The ‘Generalized Skettrup Model’ and Specific Lattice Thermal Capacity of Non-Homogeneous and Low-Dimensional Semiconductors and Insulators

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The ‘Generalized Skettrup Model’ (GSM) links features of near-band gap and intra-gap electronic as well as corresponding optical spectra of polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators to probabilities of equilibrium fluctuations in an energy of the individual quasi-particle, number of quasi-particles in a quantum grand canonical ensemble of confined acoustic phonons with static plane-wave basis (pure states), and in their aggregate energy. The essentially many-body GSM might be implemented as well at evaluations on harmonic and anharmonic contributions to the specific lattice thermal capacity of those semiconductors and insulators, as well as their low-dimensional counterparts. Herein predictions of the ‘refined’ GSM equations in these areas are compared with appropriate experimental results and outcomes of canonical Debye – Planck model.

PACS numbers: 05.70.-a; 63.20.-e; 63.20.Ry; 65.40.Ba; 65.80.Ck

1. Introduction

One of the most tremendous achievements of the ‘canonical’ quantum theory of solids had been accomplished [1, 2] in just few years preceding the World War I, mainly due to efforts of famous theorists: A. Einstein [1] and P. Debye [2]. It comprised of a comprehensive (and yet ‘first-principles’) explanation on both low-temperature and high-temperature behavior(s) of the temperature-dependent specific thermal capacity C_v(T) of bulk solids at their constant volume [1, 2]. Eventually, both archetypal branches of the experimental C_v(T) curves (i.e., C_v(T) ∝ T^3 at relatively low temperatures) and temperature-independent C_v(T) quantity (Dulong-Petit law [3] – at temperature T well exceeding the Debye’s one, θ_D) had been replicated convincingly [2] based on Debye’s fundamental long-wavelength acoustic vibrational (phonon) states with a linear dispersion and a quadratic (in the phonon energy) density-of-sates (DOS), as well as using Planck’s occupation factor for those single-phonon states. Basic equations of this canonical Debye-Planck approach with illustrations for aforementioned C_v(T) branches are summarized in the next section.

In contrast, the many-body Generalized Skettrup Model (GSM) depicted in second chapter of ref. [4] (see also references therein) is essentially based on evaluation of probabilities of equilibrated fluctuations in an energy of pure (harmonic) state(s) of individual acoustic phonons, their aggregate energy and (rational) number of quasi-particles of the (quantum) grand canonical ensemble (QGCE) of (interacting in general) acoustic phonons with static (time-independent) plane-wave basis (pure states) in polycrystalline and/or spatially non-homogeneous amorphous semiconductors and insulators with tetrahedral atomic coordination. In particular, probabilities of those fluctuations are customarily evaluated within the GSM framework via integration over available (at the given aggregate energy) mixed (anharmonic) quantum states of ensemble of (interacting) Debye’s acoustic phonons and appropriate number of those quasi-particles [4]. Furthermore, the temperature of the QGCE might (in general) fluctuate as well [5, 6], and intensity of such fluctuations could be evaluated quantitatively based on the fundamental ideas pioneered by famous Japanese physicist Takeo Matsubara elsewhere in ref. [5]. Moreover, the GSM implies that those fluctuations in QGCE of confined longitudinal acoustic phonons with the static plane-wave basis (microstates) are linked intimately to energy fluctuations in an electronic sub-system of a semiconductor (insulator) and eventually to its corresponding optical spectra: relationship among the instantaneous energies (and/or fluctuation probabilities) of single-electron and multi-phonon excitations might be established quantitatively either based on semi-empirical electron-phonon coupling parameters or via well-known ‘deformation potential’ formalism [4]. Thus, the GSM provides unambiguous physical clarification on origins of the exponential (Urbach) and ‘power-law’ (or ‘algebraic’) band tails both within band gap(s) of aforementioned semiconductors and insulators as well as of their appropriate (near-band-gap and sub-gap) optical spectra, replicates realistically spectral and temperature dependencies of key parameters for all such band tails, as well as quantitative interrelations established among those parameters: see the sixth and seventh chapters of ref. [4]. Moreover, the GSM allows one to evaluate persuasively spectral and temperature dependencies of parameters of deep defect states in the polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators: see third and seventh chapters of ref. [4].
Intensity of phonon-phonon interactions among Debye’s acoustic phonons of the GSM is defined entirely by its model parameter, \( r_1 \): see details in the third section herein and in comments to Figs.1(a), (b) of ref. [6]. In particular, the case of \( r_1 = 2.0 \) corresponds to completely non-interacting phonons, see Fig.1(b) in Ref. [6], while coherent and excited states of QGCE of the GSM yield anharmonic components in the total energy of the ensemble even in such a case. Thus, statistical parameters of the GSM might be linked directly to the specific lattice thermal capacity of (crystalline) solids, evaluated either at their constant volume or constant pressure of an environment; they will be discussed herein in comparison with features of the ‘canonical’ (essentially single-particle) quantum theory [2, 7] and results of appropriate experiments. Key features of this well-known canonical quantum approach are depicted very briefly in the next section.

2. Debye’s Acoustic Phonons and Lattice Thermal Capacity of Solids

Among the most successful (though dated by beginning of 20th century!) approximations of solid-state physics is Debye’s standing acoustic waves (phonons), or plane-wave basis [2]. Those phonons are customarily treated as non-interacting and obeying the linear dispersion: \( \omega_q = c_q \mathbf{q} \), (here \( \omega_q \) stands for the phonon frequency, \( c_q \) is sound velocity and \( \mathbf{q} \) is quasi-wave vector) [2], which is also valid for classical sound waves in solids, liquids and gases. Thus, in contrast to localized harmonic vibrations of (non-interacting) atoms, Debye’s acoustic waves (phonons) are well delocalized and might propagate as far as tens kilometers in bulk (isotropic or anisotropic) crystalline and/or amorphous solids. Therefore, they are signified by well-defined \( q \) quantities, and might be treated either within the dynamic (time-dependent) or static representations [7]. Those acoustic phonons (as well as classical sound waves) might be either longitudinal (when the direction of atomic displacement is parallel to the direction of the wave propagation, defined by the \( \mathbf{q} \) vector) or transverse (when those directions are mutually orthogonal) types. In elemental and binary solids, there are single longitudinal phonon branch, and two transverse ones [2, 7].

The total temperature-dependent lattice energy, \( U(T) \), of an ensemble of non-interacting acoustic phonons confined within a parallelepiped (crystallite) of the ribs lengths of \( L_x, L_y, L_z \) is defined as [2, 7]:

\[
U(T) = 3\nu \int P(h\omega) \frac{h\omega}{\exp(h\omega/k_BT) - 1} \ d \ h\omega ,
\]

(1)

where \( P(h\omega) \) denotes the (single-particle) static spectrum of acoustic phonons, \( \nu = L_x \cdot L_y \cdot L_z \) is volume of the non-homogeneity, \( k_B \) is the Boltzmann’s constant, while \( h \) is the reduced (‘dashed’) Planck’s one. The upper integration limit of Eq.(1) is typically associated with (or closely related to) Debye’s energy, \( k_B\theta_D \), defined eventually by a total number of atomic degrees of freedom per unit volume [2], while for truly bulk (e.g., single-crystalline) solids (i.e., at the \( L_x, L_y, L_z \rightarrow \infty \) limit), the low limit of the integration in Eq.(1) might be taken as zero. However, for polycrystalline and spatially non-homogeneous amorphous solids, the low integration limit in Eq.(1) apparently depends on the (average) sizes of the non-homogeneities [4]:

\[
E_{\min} = \frac{2\hbar c_{\text{eff}}}{\left[(L_x^2 + L_y^2 + L_z^2)/3\right]^{1/2}},
\]

(2)

where \( c_{\text{eff}} \) is an effective sound velocity, defined as follows: \( 1/c_{\text{eff}} = (1/3) \cdot (1/c_1 + 1/c_1 + 1/c_2) \); i.e., based on the single longitudinal, \( c_1 \), and two (generally non-equal!) transverse speed(s) of sounds, \( c_1 \) and \( c_2 \). Those velocities and the effective speed of various solids might be evaluated quantitatively based on (experimentally available) elastic modulus of those solids, and ‘Christoffel Matrix’ formalism (see, for instance, Appendix C in ref. [4] and references therein) for different crystalline orientations (if any) of crystalline or amorphous solids. Obtained via this way \( c_x, c_{11}, c_{12} \) and \( c_{\text{eff}} \) quantities for four specific crystalline orientations of the single-crystalline diamond, silicon, and germanium are listed in the Table 1 below.

It is noteworthy, that the simplified case of cubic crystallites (grains) of \( L = L_x = L_y = L_z \) is customarily analyzed in textbooks [7]. The temperature-dependent specific heat capacity, \( C_v(T) \) (vide infra, expressed in \( J / (m^3 \cdot K) \)), of bulk and polycrystalline metals, semiconductors and insulators, is usually dominated by their lattice thermal capacity [7], which is routinely defined based on Eq.(1) as follows [2, 7]:

\[
C_v(T) = \nu \frac{1}{\nu} \frac{\partial U(T)}{\partial T} = \frac{3}{2k_B(\pi T)^2(hc_{\text{eff}})^3} \int_{E_{\min}}^{k_B\theta_D} \frac{\exp(h\omega / k_BT)}{[\exp(h\omega / k_BT) - 1]^2} \ d \ h\omega .
\]

(3)
Sound velocities evaluated based on the ‘Christoffel Matrix’ formalism for four specific crystalline orientations of the single-crystalline diamond, silicon and germanium. \[\text{Table 1.} \]

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Crystalline orientation</th>
<th>(c_1), m/s</th>
<th>(c_{11}), m/s</th>
<th>(c_{12}), m/s</th>
<th>(c_{\text{eff}}), m/s</th>
</tr>
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<tr>
<td><strong>Diamond</strong></td>
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<td>17496.2</td>
<td>12823.3</td>
<td>12823.3</td>
<td>14076.5</td>
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<tr>
<td></td>
<td>1 1 0</td>
<td>18310.6</td>
<td>11630.9</td>
<td>12823.3</td>
<td>13725.3</td>
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<td>18574.1</td>
<td>12041.5</td>
<td>12041.5</td>
<td>13640.7</td>
</tr>
<tr>
<td></td>
<td>-1 -1 2</td>
<td>18337.5</td>
<td>12000.4</td>
<td>12438.6</td>
<td>13745.2</td>
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<tr>
<td><strong>Silicon</strong></td>
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<td>8430.48</td>
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<td>4671.62</td>
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<td>-1 -1 2</td>
<td>9162.32</td>
<td>5034.25</td>
<td>5479.18</td>
<td>6118.81</td>
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<tr>
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<td>3014.70</td>
<td>3323.49</td>
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</tr>
</tbody>
</table>

Based on the canonical quantum formalism and Eq.(3) above, lattice specific heat capacity of solids is apparently defined by the first derivative of Planck’s (Bose-Einstein) occupation factor with respect to the temperature, \(T\) – since the spectrum of Debye’s acoustic phonons is not affected by the \(T\) quantity. The Eq.(3) replicates convincingly both the low-temperature (~\(T^3\)) and high-temperature (Dulong-Petit [3]) branches of the archetypal \(C_v(T)\) dependencies (see Fig. 1(a) below), though experimental \(C_v(T)\) curves might deviate significantly from aforementioned archetypal behavior for bulk samples of \(\beta\)-boron, diamond, silicon and germanium [8 – 13], especially at elevated temperatures; see also Fig. 1(a) herein.

**FIG. 1(a), (b)** (color online). (a) Experimental temperature dependencies of lattice thermal capacity of bulk germanium (Ge), silicon (Si), \(\beta\)-boron (\(\beta\)-B), and diamond (C), replicated from original tables and plots in refs. [8 – 13]; in the latter cases – using Plot Digitizer 2.6.8 freeware, created by Joseph A. Huwaldt in 2015, see also \(\text{http://plotdigitizer.sourceforge.net}\). Vertical arrows in figure (a) indicate melting temperatures for Ge \((T_{\text{m, Ge}})\) and Si \((T_{\text{m, Si}})\), while inset to this figure exhibits low-temperature parts of \(C_v(T)\) curves and their slopes in log-log scales. (b) The \(C_v(T)\) dependencies for <100>-oriented bulk single-crystalline diamond, silicon and germanium evaluated via numerical integration of Eq.(3) at \(E_{\text{min}} = 0\). Debye’s temperature(s) of those crystals are of 2240 K, 640 K and 374 K, respectively, while corresponding effective sound velocities are listed in the last column of Table 1. Low-temperature \((1K \leq T \leq 10 K)\) log-log slope(s) for all dependencies in figure (b) equal to 3.00000±(8×10)^{-10}. 

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In particular, incremental behavior of experimental $C_p(T)$ curves at elevated temperatures (i.e., well compared to the Debye’s one) is apparently obeyed in Fig. 1(a) for all aforementioned elemental solids. Similar rising $C_p(T)$ dependencies were also reported for the samples of diamond and germanium, studied in refs. [14, 15], respectively. Moreover, the $C_p(T)$ curves recorded for beta-boron ($\beta$-B, the most stable phase of elemental boron at room temperature and atmospheric pressure [8]) and re-plotted in Fig. 1(a) herein, exceeds the Dulong-Petit limit at $T \approx 1200$ K [8], …indicating importance of anharmonicity… [8]. In general, the heat capacity measured at constant pressure, $C_p$, routinely exceeds its counterpart, $C_v$, measured for the same temperature of the given material, but at its constant volume. The (normalized by the $C_v$ quantity) $C_p - C_v$ difference is temperature-dependent: it ranges from ~0.001 to ~0.02 for the diamond [14] and from ~0.01 to ~0.05 for the germanium [15] at elevated temperatures. It is commonly attributed to the substantial impact from the thermal expansion of the crystal, which is, in turn, unambiguously related to the anharmonic (quasiharmonic) components in atomic displacement and the vibrational energy [7, 14, 15]. Though the thermal expansion effect virtually enlarges volume of a crystal and apparently reduces its harmonic thermal energy density while the temperature rises, gain in the total energy of the ensemble from the anharmonic contribution(s) clearly exceeds this effect for vast majority of solids, and routinely yields incremental $C_p(T)$ dependence at aforementioned elevated temperatures, while the $C_v(T)$ curves for the same solid(s) usually saturates in this temperature range in accordance to Dulong-Petit law [3, 7, 14, 15]. For a constant (i.e., temperature-independent) coefficient of the volume thermal expansion, $\alpha_v$, the difference between the $C_p$ and $C_v$ quantities might be approximated as follows [14]:

$$C_p^0 - C_v^0 = V_0 T \alpha_v^2,$$

where $C_p^0$ is a heat capacity of a crystal at a zero pressure, $C_v^0$ is its ‘harmonic’ counterpart, measured at zero temperature, $V_0$ is a ‘molar volume’ of a crystal at $T = 0$, while $B_0$ is its ‘bulk modulus’ [14].

On the other hand, in an apparent similarity with the archetypal Debye’s $C_v(T) \propto T^3$ behavior at $T \ll \theta_0$ (see, for instance, Fig. 1(b)), the low-temperature $C_p(T) \propto T^3$ dependencies emerge for three of four experimental curves, replicated in inset to Fig. 1(a). Indeed, though slope of the $C_p(T)$ dependencies in logarithm-logarithm plots (indicated with dashed strait lines in the inset) fluctuates significantly around exact quantity of 3 (which is, however, replicated in Fig. 1(b) with a high accuracy for $C_v(T)$ dependencies of diamond, silicon and germanium based on the canonical Debye-Planck theory), magnitudes of those fluctuations are apparently affected not only by particularities of the experimental equipment, experimentalists skills, (inevitable) experimental errors occurred during the $C_p(T)$ measurements, but also by errors acquired during the ‘digitization’ of available experimental data. It is noteworthy, that the ‘digitized’ experimental data shown in inset to Fig. 1(a) for the silicon (and partially – for germanium) apparently do not cover the temperature range, corresponding to the archetypal $C_p(T) \propto T^3$ behavior, though – based on appropriately tabulated independent experimental results – it follows very closely to the archetypal $C_v(T) \propto T^3$ function in the temperature range $1 \leq T \leq 10$ K; see, for instance, relevant $C_p(T)$ data provided for Si in Table 4 on p.12 of ref. [16] and Table 4 on p.967 of ref. [17]. Indeed, slope(s) of those low-temperature $C_p(T)$ branches for Si equals to 3.0228±0.01033 based on the data of ref. [16] and to 2.99952±5.916×10^-4 based on the data of ref. [17]; see also figure(s) in the end of the next section.

For comparison, well-known Einstein’s model of specific lattice thermal capacity at a constant volume of solids [1] is essentially based on an assumption on dominant contribution from harmonic atomic vibrations of the same frequency, $\omega_E$, and its analytical expression reads [1]:

$$C_v^E(T) = 3N_A k_B \left( \frac{\hbar \omega_E}{k_B T} \right)^2 \exp(\hbar \omega_E / k_B T) \left[ \exp(\hbar \omega_E / k_B T) - 1 \right]^2,$$

where $N_A$ is number of atoms (independent harmonic oscillators) in the given volume of a solid. In the $T \to 0$ limit, $C_v^E(T) \propto \exp(-\hbar \omega_E / k_B T)$; i.e. it apparently decays much faster with the temperature diminishment than it is observed in experiments for vast majority of solids and predicted by the canonical Debye-Planck theory [2, 7]; see also Fig. 1(b) and inset to Fig. 1(a) above, while general shape of the $C_v^E(T)$ curve(s) is quite similar to the experimental one, shown in the main panel of Fig. 1(a) for the diamond.

In order to evaluate consequences of morphological effects on features of the $C_v(T)$ dependencies for polycrystalline solids, the $E_{\text{min}}$ quantity in Eq.(3) has to be taken as a positive one, and defined based on Eq.(2) for the given sizes of crystallites (grains). The latter equation yields $E_{\text{min}}$ quantities of 0.1164 meV, 0.0538 meV and 0.0324 meV (respectively) for the polycrystalline diamond, silicon and germanium with $L = L_x = L_y = L_z = 1.0 \, \mu m$. In general, the low-energy gap is expected to be opened right below the
mentioned above \(E_{\text{min}}\) energy in the vibrational DOS distributions due to morphological cut-off in the low-energy fundamental phonon states of a polycrystalline material. It might eventually yield in a suppressed lower-temperature lattice thermal capacity of non-homogeneous materials (see fourth section) as compared to their bulk counterparts, where the morphological cut-off absents by definition. However, this gap width becomes well-comparable with the thermal energy, \(k_BT\), of the lattice(s) of 0.08616 meV even at \(T = 1\) K for \(L = L_x = L_y = L_z = 1.0\) \(\mu\)m, which makes \(\Delta\) exponential terms in Eq.(3) to be quite close to unity at \(h\omega = E_{\min}\) and effectively eliminate those morphological cut-off effect(s) in the low-temperature part(s) of the simulated \(C_v(T)\) curves for such a case. In other words, simulated \(C_v(T)\) dependencies for polycrystalline diamond, silicon and germanium at \(L = L_x = L_y = L_z = 1.0\) \(\mu\)m coincide (within the temperature range of \(1\) K \(\leq T \leq 2500\) K) with their counterparts plotted in Fig.1(b) for the aforementioned bulk elemental solids.

A more generic approach for quantitative evaluation on \(C_v(T)\) dependencies of polycrystalline, non-homogeneous amorphous, and low-dimensional solids might be developed based on essentially many-particle GSM formalism [4], which incorporates naturally both the harmonic and anharmonic fractions of the lattice thermal capacity; the latter ones – via taking into account contributions from excited and coherent states of confined (within crystallites, grains and/or non-homogeneities) Debye’s acoustic phonons. The basic features of the GSM and some results of its implementations for quantitative evaluation(s) on the specific lattice heat capacity of three elemental (poly)crystalline solids (two semiconductors and an insulator) are discussed briefly in the next section.

3. Basic Equation of GSM with Static Plane-wave Basis and Lattice Thermal Capacity

The basic equation of (an isotropic version) of the GSM links the probability of appearance of the static mixed states of QGCE to the Boltzmann-Gibbs occupation factor for those states of Debye’s acoustic phonons with the plane-wave-basis, their aggregate energy, \(E_T\), obtained at the given number \(M\) of (generally interacting) phonons, ‘normalizing’ factor, \(\Gamma(M + 1)\), and a ‘partition function’, \(Z_M\) [4]:

\[
W_D(E_T) \cong \exp \left( \frac{-E_T}{k_BT} \right) \int_{M_0}^{M} \frac{1}{\Gamma(M + 1)(Z_M)^{1/2}} \left[ 2\ell_x \ell_y F(\ell_x, \ell_y, \ell_z) \right]^{2M} \left( \frac{\ell_x \ell_y}{M^+1(hc_I^2)} \right)^{M} dM,
\]

where \(W_D(E_T)\) denotes probability density of finding of the ensemble of confined (within a parallelepiped crystallite, column, ‘wire’, etc.) Debye’s acoustic phonons of the given aggregate energy of \(E_T\), \(\Gamma(M + 1)\) is Euler’s Gamma-function [18], \(h\) is the Planck’s constant, \(c_I\) is the longitudinal sound velocity, \(\ell_x\), \(\ell_y\), \(\ell_z\) are lengths of the (orthogonal) ribs of parallelepiped phonon confinement volume, while the dimensionless function \(F(\ell_x, \ell_y, \ell_z)\) depends solely on ratios of the \(\ell_x\), \(\ell_y\) and \(\ell_z\) lengths; see also Eq.(26a) in ref. [4]. Integration in Eq.(6) is carried out over the appropriate range of the (generally rational) number \(M\) of acoustic phonons in the ensemble (this integration range is formally restricted by the \(M_M\) and \(M_0\) limits), while the dimensionless (and rational in general) model parameters \(r_1\) and \(r_2\) are typically varying in the following ranges: \(0.5 \leq r_1 \leq 2; 0.5 \leq r_2 < 1\) [4]. Furthermore, \(M_0 = (E_T/k_BT)^{(1/2)}\), while \(M_{\text{max}} = (E_T/E_{\text{min}})^{(1/2)}\), with a low limit, \(E_{\text{min}}\), of the aggregate energy of the ensemble of acoustic phonons, imposed by presence of morphology (non-homogeneities) in the studied (isotropic but spatially non-homogeneous) polycrystalline and/or columnar amorphous semiconductor (insulator), and defined by Eq.(18B) in ref. [4] (see also Eq.(2) in the previous section) for such a case.

For an ensemble of \(M\) completely non-interacting acoustic phonons (i.e., at \(r_1 \equiv 2\)), the temperature-independent (for this particular case) ‘partition function’, \(Z_M\), for Eq.(6) might be evaluated based on an \(M\)-fold algebraic product(s) of the total number(s) of single-phonon states with the plane wave-basis available for a single Debye’s acoustic phonon, which apparently equals to the volume of the phase space ‘occupied’ by such phonon, and expressed in \(h^4\) units [4]:

\[
Z_M = \left[ \frac{\ell_x \ell_y \ell_z}{3} \left( \frac{k_B \theta_D}{hc_I} \right)^3 \right]^M,
\]

see also Eq.(29a) in the section 2.3 of ref. [4].

Importantly, that the GSM in general and Eqs.(6, 7) in particular comply naturally with Heisenberg’s uncertainty principle. Furthermore, the static plane-wave basis of Debye’s acoustic phonons implemented
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essentially within the GSM framework [4] allows one to use effectively advantages of the Christoffel Matrix formalism (see Appendix C in ref. [4]), and those of conventional global vibrational (and/or electronic) DOS concept(s), simplify considerably final equation(s) of the GSM, incorporate it naturally into conventional framework(s) of the solid state and statistical physics, as well as to take into account naturally the long-range (e.g., coherent, morphological) and anisotropic effects (if any) in polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators [4], while routine implementation of others well-known sets of the basis wave functions (e.g., quantum harmonic oscillator eigenfunctions) might not allow to utilize aforementioned advantages, and eventually might yield in (much) more time- and resource-demanding computations.

Moreover, in order to evaluate statistical features of ensemble of acoustic phonons comprising of excited and coherent states of those phonons, a many-particle counterpart(s) of the fundamental basis set and the conventional (global) single-phonon DOS had been introduced within the GSM framework, and utilized in Eqs.(6, 7) herein; see Eqs.(1D, 2D) in Appendix D in ref. [4]. Though the total number of multi-phonon states available for an ensemble of M acoustic phonons is routinely evaluated based on symmetric tensor product of their single-particle Hilbert spaces [19, 20], the many-particle (though still one-dimensional and single-argument) DOS function is defined in ref. [4] is based on a (finite) Cartesian product of the M single-particle phase spaces, and yields a number of available many-particle states corresponding to the given aggregate energy, $E_T$. That definition becomes viable because of fact that the $E_T$ quantity is routinely expressed as a sum of eigenenergies $h\omega_q$ of M individual (though equivalent) acoustic phonons for an integer M. Thus, the multi-phonon statistics introduced within the GSM framework [4] replicates almost entirely the conventional statistical approach: it comprises the one-dimensional many-particle DOS function, and many-particle Boltzmann-Gibbs occupation factor, which apparently equals to just an appropriate algebraic product of the standard Boltzmann-Gibbs exponential occupation factors for each of M single-particle states. At the same time, this statistical approach apparently remains valid as well for any single phonon of the ensemble: its total number of available global states is defined by just a volume of the single-phonon phase space expressed in $\hbar^3$ units (see section 2.3 and Appendix D in ref. [4] as well as Eq.(7) above), while the Boltzmann-Gibbs occupation factor of the given single-phonon state is defined just by its energy $h\omega_q$ ($E_{\text{min}} \leq h\omega_q \leq k_B T$), and the temperature $T$ of the ensemble. Furthermore, the concept of the global many-particle phonon DOS, introduced within the GSM framework [4], allows one to retain, in principle, even quasi-wave vector(s) $q$ of all individual acoustic phonons of the ensemble, though an aggregate wave vector of aforementioned excited (and even coherent!) states becomes rather ‘ill-defined’ [6].

As it is stated in introductory section, the GSM in general and Eqs.(6, 7) in particular provides transparent physical background for quantitative evaluations on parameters of Urbach (exponential) and ‘power-law’ (‘algebraic’) band tails of electronic DOS within band gap(s) of polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators as well as parameters of those tails of (near-band-gap and sub-gap) optical absorption spectra of aforementioned materials, spectral and temperature dependencies for all such band tails, and even quantitative interrelations among relevant parameters of all aforementioned band tails [4]. It is noteworthy that all aforementioned spectral dependencies and parameters evaluated within the GSM framework become physically meaningful only at $E_T \geq k_B T$.

Furthermore, the plane-wave basis and global phonon DOS concept implemented essentially within the GSM framework, inspires its direct implementation to evaluation on the specific lattice thermal capacities of solids. However, the Eq.(6) requires some additional ‘refinement’ in order to make it suitable for evaluations on key thermal characteristics (e.g., harmonic and anharmonic lattice thermal capacity, thermal conductivity, etc.) of those materials. Indeed, mentioned above thermal characteristics are customarily evaluated based on the ‘single-particle’ spectrum of (fundamental – or pure – states of) harmonic acoustic (Debye’s) phonons with the linear dispersion, while Eq.(6) takes into account as well anharmonic many-particle excited and coherent states of those phonons. This fact is, in particular, reflected in a form of the low integration limit (M0), implemented in Eq.(6), and in the structure of its integrand. At the same time, all these particular forms of the integration limit and the integrand yield in a physically unpersuasive expression for (even excited and coherent) multi-phonon states with an (aggregate) energy not exceeding the Debye’s energy, $k_B T_D$, of those solid. Furthermore, the $c_1$ term in Eq.(6) apparently has to be replaced with the effective sound velocity, $c_{eff}$, defined in the previous section.

On the other hand, in contrast to the dominant theory of the lattice thermal capacity of solids (see, for instance, refs. [2, 7] and previous section for its basic features), which is based entirely on the assumption on involvement of purely harmonic states of Debye’s acoustic phonons, quadratic frequency dependence for their vibrational single-particle DOS, and Planck’s (Bose-Einstein in general) occupation factor(s) for
those phonon states, many-particle *mixed* (and essentially *anhmonic*) excited and *coherent* states of long-wavelength acoustic phonons (with relatively low – as compared to the \(k_B\theta_D\) quantity – energies) might contribute *significantly* as well to the total number of phononic states, and especially – to *anhmonic* fraction of the total lattice thermal capacity and even thermal conductivity of aforementioned solids, especially at elevated temperatures. Moreover, those anharmonic (quasi-harmonic) effects were studied thoroughly for decades in various systems: from thermal expansion coefficient \([14, 21]\) and electron-phonon coupling \([21]\) of solids to *molecular* vibrational spectroscopy \([22]\), where anharmonic vibrations of dipolar (diatomic) molecules routinely yield appearance of ‘overtones’ in vibrational as well as optical excitation / luminescence spectra of those molecular ensembles \([22]\). Aforementioned effects apparently originate from molecular vibrations in an anharmonic potential, which eventually caused by *electrodynamic* interactions among dipole charges (of the same or opposite signs) of neighboring molecules \([22]\).

There are several well-established computational techniques, which are currently in use for quantitative evaluations of effects(s) of anharmonicity in solids. The quasi-harmonic approximation \([23]\) presumes that phonon frequencies are affected by a (temperature-dependent in general) volume of the solid, in apparent similarity with the fundamental idea proposed by E. Grüneisen elsewhere in ref. \([24]\). More sophisticated approaches might be based on first-principles (i.e., embodied in Density Functional Theory, DFT – with plane-wave basis) ‘…calculations of the low-energy portion of the Born-Oppenheimer energy surface defined by the harmonic atomic coordinates, and exploring it to large atomic displacement, where the harmonic approximation is no longer accurate.’ \([21]\) Some others quantitative approaches for evaluations of the anharmonic effects on structural, thermal and electronic characteristics of solids are reviewed very briefly in the introductory part of ref. \([21]\).

The anharmonic contributions to the total thermal capacity of solids might be evaluated as well in a way, which is very similar to the one described in details in ref. \([4]\) (see also references therein) within framework of the GSM, though certain rectifications to its basic equation(s) are apparently required for such a case. In particular, its complete set(s) of states of acoustic phonons with the given aggregate energy, \(E_T\), (let’s assume \(E_{\text{min}} \leq E_T \leq k_B\theta_D\) for a certainty) might comprises of the harmonic *singe-particle* fundamental states (with \(N = 1\)) as well as the anharmonic *many-particle* excited and coherent ones (with \(N > 1\)) of the *same energy*. Since (integer) number of *non-interacting* particles \(N\) in the ensemble in the latter case becomes essentially variable, we have to implement again the quantum grand canonical distribution function with the semiclassical (Boltzmann-Gibbs) statistical ‘weights’ (or those of thermal ‘density matrix’) in order to evaluate probability of appearance of such single- and multi-phonon states:

\[
W_D(E_T, T) \equiv \exp\left(-\frac{E_T}{k_B T}\right) \sum_{N=1}^{N_M} \frac{1}{N! \ Z_N(T)} \left[\frac{2L_x L_y F(L_x, L_y, L_z) E_T^2}{(Nh c_{\text{eff}})^2}\right]^N, \tag{8a}
\]

with \(N_M = \text{Floor}(E_T/E_{\text{min}})\), here function Floor(x) returns an integer part of its rational argument, \(N!\) stands for the factorial of an integer particle number \(N\), while \(c_{\text{eff}}\) denotes effective sound velocity, defined in the *previous section*. Consequently, the lattice thermal energy, \(U_L\), in this case equals to the (weighted) *total energy*, \(E_T\), of the ensemble of *non-interacting* acoustic phonons confined within the parallelepiped (crystalite) of the ribs lengths of \(L_x, L_y, L_z\) and reads:

\[
U_L(T) = 3 \int W_D(E_T, T) E_T \ dE_T, \tag{9}
\]

where factor 3 reflects significant contributions from all 3 acoustic modes in an elemental and/or binary solid. As it was exemplified by Eq.(3) in the *previous section*, the harmonic lattice thermal capacity, \(C_v(T)\), of the solid (evaluated per its unit volume) is ultimately defined by the *partial derivative* of the internal energy \(U_L(T)\) – with respect to the absolute temperature of the solid, \(T\). Similarly, the \(C_p(T)\) quantity might be derived from Eqs.(8a, 9) based on the *first* partial derivative of the Boltzmann-Gibbs distribution function in Eq.(8a) with respect to the absolute temperature of the solid, \(T\):

\[
C_p(T) = \frac{\partial U_L(T)}{\partial T} \propto \frac{\partial \exp\left(-\frac{E_T}{k_B T}\right)}{\partial T} = \frac{E_T}{k_B T^2} \exp\left(-\frac{E_T}{k_B T}\right), \tag{10}
\]
Thus, the temperature-dependent total lattice thermal capacity of a solid, \( C_p^{\text{GSM}}(T) \), evaluated based on the GSM framework, might be eventually expressed as follows:

\[
C_p^{\text{GSM}}(T) = \frac{3 \cdot C_3}{k_B T^2} \int_{E_{\text{min}}}^{k_B T} \exp \left( -\frac{E_T}{k_B T} \right) \sum_{n=1}^{N_M} \frac{E_T^2}{N! Z_N} \left[ \sum_{\text{v}} \frac{2 L_x L_y L_z F\left(L_x, L_y, L_z\right) E_T^2}{(N h c_{\text{eff}})^2} \right]^N dE_T,
\]

where \( C_3 = \left[ (k_B \theta_B)^3 / \nu \right] \times \left( L_x L_y L_z / \left[ 2 \pi^2 (h c_{\text{eff}})^3 \right] \right)^{4/3} \) is a dimensional (measured in eV\(^{-1}\)m\(^3\)) constant.

Some other notations for the latter equation are introduced and explained in comments to Eqs.(6, 7) above. The dimensionless \( N \)-particle ‘partition function’, \( Z_N \), in Eqs.(8a, 11a) might be obtained based on Eq.(7) above with the following replacements: \( c_1 \rightarrow c_{\text{eff}} \), and \( M \rightarrow N \) (for an integer \( M \)).

Figs. 2(a), (b) illustrate temperature behaviors of the purely harmonic and purely anharmonic components of specific lattice thermal capacity, respectively, evaluated based on Eq.(11a) for <100>-oriented polycrystalline diamond, silicon and germanium with the cubical grains of \( L_x = L_y = L_z = 1.0 \mu m \). The purely harmonic component, \( C_{\text{HH}}(T) \) (which routinely defines conventional \( C_v(T) \) quantity), is obtained based on Eq.(11a) using the first term only in its internal sum. In other words, the single-phonon term in Eq.(11a) with a variable phonon energy: \( h \nu = E_T / l \) (\( E_{\text{min}} \leq h \nu \leq k_B \theta_B \)) is used at \( C_{\text{HH}}(T) \) evaluations; this situation formally corresponds to \( N = N_M = 1 \). On the other hand, the purely anharmonic component, \( C_{\text{AH}}(T) \), might also be evaluated based on the same Eq.(11a), but the index of internal summation commences with 2 and tops at \( N_M = \text{Floor}(k_B \theta_B / E_{\text{min}}) \) for such a case. It is noteworthy, that the archetypal \( C_{\text{HH}}(T) \propto T^3 \) behaviors at ‘low-temperature’ ranges in Fig. 2(a) emerge for the Boltzmann-Gibbs occupation factor, utilized within the GSM framework! Thus, the archetypal low-temperature Debye’s \( C_v(T) \propto T^3 \) branch might be replicated convincingly not only based on the canonical Debye-Planck statistics (see Fig. 1(b) herein), but also based on the GSM with the Boltzmann-Gibbs occupation factor: see Fig. 2(a)!

**FIG. 2(a), (b)** (color online). Temperature dependencies of (a) purely ‘harmonic’ and (b) purely ‘anharmonic’ components of the specific lattice thermal capacities for <100>-oriented polycrystalline diamond, silicon and germanium, obtained via numerical integration of Eq.(11a). Low-temperature slopes of those dependencies are quantified directly in the figure(s). The simulation parameters are specified both in the figure(s) and in main text.

On the other hand, only implementation of the canonical Debye-Planck statistics eventually yields ‘saturation’ in \( C_v(T) \) dependencies at (relatively) high temperatures, and replicates appropriately their Dulong-Petit branches [3]), while the GSM with the embedded Boltzmann distribution function apparently yields rapidly declining \( C_{\text{HH}}(T) \) (in Fig. 2(a)) and \( C_{\text{AH}}(T) \) (in Fig. 2(b)) dependencies. Those declining branches are replicated persistently at all our simulations regardless to the size(s) of the cubical crystallites (grains) and \( E_{\text{min}} \) quantity for the polycrystalline diamond, silicon and germanium (respectively). Such declining behaviour directly contradicts to the well-established experimental data.

It is noteworthy as well that slope(s) of the low-temperature branches of \( C_{\text{AH}}(T) \) dependencies become very close to 5 for all elemental crystals, represented in Fig. 2(b). Though such slope does not have any reliable direct experimental counterpart(s) for the bulk solids so far, it might be verified unambiguously...
via a comparative analysis of the available experimental and simulated \( C_p(T) \) and \( C_v(T) \) dependencies, see some examples presented below in this section.

In order to understand better the physical origins behind aforementioned similarities and differences in behaviour of aforementioned simulated and experimental dependencies, let us compare essential features of the canonical Debye-Planck approximation and of GSM one. First of all, the single-particle vibrational static DOS of Debye’s model [2] and that one of the GSM are completely identical for an isotropic case (to which the <100>-oriented elemental crystals provided the best approximation among all others crystalline orientations of such solids [4]), while – as it has been already mentioned above – difference among those models in such a case has to be attributed mainly to dissimilar occupation factors of those fundamental phonon states. At the same time, it is well-known fact [7], that the quantum Planck’s (and Bose-Einstein in general) occupation factor of the canonical Debye-Planck model and its Gibbs-Boltzmann counterpart of the GSM formally coincide for high-energy fundamental phonon states (i.e., for those states with \( \hbar \omega >> k_B T \)). This implies directly that the astonishing quantitative agreement among slopes of low-temperature branches of \( C_v(T) \) and \( C_H(T) \) dependencies plotted in Figs. 1(b), 2(a) (respectively) originate indeed from the identical features of both entirely harmonic vibrational DOS functions of Debye-Planck and GSM models (at \( N = M = 1 \) for the latter case), as well as their common semiclassical occupation factors for high-energy fundamental phonon states. It is noteworthy, that low-temperature features of various excitations in atomic and electronic sub-systems of solids are customarily attributed to entirely quantum effects [7], while their high-temperature counterparts tend to be interpreted as manifestation of classical phenomena or to behaviour of really quantum system in its so-called ‘classical limit’. In this context, remarkable quantitative coincidence in slopes of the low-temperature branches of the \( C_v(T) \) and \( C_H(T) \) dependencies plotted in Figs. 1(b), 2(a) (respectively) still remains surprising – to some extent.

Dissimilar behaviours of high-temperature branches of \( C_v(T) \) and \( C_H(T) \) curves in Figs. 1(b) and 2(a) (respectively) caused by significant differences among the Planck’s and Boltzmann’s occupation factors for the entire single-particle fundamental phonon states (especially for low-energy ones!) of the bulk and polycrystalline semiconductors and insulators at elevated temperatures. In particular, at such temperatures, the former occupation factor enlarges with the temperature as \( \sim T^2 \) (and compensates completely the \( T^2 \) prefactor of the integral in Eq.(3) above), while the semiclassical Boltzmann-Gibbs occupation factor enlarges linearly with the temperature in this range, and becomes ‘overweighed’ by the \( T^2 \) prefactor of the exponential term in Eq.(9) at relatively high temperatures. In addition, the Planck’s occupation factor well exceeds unity for majority of fundamental states of Debye’s acoustic phonons at elevated temperatures: canonical quantum statistics allows an arbitrary non-negative occupation factors for such phonon states.

General shape(s) of the \( C_H(T) \) and \( C_{AH}(T) \) curves plotted in Figs. 2(a), (b) exhibit apparent similarities with those corresponding to so-called ‘Schottky anomaly’\(^1\): a feature of a temperature-dependent specific heat capacity [25] observed routinely for so-called ‘two-level’ system(s). On the other hand, typical \( C_p(T) \) curve corresponding to the ‘Schottky anomaly’ rises with temperature as \( \sim T^2 \) before reaching its peak [25], while \( C_H(T) \propto T^3 \) are observed for all low-temperature branches of the curves plotted in Fig. 2(a), and \( C_{AH}(T) \propto T^5 \) are obeyed for low-temperature parts of the functions shown in Fig. 2(b). In addition, decay in the \( C_p(T) \) dependence corresponding to the ‘Schottky anomaly’ also usually occurs much faster than decays of \( C_H(T) \) and \( C_{AH}(T) \) curves, exhibited in Figs. 2(a), (b). Thus, aforementioned similarities in the shapes of curves plotted in Figs. 2(a), (b) and those curves corresponding to the ‘Schottky anomaly’ become rather formal, and do not reflect any common physical background(s) among them.

Based on Eqs.(26a, b) from ref.[4], for a rational \( M \) quantity, the probability of occupation of a (multi-phonon in general) level of the energy \( E_T \) (within the range of \( E_{\text{min}} \leq E_T \leq \hbar \Theta_B \)) reads:

\[
W_D(E_T) \equiv \exp \left(- \frac{E_T}{k_B T} \right)^{M} \int \frac{1}{\Gamma(M + 1) Z_M} \left[ \frac{2L_x L_y F(L_x, L_y, L_z) E_T^2}{(M \hbar c_{\text{eff}})^2} \right]^M dM,
\]

with \( M_M = (E_T / E_{\text{min}}) \) at \( r1 = 2 \) and \( r2 = 1 \). Thus, the counterpart of Eq.(11a) now reads:

\[
C_p(T) = \frac{3C_v}{k_B T^2} \int_{E_{\text{min}}}^{k_B T^2} \exp \left(- \frac{E_T}{k_B T} \right)^{M} \int \frac{E_T^2}{\Gamma(M + 1) Z_M} \left[ \frac{2L_x L_y F(L_x, L_y, L_z) E_T^2}{(M \hbar c_{\text{eff}})^2} \right]^M dM dE_T,
\]

\(^1\) This phenomenon was named after Walter Hermann Schottky (1886 – 1976), who had reported it in 1922 [25].
where the $Z_M$ quantity is expressed by Eq.(7). Thus, Eqs.(8b, 11b) entirely coincide with Eqs.(8a, 11a) ones (respectively) at $M = N$; i.e., for the rigorously integer number of acoustic phonons in the ensemble. The simulation results obtained based on Eqs.(8b, 11b) for the C, Si and Ge (but not revealed herein) are quite similar to those plotted in Figs. 2(a), (b), though the low-temperature log-log slope for the simulated $C_H(T)$ dependencies becomes close to $\pi$ (with accuracy of $3.14 \pm 0.014 \pm 3$. Though this slope seems to be even more ‘scientific’ than the archetypal one, $C_v(T) \propto T^3$, its considerable ($\sim 4.7\%$) deviation from that of the archetypal Debye’s dependence and apparent lack of reliable experimental support for such slope(s) makes the data obtained based on the two latter equations to be much less meaningful as compared to those, evaluated based on Eqs.(8a, 11a). Therefore, features of the $C_H(T)$ and $C_AH(T)$ dependencies, obtained based on Eqs.(8b, 11b) are not discussed any further in this article.

Thus, the ‘rectified’ Eqs.(8a – 11b) approximate (though with different precisions) the low-temperature $C_v(T) \propto T^3$ and/or $C_p(T) \propto T^1$ branches of the archetypal Debye’s temperature dependencies of the lattice thermal capacities for polycrystalline diamond, silicon, and germanium, while apparently fail to replicate the Dupont-Petit regime(s) even for the $C_v(T)$ curves. In order to ensure the GSM applicability for appropriate simulations on the high-temperature branches of the aforementioned $C_v(T)$ and/or $C_p(T)$ dependencies, the semiclassical Boltzmann-Gibbs occupation factor of the GSM has to be replaced – following the well-known Debye’s idea – with its fully quantum Planck’s counterpart. In principle, it might be fulfilled via ‘standard’ expansion of the exponential term(s) in Eqs.(8a, 11a) over all allowed single-phonon energies $\hbar \omega$ (which yield the given $E_i$ quantity), and consecutive differentiation of such expansion with respect to the temperature. However, herein we will not follow those well-known procedures step-by-step. Instead, below we just will use straightforwardly the following corrected counterpart of Eq.(11a):

$$C_p^{GSM}(T) = \frac{3C_3}{K_B T^2} \int_{k_B T}^{k_B \beta_B} \left[ \exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2 \frac{(h \omega)^2}{N! Z_N} \left[ \frac{2L_x L_y F(L_x, L_y, L_z)(\hbar \omega)^2}{(N h c_{eff})^2} \right] d\hbar \omega. \quad (11c)$$

The temperature dependencies of the corrected harmonic, $C_{HC}(T)$, (i.e., obtained at $N = 1$) and anharmonic, $C_{AHC}(T)$, ($2 \leq N \leq \text{Floor}(k_B \beta_B/E_{\text{min}})$) components of the $C_p^{GSM}(T)$ function simulated for polycrystalline diamond, silicon and germanium based on Eq.(11c) are revealed in Figs. 3(a), (b) below.

**FIG.3** (a), (b) (color online). The temperature-dependent contributions to the specific lattice heat capacities of the $<100>$-oriented polycrystalline diamond, silicon and germanium from (a) harmonic and (b) anharmonic components of $C_p^{GSM}(T)$ quantities evaluated based on Eq.(11c). Double – logarithmic slopes for every curve in both figures are evaluated via standard least-square-fit procedure(s) within the temperature range of $1 \text{K} \leq T \leq 10 \text{K}$ and indicated directly at the appropriate curve(s). See also main text for more simulation parameters and other details.
As it is seen from latter figure(s), every $C_{\text{HC}}(T)$ and/or $C_{\text{AHC}}(T)$ dependence shown therein saturates at elevated temperatures, in contrast to the declining behavior of high-temperature branches of the $C_{\text{H}}(T)$ and $C_{\text{AH}}(T)$ curves plotted in Figs. 2(a), (b). At the same time, low temperature log-log slopes of the $C_{\text{HC}}(T)$ curves in Fig. 3(a) are yet fairly close to 3, in good quantitative agreement with the archetypal $C_{\text{H}}(T) \propto T^3$ branches for this temperature range and features of the $C_{\text{H}}(T)$ curves plotted in Fig. 2(a). Similarly, low-temperature log-log slopes of the $C_{\text{AH}}(T)$ curves in Fig. 3(b) are in good quantitative agreement with such slopes for the $C_{\text{AH}}(T)$ curves in Fig. 2(b), and fairly close to 5, since those slopes are apparently dominated by behavior of the first anharmonic terms in Eqs. (11a, c), corresponding to the N = 2 in those equations.

At the same time, the combination of the $C_1$ pre-factor and aforementioned $Z_N$ and $(hc)^3$ terms in Eqs. (11a, c, d) apparently yields the appropriate dimension [$J / (m^3 \text{K})$] of the harmonic specific heat capacity in the right-hand sides of those equations, and makes its quantity to be entirely independent on the sizes and volumes of the cubical crystallites (grains). It is easy to verify, that in such a case the anharmonic fraction(s) of the specific heat capacity, defined by Eqs. (11a, c, d) at $2 \leq N \leq \text{Floor}(k_0 \theta_B/E_{\text{min}})$ is measured in $[J / (m^3 \text{K})]$ as well, though in contrast to the harmonic fraction – it becomes grain-size-dependent in general (see also illustrations and extended discussions on this issue in the next section).

Thus, Eqs. (11a, c, d) provide appropriate physical dimensions and comply naturally with the common physical sense(s) of both harmonic and anharmonic specific lattice thermal capacities of polycrystalline materials and powders for the case of cubical crystallite (grains) with different sizes (rib lengths), though some (relatively small) variations of even the harmonic specific lattice heat capacity might be expected for the parallelepipidal grains with non-equal lengths $L_x$, $L_y$, $L_z$ of the orthogonal ribs at alterations in the $L_x$, $L_y$, $L_z$ quantities. However, such effects will not be discussed herein in details.

It is noteworthy as well, that the fraction of the total specific heat capacity originated from the ‘anharmonic’ contribution and evaluated based on Eq. (11a) is relatively small: highest $C_{\text{HC}}(T) / C_{\text{H}}(T)$ ratios are obtained at $T \sim 2500 \text{K}$ and equal to 2.436·10^{-4}, 4.061·10^{-4}, and 4.198·10^{-4} for the diamond, silicon, and germanium (respectively) while those fractions become even smaller at low temperature and vary in the range from $-2.15·10^{-9}$ to $-1.27·10^{-7}$ at $T = 1 \text{K}$ for the elemental crystalline solids represented in Figs. 2(a), (b). Similarly, the high-temperature ($T \sim 2500 \text{K}$) $C_{\text{HC}}(T)/C_{\text{H}}(T)$ ratios for the curves shown in Figs. 3(a), (b) are of 3.265·10^{-4}, 3.721·10^{-4}, and 3.839·10^{-4} for the diamond, silicon and germanium, respectively, while their low-temperature ($T = 1 \text{K}$) fractions are of 2.822·10^{-9}, 4.285·10^{-9}, and 1.291·10^{-7} (respectively) for those polycrystalline solids. In other words, the anharmonic fraction in the total specific heat capacity, evaluated based on Eqs. (8a – 11d) are customarily couple orders of the magnitude smaller than such fraction(s) in $C_p(T)$ dependencies, obtained experimentally for real crystalline [14, 15] and amorphous solids: see, for instance, Fig. 1(a) in the previous section and discussion on it therein.

Therefore, certain correction(s) to Eqs. (8a – 11d) are still apparently required in order to make the GSM to be relevant for such evaluations. In particular, in order to increase contribution from the anharmonic terms to the total specific heat capacity of solids evaluated based on the GSM, we may consider expansion(s) of Eqs. (8a – 11d) deep into the $E_r > k_0 \theta_B$ range. In this energy range, fundamental states of Debye’s acoustic phonons simply do not exist (by definition); thus, all states of those acoustic phonons with $E_r > k_0 \theta_B$ become either excited or coherent; i.e., essentially anharmonic. In principle, such expansion(s) might be fulfilled based on Eq. (6) – since, in general, this equation valids at $E_r > k_0 \theta_B$ [4] – though alternative (and more prolific) ways of aforementioned corrections might be deliberated as well.

For instance, the following two identities, tabulated in ref. [18] (i.e., on p.262, Eq.6.5.10 as well as on p.228, Eqs.5.1.5 & 5.1.8 therein):

$$\alpha_n(z) = \int_1^\infty t^n \exp(-zt) dt = z^{-n-1} \Gamma(1 + n, z), \quad (12a)$$

$$\alpha_n(z) = \int_1^\infty t^n \exp(-zt) dt = \frac{n!}{z^{n+1}} \exp(-z) \left(1 + z + \frac{z^2}{2!} + \cdots + \frac{z^n}{n!}\right), \quad (12b)$$

might be utilized for the aforementioned purpose; here $\alpha_n(z)$ is a function related both to the ‘exponential integral’ (Eq.(12b)) and Euler’s gamma-function (Eq.(12a)) [18], while $\Gamma(1+n, z)$ stands for so-called ‘incomplete gamma-function’ [18]. At $t^2 = (E_r / E_{\text{min}})^2$, $n = 2N + 2$, $t^N = [(E_r / E_{\text{min}})^2 / N^4]^N$, and $z = (E_{\text{min}} / k_0 T)$, the Eq. (11a) might be expanded further based on the following identity:
\[ \alpha_{2(N+1)} \left( \frac{E_{\text{min}}}{k_B T} \right) = E_{\text{min}} \frac{E_{\text{min}}^{2(N+1)}}{N! N^{2N}} \int_{1}^{\infty} E_T^{2(N+1)} \frac{E_T}{k_B T} \exp \left( -E_T \frac{k_B T}{E_{\text{min}}} \right) d \left( \frac{E_T}{k_B T} \right). \]  

(13)

The latter form, in particular, comprises of the first integrand term, \( E_T^2 \), in Eq.(11a), and normalized (by the \( E_{\text{min}} \) quantity in this particular case) \( E_T \) energies. Now, based on the right-hand sides of Eqs.(12a, 13) above, the corrected (for the anharmonic contributions only!) counterpart of Eq.(11a) might be symbolized as follows:

\[ C_{\text{AH}}^*(T) = \frac{3C_3}{k_B T^2} \sum_{2}^{N_M} \alpha_{2(N+1)} \left( \frac{E_{\text{min}}}{k_B T} \right) = \frac{3C_3}{k_B T^2} \sum_{2}^{N_M} N^3 \left\{ \frac{2 \mathcal{L}_x \mathcal{L}_y \mathcal{L}_z}{h c_{\text{eff}}} \right\}^N \left( \frac{k_B T}{N} \right)^{2N^3 + 3} \Gamma \left( 2N + 3, \frac{E_{\text{min}}}{k_B T} \right). \]  

(14)

Indeed, formal extension of the upper integration range in Eqs.(12 – 14) up to infinity, i.e., well beyond its original quantity of \( E_T = k_B T \) stated in Eq.(11a), considerably amplifies anharmonic (i.e., evaluated at \( 2 \leq N \leq \text{Floor}(E_T/E_{\text{min}}) \)) contributions to a \( C_{\text{p}}^*(T) \) function as compared to its \( C_{\text{p}}(T) \) counterpart, simulated based on Eq.(11a). It is noteworthy, that the corrected anharmonic capacity defined by Eq.(14) might be evaluated for the Boltzmann-Gibbs distribution function only! The anharmonic component, \( C_{\text{AH}}^*(T) \), of the simulated \( C_{\text{p}}^*(T) \) dependencies obtained (at \( \mathcal{L}_x = \mathcal{L}_y = \mathcal{L}_z = 1.0 \mu \text{m} \) and \( N_M = \text{Floor}(E_T/E_{\text{min}}) \)) via numerical integration of Eq.(14) exhibits physically unrealistic \( C_{\text{AH}}^*(T) \propto T^{-3} \) behavior(s) for the polycrystalline diamond, silicon and germanium within the whole studied temperature range of \( 1 K \leq T \leq 2500 K \); i.e., without ‘saturation’, typical for \( C_{\text{p}}(T) \) curves in the Dulong-Petit regime. Such behavior is apparently caused by the excessive anharmonic contributions from the excited and coherent states of the GSM with the energies well exceeding the Debye’s one, \( k_B T_0 \). In contrast, the Dulong-Petit regime of \( C_{\text{p}}(T) \) curves at elevated temperatures within framework of the canonical Debye-Planck approach emerges predominantly from the contributions caused by relatively low-energy and entirely fundamental states, routinely occupied, however, with more than one particles.

In order to obtain more relevant \( C_{\text{AH}}^*(T) \) approximations, the following additional correction (tuning) of the model might be implemented. In particular, instead of Eq.(14) above, we may introduce a (pair-wise for every given integer \( N \)) difference of two weighted Euler’s gamma-functions: both of them would be expressed based on Eq.(12b) above, but with the \( E_{\text{min}} \) normalizing energy for the first term of the given pair, and with the \( k_B T_0 \) normalizing energy for the second one. Thus, on the appropriately normalized right-hand-side of Eq.(12b), a counterpart of Eq.(13) now reads:

\[ \alpha_{2(N+1)} \left( \frac{k_B T}{k_B T} \right) = k_B T \frac{(k_B T_0)^{2(N+1)}}{N! N^{2N}} \int_{1}^{\infty} E_T^{2(N+1)} \frac{E_T}{k_B T} \exp \left( -E_T \frac{k_B T}{k_B T_0} \right) d \left( \frac{E_T}{k_B T} \right) = \]  

\[ N^3 \left\{ \frac{2(N+1)}{k_B T} \right\}^{2N^3 + 3} \exp \left( -\frac{k_B T}{k_B T_0} + \frac{(k_B T)^2}{2! (k_B T_0)^2} + \cdots \right) \left( \frac{k_B T_0}{k_B T} \right)^{2(N+1)} \left( \frac{k_B T_0}{k_B T} \right)^{2(N+1)} \Gamma \left( 2N + 3, \frac{k_B T_0}{k_B T} \right). \]  

(15)

The right-hand-sides of Eqs.(12a, b) as well as their counterparts in Eqs.(13, 15) are completely identical when the number of terms of polynomial expansion in the last brackets of the right-hand side of Eq.(12b) equals exactly to \( n \) (or to \( 2N + 2 \) within the similar brackets of Eq.(15)). In such a case, all contributions to the anharmonic phonon states with \( E_T > k_B T_0 \) would be eliminated completely. In fact, such additional correction(s) effectively reduce Eqs.(14, 15) still the Eqs.(8a, 11a) ones, though – again – at the expense of rapidly descending high-temperature branches of the \( C_{\text{AH}}^*(T) \) curves, which are – even after all those additional corrections – coinciding completely with the (respective) \( C_{\text{AH}}(T) \) dependencies, plotted in Fig. 2(b) above.

If, however, these polynomial expansion(s) are truncated (e.g., some of the ‘right-hand-side’ (or ‘higher-order’) terms within the last brackets of Eqs.(12b, 15) are omitted), then the total number of the polynomial terms becomes lesser than \( n \) (or than \( 2N + 2 \)). Due to this truncation, right-hand sides of Eqs.(12a, b) as well as those of Eqs.(14, 15) apparently become not ‘balanced’ anymore even at the same integration range over \( t \) (i.e., at \( E_{\text{min}} = k_B T_0 \)), and the pair-wise differences among them emerge in those additional (though weighted) ‘higher-order’ (‘high-energy’) uncompensated correction terms, which eventually provide an additional anharmonic contribution to the Eq.(14). This strategy becomes viable in our case, and eventually yields the following form for an ‘improved’ Eq.(14):
\[ C_{AH}^{**}(T) = C_{AH}(T) - \frac{3C_3}{k_B T^2} \sum_{j=1}^{N/3} \left(2(N+1)!! \right)^2 \times \left( \frac{N^3}{N! Z_N} \left[ \frac{2\mathcal{E}_x \mathcal{E}_y \mathcal{F}(\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)}{(h \, \text{c}_{\text{eff}})^2} \right]^N \times \left( \frac{k_B T}{N} \right)^{2N+3} \right) \times \exp \left( - \frac{k_B \theta_D}{k_B T} \right) \left\{ 1 + \frac{k_B \theta_D}{k_B T} + \frac{(k_B \theta_D)^2}{2! (k_B T)^2} + \cdots + \frac{(k_B \theta_D)^{2(Q+1)}}{[2(Q+1)]! (k_B T)^{2(Q+1)}} \right\}, \] (16)

where the \( C_{AH}^{**}(T) \) function is symbolized by Eq.(14), and \( Q \leq (2N + 2) \). In general, the \( Q \) quantity apparently varies with \( N \): the higher \( Q \) is generally expected for the greater \( N \) quantities, when number of omitted high-order terms is fixed. This might create certain difficulties for the expansion terms in Eq.(16) corresponding to relatively low \( N \) quantities (e.g., at \( N = 2, 3, 4 \ldots \)); truncation of the polynomial expansion in such a case might affect the low-order ("core") polynomial terms – but not merely eliminate the high-order ones. Therefore, at practical simulations, it is more meaningful and convenient to use the polynomial approximation with a fixed number of terms for any integer (and generally variable) \( N \):

\[ 1 + \frac{\theta_D}{T} + \frac{\theta_D^2}{2!T^2} + 1.005 \frac{\theta_D^3}{3!T^3} + 0.25 \left( \frac{\theta_D^4}{4!T^4} + \frac{\theta_D^5}{5!T^5} + \frac{\theta_D^6}{6!T^6} + \frac{\theta_D^7}{7!T^7} \right). \] (17)

Though the latter polynomial expansion comprises of the fixed number (seven in this particular case) of the temperature-dependent terms, in order to fit experimental \( C_p(T) \) and \( C_{AH}(T) \) dependencies for different elemental solids, weights at major of its polynomial terms might be changed to a rational one – as compared to their entirely integer counterparts in Eqs.(12b, 15, 16). Those rational weights apparently allow additional fitting ‘degrees of freedom’ ('flexibility') for the \( C_{AH}^{**}(T) \) function(s). Again, it is worthy to highlight, that Eqs.(12b, 15, 16) define corrected anharmonic contribution to the specific lattice thermal capacity of the polycrystalline and spatially non-homogeneous amorphous solids based on the semi-classical Boltzmann-Gibbs distribution function only, imbedded into original version(s) of the GSM [4].

The (normalized) \( C_{AH}^{**}(T) \) dependencies, simulated based on the Eqs.(16, 17) are revealed in Fig. 4(b) below, while Fig. 4(a) compares corresponding simulated \( C_{H}(T) + C_{AH}(T) \) and experimental \( C_p(T) \) data.

**FIG.4 (a), (b)** (color online). (a) The \( C_{AH}^{**}(T) + C_p(T) \) and \( C_{H}(T) \) as well as (b) \( C_{AH}^{**}(T) / C_{H}(T) \) dependencies (curves) simulated using Eqs.(11c, 16, 17) for <100>-oriented polycrystalline diamond, silicon and germanium with equal cubic crystallites of the sizes of \( L = L_x = L_y = L_z = 1.0 \mu m \). The experimental \( C_p(T) \) data (symbols) in figure (a) are obtained for bulk materials, and replicated from appropriate data in refs.[9, 11 - 13, 16, 17]; see also Fig.1(a) above. Inset to figure (a) exhibits low-temperature parts of the simulated and experimental \( C_p(T) \) functions, plotted in log-log scales; slopes of linear fragments of the simulated \( C_p(T) \) dependencies are indicated directly within the inset. (b) The \( C_{AH}^{**}(T) / C_{H}(T) \) ratios (curves) simulated for the aforementioned <100>-oriented elemental (polycrystalline solids with their low-temperature slopes indicated directly at the curves), plotted against their experimental counterparts (symbols), picked up using the Plot Digitizer 2.6.8 freeware from appropriate plots provided in refs. [14, 26]. The effective sound velocities and Debye’s temperatures implemented at all these simulations are assumed to be exactly the same as their counterparts for appropriate bulk semiconductors (see details in the previous section).
As it seen from Fig. 4(a), the \( C_p(T) \) approximations (obtained for all cases based on the same Eqs. (11c, 16, 17) as well as at the fixed \( L = L_x = L_y = 1.0 \mu \text{m} \) and \( N_M^* = N_x^* = 75 \) quantities for the former two equations) reproduce general trends for their experimental \( C_p(T) \) counterparts reported for the bulk diamond, silicon and germanium, though exhibit significant deviations from \( C_p(T) \) curves at relatively high temperatures (especially at those exceeding the melting ones of the Si and Ge, indicated in this figure with the green and red vertical arrows, respectively). Those high-temperature phenomena apparently have to be attributed to the additional physical effects (e.g., diffusional motions of atoms in the liquid phases of those elemental semiconductors), which amend considerably temperature dependencies of their heat capacity above the melting temperatures of those materials, but not included into the GSM framework. Furthermore, significant discrepancies of the simulated (colored curves) and experimental (symbols) dependencies in Fig. 4(a) emerge even within intermediate (0.045 \( \leq T/\theta_0 \leq 0.45 \)) temperature ranges. Those discrepancies are routinely ascribed to contribution(s) to the lattice heat capacity from the prominent and broad peaks in appropriate vibrational DOS of the real crystalline diamond, silicon and germanium, centered at around \( \omega/2\pi \approx 2.8 \text{ THz} \) for Ge, \(-4.0 \text{ THz} \) for Si and \(-21.0 \text{ THz} \) for the diamond [27]. In fact, aforementioned prominent DOS peaks originate from saturation of dispersion curves corresponding to transverse acoustic (TA) phonon branches in vicinity of the edges of appropriate phonon Brillouin Zone(s) of those crystalline semiconductors. In other words, the mid-temperature discrepancies among the experimental and simulated \( C_p(T) \) plots in Fig. 4(a) eventually originate from significant deviation of dispersion dependencies of TA phonon branches for the aforementioned real elemental semiconductors from the simplified linear classical (Debye’s) dispersion. Furthermore, similar prominent peak(s) of the vibrational DOS emerge even in amorphous states [28] of those solid elemental semiconductors, where both quasi-wave-vectors and dispersion relations of acoustic phonons are not even really well-defined! On the other hand, both simulated (with the corrections!) and experimental \( C_p(T) \) dependencies obey the archetypal Debye’s \( C_p(T) \propto T^3 \) behavior for all aforementioned elemental solids at low temperatures: see inset to Fig. 4(a).

Furthermore, as it seen from Fig. 4(b), the refined, corrected and expanded equations of the isotropic version of the GSM (expressed by Eqs. (11c, 16, 17) above) replicate reasonably well the experimental \( [C_p(T) - C_v(T)] / C_v(T) \) data reported for the crystalline diamond and silicon in refs. [14, 26] (respectively) without any further adjustment. Moreover, the low-temperature log-log slopes for all dependencies shown in Fig 4(b) are very close to 2, well in line with an expectation based on the difference(s) of appropriate low-temperature slopes, indicated, for instance, at the curves in Figs. 3(b) and 3(a), respectively. However, similar (though relatively high-temperature) data reported in Fig. 2(b) of the ref. [15] for the crystalline germanium (but not replicated in Fig. 4(b) herein) exhibit a much smaller, \([C_p(T) - C_v(T)] / C_v(T) \propto T \), enlargement with the temperature, as compared to its counterparts for the diamond and silicon. Though such behavior is not really contradictory to the approach symbolized by Eqs. (11c, 16, 17) above, and even might be explained readily by different temperature dependencies of the simulated \( C_v(T) \) curves for the aforementioned elemental solids, caused by significant inequalities in their Debye’s temperature(s) and the effective sound velocities, some additional adjustment(s) of the rational coefficients of Eq. (17) might be required in order to replicate convincingly that experimental dependence for the case of germanium.

In principle, the GSM framework allows one to take into account effect(s) of crystalline anisotropy on features of the specific heat capacity of polycrystalline solids. Indeed, since transverse and longitudinal sound velocities (speeds of Debye’s phonons propagation) for such solids are affected significantly by their crystalline orientation(s) (see, for instance, three last columns of Table 1 in the previous section), spectral dependencies of the probabilities of both single-phonon fundamental (harmonic) and multi-phonon (anharmonic) states are also generally expected to be affected by the crystalline orientation; quantitatively such effects for the latter case might be evaluated based on an anisotropic version of the GSM equations; see, for instance, Eq. (26b) in the second chapter of ref. [4]. On the other hand, specific thermal capacity of even crystalline solids is routinely evaluated based on their effective sound velocities [7] (see also Eqs. (11a, b, 14, 16) herein), which are far more isotropic by definition: they vary in the range of just \( \sim 3\% \) for the diamond and just of \( \sim 9\% \) for the (poly)crystalline silicon and germanium at their different orientations; see the last column of the Table 1. More importantly, as it is highlighted above in this page, both canonical Debye-Planck model and the GSM one do not take into account actual features of phonon DOS even for the elemental crystals and their real phonon dispersions for relatively large wavevectors. All these make predictions of the GSM on anisotropic effects related to the crystalline orientations on features of specific heat capacity of (poly)crystalline solids to become rather indicative, than actually meaningful for such real solids. Therefore, those anisotropic effects are not discussed herein anymore.

Instead, implementation of the GSM to analysis of \( C_p(T) \) dependencies of low-dimensional semiconductors and insulators will be deliberated to some extent in the next section of this article.

Thermal capacity of various nano-structured and low-dimensional materials (metallic, semiconducting and insulating nano-wires, quantum dots, single-atomic-layer materials etc.) becomes very attractive research topic in recent decades alongside with intense studies on optical electrical, photoelectrical and magnetic properties of those materials [29], mainly due to their exceptional physical characteristics and enormous practical importance in mechanical, electronic and chemical applications, as well as for healthcare and renewable energy sectors. In particular, aforementioned materials are customarily characterized by significantly enhanced specific thermal capacitance [30, 31] in a wide temperature range as compared to that of their bulk counterparts as well as by uncommon behavior of the low-temperature \( C_\text{p}(T) \) and \( C_\text{p}(T) \) branches, which routinely deviate from the archetypal Debye’s dependence (i.e., from the \( C_\text{p}(T) \times T^3 \) one) [32–34], persistently reported (and discussed briefly in the two preceding sections of this article) for the bulk and polycrystalline insulators, semiconductors and even metals.

More specifically, the low-temperature (especially at \( T < 2 \) K) behavior of the specific thermal capacity of phosphorous-doped nano-crystalline silicon nanopowder(s) deviates significantly from the archetypal Debye’s dependence, \( C_\text{p}(T) \times T^3 \), though this deviation had been attributed to significant contributions to the \( C_\text{p}(T) \) quantities from the electronic component of those doped nanoparticles [34]. In general, the low-temperature specific lattice thermal capacitance obtained at a constant pressure is expected to follow the \( C_\text{p}(T) \times T^{d\text{dp}} \) ‘tend’, where \( d \) is (an integer) dimensionality of the system, while (the integer) factor \( p \) characterizes enlargement in phonon DOS with the phonon energy \( \hbar \omega \; (\text{h} \; \text{K}) \).

Thus, the \( C_\text{p}(T) \times T^2 \) is generally expected for the layered graphite and graphene with linear increment in the vibrational DOS with the energy (i.e., at \( d = 2 \) and \( p = 1 \), though – in the latter case – those expectations are usually not fulfilled [33] – due to dominant contribution from so-called ‘flexural’ ZA mode. The \( C_\text{p}(T) \times T^{1.6} \) was reported at experimental investigations of silicon nanowire (SiNW, with \( d = 1 \), \( p = 2 \)) [35]; (diameter(s) of those SiNWs were of 22 and 37 nm. Based on results of molecular dynamic simulations, reported elsewhere in ref. [36], the low-temperature lattice specific thermal capacity of SiNWs with different cross-sections (comprising of 4 and 7 atomic ‘layers’) follows conventional Debye’s dependence \( C_\text{p}(T) \times T^3 \), though magnitude of the \( C_\text{p}(T) \) quantities for those SiNWs is enhanced by \( \approx 5-7 \% \) as compared to those of the bulk silicon [36]. Similarly, the low-temperature specific thermal capacity of SiC ‘microwires’ with diameter ranged from 9.0 \( \mu \text{m} \) to 34.0 \( \mu \text{m} \) and lengths of 1.06 mm to 1.495 mm, follows the archetypal \( C_\text{p}(T) \times T^3 \) dependence in the temperature range 20 K \( \leq T \leq 50 \) K [37].

Below in this section, the rectified and ‘corrected’ (via implementation of the Bose-Einstein occupation factor versions of the ‘low-dimensional’ static GSM and its basic equations will be implemented for simulations on \( C_\text{p}(T) \) dependencies of graphene and quasi-one-dimensional semiconductor ‘microwires’. As a ‘zero-order’ approximation, the following equation of the static GSM will be used in the former case:

\[
C_p^{\text{GSM}}(T) = \frac{2C_2}{k_B T_2^2} \int_{E_{\min}}^{k_B T_2} \frac{\exp(h\omega/k_BT)}{\exp(h\omega/k_BT) - 1} \sum_{1}^{N} \left[ \frac{2L_x L_y}{N!} \frac{Z_2^N}{Z_2^N} \right] \frac{(h\omega)^2}{N h c_{\text{eff}}} \frac{N}{h c_{\text{eff}}} \frac{\exp(h\omega/k_BT)}{\exp(h\omega/k_BT) - 1} dh\omega, \tag{11d}
\]

here \( L_x, L_y \) are lengths of mutually orthogonal ribs of a rectangular piece (cluster) of the 2-dimensional semiconductor, insulator or metal, \( F_2(L_x, L_y) \) is a dimensionless function (a two-dimensional counterpart of the \( F(L_x, L_y, L_z) \) function in Eqs.(6, 8a, 8b, 11a, 11b, 11c, 11d)), \( C_2 \) is a dimensional (of \( \text{eV}^{-1}\text{cm}^{-2} \)) constant (defined as \( C_2 = [k_B d^2]/(L_x L_y) \times L_x L_y / \{2\pi^2 (h c_{\text{eff}})^3\}^{3/2} \)), while \( Z_2^N \) is a ‘two-dimensional’ \( N \)-particle temperature-independent ‘partition function’, which might be defined in a way, very similar to that one expressed by the Eq.(7) from the previous section:

\[
Z_2^N = \left[ \frac{L_x L_y}{2} \frac{k_B \theta_D}{\hbar c_{\text{eff}}} \right]^N. \tag{7a}
\]

For the graphene, Debye’s temperature equals to \( \theta_D \equiv 2100 \) K [33], while the \( c_{\text{eff}} \equiv 16600.57 \) m/s is evaluated based on the \( c_{\text{TA}} \equiv 13600 \) m/s and \( c_{\text{LA}} \equiv 21300 \) m/s quantities, provided in ref. [33]. Similar to Eqs.(8a, 11a) above, Eqs.(7a, 11d) yield both the ‘harmonic’ (obtained at \( N \equiv 1 \)) and ‘anharmonic’ (for the
integer N ranging from 2 to \(N_M = \text{Floor}(E_f/E_{\text{min}})\) contributions to the specific lattice heat capacity of the graphene (graphite). Figs. 5(a), (b) illustrate the \(C_{\text{CH}}(T)\) and \(C_{\text{CAH}}(T)\) dependencies, simulated based on Eqs.(7a, 11d) herein for the square pieces (‘crystallites’) of graphene at different lengths of the orthogonal ribs, \(L = L_x = L_y\). Contributions from the ‘flexural’ outplane acoustic mode \cite{33} and interlayer coupling(s) to the \(C_{\text{CH}}(T)\) and \(C_{\text{CAH}}(T)\) quantities of the graphene are completely ignored at all these simulations.

FIG. 5 (a), (b) (color online). Temperature dependencies of (a) ‘harmonic’ and (b) ‘anharmonic’ contributions to the corrected (with the Planck’s occupation factor) GSM specific lattice heat capacities of graphene (graphite), simulated based on the state Eqs.(7a, 11d) at different L quantities (shown directly in the panels). The log-log slopes of those dependencies evaluated for the mid-temperature ranges are indicated directly within the both panels of the figure. See main text for more simulation parameters and other details.

As it seen from Fig. 5(a), the \(C_{\text{CH}}(T)\) dependencies, simulated for the graphene based on Eqs.(7a, 11d) are not affected by the sizes of the square ‘pieces’ of graphene (unless \(L\) becomes as low as \(L = 0.1\) \(\mu\)m and the temperature \(T\) drops below 20 K), and exhibit apparent qualitative similarities with their counterparts plotted in Figs. 3(a), (b) for the \(<100>\)-oriented polycrystalline diamond, silicon and germanium, though quantitative parameters of those dependencies are significantly different. In particular, the ‘mid-temperature’ (11 K \(\leq T \leq 101\) K) branches of the \(C_{\text{CH}}(T)\) curves in Fig. 5(a) obey (with a reasonable accuracy) the \(C_{\text{CH}}(T) \propto T^2\) ‘law’, in distinctions from the archetypal Debye’s \(C_{\text{CH}}(T) \propto T^3\) behavior for the simulated low-temperature branches presented for the ‘3-dimensional’ polycrystalline diamond, silicon and germanium in Figs. 2(a), 3(a) and 4(a). On the other hand, the \(C_{\text{CH}}(T) \propto T^2\) branches in Fig. 5(a) are in reasonable quantitative agreement with the \(C_{\text{H}}(T) \propto T^2\) dependencies, expected for the graphene (graphite) based on the generic physical considerations, provided elsewhere in ref. \cite{33}, and replicated above using the appropriate GSM equations for the two-dimensional materials with the linear dependence for the phonon DOS of the fundamental vibrational states, on condition of the absence of significant contributions from the ‘flexural’ and ‘outplane’ modes, as well as from ‘interlayer’ interactions.

The mid-temperature-range log-log slope of the \(C_{\text{CAH}}(T)\) dependencies in Fig. 5(b) becomes much steeper (\(~ 3.0\) for all simulated curves) as compared to that of the \(C_{\text{CH}}(T)\) curves in Fig. 5(a) – in apparent qualitative similarities with the steeper slope(s) of, for instance, the \(C_{\text{CAH}}(T)\) curves in Fig. 2(b) – as compared to slopes of \(C_{\text{AH}}(T)\) dependencies in Fig. 2(a). Furthermore, the \(C_{\text{CH}}(T)\) curve in Fig. 5(a) obtained for \(L = 0.1\) \(\mu\)m exhibit a significant low-temperature ‘anomaly’, which is apparently caused by the morphological ‘cut-off’ in the low-energy (bottom) part (located just below the appropriate \(E_{\text{min}}\) quantity) of the phonon spectrum of the ‘polycrystalline’ graphene. Quantitatively, the cut-off energies, \(E_{\text{min}}\), are evaluated based on a two-dimensional counterpart of Eq.(2) from the second section:

\[
E_{\text{min}} = \left[\frac{2\hbar c_{\text{eff}}}{(L_x^2 + L_y^2)/2}\right]^{1/2}.\tag{2a}
\]
The latter equation yields: $E_{\text{min}} = 0.0137309 \text{ meV (at } L = 10.0 \mu \text{m}, E_{\text{min}} = 0.137309\text{ meV (at } L = 1.0 \mu \text{m})$, and $E_{\text{min}} = 1.37309\text{ meV (at } L = 0.1 \mu \text{m)}$ for the case of graphene. Since the latter quantity is more than an order of the magnitude larger than the $E_{\text{min}} = 0.1164 \text{ meV}$, obtained based on Eq.(2) from the second section for the polycrystalline diamond with the cubical grains of the sizes of $L_x = L_y = L_z = 1.0 \mu \text{m}$, the corresponding Boltzmann-Gibbs occupation factors of phonon states drops till $\sim 1.2 \times 10^{-7}$ (!) at $T = 1 \text{K}$ for the case of graphene with $L_x = L_y = 0.1 \mu \text{m}$, and the morphological ‘cut-off’ effect (which results in the mentioned above low-temperature ‘anomaly’ for the appropriate $C_{\text{CAH}}(T)$ curve) becomes apparent in Fig. 5(a) only for such a case. It is noteworthy, that the experimental $C_p(T)$ and $C_{\text{CAH}}(T)$ curves might not exhibit such low-temperature ‘anomalies’ neither for the graphene nor for other two-dimensional materials due to significant contributions from ‘zero-temperature’ and ‘outplane’ phonon vibrations, as well as because of impact from the ‘grain boundaries’, dangling bonds, other defect states etc.

The high-temperature branches of the $C_{\text{CAH}}(T)$ and $C_{\text{CAH}}(T)$ dependencies, revealed in Figs. 5(a), (b), respectively, saturate in accordance to the Dulong-Petit law and in apparent similarities with behavior of their bulk counterparts, presented in Figs. 3(a), (b). This similarity implies that the corrected version(s) of the GSM replicate convincingly the 3-dimensional (3D) polycrystalline semiconductors and insulators and/or for the 2-dimensional (2D) ones – due to fully quantum Planck’s (Bose-Einstein) occupation factor of the fundamental phonon states of the corrected 2D and 3D versions of the static GSM; see also some extended discussion on this issue in the end of the previous section.

The fraction, $C_{\text{CAH}}(T)/C_{\text{CH}}(T)$, of the anharmonic to harmonic contributions of the lattice thermal capacity of graphene, obtained based on Eqs.(2a, 7a, 11d) equals to $1.579 \times 10^{-4}$ (for $L = 10.0 \mu \text{m}$), $1.581 \times 10^{-5}$ (L = 1.0 mm), and 0.0160 (L = 0.1 mm) at $T \geq 2500 \text{ K}$, while this fraction becomes of $1.240 \times 10^{-6}$ (L = 10.0 mm), 1.261 $\times 10^{-5}$ (L = 1.0 mm), and turns to be $2.228 \times 10^{-4}$ (for $L = 0.1 \mu \text{m}$) at $T = 3 \text{ K}$. Thus, in contrast to situation with the polycrystalline diamond, germanium and silicon of L = $L_x = L_y = L_z = 1.0 \mu \text{m}$ (see also Figs. 3(a), (b) in the previous section), where the anharmonic fractions of the total lattice thermal capacities are apparently underestimated, those fractions evaluated for the graphene based on Eqs.(7a, 11d) become much larger both at high ($T \geq 2500 \text{ K}$) and low ($T = 3 \text{ K}$) absolute temperatures. Thus, the specific way of an additional ‘enhancement’ of the anharmonic lattice heat capacity, described in the end of the previous section, and implemented therein to the 3-dimensional polycrystalline semiconductors (see simulation results plotted in Fig. 4(b)) is apparently not required for the case of graphene.

Indeed, the whole $C_{\text{CAH}}(T)$ dependencies shown in Fig. 5(b), are affected significantly by the size (rib length L) of square graphene ‘pieces’: the temperature-dependent magnitude for whole those dependencies becomes almost inversely proportional to the L ($C_{\text{CAH}}(T) \sim 1/L$); though the low-temperature part of the $C_{\text{CAH}}(T)$ curve obtained at L = 0.1 mm exhibits the ‘additional’ low-temperature ‘anomaly’ due to morphology-induced ‘cut-off’ in the bottom part of phonon spectrum (discussed to some extent just above on this page). Similar size-dependent effects are well-known and documented repeatedly for nanocrystalline solids, where the $C_p(T)$ quantities usually enlarges considerably with the diminishment in sizes of nano-crystallites [30, 31], though the $C_p(T)$ enhancement in the latter case is routinely ascribed to contributions from a surface (interface) energy (due to well-developed interfaces of nano-structured materials), rather than to that from anharmonic components of the vibrational energy. In addition, magnitude of the enhancement is usually limited by few tens percent for the materials with nanometer-sized morphology [30, 31], while even high-temperature ($T \geq 2500 \text{ K}$) fraction of the anharmonic lattice heat capacity in our case does not exceed $\sim 1.6\%$ of the total grahen lattice heat capacity at $L = 0.1 \mu \text{m}$. On the other hand, it is expected to be as high as $\sim 16\%$ at $L = 0.01 \mu \text{m}$ (10 nm); i.e. for truly nano-sized pieces of the graphene. Thus, the high-temperature $C_{\text{CAH}}(T)$ fractions evaluated based on Eq.(7a, 11d) become high enough indeed, and no further corrections to those equations are apparently required in such a case.

As for quasi-one-dimensional diamond, silicon and germanium ‘microwires’, the following ‘low-dimensional’ static GSM equation might be implemented at simulations on their lattice heat capacity:

$$C_{p,\text{GSM}}(T) = \frac{3C_3\theta_T}{k_B T^2} \int_{E_{\text{min}}}^{k_B \theta_T} \frac{\exp(h\omega/k_B T)}{[\exp(h\omega/k_B T) - 1]^2} \sum_{N=1}^{N_m} \left(\frac{(h\omega)^2}{N! Z_N^2} \left(\frac{N^2 L_x L_y L_z}{8 (N h \epsilon_{\text{eff}})^2}\right)^N\right) d\omega, \quad (11e)$$

which is essentially based on the single-particle Eq.(17B) for the harmonic static vibrational DOS, derived in Appendix B of ref. [4]; see also references therein. Simulation results obtained based on Eqs.(7, 11e) for the ‘harmonic’ (at $N = 1$) and ‘anharmonic’ ($2 \leq N \leq \text{Floor}(k_B \theta_T/E_{\text{min}})$) fractions of the $C_{p,\text{GSM}}(T)$ function,
for the <100>-oriented diamond, silicon, and germanium ‘microwires’ of squared cross-sections with \( L = L_x = L_y = 0.1 \mu m \) and \( L_z = 10.0 \mu m \) (i.e., with the ‘aspect ratio’ of 1:100) are revealed in Figs. 6(a), (b).

![Diagram](attachment:image.png)

**FIG. 6 (a), (b) (color online).** Temperature dependencies of (a) ‘harmonic’, \( C_{HC}(T) \), and (b) ‘anharmonic’, \( C_{AHC}(T) \) components of the \( C_p^{GSM}(T) \) dependencies evaluated based on Eqs.(7, 11e) for the <100>-oriented diamond, silicon and germanium ‘microwires’ with squared \( xy \) cross-section(s), but elongated in \( z \) direction. Simulation parameters are specified both within the figures and in the main text. The log-log slopes of the low-temperature branches of the \( C_{HC}(T) \) and \( C_{AHC}(T) \) curves are indicated directly near the appropriate curve(s).

As it seen from Figs. 6(a), (b), the high-temperature branches of all curves shown in these figures ‘saturate’ at relatively high temperature(s) (well-compared with the appropriate Debye’s ones), while the low-temperature slopes of the \( C_{HC}(T) \) dependencies revealed in Figs. 6(a) remain fairly close to 3 in the log-log plots, obeying the archetypal Debye’s behavior. In these respects, behavior of the \( C_{HC}(T) \) and \( C_{AHC}(T) \) dependencies plotted in the latter figures are fairly similar to behavior of the specific lattice heat capacity of polycrystalline diamond, silicon and germanium, exhibited in Figs. 3(a), (b), 4(a), 4(b) from the previous section, though the temperature-dependent anharmonic contribution(s) to the specific lattice heat capacity exhibited in Fig. 6(b) exceeds their counterparts shown in Fig. 3(b) approximately by a factor of 2 (when compared at the fixed temperature).

Those similarities apparently originate from the canonical Debye’s spectrum of acoustic phonons (with quadratic enlargement in its static vibrational DOS with the phonon energy increment) assumed both for the 3-dimensional polycrystalline solids with the cubical grains and for the elongated quasi-one-dimensional ‘microwires’ (compare Eqs.(11c, 11e)).

On the other hand, as it is discussed above in this section, the mid-temperature lattice specific heat of the two-dimensional ‘polycrystalline’ graphene increases with the temperature as \( C_p(T) \propto T^2 \) at a negligible contribution from theZA ‘flexural’ phonon modes (see Fig. 5(a) above and ref. [33]), in contrast to the archetypal Debye’s behavior of the low-temperature mid-temperature branches of the bulk and polycrystalline metals, semiconductors and insulators. This amendment in the log-log slope of the low-temperature \( C_p(T) \) dependencies simulated above for graphene based on the ‘two-dimensional’ version of the static GSM has to be attributed entirely to the crucial alteration in the key features of its vibrational static DOS [33]: it increases linearly with the phonon energy for the graphene instead of its quadratic enlargement for the polycrystalline semiconductors and ‘microwires’. Similarly, key features of low-temperature branches of the specific lattice heat capacity of non-homogeneous metals, semiconductors and insulators with nanometer-sized non-homogeneities customarily deviate considerably from those of the archetypal Debye’s \( C_p(T) \propto T^2 \) function regardless of dimensionality of such materials [34, 35]. However, herein we will not discuss physical origins behind such deviations.

All simulation results presented above in this article so far are formally obtained for the crystalline modification of the bulk, polycrystalline, and low-dimensional semiconductors and insulators, whereas the original scope of the static GSM naturally comprises as well the case of their solid amorphous (structurally disordered) counterparts: see the third, sixths and sevenths chapters of the ref. [4]. Indeed, the static plane-
wave basis of Debye’s acoustic phonons apparently remains viable even for the case of solid spatially non-homogeneous amorphous semiconductors and insulators with the ‘convex’ phonon confinement volumes, though sound velocities of such solids are significantly lower (up to ~30%) in magnitude as compared to those for their crystalline counterpart [38], and apparently become even ‘more isotropic’ – i.e., less dependent on the specific spatial orientation. Furthermore, essential features (e.g., quadratic dependence on the phonon energy) of the archetypal static DOS function of the fundamental states of Debye’s acoustic phonons are not affected considerably at a transition from (poly)crystalline to amorphous phases of the given solid semiconductor and/or insulator. Moreover, the ‘Christoffel Matrix’ formalism, implemented essentially within the GSM framework is equally applicable to the bulk crystalline and/or amorphous solids, as well as to their polycrystalline and spatially non-homogeneous amorphous counterparts, though amorphous solids with the tetrahedral atomic coordination commonly comply with a specific ‘isotropic condition’ for their elasticity modulus, which is, however, not obeyed for majority of elemental crystalline semiconductors and insulators even with the highly-symmetric diamond and/or zinc blend primitive cells (see Appendix C in ref. [4] and references therein). In addition, though Debye’s temperature of amorphous semiconductors is typically lower (by ~10 – 15 %) as compared to that of their crystalline counterparts, it remains a well-defined quantitative parameter of the canonical Debye-Planck and GSM approaches even in such a case [38]. Therefore, the (refined) basic equations of the isotropic GSM become equally applicable for quantitative evaluations on the specific lattice thermal capacity of the polycrystalline and spatially non-homogeneous amorphous semiconductors (at least for those with the tetrahedral atomic coordination), as well as for realistic simulations on their $C_v(T)$ and $C_p(T)$ dependencies. Moreover, archetypal features of those simulated dependencies (not shown herein) obtained for 3D amorphous semiconductors are found to be quite similar to their counterparts, presented in the previous section of this article for the polycrystalline modifications of elemental semiconductors and insulators, though certain amendments in quantitative parameters of the experimental $C_v(T)$ and $C_p(T)$ dependencies (e.g., significant ‘excessive’ heat capacity of amorphous solids at $1 K \leq T \leq 20 K$ [39], which is caused by various atomic and electronic excitations and a ‘shift’ in temperature of transition from the archetypal (Debye’s) $C_v(T) \propto T^3$ behavior to the Dulong-Petit regime) had been reported for real amorphous materials (especially for glasses) [38, 39]. However, predictions of refined 3D GSM for the high- and medium- ($20 K \leq T \leq 100 K$) temperature ranges are in fairly reasonable quantitative agreement with experimental $C_p(T)$ data reported elsewhere in ref. [38] (see, in particular, Fig.2 therein) for the thin films of amorphous silicon.

5. Conclusions

The (refined) basic equation(s) of the isotropic version of the Generalized Skettrup Model (GSM, presented in details in the second chapter of ref. [4]; see also very brief review of those equations in the third section herein), incorporates naturally contributions to the total energy of quantum grand canonical ensemble (QGCE) of confined Debye’s acoustic phonons with the static plane-wave basis both from their pure states as well as from the excited and coherent states of those phonons, are implemented herein at quantitative evaluations on the harmonic and anharmonic contributions to the temperature-dependent lattice thermal capacities, $C_v(T)$ and $C_p(T)$ (i.e., those measured at a constant volume of a solid and at a constant environmental pressure, respectively), of polycrystalline and low-dimensional solids.

Since the GSM retains essential features of the semi-classical static (time-independent) ‘global’ states of non-interacting acoustic phonons with the plane-wave basis and the archetypal vibrational DOS introduced by P. Debye elsewhere in ref. [2] (and briefed in the second and third sections herein), its implementation to evaluation on the harmonic and anharmonic fractions of the specific lattice thermal capacities of solids becomes very straightforward and ‘intuitive’. The Debye’s static plane acoustic wave (phonon) basis is proven to be simply the best choice for evaluation on lattice thermal capacities as well as on other key thermal characteristics of the bulk (both crystalline and amorphous) metals (even with strong electron-phonon interactions!), semiconductors and insulators, their polycrystalline and spatially non-homogeneous amorphous counterparts with the micrometer- and sub-micrometers sized crystallites (non-homogeneities), as well as low-dimensional and even nano-structural materials: the history of successful implementation of such basic sets for all aforementioned purposes is enduring for many decades [7, 33].

On the other hand, the semiclassical Boltzmann-Gibbs occupation factor implemented essentially in the original version of the GSM [4] for (generally many-particle) states of acoustic phonons with the plane-wave basis might yield significant deviations of the high-temperature branches of the simulated temperature dependencies of the lattice thermal capacity from their well-known (Dulong-Petit)
experimental counterparts and predictions of the canonical Debye-Planck model. In particular, though the refined isotropic GSM equation(s) implemented for the $C_v(T)$ and $C_p(T)$ simulations replicate convincingly the archetypal (Debye’s) low-temperature $C_v(T) \propto T^3$ branches of elemental polycrystalline solid(s) composed from atoms of IV group of the periodic table (i.e., diamond, silicon and germanium) at different sizes of their crystallites (varied well within the sub-micrometer- and micrometer- ranges), it persistently yields declining harmonic and anharmonic components of the $C_v(T)$ and $C_p(T)$ dependencies at relatively high temperatures, well comparable with the Debye’s temperature of the given solid, see discussion on this issue in the third section of this article. The latter predictions of the GSM apparently contradict to the well-established experimental data sets (both for the aforementioned elemental and many others crystalline and amorphous solids) as well as to outcomes of the canonical Debye-Planck approximation. However, aforementioned drawback of the (refined) GSM might be corrected via direct replacement of the semi-classical Boltzmann-Gibbs occupation factor with the fully quantum Planck’s (Bose-Einstein in general) one for both fundamental (single-particle) as well as essentially many-particle excited and coherent states of those phonons. For those latter states, a many-particle counterpart of the conventional global DOS concept (see Appendix D of ref. [4]) becomes especially meaningful and convenient. Aforementioned replacement (correction) becomes eloquent for polycrystalline semiconductors and insulators (see discussion and some simulation results in the third section), as well as for their low-dimensional and spatially non-homogeneous amorphous counterparts (see fourth section for details). Simulation results presented herein are predominantly obtained for the (simplified) cases of square (for graphene) or cubical (for polycrystalline diamond, silicon, and germanium) ‘crystallites’ (mainly of the rib length of 1.0 μm), though more generic cases of the rectangular and parallelepiped two- and three-dimensional ‘crystallites’ might be analyzed readily within the GSM framework; see, for instance, Eq.(11e) in the fourth section herein.

In contrast to the harmonic lattice heat capacity evaluated based on the GSM, its anharmonic counterpart becomes essentially size-dependent both for the 3-dimensional (polycrystalline) and for the low-dimensional materials, resembling behavior of the size-dependent lattice heat capacity of nano-structural solids, though the physical essences of those size-dependent effects are essentially different (see the fourth section for details). The anharmonic fractions of the lattice heat capacity evaluated based on the GSM are routinely underestimated for the elemental polycrystalline solids as compared to such fractions measured for their bulk (single-crystalline) counterparts. In order to overcome this problem, appropriate GSM equations might be is expanded well into entirely anharmonic regime for the excited and coherent states of the GSM, with the total energy of the QGCE well exceeding Debye’s energy of the given solid. A combination of the ‘exponential integral’ and ‘incomplete gamma-function’ [18] is used essentially at such expansion, which allows one to re-formulate substantially the basic equation(s) of the GSM; see Eqs.(12a – 17) in the third section. As a result, the simulated $C_p(T)$ and $\{[C_p(T) – C_v(T)]/C_v(T)\}$ dependencies replicate reasonably well their experimental counterparts obtained for the bulk diamond and silicon within the absolute temperature range from 1K up to ~ 1700 K; see figures in the end of the third section herein.

Thus, the basic physical ideas as well as refined, expanded and corrected version(s) of the isotropic static equations of the GSM (which are originally depicted in details in the second chapter of the ref. [4] – see also references therein as well as the third and fourth sections above – and provide appropriate quantitative descriptions on statistical characteristics of the fundamental, excited and coherent states of Debye’s acoustic phonons with the static plane-wave basis as well as on key features of closely related to them near-band-gap and intra-gap electronic and optical characteristics of polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators [4]), might be implemented readily at realistic simulations on both harmonic and anharmonic specific lattice thermal capacities of the polycrystalline, spatially non-homogeneous amorphous, and low-dimensional solids, as well as of their temperature dependencies within a wide temperature range. At the same time, the mentioned above rectification of basic static equation(s) of the GSM discussed in details in the third section of this article allows one to clarifies as well the original scope of (both isotropic and/or anisotropic versions of the) GSM [4]; it might be implemental unambiguously for realistic simulations on key features of the near-band-gap and intra-gap electronic and optical spectra of aforementioned semiconductors and insulators only when the energy of the many-particle phononic and caused by them single-particle electronic excitations exceeds the Debye’s energy of the given crystalline and/or amorphous solid. Furthermore, in principle, those refined, expanded and corrected isotropic static GSM equations might be developed even further and implemented (after their fairly trivial modifications) at quantitative evaluations on characteristics of thermal transport in all aforementioned non-homogeneous solids within framework of the ‘relaxation time’ approximation [40]. Though this potential of the GSM and its basic equations is not explored herein, it might be considered as a subject of their upcoming development(s).
References


Acknowledgements. The simulation results exhibited in the Table 1 as well as represented by color curves in Figs. 1(a), 2(a), 2(b), 3(a), 3(b), 4(a), 4(b), 5(a), 5(b), 6(a), 6(b) are obtained using Octave 3.6.4 free software: Copyright (C) 1996 – 2011 John W. Eaton iwe@octave.org; see also http://www.octave.org.

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