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-particle 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 are discussed herein in comparison to those of quantum statistics pioneered by 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 (grains) of polycrystalline 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) states 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 bosonic (phononic) excitations with static (time-independent) plane-wave basis (pure states) in amorphous and/or crystalline solids. 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, which yield the given aggregate energy of the ensemble [1]. Furthermore, the GSM implies that those fluctuations in the ensemble of confined longitudinal acoustic phonons with 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 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 [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, proportional to the inverse 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 significant or dominant. Herein consequences of aforementioned effects are evaluated only for solid polycrystalline and amorphous semiconductors and insulators, including nano-structured ones, and discussed in comparison with features of the GSM [1].
2. Key Features of Matsubara statistics

In a thermal equilibrium, averaged (statistical) characteristics of pure or mixed (static 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, $\rho_D$ [3]:

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

where $\text{Tr}[\exp(-H_0/k_B T)]$ denotes trace (i.e., sum of its diagonal elements) of the matrix exponential of the weighted ‘thermal’ Hamiltonian matrix ($H_0/k_B T$), and $k_B$ is the Boltzmann constant. This $\rho_D$ operator is Hermitian, positive definite and normalized: $\text{Tr}[\rho_D] = 1$ [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 are time-independent (static), while the operators (Hamiltonian) does change in time.

Essential generalization of concept of equilibrium statistics of (bosonic or fermionic) ensemble with a time-dependent (dynamic) basis was achieved via introduction of a single-particle two-points Matsubara ‘Green Function’ (GF), expressed herein using a coordinate representation [4]:

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

where $\vec{r}_1$, $\tau_1$ and $\vec{r}_2$, $\tau_2$ stand for spatial and imaginary time ‘coordinates’ of the first and second points of an Euclidian space-time continuum, $\mu$ is a chemical potential of the ensemble, $\Psi_\alpha(\vec{r}, \tau)$ is imaginary-time-dependent operator, acting on (time-independent) wavefunction(s) (eigenstates) (enumerated by their index $\alpha$) of the ensemble, and $\Psi_\alpha^*(\vec{r}, \tau)$ is its complex-conjugate (adjoint), $T_\tau$ is so-called ‘time-ordering’ operator with respect to the imaginary time, while $N(1/T)$ is a form of ‘density matrix’, defined (based on a generic identity) as follows [4]:

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

where $i = \sqrt{-1}$, $\beta = 1/(k_B T)$, $\tau = \beta i$, and $H_{\text{int}}(t)$ is a (time-dependent) ‘interaction Hamiltonian’ 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 $\bar{G}(\vec{r}_1, \tau_1, \vec{r}_2, \tau_2)$, the Matsubara’s ‘equilibrium’ two-point GF $\bar{G}_M(\vec{r}_1, \tau_1, \vec{r}_2, \tau_2)$ specified by Eq.(2), was established in ref. [2] via substitution of real-time variable $t$ of the conventional GF with its ‘imaginary time’ counterpart $\tau = -it$, which is also related directly to the inverse temperature $\beta$ of the ensemble (i.e., via so-called ‘Wick rotation’). This idea was apparently inspired by the structure of the Minkowski (relativistic) space-time metric, which comprises of imaginary time axis. Furthermore, in an equilibrium 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 fluctuation(s) in its local temperature.

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]. The Eq.(3) might be eventually re-formulated in a more compact (and yet generic) form [3]:

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

here $t_0$ is 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 (time-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 $\omega_n$, which are routinely defined for bosonic ensemble based on periodicity conditions of those exponential terms: $\exp(i \omega_n \mathbf{q}) \equiv 1$ [2–4]. Consequently, in general, integration over imaginary time in Eq.(3) might be replaced with (finite) summation over the Matsubara frequencies. However, in apparent contradiction with Eqs.(3, 4), those Matsubara frequencies 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 mentioned above periodicity condition, one readily obtains: $\beta \omega_n = 2 \pi n [5]$ or $\omega_n = 2 \pi k_B T_n$ (n herein is an integer index) [2, 3]. At $T = 1 \text{K}$ and $n = 1$, this periodicity condition yields: $\omega_1 = 2 \pi k_B T = 5.414 \times 10^4 \text{eV}$. The higher Matsubara frequencies are just proportional (topple) to the $\omega_1$ quantity. Similar Matsubara frequencies might be defined readily as well for a fermionic ensemble [2–4]. Thus, fluctuations (and ‘interactions’) in parameters of either bosonic or fermionic ensemble might be taken into account via appropriate expansion over the imaginary time scale 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 quantum statistic of condensed systems [3, 4]. In addition, it was advanced further by T. Matsubara in order to set up diagrammatic perturbation theory for grand partition function 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 (confined) plane-wave-functions (pure states of Debye acoustic phonons) as well as its ‘partition function’, $Z_M [1]$:

$$W_P(E_T) \equiv \exp \left( - \frac{E_T}{k_B T} \right) \int_{\Omega_0} \frac{1}{\Gamma(M + 1)(Z_M)^{\frac{1}{2}}} \left[ \frac{2 \mathcal{L}_x \mathcal{L}_y \mathcal{F}(\mathcal{L}_x, \mathcal{L}_y, \mathcal{L}_z) E_T^2}{\mathcal{M}^{(M)}(hc)^2} \right] dM,$$

where $W_P(E_T)$ denotes probability density of finding of the ensemble of confined (within a parallelepiped crystalline, column, cone, etc.) Debye acoustic phonons in a mixed state with its aggregate energy of $E_T$, $\Gamma(M)$ is Euler’s Gamma-function [5], $h$ is the Planck’s constant, $c_i$ 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 $\mathcal{F}(\mathcal{L}_x, \mathcal{L}_y, \mathcal{L}_z)$ 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 $M_0$ and $M_0$ limits), while the (rational) model parameters $r_1$ and $r_2$ are typically varying in the following ranges: $0.5 \leq r_1 \leq 2$; $0.5 \leq r_2 \leq 1 [1]$. In spite of significant differences in notations, structures of Eq.(2, 5) exhibit apparent similarities, in particular, at $\mu = 0$. Furthermore, close formal interrelations among those equations might be established readily for a specific case of the ensemble of acoustic phonons with the plane-wave basis and ‘classical’ linear dispersion: $\omega_0 = c_q q$ (here $\omega_0$ corresponds to the quasi-wave vector $q$).

Indeed, first of all, unambiguous interrelations between ‘conventional’ two-points GF $\tilde{G}(\mathbf{r}_1, \mathbf{t}_1, \mathbf{r}_2, \mathbf{t}_2)$ and the ‘conservative’ Eq.(5) really do exist in such a case due to the following well-known identities [5]:

$$\exp \left[ - i \omega_q (t - t') \right] \exp \left[ - i \mathbf{q} \cdot (\mathbf{r}' - \mathbf{r}) \right] = \delta(t - t') \delta(\mathbf{r}' - \mathbf{r}) = \delta(t = t') \delta(\mathbf{r}' = \mathbf{r}).$$

Thus, based on those identities, parameters of the ‘conventional’ GF, defined at two points $[(\mathbf{r}, t), (\mathbf{r}', t')]$ of Euclidian space-time continuum are linked directly to a number of single-point (with coordinates of $(\mathbf{r}, t)$) poles (states) of the plane wave with the angular frequency $\omega_q$, propagating within the continuum. On the other hand, number of single-phonon states in integrand of Eq.(5) 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. Similar interrelations might be established as well between Eq.(5) and Matsubara GF, defined in space-time metric with an imaginary time axis. Furthermore, an appropriate sum (over all available indexes α) of the products \( \{ \Psi_\alpha(\mathbf{r}, \tau) \cdot \Psi_\alpha(\mathbf{r}, \tau) \} \) 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 \( V_p = \mathbf{L}_1 \cdot \mathbf{L}_2 \cdot \mathbf{L}_3 \) has to be defined by integration over the aforementioned phonon density, and over the whole volume, \( V_p \). Furthermore, 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 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, for instance, 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 \( \mathbf{q} \) quantity for all its components) and/or excited (with non-equivalent \( \mathbf{q} \) 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: \( \sim (n!c!)^{1/2} \exp(-i\mathbf{q}_c \cdot \mathbf{r}) \) \([6, 7]\); here \( n \) 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 \( \Gamma(M+1)^{1/3} \) term in Eq.(5) at \( M = n \). 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’ \( \mathcal{N}(1/T) \), 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 \( \mathcal{N}(1/T) \) term might be introduced readily for the Eq.(5). Indeed, formally, the given scalar \( \mathcal{E}_T \) quantity in the exponential term of Eq.(5) might be treated as particular case of a (single-valued) equilibrium (static) Hamiltonian, which causes the system evolution only on the imaginary time scale \( \tau \). However, 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) \( \Theta_{\alpha}(\mathcal{E}_T, \tau) \) function might be introduced based on a meaningful number of poles of the exponential term in Eq.(5), which is are apparently affected by the (aggregate) energy of the mixed state of the phononic ensemble, as well as by its temperature, see Fig. 1(a). Indeed, \( \beta = 1/\mathcal{E}_T \mathcal{T} \equiv 11605 \text{ eV}^{-1} \) at \( T = 1 \text{ K} \), while its dimensionless counterpart reads: \( \beta = (\mathcal{E}_T/\mathcal{T}) \equiv 11605 \) at \( \mathcal{E}_T = 1 \text{ eV} \). Furthermore, now the (dimensional and dimensionless) Matsubara frequencies might be defined as follows: \( \omega_\alpha = 2\pi\mathcal{E}_T n \) \([2, 3]\) and \( \omega_\alpha = (2\pi\mathcal{E}_T n) / \mathcal{E}_T \) (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. 1(a). (b).

Thus, the physically meaningful number (range) of those frequencies might be truncated, and evaluated following an idea formalized by Eq.(3), where the integration range \([0, \beta]\) is implemented. Consequently, the following ‘Matsubara’ correction function \( \Theta_{\alpha}(\mathcal{E}_T, \tau) \) to the Eq.(5) – the counterpart of the \( \mathcal{N}(1/T) \) term – might be introduced based on the meaningful number of poles of its exponential term:
\[
\Theta_m \left( E_T , T \right) = \exp \left( -i \int_0^{\beta} E_T \, d\tau \right) = \text{Int} \left( \frac{E_T}{2\pi k_B T} \right) + 1, \quad (7)
\]

where \( \text{Int} \) denotes a function, which return the integer part of its argument, and unity term in right-hand side arises due to the zeroth Matsubara frequency of the phononic ensemble, see Fig.1(b). Spectral and temperature dependencies of the \( \Theta_m(E_T, T) \) function are illustrated in Fig. 2(a), (b).

**FIG. 1** (a), (b) (color online). Schematic illustration of (a) periodic behavior of the inverse exponential term in Eq.(5) 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.

**FIG. 2** (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 Eq.(7). The plotted curves are obtained via replacement of the \( \text{Int} \) function in this equation with its rational argument. Mind double-logarithmic scale(s) for both panels of the figure.
Subsequently, Eq.(5) might be modified as follows:

$$W_D(E_T) \cong \Theta_M(E_T, T) \exp \left( -\frac{E_T}{k_B T} \right) \int_{0}^{M_M} \frac{1}{\Gamma(M + 1)} (Z_M)^{M} \left[ \frac{2L_x L_y F(L_x, L_y, L_z)}{M^{r+1} (\hbar c)^2} \right]^M dM. \quad (8)$$

It is noteworthy, that left-hand half of the complex plane in Fig.1(a) corresponds to negative Re[$\exp(iE_T\beta)$] quantities, which formally implies negative probability [$W_D(E_T)$ function(s)] defined by Eq.(8). In order to overcome this problem, total contribution from ‘Matsubara correction(s)’ (expressed by $\Theta_M(E_T, T)$ term – or Eq.(7)), is routinely evaluated via integration (summation) over Matsubara frequencies $\omega_n$ defined on the complex frequency plane – following refs. [2, 3] and discussion just above herein, see also Fig.1(b).

Based on Eq.(7), as well as on (physically meaningful) number of poles of exponential term of Eq.(5) evaluated above in the main text and illustrated in Fig. 2(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 $T$:

$$\Theta_M(E_T, T) = \Theta_M^{(0)}(E_{\text{min}}, T) \ast E_T. \quad (9)$$

where $E_{\text{min}}$ is a low limit of aggregate energy of the ensemble of acoustic phonons, imposed by presence of morphology (non-homogeneities) in the studied (isotropic but spatially non-homogeneous) polycrystalline or amorphous semiconductor (insulator), and defined by the Eq.18B in ref. [1], while $\Theta_M^{(0)}(E_{\text{min}}, T) = [\Theta_M(E_{\text{min}}, T) / E_{\text{min}}]$ is a dimensional (of eV$^{-1}$) and temperature-dependent factor; Eq.(9) valids at ($E_T \geq E_{\text{min}}$) and ($E_T \geq k_B T$).

Therefore, based on Eq.(15D) in ref. [1], the ‘partition function’, $Z_M$, for the ‘isotropic version’ of the Eq.(8) reads:

$$Z_M = \Theta_M^{(0)}(E_{\text{min}}, T)(k_B T)^{2(M+2)} \Gamma \left[ (2M + 2), \left( \frac{E_{\text{min}}}{k_B T} \right), \left( \frac{M k_B T}{k_B T} \right) \right] \left[ \frac{2L_x L_y F(L_x, L_y, L_z)}{M^{r+1} (\hbar c)^2} \right]^M, \quad (10)$$

where $\Gamma(m, z_0, z_1)$ is the ‘generalized incomplete Gamma function’ [5] with $m = (2M + 2)$, $z_0 = (E_{\text{min}} / k_B T)$, $z_1 = [M \cdot k_B T / (k_B T)] = M \Theta_M^{(0)} / T$. It is noteworthy that the dimension of $Z_M$ functions defined by Eq.(9) 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 ($k_B T$) term is ‘compensated’ by appearance of the dimensional $\Theta_M^{(0)}(E_{\text{min}}, T)$ one. Thus, though the dimensionless ‘Matsubara correction’ function $\Theta_M(E_T, T)$ well exceeds $10^9$ at $T \approx 1$ K and $E_T \geq 1$ eV (Fig. 2(b)), its ultimate effect on the $W_D(E_T)$ distribution defined by the Eq.(8) 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, the depicted above ‘Matsubara correction’ is expected to work well for crystalline semiconductors and insulators at a finite temperature. Furthermore, the ‘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 ‘freezing-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) ‘freezing-in’ temperature – than to 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-band-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 varies, mainly due to relatively low \( h \) quantity (the dimensional \( k_B T/h \) ratio is \( 1.309 \times 10^{11} \) 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 sum Lagrangian formalisms [10–12].

The overall contribution even from non-normalized ‘Matsubara correction’ to the basic equations of the GSM is expected to be relatively small for polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators with the typical sizes of non-homogeneities (grains) of the order of \( 1 \) \( \mu \)m – 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 \( r_1 \) and \( r_2 \) in Eqs.(5, 8). Indeed, contribution from the ‘Matsubara correction’ function is expected to yield just a small contribution from the ‘Matsubara correction’ function \( \Theta_M(E_T, T) \) to relatively small \( (E_T < 1 \) eV) aggregate energy of the phonon ensemble as compared to effects caused by variation in the GSM model parameters \( r_1 \) and \( r_2 \) in Eqs.(5, 8). Indeed, contribution from the main integrand term in Eqs.(5, 8) (located within square bracket in those equations) is \( \approx \frac{2.40x10^9}{E_T = 1 \) eV, \( M = 1, \) \( r_1 = 2 \) and \( r_2 = 1 \) for the \( <100> \)-oriented polycrystalline diamond with \( L_x = L_y = L_z = 1 \) \( \mu \)m, and exceeds even low-temperature contribution from \( \Theta_M(E_T, T) \) term by a factor of \( \approx 1.30x10^6 \), though this ratio apparently becomes much large 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 \( L_x, L_y, \) and \( L_z \) of their non-homogeneities are of \( L_x \approx L_y \approx L_z = 1 \) \( \mu \)m. 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 nanostructured semiconductors and insulators (e.g., when \( L_x \approx L_y \approx L_z = 10 \) nm), especially at low temperature and relatively high aggregate energy of the ensemble. Indeed, in such a case, contribution from the integrand term in Eqs.(5, 8, 10) 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.

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 \( r_1 \) and \( r_2 \) 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. 2.(a, b). Furthermore, the static plane-wave-function basis of the GSM [1] might be expanded readily in the time domain.

4. Dynamic Expansion of Plane-wave Basis for GSM and its Relation to GF Formalism

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 ‘classical’ linear dispersion \( \omega_0 = c_0 q \), might be expanded readily both in time and spatial domains (i.e., represented within framework of Schrödinger’s picture of quantum mechanics with time-dependent eigenstates), and linked to its characteristic frequency \( \omega_0 \) using analytical properties of the exponential (direct and inverse) Fourier transform(s) and well-known identities for Dirac’s \( \delta \)-function [6]:

\[
\phi(\mathbf{r}, t) \propto \exp[-i\omega_q (t-t')] \exp[-i q (\mathbf{r'}-\mathbf{r})] = \delta(t-t') \delta(\mathbf{r'}-\mathbf{r}) = \delta(t-t') \delta(\mathbf{r'}=\mathbf{r}), \quad (11)
\]
where the quasi-wave-vector \( \mathbf{q} \) 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.(11) 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 longitudinal Debye’s acoustic phonon apparently yields equal numbers of the poles (states) in the spatial and time domains. 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 \( \omega_0 = c q \) 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.(11) 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 \( \tilde{G}(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2) \) with such basis (pure states), even though – in apparent distinction from the GSM – the \( \tilde{G}(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2) \) 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) \( \{2 \rightarrow 4\} \). On the other hand, interrelations between 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 a complex 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 essentially 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 (equilibrium) Matsubara GF \( \{2 \rightarrow 4\} \). 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 \( \omega_0 \) (which characterize oscillations of the plane waves propagating in a direction defined by the quasi-wave vector \( \mathbf{q} \)) and the imaginary Matsubara frequencies \( \omega_n \) (which are rather related to lifetime of those plane waves between two consecutive scattering events and/or their spatial decay) [6].

\[
\Phi(\omega_n, \omega_q) = \frac{1}{i \omega_n + \omega_q} - \frac{1}{i \omega_n - \omega_q} = \frac{2 \omega_q}{\omega_n^2 + \omega_q^2}, \quad (12)
\]

with \( \omega_n = c q \). The latter equation is valid for bosonic excitations with plane-wave basis [4]. The denominator of very last term in right-hand side of Eq.(12) is also known as spectral representation of ‘Matsubara thermal propagator’ [6].

As it is discussed briefly in the previous section (see also Fig.1(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 imaginary time axis. However, summation even over infinite set of the ‘Matsubara thermal propagators’ (with the conventional Matsubara frequencies \( \omega_n \), evaluated based on the periodicity of Fourier expansion coefficients) often yields a finite (convergent) expression [6]:

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

where the ‘conventional’ Matsubara frequencies \( \omega_n \) are numerated here by their integer (summation) index \( n \), while \( \coth(\beta \omega_q/2) \) denotes hyperbolic cotangent (of its argument), and \( n_{\text{BE}}(\omega_q) = [\exp(\beta \omega_q/2) - 1]^{-1} \) stands for the conventional (dimensionless) Bose-Einstein occupation factor of the phononic state corresponding to the frequency \( \omega_n = c q \) [6]. This implies, that the right-hand side of Eq.(13) might be
treated as an ‘effective’ occupation factor \( n_{\text{eff}}(\hbar \omega_q) \) of a ground Debye’s phononic state (with the plane-wave basis) of the (real and positive) frequency of \( \omega_q \). Since \( \omega_q(\omega_q) = 0 \) for a bosonic ensemble [2–4] (see also Fig. 1(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 \( n_{\text{BE}}(\hbar \omega_q) \) of the ‘standard’ Bose-Einstein occupation factor). However, even in polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators with micrometer-size of the grains (non-homogeneities), the \( \omega_q \) is always expected to be non-zeros due to effect of phonon confinement imposed by the limited spatial extent of those non-homogeneities (see also Fig. 4D in Appendix D of ref. [1]). Therefore, the divergence in both \( n_{\text{eff}}(\hbar \omega_q) \) and \( n_{\text{BE}}(\hbar \omega_q) \) dependencies become avoidable even for those materials – not only for nanostructured semiconductors and insulators, where the phonon confinement effects are expected to be manifested in much more profound way.

As it is shown in Fig. 3, spectral behavior of the room-temperature effective occupation factor \( n_{\text{eff}}(\hbar \omega_q) \) differs considerably from that of the standard Bose-Einstein one, \( n_{\text{BE}}(\hbar \omega_q) \), for ground states of ensemble of acoustic phonons of the diamond.

![Graph](image_url)

**FIG. 3** (color online). The room-temperature spectral dependencies of the ‘standard’ Bose-Einstein occupation factor \( n_{\text{BE}}(\hbar \omega_q) \) and its ‘effective’ counterpart \( n_{\text{eff}}(\hbar \omega_q) \), 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 \( k_B \theta_D = 193.0 \text{ meV} \) \((\theta_D = 2240 \text{ K})\), indicated in the figure with the vertical dashed line. See further details in the main text.

In particular, it decays faster than \( n_{\text{BE}}(\hbar \omega_q) \) with the \( \hbar \omega_q \) enlargement at relatively low phonon energies \((\hbar \omega_q < 20 \text{ meV})\), but much slower than that at relatively high \((\hbar \omega_q > 50 \text{ meV})\) those energies, Fig. 3. 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 the Debye energy, \( k_B \theta_D \): conventional (ground) single-phonon states with higher energies simply do not exist in an equilibrium state of the ensemble of acoustic phonons! Thus, both dependencies plotted in Fig. 3 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 (with generally non-equivalent \( \mathbf{q} \) quantities for all its basic components in an appropriate Hilbert space) and coherent (with the same \( \mathbf{q} \) parameter for all its components) states naturally. 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 vector \( \mathbf{q} \) is well-defined and always located within the first phononic Brillouin Zone (BZ). On the other hand, aforementioned 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. In contrast, Klauder’s bosonic coherent states \(-\langle n_c! \rangle^{1/2} \exp(-i\mathbf{q}_c \cdot \mathbf{r})\) \([6, 7]\) 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 the first BZ of (longitudinal acoustic) phonons. Moreover, based on the ‘classic’ dispersion relation \(\omega = c|\mathbf{q}|\), the phonon energy \(\hbar \omega\) would routinely exceed their upper limit — the Debye’s energy \((k_B\theta_D)\) — defined for the ground states of acoustic phonons; see comments to Fig.3 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 consideration at a quantitative description of electron interactions with such 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 mixed (coherent and excited) states of ensemble of acoustic phonons within framework of modified dynamic version of the GSM is generally expected to deviate significantly from the Gibbs-Boltzmann occupation factor of non-interacting phonon states in its original version, depicted in ref. [1] (i.e., at the following ‘model parameters’: \(r_1 = 2, r_2 = 1\)). 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 Eq.(7) therein. Consequently, within the GSM framework, spectral density of ensemble of acoustic phonons [6] (which generalizes concept of conventional one-dimensional phononic DOS spectrum — since the latter one is not applicable directly within framework of the second quantization formalism) with the dynamic plane-wave basis might be linked straightforwardly to the dynamic DOS function, multiplied by the \(\Theta_\beta(E_T, T)\) term, while a dynamic counterpart of Eq.(5) now reads:

\[
W_D(E_T) \equiv \exp(-E_T/k_B T) \int_{M_0}^{M} \frac{1}{\Gamma(M+1)} (Z_M)^2 \left[ \frac{4L_x L_y F(L_x, L_y, L_z) \Theta_M(E_T, T) E_T^2}{M^{1/2} (\hbar c_l)^2} \right] dM. \quad (14)
\]

The ‘partition function’ \(Z_M\) for the Eq.(5), expressed by Eq.(9) above, now has to be amended as well:

\[
Z_M = (k_B T)^{2(M+1)} \Gamma \left( 2M + 1 \right) \left( \frac{E_{\text{min}}}{k_B T} \right)^{1/2} \left( \frac{k_B \theta_D}{k_B T} \right)^{1/2} \left[ \frac{4L_x L_y F(L_x, L_y, L_z) \Theta_M(E_T, T)}{M^{1/2} (\hbar c_l)^2} \right] \quad (15)
\]

Again, in a \(T \to \infty\) limit, the Eq.(15) is expected to coincide with the conventional ‘partition function’ \([7]\), expressed for this particular case by the Eq.(15D) in ref.[1]; see also Fig. 2(b) in the previous section.

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 aforementioned particular cases of ensemble(s) of acoustic phonons confined within polycrystalline and spatially non-homogeneous amorphous semiconductors and insulators with micrometer- and sub-micrometer sizes of non-homogeneities (grains), 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 GF formalism(s) \([3]\).
On the other hand, the static plane wave-functions basis of Debye acoustic phonons implemented within the GSM framework [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. At the same time, 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 phononic states (microstates). Importantly, that such dynamic expansion allows one to retain almost entirely principal features of the conventional (static) phononic DOS concept (essentially used in original version of the GSM [1]) and 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) GSM and those of equilibrium conventional and Matsubara Green Functions. In addition, the model parameters r1 and r2 of 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 the original static and modified dynamic version of) the GSM, and inspire its direct implementation to the appropriate quantitative descriptions of statistical characteristics of phononic excitations with the plane-wave basis in nano-structured semiconductors and insulators as well as of their near-band-gap and intra-gap electronic and optical spectra.

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