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Pressure dependence of phonon populations and non-standard quasiadditive integrals of motion

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The existing equilibrium statistical physics is based on application of standard quasiadditive integrals of motion, which include energy, momentum, rotation momentum, and number of particles. It is shown that this list is far from complete and that any quasiadditive dynamic variable can be mapped to corresponding quasiadditive integral of motion. As a result an ensemble with a given external pressure is constructed. It provides the first example of the distribution in which phonon populations depend on pressure differently than in the canonical Gibbs ensemble. Obtained results indicate the need to continue the studies of phonon populations based on Raman scattering, which were fulfilled earlier in LFTI and initiated this work.

Keywords:: Phonon populations, phonon frequencies, quasiharmonic approximation, canonical Gibbs ensemble, ensemble with given pressure, additive integral of motion, Gruneisen factor, Raman scattering.

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Introduction

Raman light scattering, along with inelastic neutron scattering, belongs the basic experimental methods for studying lattice vibrations in crystals. In this case, the most important part of the knowledge necessary for interpreting the results obtained is the existing ideas about the equilibrium distribution of phonons, supplied by equilibrium statistical physics. They are based on canonical Gibbs distributions [1–4]. To justify these distributions, a large system consisting of large subsystems is usually reviewed. Then from the assumption of quasi-independence of the subsystems it follows that the statistical operator logarithm of the system ρ is quasi-additive with respect to the logarithms of the statistical operators of the subsystems ρ_a:

$$\ln\rho = \sum_a \ln\rho_a. \tag{1}$$

This equality is valid when surface effects are neglected. It immediately results in the canonical Gibbs distributions, since it is assumed that all quasi-additive integrals of motion are exhausted by the total energy, the total number of particles, and the total values of momentum and angular momentum.

The informational view on the problem [2,5,6] is based on the quasi-additivity and maximality of the entropy of the equilibrium distribution. It leads to the same conclusions because it uses the same integrals I_μ of motion to impose the conditions

$$\langle I_\mu\rangle = \mathrm{Tr} I_\mu \rho = I_\mu^{(\mathrm{ex})}, \tag{2}$$

limiting the variation of $\delta\rho$ in the search for the maximum entropy

$$S = -\langle \ln\rho\rangle. \tag{3}$$

As a result,

$$\rho = \exp\Big(-\sum_{\mu=1}^{\nu} A_\mu I_\mu\Big), \tag{4}$$

where ν — the number of conditions (2) that serve as equations for determining the Lagrangian factors A_μ for a given set of values $\{I_\mu^{(\mathrm{ex})}\}$. The maximum of entropy realizes the distribution corresponding to the presence of a minimum of information about the system under conditions (2).

To describe many phenomena associated with the anharmonicity of lattice vibrations, the so-called quasi-harmonic approximation is sufficient, in which the vibrations remain small, but their frequencies depend on the volume of the crystal and, accordingly, on the external pressure $P^{(\mathrm{ex})}$. Meanwhile, the dependence of the average occupation numbers (populations) of $n_k = \langle c_k^+ c_k\rangle$ phonons on $P^{(\mathrm{ex})}$ manifests itself only through the pressure dependence of the phonon frequencies $\omega_k(P^{(\mathrm{ex})})$ [7–9]. Under these conditions, one of the consequences of the equivalence of Gibbs ensembles [1–4] for non-small systems is that

$$n_k = n_k^{(0)}(P^{(\mathrm{ex})}) = \Big[\exp(\beta\omega_k(P^{(\mathrm{ex})})) - 1\Big]^{-1}. \tag{5}$$

Here $\beta = 1/T$ — the inverse temperature, and c_k^+ and c_k — the phonon creation and annihilation operators in the state with condition number k

A direct measurement of the dependence $n_k(P^{(\text{ex})})$ was undertaken in [10,11] based on a comparison of the intensities of the Stokes and anti-Stokes components in Raman light scattering. These papers continued the study [12] of Raman light scattering in strained crystalline silicon plates. Their results are much better described by the relation

$$n_k(P^{(\text{ex})}) = \left\{\exp\left[\beta(\omega_k(P^{(\text{ex})}) + \Delta_k(P^{(\text{ex})}))\right] - 1\right\}^{-1}, \quad (6)$$

where

$$\Delta_k(P^{(\text{ex})}) = \omega_k(P^{(\text{ex})}) - \omega_k(0),$$

than by the formula (5). Naturally, the measurements were carried out at $\Delta_k(P^{(\text{ex})}) \ll \omega_k(P^{(\text{ex})})$.

This conclusion was obtained by a highly qualified team in one of the largest physical centers. Nevertheless, it did not attract wide attention of researchers, apparently because it did not receive a convincing theoretical justification. Existing statistical physics does not offer anything except the relation (5).

Let us note that the actual measurement [10,11] was carried out under somewhat more complex conditions than isotropic tension or compression, but we restrict ourselves here to only this case in order to highlight the most important conceptual part of the problem.

In this paper, it is shown that the list of quasi-additive integrals of motion is far from exhausted by the above standard dynamic variables, and on this basis a new statistical operator is constructed that ensures the fulfillment of an additional condition imposed on the pressure in the system. It results for the first time in other phonon populations than canonical Gibbs distributions.

The new statistical operator does not coincide with the known $P-T$-distribution (see, for example, item 9.6 in [2], Ch. 1, §13 in [3] or problem 11 on page 91 in [4]), which corresponds to the inclusion in (2) of an additional condition not on the pressure, but on the volume of the system [2]. $P-T$-distribution for large systems is equivalent to the usual canonical distribution.

1. Pressure as a dynamic variable and an ensemble with a given pressure

We will relate the quasi-additive dynamic variable

$$Q(p,q) = -\frac{1}{d}\frac{\partial}{\partial\lambda}H(p/\lambda, q\lambda)|_{\lambda=1}. \quad (7)$$

to the pressure. Here $H(p,q)$ — Hamiltonian of the system, d — its spatial dimension, p and q denote the totality of all momenta and coordinates, and the numerical parameter λ is assumed to be equal to one after calculating the derivative $\partial/\partial\lambda$. This choice is due both to the general statement [1] that the pressure is determined by the relation

$$p^{(\text{ex})} = -\left\langle\frac{\partial H}{\partial V}\right\rangle,$$

and to the fact that in the canonical ensemble the mean pressure is

$$p^{(\text{ex})} = -\left\langle\frac{\partial H}{\partial V}\right\rangle = -\frac{\partial F(\beta, V)}{\partial V}$$

$$= \frac{1}{V}\sum_n \langle n|Q|n\rangle \exp\big(-\beta(F - \langle n|H|n\rangle)\big) = \frac{\langle Q\rangle}{V}. \quad (8)$$

Here F — free energy, and the vectors $|n\rangle$ are eigenstates for the Hamiltonian H. A similar relation is also valid in the grand canonical ensemble. A fairly complete derivation of the relation (7) can be found in the papers [2,13–15]. It is a specification of the calculation of the operator $\partial H/\partial V$ in case when the total Hamiltonian of the system is $H_{\text{tot}} = H(p,q) + U_b(q/L)$, where the term $U_b(q/L)$ describes the influence of the boundary, the volume of the system is $V \sim L^d$, and $H(p,q)$ does not contain an explicit dependence on V in the coordinate representation.

In a standard three-dimensional dynamical system with the Hamiltonian

$$H(p,q) = \sum_{j=1}^{N}\frac{p_j^2}{2m} + \frac{1}{2}\sum_{i\neq j}\Phi(\mathbf{q}_i - \mathbf{q}_j), \quad (9)$$

where N is the number of particles in the system, m is the particle mass, and $\Phi(\mathbf{q}_i - \mathbf{q}_j)$ is the interparticle interaction energy, we have ’

$$Q(p,q) = \frac{1}{3}\left[2\sum_{j=1}^{N}\frac{p_j^2}{2m} - \frac{1}{2}\sum_{i\neq j}\mathbf{q}_{ij}\partial\Phi(\mathbf{q}_{ij})/\partial\mathbf{q}_{ij}\right]. \quad (10)$$

Analyzing the time dependence of the densities of standard quasi-additive integrals of motion also leads to the similar representations for pressure [14,16–18].

Let us note that only the diagonal elements $\langle n|Q|n\rangle$ appear in (8).

With a sufficiently rapid decrease in the interaction $\Phi(\mathbf{q}_{ij})$ with an increase in $\mathbf{q}_{ij} = \mathbf{q}_i - \mathbf{q}_j$, the operator $Q(p,q)$ is quasi-additive, as is the Hamiltonian (9). Accordingly, its diagonal part

$$Q_D = \sum_n |n\rangle\langle n|Q|n\rangle\langle n| \quad (11)$$

is also quasi-additive and, unlike $Q(p,q)$, is an integral of motion. Indeed, let the system consist of two parts, and neglecting the interaction on the boundary

$$H(p,q) = H_1(p_1,q_1) + H_2(p_2,q_2),$$

$$Q(p,q) = Q_1(p_1,q_1) + Q_2(p_2,q_2).$$

Here (p_a, q_a) — the set of impulses and coordinates of the a-th subsystem. Accordingly, $|n\rangle = |n_1\rangle|n_2\rangle$, where $|n_a\rangle$ — eigenvector of the Hamiltonian $H_a(p_a, q_a)$. Therefore,

$$Q_D = \sum_n |n\rangle\langle n|Q|n\rangle\langle n| = \sum_{n_1}|n_1\rangle\langle n_1|Q_1|n_1\rangle\langle n_1|$$

$$+ \sum_{n_2}|n_2\rangle\langle n_2|Q_2|n_2\rangle\langle n_2| = Q_{1D} + Q_{2D},$$

which proves the quasi-additivity Q_D.

Therefore, the statistical operator

$$\rho = \exp\bigl[\beta(G - H - \tau Q_D)\bigr] \qquad (12)$$

is an integral of motion and represents an equilibrium distribution that satisfies requirement (1) and additional conditions

$$\langle H\rangle = E, \quad \langle Q\rangle = Q^{(\mathrm{ex})}, \quad \langle 1\rangle = 1, \qquad (13a)$$

from which β, τ and $G(\beta, \tau)$ are determined. Here $Q^{(\mathrm{ex})} = P^{(\mathrm{ex})}V^{(\mathrm{ex})}$, and $V^{(\mathrm{ex})}$ — average volume. Obviously,$\langle Q_D\rangle = \langle Q\rangle$.

In the distribution (12), we have written the exponent in the „standard“ form [1–4], when the thermodynamic parameter τ appears as a factor for the quasi-additive integral of motion Q_D. In the nature of things, other representations are also possible, and the choice among them is currently not limited by anything, except for the condition of maximum entropy when the imposed conditions (13) are satisfied. So, for example, instead of the conditions on the energy and the pressure representative $\langle Q\rangle$ from (13), the conditions on the density of these quantities can be used:

$$\langle H/V\rangle = \varepsilon, \quad \langle Q/V\rangle = P^{(\mathrm{ex})}. \qquad (13b)$$

The equivalence of the distributions corresponding to conditions (13a) and (13b) becomes apparent after passing to the density matrix ρ_1 introduced below by formula (21) in section 3.

Let us note that relation (12) is also valid in the classical theory for

$$Q_D(p, q) = \lim_{\vartheta\to\infty}\int_{-\vartheta}^{\vartheta}\frac{dt}{2\vartheta}\,Q\bigl(p_c(t), q_c(t)\bigr),$$

where $p_c(t)$ and $q_c(t)$ represent the classical trajectory with the initial condition

$$p_c(t = 0) = p, \quad q_c(t = 0) = q.$$

2. Equilibrium statistical operators with nonstandard quasi-additive integrals of motion

The method of constructing the quasi-additive integral of motion Q_D formulated above is completely general and is not tied to a specific representation (10). It allows for any quasi-additive dynamical variable $Q^{(\mu)}(p, q)$ to construct a quasi-additive integral of motion $Q_D^{(\mu)}$, which is the diagonal part of $Q^{(\mu)}(p, q)$. The new quasi-additive integrals of motion thus obtained can be further included in the list I_μ for constructing new statistical operators according to the rule (4).

3. Phonon occupation numbers in the presence of constant external pressure

Let us consider a crystal consisting of atoms of the same type. We write the corresponding lattice Hamiltonian as [1] in the approximation quadratic in displacements $\mathbf{u}_{\mathbf{n}s}$ of atoms from their average positions $\mathbf{r}_{\mathbf{n}s}$ in the cell numbered $\mathbf{n}$:

$$H(p, u, V) = \sum_{\mathbf{n}s}\frac{p_{\mathbf{n}s}^2}{2m} + \frac{1}{2}\sum_{\mathbf{n}\mathbf{n}'ss'}\Lambda_{ss'}^{\alpha\beta}(\mathbf{n}-\mathbf{n}', V)u_{\mathbf{n}s}^{\alpha}u_{\mathbf{n}'s'}^{\beta} + U_0(V). \qquad (14)$$

Here, the index s enumerates the atoms in the elementary cell, while α and β enumerate the Cartesian components. In (14), in contrast to (9), and due to the application of the harmonic approximation, the energy of the mean position $U_0(V)$ and coefficients $\Lambda_{ss'}^{\alpha\beta}(\mathbf{n}-\mathbf{n}', V)$ appeared, which explicitly depend on the volume V. Taking this into account the relation

$$\begin{aligned}Q(p, u, V) &= -\left(\frac{1}{d}\frac{\partial}{\partial\lambda} + V\frac{\partial}{\partial V}\right)H(p/\lambda, u\lambda, V)|_{\lambda=1}\\ &= \frac{2}{d}\left[\sum_{\mathbf{n}s}\frac{p_{\mathbf{n}s}^2}{2m} - \frac{1}{2}\sum_{\mathbf{n}\mathbf{n}'ss'}\Lambda_{ss'}^{\alpha\beta}(\mathbf{n}-\mathbf{n}', V)u_{\mathbf{n}s}^{\alpha}u_{\mathbf{n}'s'}^{\beta}\right]\\ &\quad - \frac{1}{2}\sum_{\mathbf{n}\mathbf{n}'ss'}\frac{\partial\Lambda_{ss'}^{\alpha\beta}(\mathbf{n}-\mathbf{n}', V)}{\partial\ln V}u_{\mathbf{n}s}^{\alpha}u_{\mathbf{n}'s'}^{\beta} - \frac{\partial U_0(V)}{\partial\ln V}.\end{aligned} \qquad (15)$$

is obtained instead of (7) and (10).

When written using the operators of creation c_k^+ and annihilation c_k of phonons in the state k, the Hamiltonian (14) becomes

$$H = \sum_k \omega_k(c_k^+c_k + 1/2) + U_0(V). \qquad (16)$$

The Q operator in this representation looks much more complicated, mainly due to the member associated with $\partial\Lambda/\partial\ln V$, which generates interzone transitions. But the diagonal part (11) is simple:

$$Q_D = -\frac{\partial}{\partial\ln V}\left(U_0(V) + \frac{1}{2}\sum_k\omega_k\right) - \sum_k\frac{\partial\omega_k}{\partial\ln V}c_k^+c_k. \qquad (17)$$

The results obtained in [7–9] for pressure within the canonical ensemble lead to the same form for Q_D.

From relations (12), (16) and (17) it naturally follows that

$$n_k = \Bigl\{\exp\bigl[\beta(\omega_k - \tau\,\partial\omega_k/\partial\ln V)\bigr] - 1\Bigr\}^{-1}. \qquad (18)$$

Here $V = V_0(P^{(\mathrm{ex})})$. The method for calculating this value is described below.

Calculations with the statistical operator (12), as well as calculations in the $P-T$ ensemble, include integration over the volume of the system V. For instance,

$$\exp(-\beta G) = \Omega^{-1} \int\limits_{\tilde{V}} dV \mathrm{Tr} \exp[-\beta(H + \tau Q_D)], \qquad (19)$$

where the formal parameter Ω with the dimension of volume is introduced so that the distribution (12) is dimensionless, and the region of integration over volume $\tilde{V}$ is concentrated near the point V_0 indicated below. In standard calculations of such quantities as G, $\langle H \rangle$, $P = \langle Q/V \rangle$ and n_k it is natural to calculate this integral after calculating the trace over other degrees of freedom. Meanwhile (as in the $P-T$ ensemble), the result for large systems is determined by the presence of a sharp maximum in V near some value of V_0, and the relative width of this maximum is small in the parameter $N^{-1/2}$, where N — the number of particles in the system. Therefore, according to the rules of saddle point method, the value of $V = V_0$ is determined by the equation

$$\frac{\partial}{\partial V} \ln \mathrm{Tr} \exp[-\beta(H + \tau Q_0)] = \beta \left(P_1 - \tau \left\langle \frac{\partial Q_D}{\partial V} \right\rangle_1 \right) = 0. \qquad (20)$$

Here $P_1 = -\langle \partial H/\partial V \rangle_1$, $\langle B \rangle_1 = \mathrm{Tr} B \rho_1$ for any operator B, and

$$\rho_1 = \exp\left[-\beta(H + \tau Q_D\right] / \mathrm{Tr} \exp\left[-\beta(H + \tau Q_D)\right]. \qquad (21)$$

Taking into account (13) we have $P_1 = P^{(\mathrm{ex})}$. Therefore, for $P^{(\mathrm{ex})} = 0$, from (20) follows $\tau = 0$, and the distributions (12) and (21) are reduced to the canonical one with volume $V = V_0 = V_T$, where V_T — the usual equilibrium volume in the absence of external pressure. In general case, τ and V_0 are defined by a pair of relations

$$P_1(V, \tau) = P^{(\mathrm{ex})}, \quad \tau \langle \partial Q_D/\partial V \rangle_1 = P^{(\mathrm{ex})}. \qquad (22)$$

The ground experimental data of the papers [9,10] refer to deformations much larger than the thermal change in the cell parameter associated with the last term in (17) [7–9]. Therefore, when calculating τ, this term can be neglected. In the result

$$\tau = P^{(\mathrm{ex})} \Big/ \left\langle \frac{\partial Q_D}{\partial V_0} \right\rangle_1 \approx P^{(\mathrm{ex})} \Big/ \frac{\partial (V_0 P^{(\mathrm{ex})})}{\partial V_0} \approx V_T^{-1}(V_0 - V_T). \qquad (23)$$

Here it is taken into account that $(V_0 - V_T)/V_T \ll 1$ and $V_0 - V_T$ are linear in $P^{(\mathrm{ex})}$. Now, substitution (23) into (18) together with taking into account the relative smallness of the change in phonon frequencies $\omega_k(P^{(\mathrm{ex})}) - \omega_k(0) \ll \omega_k(P^{(\mathrm{ex})})$ leads to

$$n_k(P^{(\mathrm{ex})}) = \left\{ \exp\left[\beta(\omega_k(P^{(\mathrm{ex})}) - \Delta_k(P^{(\mathrm{ex})})\right] - 1 \right\}^{-1}$$

$$\approx \left\{ \exp\left[\beta(\omega_k(P^{(\mathrm{ex})} = 0))\right] - 1 \right\}^{-1}. \qquad (24)$$

4. Temperature

The question of the relationship between the parameters β and τ introduced in (12) and the standard thermodynamic temperature $T_t = 1/\beta_t$ requires a special study. We will not give here a complete solution of this problem, but we hope that the material presented below forms an important part of it.

It is known that in case of a three-dimensional ($d = 3$) ideal gas, the pressure operator is proportional to the Hamiltonian: $P = 2H/(3V)$. In this case, formula (12) coincides with the usual canonical distribution and $\beta_t = \beta(1 + 2\tau/3)$.

The distribution (12) is no longer reduced to those known earlier for phonon systems. Therefore, we first overview the classical limit, when it is natural to expect that the temperature is determined by the average value of the kinetic energy per vibrating atom:

$$\left\langle \sum_{j=1}^{N} p_j^2/2m \right\rangle \Big/ N = 3T_t/2.$$

A simple calculation in this case gives

$$\beta_t = \beta(1 + \tau \gamma_{\mathrm{eff}}^c). \qquad (25)$$

Here the effective Gruneisen parameter γ_{eff}^c is introduced, which is related to the mode [7,8] Gruneisen parameters $\gamma_k = -\partial \ln \omega_k / \partial \ln V$ by the relation

$$(1 + \tau \gamma_{\mathrm{eff}}^c)^{-1} = \sum_k (1 + \tau \gamma_k)^{-1}/(3N). \qquad (26)$$

In the general situation, it is natural to consider a separate macroscopic subsystem with known properties as a thermometer. Let the thermometer be an ideal gas with a given volume V_t, Hamiltonian H_t and temperature T_t, which is in equilibrium with the crystal described by the density matrix (21). Let us consider the evolution of the system when the weak interaction H_1 between the thermometer and the crystal is switched on. Let us assume that initially, at $t = 0$, the density matrix of the system consisting of a sample and a thermometer has the form

$$\rho_g = \rho_1(\beta, \tau) \rho_t(\beta_t, V_t), \qquad (27)$$

where $\rho_1(\beta, \tau)$ is defined by relation (21). From the standard theory of linear reaction [2] it follows that the rate of change of thermometer energy is

$$\frac{\partial}{\partial t} \left\langle H_t(t) \right\rangle = \int\limits_0^\infty dt' \mathrm{Tr}[H_1(t'), H_t][H_1, \rho_g]. \qquad (28)$$

Here $H_1(t) = \exp(iH_g t) H_1 \exp(-iH_g t)$, and the Hamiltonian $H_g = H + H_t$. The relation (28) is valid at the beginning of the evolution, when $|\langle H_t(t) \rangle - \langle H_t(0) \rangle| \ll |\langle H_t(0) \rangle|$, but $t > \tau_c$, where τ_c — the decay time of the integrand. Let us rewrite (28) using the eigenvectors $|n_g\rangle = |n\rangle |n_t\rangle$ and the eigenvalues

$E_{ng} = E_n + E_{tn}$ of the Hamiltonian H_g, constructed from the eigenvectors and values of the Hamiltonians H and H_t. Meanwhile,

$$\frac{\partial}{\partial t}\Big\langle H_t \Big\rangle = \sum_{n_g m_g} \pi\delta(E_{gn} - E_{gm})|\langle n_g|H_1|m_g\rangle|^2 (E_{m_t} - E_{n_t})$$

$$\times \Big\{1 - \exp\big[-(\beta_t - \beta)(E_n - E_m) + \beta\tau(Q_{Dn} - Q_{Dm})\big]\Big\}\rho_{gn}. \tag{29}$$

Here

$$\rho_{gn} = \exp(-\beta(E_n + \tau Q_{Dn}) - \beta_t E_{nt})/$$

$$\operatorname{Tr}\exp(-\beta(H + \tau Q_D) - \beta_t H_t)$$

is the eigenvalue of the density matrix ρ_g on the vector $|n_g\rangle = |n\rangle|n_t\rangle$.

It is natural to expect that when the thermometer is in equilibrium with the crystal

$$\partial\langle H_t(t)\rangle/\partial t = 0. \tag{30}$$

If $\tau = 0$, then this condition is satisfied for $\beta = \beta_t$ regardless of the explicit form of H_1, as it should be in the canonical ensemble. In general case, condition (30) is an equation for $\beta = \beta(\beta_t, \tau)$, the solution of which depends on H_1.

Let us show that there is a natural approximation for this solution, which does not depend on H_1. Let us place $H = H^{(\mathrm{el})} + H^{(\mathrm{ph})}$ and $Q_D = Q_D^{(\mathrm{el})} + Q_D^{(\mathrm{ph})}$. Here, the phonon parts $H^{(\mathrm{ph})}$ and $Q_D^{(\mathrm{ph})}$ include terms that are quadratic in the operators c_k^+ and c_k, while the elastic parts $H^{(\mathrm{el})}$ and $Q_D^{(\mathrm{el})}$ do not contain operators. Obviously, both the density matrix ρ_1 and the right side in (29) do not depend on $H^{(\mathrm{el})}$ and $Q_D^{(\mathrm{el})}$, because their contributions to the numerator and denominator from (21) cancel out. Similarly, we can place

$$\rho_1 = \exp\Big[-\beta\big((1 + \tau u)H^{(\mathrm{ph})} + \tau(\Delta Q_D^{(\mathrm{ph})} - u\Delta H^{(\mathrm{ph})})\big)\Big]/Z, \tag{31}$$

where $\Delta B = B - \langle B\rangle_1$, and Z — normalization factor. Parameter u will be chosen in such a way as to minimize

$$\Phi = \Big\langle(\Delta Q_D^{(\mathrm{ph})} - u\Delta H^{(\mathrm{ph})})^2\Big\rangle_1.$$

Meanwhile,

$$u = \Big\langle(\Delta Q_D^{(\mathrm{ph})}\Delta H^{(\mathrm{ph})}\Big\rangle_1 \Big/ \Big\langle(\Delta H^{(\mathrm{ph})})^2\Big\rangle_1. \tag{32}$$

Now, in the leading order in $\Delta Q_D^{(\mathrm{ph})} - u\Delta H^{(\mathrm{ph})}$, we obtain

$$\rho_1 = \exp[-\beta(1 + \tau u)H^{(\mathrm{ph})}]/Z,$$

and equation (30) has a solution

$$\beta = \beta_t/(1 + u\tau), \tag{33}$$

not depending on H_1. Calculation by formulas (32) and (31) leads to

$$u = \sum_k \gamma_k\omega_k^2 n_k(n_k + 1)\Big/\sum_k \omega_k^2 n_k(n_k + 1). \tag{34}$$

Here,

$$n_k = \Big\{\exp[\beta(1 + \tau\gamma_k)\omega_k] - 1\Big\}^{-1}$$

as in (18). As a rule $|\gamma_k| \sim 1$ [7,8]. To reveal in n_k effects of the main order by $\tau \ll 1$ in n_k , it is enough to place $\tau = 0$ in (34). In this limit u coincides with the so-called total Gruneisen parameter γ (see formula (25.19) from [8]), for which there are many numerical estimates in the literature . Apparently, the value of $\gamma \approx 0.5$ given in [19] for silicon at room temperature and $P^{(\mathrm{ex})} = 0$ did not undergo significant changes in subsequent papers [20,21].

In the classical limit $u = \gamma_{\mathrm{eff}}^c(1 + Q(\tau))$. Moreover, relations (31) and (25) are equivalent.

Analyzing the thermodynamic relations following directly from the distribution (12) also leads to similar conclusions. It is easy to check that

$$\frac{\partial G}{\partial\beta} = \frac{S}{\beta^2}, \quad \frac{\partial G}{\partial\tau} = \langle Q\rangle = Q^{(\mathrm{ex})}, \tag{35}$$

i.e.

$$dG = -SdT + Q^{(\mathrm{ex})}d\tau. \tag{36}$$

Hence, taking into account that $E = \langle H\rangle = G - \tau Q^{(\mathrm{ex})} + TS$,

$$dE = \left(T - \tau\left(\frac{\partial Q^{(\mathrm{ex})}}{\partial S}\right)_V\right)dS - \tau\left(\frac{\partial Q^{(\mathrm{ex})}}{\partial V}\right)_S dV. \tag{37}$$

is obtained. Let's compare this expression with the standard thermodynamic relation

$$dE = T_t dS_t - pdV. \tag{38}$$

Here T_t and S_t — standard thermodynamic temperature and entropy respectively. Relations (37) and (38) will match if

$$\tau\left(\frac{\partial Q^{(\mathrm{ex})}}{\partial V}\right)_S = p. \tag{39}$$

Then it can be assumed that $S = S_t$, and

$$T_t = T - \tau\left(\frac{\partial Q^{(\mathrm{ex})}}{\partial S}\right)_V. \tag{40}$$

Comparison of relations (22) and (39) shows that (39) is performed at least in the leading order in τ. With the same accuracy, relation (40) reduces to (34).

5. Conclusions

The construction of a new ensemble carried out in the present work essentially uses the possibility of explicitly constructing a new quasi-additive integral of motion based on the presence of a phonon representation for crystal vibrations. Apparently, it can be easily generalized to any other objects in which the Hamiltonian of free quasiparticles is a good approximation, for example, to magnon systems. In a more general situation, the problem may turn out to be as difficult as the ergodic problem.

The resulting new dependence of phonon occupation numbers on external pressure (24) differs significantly from that for previously known Gibbs ensembles (5), but does not agree with the results (6) of the experiment [10,11] even with allowance for temperature redefinition , which was discussed in Section 4. This indicates the need for further experimental and theoretical studies. In particular, it becomes much more important to study the correspondence between the experiment and the ensemble compared to it. Let us note that, along with optical and magnetic resonance methods for measuring phonon and magnon populations, it is also desirable to use inelastic neutron scattering, since in this case the influence of effects such as a narrow phonon throat is minimized.

At present, in the absence of ergodic theorems, the kinetic equations are usually formulated in such a way that their equilibrium solutions coincide with the results of the equilibrium theory. Actually, this requirement is purely phenomenological, and an example of how a consistent theory can be in conflict with it is given in [22]. Therefore, the extension of the class of admissible equilibrium states revealed in this paper, which arises when nontraditional quasi-additive integrals of motion are taken into account, should lead to a modification of not only equilibrium, but also nonequilibrium statistical physics. First of all, this may refer to problems in the theory of destruction of materials. The papers [10–12] were directed to them and stimulated the present study. To apply our results in the general theory of kinetic equations, the problem of finding convenient representations for the densities of non-standard quasi-additive integrals of motion, which could be used along with standard densities in constructing, for example, a description of the hydrodynamic stage of evolution, should be among the first to be solved.

Let us note that the discovery of a new quasi-additive integral of motion in the quasi-harmonic approximation does not yet mean that it will appear in the completely equilibrium density matrix of the system. For a theoretical solution of such a question, it would be necessary to prove the corresponding ergodic theorem. But the new integral is at least important in quasi-equilibrium distributions that describe the system at the stage of approaching full equilibrium. Examples of such situations are well known. Thus, in many problems of the dynamics of isolated spin systems, most of the evolution and many effects are described under the assumption that there is an equilibrium inside the Zeeman and dipole subsystems, each of which has its own temperature, and their Hamiltonians are integrals of motion, neglecting the nonsecular terms of dipole-dipole interactions [23]. Meanwhile, there is no doubt that the complete equilibrium of an isolated spin system corresponds to a canonical distribution with one temperature and with a total Hamiltonian that is an exact integral of motion.

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Conflict of interest

The author declares that he has no conflict of interest.

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