this “mixed” situation is typical for nanoparticles having the size of order of several nanometers which were investigated in recent experiment\cite{app4}. At last, with further increase of disorder the line widths become so wide that they fill in even the first (largest) gap, making the entire spectrum continuous, see Fig. 3d.

We presented above this very detailed picture of the line broadening in order to highlight the importance of the main statement of the present papers (which, however, sounds quite evident from general point of view). Namely, we argue that the principle characteristics of the phonon spectral line widths in nanoparticles vary dramatically depending on either it is separated level or this level belongs to the continuum. More specifically, for disorder induced broadening of the optical phonon spectral line we observe its linear dependence on the disorder strength parameter $S$ and its inverse proportionality to the particle size $L$, $\Gamma \propto S/L$, when the broadened spectral levels are overlapped, while for separated levels the line width behaves as $\Gamma \propto \sqrt{S}/L^{3/2}$. Here the strength parameter $S$ is defined as a product of (dimensionless) impurity concentration $c_{\text{imp}}$ and the squared normalized disorder induced variation of the random parameter of the theory (here, the atom mass $m$), which yields $S = c_{\text{imp}} (\delta m/m)^2$.

In particular, it means that for a given intermediate nanoparticle size and strength of disorder various groups of finite size quantization induced spectral levels that altogether constitute the main Raman peak may exist in different regimes, separated or continuous, so the entire Raman peak dependence on these parameters is the result of interplay of corresponding contributions. Simulta-
neously, for small enough quasiparticles and/or for weak enough disorder the line broadening occurs following the “separated” scenario. This, however, does not guarantee the same dependence of the entire Raman peak, which becomes to be the integral characteristics of many levels (mostly, of the first triple line and one or two highest active bands). On the contrary, biggest or dirtiest nanoparticles reveal “continuous” properties. Generally, for a given impurity strength there exists a crossover particle size \( L_c \propto a_0 S^{-1} \) between these regimes, with \( a_0 \) being the lattice constant.

We also address the problem of strong level shape asymmetry in the continuous regime of level broadening. It is caused by the fact that the main contribution to the phonon self energy comes from scattered phonons with intermediate momenta lying in the vicinities of van Hove singularities of the spectrum (model free argument). Furthermore, we investigate the possibility to form the bound state of optical phonon and strong impurity. The role of nanoparticle size distribution in a powder for the Raman peak shape is also discussed.

The work consists of two papers, and this is the first one (hereinafter, I). Within the framework of a set of simple models of disorder it theoretically treats the line width problem for both cases of separated and overlapped levels. Second paper (Ref. \(^{25}\), hereinafter, II) is devoted to numerical simulations of the disordered Raman problem, necessary for both verification and justification of analytical results of paper I. In line with paper I numerical paper II allows us to represent the all-round picture of our general approach (EKFG method, cubic particles) for the treatment of surface particle imperfections.

Technically, our approach in I can be described as follows. In order to address the problem comprehensively, we successively evaluate the broadening of the optical phonon spectral lines in nanoparticles due to scattering off (i) weak point-like Gaussian (Born) impurities and in (ii) weak smooth random Gaussian potential, as well as by (iii) strong rare identical impurities. Treating the case of separated levels we apply self-consistent Born approximation for the first two problems, the diagram technique is formulated in the basis of eigenfunctions of the problem considered. Strong impurities are treated within the T-matrix approximation for both cases. When investigating the overlapped levels we utilize the fact that the eigenfunctions are essentially extended in this case. It allows us to replace them by plane waves thus considering the ordinary bulk problem within the momentum representation and making the size quantization replacement of the momentum \( q \to q_n(L, p) \) in final formulas. Here \( n = n(p) \) are generalized quantum numbers of the corresponding size quantization problem, and nanoparticle shape enters the formulas via the effective faceting number \( p \).

For example, in cubic particles \( p = 6 \) and \( q_n = (\pi/L)P_6 \sqrt{n_x^2 + n_y^2 + n_z^2} \), where \( n_x, n_y, n_z \) are quantum numbers related to size quantization in Cartesian coordinates, with \( P_6 \) being the factor converting natural linear measure of a particle with faceting number \( p \) (for the case of cube, it is the cube edge) into the diameter of a sphere which contains the same amount of atoms, \( P_6 = (\pi/6)^{-1/3} \).

In paper II we focus on numerical studies of disorder induced broadening of vibrational modes in nanoparticles. We use the atomistic DMM (the “ball-spring” model) in order to obtain phonon eigenfunctions and corresponding eigenfrequencies. It allowed to implement the “model” Gaussian disorder for a direct comparison with analytics and to investigate Gaussian and binary disorder, vacancies and NV centers within the unified scheme. This scheme includes numerical evaluation of phonon Green’s functions for each state of a pure particle with their further averaging over disorder realizations. The typical statistical sampling was no less than several hundreds. Also, we use continuous EKFG model for the treatment of surface particle imperfections.

Some preliminary results of present work have been reported in Ref. \(^{27}\).

Paper I is organized as follows. Section II contains a short description of the results of papers \(^{20,24}\) necessary to make understanding of the line broadening problem more closed and fluent. In Section III we introduce the Hamiltonian and sketch general Green’s functions formalism for dirty optical phonons in situations when the energy levels are separated and/or overlapped. Then we calculate the spectral line broadening within the weak delta-correlated Gaussian impurity potential (point-like Born impurities). In Section IV we extend our treatment onto weak but smooth random potential, while in Section V we elaborate the case of strong rare impurities, the latter being evaluated within the T-matrix method. At last, Section VI summarises our analytical results. The comparative discussion of separated and overlapped levels broadening is also presented. Example of application of our general approach (EKFG method, cubic particles) can be found in Appendix.

II. BRIEF OVERVIEW OF DMM-BPM AND EKFG APPROACHES

Generally, paper I is devoted to analytical treatment of the role of disorder in the problem of vibrational eigenmodes broadening as far as the spectra of nanoparticles of nonpolar crystals are investigated. No detailed knowledge is needed about the theory used to evaluate the “clean” spectra. Nevertheless, for the sake of clarity and integrity of presentation we provide paper I with a short presentation of two theoretical methods (DMM-BPM and EKFG) we advocate for spectral calculations. Their detailed description can be found in Refs. \(^{20,24}\).

Altogether, the program of processing of Raman peaks for the powder of nanoparticles of particular sort and shape consists of four steps. The first one is the evaluation of the corresponding vibrational eigenproblem providing us with a set of phonon eigenfrequencies and eigen-
functions. In our first approach\cite{26}, this step is implemented with the use of dynamical matrix method\cite{26} which is a direct solution of $3N \times 3N$ matrix equation of motion for mechanical vibrations:

$$m \omega^2 r_{i,\alpha} = \sum_{j=1}^{N} \sum_{\beta=x,y,z} \frac{\partial^2 \Phi}{\partial r_{i,\alpha} \partial r_{j,\beta}} r_{j,\beta}, \quad (1)$$

where $N$ is the number of atoms in a particle, $r_{i,\alpha}$ is the $i$-th atom displacement along direction $\alpha$, $m$ is the mass of the atom, $\omega$ is the frequency, and $\Phi$ is the total energy of the particle as a function of atomic displacements. The function $\Phi$ could be extracted from any mechanicistic theory of crystals; we use the Keating model\cite{42}. This straightforward approach has the only disadvantage: it takes quite a long time to evaluate numerically\cite{3}. One of the ways to avoid this difficulty is realized by our second approach, see Ref.\cite{26}. It has been demonstrated in this paper that the long wave length limit of discrete DMM problem\cite{1} for optical phonons near the Brillouin zone center is governed by the continuous Klein-Fock-Gordon equation in the Euclidean space (EKFG) with Dirichlet boundary conditions:

$$(\partial_t^2 + C_1 \Delta + C_2) Y = 0, \quad Y|_{\partial \Omega} = 0. \quad (2)$$

Here $C_{1,2}$ are the positive constants which can be expressed via the parameters of microscopic theory, $Y$ are the eigenfunctions to be obtained in the course of solution of the problem, $\partial \Omega$ is the nanoparticle boundary. The latter equation is much easier to solve for arbitrary particle shape even for size essentially larger than 6 nm with the use of routine Mathematica\cite{43} apparatus.

The second step of calculations is the elaboration of spectral characteristics obtained at the first step in order to achieve how they manifests themselves in the optical experiment, i.e., as a result of certain effective photon-phonon interaction. For this aim we used the bond polarization model (BPM) which is shown to be appropriate for the description of photon scattering in nonpolar crystals under the Raman experimental conditions\cite{27}. In this model the polarization tensors $P_{\alpha\beta}(\nu)$ for $\nu$-th phonon mode are given by

$$P_{\alpha\beta}(\nu) = \sum_{i=1}^{N} \sum_{\gamma} M_{i,\alpha,\beta,\gamma} r_{i,\gamma}(\nu), \quad (3)$$

with $M_{i,\alpha,\beta,\gamma}$ being some combinations of atomic radius vectors and material constants, which could be expressed via the microscopic parameters of the theory\cite{26} as well.

Analyzing theoretically the spectral properties of diamond nanocrystals of various shapes, we observe a very helpful common feature of them, namely, existence of Raman “active” (strongly contributing) and “silent” (almost not contributing) modes in the spectrum. This allows us to formulate the simplified analytical version of the DMM-BPM\cite{26} which is much easier to calculate thus making it applicable for larger particles than the regular DMM-DPM allows. Furthermore, for EKFG we developed the continuous version of the BPM; the Raman intensity of $\nu$-th mode is given now by

$$I_\nu = \left| \int Y_\nu \, dV \right|^2. \quad (4)$$

This feature makes it possible to present the outcome of EKFG calculations for Raman spectra on almost the same level of accuracy as it has been done with the use of more direct DMM-BPM method.

As a result of first two steps the Raman spectra evaluated within both approaches are given by dense series of zero-width spectral lines with an intrinsic structure peculiar and characteristic for shape and sort of nanoparticles studied. The third step needed to describe the Raman experiment is to broaden these lines replacing zero-width delta functions by Lorentzians and thus introducing the damping of individual eigenmodes. This damping is known to be much larger for nanoparticles than for corresponding bulk materials\cite{44}. In our previous calculations, we treated the line width $\Gamma$ as a fitting parameter. The present two papers are intended to certify the disorder as the main microscopic source of line broadening in Raman spectra and to interconnect the fitting parameters with microscopic characteristics of disordered nanocrystals.

After the spectral lines are properly broadened, we end up with the Raman peak (and/or peaks) as they would exist for a powder of particles all having one single size. Therefore, the fourth step of calculations is to involve the size distribution function. The easiest way to do it is to apply for spectral lines the scaling arguments developed in\cite{27} within the EKFG method:

$$I_{L_2}(\omega) = \left( \frac{L_2}{L_1} \right)^3 I_{L_1}(\omega_0 - (\omega_0 - \omega) \left( \frac{L_2}{L_1} \right)^2). \quad (5)$$

Here $I_{L_{1,2}}(\omega)$ are the Raman spectra of identical particles with sizes $L_{1,2}$, respectively, both having the same shape; $L_2$ being slightly different from $L_1$.

Empirically, the EKFG scaling\cite{5} may be extended onto DMM-BPM approach, as well, which can be justified by similarity of spectra obtained with the use of both these methods. It allows to incorporate the size distribution into the theory rapidly and without cumbersome recalculation of Raman spectra for each particle size containing in the distribution function, as one should do at the first glance.

Notice that the Raman peaks calculated within the DMM-BPM and EKFG methods look very similar. They also fit existing experimental data for small nanoparticles much better than previous theories even with empirical broadening procedure undertaken instead of the third step of this Section approach (see\cite{26,27} and Fig. 2).
III. WEAK POINT-LIKE IMPURITIES

In this Section we discuss the so-called Born impurities in two qualitatively different regimes of separated and overlapped energy levels.

A. General formalism

Let us start the derivation of the Hamiltonian of “dirty phonons” from the more general one:

$$\mathcal{H} = \sum_l \frac{p_l^2}{2m_l} + \frac{1}{2} \sum_{ll'} K_{ll'} (r_l - r_{l'})^2,$$

where the first sum runs over all the atom sites \( l \), and the atom mass \( m_l \) vary from site to site. The second sum includes all pairs of atoms, with spring rigidities being \( K_{ll'} \), and \( r_l \) are the corresponding displacements.

As we mentioned above the phonon line broadening problem in a nanoparticle should be treated separately depending on whether this broadening procedure results in levels overlaps or not. For weak enough disorder and/or large enough inter level distances we are definitely in the regime of separated levels. In order to describe this regime it is convenient to use the Green’s functions formalism formulated in the basis of eigenfunctions of the corresponding vibrational problem.

In the particle containing \( N \) atoms there are \( 3N \) normalized to unity vibrational modes \( Y_n(R_l) \) with energies \( \omega_n \). Here \( n \) is the generalized (multicomponent) quantum number of the eigenproblem. Then, assuming all the masses to be equal to each other (as, e.g., in diamond) for atom displacements and momenta we have

$$r_l = \frac{1}{\sqrt{2m}} \sum_n Y_n(R_l) \sqrt{\omega_n} (b_n + b_n^\dagger)$$

and

$$p_l = i\frac{\sqrt{m}}{\sqrt{2}} \sum_n Y_n(R_l) \sqrt{\omega_n} (b_n^\dagger - b_n),$$

respectively. Using Eqs. (7) and (8) one gets the Hamiltonian in the form \( \mathcal{H} = \mathcal{H}_{ph} + \mathcal{H}_{imp} \), where the first term yields the phonon energy

$$\mathcal{H}_{ph} = \sum_n \omega_n \left( b_n^\dagger b_n + 1/2 \right).$$

The second term \( \mathcal{H}_{imp} \) specifies how disorder affects vibrational modes. Hereinafter, we shall assume for simplicity that the disorder appears in the problem via the mass variation only (another source of disorder would be random rigidities). For simplest point-like impurities the perturbation of the bare Hamiltonian \( \mathcal{H}_{ph} \) reads:

$$\mathcal{H}_{imp} = \frac{1}{2} \sum_l \delta m_l^{-1} p_l^2,$$

with the inverse mass variation \( \delta m_l^{-1} \) given by

$$\delta m_l^{-1} = \frac{1}{m + \delta m_l} - \frac{1}{m} \approx - \frac{\delta m_l}{m^2},$$

where

$$m = \langle m_l \rangle,$$

and the random masses are supposed to be the Gaussian delta-correlated quantities with zero averages:

$$\langle \delta m_l^{-1} \rangle = 0, \quad \langle \delta m_l \rangle = 0,$$

and delta-functional pairwise correlators:

$$\langle \delta m_l^{-1} \delta m_{l'}^{-1} \rangle = \langle \delta m_l \delta m_{l'} \rangle / m^2 = \delta_{ll'} S.$$  

Here \( S \ll 1 \) is the dimensionless strength of impurities. “Strong” impurities \( (S \lesssim 1) \) with nonzero average will be considered in Section V of this paper.

Using Eqs. (7) and (8) we can write the impurity-induced perturbation in the form

$$\mathcal{H}_{imp} = \frac{m}{4} \sum_{l,n,n'} Y_n(R_l) \cdot Y_{n'}(R_l) \delta m_l^{-1} \sqrt{\omega_n \omega_{n'}} (b_n^\dagger - b_n) (b_{n'}^\dagger - b_{n'}).$$

We introduce Green’s functions \(-i\langle T\phi_n\phi_n \rangle\) for operators \( \phi_n = i(b_n^\dagger - b_n) \). Upon averaging over impurity configurations, the self-energy term \( \Pi_n(\omega) \) arising due to phonon scattering by disorder enters this Green’s function on the following way:

$$D_n(\omega) = \frac{2\omega_n}{\omega^2 - \omega_n^2 - 2\omega_n \Pi_n(\omega)}.$$  

To the leading order in the impurity strength \( S \) only the diagram shown in Fig. 3(b) contributes to the phonon self-energy (diagram Fig. 3(a) is zero due to condition (13)), the corresponding quantity reads:

$$\Pi_n(\omega) = \frac{S \omega_n}{16} \sum_{l,n,n'} |Y_n(R_l) \cdot Y_{n'}(R_l)|^2 \omega_n D_n(\omega).$$

This equation will be solved in the next Subsection.

When disorder increases the levels start to overlap. Another way to obtain the overlapped states is to treat large enough particles. For both these situations it is convenient to use the ordinary (bulk) diagram technique in the momentum space and then utilize the finite size quantization \( q \rightarrow q_n(L,p) \) in final formulas. The quantization rule \( q_n(L,p) \) depends on the shape of a particle via the faceting number \( p \).

For bulk crystals one can use the standard expressions for atomic displacements and momenta via the phonon creation-annihilation operators \( b_{nq}^\dagger (b_{nq}) \):}

$$r_l = \frac{1}{\sqrt{2Nm}} \sum_{nq} \frac{P_{nq}}{\sqrt{\omega_{nq}}} \left( b_{nq}^\dagger e^{-iqR_l} + b_{nq} e^{iqR_l} \right),$$

and
where H.C. stands for Hermitian conjugate. The diagram technique developed for Hamiltonian (20) and (23) (see, e.g., Refs. [29] and [30]) has the conventional form of disordered technique very similar to the one widely used in the fermionic case (cf. Ref. [29]). The phonon Green's function $D(\omega, \mathbf{q})$ is built up for (bosonic) field operators $\phi(\mathbf{q}) \propto b_{\mathbf{q}} - b_{\mathbf{q}}^\dagger$. The bare (noninteracting) Green’s function is given by

$$D_0(\omega, \mathbf{q}) = \frac{2\omega_{\mathbf{q}}}{\omega^2 - \omega_{\mathbf{q}}^2 + i0} \tag{24}$$

Upon averaging over impurity configurations, the self-energy term $\Pi_\alpha(\omega)$ arising due to phonon scattering by disorder enters this equation on the following way:

$$D^{-1}(\omega, \mathbf{q}) = D_0^{-1}(\omega, \mathbf{q}) - \Pi_\alpha(\omega). \tag{25}$$

Furthermore, to the leading order in $S$ the counterpart of Eq. (17) reads:

$$\Pi_\alpha(\omega) = \frac{\sqrt{\omega}}{16N} \sum_k \omega_k D_0(\omega, k), \tag{26}$$

where we take into account that the proper choice of coordinates eliminates the contribution of one of the branches to $\Pi_\alpha(\omega)$.

It should be mentioned the similarity between the formulas for separated and overlapped levels, cf. Eqs. (16) and (25) as well as Eqs. (17) and (26). However, the results for these two cases are drastically different as it is shown below.

### B. Separated levels

When using the formal perturbation theory in the parameter $S$ the phonon self-energy on the r.h.s. of Eq. (17) should be omitted. It can be shown that no broadening of the phonon line appears within the framework of this approximation. Correspondingly, we shall use the self-consistent Born approximation keeping self-energy on the r.h.s. of Eq. (17) finite, and thus obtaining $\Pi_n(\omega)$ self-consistently. This method resembles the approach used for disorder-induced broadening of Landau levels in the two-dimensional degenerate electron gas in high magnetic fields [22]. Following the same line we consider equation

$$\Pi_n(\omega) = \frac{S\omega_n}{8} \sum_{l,n'} \frac{[\mathbf{Y}_n(\mathbf{R}_l) \cdot \mathbf{Y}_{n'}(\mathbf{R}_{n'})]^2 \omega_{n'}^2}{\omega^2 - \omega_{n'}^2 - 2\omega_n \Pi_n(\omega)}. \tag{27}$$

One can easily see that for non-overlapped levels this equation contains effectively only the term with $n' = n$. For non-degenerate level it yields:

$$\Pi_n(\omega) = \frac{2^2 e_n^3(p) S \omega_n^4}{N} \frac{1}{\omega^2 - \omega_n^2 - 2\omega_n \Pi_n(\omega)}. \tag{28}$$

Here $e_n^2(p) = N \sum_l [\mathbf{Y}_n(\mathbf{R}_l)]^4 / 16$ is certain shape $p$ and quantum number $n$ dependent coefficient of order of unity.
FIG. 5. The shape of spectral line in the regime of separated levels (blue solid line) vs. its on-shell Lorentzian counterpart (red dashed line).

to be determined numerically. Solving Eq. (28) we obtain:

$$\Pi_n(\omega) = \frac{\omega^2 - \omega_n^2 - \sqrt{\left(\omega^2 - \omega_n^2\right)^2 - \frac{16c_n^2(p)S\omega_n^2}{N}}}{4\omega_n}. \quad (29)$$

When the square root in Eq. (29) is imaginary it determines the phonon damping which leads to the well-known semi-circle law for density of states. Similar to the case of disordered electrons in high magnetic field, the range of validity for this self-consistent solution is limited by proximities of semi-circles maxima, whereas near their edges one should take into account the phonon scattering by rare configurations of impurities which results in exponential tails in DOS (see Ref. 47 and references therein).

However, if we are not interested in these details, one can use the crude Lorentzian (on-shell) approximation. This approximation ($\omega = \omega_n$) in Eq. (29) leads to the phonon damping in the form

$$\Gamma_n = \omega_n c_n(p) \sqrt{\frac{S}{N}}. \quad (30)$$

Notice that the definition of $\Gamma$ we shall use throughout papers I and II differs from that of Refs. 24,25,26,27,28 where the Lorenzian width has been parametrized by $\Gamma/2$ rather than $\Gamma$ of present work.

Semi-circle shape of a spectral line in separated levels approximation and its simplified Lorentzian form are shown in Fig. 5.

Next, we express the number of atoms $N$ in a particle via its effective size $L$. For example, cubic particles provide $N \rightarrow \left(2L/P_0 a_0\right)^3$, the lattice assumed to be cubic with two atoms in the unit cell. This finally yields:

$$\Gamma_n = \omega_n \mu_n(p) \sqrt{\frac{S}{L}} \left(\frac{a_0}{L}\right)^{3/2}. \quad (31)$$

Here we absorbed the shape-dependent parameter $P_p$ into $\mu_n(p) = c_n \sqrt{P_p^3/8}$. Evidently, the constant $\mu_n(p)$ can be calculated for any specific shape of particles numerically.

The impurity strength parameter could be rewritten via the dimensionless impurity concentration $c_{imp}$ and the impurity-induced mass variation $\delta m$ as follows:

$$S = c_{imp} \left(\frac{\delta m}{m}\right)^2. \quad (32)$$

Notice that the damping (31) is (i) proportional to the square root of the impurity concentration rather than to the first power as one should expect at the first glance, (ii) linear in the parameter $\delta m/m$, (iii) it contains the information about the particle shape (parameterized by the effective faceting number $p$), (iv) weakly depends on the quantum level number $n$ and (v) depends on the particle size as $L^{-3/2}$. For degenerate levels the r.h.s. of Eq. (31) should be multiplied by the effective degeneracy coefficient $g$ which could be calculated for any particular model separately (see Appendix).

The real correction to the phonon self-energy stemming from other energy levels can be found from Eq. (27) without self-consistency:

$$\Pi_n(\omega) = \frac{S\omega_n}{8} \sum_{l,n' \neq n} \left|Y_{n}(R_l) \cdot Y_{n'}(R_l')\right|^2 \omega_n^2 \omega_n'. \quad (33)$$

This weakly $\omega$-dependent correction originates from the whole bunch of phonon modes in the spectrum and results mainly in the effective renormalization of $\omega_0$ for highest (i.e., closest to the Brillouin zone center) modes.

### C. Overlapped levels

The difference between separated and overlapped levels is evident already when comparing Eq. (17) and Eq. (26). First, the sum in $n'$ in (17) could be safely omitted within the independent levels approximation while the integration over intermediate momenta in Eq. (26) is an essential ingredient of the theory. Second, the non-zero line width for separated levels appears only due to self-consistent treatment while the finite phonon line broadening in continuum is provided by the regular perturbation theory in $S$. In the latter case one gets:

$$\text{Im}\Pi_q(\omega) = -\frac{\pi S \omega_0}{16N} \sum_{k} \omega_k \left[\delta(\omega + \omega_k) + \delta(\omega - \omega_k)\right]. \quad (34)$$

Eq. (34) contains two delta-functional terms. Since we are interested in its behavior in the vicinity of the positive pole $\omega \approx \omega_q$ of the Green’s function, the phonon dispersion does not allow the argument of delta-function $\delta(\omega + \omega_k)$ to reach zero value anywhere in the Brillouin zone, so this term gives zero contribution to the integral. Hence, the only delta-function which contributes is $\delta(\omega - \omega_k)$. Notice that in the vicinity of the negative pole $\omega \approx -\omega_q$ the situation is opposite. Then using the expansion of phonon spectrum near its maximum one
obtains:

\[ \text{Im}\Pi_q(\omega) = -\frac{S a_0^3 \omega q}{64 \pi \alpha^{3/2}} \theta(\omega_0 - \omega) \omega \sqrt{\omega_0 - \omega}, \]  

where we take into account different phonons modes and perform the angular averaging of polarization factors. We see that the imaginary part of \( \Pi_q(\omega) \) is nonzero only for frequencies lower than \( \omega_0 \). Furthermore, the self-energy reveals the square-root non-analytical behavior when \( \omega \rightarrow \omega_0 \) originated from van Hove singularity in the phonon density of states that occurs at this energy.

The real part of \( \Pi_q(\omega) \) can be calculated on similar manner, and the result is given by

\[ \text{Re}\Pi_q(\omega) = -\frac{S a_0^3 \omega q}{64 \pi \alpha^{3/2}} \theta(\omega - \omega_0) \omega \sqrt{\omega - \omega_0}. \]  

This result is essentially frequency-dependent in the vicinity of the phonon pole \( \omega \approx \omega_q \). Likewise the contribution (35) to the imaginary part of \( \Pi_q(\omega) \) it stems from van Hove singularity in spectra of intermediate phonons with momenta lying near the center of the Brillouin zone scattered by disorder. It can be evaluated either directly or from the imaginary part of \( \Pi_q(\omega) \) with the use of Kramers-Kronig relations, see (29).

In addition to Eq. (36), near the pole \( \omega \approx \omega_q \) there appears almost constant term proportional to Debye momentum \( q_D \) that comes from the upper limit of integration over the Brillouin zone in Eq. (26). It is the momentum region where the details of the phonon band structure become important, and the Debye approximation is valid only qualitatively. Moreover, the Keating model we use in our calculations essentially fails in this area. This makes the numerical prefactor in front of the high-momenta contribution very unreliable. Also, similar contributions stems in this case from both \( (\omega \pm \omega_q)^{-1} \) poles of the integrand in Eq. (26). In fact, this term has the same origin as the contribution discussed in previous Section for certain types of disorder with nonzero mean value \( \langle \delta m_t^{-1} \rangle \) which also provides the constant shift of the real part of phonon self-energy. Therefore, in what follows we shall concentrate on strongly frequency- and momentum- dependent part of the self-energy assuming that constant \( (q, \omega\text{-independent}) \) terms are already absorbed into \( \omega_0 \) (see, however, Section V and paper II for discussion).

Notice that the real and the imaginary parts of \( \Pi_q(\omega) \) can be conveniently rewritten altogether as follows:

\[ \Pi_q(\omega) = -\frac{S a_0^3 \omega q}{64 \pi \alpha^{3/2}} \omega \sqrt{\omega - \omega_0}. \]  

Substituting Eq. (37) into Eq. (28) we can draw the spectral weight of the Green’s function

\[ A_q(\omega) = \frac{1}{\pi} \text{Im}D_q(\omega). \]  

This function depicted in Fig. 6 (blue curve) represents the broadened spectral line of the optical phonon (rigorously speaking, in the bulk). Our first observation is that the shape of the line is quite asymmetric. This asymmetry originates from nontrivial frequency dependencies of both real and imaginary parts of the self-energy which take place in different frequency domains. It is the common feature in many physical problems where the self-energy demonstrates visible frequency variation near the quasiparticle pole (see, e.g., Ref. 23). Let us perform, however, the on-shell approximation:

\[ \Gamma_q(\omega) = \frac{-2\omega_q \text{Im}\Pi_q(\omega)}{\omega + \omega_q} \rightarrow \Gamma_q(\omega = \omega_q) = \Gamma_q. \]  

Making this substitution in Eq. (38) we observe that the resulting curve becomes Lorentzian (see Fig. 6 red dashed curve), i.e., symmetric near its maximum, the width of the peak being close to the real one as far as the interaction-induced corrections are small. Here \( \Gamma_q \) plays the role of the phonon line width.

Ignoring the line shape asymmetry for the sake of qualitative description yields the phonon line width in the form

\[ \Gamma_q = \omega_q^2 \frac{S a_0^3}{64 \pi \alpha} q = \omega_q \frac{S}{64 \pi F}(q a_0). \]  

The linear-in-\( q \) dependence of the broadening parameter \( \Gamma_q \) here is our second observation in this Subsection. It is of prime importance and constitute one of the main results of the present paper. Indeed, until now our consideration was related to the bulk phonon-impurity model. Following the main strategic line of this paper we perform the finite-size quantization \( q \rightarrow q_n(L, p) \) in Eq. (40). It immediately yields the line width dependence on the particle size in the following desirable \( 1/L \) form:

\[ \Gamma_n = \omega_n \nu_n(p) \frac{S a_0}{L}. \]  

Here \( \nu_n(p) \) is the shape-dependent coefficient which contains: (i) numerical prefactor \( 1/64 \), (ii) spectrum flatness parameter \( F \) in denominator, and (iii) strong dependence on the quantum number \( n \). From the above consideration it follows that the higher order spectral lines have their widths larger than the first one. In particular, for cubic particle they are related to each other by

\[ \Gamma_{nx,ny,nz} = \sqrt{n_x^2 + n_y^2 + n_z^2} \frac{S}{3} \Gamma_1. \]  

Notice that for Raman active modes all quantum numbers \( n_i \) are odd in this case.

To conclude this Section, we investigated how the simplest model of disorder (point-like delta-correlated weak (Born) impurities) affects the line shapes in the Raman spectrum. We calculated the phonon line width in regimes of separated and overlapped levels. For separated levels we used the self-consistent Born approximation and observed the semi-circle law in phonon DOS and \( \sqrt{S}/L^{3/2} \) impurity strength and particle size dependence of the spectral line width, the prefactor is found to
be weakly shape and quantum number dependent quantity. For overlapped levels we found that the phonon line shape is visibly asymmetric due to van Hove singularity in the spectrum. By applying Lorentzian approximation and further quantizing the phonon momentum we obtain the damping proportional to $S/L$ with prefactor strongly dependent on particle shape and quantum number.

IV. SMOOTH RANDOM POTENTIAL

Section III has been devoted to the treatment of weak point-like (delta-correlated) Gaussian disorder. Now we shall consider how the smooth character of the (still, weak) random impurity potential affects the result of previous Section. More specifically, instead of point-like impurities \[\text{[14]}\] we shall assume the long-range character of the impurity-impurity correlation function

\[
\langle \delta m_\perp^{-1} \delta m_\perp \rangle m^2 = \langle \delta m_\parallel \delta m_\parallel \rangle m^{-2} = S W(|R_\perp - R_\parallel|, \sigma), \tag{43}
\]

where the characteristic scale $\sigma$ of the potential is much longer than the lattice parameter, $\sigma \gg a_0$, and the correlation function is Gaussian:

\[
W(r, \sigma) = \frac{a_0^3}{(2\pi \sigma^2)^{3/2}} \exp\left(-\frac{r^2}{2\sigma^2}\right), \tag{44}
\]

the prefactor is introduced for proper normalization.

We notice that particular spatial dependence of correlator in \[\text{[14]}\] is not essential; the only property needed is its rapid decay on scale $\sigma$. For instance, we observe that replacing the Gaussian correlator in \[\text{[14]}\] by the exponential one does not change qualitatively our results.

A. Separated levels

Here we present our results for separated levels. We obtain self-consistent equation for the phonon self-energy in the following form:

\[
\Pi_n(\omega) = \frac{S\omega_n}{8} \sum_{l,l',n'} |Y_n(R_l) \cdot Y_{n'}(R_{l'})| |Y_{n'}(R_{l'}) \cdot Y_n(R_l)| W(|R_l - R_{l'}|, \sigma) \frac{\omega_{n'}^2}{\omega^2 - \omega_{n'}^2 - 2\omega_{n'}^{}}. \tag{45}
\]

For non-degenerate separated levels it yields

\[
\Pi_n(\omega) = \frac{2d_n^2(p) S\omega_n^3}{N} \frac{1}{\omega^2 - \omega_n^2 - 2\omega_n^{}} = \frac{1}{\omega_n^{}}. \tag{46}
\]

where the shape and quantum number dependent parameters $d_n(p)$ are given by

\[
d_n^2(p) = \frac{N}{16} \sum_{l,l'} |Y_n(R_l)|^2 |Y_{n'}(R_{l'})|^2 W(|R_l - R_{l'}|, \sigma). \tag{47}
\]

These constants could be calculated for any particular model and particle shape. After determining new parameters $d_n^2(p)$ instead of $c_n^2(p)$ all the results of Subsection III B are applicable for the smooth potential. Once again, using the on-shell approximation we obtain the line broadening in the form:

\[
\Gamma_n = \omega_n \rho_n(p) \sqrt{S} \left(\frac{a_0}{T}\right)^{3/2}, \tag{48}
\]

where $\rho_n(p)$ are the novel shape and quantum number dependent parameters, $\rho_n(p) = d_n \sqrt{P_\parallel^3/8}.$

In general, finite disorder induced length scale $\sigma$ leads to diminishing of the constant $\rho_n(p)$ in comparison with the delta-correlated case (see Appendix). Two regimes should be distinguished. The first one could be analyzed via expansion in the parameter $q_n \sigma \ll 1$, where $q_n(\delta, p)$ is the finite size quantization induced momentum (notice that it has the meaning of the phonon eigennumber, $\omega_n = \omega_0 - \alpha q_n^2$). To the leading order it coincides with the result for the point-like potential, the first correction being of the order of $(q_n \sigma)^2$.

The second regime that occurs at $q_n \sigma \gg 1$ appears due to smoothness of the random potential. In this regime the wave-functions in Eq. \[\text{[17]}\] experience fast oscillations on the scale $\sigma$ and therefore could be replaced by their average values $\sim 1/\sqrt{N}$. As a result, the line width as a function of particle size $L$ saturates:

\[
\Gamma_n = \omega_n \frac{1}{4(2\pi)^{3/4}} \sqrt{S} \left(\frac{a_0}{\sigma}\right)^{3/2}. \tag{49}
\]

The damping in this regime is small as compared to the delta-correlated potential case (cf. Subsection III B).
B. Overlapped levels

The leading contribution to $\text{Im}\Pi_q(\omega)$ is determined by the same diagram Fig. 2 as for delta-correlated impurities. The corresponding analytical expression reads:

$$
\text{Im}\Pi_q(\omega) = -\frac{\pi S \omega_q}{16 N} \sum_k \omega_k \widetilde{W}(k - q, \sigma) \delta(\omega - \omega_k),
$$

(50)

where $\widetilde{W}(q, \sigma)$ is the Fourier transform of Eq. (44):

$$
\widetilde{W}(q, \sigma) = \exp \left( -\frac{q^2 \sigma^2}{2} \right).
$$

(51)

Integrating in (50) one obtains for the phonon damping

$$
\Gamma_q(\omega) = -\frac{S a_0^3 \omega_q}{64 \pi} \frac{\omega(\omega_0 - \omega)}{2 \alpha \sigma^2 q}
\times \exp \left[ \frac{\sigma^2}{2 \alpha} (\sqrt{k^2 - \omega_0^2} - \sqrt{q^2 - \omega^2}) \right]
- \exp \left[ \frac{\sigma^2}{2 \alpha} (\sqrt{k^2 + \omega_0^2} + \sqrt{q^2 + \omega^2}) \right].
$$

(52)

The next step is to apply for (52) the on-shell approximation $\omega \rightarrow \omega_q$. This yields:

$$
\Gamma_q = \Gamma_0 f(q\sigma),
$$

(53)

where $\Gamma_0$ is the bulk phonon damping for delta-correlated disorder (see Eq. [40]), and the spreading function $f(x)$ is given by

$$
f(x) = 1 - \exp \left( -\frac{2x^2}{2x^2} \right)
$$

(54)

Now we apply the finite size quantization rule $q \rightarrow q_n(L, p)$ to Eqs. (53) and (54):

$$
\Gamma_n = \Gamma_0 f(q_n \sigma),
$$

(55)

where $\Gamma_0$ is given by Eq. (41). This equation determines the damping of overlapped vibrational eigenmodes for finite nanoparticles subjected to the smooth random potential at arbitrary relation between $L$ and $\sigma$.

It is instructive to investigate Eq. (55) in the limiting cases of small $q_n \sigma \ll 1$ and large $q_n \sigma \gg 1$ discrete momenta. The first asymptote yields $f(x) \rightarrow 1$ and therefore $\Gamma \approx \Gamma_0$; in the leading order the scale $\sigma$ drops down from the formula. Thus the damping function for smooth disorder qualitatively retains its behavior peculiar for point-like impurities. We conclude that for finite nanoparticles which are essentially nonuniform on the scale of its size, $L \geq \sigma$, the model of point-like impurities qualitatively describes the finite-scale disorder, as well, and the resulting line width is still mainly given by $\Gamma \propto 1/L$ law.

However, when the discrete momentum is large enough, $q_n \sigma \gg 1$, then $f(x) \approx 1/(2x^2)$, and the asymptotic behavior of damping in smooth disorder described by (53) becomes $\Gamma \propto 1/q_n \sigma^2$ thus being drastically different from the aforementioned point-like case. In terms of finite size particles it means that, while the variation of disorder appears only on scales of order of or longer than the particle size, $\sigma \geq L$, the novel regime $\Gamma \propto L$ emerges:

$$
\Gamma_n = \frac{\omega_n}{2 \nu_n^{-1}(p)} \left( \frac{a_0}{\sigma} \right)^2 S \frac{L}{a_0},
$$

(56)

Physically, two regimes of $\Gamma$ momentum dependence could be understood from the general scattering theory after we recognize that the particle velocity $v_n \propto \partial_q \omega_q$ is proportional to the momentum $q$. Then the first regime corresponds to the “slow” particles scattering and the second one describes the “fast” particles scattering off the soft-core spheres with radius $\sigma$ (see corresponding problems in Ref. [94]).

This Section has been devoted to the treatment of effects of long-range character of the impurity potential. Introducing the characteristic potential scale, $\sigma$, we observed, that the relation between the nanoparticle size, $L$, and the scale $\sigma$ is responsible for two crossovers in the behavior of the phonon line width. Namely, when the particle size is larger than the impurity length scale, i.e., when the nanoparticle is essentially inhomogeneous, the damping reveals ordinary $1/L^{3/2}$ dependence for separated and $1/L$ dependence for overlapped phonon levels. Otherwise, the particle could be regarded as “almost homogeneous”. Then the damping behavior changes to saturation for separated and to the linear-in-$L$ law for overlapped levels, the crossovers occur at $L \sim \sigma$ (to be precise, the numerical factor $2\pi$ entering expansion moves
the masses are given by $m$. In particular, it means that surface inhomogeneities of particles lead to deviations from $1/L$ dependence.

V. STRONG IMPURITIES

In this Section we investigate the influence of strong impurities (the amplitude may exceed the phonon band width) with low concentration $c_{imp} \ll 1$ on the vibrational spectrum of nanoparticles. We apply the standard T-matrix approach (see, e.g., Ref. [24]) which takes into account multiple scattering off a single impurity. It gives the correct result to the first order in $c_{imp}$ (see Fig. 4(c)). The possibility to form the localized phonon state on the impurity site we noticed that at $\delta m < 0$ the localization of the optical phonon with $\omega > \omega_0$ can appear, as lighter atoms have higher vibrational frequencies. The corresponding analysis takes into account all phonon modes $n$, in Eq. (59), and sum up all contributions of different orders in $k$. This program can be realized for any particular set of model wave functions $Y_n$, numerically, but hardly achieved in general terms. Nevertheless, since the states localized inside the particle barely feel its boundary they can be analyzed within the bulk approximation, see next Subsection. We also address this problem numerically in paper II.

A. Separated levels

As we mentioned above the T-matrix approach consists of the exact solution of the single-impurity problem as the first step with subsequent averaging over disorder configurations as the second one. The former procedure implies the summation of all the multiple-scattering diagrams for one impurity (see Fig. 4(c)). As before, the solution for separated levels will be found self-consistently. Expression for the impurity located at the $l$-th site reads:

$$
\Pi_n^{(1)}(\omega) = \omega_n \sum_{k=1}^{\infty} \sum_{n_1, \ldots, n_k} \left( \frac{U}{4} \right)^k [Y_n(R_i) \cdot Y_{n_1}(R_i)] \\
\times \left[ Y_{n_2}(R_i) \cdot Y_{n_3}(R_i) \right] \ldots \left[ Y_{n_{k-1}}(R_i) \cdot Y_{n_k}(R_i) \right] \\
\times \omega_{n_1} D_{n_1}(\omega) \ldots \omega_{n_{k-1}} D_{n_{k-1}}(\omega),
$$

and the $k$-th term corresponds to the $k$-fold scattering off the same impurity.

As the next step, one should sum up the r.h.s. of Eq. (59) over all impurities and average over disorder configurations. The technical problem when solving this equation is the necessity to sum up over repeated quantum numbers the scalar products of wave functions stemming from different orders in scattering. This makes impossible to represent the result of this procedure in a simple form of geometrical progression. It should be contrasted with the conventional situation of extended states, when the wave functions are the plane waves and this summation occurs automatically.

Nevertheless, the separated levels approximation for non-degenerate levels allows to solve this problem by putting all $n_i$ in Eq. (59) to be equal to $n$. Simple argument $|Y(R)| \sim 1/\sqrt{N}$ allows to estimate the $k$-th contribution to Eq. (59) as $1/N^k$. So, there are only two terms in the entire series shown by diagrams (a) and (b) in Fig. 4 that should be taken into account if $|U| \sim 1$. The first one is the (almost constant) correction to the phonon frequency $\omega_0$ due to the change in the average mass of nanoparticle atoms (cf. paper II):

$$
\Pi_n^{(1)} = -\frac{1}{4} \omega_n U c_{imp}.
$$

The second term in Eq. (59) results in the self-consistent equation for $\Pi_n(\omega)$ which is equivalent to Eq. (28) where for $S$ one should insert $c_{imp} U^2$. Finally, the counterpart of Eq. (31) reads:

$$
\Gamma_n = \omega_0 n_\mu p_n(p) \sqrt{c_{imp}} |U| \left( \frac{a_0}{L} \right)^{3/2}.
$$

Addressing the problem of phonon localization on the impurity site we notice that at $\delta m < 0$ the localization of the optical phonon with $\omega > \omega_0$ can appear, as lighter atoms have higher vibrational frequencies. The corresponding analysis takes into account all phonon modes $n_i$ in Eq. (59), and sum up all contributions of different orders in $k$. This program can be realized for any particular set of model wave functions $Y_n$, numerically, but hardly achieved in general terms. Nevertheless, since the states localized inside the particle barely feel its boundary they can be analyzed within the bulk approximation, see next Subsection. We also address this problem numerically in paper II.

B. Overlapped levels

In contrast to the regime of separated levels (see Eq. (59)) in bulk all the contributions shown in Fig. 4(c) can be easily summed up as a geometrical progression. After averaging over disorder configurations the phonon self-energy has the following standard form:

$$
\Pi_\Omega(\omega) = -\frac{\omega \sqrt{c_{imp}} U / 4}{1 + \frac{\pi}{4} \sum_k \omega_k D_0(\omega, k)}.
$$

It is worth to mention that $\Pi_\Omega(\omega)$ in Eq. (62) remains finite even for infinitely strong $U$ (so-called “unitary limit”).

Integration in (62) is performed similarly to the Born case. One important difference comes from the fact that due to slightly different model of disorder (disorder with
nonzero average) now we could not absorb the constant terms into $\omega_0$ as we did for Born impurities. As a result we get:

$$
\frac{1}{N} \sum_k \omega_k D_0(\omega, k) = \frac{\omega_0}{4\pi \alpha} \left[ \frac{q_D}{\pi/2} - \sqrt{\frac{\omega - \omega_0}{\alpha}} \right], \tag{63}
$$

where $q_D$ is the Debye momentum (upper limit of integration). The Debye momentum is in fact a sort of adjustable parameter since its determination presumes that the spherical symmetry of the spectrum characteristic for phonons near the Brillouin zone center extents onto large momenta. Therefore, the factor $\pi/2$ in Eq. (63) could not be treated seriously, and hereafter we just absorb it into the definition of Debye momentum using $q'_D = q_D/\pi/2$ instead of $q_D$.

Plugging Eq. (63) into Eq. (62) and using the definition (22), at $\omega < \omega_0$ we obtain:

$$
\Pi_q(\omega) = -\omega_q 4\pi F^2 \frac{c_{imp} \omega_0}{\omega_{loc} - \omega} \left[ \frac{a_0}{\zeta} + i \sqrt{\frac{\omega - \omega_0}{F \omega_0}} \right], \tag{64}
$$

where the resonant frequency $\omega_{loc}$ (see below) is determined as follows:

$$
\omega_{loc} = \omega_0 + \alpha \zeta^{-2}, \tag{65}
$$

and the characteristic length $\zeta$ is given by

$$
\zeta^{-1} = q'_D \left( 1 + \frac{16\pi F}{U a_0} \right). \tag{66}
$$

This length is of order of $1/q'_D \sim a_0$ for regular $U$ and infinitely increases when $U < 0$ and $|U| \rightarrow |U_{min}| = 16\pi F/q'_D a_0$. At $\omega > \omega_0$ we have $\text{Im} \Pi_q(\omega) = 0$, i.e., the damping is absent.

First, we consider the on-shell ($\omega \rightarrow \omega_k$) approximation. The damping acquires the form:

$$
\Gamma_q = \omega_q 4\pi F c_{imp} \left( \frac{\zeta}{a_0} \right) \frac{q \zeta}{1 + (q \zeta)^2}, \tag{67}
$$

which after applying the finite size quantization trick $q \rightarrow q_n (L, p)$ yields:

$$
\Gamma_n = \omega_n 4\pi F c_{imp} \left( \frac{\zeta}{a_0} \right) \frac{q_n \zeta}{1 + (q_n \zeta)^2}, \tag{68}
$$

We see that the behavior of the line width strongly depends on parameter $\zeta$. When the spatial scale generated by this quantity is the short-range one, i.e., when $\zeta \sim a$, the line width reveals conventional $1/L$ behavior. If, however, the characteristic scale $\zeta$ is a sort of critical quantity (this happens when $|U| \approx |U_{min}|$), then it generates the long scale to be compared with $L$. For large enough $L \gg \zeta$ equation (68) yields $1/L$ particle size dependence, with additional enhancement factor $(\zeta/a_0)^2$. In the opposite case $\zeta \gg L$ the size dependence in Eq. (68) changes to linear-in-$L$. Generally, the situation resembles crossover observed for smooth random potential (see Section IV).

Let us also present the formula for the phonon line width in the unitary limit $|U| \rightarrow \infty$ (which is realized for $\delta m \approx -m$, very light atoms or vacancies):

$$
\Gamma_n = \omega_n \left( \frac{32F}{a_0 q'_D} \right)^2 c_{imp} \nu_n(p) a_0 \frac{a_0}{L}. \tag{69}
$$

the strength of disorder does not enter the final formula. In contrast, for large positive $\delta m \gg m$ (heavy impurity atoms) disorder strength saturates at $U \sim 1$ and there is no unitary limit.

We plot the phonon line width dependence on the disorder strength $U$ in Fig. 8. We investigate the first phonon mode for a spherical 3nm nanodiamond. One can see quadratic dependence at $|U| \ll 1$ which corresponds to familiar weak point-like impurities (see Sec. III C), the resonant scattering when $U$ is close to $U_{min} \approx -0.2$ and the unitary limit at $U \lesssim -1$, when the damping is almost constant.

Importantly, Eq. (63) allows to study the possibility to form the localized phonon-impurity bound states by investigating zeros of denominator of Eq. (62) which determine the resonant energies of these states. Evidently, for $\delta m > 0$ localized states with $\omega > \omega_0$ do not appear because the denominator is positive in this frequency domain. There is no resonant states with $\omega_{res}$ close to $\omega_0$ for the same reason. Thus, significant perturbations of DOS can only be observed at frequencies corresponding to short wave length optical phonons (this would lead to their rapid decay) or even below the band of opical phonons. Obviously, these states are unessential for the analysis of Raman spectra.

In the meantime, at $\delta m < 0$ the situation is very different. Equation

$$
1 + \frac{U a_0}{16\pi F} \left( q'_D - \sqrt{\frac{\omega_0 - \omega}{\alpha}} \right) = 0 \tag{70}
$$

has solution (65) for $|U| \geq |U_{min}|$ (remember that $U < 0$ in this case). If $U \approx U_{min}$ then the frequency of localized level $\omega_{loc}$ is close to $\omega_0$ and the phonon damping is drastically enhanced due to the resonant character of scattering off the impurities (see above). With further increasing of $U$ towards the unitarity the main contribution to the integral in Eq. (62) comes from momenta lying beyond the range of applicability of spectral expansion (21) and Eq. (63) fails. Here we just mention that in the improved theory $\omega_{loc} \sim |U|^{1/2}$.

To conclude this Section, we investigate the optical phonon damping due to strong point-like impurities within the framework of $T$-matrix approximation. In the regime of separated levels besides the trivial “mean-field” correction to phonon eigenfrequencies $\omega_n$ we observe the damping similar to the weakly disordered case (see Subsection III B): it is proportional to the square root of the impurity concentration and decays with increasing of the particle size as $L^{-3/2}$. For overlapped levels in the long-wavelength limit we find the linear-in-$q$ momentum
dependence of phonon damping in the bulk which could be converted into $1/L$ dependence for finite-size particles. In the “critical” regime of nearly resonant impurity scattering we obtain the parametrical enhancement of $1/L$ damping for largest particles and the crossover to linear-in-$L$ behavior for smallest ones. We also study the possibility to form the localized phonon-impurity bound state near the zone edge for both positive and negative impurity mass defects.

VI. DISCUSSION AND INTERMEDIATE CONCLUSIONS

This Section is intended to present the discussion of intermediate (analytical) results elucidating the role of disorder in crystalline nanoparticles. More complex and detailed summary which includes the comparative analysis of both analytical and numerical approaches to this problem could be found in paper II. In the meanwhile, two general remarks are in order right now.

First, we would like to point out that in the above consideration we did not present the unified analytical theory of phonons in disordered nanoparticles. Instead, we investigate important features of this problem by studying several simplest models which probably exaggerate and oversimplify the real experimental situation (cf. paper II). It allows to extract characteristic spatial scales associated with these features and, more importantly, to formulate the qualitative model free picture of the phonon-impurity scattering in nanoparticles.

Our second remark is related to the object we addressed in this paper. We would like to emphasize that we evaluated the broadening of individual lines in the spectrum of vibrational eigenmodes in nanoparticles of a given shape. Only all these lines treated together, properly broadened, and elaborated with the use of the theory of photon-phonon interaction constitute the Raman peak in real experiments. This approach should be contrasted with PCM-like theories wherein the line width is a single parameter for the entire Raman peak.

We started our analysis from the treatment of simplest weak point-like impurities. We observe that there exist two drastically different regimes depending on either the eigenmodes are separated or they belong to the (quasi)continuum. In particular, for separated levels the phonon damping behaves as $\Gamma_n \propto \sqrt{S/L^{3/2}}$, where $L$ is the particle size and the disorder strength $S$ is a product of impurity concentration $c_{imp}$ and the squared relative variation of the random parameter of the theory (in our case, the atomic mass $m$). For overlapped levels we find $\Gamma_n \propto S/L$. In the latter case we solve the bulk problem performing the finite-size quantization only in final formulas. This (definitely, approximate) trick is justified due to evident similarity between the continuous spectra of propagating wave modes and the ones of plane waves, the difference supposed to be negligible.

These results were obtained within the on-shell (Lorentzian) approximation. Beyond this approximation the line shape in the latter case is shown to be strongly asymmetric due to Hove singularity in the optical phonon spectrum, whereas in the former one it obeys the semi-circle law. We also establish simple relations between the line widths of low-lying eigenmodes with different quantum numbers. The dependence of $\Gamma_n$ on the quantum number of the level is observed to be stronger in the overlapped regime than in the separated one.

Considering weak but smooth disorder with characteristic length scale $\sigma$ we obtain the damping at $\sigma \ll L$ similar to the one for point-like impurities. In the opposite limit $\sigma \gg L$ it is proportional to $L$ in overlapped regime and saturates as a function of particle size if the levels are separated. Such a behavior of the phonon line width for overlapped levels could be understood from general quantum mechanical picture of fast vs. slow particles scattered off the “soft spheres” potential.

At last, we treated the case of strong impurities with low concentration $c_{imp} \ll 1$ using the $T$-matrix approach borrowed from the theory of dirty fermions. We consider the replacement impurities of a single sort to be strong so the effective local potential generated by mass defect may even exceed the phonon band width. Our main observation concerning separated levels is that the result for damping is almost the same as for the weak impurities case. The only difference is additional shift of the maximal optical phonon frequency $\omega_0$. When regarding the damping for overlapped levels we observe the same particle size and concentration dependence as we found for Born impurities with prefactor enhancement for light impurity atoms.
The T-matrix approach allows also to investigate the bound state of a phonon localized on the impurity. Since the wave functions of phonons localized in the depth of the particle rapidly decay with distance they barely feel the boundary. Thus we can analyze them within the particle rapidly decay with distance they barely feel the wave functions of phonons localized in the depth of the bound state of a phonon localized on the impurity. Since Eq. (72) can be inverted, thus determining the critical and the phonon life time $1/\Gamma_n$ for a phonon to fly ballistically throughout the particle) could be in different regimes if say the states $\omega_{n-1}$ and $\omega_n$ are already overlapped while $\omega_{n}$ and $\omega_{n+1}$ are not).

Next, since the line widths in different regimes reveal different size and disorder dependence, it is instructive to determine the characteristic size for these two quantities to be equal to each other. Roughly, dropping the coefficients one obtains:

$$L_c \sim \frac{a_0}{S}, \quad (72)$$

Remarkably, the line width (in both regimes) reaches the inter level distance on the same scale. In other words, $L_c$ is the spatial scale for ballistic Thouless time (the time for a phonon to fly ballistically throughout the particle) and the phonon life time $1/\Gamma_n$ to coincide. Moreover, Eq. (72) can be inverted, thus determining the critical disorder strength for a given particle size:

$$S_c \sim \frac{a_0}{L_c}, \quad (73)$$

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Appendix A: Disorder in EKFG formalism

The consideration given in the main body of this paper is presented in maximally general form applicable for various theories (DMM-BPM, EKFG) we developed. It provides the limitations on final results including the coefficients and some relevant dependencies. In this Appendix we illustrate how the problem can be solved completely for some particular case. As an example we choose the EKFG theory of a cubic particle which can be treated analytically. Since the overlapped regime is a sort of trivial we concentrate on separated levels.

1. Hamiltonian and quantization

We start from the Hamiltonian of EKFG model

$$\mathcal{H}_0 = \int d^3r \frac{1}{2} \left[ \Pi^2 - C_1(\nabla\Phi)^2 + C_2\Phi^2 \right]. \quad (A1)$$

Here quantized field in Schrodinger representation

$$\Phi(r) = \sum_n \frac{1}{\sqrt{2\omega_n}} \left( b_n Y_n(r) + b_n^+ Y_n^*(r) \right) \quad (A2)$$

and momentum operator

$$\Pi(r) = -\sum_i \frac{i}{2} \sqrt{\omega_n} \left( b_n Y_n(r) - b_n^+ Y_n^*(r) \right) \quad (A3)$$

are expressed via the phonon creation-annihilation operators $b_n^+, b_n$ and the eigenfunctions of EKFG model $Y_n$. They obey conventional commutation relation:

$$[\Phi(r), \Pi(r')] = -i\delta(r - r'). \quad (A4)$$

It is easy to show that the quantized Hamiltonian reads:

$$\mathcal{H}_0 = \sum_n \omega_n (b_n^+ b_n + 1/2). \quad (A5)$$

Furthermore, we can define the causal phonon Green’s function

$$D(r_1, t_1; r_2, t_2) = -i \langle 0 | \tilde{T} (\Phi(r_1, t_1)\Phi(r_2, t_2)) | 0 \rangle. \quad (A6)$$

Here $\tilde{T}$ is the time ordering operator for the field $\Phi(r, t)$ in Heisenberg representation. After simple calculations and Fourier transform we obtain

$$D_0(r_1, r_2, \omega) = \sum_n \frac{Y_n(r_1)Y_n(r_2)}{\omega^2 - \omega_n^2 + i\Gamma_n}. \quad (A7)$$

where the eigenfunctions $Y_n$ are real.

Considering the solution of Eq. (2) for a given frequency $\omega$ we get

$$(\omega^2 - C_1) Y - C_2 \Delta Y = 0. \quad (A8)$$
First, we should solve the eigenproblem
\[ \triangle Y + q^2 Y = 0, \quad Y|_{\partial \Omega} = 0, \quad (A9) \]
where \( q \) will be referred to as the momentum. Thus, the spectrum of the problem has the form:
\[ \omega^2 = C_2 - C_1 q^2. \quad (A10) \]
This is the equivalent of Eq. (21):
\[ \omega_k = \omega_0 - \alpha q^2, \quad (A11) \]
where we put \( \omega_0 = \sqrt{C_2} \) and \( \alpha = C_1/2\sqrt{C_2}. \)

As an example we consider the cubic nanoparticle with the edge \( b \). In that case EKFG has obvious solution normalized to unity:
\[ Y_n = \sqrt{\frac{8}{b^3}} e^{-i \omega t} \sin \frac{\pi n_1 x}{b} \sin \frac{\pi n_2 y}{b} \sin \frac{\pi n_3 z}{b}, \quad (A12) \]
where vector \( n = (n_1, n_2, n_3) \) enumerates the eigenstates, and the corresponding eigenvalues are
\[ \omega_n = \omega_0 - \frac{\pi^2}{b^2} (n_1^2 + n_2^2 + n_3^2). \quad (A13) \]

2. Point-like impurities

In the lattice model disorder in atom masses corresponds to variation of parameters \( C_1 \) and \( C_2 \) of the Hamiltonian. In the range of EKFG approach validity \( q a_0 \ll 1 \) we can neglect the variation of \( C_1 \). Thus, the disorder-induced perturbation to the Hamiltonian reads:
\[ \delta \mathcal{H} = \int d^3r \frac{C_2(r) - C_2}{2} \Phi^2. \quad (A14) \]
Here \( C_2 = \omega_0^2 \) stands for the average value of \( C_2(r) \). Obviously, \( C_2(r) - C_2 \approx -\omega_0^2 \delta m(r)/m \). Using this fact we can write:
\[ \delta \mathcal{H} = -\sum_{n,n'} \int d^3r \frac{\omega_0^2}{4\omega_0 \omega_{n'n'}} \delta m(r) \frac{m}{m} \quad (A15) \]
\[ \times (a_n + a^+_n)(a_{n'} + a^+_{n'}) Y_n(r) Y_{n'}(r). \]
Within the EKFG approximation the disorder correlation function for weak point-like impurities is given by
\[ \langle \delta m(r_1) \delta m(r_2) \rangle = S V_0 \delta(r_1 - r_2). \quad (A16) \]
where \( V_0 \) is the unit cell volume.

In the limit of weak impurities only the second diagram in Fig. 4(b) is relevant. By virtue of Eq. (A15) the correction to the phonon Green’s function yields:
\[ \delta D(r_1, r_2, \omega) = \frac{S V_0 \omega_0^4}{4} \int d^3r \sum_n Y_n(r_1) Y_n(r_2) \quad (A17) \]
\[ \sum_{n'} Y_{n'}(r) Y_{n'}(r_2) \frac{Y_n(r) Y_n(r_2)}{\omega^2 - \omega_{n'n'}^2 + i0}. \]

For further analysis it is useful to perform the discrete Fourier transform of equation
\[ D(r_1, r_2, \omega) = D_0(r_1, r_2, \omega) + \delta D(r_1, r_2, \omega). \quad (A18) \]
In order to execute this transformation we multiply Eq. (A18) by \( Y_n(r_1) Y_{n'}(r_2) \) and integrate it over \( r_1 \) and \( r_2 \). This procedure eliminates the sum in Eq. (A7) and sums over \( n \) and \( n'' \) in Eq. (A17) due to orthogonality of eigenfunctions \( Y_n \). We can rewrite Eq. (A18) introducing renormalized complex eigenfrequencies \( \omega_n \) as follows:
\[ \omega^2 - \omega_n^2 = \omega^2 - \omega_{n'}^2 - \Pi_n(\omega), \quad (A19) \]
where
\[ \Pi_n(\omega) = \frac{S V_0 \omega_0^4}{32 V} \sum_n \prod_{i=x,y,z} \frac{(2 + \delta_{n_i n''_i})}{\omega^2 - \omega_{n''_i}^2 + i0}, \quad (A20) \]

Using eigenfunctions (A12) we calculate the self-energy (A20):
\[ \Pi_n(\omega) = \frac{27 S V_0 \omega_0^4}{32 V} \frac{1}{\omega^2 - \omega_n^2 - \Pi_n(\omega)}. \quad (A21) \]

Solving this equation, we obtain:
\[ \Pi_n(\omega) = (\omega^2 - \omega_n^2) - \sqrt{(\omega^2 - \omega_n^2)^2 - \frac{47 S V_0 \omega_0^4}{32 V}}, \quad (A22) \]

One can see, that the phonon line obeys familiar semi-circle form (see Fig. 5), and the width of the phonon line is given by:
\[ \Gamma_n = \omega_0 \sqrt{\frac{27 S}{32 V}}. \quad (A23) \]

For degenerate level \( n \) only the coefficient in Eq. (A24) should be modified. If two quantum numbers in \( n \) are equal to each other then the level is three-fold degenerate and instead of 27/32 we get \((27 + 4)/32 = 51/32\). For six-fold degenerate level with all three quantum numbers different the multiplier is 79/32.

Furthermore, from Eq. (A21) one can find the real part of the correction to the phonon self-energy energy (see subsection III.B. This contribution is proportional to \( S \).

Finally, from Eq. (A24) we precisely determine the characteristic crossover scale \( L_c \):
\[ L_c \approx 15 \pi^4 F^2 \frac{a_0}{S}. \quad (A25) \]

For a diamond \( F \approx 0.008 \), and prefactor in front of the model-free second term in (A25) turns out to be not too small \((\approx 0.093)\).
3. Smooth disorder

Now we consider smooth disorder with some characteristic length scale $\sigma$. The correlator reads:

$$\frac{\langle m(r_1)m(r_2) \rangle}{m^2} = \frac{S}{\sigma^4 (2\pi)^{3/2}} e^{-\frac{(r_1-r_2)^2}{2\sigma^2}}. \quad (A26)$$

Using this correlator we obtain the following correction to the phonon Green’s function:

$$\delta D(r_1, r_2, \omega) = \frac{S \omega^4}{4} \int d^3r d^3r' \left[ \sum_n \frac{Y_n(r_1)Y_n(r)}{\omega^2 - \omega_n^2 + i0} \sum_{n'} \frac{Y_{n'}(r')Y_{n'}(r_2)}{\omega^2 - \omega_{n'}^2 + i0} e^{-\frac{(r-r')^2}{2\sigma^2}} \sigma^3 (2\pi)^{3/2} \right].$$

For non-degenerate level $n$ and $q_n^2\sigma^2 \ll 1$ we have only small correction to damping:

$$\Gamma_n = \omega_0 \sqrt{\frac{27 S}{32 N} \left(1 - \frac{2}{3}q_n^2\sigma^2\right)}. \quad (A27)$$

For three-fold degenerate level $(n_1, n_2, n_2)$ the damping reads:

$$\Gamma_n = \omega_0 \sqrt{\frac{51 - 42\pi^2 n_1^2 \sigma^2 - 76 \pi^2 n_2^2 \sigma^2}{32N} S}, \quad (A28)$$

and for six-fold one the result is as follows:

$$\Gamma_n = \omega_0 \sqrt{\frac{79 - 66 q_n^2 \sigma^2}{32 N} S}. \quad (A29)$$

Thus, at $q_n^2\sigma^2 \ll 1$ the smooth random potential leads to almost the same result as the point-like impurities. For first modes with highest frequencies this condition is equivalent to $\sigma \ll L$, i.e., the length scale of the random potential must be much smaller than the particle size.

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