The 'Generalized Skettrup Model' and Matsubara Statistics

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The 'Generalized Skettrup Model' (GSM) [1] 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 *fluctuations* in an energy of the individual quasi-particle, number of quasi-particles in a quantum grand canonical ensemble (QGCE) of *confined acoustic phonons* with *static* plane-wave basis (pure states), and in their aggregate energy. Features of the GSM [1] are discussed herein in comparison to those of quantum statistics pioneered by famous Japanese physicist T. Matsubara [2], which is based essentially on two-points 'Green Function' (GF) formalism, and takes into account fluctuations in *temperature* of QGCE. The GSM [1] might be ultimately treated as a 'conservative' (and essentially *static*) ***counterpart*** of the generic Matsubara statistics for the specific case of ensemble of acoustic phonons confined within micrometer- and sub-micrometer-sized non-homogeneities (crystallites) of poly-crystalline and spatially non-homogeneous amorphous semiconductors and insulators. However, unambiguous links among *spectral characteristics* of the GSM and Matsubara GF might be established for equilibrated phononic ensembles with static and/or dynamic plane-wave basis. Moreover, original scope of the GSM might be expanded further based on the fundamental ideas, pioneered by T. Matsubara.

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1. Introduction

The Generalized Skettrup Model (GSM) depicted in the *second* chapter of ref. [1] (see also references therein) is essentially based on evaluation of probabilities of *fluctuations* in an *energy* of pure state(s) of individual acoustic phonons, their *aggregate energy* and (generally rational) *number* of quasi-particles of the (quantum) *grand canonical* ensemble (QGCE), corresponding to many-particle phononic excitations with *static* (time-independent) plane-wave basis (pure states) in polycrystalline and/or spatially non-homogeneous amorphous semiconductors and insulators. In particular, within the GSM framework, those fluctuation probabilities are customarily evaluated via an *integration* (averaging) over available (at the given aggregate energy) *mixed* quantum states of ensemble of Debye's acoustic phonons and appropriate number of those quasi-particles [1]. Furthermore, the GSM implies that those fluctuations in the ensemble 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 between the *instantaneous* aggregate energies (fluctuation probabilities) of electronic and phononic sub-systems might be established quantitatively either based on semi-empirical electron-phonon coupling parameters or via the 'deformation potential' formalism [1].

Thus, aforementioned GSM approach essentially implies that the individual and aggregate *energies* as well as *number* of quasi-particles in the phononic ensemble have to be treated as *real* (generally rational) *variables*, while temperature of the ensemble is usually treated as a *fixed* (constant) quantity for the given environmental conditions; i.e., as a *parameter* of an external 'thermal reservoir'.

In contrast, quantum statistical mechanics pioneered (in particular) by famous Japanese physicist ***Takeo Matsubara*** for a quantum ensemble with a time-dependent (*dynamic*) basis (comprises either electrons (fermions) or phonons (bosons)) [2] is based essentially on properties of 'equilibrium' two-points 'Green Function' (GF), and treats the *temperature* of QGCE as a *variable complex parameter*. This implies that the *temperature* of the ensemble *fluctuates* as well – *in addition* to fluctuations in total number of its quasi-particles and in their individual and aggregate energies for the given QGCE. Furthermore, quantitative parameters of the conventional two-points GF might be evaluated appropriately via substitution of real-time variable of the GF defined in Euclidian space-time continuum with its 'imaginary time' counterpart, which is *inversely proportional* to the temperature of the ensemble [2]. Such treatment becomes essential for *interacting* systems: *condensed* matter, dense plasmas, neutron stars etc., where local temperature *fluctuations* are expected to be considerable or dominant. Herein significances of aforesaid effects are evaluated only for *solid* crystalline and non-homogeneous amorphous semiconductors and insulators, including nano-structured ones, and discussed in comparison with predictions of the GSM [1].

2. Key Features of Matsubara Statistics

In a thermal equilibrium, averaged (statistical) characteristics of *pure* or *mixed* (static and/or dynamic) many-body state(s) of a *non-interacting* (either fermionic or bosonic) ensemble at the given (absolute) temperature T are routinely evaluated based on the quantum grand canonical density operator, ρ_D [3]:

$$\rho_D \quad \equiv \quad \frac{\exp\left(-H_0/k_B T\right)}{Tr\left[\exp\left(-H_0/k_B T\right)\right]}\,, \qquad (1)$$

where $Tr[\exp(-H_0/k_BT)]$ denotes *trace* (i.e., sum over its *diagonal* elements) of the matrix exponential of the weighted 'thermal' Hamiltonian matrix (H_0/k_BT), and k_B is the Boltzmann constant. This ρ_D operator is Hermitian, 'positive definite' and normalized: $Tr\{\rho_D\} \equiv 1$ [3]. Importantly, that Eq.(1) remains valid even for *Heisenberg representation* of the quantum mechanics, which presumes that *wavefunctions* (set of basic states) of the system and its Hamiltonian are *time-independent* (static), while *operators* do *change in time*.

Essential generalization of concept of equilibrium statistics for an (bosonic or fermionic) ensemble with a time-dependent (*dynamic*) basis had been achieved [2] via implementation of a single-particle two-points Matsubara 'Green Function' (GF), expressed herein using a coordinate representation [4]:

$$\breve{G}_M\left(\vec{r}_1,\,\tau_1,\,\vec{r}_2,\,\tau_2\right) = -\frac{Tr\left\{\exp\left[-\left(\mu N - H_0\right)/\left(k_B T\right)\right]\,T_\tau\left[\Psi_\alpha\left(\vec{r}_1,\,\tau_1\right)\Psi_\alpha^+\left(\vec{r}_2,\,\tau_2\right)\aleph\left(1/T\right)\right]\right\}}{Tr\left\{\exp\left[\left(\mu N - H_0\right)/\left(k_B T\right)\right]\aleph\left(1/T\right)\right\}}\,, \quad (2)$$

where $\mathbf{r}_1$, τ_1 and $\mathbf{r}_2$, τ_2 stand for spatial and *imaginary* time 'coordinates' of the first and second points of an Euclidian space-time continuum, N is number of particles in the ensemble, μ is its chemical potential, $\Psi_\alpha(\mathbf{r}, \tau)$ is *imaginary-time-dependent* <u>operator</u>, acting on (time-independent) wavefunction(s) (eigenstates, numerated by their index α) of the ensemble, and $\Psi_\alpha^+(\mathbf{r}, \tau)$ is its complex-conjugate (adjoint), T_t is so-called 'time-ordering' operator with respect to the imaginary time, while $\aleph(1/T)$ is a form of 'density matrix', defined (based on a generic identity) as follows [4]:

$$\aleph\left(1/T\right) \quad \equiv \quad T_\tau \exp\left[-i\int_0^{-i\beta} H_{\text{int}}\left(t\right)dt\right] \quad = \quad T_\tau \exp\left[-\int_0^{\beta} H_{\text{int}}\left(\tau\right)d\tau\right], \qquad (3)$$

where $i = \sqrt{-1}$, $\beta = i/(k_BT)$, $\tau = it$, and $H_{int}(t)$ is a (time-dependent) '<u>interaction Hamiltonian</u>' of the ensemble [4]. Thus, Eqs.(2, 3) manifest a two-points *generalization* (in coordinate representation) of the conventional ('thermal') density matrix, as well as density operator, expressed by Eq.(1). In particular, Eq.(1) might be 'restored' from Eq.(2) in the 'equal times' limit, i.e., at $\tau_1 = \tau_2$. The Eq.(2) is *formally* compatible with Heisenberg representation of quantum mechanics. An integration over the 'imaginary time' in Eq.(3) seemingly yields an '*interaction representation*' for the statistical ensemble [2 – 4].

In apparent distinction from the 'conventional' GF $\breve{G}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$, the Matsubara's 'equilibrium' two-point GF $\breve{G}_M(\mathbf{r}_1, \tau_1, \mathbf{r}_2, \tau_2)$ specified by Eqs.(2, 3), was established in ref. [2] via *substitution* of real-time variable t of the conventional GF with its 'imaginary time' counterpart $\tau = it$ (i.e., via so-called 'Wick rotation'), which is also related directly to the *inverse* temperature, 1/T, of the ensemble. This idea was apparently inspired by the structure of Minkowski (relativistic) space-time metric, which comprises of *imaginary* time axis. Formally, the *equilibrium* GFs, $\breve{G}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ and $\breve{G}_M(\mathbf{r}_1, \tau_1, \mathbf{r}_2, \tau_2)$ one, depend only on the *time difference(s)* [3]. Furthermore, in an <u>*equilibrium*</u> state, the Hamiltonian H_0 of the system is expected to be static (*time-independent*), and evolution (fluctuations) of the ensemble parameters have to be attributed entirely to its evolution on the *imaginary time* axis, or <u>*fluctuation(s)*</u> *in its* <u>*local temperature*</u>.

This kind of evolution (fluctuation) might be formally depicted by Eqs.(2, 3), as long as integration in Eq.(3) is fulfilled along the straight line, parallel to the 'imaginary time' axis on the complex time plane [2 – 4]. In such a case, Eq.(3) might be re-formulated in a more compact (and yet generic) form [3]:

$$U\left(t_0 - \beta,\, t_0\right) \quad \equiv \quad \exp\left(i\,\beta\,\hat{H}_0\right), \qquad (4)$$

here U denotes an evolution operator, and t_0 stands for an 'origin' of the real time axis. It is noteworthy, that evolution of the bosonic ensemble is *periodic* on the imaginary time scale, while evolution of the fermionic ensemble is 'antiperiodic' [2 – 4].

Alternatively, *any* (temperature-dependent) function in Euclidian space (e.g., phonon eigenfunction, conventional GF, creation and/or annihilation operator, thermal 'propagator' etc.) might be expanded readily in an *infinite* exponential Fourier series over *imaginary* time with (Matsubara) frequencies ω_n, which are routinely defined for bosonic ensemble based on *periodicity* conditions of those exponential terms: $\exp(\beta\omega_n) \equiv 1$ [2 – 4]. Consequently, in general, integration over imaginary time in Eq.(3) might be replaced with a (infinite) summation over the Matsubara frequencies. However, in *apparent contradiction* with Eqs.(3, 4), those Matsubara frequencies ω_n naturally become *temperature-dependent, but not affected* neither by frequencies of pure states (individual modes) of the phononic ensemble nor by their aggregate energy. In particular, based on the mentioned above periodicity condition, one readily obtains: $\beta\omega_n = 2\pi n$ [5] or $\omega_n = -2\pi i k_B T n$ (n herein is an integer index) [2, 3]. At T = 1 K and n = –1, this periodicity condition yields: $\omega_{-1} = 2\pi i k_B T \cong 5.414{*}10^{-4}\, i$ eV. Higher Matsubara frequencies are just proportional to the ω_{-1} quantity. Similar Matsubara frequencies might be defined readily as well for a fermionic ensemble [2 – 4]. Thus, fluctuations (and interactions) in either bosonic or fermionic ensemble might be taken into account via *appropriate expansion* over the *imaginary* time or frequency domain(s) of the given ensemble.

The original Matsubara's idea is *tremendously fruitful* and was further developed and implemented for decades in GF-based formalisms of a finite-temperature quantum statistic of condensed systems [3, 4]. In addition, it was advanced further by T. Matsubara in order to establish *diagrammatic* perturbation theory for their grand partition functions within framework of the field-theoretical basis [2 – 4]. However, 'orthodox' GF and diagrammatic formalisms *do not apply* to '…Bose systems below points of the Bose condensation…' and '…Fermi systems in which superconductivity exists…' [4].

3. 'Matsubara Correction' for GSM with *Static* Plane-wave Basis

The basic feature of the briefly depicted in the previous section Matsubara's generalization of the fluctuation concept might be incorporated *naturally* into the framework of essentially *static* GSM [1]. Indeed, basic equation of (isotropic version) of the GSM comprises of the Gibbs (Boltzmann) term, total number of available static *mixed* states of QGCE of Debye *acoustic* phonons with the plane-wave-functions (pure states) as well as its 'normalizing' factor, $\Gamma(M + 1)^{-1}$, and a 'partition function', Z_M [1]:

$$W_D(E_T) \cong \exp\left(-\frac{E_T}{k_B T}\right) \int_{M0}^{M_M} \frac{1}{\Gamma(M+1)(Z_M)^{r2}} \left[\frac{2\mathcal{L}_x \mathcal{L}_y \,\mathrm{F}(\mathcal{L}_x, \mathcal{L}_y, \mathcal{L}_z)\, E_T^2}{M^{r1}(hc_l)^2}\right]^M dM, \qquad (5)$$

where $W_D(E_T)$ denotes probability density of finding of the ensemble of confined (within a parallelepiped crystallite, column, cone, etc.) Debye acoustic phonons in a *mixed* state with its aggregate energy of E_T, $\Gamma(M + 1)$ is Euler's Gamma-function [5], *h* is the Planck's constant, c_l is *longitudinal* sound velocity, $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ are lengths of the (orthogonal) ribs of parallelepiped phonon confinement volume, while the dimensionless function $\mathbf{F}(\mathcal{L}_x, \mathcal{L}_y, \mathcal{L}_z)$ depends solely on *ratios* of the $\mathcal{L}_x$, $\mathcal{L}_y$ and $\mathcal{L}_z$ lengths; see also Eq.(26a) in ref. [1]. Integration in Eq.(5) is expected to be carried out over the appropriate range of (generally rational) number M of acoustic phonons in the ensemble (this integration range is restricted by the M_M and M0 limits), while dimensionless (and rational in general) model parameters r1 and r2 are typically varying in the following ranges: $0.5 \le r1 \le 2$; $0.5 \le r2 \le 1$ [1]. Furthermore, $M0 = (E_T/k_B\theta_D)^{(2/r1)}$, with Debye energy of the solid equals to $k_B\theta_D$ (and Debye temperature of θ_D), while $M_{max} = (E_T/E_{min})^{(2/r1)}$, with a low limit, E_{min}, of the aggregate energy of the ensemble of acoustic phonons, imposed by presence of *morphology* (non-homogeneities) in studied (isotropic but spatially non-homogeneous) polycrystalline or amorphous semiconductor (insulator), and defined by Eq.(18B) in ref. [1] for such a case.

In spite of significant differences in notations, *structures* of Eq.(2, 5) exhibit apparent *similarities*, in particular, at $\mu = 0$ and M = 1. Furthermore, close *formal interrelations* among those equations might be established readily for a specific case of the ensemble of Debye acoustic phonons with the plane-wave basis and 'classical' linear dispersion: $\omega_q = c_l q$ (here ω_q corresponds to the quasi-wave vector **q**).

Indeed, first of all, unambiguous interrelations between *equilibrium* two-points $\breve{G}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ function and the 'conservative' Eq.(5) really do exist in such a case due to the following well-known identities [5]:

$$\exp\left[-i\omega_q\left(t-t'\right)\right]\exp\left[-i\,\vec{q}\left(\vec{r}\,'-\vec{r}\right)\right] \;=\; \delta\left(t-t'\right)+\delta\left(\vec{r}\,'-\vec{r}\right) \;\equiv\; \delta\left(t=t'\right)+\delta\left(\vec{r}\,'=\vec{r}\right). \qquad (6)$$

Thus, based on those identities, *eigenfunctions* of the *equilibrium* 'conventional' GF, defined at *two points* [(**r**, *t*), (**r**', *t'*)] of Euclidian space-time continuum are linked *directly* to a number of single-point (with coordinates of (**r**, *t*)) **poles** (states) of the plane wave with the angular frequency ω_q, propagating within the continuum. On the other hand, number of single-phonon states in integrand of Eq.(5) at M = 1 equals to number of **poles** of *static* plane-wave basis of Debye phonons: i.e., only right-hand terms in all equalities expressed by the Eq.(6) have to be taken into account in such a case. However, quantitative interrelations among *eigenfunctions* of Eq.(5) and those of Matsubara GF, defined by Eq.(2) are *not so straightforward*, see next section for details. Furthermore, an appropriate sum (over all available indexes α) of the products $[\Psi_\alpha^+(\mathbf{r}, \tau) * \Psi_\alpha(\mathbf{r}, \tau)]$ of the 'one-body' and 'equal-times' annihilation and creation operators (acting on the given set of ground (basis) plane-wave-functions) would yield a *total density* of Debye phonons in Eq.(2) at the particular point of Euclidian space [4, 6, 7]. Consequently, the *total number* of such phonons confined within the parallelepiped volume of $V_p = \mathcal{L}_x\mathcal{L}_y\mathcal{L}_z$ has to be defined by *integration* over the afore-mentioned phonon density, and over the whole volume, V_p. Moreover, since Eq.(2) is formulated within the 'second quantization' framework [4, 6, 7], actual spectrum of excitations of the 'ground' states of the (bosonic or fermionic) ensemble is routinely described based on spectral characteristics of its *individual* quasi-particles and appropriate *occupation factor* for the single-particle (ground) states; see also next section for an example. Thus, implementation of the 'second quantization' approach and GF formalism to an ensemble of bosons or fermions typically yields *scalar* (though generally time-dependent) parameters of the ensemble (e.g., average total number of particles in the ensemble, their average aggregate energy etc.), even though its basis wave-functions may contain vital information on *direction* of their spatial propagation and angular frequency, morphological and *anisotropic* effects in crystalline lattice, etc.

In contrast, the integrand term located within the square brackets of Eq.(5) is linked directly to parameters of the *static* plane-wave-functions (pure states) of the ensemble of (longitudinal) Debye acoustic phonons, and retains essentially the long-range (e.g., *anisotropic* and/or *coherent*) effects, 'inherited' from those plane-wave-functions; see, in particular, Eq.(26b) in ref. [1]. Moreover, the number of acoustic phonons is introduced explicitly as a (generally rational) parameter M of the integrand term in Eq.(5). However, this GSM parameter rather characterize number of quasi-particles in a *coherent* (i.e., with the *same* **q** quantity for *all* its components) and/or *excited* (with non-equivalent **q** quantities of its components) *mixed state* of acoustic phonons, than in their ground states (though M ≡ 1 formally matches to the *ground* state). On the other hand, – in apparent similarity with the 'second quantization' approach – the integrand term located within the square brackets of Eq.(5) is defined merely based on the (idealized) *single-particle* spectrum of the (isotropic) Debye acoustic phonon and its first Brillouin Zone (BZ); this similarity is also accomplished with appropriate low integration limit in the Eq.(5) [1]. It is noteworthy, that the 'second quantization' and Matsubara GF formalisms also allow one to incorporate bosonic *coherent states* with the plane-wave basis: e.g., 'normalized' Klauder's state: $\sim (N_C!)^{-1/2} \exp(-i\mathbf{q}_C\,\mathbf{r})$ [6, 7]; here N_C is an integer, while $\mathbf{q}_C$ is its quasi-wave vector. Notably, that its squared 'normalizing' coefficient $(1/N_C!)$ formally *coincides* with the $\Gamma(M{+}1)^{-1}$ term in Eq.(5) at $M = N_C$. However, the $\mathbf{q}_C$ vector of Klauder's *phononic coherent state* routinely *exceeds* edge of the first phononic BZ. This implies that the $\mathbf{q}_C$ parameter is 'ill-defined' for the phononic states, and such coherent states could not be treated as *pure states* (microstates) of the ensemble of (longitudinal) acoustic phonons; see also next section for further discussion.

The only term, which appears in the Eq.(2), but apparently absents in Eq.(5) – is the 'density matrix' $\aleph(1/T)$, defined by the Eq.(3) in the previous section. However, based on the fundamental idea, pioneered by T. Matsubara [2], an appropriate *counterpart* of the $\aleph(1/T)$ term might be introduced readily for the Eq.(5). Indeed, formally, the given *scalar* E_T quantity in the exponential term of Eq.(5) might be treated as particular case of a (single-valued) *equilibrium* (static) Hamiltonian. However, the E_T quantity apparently comprises of both the sum of the 'self-energies' of the ensemble of the confined acoustic phonons, as well as a contribution caused by their interactions, while the 'density matrix' $\aleph(1/T)$ defined by Eq.(3) is based entirely on an 'interaction Hamiltonian' [4]. Nonetheless, two aforementioned contributions to the E_T term in Eq.(5) might be *separated readily* within the GSM framework. Indeed, at the given energy of acoustic phonon, $\hbar\omega$, the aggregate 'self-energy' of the *sub-set* of M such *equivalent* acoustic phonons in the ensemble is just of $E_T^S = E_T = M{*}\hbar\omega$. However, an *actual number* of such phonons in the ensemble is apparently *smaller* due to presence of the model parameter r1, and equals just to $M^{(r1/2)}$; see terms in square brackets in integrand of Eq.(5) above. Thus, the difference, $E_T - \hbar\omega{*}M^{(r1/2)} = M\hbar\omega[1 - M^{(r1/2-1)}]$, defines the effective interaction energy, E_{int}, for the given sub-set (comprising M equivalent acoustic phonons) of the ensemble. Now, the *'normalized' interaction energy*, E_{int}^{nrm}, of GSM at the given E_T and M quantities is defined by the equation: $E_{int}^{nrm} = E_T[1 - M^{(r1/2-1)}]/M$; herein it is calculated per phonon. Consecutive integration of such *'normalized' interaction energy* (over the M0 ≤ M ≤ M_{max} range), and its additional 'normalization' by the ∫(E_T/M) dM integral (taken also over the M0 ≤ M ≤ M_{max} range) eventually yields:

$$E_{\rm int}^{avr} \;=\; E_T\left[1 \;-\; \frac{\left(M_{max}\right)^{(r1/2-1)} - \left(M0\right)^{(r1/2-1)}}{\left(r1/2-1\right)\,\ln\left(M_{max}/M0\right)}\right]. \qquad (7)$$

The Eq.(7) is apparently *non-linear* in general, though yields: $\mathbf{E_{int}^{avr} \to 0}$ at **r1 → 2.** Behavior of the $E_{int}^{avr}(E_T)$ dependencies obtained based on Eq.(7) at different r1 quantities is illustrated in Fig.1 below for a specific case of <100>-oriented polycrystalline diamond with the crystallite sizes of $\mathcal{L}_x = \mathcal{L}_y = \mathcal{L}_z$ = 1.0 μm.

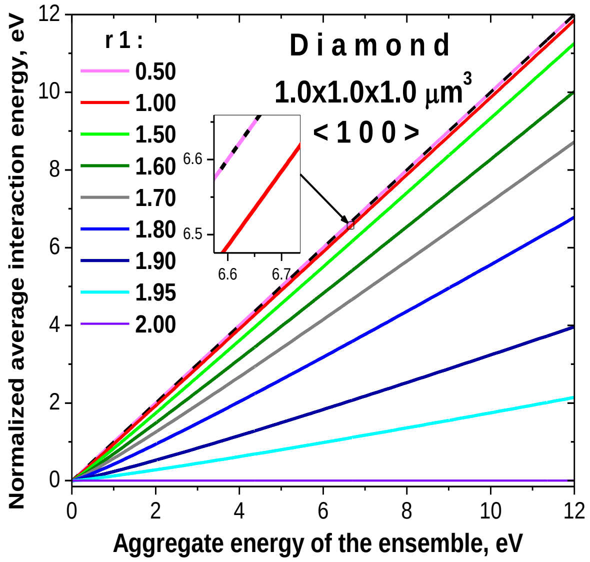

FIG. 1 (color online). Effect of GSM parameter, r1, and aggregate energy, E_T, of ensemble of acoustic phonons on their *normalized* average interaction energy, E_{int}^{avr}, evaluated for <100>-oriented polycrystalline diamond based on Eq.(7). The black *dashed* straight line in this figure corresponds to $E_{int}^{avr} = E_T$. As a 'zero-order' approximation, all $E_{int}^{avr}(E_T)$ dependencies in this figure might be fitted with *straight* lines. See also main text for details.

Simulation results revealed in Fig.1 imply that the *average fraction*, $E_{int}^{avr}(E_T)/E_T$, of the *normalized interaction energy* in the total aggregate energy E_T of the ensemble of confined acoustic phonons depends essentially by the GSM parameter, r1. Indeed, this fraction equals exactly to *zero* at r1 = 2.0, but becomes fairly close to unity ($0.999989 \pm 1.016 \cdot 10^{-4}$ to be exact) at r1 = 0.5, Fig. 1. In other words, the aggregate energy E_T of the ensemble is almost entirely composed of 'self-energies' of acoustic phonons at r1 → 2.0, while contribution from phonon-phonon interactions comprises of ~99.999% of the E_T term at r1 = 0.5.

In contrast to the 'conventional' (and infinite) set of Matsubara frequencies customarily defined based on periodicity conditions of the exponential term(s) in the Fourier expansion of an Euclidian propagator [2 – 4] (see also end of the previous section), the dimensionless (and *always* finite) $\Theta_M(E_T, T)$ function might be introduced based on a physically *meaningful* number of poles of the exponential term in Eq.(5), which is apparently *affected* both by the *interaction* component of its total Hamiltonian (Fig. 1), as well as by its temperature, see Fig. 2(a). Indeed, $|\beta| = 1/k_BT \cong 11605$ eV^{-1} at T = 1 K, while its *dimensionless* counterpart reads: $|\underline{\beta}| = [E_{int}^{avr}(E_T) / k_BT] \cong 11605$ at $E_{int}^{avr}(E_T)$ = 1 eV. Furthermore, now the (dimensional and dimensionless) Matsubara frequencies might be defined as follows: $\omega_n = 2\,\pi\,i\,k_B\,T\,n$ [2, 3] and $\underline{\omega}_n = (2\,\pi\,i\,k_B\,T\,n) / E_{int}^{avr}(E_T)$ (respectively). It is noteworthy, that poles of the exponential term in Eq.(5) as well as just defined above Matsubara frequencies are *always* located on the *imaginary* axes of the appropriate *complex plane*, see Fig. 2(a), (b).

Thus, the *physically meaningful* number of those poles might be evaluated based on an idea formalized by Eq.(3), where the *limited* integration range of [0, β] is implemented. Consequently, the 'Matsubara' correction function $\Theta_M(E_T, T)$ to Eq.(5) – the counterpart of the ℵ(1/T) term – might be introduced based on the meaningful number of the poles of its exponential term, emerged in the *complex time* domain:

$$\Theta_M\left(E_T, T\right) = \exp\left[-\int_0^{\beta} E_{\rm int}^{avr}(E_T)\,d\tau\right] = Int\left[\frac{E_{\rm int}^{avr}(E_T)}{2\pi k_B T}\right] + 1, \qquad (8)$$

here *Int* denotes a function, which returns the *integer* part of its *rational* argument, and with the unity term in right-hand side yields the *total* integer number of poles, located *within* the *imaginary* integration range of [0, β]; while the $E_{int}^{avr}(E_T)$ function 'embedded' in the latter equation is defined by Eq.(7) above.

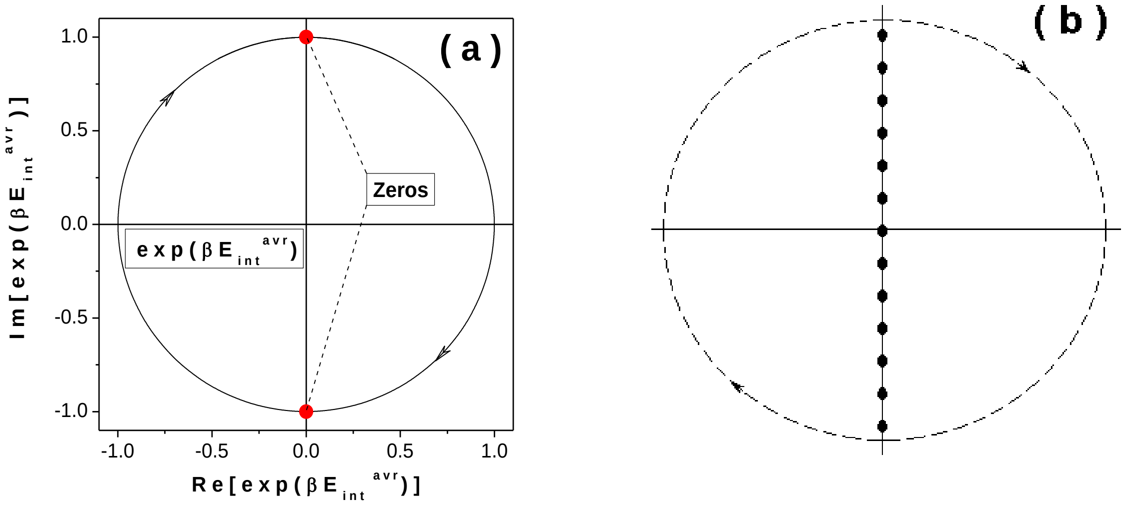

FIG. 2 (a), (b) (color online). Schematic illustration of (**a**) periodic behavior of the *inverse* exponential term in Eq.(5) (comprises of only *'interaction'* component of its total Hamiltonian!) on the complex plane with two its zeros located on the imaginary axis, and (**b**) the Matsubara integration contour (dashed curve). The black dots in figure (**b**) are located on the *imaginary* frequency axis and indicate positions of *bosonic* Matsubara frequencies on the complex frequency plane. See also figure (**a**) and main text for more details.

Spectral and temperature dependencies of the $\Theta_M(E_T, T)$ function, defined by Eqs.(7.8) are illustrated in Fig. 3(a), (b) for a case of r1 = 1, and <100>-oriented polycrystalline diamond with $\mathcal{L}_x = \mathcal{L}_y = \mathcal{L}_z = 1.0$ μm.

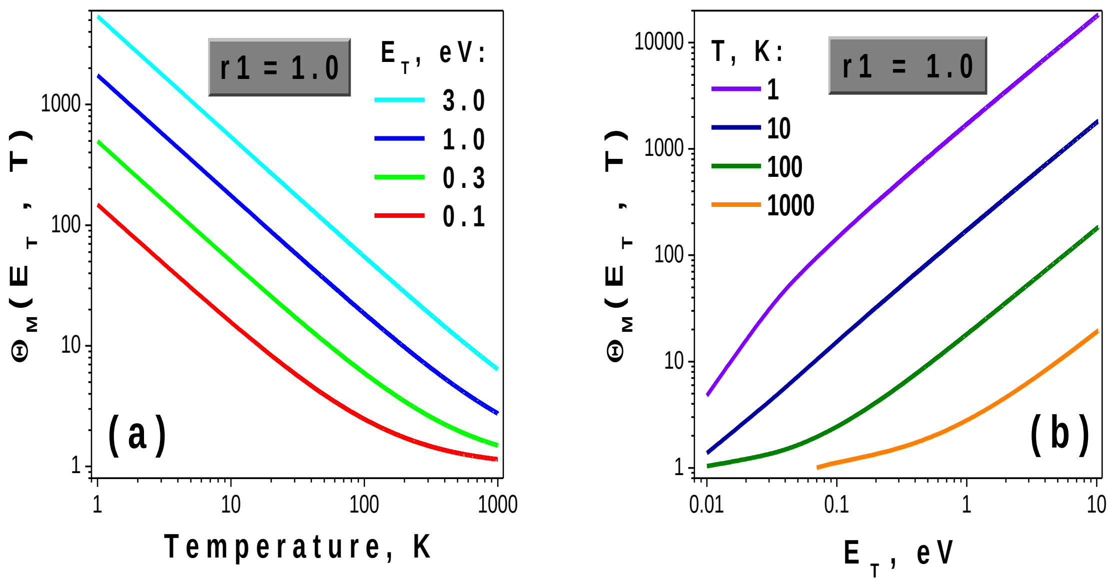

FIG. 3 (a), (b) (color online). Effects of (**a**) the absolute temperature T and (**b**) aggregate energy E_T of the phonon ensemble on the $\Theta_M(E_T, T)$ function, defined by Eqs.(7, 8) at r1 = 1.0 for a case of <100>-oriented polycrystalline diamond with $\mathcal{L}_x = \mathcal{L}_y = \mathcal{L}_z = 1.0$ μm. The plotted curves are eventually obtained via replacement of the *Int* function in Eq.(8) with its *rational* argument. Mind double-logarithmic scale(s) for both panels of the figure.

Subsequently, Eq.(5) might be modified as follows:

$$W_D(E_T) \cong \Theta_M(E_T,T)\, exp\left(-\frac{E_T}{k_BT}\right) \int_{M0}^{M_M} \frac{1}{\Gamma(M+1)(Z_M)^{r2}} \left[\frac{2\mathcal{L}_x\mathcal{L}_y\, \mathrm{F}(\mathcal{L}_x,\mathcal{L}_y,\mathcal{L}_z)\, E_T^2}{M^{r1}(hc_l)^2}\right]^M dM\,. \quad (9)$$

It is noteworthy, that left-hand half of the complex plane in Fig. 2(a) corresponds to *negative* Re{exp[$\beta E_{int}^{avr}(E_T)$]} quantities, which formally implies *negative probability* [$W_D(E_T)$ function(s)] defined by Eq.(9). In order to overcome this problem, total contribution from 'Matsubara correction(s)' (expressed by $\Theta_M(E_T, T)$ term – or Eq.(8)), is routinely evaluated via integration (summation) over *poles* of the Gibbs-Boltzmann term (with the purely *interaction* Hamiltonian!) in Eq.(5) in its *complex* time (or frequency) domain(s), following refs. [2, 3] and discussion just above herein.

Based on Eqs.(7, 8), which provide the physically meaningful number of poles of exponential term of Eq.(5), and evaluation results illustrated in Fig. 3(b), the *dimensionless* 'Matsubara correction' term $\Theta_M(E_T, T)$ apparently might be approximated with a *linear function* of E_T at a given temperature T:

$$\Theta_M(E_T,T) \;=\; \Theta_M^0(E_{\min},\, T) * E_T\,, \qquad (10)$$

where E_{min} is a low limit of aggregate energy of the ensemble of acoustic phonons, imposed by presence of morphology (non-homogeneities), while $\Theta^0_M(E_{min}, T) = [\Theta_M(E_{min}, T)/E_{min}]$ is a *dimensional* (of eV^{-1}) and *temperature-dependent* factor; Eq.(10) valids at ($E_T \geq E_{min}$) and ($E_T \geq k_BT$). Therefore, due to Eq.(15D) in ref. [1] and Eq.(10) above, the 'partition function', Z_M, for the 'isotropic version' of the Eq.(9) reads:

$$Z_M = \Theta_M^0(E_{min},T)(k_BT)^{[2(M+2)]}\, \Gamma\left[(2M+2), \left(\frac{E_{min}}{k_BT}\right), \left(M\frac{k_B\theta_D}{k_BT}\right)\right] \left[\frac{2\mathcal{L}_x\mathcal{L}_y\, \mathrm{F}(\mathcal{L}_x,\mathcal{L}_y,\mathcal{L}_z)}{M^{r1}(hc_l)^2}\right]^M, \quad (11)$$

where $\Gamma(m, z_0, z_1)$ is the 'generalized incomplete Gamma function' [5] with m = (2M + 2), z_0 = (E_{min}/k_BT), $z_1 = [M * k_B\theta_D/(k_BT)] = M\theta_D/T$. It is noteworthy that the *dimension* of Z_M functions defined by Eq.(11) is still expressed in eVs; i.e., it remains *unchanged* as compared to its counterpart expressed by Eq.(15D) in ref. [1]: enlargement in the (rational) power of the (k_BT) term is 'compensated' by appearance of the dimensional $\Theta^0_M(E_{min}, T)$ one. Thus, though the dimensionless 'Matsubara correction' function $\Theta_M(E_T, T)$ well exceeds 10^3 at T ≈ 1 K and $E_T \geq 1$ eV [Fig. 3(b)], its ultimate effect on the $W_D(E_T)$ distribution defined by the Eq.(9) would be eventually reduced due to 'normalizing' effect of the partition function Z_M (statistical sum). Similar 'Matsubara correction' might be also 'embedded' readily into an *anisotropic* version of the basic equation of GSM [1].

Thus, depicted above 'Matsubara correction' is expected to work well for *polycrystalline* semiconductors and insulators at a *finite* temperature. Furthermore, such 'Matsubara correction' is expected to *remain valid* even at *zero* temperature for many *amorphous* solid semiconductors and insulators, where spatial atomic positions are commonly expected to be *time-independent* (static) – though generally *affected* by the 'freeze-in' temperature, established at the material formation (e.g., Eq.(37) on p.81 of ref. [1]). In other words, those atomic positions are still subjected to evolution in the 'imaginary time', though 'traditional' meaning [2] of the 'imaginary time' has to be amended, and rather linked to the (inverse) *'freeze-in'* temperature – than to inverse actual absolute temperature of the material. It is noteworthy, that different versions of the *GSM* enable such kind of 'Matsubara correction(s)' readily, while many others well-known approaches to simulation on near-band-gap and intra-gap electronic density-of-states (DOS) in disordered semiconductors (e.g., the semi-classical [8] and Halperin-Lax [9] ones) do not comprise the exponential Gibbs-Boltzmann term and might not be 'corrected' in this way. Furthermore, in spite of certain *formal* similarity among the path-integral-based formalism [10] and Matsubara one, the physical backgrounds of those formalism and even their mathematical expressions are significantly different. Indeed, the *real-time action* (i.e. a time-dependent integral over a potential) in the canonical path integral formalism has to be transformed into *imaginary-time* integration within framework of Matsubara's approach via (formal) implementation of so-called 'Wick rotation', see ref. [7], p.12. In general, both path-integral and Matsubara formalisms are equally applicable to bosonic and fermionic ensembles, though the path-integral usually *oscillates far more strongly* (with alterations in its sign!) as its argument vary, mainly due to relatively low $\hbar$ quantity (the *dimensional* $k_BT/\hbar$ ratio is ~1.309 x 10^{11} at T = 1 K in appropriate SI units).

Therefore, the path-integral technique was widely implemented (e.g., refs. [10 – 12]) to relatively small (with the typical spatial extent of just very few Angstroms) parts of *electronic* sub-system, *interacting* with their ionic counterparts, while direct contributions from the quantized atomic vibrations (phonons) are usually 'integrated out' (eliminated) within the path-integral cum Lagrangian formalisms [10 – 12].

The overall contribution even from non-normalized 'Matsubara correction' to the basic equations of the GSM [1] is expected to be relatively *small* for *polycrystalline* and *spatially non-homogeneous amorphous semiconductors and insulators* with typical sizes of non-homogeneities (grains) of the order of **~ 1 μm** – or even sub-micrometer – (especially at elevated – e.g., room – temperature T and relatively low (E_T < 1 eV) aggregate energy of the phonon ensemble) as compared to effects caused by variation in the GSM model parameters, r1 and r2, in Eqs.(5, 9). Indeed, contribution from the main integrand term in Eqs.(5, 9) (located within square brackets in those equations) is ~$2.40\text{x}10^{9}$ at E_T = 1 eV, M = 1, r1 = 1 and r2 = 1 for the <100>–oriented polycrystalline *diamond* with $\mathcal{L}_x = \mathcal{L}_y = \mathcal{L}_z$ = 1 μm, which *exceeds* even low-temperature contribution from the $\Theta_M(E_T, T)$ term by a factor of ~$1.37\text{x}10^{6}$, though this ratio apparently becomes *much larger* at elevated (e.g., 'room') temperatures. Similar ratios are expected as well for others polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators, when dimensions $\mathcal{L}_x$, $\mathcal{L}_y$ and $\mathcal{L}_z$ of their non-homogeneities are of $\mathcal{L}_x \approx \mathcal{L}_y \approx \mathcal{L}_z \approx$ 1 μm. Thus, relatively *small* room-temperature 'Matsubara corrections' are generally expected for an ensemble of acoustic phonons confined within grains, columns, cones (etc.) of those *polycrystalline* and *spatially non-homogeneous amorphous semiconductors and insulators* at *elevated temperatures*. This statement might be verified independently: integration over the imaginary time is expected to yield just a *partition function* (for the aforementioned bosonic ensemble) at $\beta \to 0$ (i.e., at $T \to \infty$) limit(s), see details on p.13 of the ref. [7].

On the other hand, contribution from the 'Matsubara correction' function might be significant or even dominant for ***nano-structured*** semiconductors and insulators (e.g., when $\mathcal{L}_x \approx \mathcal{L}_y \approx \mathcal{L}_z \approx$ 10 nm), especially at low temperature and relatively high aggregate energy of the mixed states of the confined ensemble of acoustic phonons. Indeed, in such a case, contribution from the integrand term in Eqs.(5, 9, 11) is expected to be diminished by ~6 orders of the magnitude (as compared to the discussed above case of the <100>-oriented polycrystalline diamond), while contribution from the 'Matsubara correction' function $\Theta_M(E_T, T)$ *remains unaffected* by alterations in the sizes of the non-homogeneities (crystallites).

Thus, following the fundamental idea pioneered by T. Matsubara in ref. [2], basic (and essentially *static*) equations (of original versions) of the GSM [1] might be 'corrected' in order to take into account effects of fluctuations in the absolute and/or 'freeze-in' temperature(s) of the ensemble of the confined acoustic phonons (via implementation of the dimensionless $\Theta_M(E_T, T)$ function, as it discussed above in this section), though such corrections are expected to be relatively small for polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators with micrometer- and sub-micrometer sizes of non-homogeneities (grains), but might be significant or even dominant for their nano-structured counterparts. In addition, the model parameters, r1 and r2, of the GSM, are typically invariable (fixed) for the given set of simulations even though the T and E_T quantities may vary for this set [1], while the introduced above $\Theta_M(E_T, T)$ function is apparently temperature- and energy- dependent, see Fig. 3(a), (b). Furthermore, the *static* plane-wave basis of the GSM [1] might be expanded readily in the time domain.

4. Dynamic Expansion of Plane-wave Basis for GSM

In contrast to the original *static* version of the GSM and closely related to it *static* Born-Huang expansion (see Appendix A and Appendix B in ref. [1]), the *single* plane-wave eigenfunction $\phi(\mathbf{r}, t)$ of the *pure state* (microstate) of the *longitudinal* Debye's acoustic phonon with the 'classical' linear dispersion $\omega_q = c_l q$, might be *expanded* readily ***both in time and spatial*** domains (i.e., formally represented within framework of Schrödinger's picture of quantum mechanics with *time-dependent* eigenstates), and linked to its characteristic frequency ω_q using analytical properties of the exponential (direct and inverse) Fourier transform(s) and well-known identities for Dirac's δ-function [6]:

$$\phi(\vec{r}, t) \propto \exp\left[-i\omega_q\left(t-t'\right)\right]\exp\left[-i\,\vec{q}\left(\vec{r}\,'-\vec{r}\right)\right] = \delta\left(t-t'\right)+\delta\left(\vec{r}\,'-\vec{r}\right) \equiv \delta\left(t=t'\right)+\delta\left(\vec{r}\,'=\vec{r}\right), \quad (6a)$$

where the quasi-wave-vector **q** of the plane wave (pure state of acoustic phonon) defines spatial orientation of the plane-wave-function and its evolution in the *space domain*; see also Eq.(6) in the previous section. Thus, in **contrast** to the *purely static* wavefunctions of the GSM and canonical Born-Huang expansion [1], the plane-wave-function expressed by Eq.(6a) apparently becomes *time-dependent* (dynamic) due to its *first* term in the right-hand side(s), but retains spatial *propagation direction* of the plane wave due to the *second* one. Furthermore, it is easy to show that the given plane wave (eigenfunction) of the confined *longitudinal* Debye's acoustic phonon apparently yields ***equal numbers*** of the poles (states), 'located' at $t_n = (2n + 1)\pi/(2\omega_q)$ and $\mathbf{r}_n = (2n + 1)\pi/(2\mathbf{q})$ in the time and spatial domains (respectively); here n is an *integer* index, varying in the range: $-Int(2L/d) \leq n \leq Int(2L/d)$, $L = [(\mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2)/3]^{1/2}$, while d is an *average* interatomic distance. This immediately implies that the crucially important (for generic solid state physics) **concept** of the **phononic DOS** implemented essentially in the original (static) versions of the GSM [1] **might be retained** even for the case of dynamic (time-dependent) expansion of the plane-wave basis of the GSM, though *actual number* of the ground phononic states corresponding to the given frequency $\omega_q = c_l q$ has to be *just multiplied* by the factor of 2 as compared to its original static version. Furthermore, as it was discussed in the previous section (see also Eq.(6) therein and Eq.(6a) above), the *dynamic* (time-dependent) *expansion* of the plane-wave basis expressed by the latter equation allows one to establish *a direct link* among *spectral characteristics* of the GSM and those of the conventional *equilibrium* GF $\check{G}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ with such basis (pure states), even though – in apparent distinction from the GSM – the $\check{G}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ function is rather defined based on parameters of *second-quantization operators* acting on the time-dependent wave-functions (of the phononic ensemble), than based on actual dynamic characteristics of those wavefunctions (pure states of the ensemble) [2 – 4]). On the other hand, interrelations among key features of the GSM (even with the dynamic plane-wave basis) and those of the *equilibrium Matsubara GF* even with the *same basis functions* (pure states) are far less straightforward.

Indeed, based on the fundamental idea pioneered by T. Matsubara in ref. [2], the *inverse* temperature of the (bosonic or fermionic) ensemble has to be treated as an *imaginary time*, and the first (exponential, Gibbs-Boltzmann) and the rest (i.e., evaluated based on the DOS concept) terms of the 'dynamic' version of the GSM (see also Eq.(5) herein) should *not* be any more considered as truly *independent* ones, but become *related intimately* and affected by the system evolution on its *complex* time plane. It is noteworthy, that such approach to description of excitations of the bosonic or fermionic ensembles at a *finite temperature* is the *genuine essence* of the whole Matsubara statistics and the (equilibrium) Matsubara GF [2 – 4]. One of the most straightforward consequences of implementation of this 'ideology' to a quantum ensemble with plane-wave basis is that the *spectral representation* (direct Fourier transform) of the basis time-dependent plane-wave-function (e.g., pure state of acoustic phonon) now becomes a function of two frequencies: the *real* plane-wave circular frequency ω_q (which characterize spatial *oscillations* of the plane waves, propagating freely in a direction defined by the quasi-wave vector $\mathbf{q}$) and the *imaginary* Matsubara frequencies ω_n (which are rather related to inverse *lifetime* of those plane waves between two consecutive scattering events and/or their spatial *decay*) [6]:

$$\Phi\left(\omega_n, \omega_q\right) = \frac{1}{i\omega_n + \omega_q} - \frac{1}{i\omega_n - \omega_q} \equiv \frac{2\omega_q}{\omega_n^2 + \omega_q^2}, \qquad (12)$$

with $\omega_q = c_l q$. The latter equation is valid for bosonic excitations with plane-wave basis [4]. The inverse *denominator* of very last term in right-hand side of Eq.(12) is also known as *spectral representation* of 'Matsubara thermal propagator' [6]. Indeed, its poles (on the complex frequency plane) are apparently defined by the characteristic frequencies, ω_q and ω_n, of the *dynamic* plane-wave function. In contrast, spectral characteristics of both static and dynamic versions of the GSM are eventually defined by the poles in their *spatial* and *complex time* domains, which are, however, linked *directly* to *real* frequencies of (either static or dynamic) *plane-wave* basis functions (microstates), and *imaginary* (Matsubara) frequencies of the exponential (Gibbs-Boltzmann) term in Eq.(5). This similarity establishes an unambiguous link among spectral characteristics of the GSM and those of equilibrium GF formalism(s), even though *traditional representation* of the plane-wave Debye acoustic phonon(s) would be *affected significantly* within framework of Matsubara GF formalism due to *strong temporal 'confinement' and decay* of those phonons, imposed by existence of the *imaginary* Matsubara frequencies, and *'truncating' effect* of the 'time-ordering' operator(s), which virtually impose considerable restrictions on *lifetimes* of those phonons. Instead, significant *lifetime restriction* of their *mixed states* within framework of the original GSM version(s) [1] is rather imposed by the *combined effects* of the freely propagating (within whole volume(s) of crystallites and non-homogeneities) plane waves (pure states) of Debye acoustic phonons – see Figs. 2D and 5D in Appendix D of ref. [1], as well as further discussion on this issue shortly below in this section.

As it is discussed briefly in the previous section (see also Fig. 2(a), (b) therein), in general, a whole (ultimately – *infinite*) set of Matsubara frequencies has to be taken into account at analysis of evolution of an ensemble on its *complex frequency* plane. However, summation even over an *infinite* set of the 'Matsubara thermal propagators' (with the conventional Matsubara frequencies, ω_n, evaluated based on the periodicity of Fourier expansion coefficients) often yields a *finite* (converging) expression [6]:

$$\frac{1}{\hbar|\beta|}\sum_{n=-\infty}^{n=\infty}\frac{1}{\omega_n^2+\omega_q^2} = \frac{1}{2\hbar\omega_q}\coth\left(\frac{|\beta|\hbar\omega_q}{2}\right) = \frac{1}{2\hbar\omega_q}\left[1+2n_{BE}\left(\hbar\omega_q\right)\right] \equiv n_{eff}\left(\hbar\omega_q\right), \quad (13)$$

where the 'conventional' Matsubara frequencies ω_n are numerated here by their *integer* (summation) index *n*, while $\coth(|\beta|\hbar\omega_q/2)$ denotes hyperbolic cotangent (of its argument), and $n_{BE}(\hbar\omega_q) = [\exp(\hbar\omega/k_BT) - 1]^{-1}$ stands for the *conventional* Bose-Einstein occupation factor of the phononic state corresponding to the frequency $\omega_q = c_l q$ [6]. This implies, that the right-hand side of Eq.(13) might be treated as an 'effective' occupation factor $n_{eff}(\hbar\omega_q)$ of a ground Debye's phononic state (with the plane-wave basis) of the (real and positive) frequency of ω_q. Since $\omega_{(n=0)} = 0$ for a bosonic ensemble [2 – 4] (see also Fig.2(b) in the previous section), the sum(s) in the right-hand side of Eq.(13) might diverge at $\omega_q \rightarrow 0$ (i.e., in this limit, behaves *similar* to the spectral dependence $n_{BE}(\hbar\omega_q)$ of the 'standard' Bose-Einstein occupation factor). However, even in polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators with micrometer-sized crystallites (non-homogeneities), the ω_q quantity is *always* non-zeroth due to effect of *phonon confinement* imposed by the limited spatial extent of those non-homogeneities. Therefore, the divergence in both $n_{eff}(\hbar\omega_q)$ and $n_{BE}(\hbar\omega_q)$ dependencies become *avoidable* even for those materials – not only for nano-structured semiconductors and insulators, where the phonon confinement effects are expected to be manifested in much *more profound* way (see, for instance, Fig. 4D in Appendix D of ref. [1]).

As it is shown in Fig. 4, spectral behavior of the room-temperature effective occupation $n_{eff}(\hbar\omega_q)$ factor *differs considerably* from that of the standard Bose-Einstein one, $n_{BE}(\hbar\omega_q)$, for ground states of ensemble of acoustic phonons of the diamond.

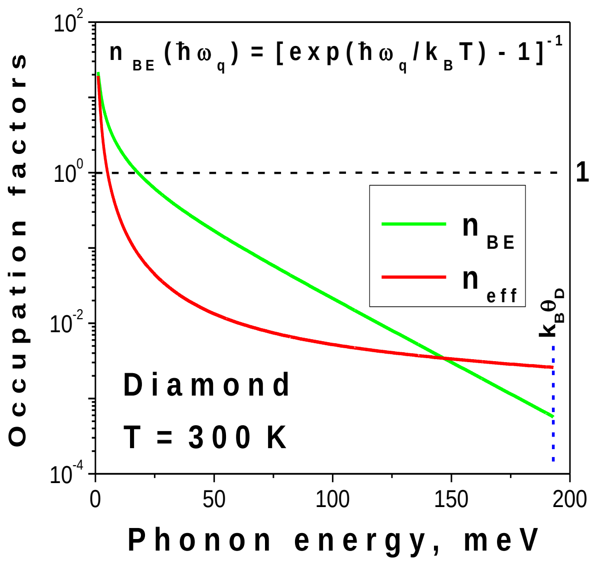

FIG. 4 (color online). The room-temperature spectral dependencies of the 'standard' Bose-Einstein occupation factor $n_{BE}(\hbar\omega_q)$ and its 'effective' counterpart $n_{eff}(\hbar\omega_q)$, defined by Eq.(13). Both dependencies are evaluated for *ground single-particle* states of Debye acoustic phonons of the diamond with its Debye energy of $k_B\theta_D = 193.0$ meV ($\theta_D = 2240$ K), indicated in the figure with the *vertical* dashed line. See further details in the main text.

In particular, it decays faster than the $n_{BE}(\hbar\omega_q)$ one with the $\hbar\omega_q$ enlargement at relatively low phonon energies ($\hbar\omega_q < 20$ meV), but much slower than that at relatively high ($\hbar\omega_q > 50$ meV) those energies, Fig. 4. It is noteworthy, that in case of a real semiconductor or insulator (e.g., diamond), both dependencies remain meaningful only within the phonon energy range, limited by *Debye energy*, $k_B\theta_D$: conventional (ground) single-phonon states with higher energies simply <u>*do not exist*</u> in an equilibrium state of the ensemble of acoustic phonons! Thus, both dependencies plotted in Fig. 4 become *truncated* at the $k_B\theta_D$ energy. Furthermore, average occupation factors of the *excited* and *coherent* states of the ensemble of *interacting* acoustic phonons might deviate from that derived routinely based on the standard Bose-Einstein statistics: see, for instance, Eq.(13) above.

The basic equation(s) of (static and dynamic versions) of the GSM incorporate such *interacting* excited states naturally: see Eq.(7), Fig. 1, and comments to them in the previous section. Furthermore, within the GSM framework, spectral characteristics of such excited and coherent states of longitudinal acoustic phonons are *always* composed based on eigenenergies of single Debye acoustic phonons, which allows one to retain traditional concept of the phononic DOS for those individual phonons, and insure that their basic quasi-wave vectors **q** are well-defined and always located within the first phononic Brillouin Zone (BZ). On the other hand, those excited and coherent states are always composed as *mixed* quantum states of the ensemble of acoustic phonons within the GSM framework, which eventually implies that quasi-wave vector of such mixed states becomes 'ill-defined' quantity – since their 'aggregate' quasi-wave vector is expected to *exceed significantly* the edge of the *first* phononic BZ. Moreover, typical *spatial extent* of those mixed states is *well comparable* with an *inter-atomic distance d* of a semiconductor (insulator): see Figs. 3D, 6D in Appendix D of ref. [1]. In other words, this spatial extent is (many) *orders* of the magnitude *shorter* than typical sizes of crystallites (non-homogeneities) in polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators. Thus, such mixed states are essentially *localized*, and could hardly be characterized by any meaningful wave-vector, even though longitudinal acoustic plane waves (*pure states* of Debye phonons) might propagate within the *whole volume* of those non-homogeneities without disruption [1], and are described by their well-defined vectors **q**, see Eq.(6a).

In contrast, Klauder's bosonic coherent states $\sim(N_C!)^{-1/2}\exp(-i\mathbf{q}_C\mathbf{r})$ [6, 7] are apparently well-defined for *photonic excitations* in vacuum, though they are usually characterized by a quasi-wave vector $\mathbf{q}_C$, located *well beyond* of the first BZ of the (longitudinal acoustic) *phonons*. Moreover, based on the 'classic' dispersion relation, $\omega = c_l q_C$, the phonon energy $\hbar\omega$ would routinely exceed its upper physical limit – the Debye's energy ($k_B\theta_D$) – defined for the ground states of acoustic phonons; see also comments to Eq.(5) and Fig. 4 above. All these apparently imply that the $\mathbf{q}_C$ quantity becomes 'ill-defined' as well even for Klauder's coherent *phononic* states, and so-called *Umklapp* processes have to be taken into account at a quantitative description of electron interactions with those phononic states and phonon-phonon interactions. Thus, similar to the *excited* and *coherent* states of the GSM, Klauder's phononic coherent states could hardly be associated as well with *propagating* thermal plane waves in solids, and should not be identified neither as *pure states* (microstates) of the phononic ensemble.

As a result, an effective occupation factor of *interacting* states of ensemble of acoustic phonons within framework of modified dynamic version of the GSM at r1 < 2 is generally expected to *deviate significantly* from Bose-Einstein occupation factor (originally obtained for *non-interacting* bosonic ensembles), which corresponds to 'model parameters' of r1 = 2 and r2 = 1 of the original version of GSM, depicted in ref. [1].

It is noteworthy as well, that the set of (dimensionless in such a case) Matsubara frequencies is *limited* (truncated) for the GSM – since it is defined based on the periodicity condition of the exponential term in Eq.(5); see also brief discussion in the previous section, and Eqs.(7, 8) therein. Consequently, within the GSM framework, *spectral density* of ensemble of acoustic phonons [6] (which generalizes traditional concept of conventional one-dimensional phononic DOS spectrum – since the latter one is not applicable directly within framework of the GF formalism) with the dynamic plane-wave basis might be linked in such a case directly to the *dynamic* DOS function, multiplied by the $\Theta_M(E_T, T)$ term. Thus, a *dynamic* counterpart of Eq.(9) now reads:

$$W_D(E_T) \cong \ exp\left(-\frac{E_T}{k_BT}\right)\int_{M0}^{M_M}\frac{1}{\Gamma(M+1)(Z_M)^{r2}}\left[\frac{4\mathcal{L}_x\mathcal{L}_y\,\mathrm{F}(\mathcal{L}_x,\mathcal{L}_y,\mathcal{L}_z)\,\Theta_M(E_T,T)\,E_T^2}{M^{r1}(hc_l)^2}\right]^M dM\,. \quad (14)$$

The 'partition function' Z_M for the Eq.(9), expressed by Eq.(11) above, now has to be amended as well:

$$Z_M = \ (k_BT)^{[2(M+1)]}\,\Gamma\left[(2M+1),\left(\frac{E_{min}}{k_BT}\right),\left(M\,\frac{k_B\theta_D}{k_BT}\right)\right]\left[\frac{4\mathcal{L}_x\mathcal{L}_y\,\mathrm{F}(\mathcal{L}_x,\mathcal{L}_y,\mathcal{L}_z)\,\Theta_M(E_T,T)}{M^{r1}(hc_l)^2}\right]^M. \quad (15)$$

Again, in the $T \to \infty$ limit, Eqs.(14, 15) are expected to coincide with their 'conservative' counterparts expressed for this case by the Eqs.(26a, 15D) in ref. [1] (respectively). In particular, Eq.(15) would yield the conventional 'partition function' at $\beta \to 0$ ($T \to \infty$) [7], see also Fig. 3(b) in the previous section. The Eq.(14) allows one to re-define the GSM parameter r1 as the energy– and temperature–dependent one: $r1(E_T, T, M) = 2 - \ln[\Theta_M(E_T, T)]/\ln(M)$; here $\ln(x)$ denotes the *'natural' logarithm* of x. Similarly, the r1 counterpart for Eq.(9) in previous section reads: $r1(E_T, T, M) = 2 - \ln[\Theta_M(E_T, T)]/[M_* \ln(M)]$. Both latter expressions apparently yield: $\underline{r1(E_T, T, M) = 2}$ at $\Theta_M(E_T, T) = 1$, though *diverge* at $M = 1$. It is noteworthy as well, that the $\Theta_M(E_T, T)$ function depends, in turn, on the *interaction Hamiltonian* of the GSM, defined by Eq.(7) in the previous section, and it is affected *decisively* by variations in the GSM parameter, r1: see Fig.1 and comments to it above.

Thus, the essentially *dynamic* formalism, depicted above in this section, might be implemented readily for quantitative evaluation of statistical properties of ensembles of acoustic phonons in polycrystalline and even spatially non-homogeneous *amorphous* semiconductors and related to them electronic and optical characteristics of those materials at a *finite temperature*, though original static plane-wave basis might be probably retained for amorphous semiconductors at zero temperature. This also expands further scope of the GSM, establishes its intimate relationship with the *equilibrium* conventional and Matsubara GFs, and inspires its direct implementation to the nano-structured semiconductors and insulators.

5. Conclusions

In summary, the GSM presented in ref. [1] might be treated as a kind of 'conservative' (and essentially *static*) ***counterpart*** to the well-known quantum Matsubara statistics (and closely related to it equilibrium conventional and Matsubara Green Functions formalisms [2 – 4]) for the particular cases of ensemble(s) of acoustic phonons confined within polycrystalline and spatially non-homogeneous amorphous semiconductors (insulators) with micrometer- and sub-micrometer sizes of non-homogeneities (crystallites), though the GSM apparently is not applicable directly to the ensemble of fermions and essentially uses the *static* Debye's *plane wavefunctions basis* (*pure* quantum states), while other convenient sets of basis functions (e.g., time-dependent eigenfunctions of the quantum harmonic oscillator, QHO) might be used as well within the generic framework of GF formalism(s) [3].

On the other hand, the *static* plane wave-functions basis of Debye acoustic phonons implemented within the GSM [1] allows one to use effectively advantages of the phononic *DOS concept* and *Christoffel Matrix* formalism (see Appendix C in ref. [1]), *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 long-range (e.g., *coherent*, *morphological*) and anisotropic effects (if any) in polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators [1], while routine implementation of others sets of the basis wave functions (e.g., QHO eigenfunctions) might not allow to utilize aforementioned advantages [3], and apparently would yield in (much) more time- and resource-demanding computations. Moreover, mentioned above long-range, morphological and anisotropic effects could hardly be expected to be taken into account appropriately within framework of GF formalism even at implementation of the plane-wave basis (eigenfunctions); e.g. those of the ensemble of Debye acoustic phonons; mainly due to *strong temporal 'confinement' and decay* of those phonons, imposed by presence of the *imaginary* Matsubara frequencies in the spectrum of this ensemble, and *'truncating' effect* of the 'time-ordering' operator(s). Both aforesaid effects virtually restrict *nominal* spatial propagation ranges and lifetimes of those phonons, and make *questionable* an implication of the *conventional concept* of phononic DOS within framework of GF formalism. On the other hand, the basis and scope of the GSM might be expanded even further based on the fundamental ideas, pioneered by Takeo Matsubara in ref. [2].

In particular, the *essentially static* set of the basis wavefunctions of the original version of the GSM [1] might be expanded readily using the *time-dependent* (dynamic) plane-wave basis for *pure* states (microstates) of Debye acoustic phonons. Importantly, that such dynamic expansion allows one to retain almost entirely *vital features* of the conventional (static) phononic DOS concept (essentially used in original versions of the GSM [1]) and *key* structures of its *basic equations*. Furthermore, such kind of dynamic expansion allows one to establish physically *unambiguous link* among spectral characteristics of the (original, *static*, and modified, *dynamic*, versions of) GSM and those of *equilibrium* conventional and Matsubara Green Functions. In addition, the fixed model parameters r1 and r2 (which are linked closely to the number of available states in the phase space of a single acoustic phonon, and intensity of phonon-phonon interactions in the original version of the GSM [1]) might be re-defined readily as the energy- and temperature-dependent ones, following the 'Matsubara style'. All these validate rigorous physical background for the basic ideas and principal equations of (both original, *static*, and modified, *dynamic*, versions of) the GSM, and inspire its direct implementation to appropriate quantitative descriptions of statistical characteristics of phononic excitations with the plane-wave basis in *nano-structured* semiconductors and insulators as well as to their near-band-gap and intra-gap electronic and optical spectra.

References

1. V. Ligatchev, *Polycrystalline and Spatially Non-Homogeneous Amorphous Semiconductors and Insulators*. Nova Science Publishers, Hauppauge, N.Y.: 2017, pp 1 – 289.
2. T. Matsubara, *Prog. Theor. Phys.* **14**, 351 (1955).
3. K. Balzer, M. Bonitz, *Nonequilibrium Green's Functions Approach to Inhomogeneous Systems*. Springer, 2013, **XII**, pp 1 – 130.
4. A. A. Abrikosov, L. P. Gor' kov, and I. E. Dzyaloshinskii, *Soviet Physics JETP*, **36**, 636 (1959).
5. *Handbook of mathematical functions: with formulas, graphs, and mathematical tables* / Abramowitz, M.; Stegun, I. A. Eds.: Dover, New-York, N.Y.: 1965, pp 1 – 1046.
6. Ch. G. van Weert, *An Introduction to Real- and Imaginary-time Thermal Field Theory*, Amsterdam, 2001, pp 1 – 99.
7. N. Dipius, Chapter 1, In: *Functional Integrals*, 2014, pp 1 – 172.
8. E. O. Kane, *Phys. Rev.* **131**, 79 (1963).
9. B. I. Halperin, M. Lax, *Phys. Rev.* **148**, 722 (1966), *ibid* **153**, 802 (1967).
10. R. P. Feynman, A. R. Hibbs, *Quantum Mechanics and Path Integrals*, McGraw Hill, New York, 1965.
11. C. H. Grein, Sajeev John, *Phys. Rev. B* **39**, 1140 (1989).
12. S. Fratini, P. Quémerais, *Eur. Phys. J. B* **14**, 99 (2000).

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