Eur. Phys. J. B **28**, 271–276 (2002)
DOI: 10.1140/epjb/e2002-00229-3

THE EUROPEAN PHYSICAL JOURNAL B

High-order vibrational relaxation: a nonperturbative theory

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Received 2 May 2002
Published online 31 July 2002 –

Abstract. A nonperturbative theory of the multiphonon relaxation of a localized vibrational mode, caused by a high-order anharmonic interaction with the nearest atoms of the crystal lattice, is proposed. It relates the rate of the process to the positive frequency part of the time-dependent non-stationary displacement correlation function of atoms. The nonlinear integral equation for this function is derived and solved numerically. We have found that the rate exhibits a critical behavior: it sharply increases near a specific (critical) value(s) of the interaction; the corresponding dependence is characterized by the critical index $k-1$, where k is the number of the created phonons.

PACS. 63.50.+x Vibrational states in disordered systems – 71.23.An Theories and models; localized states

1 Introduction

Physical processes in solids usually involve the relaxation of the vibrational energy. The vibrational quanta of light impurity molecules in crystals may exceed many times the maximal energy of phonons. In such a case the energy relaxation of a molecule takes place as a multiphonon emission. Pulse laser sources give a possibility to study these processes in the time domain (see, *e.g.* [1–3] and the references therein). If one considers the relaxation of lower vibrational levels, then the interaction of the molecular vibration with phonons is usually weak and the process can be explained in terms of a standard perturbation theory [4–9]. However, modern methods allow one to excite molecules to very high vibrational levels [3]. In such cases the anharmonic interaction is strong. To interpret the results of measurements in these cases, a nonperturbative theory of multiphonon relaxation is needed. The goal of this communication is to propose such a theory.

When considering the decay of a nonstationary state of a quantum subsystem interacting with the medium, one usually proceeds from the calculation of the time dependence of the characteristics of the subsystem (*e.g.* its density matrix). Here we apply another method, which is based on the consideration of the rate of creation of phonons in a nonstationary state (here in the excited state of the localized mode). The method was proposed in [10] for two phonon relaxations of a classical local mode; in [11] it was extended to quantum transitions between the vibrational levels caused by cubic anharmonicity. According to this theory the transition rate is strongly enhanced near the critical value(s) V_{cr} of the nondiagonal vibronic interaction V and it is remarkably reduced when this interaction is strong (above V_{cr}). This kind of dependence of a two-phonon relaxation on V was observed in [12], where a sharp maximum of the relaxation rate at vibrational level number $n = 22$ of a Xe_2^* molecule was observed in a hot luminescence spectrum of a self-trapped exciton in a solid Xe (in this case $V \propto \sqrt{n}$).

To explain the idea of the method [10,11] let us consider a two-phonon decay of a highly excited local mode caused by the interaction $\hat{H}_{int} = \hat{Q}\sum_{ii'} V_{3,ii'}\hat{x}_i\hat{x}_{i'}$, where $V_{3,ii'}$ are the cubic anharmonicity interaction parameters, $\hat{Q}$ is the coordinate operator of the mode, $\hat{x}_i = \sqrt{\hbar/2\omega_i}(\hat{a}_i + \hat{a}_i^+)$ are the coordinate operators of the phonons, $\hat{a}_i$ and $\hat{a}_i^+$ are the initial destruction and creation operators. The highly-excited mode can be considered classically. In this approximation the phonon Hamiltonian takes the form

$$\hat{H} \simeq \hbar\sum_i \omega_i(\hat{a}_i^+\hat{a}_i + 1/2) + Q(t)\sum_{ii'} V_{3,ii'}\hat{x}_i\hat{x}_{i'},$$

where $Q(t)$ is the time-dependent classical coordinate of the mode. This Hamiltonian can be diagonalized by standard methods of local dynamics. This is achieved by means of the new, time-dependent destruction ($\hat{b}_{j,t}$) and creation ($\hat{b}_{j,t}^+$) operators of phonons. The latter are determined by the time-dependent Bogolubov transformation $\hat{b}_{j,t} = \sum_i(\mu_{ji,t}\hat{a}_i + \nu_{ji,t}\hat{a}_i^+)$ (for the expressions for $\mu_{ji,t}$ and $\nu_{ji,t}$ see in [10]). For a large time t as compared to the reciprocal frequency of the phonons ω_i^{-1} the

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transformation coefficients of phonon operator simplify to [11] $\mu_{ji,t} \simeq \delta_{ji}\mu_{i,t}$, $\nu_{ji,t} \simeq \delta_{ji}\nu_{i,t}$ so that

$$\hat{b}_{i,t} \simeq \mu_{i,t}\,\hat{a}_i + \nu_{i,t}\,\hat{a}_i^+; \tag{1}$$

where $|\mu_{i,t}|^2 = 1+|\nu_{i,t}|^2$. One can see that the initial zero-point state of phonons, $|0\rangle$, is not the zeroth state of the operators $\hat{b}_{i,t}$. This means that phonons are generated in the lattice. The number of created phonons for the normal mode i at $T = 0$ equals $n_{i,t} = |\nu_{i,t}|^2$. This allows one to find the rate of the energy loss (relaxation) of the mode as follows:

$$\dot{E} = (\hbar\omega_l/k)\sum_i \mathrm{d}|\nu_{i,t}|^2/\mathrm{d}t \tag{2}$$

(here $k = 2$ is the number of phonons emitted for each quantum $\hbar\omega_l$ of the mode). The effect of temperature can be included in a standard way by adding the stimulated transitions. The described approach to relaxation holds for an arbitrary interaction as far as the dependence of $|\nu_{i,t}|^2$ on time is slow as compared to the characteristic phonon frequency $\bar{\omega}$.

From the given expression for $\dot{E}$ it follows that, in fact, one does not need the full knowledge of the operator transformation (*i.e.*, one does not need to know the complex parameters $\mu_{i,t}$ and $\nu_{i,t}$); it suffices to find $|\nu_{i,t}|^2$. To obtain the latter parameter, one does not obligatorily need to diagonalize the Hamiltonian. It is much easier to obtain this parameter from the $\sim \mathrm{e}^{\mathrm{i}\omega_i\tau}$ (negative frequency) term of the large-time asymptotic form of the phonon correlation function $\mathcal{D}_i(t,\tau) = \langle 0|\hat{x}_i(t+\tau)\hat{x_i}(t)|0\rangle$ with t averaged over a vibrational period. Indeed, taking $\hat{x}_i(t) = (\hbar/2\omega_i)(\hat{b}_{i,t}^+\mathrm{e}^{\mathrm{i}\omega_i t} + \hat{b}_{i,t}\mathrm{e}^{-\mathrm{i}\omega_i t})$, where the operator $\hat{b}_{i,t}$ is given by equation(1), one finds

$$\mathcal{D}_i(t;\tau) \simeq \mathcal{D}_i(\tau) = (\hbar/2\omega_i)\big(|\mu_{i,t}|^2\mathrm{e}^{-\mathrm{i}\omega_i\tau} + |\nu_{i,t}|^2\mathrm{e}^{\mathrm{i}\omega_i\tau}\big). \tag{3}$$

The terms $\propto \mathrm{e}^{\pm 2\mathrm{i}\omega_i t}$ drop out when averaging t over a vibrational period. For what follows it is essential to note that, under rather general assumptions, the asymptotic phonon correlation function $\mathcal{D}_i(t,\tau)$ at large times has the form (3) also in the case when the interaction Hamiltonian comprises more than two phonon operators and when the Hamiltonian cannot be diagonalized [11,13]. This allows one to apply the described method also for the description of multiphonon relaxation caused by higher-order anharmonicities.

2 Multiphonon emission

Let us consider first the decay of a strongly-excited local mode due to a simultaneous emission of $k \geq 2$ phonons. The Hamiltonian of the system under consideration is

$$\hat{H} = \hat{H}_0 + \hat{H}_{int}, \quad \hat{H}_0 = \sum_i \hbar\omega_i(\hat{a}_i^+\hat{a}_i + 1/2),$$
$$\hat{H}_{int} = \hat{Q}\sum_m V_{m,k}\,\hat{q}_m^k. \tag{4}$$

Here $\hat{H}_{int}$ is the anharmonic interaction in the collinear configurational approximation [7,9], $V_{m,k} = \sqrt{n_l\hbar/2\omega_l}U_m^{(k+1)}$. $U_m^{(k)}$ are the parameters of the k'th order anharmonicity, $\hat{q}_m = \sum_i e_{im}\hat{x}_i$ are the mutually orthogonal displacement operators of the host atoms with respect to the atom(s) of the mode ($\sum_i e_{im}e_{im'} = \delta_{mm'}$). We take into account that the strongly-excited mode can be considered classically and replace the operator $\hat{Q}$ by $Q(t) \simeq A\cos\omega_l t$, where A is the initial amplitude of the mode. Then

$$\hat{H}_{int} \simeq A\cos\omega_l t\sum_m V_{m,k}\,\hat{q}_m^k.$$

This interaction Hamiltonian describes the k-phonon emission due to a periodical local field.

2.1 Phonon correlation function

To calculate the rate of the multiphonon emission, let us consider the phonon correlation function $D_i(t)$. We proceed from the equation of motion of a phonon

$$\ddot{\hat{x}}_i(t) + \omega_i^2\hat{x}_i(t) + ke_iV_kQ(t)\hat{q}^{k-1}(t) = 0$$

(the subscript m is omitted); its integral form reads:

$$\hat{x}_i(t) \simeq \hat{x}_{0i}(t) - k\bar{e}_iAV_k \times\int_0^t \mathrm{d}t_1\sin(\omega_i(t-t_1))\hat{q}^{k-1}(t_1)\cos\omega_l t_1, \tag{5}$$

where $\bar{e}_i = e_i/\omega_i$, $\hat{x}_{0i}(t) = (\hbar/2\omega_i)(\hat{a}_i\mathrm{e}^{-\mathrm{i}\omega_i t} + \hat{a}_i^+\mathrm{e}^{\mathrm{i}\omega_i t})$. Inserting (5) into (3), one gets

$$\mathcal{D}_i(t;\tau) \simeq (\hbar/2\omega_i)\mathrm{e}^{-\mathrm{i}\omega_i\tau} + \big(k^2V_k^2A^2\bar{e}_i^2/4\big) \times\int_0^{t+\tau}\mathrm{d}t_1\int_0^t\mathrm{d}t_2D_{k-1}(t_1,t_2) \times\cos\left(\omega_i(t_1-t_2-\tau)\right)\cos\left(\omega_l(t_1-t_2)\right), \tag{6}$$

where $D_{k-1}(t_1,t_2) = \big\langle 0|\hat{q}^{k-1}(t_1)\hat{q}^{k-1}(t_2)|0\big\rangle$ is the multiparticle displacement correlation function. Here we took into account the relations

$$\cos\omega_l t_1\cos\omega_l t_2 = [\cos\left(\omega_l(t_1+t_2)\right) + \cos\left(\omega_l(t_1-t_2)\right)]/2,$$

$$\sin\left(\omega_i(t+\tau-t_1)\right)\sin\left(\omega_i(t-t_2)\right) = [\cos\left(\omega_i(t_1-t_2-\tau)\right) - \cos\left(\omega_i(2t+\tau-t_1-t_2)\right)]/2$$

and neglected fast-oscillating terms having the factors $\cos\left(\omega_l(t_1+t_2)\right)$, $\cos\left(\omega_l(t_1+\tau)\right)$, $\cos\omega_l t_2$ and $\cos\left(\omega_i(2t+\tau-t_1-t_2)\right)$ under the integrals since at large t these terms drop out when averaging t over a vibrational period.

The function $D_{k-1}(t_1,t_2)$ under the integral (6) essentially differs from zero for $|t_1-t_2| \lesssim (k-1)\Gamma \ll t$ where $(k-1)\Gamma$ is the characteristic width of $(k-1)$-phonon transitions (Γ is the characteristic width of the phonon spectrum). Therefore in the large time limit $t \gg \tau$ this integral

is $\propto t$; this allows one to replace the upper limit $t+\tau$ by t. Then the residual τ dependence of the integral in equation (6) is given by the factor $\cos(\omega_i(t_1-t_2-\tau))$, *i.e.* the dependence on τ of the phonon correlation function indeed has the form (3). The factor of the $\propto \mathrm{e}^{\mathrm{i}\omega_i\tau}$-term equals

$$|\nu_{i,t}|^2 \simeq \frac{A^2V_k^2e_i^2}{4\hbar\omega_i}\iint_0^t \mathrm{d}t_1\mathrm{d}t_2\mathrm{e}^{\mathrm{i}\omega_i(t_2-t_1)} \times\cos(\omega_l(t_2-t_1))D_{k-1}(t_1,t_2). \quad (7)$$

The derived relation holds if the rate of the process is sufficiently small as compared to $k\Gamma$. The fact that in this case equation (3) holds also for $k>2$ means that phonons remain almost harmonic. This allows one to use in (7) the pair correlation approximation

$$D_{k-1}(t_1,t_2)\approx(k-1)!\,D^{k-1}(t_1,t_2)$$

where $D(t,t')=\langle 0|\hat{q}(t)\hat{q}(t')|0\rangle$ is the displacement pair correlation function. Here the same time pairings are neglected, as they give contribution to $k-2,k-4,\ldots$ –phonon transitions and, therefore, result in the renormalization of the anharmonic constants V_k. This renormalization is usually small but it can be incorporated in the theory if needed.

Note that the validity of equation (3) with a non-zero value of $|\nu_{i,t}|$ means the existence of the anomalous correlations $\langle\hat{b}_{it}^2\rangle=\nu_{i,t}\mu_{i,t}$. Unlike a superconducting state of a metal, which is also characterized by the existence of anomalous correlations, here these correlations depend on time.

2.2 Rate of energy loss

To find the rate of the energy loss of the mode, one should insert equation (7) into equation (2). Taking into account the integral relation

$$\iint_0^t \mathrm{d}t_1\mathrm{d}t_2=\int_0^t\mathrm{d}t'\int_{-t'}^{t'}\mathrm{d}t'',$$

where $t'=(t_1+t_2)/2$ and $t''=t_1-t_2$, and replacing the limits $\pm t'$ by $\pm\infty$ (which can be done in the case under consideration $t,t'\gg 1/k\Gamma$), one gets in the pair correlation approximation

$$\dot{E}\simeq(A^2k!V_k^2\omega_l/4\hbar)\int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{\mathrm{i}\omega_l t}\,d_0(t)D^{k-1}(t), \quad (8)$$

where $d_0(t)=\sum_i(\hbar/2\omega_i)e_i^2\mathrm{e}^{-\mathrm{i}\omega_i t}$. Thus, in order to find the rate of the nonradiative transitions one needs to calculate the displacement correlation function $D(t)$. If the anharmonic interaction is weak, then $D(t)\approx d_0(t)$. In this approximation the equation (8) coincides with the corresponding equation of the standard time-dependent perturbation theory which gives

$$\dot{E}^{(0)}\simeq(A^2k!V_k^2\omega_l/4\hbar)\int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{\mathrm{i}\omega_l t}\,d_0^k(t).$$

2.2.1 Displacement correlation function

To get beyond the perturbation theory we consider the equation of motion for the displacement operator(s) $\hat{q}$. From (5) it follows that

$$\hat{q}(t)=\hat{q}_0(t)-kAV_k\int_0^t\mathrm{d}t_1G(t-t_1)\hat{q}^{k-1}(t_1)\cos\omega_l t_1,$$

where $\hat{q}_0(t)=\sum_i e_i\hat{x}_{0i}(t)$, $G(t)=\theta(t)\sum_i(e_i^2/\omega_i)\sin\omega_i t$ is the Green function of the lattice dynamics [14], $\theta(t)$ is the Heaviside step-function. By using this equation for the first operator $\hat{q}(t_1)$ under the integral, one gets

$$\hat{q}(t)=\hat{q}_0(t)-kAV_k\int_0^t\mathrm{d}t_1G(t-t_1)\big[\hat{q}_0(t_1)-kAV_k \times\int_0^{t_1}\mathrm{d}t_2G(t_1-t_2)\hat{q}^{k-1}(t_2)\cos\omega_l t_2\big]\hat{q}^{k-2}(t_1)\cos\omega_l t_1.$$

Let us insert this equation into the displacement correlation function $D(t,t')=\langle 0|\hat{q}(t)\hat{q}(t')|0\rangle$ and apply once again the pair correlation approximation. In this approximation

$$\langle 0|\hat{q}^{k-1}(t_2)\hat{q}^{k-2}(t_1)\hat{q}(t')|0\rangle\approx(k-1)!D(t_2,t_1)^{k-2}D(t_2,t')$$

(the same time pairings are neglected). As a result, we obtain the following integral equation

$$D(t,t')\simeq d^*(t,t')+\tilde{V}_k^2\int_0^t\mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2\,\mathrm{e}^{\mathrm{i}\omega_l(t_2-t_1)}G(t-t_1) \times G(t_1-t_2)D^{k-2}(t_2,t_1)\,D(t_2,t'), \quad (9)$$

where $\tilde{V}_k=V_kA\sqrt{kk!}/2$, $d^*(t,t')=\langle 0|\hat{q}_0(t)\hat{q}(t')|0\rangle=\langle 0|\hat{q}(t')\hat{q}_0(t)|0\rangle^*$. The terms $\sim q^{(0)}(t_1)$ under the integrals lead to same time pairing; they are small and therefore neglected; the terms $\sim\mathrm{e}^{\mathrm{i}\omega_l(t_1+t_2)}$ are also neglected as they oscillate fast and therefore give also a very small contribution. Analogously one finds

$$d(t,t')\simeq d_0(t-t')+\tilde{V}_k^2\int_0^t\mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2\,\mathrm{e}^{\mathrm{i}\omega_l(t_2-t_1)}G(t-t_1) \times G(t_1-t_2)D^{k-2}(t_2,t_1)\,d(t_2,t'). \quad (10)$$

2.2.1.1 Spectral representation

Taking into account that in the time interval under consideration the functions $D(t,t')$ and $d(t,t')$ depend only on the time difference, the above equations can be simplified by means of the spectral representation

$$D(\omega)=\int_{-\infty}^{\infty}\mathrm{d}t\mathrm{e}^{\mathrm{i}\omega t}D(t)$$

(and an analogous representation of $d(t)$). Indeed, when using the transformations

$$\int_0^\infty\mathrm{d}t\int_0^t\mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2=\int_0^\infty\mathrm{d}t_2\int_{t_2}^\infty\mathrm{d}t_1\int_{t_1}^\infty\mathrm{d}t,$$

$$\int_0^\infty\mathrm{d}t\mathrm{e}^{\mathrm{i}\omega t}D(t-t')\simeq\mathrm{e}^{\mathrm{i}\omega t'}D(\omega),$$

$t' \gg 1/k\Gamma$, these equations in the spectral representation take the form

$$D(\omega) = d^*(\omega) + G(\omega)\tilde{V}_k g_k(\omega - \omega_l)\tilde{V}_k D(\omega),$$

$$d(\omega) = d_0(\omega) + G(\omega)\tilde{V}_k g_k(\omega - \omega_l)\tilde{V}_k d(\omega),$$

where $d_0(\omega)$ and $G_(\omega)$ are the spectral representations of $d_0(t)$ and $G(t)$, respectively, and

$$g_k(\omega - \omega_l) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\omega-\omega_l)t} G(t) D^{k-2}(-t). \qquad (11)$$

This gives

$$D(\omega) = d_0(\omega)|1 - G(\omega)\tilde{V}_k g_k(\omega - \omega_l)\tilde{V}_k|^{-2}. \qquad (12)$$

Within the given notations the rate of the energy loss in the spectral representation takes the form:

$$\dot{E} = \frac{\omega_l \tilde{V}_k^2}{k\hbar} \iint\cdots\int d_0(\omega_1) \prod_{j=2}^{k} D(\omega_j) \frac{d\omega_j}{2\pi}, \qquad (13)$$

where $\omega_1 = \omega_l - \sum_{j=2}^{k} \omega_j$. The expression under the integral gives a partial probability of the k-phonon transitions at $T = 0$.

2.2.2 The rate of multiphonon transitions

Although the above-given expression for the rate of the energy loss was derived for a classical mode, it is also applicable for the description of the decay of energy levels. Indeed, taking into account that the decay is due to the k-phonon transitions between the adjoining levels n_l and $n_l - 1$, we get for the rate of the k-phonon transitions $\gamma_k \equiv \dot{E}/\hbar\omega_l$ the following expression [13]:

$$\gamma_k \simeq (\tilde{V}_k^2/4k\hbar^2) \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega_l t}\, d_0(t) D^{k-1}(t), \qquad (14)$$

where $\tilde{V}_k = V_k\sqrt{n_l k k!\hbar/2\omega_l}$ and $A = \sqrt{2n_l\hbar/\omega_l}$. In the case under consideration the rate of the generation of phonons is small as compared to $\bar{\omega}$ and ω_l. This means that the account of all other levels, except n_l and $n_l - 1$, does not give any remarkable contribution to the transition rate. Therefore the origin of the levels n_l and $n_l - 1$ is not essential, *i.e.* equation (14) is applicable not only for the description of the k-phonon decay of high levels but also of any excited level. In the case of small $|\tilde{V}_k|$ one can take $D(t) \approx d_0(t)$. Then equation (14) coincides with the one given by the Fermi golden rule for arbitrary n_l.

Note that equation (14) does not include the finite lifetime broadenings of the initial and final levels. To take them into account one should add under the integral the factor $\exp\{-\gamma|\tau|\}$, where γ is the sum of the decay constants (rates) of these levels; the latter should be determined self-consistently.

2.2.3 Effect of temperature

The finite temperature effect can be described as usual: one should take into account the stimulated transitions. As a result, one gets an additional factor $(1 - \mathrm{e}^{-\hbar\omega_l/k_BT}) \prod_{j=1}^{k}(1 + \bar{n}_j)$ (which takes into consideration phonon-induced transitions) [15,16,13], where $\bar{n}_j = 1/(\mathrm{e}^{\hbar\omega_j/k_BT} - 1)$. In the case of multiphonon transitions in a two-level system, the first factor should be replaced by $(1 + \mathrm{e}^{-\hbar\omega_l/k_BT})$ [13,15,16].

3 Discussion

Equations (11–14) give a solution of the problem: by solving the nonlinear integral equation (11), one finds $g_k(\omega)$ and $D(\omega)$, which allows one to calculate the rate γ_k. The main properties of the solution are:

1. In the weak coupling limit $D(\omega) = d_0(\omega)$ and $\gamma_k \sim |\tilde{V}_k|^2$ in accordance with the perturbation theory. In the opposite limit of a very strong coupling, as it follows from (12), $D \sim |\tilde{V}_k|^{-4/(2k-3)}$, which gives $\gamma_k \sim |\tilde{V}_k|^{-2/(2k-3)}$; *i.e.* $\gamma_k \to 0$ if $\tilde{V}_k \to \infty$ (see also [13] where an analogous conclusion was made on the basis of some qualitative arguments). This is the opposite behavior as compared to the perturbation theory. Yet the interpretation of this surprising result is straightforward – the multiphonon decay is of a purely quantum-mechanical origin and, therefore, it should disappear in the classical limit $n_l \sim \tilde{V}_k^2 \to \infty$.
2. $G(\omega)$ is the sign-alternating complex function. Therefore there are some frequencies ω_{cr} for which the imaginary part of the denominator in (12) turns to zero. Besides, for some specific value(s) of the interaction $\tilde{V}_{k,cr}$ the real part of the denominator also vanishes at ω_{cr}. This means that γ_k has a sharp peak(s) at $\tilde{V}_{k,cr}$. To find out how γ_k depends on $\tilde{V}_k$ in the vicinity of $\tilde{V}_{k,cr}$ we expand the denominator $|R(\omega)|^2$ in (12) near ω_{cr}: $|R(\omega)|^2 \approx |R + \mathrm{i}(\omega - \omega_{cr})R'|^2$ where R is real and R' is imaginary. This gives $D(\omega) \sim [(\tilde{V}_k - \tilde{V}_{k,cr})^2 + (\omega - \omega_{cr})^2|R'/R|^2]^{-1}$. If $\tilde{V}_k \to \tilde{V}_{k,cr}$ then $D(\tau)$ diverges like $|\tilde{V}_k - \tilde{V}_{k,cr}|^{-1}$. This means that γ_k also diverges like $|\tilde{V}_k - \tilde{V}_{k,cr}|^{-k+1}$. Consequently, the behavior of the system in the vicinity of $\tilde{V}_{k,cr}$ is critical; *i.e.* it resembles a phase transition. The order parameter is connected with the mean field associated with the anomalous correlations, which is changed stepwise on the transition. The critical index equals $k - 1$.

4 Numerical example

As an example, we consider the multiphonon relaxation of a local mode caused by an anharmonic interaction with a narrow-phonon band. We suppose that the mode is localized on an atom and take into account two diagonal elements of the Green function which stand for the contribution of two nearest atoms of the lattice to the interaction; the non-diagonal elements are usually much smaller [14]

and approximate the density of states of the phonon band by the parabolic distribution

$$\rho(\omega) = (3/4\Gamma)[1 - (\omega - \omega_1)^2)/\Gamma^2]; \;\; |\omega - \omega_1| < \Gamma \ll \omega_1;$$

$\rho(\omega) = 0$ if $|\omega - \omega_1| \geq \Gamma$. Here ω_1 is the mean frequency and Γ is the half-width of the band.

By using the dimensionless frequency $\Omega = (\omega - \omega_1)/\Gamma$ and the time $\tau = t\Gamma$, the equation (14) takes the form

$$\gamma_k = \frac{2w_k^2\Gamma}{k}\int_0^\infty \mathrm{d}\tau d_0(\tau)D^{k-1}(\tau),$$

where $w_k = (|\tilde{V}_k|/k\hbar\Gamma)(\hbar/2\omega_1)^{k/2}$ is the dimensionless interaction parameter, $D(\tau)$ is the Fourier transform of the function $D(\Omega)$. This function should be determined from the following nonlinear equations:

$$g_k(\Omega) = \int_0^\infty \mathrm{d}\tau \mathrm{e}^{\mathrm{i}\Omega\tau}G(\tau)^* D^{k-2}(\tau), \qquad (15)$$

$$D(\Omega) = \frac{d_0(\Omega)}{|1 - w^2 G(\Omega)g_k(\Omega)|^2}, \qquad (16)$$

where $d_0(\Omega) = 2\mathrm{Im}G(\Omega)$,

$$d_0(\tau) = \mathrm{i}G(\tau) = (3/2\tau^3)(\sin\tau - \tau\cos\tau),$$

$$G_0(\Omega) = \frac{3}{4}\left[(1-\Omega^2)\ln\left|\frac{1-\Omega}{1+\Omega}\right| - 2\Omega + \mathrm{i}\pi(1-\Omega^2)\theta(1-\Omega^2)\right].$$

For small w_k (smaller than $w_{k,cr}$) the equations (15, 16) can be solved by using the standard iteration procedure. However, for $w_k > w_{k,cr}$ this procedure diverges. In this case the approximate solutions of the given equations have been found by means of the following approximation:

$$D(\Omega) = A\left[1 - \left(\Omega^2 + c^2\right)^\beta / \left(1 + c^2\right)^\beta\right];$$

parameters A, β and c have been found from the best fit of the input and the output functions. The results of calculations of γ_k at $T = 0$ in dependence of the dimensionless interaction parameters w_k are given in Figures 1, 2. For small $w_k \ll 1$ the rates linearly increase with the w_k^2 (in accordance with the Fermi golden rule). For larger w_k this dependence is changed to a superlinear one; the superlinearity increases with k. The rates have sharp peaks at $w_{k,cr} \lesssim 1$. Thereby, as expected from a general consideration, $\gamma_k \propto |w_k - w_{k,cr}|^{-k+1}$ if $\gamma \to \infty$. However, only the rates satisfying the condition $\gamma_k \ll k\Gamma$ are consistent with the assumptions of the theory. In the case of a high-order multiphonon relaxation ($k \gg 1$) for large w_k (larger than $w_{k,cr}$) the rate very slowly decreases with the increasing of the interaction parameter (as $w_k^{2/2(k-3)}$) and is very high ($\sim \Gamma$) practically for all reasonable values of $w_k \gtrsim w_{k,cr}$.

The temperature dependence of the rate in this model is given by the factor $(1 - \mathrm{e}^{-k\hbar\omega_1/k_BT})/(1 - \mathrm{e}^{-\hbar\omega_1/k_BT})^k$.

To clarify the question in which systems the described effects could be expected to be observed we present an estimation of w_k. Supposing that atoms interact *via* the Lennard-Jones potential, and taking into account that for large k the main contribution to the anharmonic interaction constants is given by the repulsive part r^{-12} of the potential, one obtains

$$w_k \sim \sqrt{n_l(k-1)!}[(13+k)!/13!](a_0/r)^{k+1},$$

where a_0 is the zero-point amplitude of the host atoms, r is the distance to the nearest atom (see also [9], where an analogous estimation is given). According to this formula, in quantum crystals and in other crystals with a large ratio $a_0/r \geq 0.2$, a value $w_k \sim 1$ can be reached for a vibration level as low as $n_l \lesssim 10$ (we remind that $w_k \sim \sqrt{n_l}$). In the case of the Xe_2^* molecule in a Xe crystal, studied in [12], $M_0/M = 2$, $a_0/r \sim 0.1$ and this formula gives $w_2 \sim 1$ for $n_l \approx 20$. This agrees well with the critical number $n_l = 22$ obtained experimentally in [12].

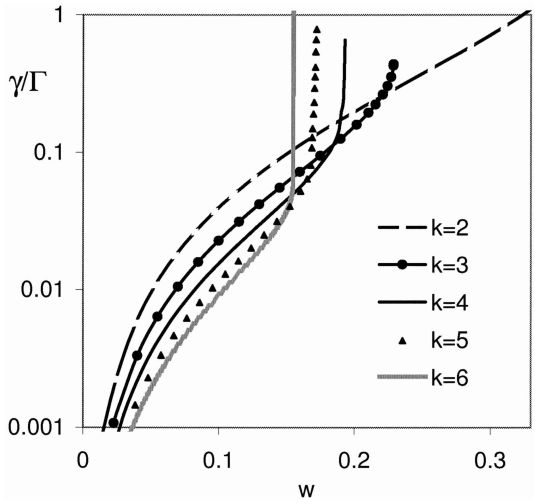

Fig. 1. The dependence of the transition rates γ_k (in Γ units) on the dimensionless interaction parameters w_k below $w_{k,cr}$.

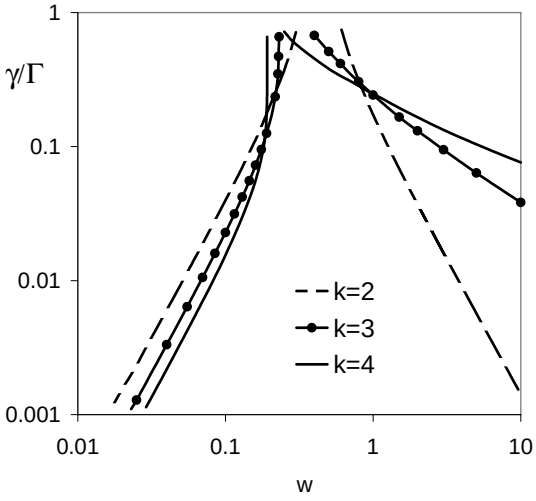

Fig. 2. The dependence of the rates γ_k (in Γ units) of two-phonon ($k = 2$), three-phonon ($k = 3$) and four-phonon ($k = 4$) transitions on the dimensionless interaction parameters w_k.

5 Conclusion

In summary, we have developed a nonperturbative theory of a multiphonon relaxation of a local mode, caused by a high-order anharmonic interaction. The relaxation process is characterized by time-dependent anomalous correlations of phonons. The rate of the relaxation is expressed through the positive frequency part of the nonstationary displacement correlation functions. The nonlinear integral equations for these functions have been derived and solved numerically.

We have found that the relaxation rate exhibits a critical behavior: it is sharply increased near a specific (critical) value(s) of the interaction. The corresponding dependence is characterized by the critical index $k-1$, where k is the number of the created phonons. In the close vicinity of the critical point(s) the rate attains a very high value comparable to the frequency of phonons. In the weak coupling limit the obtained results agree with the predictions of the standard perturbation theory.

The research was supported by the ETF Grants No. 3864 and No. 4032.

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