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Classical Theory of Nonlinear Oscillators Interacting with a Medium

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The correlation function $Q_\varkappa(t)$ of the normal coordinates of singled out nonlinear vibrations interacting with the vibrations of the continuous spectrum of a medium (e.g. of local or quasi-local vibrations in crystals) as well as its spectral representation $Q_\varkappa(\omega)$ were investigated. The calculations have been carried out for the case of high temperatures when the classical approach is applicable. The use of asymptotic methods of nonlinear mechanics and some results of the theory of random processes allowed to consider the case of an arbitrary ratio between the constants characterizing the non-linearity of singled out oscillators and their energy of interaction with the medium (but with the assumption that both these constants are small). In this general case asymptotic explicit expressions were derived for $Q_\varkappa(t)$ and $Q_\varkappa(\omega)$. Using the Fokker-Planck equation for this problem we have also derived the difference equations which determine $Q_\varkappa(\omega)$.

Рассмотрена корреляционная функция $Q_\varkappa(t)$ нормальных координат выделенных нелинейных колебаний, взаимодействующих с колебаниями непрерывного спектра среды (например, локальных или квазилокальных колебаний в кристалле), и ее спектральное представление $Q_\varkappa(\omega)$. Расчет проведен в пренебрежении тонкой структурой спектра для случая высоких температур, когда применимо классическое приближение. Использование асимптотических методов нелинейной механики и некоторых результатов теории случайных процессов позволило рассмотреть случай произвольного соотношения между константами, характеризующими нелинейность выделенных осцилляторов и энергию их взаимодействия со средой (но в предположение, что эти константы невелики). В этом общем случае получены асимптотические явные выражения для $Q_\varkappa(t)$ и $Q_\varkappa(\omega)$. В приложении при помощи рассмотрения уравнения Фоккера-Планка для этой задачи получены разностные уравнения, определяющие $Q_\varkappa(\omega)$.

1. Introduction

The interaction of singled out linear oscillators with a medium was the subject of a number of papers. This problem was considered in connection with both the general problem of investigating the process of approaching the equilibrium state in a sub-system (see, for example, [1] to [3]) and some special problems in the theory of lasers (see, e.g., [4] and [5]) and in the theory of local (LV) and quasi-local vibrations (QV) near impurity centres in crystals (see, for example, [6]). In the latter case, the spectral distribution $Q_\varkappa(\omega)$ of the time correlation function $Q_\varkappa(t)$ of the coordinates of LV or QV which determines the spectral distribution of the infrared absorption coefficient or the inelastic neutron scattering cross-section was investigated in detail.

However, some results are significantly changed if the non-linearity of the singled out oscillators is taken into account. In particular, the width and shape

of the distribution $Q_\varkappa(\omega)$ should be strongly affected by the non-equidistance of the energy levels of the nonlinear oscillator. As it is shown in the papers [7] and [8], such a non-equidistance depending on the ratio between its value $\Delta\omega$ and the reciprocal lifetime of the localized modes, $1/\tau$, may lead to the appearance of a fine structure in the spectral distribution in the frequency range near the frequency of LV or QV, or to the formation of a single broadened distribution. Its width is not connected with a finite lifetime of the localized state and may greatly predominate over $1/\tau$.

Calculations of the spectral distribution with all these effects being taken into account were carried out in the works [7] and [8] by the method of the Green's temperature function, but expressions for the Green's function and for the correlation function had been found only in the extreme cases $\Delta\omega \gg \tau^{-1}$ and $\Delta\omega \ll \tau^{-1}$, while in the general case the expression for $Q_\varkappa(\omega)$ has not been derived.

The problem apparently becomes simpler at high temperatures when $kT \gg \hbar\,\omega_\varkappa$ and the occupation number of QV (or LV) $n_\varkappa \gg 1$. If here the fine structure of the spectral distribution is smeared or if only the distribution averaged over the fine structure is of interest, the calculation may be carried out by the classical theory (the fine structure which is defined by the level discreteness may be investigated only by the quantum theory). This allows to use the developed asymptotic methods of nonlinear mechanics [9] and some results of the theory of random processes. Hence, as will be shown below, it seems to be possible to determine the time correlation functions and their spectral representations for any ratios between $\Delta\omega$ and $1/\tau$.

The solution of the problem may be quite different depending on the fact whether the frequencies $\omega_\varkappa$ of different LV (or QV) are coincident (close) or strongly different. Below we shall consider the simpler case of centres of low symmetry where the degeneracy is absent and the $\omega_\varkappa$ are highly different. We shall restrict ourselves to the case when the $\omega_\varkappa$ are not close to some combination of the frequencies $\omega_{\varkappa'} \pm \omega_{\varkappa''}$.

Consideration will be made with the help of the model of a weakly bound impurity atom already used for the investigation of the spectral distribution QV (see, e.g., [8]). It is supposed in this model that the force constants of interaction of the impurity atom with the crystal atoms are much smaller than that of the interaction of the crystal atoms with each other.

If the impurity atom mass is comparable with that of the crystal atoms, then the frequencies $\omega_\varkappa$ lie in the low-frequency range of vibrations of the continuous spectrum, and if the state density is sufficiently low, then QV appears. But in the case of very light impurity atoms, when $\omega_\varkappa$ does not coincide with the frequencies of the continuous spectrum, LV appears. It is noteworthy that some results obtained in the model under consideration are qualitatively applicable to more general models of vibrations of impurity atoms and molecules. It will as well be supposed that the anharmonicity is sufficiently low and hence the anharmonic corrections to the frequencies $\omega_\varkappa$ are much smaller than these frequencies.

2. Exclusion of the Vibrations of the Continuous Spectrum

The oscillation amplitude of a weakly bound impurity atom greatly predominates over that of the crystal atoms and in a zero approximation the latter may be regarded as immovable. In this approximation even QV of the impurity may be considered as LV of nonlinear oscillators, and the interaction of these oscillations with that of the continuous spectrum (harmonic and anharmonic)

may be treated as a small perturbation which turns LV into QV. The vibration of the continuous spectrum at the frequencies ω_k corresponds in the zeroth approximation to the oscillation of, generally speaking, an imperfect crystal from which the impurity atom is taken away (the index k characterizes the branch number and the wave vector of a plane wave distorted by the defect). For simplicity we shall assume that LV or QV of another type do not appear in the vicinity of the impurity.

It is convenient to choose the normal coordinates and momenta of LV, $q_\varkappa$ and $p_\varkappa$, and of the vibration of the continuous spectrum, q_k and p_k, in such a way that with neglect of the above mentioned interaction they may diagonalize the harmonic part of the Hamiltonian. Then for the impurity atom located in the position which has an inversion centre, the Hamiltonian of the system may be written as

$$\left.\begin{aligned} H &= H_0 + \sum_k H_k\, q_k + \frac{1}{2}\sum_{kk'} H_{kk'}\, q_k\, q_{k'}\,; \\ H_0 &= \sum_\varkappa \left(\frac{1}{2}\, p_\varkappa^2 + \frac{1}{2}\,\omega_\varkappa^2\, q_\varkappa^2 + \frac{1}{4}\,\gamma_{\varkappa\varkappa}\, q_\varkappa^4\right) + \\ &\quad + \frac{3}{8}\sum_{\varkappa\varkappa'}{}'\,\gamma_{\varkappa\varkappa'}\, q_\varkappa^2\, q_{\varkappa'}^2 + \frac{1}{2}\sum_k (p_k^2 + \omega_k^2\, q_k^2)\,, \\ H_k &= \sum_\varkappa \varepsilon_{\varkappa k}\, q_\varkappa + \sum_{\varkappa\varkappa'} \zeta_{\varkappa\varkappa' k}\, q_\varkappa\, q_{\varkappa'}\,, \\ H_{kk'} &= \sum_\varkappa \xi_{\varkappa kk'}\, q_\varkappa + \sum_{\varkappa\varkappa'} \eta_{\varkappa\varkappa' kk'}\, q_\varkappa\, q_{\varkappa'}\,. \end{aligned}\right\} \tag{1}$$

Here and below the prime at the sum over $\varkappa\,\varkappa'$ (or over $\varkappa'$) means that in the summation one should omit the term with $\varkappa' = \varkappa$. The factors γ, ε, ξ, η, and ζ, according to our assumption, include small parameters. In equation (1) the terms are omitted connected with the anharmonicity of higher order as well as terms (of the type $\gamma_{\varkappa\varkappa'\varkappa''}\, q_\varkappa^2\, q_{\varkappa'}\, q_{\varkappa''}$) which lead to corrections of higher order of smallness as compared to the terms taken into account.

In the following for the system with the Hamiltonian (1) we shall determine the time correlation function $Q_\varkappa(t) = \langle\langle q_\varkappa(t)\, q_\varkappa(0)\rangle\rangle$ ($\langle\langle \ldots \rangle\rangle$ denotes statistical averaging) and its spectral representation $Q_\varkappa(\omega)$. The function $Q_\varkappa(\omega)$ with the accuracy to factors weakly dependent on frequency determines the spectral distribution for the peak of the infrared absorption by LV or QV in the range $\omega \approx \omega_\varkappa$ or for the neutron inelastic scattering in the range of transmitted energy $\approx \hbar\,\omega_\varkappa$.

From equation (1) it follows that the equations of motion are of the form

$$\ddot{q}_k + \omega_k^2\, q_k = -\,H_k - \sum_{k'} H_{kk'}\, q_{k'}\,, \tag{2}$$

$$\ddot{q}_\varkappa + \omega_\varkappa^2\, q_\varkappa + \gamma_{\varkappa\varkappa}\, q_\varkappa^3 + \frac{3}{2}\sum_{\varkappa'}{}'\,\gamma_{\varkappa\varkappa'}\, q_\varkappa\, q_{\varkappa'}^2 = -\sum_k H_k^\varkappa\, q_k - \frac{1}{2}\sum_{kk'} H_{kk'}^\varkappa\, q_k\, q_{k'}\,; \tag{3}$$

$$H_k^\varkappa = \frac{\partial H_k}{\partial q_\varkappa}, \qquad H_{kk'}^\varkappa = \frac{\partial H_{kk'}}{\partial q_\varkappa}.$$

It is convenient to exclude from these equations the vibrations of the continuous spectrum and to derive the equation dependent only on the coordinates of LV or QV and some random function (Bogolubov was the first who made this

exclusion when solving the problem of the relaxation of the harmonic oscillator [1]). We shall begin with the consideration of those QV for which the interaction with two modes of the continuous spectrum (the last term in (1)) is of much less importance than that with a single mode. Accordingly let us set $\xi_{\varkappa kk'} = 0$, $\eta_{\varkappa\varkappa' kk'} = 0$. Then the general solution of (2) may be written as

$$q_k(t) = A_k \cos(\omega_k t + \varphi_k) - \frac{1}{\omega_k}\int_0^t H_k(\tau) \sin\omega_k (t-\tau)\, d\tau . \tag{4}$$

Here the amplitude and phase, A_k and φ_k, are determined from initial conditions and have the meaning of random values. Substituting equation (4) into (3) we get the integro-differential equation containing only normal coordinates of QV under consideration:

$$\ddot{q}_\varkappa + \omega_\varkappa^2 q_\varkappa + \gamma_{\varkappa\varkappa} q_\varkappa^3 + \frac{3}{2}\sum_{\varkappa'}{}' \gamma_{\varkappa\varkappa'} q_\varkappa q_{\varkappa'}^2 = f_\varkappa + L_\varkappa . \tag{5}$$

Here $q_\varkappa \equiv q_\varkappa(t)$ and

$$\left.\begin{aligned} f_\varkappa &= -\sum_k H_k^\varkappa(t)\, A_k \cos(\omega_k t + \varphi_k) , \\ L_\varkappa \equiv L_\varkappa[q] &= \int_0^t \sum_k \frac{1}{\omega_k} H_k^\varkappa(t)\, H_k(\tau) \sin\omega_k (t-\tau)\, d\tau . \end{aligned}\right\} \tag{6}$$

In the case of LV the relaxation processes are due to their interaction with two modes of the continuous spectrum, and hence it is necessary to take into account the last terms in equations (1), (2), and (3). When doing this care must be taken of the smallness of the values ε, ξ, η, and ζ, while the higher terms (higher than the second order) with respect to these values must be neglected. We shall solve equation (2) by the iteration method. Taking last term in (2) into account, the term $H_k(\tau)$ in (4) should be substituted by $H_k(\tau) + \sum_{k'} H_{kk'}(\tau)\, q_{k'}(\tau)$. We then put the generalized equation (4) into (3) fulfilling the decoupling (see [10]) that is taking instead of $q_{k'}(t)\, q_{k''}(\tau)$ their average value obtained in the zeroth approximation, $\langle\langle q_{k'}(t)\, q_{k''}(\tau)\rangle\rangle = \delta_{k'k''} kT\, \omega_{k'}^{-2} \cos\omega_{k'}(t-\tau)$, and eliminating those terms which will not contribute (in the approximation under study) to damping and shift. It will be found that $q_\varkappa(t)$ is determined by equation (5) if we substitute $f_\varkappa$ and $L_\varkappa$ for $\tilde{f}_\varkappa$, $\tilde{L}_\varkappa$. Here

$$\left.\begin{aligned} \tilde{f}_\varkappa &= f_\varkappa - \frac{1}{2}\sum_{kk'} H_{kk'}^\varkappa A_k A_{k'} \cos(\omega_k t + \varphi_k) \cos(\omega_{k'} t + \varphi_{k'}) , \\ \tilde{L}_\varkappa &= L_\varkappa + kT \sum_{kk'} \frac{1}{\omega_{k'}\omega_k^2} H_{kk'}^\varkappa(t) \int_0^t H_{k'k}(\tau) \sin\omega_{k'}(t-\tau) \cos\omega_k (t-\tau)\, d\tau . \end{aligned}\right\} \tag{7}$$

3. Determination of the Time Correlation Functions

Of the utmost interest are the functions $Q_\varkappa(t)$ in the large time range $t \gg t_0$ where t_0 is the highest of the values $\omega_\varkappa^{-1}$, ω_{m}^{-1} (ω_{m} is the maximum frequency of phonons). To determine $Q_\varkappa(t)$ in this range it is useful to seek the solution of equation (5) with the aid of asymptotic methods of perturbation theory which

give approximate solutions slightly different from the exact solution in the whole time interval. We shall illustrate the use of these methods at first on the example of QV where we can neglect the anharmonic interaction with the vibrations of the continuous spectrum and set $\xi = \eta = \zeta = 0$ (later the results will also be formulated for the more general case). In this case $f_\varkappa$ and $L_\varkappa$ in equation (5) have the form

$$\left.\begin{aligned} f_\varkappa &= -\sum_k \varepsilon_{\varkappa k} A_k \cos(\omega_k t + \varphi_k), \\ L_\varkappa[q] &= \int_0^t \sum_{\varkappa'} K_{\varkappa\varkappa'}(t-\tau)\, q_{\varkappa'}(\tau)\, \mathrm{d}\tau; \\ K_{\varkappa\varkappa'}(\tau) &= \sum_k \frac{1}{\omega_k} \varepsilon_{\varkappa k}\, \varepsilon_{\varkappa' k} \sin \omega_k \tau . \end{aligned}\right\} \tag{8}$$

For determining the asymptotic (on small parameters $\varepsilon_{\varkappa k}$) solution of equation (5) with the right-hand side (8) we use the method analogous to that of averaging in nonlinear mechanics [9]. For this we shall go from the unknown functions $q_\varkappa$ and $\dot{q}_\varkappa$ to the new unknown functions $u_{\varkappa 1}$ and $u_{\varkappa 2}$:

$$q_\varkappa = \sum_\alpha u_{\varkappa\alpha} \exp(i\,\omega_{\varkappa\alpha} t), \quad \dot{q}_\varkappa = i \sum_\alpha \omega_{\varkappa\alpha} u_{\varkappa\alpha} \exp(i\,\omega_{\varkappa\alpha} t). \tag{9}$$

Here $\alpha = 1, 2$; $\omega_{\varkappa 1} \equiv \omega_\varkappa$; $\omega_{\varkappa 2} = -\omega_\varkappa$; $u_{\varkappa 1} = u^*_{\varkappa 2}$. From equation (9) it follows that $\sum_\alpha \dot{u}_{\varkappa\alpha} \exp(i\,\omega_{\varkappa\alpha} t) = 0$ and $\ddot{q}_\varkappa + \omega_\varkappa^2 q_\varkappa = i \sum_\alpha \omega_{\varkappa\alpha} \dot{u}_{\varkappa\alpha} \exp(i\,\omega_{\varkappa\alpha} t)$. Having in mind these equalities by substitution of the values (9) into (5) (with the right-hand side (8)) we get

$$\dot{u}_{\varkappa\alpha} = -\frac{3}{2i\omega_{\varkappa\alpha}} \sum_{\varkappa'} \gamma_{\varkappa\varkappa'}\, y_{\varkappa'}\, u_{\varkappa\alpha} + \frac{1}{2i\omega_{\varkappa\alpha}} \mathrm{e}^{-i\omega_{\varkappa\alpha} t} f_\varkappa + \Lambda_{\varkappa\alpha}[u]; \tag{10}$$

$$\Lambda_{\varkappa\alpha}[u] = \frac{1}{2i\omega_{\varkappa\alpha}} \sum_{\varkappa'\alpha'} \mathrm{e}^{i(\omega_{\varkappa'\alpha'} - \omega_{\varkappa\alpha})t} \int_0^t K_{\varkappa\varkappa'}(\tau)\, \mathrm{e}^{-i\omega_{\varkappa'\alpha'}\tau}\, u_{\varkappa'\alpha'}(t-\tau)\, \mathrm{d}\tau ,$$

$$y_\varkappa = u_{\varkappa 1}\, u_{\varkappa 2} .$$

In equation (10) according to the idea of the averaging method all terms of the type $(3\,\gamma_{\varkappa\varkappa}/2\,i\,\omega_\varkappa)\, u_{\varkappa 1}\, u_{\varkappa 2}^2 \exp(-2\,i\,\omega_{\varkappa\alpha} t)$, proportional both to the small parameter γ and to the fast oscillating factor $\exp(\pm 2\,i\,\omega_\varkappa t)$, are neglected (as well as the terms $\sim \exp[\pm i\,(\omega_\varkappa \pm \omega_{\varkappa'})\, t]$). They are of importance only for the investigation of the spectral distribution in the range of multiple and combination frequencies. Since in the present work we are concerned only with the range of main frequencies $\omega \approx \omega_\varkappa$, the small terms pointed out must not be taken into account. For the same reason we may preserve only the term with $\varkappa' = \varkappa$, $\alpha' = \alpha$ in the sum over $\varkappa'\,\alpha'$ in the expression $\Lambda_{\varkappa\alpha}[u]$ in equation (10). All these terms having been neglected, the function $u_\varkappa$, contains only the smooth slowly varying (at times $\approx t_0$) and the random parts. In this respect it is more convenient that the initial unknown function $q_\varkappa$ also includes fast oscillating factors $\exp(\pm i\,\omega_\varkappa t), \cdots$.

Introducing the function

$$g_\varkappa(\omega)\, \mathrm{d}\omega = \sum_{\omega < \omega_k < \omega + \mathrm{d}\omega} \frac{\varepsilon_{\varkappa k}^2}{\omega_k^2}; \tag{11}$$

we may go from the sum over k in $K_{\varkappa\varkappa'}(\tau)$ to an integral over ω and after elementary transformation we may write the term $\Lambda_{\varkappa\alpha}[u]$ in (10) in the form

$$\Lambda_{\varkappa\alpha}[u] = -\frac{1}{4\,\omega_{\varkappa\alpha}} \int_0^\infty \mathrm{d}\omega\; \omega\; g_\varkappa(\omega) \int_0^t \mathrm{d}\tau\; [\mathrm{e}^{-i(\omega_{\varkappa\alpha}-\omega)\tau} - \mathrm{e}^{-i(\omega_{\varkappa\alpha}+\omega)\tau}]\; u_{\varkappa\alpha}(t-\tau)\;. \tag{12}$$

In the range of large times $|t| \gg t_0$, neglecting the terms $\sim \varepsilon^2$ or $t_0/|t|$, we may substitute $u_{\varkappa\alpha}(t)$ for $u_{\varkappa\alpha}\,(t-\tau)$ in (12) and take this quantity before the integral sign (one can become sure in this when considering the next expansion term of $u_{\varkappa\alpha}\,(t-\tau)$ in powers of τ). Then

$$\Lambda_{\varkappa\alpha}[u] = (-\Gamma_\varkappa \operatorname{sign} t + i\,P_{\varkappa\alpha})\,u_{\varkappa\alpha}; \qquad |t| \gg t_0; \tag{13}$$

$$\Gamma_\varkappa = \frac{\pi}{4}\,g_\varkappa(\omega_\varkappa)\,, \quad P_{\varkappa\alpha} = \frac{1}{2\,\omega_{\varkappa\alpha}}\,\mathrm{P}\int_0^\infty \frac{\omega^2\,g_\varkappa(\omega)}{\omega_\varkappa^2-\omega^2}\,\mathrm{d}\omega$$

("P" denotes principal value).

Once the substitution of equation (13) is made the integro-differential equation (10) is turned into a stochastic differential equation. Markov's random process corresponds to its solution and therefore this solution may be found by the consideration of the Fokker-Planck equation. This method is explained in the Appendix. Here we shall use another method allowing to find the time correlation functions in the explicit form.

The term containing $y_{\varkappa'}\,u_{\varkappa\alpha} = u_{\varkappa' 1}\,u_{\varkappa' 2}\,u_{\varkappa\alpha}$ transforms the differential equation under study into a nonlinear one. But formally we may consider it as a linear one assuming $y_{\varkappa'}$ to be a known function. Then its solution may be written as

$$u_{\varkappa\alpha}(t)\;\mathrm{e}^{-iP_{\varkappa\alpha}t} = u_{\varkappa 0}\,\mathrm{e}^{i\varphi_{\varkappa\alpha}}\,\mathrm{e}^{F_{\varkappa\alpha}(t)-\Gamma_\varkappa|t|} + \mathrm{e}^{F_{\varkappa\alpha}(t)}\,x_{\varkappa\alpha}(t); \tag{14}$$

$$x_{\varkappa\alpha}(t) = \sum_{k\alpha_1} x_{k\varkappa\alpha\alpha_1}(t)\,\mathrm{e}^{i\varphi_{k\alpha_1}}\,,$$

$$x_{k\varkappa\alpha\alpha_1}(t) = i\,\frac{\varepsilon_{\varkappa k}\,A_k}{4\,\omega_{\varkappa\alpha}}\,\mathrm{e}^{-\Gamma_\varkappa|t|}\int_0^t \mathrm{e}^{i(\omega_k\alpha_1-\tilde{\omega}_{\varkappa\alpha})t_1}\exp\left[\Gamma_\varkappa|t_1| - F_{\varkappa\alpha}(t_1)\right]\mathrm{d}t_1\,,$$

$$F_{\varkappa\alpha} = \frac{3\,i}{2\,\omega_{\varkappa\alpha}}\int_0^t \sum_{\varkappa'} \gamma_{\varkappa\varkappa'}\,y_{\varkappa'}(t_1)\,\mathrm{d}t_1\,.$$

Here $u_{\varkappa 0}$ and $\varphi_\varkappa$ are the initial amplitude and the phase of vibration $\varkappa$, $\varphi_{\varkappa 1} = \varphi_\varkappa$, $\varphi_{\varkappa 2} = -\varphi_\varkappa$, $\varphi_{k1} = \varphi_k$, $\varphi_{k2} = -\varphi_k$, $\tilde{\omega}_{\varkappa\alpha} = \omega_{\varkappa\alpha} + P_{\varkappa\alpha}$, $x_{\varkappa 1}(t) = x^*_{\varkappa 2}(t)$.

In fact equation (14) is an integral equation which defines $u_{\varkappa\alpha}$ but has a convenient form for the averaging necessary for the calculation of the correlation functions. Such a calculation is reduced to the determination of the averages $\langle \exp F_{\varkappa\alpha}(t)\rangle$ and $\langle \mathrm{Re}\; x_{\varkappa\alpha}(t) \exp[F_{\varkappa\alpha}(t) - i\,\varphi_{\varkappa\alpha}]\rangle$ over the random phases $\varphi_{k\alpha}$, $\varphi_{\varkappa\alpha}$ and the amplitudes A_k (averaging over $u_{\varkappa 0}$ will be carried out separately). The corresponding averaging may be performed because the random process $x_{\varkappa\alpha}(t)$, as will be shown below, turns to be normal (if neglecting the corrections $\sim \varepsilon^2$).

Such a process is characterized by the correlation function

$$\langle x_{\varkappa\alpha}(t)\, x^*_{\varkappa'\alpha'}(t')\rangle =$$

$$= \frac{1}{16\,\omega_{\varkappa\alpha}\,\omega_{\varkappa'\alpha'}}\left\langle \sum_{kk'}\sum_{\alpha_1\alpha_2} \varepsilon_{\varkappa k}\,\varepsilon_{\varkappa' k'}\,A_k\,A_{k'}\,\mathrm{e}^{-\Gamma_\varkappa|t|-\Gamma_{\varkappa'}|t'|}\int_0^t\int_0^{t'} \exp\left[i\,(\omega_{k\alpha_1}-\tilde{\omega}_{\varkappa\alpha})\,t_1-\right.\right.$$

$$\left.\left.-i\,(\omega_{k'\alpha_2}-\tilde{\omega}_{\varkappa'\alpha'})\,t_2+i\,(\varphi_{k\alpha_1}-\varphi_{k'\alpha_2})+\Gamma_\varkappa|t_1|+\Gamma_{\varkappa'}|t_2|-F_{\varkappa\alpha}(t_1)+F_{\varkappa'\alpha'}(t_2)\right]\mathrm{d}t_1\,\mathrm{d}t_2\right\rangle\approx$$

$$\approx\delta_{\varkappa\varkappa'}\delta_{\alpha\alpha'}\frac{kT}{\omega_\varkappa^2}\frac{\pi}{4}g_\varkappa(\omega_\varkappa)\,\mathrm{e}^{-\Gamma_\varkappa|t|-\Gamma_{\varkappa'}|t'|}\int_0^t\mathrm{d}t_1\int_0^{t'}\mathrm{d}t_2\exp\left[\Gamma_\varkappa|t_1|+\Gamma_\varkappa|t_2|-F_{\varkappa\alpha}(t_1)+F_{\varkappa\alpha}(t_2)\right]\times$$

$$\times\,\delta\,(t_1-t_2) = 2\,A(t,t')\,\delta_{\varkappa\varkappa'}\,\delta_{\alpha\alpha'}; \qquad (15)$$

$$A(t,t') = \frac{kT}{4\,\omega_\varkappa^2}\exp\left[-\Gamma_\varkappa\,(|t|+|t'|)\right]\left[\exp\left(2\,\Gamma_\varkappa|t_{\min.}|\right)-1\right].$$

Here $|t_{\min.}|$ is the smallest of the values $|t|$, $|t'|$, and account is taken of the fact that $\langle A_k^2\rangle = 2\,kT\,\omega_k^{-2}$ and that $g_\varkappa(\omega_\varkappa)$ is related with $\Gamma_\varkappa$ by equation (13). When calculating (15) we preserve only the terms $k = k'$, $\alpha_1 = \alpha_2 = \alpha$, while the integral over the frequencies, $\int_0^\infty g_\varkappa(\omega)\,\exp\left[i\,(\omega-\tilde{\omega}_\varkappa)\,(t_1-t_2)\right]\mathrm{d}\omega$, is reduced to the δ-function $2\,\pi\,g_\varkappa(\omega_\varkappa)\,\delta\,(t_1-t_2)$. In the range of time significant for further study $|t-t'| \gg t_0$, this leads to a small correction $\sim\varepsilon^2$ or $t_0/|t-t'|$. Of the same order is the expression under consideration at $\varkappa \neq \varkappa'$ or $\alpha \neq \alpha'$ when in the integrand a fast oscillating function occurs. Since, as it is evident from equation (14), the expansion $\exp\left[-F_{\varkappa\alpha}(t)\right]$ includes terms with random quantities $\exp\left[i\,(\varphi_{k\alpha_1}-\varphi_{k'\alpha_2})\right]$, one should also take into account the terms with $k \neq k'$ in the sum (15). However, the integration over the frequencies ω_k and $\omega_{k'}$ will lead to the appearance of the δ-functions $\delta\,(t_1-t_3)\,\delta\,(t_2-t_4)$ in the integrand where t_3 and t_4 are always less than one of the variables t_1 or t_2. Hence the terms with $k \neq k'$ lead only to the corrections $\sim\varepsilon^2$ and may be neglected. Important is the fact that the average $\langle x_{\varkappa\alpha}(t)\,x^*_{\varkappa'\alpha'}(t')\rangle$ was obtained asymptotically in such a form as if the value $x_{\varkappa\alpha}$ had not comprised the random function $\exp\left[-F_{\varkappa\alpha}(t_1)\right]$.

In the same way, neglecting small corrections and taking into account the appearance of a δ-function with argument differences in the integrand (these arguments are always different in the integration interval under study), it is possible to show that the $F_{\varkappa\alpha}$ are omitted in the expression for the averages $\langle x_{\varkappa\alpha}(t_1)\ldots x^*_{\varkappa'\alpha'}(t_4)\rangle$ which define the fourth moment of the distribution, and for the averages of the larger number of factors determining the highest moments.[1]) Therefore asymptotically the presence of $F_{\varkappa\alpha}$ in (14) does not affect all the moments and hence the distribution of the random quantity $x_{\varkappa\alpha}(t)$ which may be considered as the sum of independent random terms of the type $A_k\exp\left(i\,\varphi_{k\alpha}\right)$ (with fixed coefficients).

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[1]) If in the $2\,p$-multiple sum over k_i some of the $k_i = k_j$ coincide, the summation over these k_i (as it was in equation (15)) causes the appearance of the δ-functions $\delta\,(t_i-t_j)$ and cancellation of the factors $\exp\left[F_{\varkappa\alpha}(t_i)-F_{\varkappa\alpha}(t_j)\right]$; hence this part of the expression is reduced to a $2\,p-2$-multiple sum and may be considered by the induction method. But when all k_i are different, then, as may be seen from the integral form of (14) for $F_{\varkappa\alpha}(t)$, the largest from the arguments of the functions $x_{\varkappa\alpha}(t)$ always predominates over all the other times which may enter into the arguments of the δ-functions.

The distribution of such random function may be determined with the aid of the Bogolubov theorem [1]. According to this theorem, if in the sum of N terms, $x_\varkappa(t)=\sum\limits_{k\alpha} x_{\varkappa k\alpha}(t)\exp(i\varphi_{k\alpha})$ the quantities $x_{\varkappa k\alpha}$ are independent random variables, $\varphi_{k\alpha}$ are random phases uniformly distributed from 0 up to 2π, and at $N\to\infty$ $2A(t,t')=2\sum\limits_{k} x_{\varkappa k\alpha}(t)\,x^*_{\varkappa k\alpha}(t')$ tends to coefficients of positively determined form while $\sum\limits_{k} x_{\varkappa k\alpha}(t_1)\ldots x^*_{\varkappa k\alpha}(t_4)\to 0$, then the distribution of the random function in the limit $N\to\infty$ appears to be normal. This means that the probability of the values $x'_\varkappa(t_n)$ ($x_\varkappa = x'_\varkappa + i\,x''_\varkappa$) at times $t_1, t_2, \ldots, t_m$ has the form

$$w\left(\ldots x'_\varkappa(t_n)\ldots\right) = w\left(\ldots x''_\varkappa(t_n)\ldots\right) =$$

$$= (2\pi)^{-m/2}\,|A_{\varkappa n n'}|^{-1/2}\exp\left[-\frac{1}{2}\sum_{n,n'=1}^{m} A^{-1}_{\varkappa n n'}\,x'_\varkappa(t_n)\,x'_\varkappa(t_{n'})\right]; \qquad (16)$$

$$A_{\varkappa n n'} = \frac{1}{2}\langle x_\varkappa(t_n)\,x^*_\varkappa(t_{n'})\rangle = \frac{1}{2}\,\langle x'_\varkappa(t_n)\,x'_\varkappa(t_{n'})\rangle + \frac{1}{2}\langle x''_\varkappa(t_n)\,x''_\varkappa(t_{n'})\rangle\,,$$

where $|A_{\varkappa n n'}|$ is the determinant of the matrix $A_{\varkappa n n'}$.

In equation (14) for $F_\varkappa \equiv F_{\varkappa 1}$ it is convenient to go from the integral over t_1 to the sum over the close equidistant points t_n. Then, taking into account that $y_{\varkappa'} = u_{\varkappa' 1}\,u_{\varkappa' 2}$ is also determined by (14), we get

$$F_\varkappa(t_m) = F^0_\varkappa(t_m) + \sum_{\varkappa'} F_{\varkappa\varkappa'}(t_m);$$

$$F^0_\varkappa(t_m) = \sum_{\varkappa'} F^0_{\varkappa\varkappa'}(t_m)\,,$$

$$F^0_{\varkappa\varkappa'}(t) = \frac{3\,i}{4\,\omega_\varkappa}\,\frac{\gamma_{\varkappa\varkappa'}}{\Gamma_{\varkappa'}}\,u^2_{\varkappa' 0}\,[1-\exp(-2\,\Gamma_{\varkappa'}|t|)]\,,$$

$$F_{\varkappa\varkappa'}(t_m) = \Delta\sum_{n=1}^{m}[\mu_{\varkappa\varkappa'}(t_n)\,\mathrm{Re}\left(e^{i\varphi_{\varkappa'}}\,x^*_{\varkappa' 1}(t_n)\right) + \nu_{\varkappa\varkappa'}|x_{\varkappa' 1}(t_n)|^2];$$

$$\nu_{\varkappa\varkappa'} = \frac{3\,i}{2\,\omega_\varkappa}\gamma_{\varkappa\varkappa'}\,, \quad \mu_{\varkappa\varkappa'}(t_n) = 2\,\nu_{\varkappa\varkappa'}\,u_{\varkappa' 0}\,e^{-\Gamma_{\varkappa'}|t_n|}\,, \quad \Delta = \frac{t_m}{m}. \qquad (17)$$

Let us write the results of averaging $\exp[F_{\varkappa\varkappa'}(t)]$ as $\exp h_{\varkappa\varkappa'}(t)$. Then it is evident that

$$\langle\exp F_\varkappa(t)\rangle = \exp\left[F^0_\varkappa(t) + \sum_{\varkappa'} h_{\varkappa\varkappa'}(t)\right]; \qquad (18)$$

$$\dot{h}_{\varkappa\varkappa'}(t) = \mu_{\varkappa\varkappa'}(t)\,\mathrm{Re}\,\overline{\exp(i\,\varphi_{\varkappa'})\,x^*_{\varkappa' 1}(t)} + \nu_{\varkappa\varkappa'}\overline{|x_{\varkappa' 1}(t)|^2}\,,$$

where the bar denotes averaging with the statistical weight, $w(\ldots x_{\varkappa'}(t_n)\ldots)\times$ $\times\exp F_{\varkappa\varkappa'}(t_m)$. Calculating the average value with such a normal distribution which is determined by formulae (16) and (17), we have

$$\dot{h}_{\varkappa\varkappa'}(t_m) = \mu_{\varkappa\varkappa'}(t_m)\,E_{\varkappa\varkappa'} + 2\,\nu_{\varkappa\varkappa'}\,\beta^{-1}_{\varkappa' m m} + \nu_{\varkappa\varkappa'}\,E^2_{\varkappa\varkappa'}; \qquad (19)$$

$$E_{\varkappa\varkappa'} = \Delta\sum_{n=1}^{m}\mu_{\varkappa\varkappa'}(t_n)\,\beta^{-1}_{\varkappa' m n}\,; \quad \beta_{\varkappa' n n'} = A^{-1}_{\varkappa' n n'} - 2\,\Delta\,\nu_{\varkappa\varkappa'}\,\delta_{n n'}\,.$$

Here the relation is valid

$$\langle x_{\varkappa 1}(t_m)\,e^{-i\varphi_\varkappa}\,e^{F_\varkappa(t_m)}\rangle = E_{\varkappa\varkappa}\exp\left[F^0_\varkappa(t_m) + \sum_{\varkappa'} h_{\varkappa\varkappa'}(t_m)\right], \qquad (20)$$

which is used below for the determination of $Q_\varkappa(t)$.

The matrix $\beta_{\varkappa'}^{-1}$ satisfies the matrix equation $\beta_{\varkappa'}^{-1}(A_{\varkappa'}^{-1} - 2\,\Delta\nu_{\varkappa\varkappa'}\,I) = I$ (I is the identity matrix) or $\beta_{\varkappa'}^{-1}(I - 2\,\Delta\nu_{\varkappa\varkappa'}\,A_{\varkappa'}) = A_{\varkappa'}$. Replacing in this matrix equation the sum over n again by the integral and introducing the notation $\beta_{\varkappa'}^{-1}{}_{m\,n} = X_{\varkappa'}(t_n)$ (m is fixed) we get an integral equation which determines the function $X_{\varkappa'}(t)$ that is the $\beta_{\varkappa'}^{-1}{}_{m\,n}$ comprised in (19):

$$X_{\varkappa'}(t') - 2\,\nu_{\varkappa\varkappa'}\int_0^t X_{\varkappa'}(t'')\,A_{\varkappa'}(t'', t')\,\mathrm{d}t'' = A_{\varkappa'}(t, t')\,. \tag{21}$$

Taking into account equation (15) for $A_{\varkappa'}(t', t'')$ we shall rewrite this equation in the form of

$$X_{\varkappa'}(t') - \frac{kT}{\omega_{\varkappa'}^2}\nu_{\varkappa\varkappa'}\,\mathrm{e}^{-\Gamma_{\varkappa'}t}\int_0^t \sinh(\Gamma_{\varkappa'}\,t'')\,X_{\varkappa'}(t'')\,\mathrm{d}t'' -$$

$$-\frac{kT}{\omega_{\varkappa'}^2}\nu_{\varkappa\varkappa'}\sinh\Gamma_{\varkappa'}\,t'\int_{t'}^t \mathrm{e}^{-\Gamma_{\varkappa'}t''}\,X_{\varkappa'}(t'')\,\mathrm{d}t'' = \frac{kT}{2\,\omega_{\varkappa'}^2}\mathrm{e}^{-\Gamma_{\varkappa'}t}\sinh\Gamma_{\varkappa'}\,t'\,. \tag{22}$$

After this equation was differentiated twice with respect to t' and the initial equation multiplied by $\Gamma_{\varkappa'}^2$ was subtracted from the result, we may reduce it to the differential equation

$$\ddot{X}_{\varkappa'}(t') - a_{\varkappa\varkappa'}^2\,X_{\varkappa'}(t') = 0; \tag{23}$$

$$a_{\varkappa\varkappa'}^2 = \Gamma_{\varkappa'}^2 - \frac{kT}{\omega_{\varkappa'}^2}\Gamma_{\varkappa'}\,\nu_{\varkappa\varkappa'} = \Gamma_{\varkappa'}^2 - i\frac{3\,kT\,\Gamma_{\varkappa'}\,\gamma_{\varkappa\varkappa'}}{2\,\omega_{\varkappa}\,\omega_{\varkappa'}^2}.$$

The constants of the solution of this equation depend on t. They may be defined from the requirement that the solution should also satisfy the initial equation (22). Then

$$X_{\varkappa'}(t') = \frac{kT\,\Gamma_{\varkappa'}}{2\,\omega_{\varkappa'}^2}\left[a_{\varkappa\varkappa'}\cosh a_{\varkappa\varkappa'}\,t + \Gamma_{\varkappa'}\sinh a_{\varkappa\varkappa'}\,t\right]^{-1}\sinh a_{\varkappa\varkappa'}\,t'; \quad t > 0\,. \tag{24}$$

Substituting the obtained quantities $X_{\varkappa'}(t_n)$ into (19) instead of $\beta_{\varkappa'}^{-1}{}_{mn}$ and replacing the sum over n by an integral we may find $\dot{h}_{\varkappa\varkappa'}(t)$ and then $h_{\varkappa\varkappa'}(t)$:

$$h_{\varkappa\varkappa'}(t) + F_{\varkappa\varkappa'}^0(t) = \frac{3\,i}{2\,\omega_{\varkappa}}\gamma_{\varkappa\varkappa'}\,u_{\varkappa'0}^2\,\frac{\tanh a_{\varkappa\varkappa'}\,t}{a_{\varkappa\varkappa'} + \Gamma_{\varkappa'}\tanh a_{\varkappa\varkappa'}\,t} -$$

$$-\ln\left(\cosh a_{\varkappa\varkappa'}\,t + \frac{\Gamma_{\varkappa'}}{a_{\varkappa\varkappa'}}\sinh a_{\varkappa\varkappa'}\,t\right) + \Gamma_{\varkappa'}\,t; \quad t > 0\,. \tag{25}$$

Subsequent determination of $\langle\exp F_{\varkappa}\rangle$ and $\langle x_{\varkappa 1}(t)\exp[F_{\varkappa 1}(t) - i\,\varphi_{\varkappa}]\rangle$ from equations (18), (20), and (25), the use of equation (9) and (14), and integration over $u_{\varkappa' 0}$ with the statistical weight

$$w(u_{\varkappa' 0}) = \frac{4\,\omega_{\varkappa'}^2}{kT}\,u_{\varkappa' 0}\exp\left(-\frac{2\,\omega_{\varkappa'}^2}{kT}\,u_{\varkappa' 0}^2\right)$$

yields the time correlation function of the oscillation $\varkappa$:

$$Q_\varkappa(t) = \langle\langle q_\varkappa(t)\, q_\varkappa(0)\rangle\rangle = e^{i\tilde{\omega}_\varkappa t}\langle\langle u_{\varkappa 1}(t)\, e^{-i P_\varkappa t}\, u^*_{\varkappa 1}(0)\rangle\rangle + \text{c.c.} = 2\,\mathrm{Re}\,[e^{i\tilde{\omega}_\varkappa |t|}\,\tilde{Q}_\varkappa(|t|)]; \tag{26}$$

$$\tilde{Q}_\varkappa(t) = \frac{kT}{2\omega_\varkappa^2}\psi^{-1}_{\varkappa\varkappa}(t)\prod_{\varkappa'}[\psi^{-1}_{\varkappa\varkappa'}(t)\, e^{\Gamma_{\varkappa'} t}],$$

$$\psi_{\varkappa\varkappa'}(t) = \cosh a_{\varkappa\varkappa'} t + \frac{\Gamma_{\varkappa'}(1 - 2i\varkappa_{\varkappa\varkappa'})}{a_{\varkappa\varkappa'}}\sinh a_{\varkappa\varkappa'} t,$$

$$\alpha_{\varkappa\varkappa'} = \frac{3\,kT\,\gamma_{\varkappa\varkappa'}}{8\,\omega_\varkappa\,\omega^2_{\varkappa'}\,\Gamma_{\varkappa'}}.$$

Here the $a_{\varkappa\varkappa'}$ are determined by equation (23). Equation (26) defines the correlation function $Q_\varkappa(t)$ in the explicit form. Due to the fact that above we have used asymptotic methods which preserve the terms $\sim \varepsilon^2|t|$ but neglect the corrections $\sim \varepsilon^2$ being not proportional to the large time $|t|$, this expression is valid only in the most interesting range of large times and is inapplicable for $|t| \lessapprox t_0$.

The results given above were obtained for the case QV for which only harmonic interaction with the vibrations of the continuous spectrum is essential. But in the same way one may consider LV and QV for which anharmonic interaction proportional to $q_\varkappa\, q_k\, q_{k'}$ is also of great importance. Performing the same calculations as were done above (with the evident difference that now $x_{\varkappa\alpha}(t)$ will be a double sum of random functions $\exp[i(\varphi_{k\alpha_1} + \varphi_{k'\alpha_2})]$ but not the sum of $\exp(i\varphi_{k\alpha})$), it is easy to see that if this interaction is taken into account, then $Q_\varkappa(t)$ is again defined by equation (26) and only in $\Gamma_\varkappa$ and in $P_\varkappa$ new terms $\Gamma'_\varkappa$, $P'_\varkappa$ will appear where

$$\Gamma'_\varkappa = \frac{\pi}{16} kT\,[g^+_\varkappa(\omega_\varkappa) + 2\,g^-_\varkappa(\omega_\varkappa)],$$

$$P'_\varkappa = \frac{kT}{8\,\omega_\varkappa}\,\mathrm{P}\int_{-\infty}^{\infty}\frac{[g^+_\varkappa(\omega') + g^-_\varkappa(\omega')]\,\omega'^2}{\omega_\varkappa^2 - \omega'^2}\,d\omega';$$

$$g^\pm_\varkappa(\omega')\,d\omega' = \sum_{\substack{k'k \\ \omega' < \omega_k \pm \omega_{k'} < \omega' + d\omega'}} \frac{\xi^2_{\varkappa k k'}}{\omega_k^2\,\omega_{k'}^2}. \tag{27}$$

Consideration of those terms in the Hamiltonian of anharmonicity which are proportional to $q_\varkappa\, q_{\varkappa'}\, q_k$ or $q_\varkappa\, q_{\varkappa'}\, q_k\, q_{k'}$, i.e. containing the product of two coordinates of LV or QV, causes more significant change in the results and leads to both renormalization of the quantities $\gamma_{\varkappa\varkappa'}$ (proportional to ζ^2, η^2) and modification of the form of the function $Q_\varkappa(t)$. But in the present case of weakly coupled impurity atoms the corresponding corrections are usually not large and we shall not consider them here. (In the case of high-frequency LV where $g_\varkappa(\omega_\varkappa) = 0$, $g^\pm_\varkappa(\omega_\varkappa) = 0$ and the main contribution into damping comes from the terms of the type $q^2_\varkappa\, q_k\, q_{k'}$ in the Hamiltonian, the joint consideration of these terms and the terms with $q^2_\varkappa\, q^2_{\varkappa'}$ have been already done in the quantum theory [7].)

Of greater importance is the renormalization of the $\gamma_{\varkappa\varkappa'}$ when impurity atoms are in sites which are not centres of inversion and H_0 contains terms $\sum'_{\varkappa\varkappa'}\beta_{\varkappa\varkappa'}\, q_\varkappa\, q^2_{\varkappa'}$

which were not taken into account in (1). It is not difficult to see that they lead to the correction

$$\gamma_{\varkappa\varkappa}^{\text{eff.}} = \gamma_{\varkappa\varkappa} - \frac{4}{3}\sum_{\varkappa'}\frac{\beta_{\varkappa\varkappa'}^2}{\omega_{\varkappa'}^2} + \frac{2}{3}\sum_{\varkappa'}\frac{\beta_{\varkappa\varkappa'}^2}{4\,\omega_{\varkappa}^2 - \omega_{\varkappa'}^2} - \frac{10\,\beta_{\varkappa\varkappa}^2}{\omega_{\varkappa}^2},$$

$$\gamma_{\varkappa\varkappa'}^{\text{eff.}} = \gamma_{\varkappa\varkappa'} - 8\,\beta_{\varkappa\varkappa'}^2\frac{\omega_{\varkappa}^2 + \omega_{\varkappa'}^2}{(4\,\omega_{\varkappa}^2 - \omega_{\varkappa'}^2)\,(4\,\omega_{\varkappa'}^2 - \omega_{\varkappa}^2)} - 4\frac{\beta_{\varkappa\varkappa}\,\beta_{\varkappa\varkappa'}}{\omega_{\varkappa}^2} -$$

$$- 4\frac{\beta_{\varkappa'\varkappa'}\,\beta_{\varkappa'\varkappa}}{\omega_{\varkappa'}^2} - \frac{4}{3}\sum_{\substack{\varkappa'' \\ (\varkappa''\neq\varkappa,\varkappa')}}\frac{\beta_{\varkappa'\varkappa}\,\beta_{\varkappa'\varkappa''}}{\omega_{\varkappa'}^2}; \quad \varkappa \neq \varkappa'.$$

4. Investigation of the Spectral Representation

We may use equation (26) for $Q_{\varkappa}(t)$ for determining the spectral representation

$$Q_{\varkappa}(\omega) = Q_{\varkappa}^{*}(-\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} Q_{\varkappa}(t)\,\mathrm{e}^{-i\omega t}\,\mathrm{d}t \approx \frac{1}{\pi}\,\mathrm{Re}\int_{0}^{\infty}\tilde{Q}_{\varkappa}(t)\,\mathrm{e}^{-i\,\Omega_{\varkappa}t}\,\mathrm{d}t; \qquad (28)$$

$$\Omega_{\varkappa} = \omega - \tilde{\omega}_{\varkappa}, \quad |\Omega_{\varkappa}| \ll \omega_{\varkappa}, \omega_{\mathrm{m}}$$

of the time correlation function. Since equation (26) is valid only in the range of large times $|t| \gg t_0$, the spectral distribution may be obtained by such an asymptotic method at small $|\Omega_{\varkappa}| \ll t_0^{-1}$, i.e. in the region of the peak of the spectral distribution, $\omega \approx \tilde{\omega}_{\varkappa}$. On the far wings of the distribution at $|\Omega_{\varkappa}| \approx \mathrm{Min}\,\{\omega_{\varkappa}, \omega_{\mathrm{m}}\}$ the deduced formulae ceased to be valid, but $Q_{\varkappa}(\omega)$ in this region may be easily obtained with the aid of common perturbation theory.

Equations (28) and (26) determine $Q_{\varkappa}(\omega)$ as the integral of elementary functions and may be used for numerical calculations by a computer. An alternative way of numerical determination of $Q_{\varkappa}(\omega)$ based on the solution of the difference equation system is described in the Appendix. If we may ignore the interaction of the singled out oscillations with each other, then $Q_{\varkappa}(\omega)$, which is considered as the function $\Omega_{\varkappa}/\Gamma_{\varkappa}$, depends only on the single parameter $\alpha = \alpha_{\varkappa\varkappa}$ where $\alpha_{\varkappa\varkappa'} = 3\,kT\,\gamma_{\varkappa\varkappa'}/(8\,\omega_{\varkappa}\,\omega_{\varkappa'}^2\,\Gamma_{\varkappa'})$. The curves of the dependences of $Q_{\varkappa}(\omega)$ on $\Omega_{\varkappa}/\Gamma_{\varkappa}$ at different values of α, calculated from (26) and (28), are shown in Fig. 1. Fig. 2

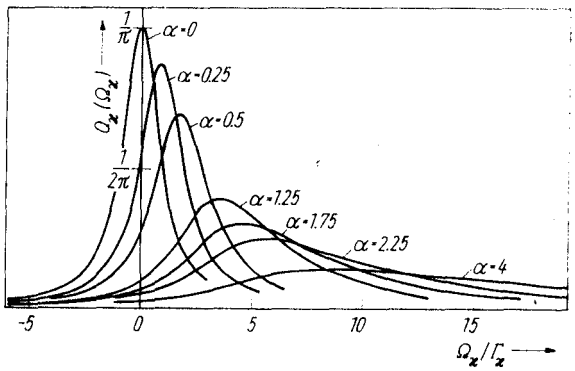

Fig. 1. The spectral distributions $Q_{\varkappa}(\omega)$ for different values of the dimensionless parameter α

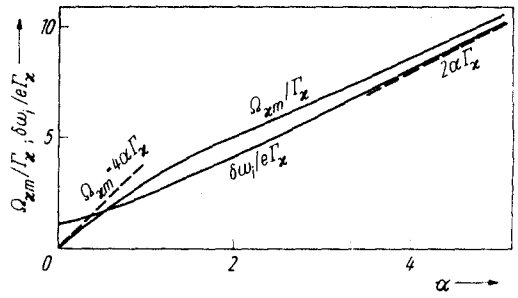

Fig. 2. The dependences of the position of the maximum $Q_{\varkappa m}$ and the integral width of the spectral distribution $\delta\omega_1$ on the parameter α

gives the position of the maximum $\Omega_{\varkappa m}$ and the integral width of the spectral distribution, $\delta\omega_1 = Q_\varkappa^{-1}(\Omega_{\varkappa m})$ (the integral intensity is normalized to 1), expressed in units $\Gamma_\varkappa$, as a function of α.

For $\alpha_{\varkappa\varkappa'} = 0$, $Q_\varkappa(\omega)$ is described by a Lorentzian curve with maximum at $\omega = \tilde{\omega}_\varkappa$ and with integral width $\delta\omega_1 = \pi\Gamma_\varkappa$. As α grows the maximum is shifted (to lower frequencies at $\gamma_{\varkappa\varkappa} < 0$), the spectral distribution becomes more and more asymmetric, and the ratio $\delta\omega_1/\Gamma_\varkappa$ is increased tending to an asymptotic value of $2e\alpha \approx 5.44\alpha$. In the case of QV, if $\Gamma_\varkappa$ does not depend on temperature, α is proportional to T, i.e., the asymmetry and the width of the distribution should grow with increasing temperature. If in the case of LV we have $\Gamma_\varkappa \sim T$, then with increasing temperature the width of the distribution grows proportionally to T but its form remains unchanged.

The expression for $Q_\varkappa(\omega)$ may be reduced to elementary functions at low and high α. When α is low, then, expanding (26) into powers of $\gamma_{\varkappa\varkappa'}/\Gamma_{\varkappa'}$ up to quadratic terms inclusively, we find that

$$\tilde{Q}_\varkappa(t) = \frac{kT}{2\omega_\varkappa^2}\exp\left[-\Gamma_\varkappa t + 2i\sum_{\varkappa'}\alpha_{\varkappa\varkappa'}\Gamma_{\varkappa'}(1+\delta_{\varkappa\varkappa'})t\right]\times$$
$$\times\left\{1+\sum_{\varkappa'}\alpha_{\varkappa\varkappa'}^2(1+\delta_{\varkappa\varkappa'})(1-e^{-2\Gamma_{\varkappa'}t}-2\Gamma_{\varkappa'}t)\right\}, \qquad (29)$$

i.e.

$$\left.\begin{aligned} Q_\varkappa(\omega) &= \frac{1}{2\pi}\frac{kT}{\omega_\varkappa^2}\left\{\frac{\Gamma_\varkappa}{\Gamma_\varkappa^2+\Omega_\varkappa'^2}+\sum_{\varkappa'}\alpha_{\varkappa\varkappa'}^2(1+\delta_{\varkappa\varkappa'})\times\right.\\ &\left.\times\left[\frac{\Gamma_\varkappa}{\Gamma_\varkappa^2+\Omega_\varkappa'^2}-\frac{\Gamma_\varkappa+2\Gamma_{\varkappa'}}{(\Gamma_\varkappa+2\Gamma_{\varkappa'})^2+\Omega_\varkappa'^2}-2\frac{\Gamma_{\varkappa'}(\Gamma_\varkappa^2-\Omega_\varkappa'^2)}{(\Gamma_\varkappa^2+\Omega_\varkappa'^2)^2}\right]\right\};\\ \Omega_\varkappa' &= \Omega_\varkappa - 2\sum_{\varkappa'}\alpha_{\varkappa\varkappa'}\Gamma_{\varkappa'}(1+\delta_{\varkappa\varkappa'}) = \Omega_\varkappa - \frac{3}{4}\sum_{\varkappa'}\frac{kT\gamma_{\varkappa\varkappa'}}{\omega_\varkappa\omega_{\varkappa'}^2}(1+\delta_{\varkappa\varkappa'}). \end{aligned}\right\} \qquad (30)$$

It may be seen from equation (30) that in this extreme case of small nonlinearity of singled out oscillations the spectral distribution is described by a symmetric (if we neglect higher terms with regard to $\gamma_{\varkappa\varkappa'}/\Gamma_{\varkappa'}$) curve. Its maximum is shifted with respect to the point $\Omega_\varkappa = 0$ by a quantity proportional to temperature and linearly dependent on $\gamma_{\varkappa\varkappa'}$. The integral width of the curve (30) is equal to $\pi\Gamma_\varkappa[1+4\sum_{\varkappa'}\alpha_{\varkappa\varkappa'}^2(1+\delta_{\varkappa\varkappa'})\Gamma_{\varkappa'}^2\Gamma_\varkappa^{-1}(\Gamma_\varkappa+2\Gamma_{\varkappa'})^{-1}]$. These results with an accuracy to terms of the higher order of smallness coincide with the results obtained for the case of low $\gamma_{\varkappa\varkappa'}/\Gamma_{\varkappa'}$ in the quantum theory [7, 8].

In the opposite case of large $\alpha_{\varkappa\varkappa'} \gg 1$ we may set in (26) according to (23) $a_{\varkappa\varkappa'} = 2\,i\sqrt{i}\,\alpha_{\varkappa\varkappa'}^{1/2}\,\Gamma_{\varkappa'}$. The width of the distribution $Q_\varkappa(\omega)$ is $\delta\omega_i \sim \alpha_{\varkappa\varkappa'}\,\Gamma_{\varkappa'}$. For the definition of $Q_\varkappa(\omega)$ in the range $\Omega_\varkappa \sim \delta\omega_i$, the region of low t is essential when $\psi_{\varkappa\varkappa'}(t)\exp(-\Gamma_{\varkappa'}t) \approx 1 - 2\,\alpha_{\varkappa\varkappa'}\,\Gamma_{\varkappa'}\,t - 4/3\,\alpha_{\varkappa\varkappa'}^2\,\Gamma_{\varkappa'}^3\,t^3$. But if $\Omega_\varkappa \to 0$ then the general expression (26) for $\psi_{\varkappa\varkappa'}(t)$ should be used.

In the limit of $\Gamma_{\varkappa'} \to 0$ equations (26) and (28) determine in this case the distribution obtained before [8] neglecting relaxation while at finite but small $\Gamma_{\varkappa'}$ they determine the correction for this distribution. If, for example, we can neglect the interaction of a given singled out vibration with another one then obtains

$$\left.\begin{aligned} Q_\varkappa(\omega) &= \frac{kT}{2\,\omega_\varkappa^2\,\Omega_0}\left[\frac{|\Omega_\varkappa|}{\Omega_0}\exp\left(-\frac{\Omega_\varkappa}{\Omega_0}\right) + \frac{1}{6\,\pi\,\alpha}\,\chi\left(\frac{\Omega_\varkappa}{\Omega_0}\right)\right] \quad \text{at} \quad |\Omega_\varkappa| \gg \Gamma_\varkappa|\alpha|^{1/2};\\ \chi(x) &= (3-3\,x+x^2)\,e^{-x}\,P\int_{-\infty}^{x}\frac{e^{x'}}{x'}\,dx' - \frac{2}{x} + 2 - x\,, \quad \Omega_0 = 2\,\alpha\,\Gamma_\varkappa = \frac{3\,kT\,\gamma_{\varkappa\varkappa}}{8\,\omega_\varkappa^3}, \end{aligned}\right\} \tag{31}$$

$$\left.\begin{aligned} Q_\varkappa(\omega) &= M\,\frac{kT}{\omega_\varkappa^2\,\Omega_0}\,\frac{1}{|\alpha|^{1/2}} \quad \text{at} \quad \Omega_\varkappa = 0;\\ M &\approx 1, \quad \theta(x) = 1 \quad \text{at} \quad x > 0\,, \quad \theta(x) = 0 \quad \text{at} \quad x < 0\,. \end{aligned}\right\} \tag{32}$$

The distribution (31) has the integral width $\delta\omega_i = e\,\Omega_0\,[1 + 0.044\,\alpha]$ ($\Omega_{\varkappa m} \approx \approx 2\,\alpha + 0.17$). In the wings of the distribution at $|\Omega_\varkappa| \gg |\Omega_0|$, $Q_\varkappa(\omega) = = (kT/2\,\pi\,\omega_\varkappa^2)\,(\Gamma_\varkappa/\Omega_\varkappa^2)$ decreases as $\Omega_\varkappa^{-2}$.

It should be kept in mind that for sufficiently small $\Gamma_\varkappa$, when $\Gamma_\varkappa \ll \Delta\omega$, the fine structure of the distribution $Q_\varkappa(\omega)$ must appear. Since $\Delta\omega \sim \delta\omega_i \times \times (kT/\hbar\,\omega_\varkappa)^{-1}$, the results of the classical theory are applicable only at $\hbar\,\gamma_{\varkappa\varkappa} < < \omega_\varkappa^2\,\Gamma_\varkappa$ (this condition may be satisfied simultaneously with the criterion of equations (31) and (32)), $\gamma_{\varkappa\varkappa} \gg (\omega_\varkappa^3\,\Gamma_\varkappa/kT)$). But if $\hbar\,\gamma_{\varkappa\varkappa} \gg \omega_\varkappa^2\,\Gamma_\varkappa$, then the classical theory determines only the average distribution $Q_\varkappa(\omega)$. For investigating the fine structure of the spectrum even at high temperatures the results of quantum theory should be used.

Appendix

When considering the stochastic differential equations for $u_{\varkappa\alpha}$ we shall confine ourselves here for brevity with the case of non-interacting (one with the other) singled out vibrations, and hence we may investigate ony a single vibration $\varkappa$ omitting the indices $\varkappa$, $\varkappa'$. Then equations (10) and (13) for u' and u'' ($u + i\,u'' = = u_{\varkappa 1}\,e^{-i\,P\varkappa t}$) will be written as

$$\left.\begin{aligned} \dot{u}' &= -\Gamma u' - C\,(u'^2 + u''^2)\,u'' + f'\,,\\ \dot{u}'' &= -\Gamma u'' + C\,(u'^2 + u''^2)\,u' + f'';\\ C &= \frac{3}{2}\,\frac{\gamma_{\varkappa\varkappa}}{\omega_\varkappa}, \quad f' + i\,f'' = \frac{1}{2\,i\,\omega_\varkappa}\,e^{-i\omega\varkappa t}\,f_\varkappa(t); \quad t \geqq 0. \end{aligned}\right\} \tag{A1}$$

Taking into account the definition (8) for $f_\varkappa(t)$ and equations (11), (13) we shall find that the correlators of the random functions, f' and f'', for markedly different times $|t - t'| \gg t_0$ after integration over ω_k may be conditionally reduced to

δ-functions (strictly speaking, one should consider δ-shaped functions with the width $\approx t_0$):

$$\left.\begin{aligned} \langle f'(t)\, f'(t')\rangle = \langle f''(t)\, f''(t')\rangle = B\,\delta\,(t-t');\\ B = \frac{kT}{2\,\omega_\varkappa^2}\,\Gamma\,,\quad \langle f'(t)\, f''(t')\rangle = 0\,. \end{aligned}\right\} \tag{A2}$$

Thus for time intervals large as compared with t_0 the random process described by equations (A1) may be regarded as a Markov process and may be characterized by the transition probability $v(u', u'', t; u_0', u_0'', t_0)$. The Fokker-Planck equation (the second Kolmogorov equation) corresponding to equations (A1) has the form

$$\frac{\partial v}{\partial t} = \frac{\partial}{\partial u'}\left[\Gamma u'\, v + C\,(u'^2 + u''^2)\, u''\, v\right] + \frac{\partial}{\partial u''}\left[\Gamma u''\, v - C\,(u'^2 + u''^2)\, u'\, v\right] + \\ + \frac{1}{2}\,B\left(\frac{\partial^2 v}{\partial u'^2} + \frac{\partial^2 v}{\partial u''^2}\right), \tag{A3}$$

where $v(u', u'', t_0; u_0', u_0'', t_0) = \delta\,(u' - u_0')\,\delta\,(u'' - u_0'')$. Going from the variables $u' = r\cos\varphi$, $u'' = r\sin\varphi$ to the amplitude and phase r, φ (to the polar coordinates) we shall rewrite the equation for $V = r\,v$ [$V(r, \varphi, t_0; r_0, \varphi_0, t_0) = \delta\,(r - r_0)\,\delta\,(\varphi - \varphi_0)$] as

$$\frac{\partial V}{\partial t} = \Gamma\,\frac{\partial (r\,V)}{\partial r} - C\,r^2\,\frac{\partial V}{\partial \varphi} + \frac{1}{2}\,B\left(\frac{\partial^2 V}{\partial r^2} - \frac{1}{r}\,\frac{\partial V}{\partial r} + \frac{V}{r^2} + \frac{1}{r^2}\,\frac{\partial^2 V}{\partial \varphi^2}\right). \tag{A4}$$

The desired correlation function $Q(t)$ may be expressed according to (26) by V in the form of an integral:

$$Q(t - t_0) = \langle r(t)\, r_0 \exp\left[i\,\varphi(t) - i\,\varphi_0\right]\rangle\, e^{i\,\tilde{\omega}_\varkappa t} + \text{c.c.} = \\ = \frac{1}{2\,\pi}\int_0^\infty\int_0^\infty dr\, dr_0 \int_0^{2\pi}\int_0^{2\pi} d\varphi\, d\varphi_0\, w(r_0) \times \\ \times V(r, \varphi, t; r_0, \varphi_0, t_0)\, r\, r_0 \exp\left[i\,(\varphi - \varphi_0)\right] e^{i\,\tilde{\omega}_\varkappa t} + \text{c.c.}\,;$$

$$w(r_0) = \frac{2\,\Gamma\, r_0}{B}\exp\left(-\frac{\Gamma}{B}\,r_0^2\right);\quad \left(\frac{kT}{2\,\omega_\varkappa^2} = \frac{B}{\Gamma}\right). \tag{A5}$$

It is seen from this formula that for determining $Q(t)$ one should in fact know not the function V but only the integral

$$W(r, t) = \frac{1}{2\,\pi}\int_0^\infty dr_0 \int_0^{2\pi}\int_0^{2\pi} d\varphi\, d\varphi_0\, w(r_0)\; V(r, \varphi, t; r_0, \varphi_0, 0)\, r_0\, e^{i\,(\varphi - \varphi_0)}\,. \tag{A6}$$

Going further from $W(r, t)$ to its Laplace transform

$$W(r, s) = \int_0^\infty \exp\,(-s\,t)\; W(r, t)\, dt; \tag{A7}$$

$$\int_0^\infty \exp\,(-s\,t)\,\frac{\partial W(r, t)}{\partial t}\, dt = s\; W(r, s) - W(r, t = 0) = s\; W(r, s) - r\; w(r)\,,$$

we get from (A4) an ordinary differential equation for $W(r, s)$:

$$\frac{\mathrm{d}^2 W(r,s)}{\mathrm{d}r^2} + \left(\frac{2\,\Gamma}{B} r - \frac{1}{r}\right)\frac{\mathrm{d}W(r,s)}{\mathrm{d}r} + \left(\frac{2\,\Gamma}{B} - \frac{2\,s}{B} + \frac{2\,i\,C}{B} r^2\right) W(r,s) =$$

$$= -\frac{4\,\Gamma}{B^2} r^2 \exp\left(-\frac{\Gamma}{B} r^2\right). \tag{A8}$$

Let us introduce instead of the function $W(r, s)$ its moments $W_n(s) = \int_0^\infty r^n\, W(r,s)\,\mathrm{d}r$ ($W(r, s)$ tends exponentially to zero with $r \to \infty$). Then (A8) is reduced to the difference equation system

$$(n^2 - 1)\, W_{n-2} - \frac{2}{B}(\zeta + \Gamma n)\, W_n + \frac{2\,i\,C}{B} W_{n+2} = -2\,\Gamma\left(\frac{n+3}{2}\right)\frac{1}{B}\left(\frac{B}{\Gamma}\right)^{\frac{n+1}{2}}; \tag{A9}$$

with $n \geqq 1$,

where $\Gamma\left((n+3)/2\right)$ is the Γ-function, and it is kept in mind that $W(0, s) = 0$. Here it is necessary to study the partial solution of (A9) which turns into zero together with the right-hand part of these equations.

Equations (A5) to (A7) show that the spectral representation $Q(\omega)$ of the function $Q(t)$ is expressed by the first moment $W_1(s)$ for the complex argument $s = i\,\Omega$:

$$Q(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} Q(t)\, \mathrm{e}^{-i\omega t}\,\mathrm{d}t = \frac{1}{\pi}\,\mathrm{Re}\; W_1(i\,\Omega)\,. \tag{A10}$$

The quantity W_1 may be found by solving (A9). For example, at $C = 0$ from the equation with $n = 1$ we obtain $W_1 = B\,\Gamma^{-1}(s + \Gamma)^{-1}$ from which, according to (A10), the common Lorentzian distribution $Q(\omega)$ follows, with the width $2\,\Gamma$. At small C, equations (A9) may be considered with $n = 1, 3, 5, \ldots, n_1$ and the chain may be broken with the assumption $W_{n_1+2} = 0$ in the last equation. If we consider e.g. three equations with $n = 1, 3, 5$ and set $W_7 = 0$, then after an expansion into C we get equation (30) for $Q_x(\omega)$ which had already been obtained by another method.

The complex equations (A9) for $s = i\,\Omega$ may be represented in the real form. For example, assuming $W_n = \Gamma\left((n+1)/2\right)(B/\Gamma)^{(n-1)/2}\, Y_n$ we derive from (A9) the equations for the real variables:

$$\left.\begin{aligned} &(n+1)\, Y'_{n-2} - n\, Y'_n + \frac{\Omega}{\Gamma} Y''_n - \frac{C\,B}{2\,\Gamma^2}(n+1)\, Y''_{n+2} = -\frac{1}{2}(n+1)\frac{B}{\Gamma^2}, \\ &(n+1)\, Y''_{n-2} - n\, Y''_n - \frac{\Omega}{\Gamma} Y'_n + \frac{C\,B}{2\,\Gamma^2}(n+1)\, Y'_{n+2} = 0\,. \end{aligned}\right\} \tag{A11}$$

At large n the Y_n are smooth functions of n and may be determined approximately from the asymptotic formula

$$Y'_n + i\, Y''_n = \frac{B}{4\,\Gamma^2}\left(1 - i\,\frac{C\,B}{2\,\Gamma^2}\right)^{-1} \exp\left[-\varphi(n)\right]\int_0^n \exp\varphi(x)\,\mathrm{d}x\,; \tag{A12}$$

$$\varphi(x) = -\frac{1 - i\,\Omega/\Gamma}{2\left[1 - i\,(C\,B/2\,\Gamma^2)\right]}\ln x - i\,\frac{C\,B}{4\,\Gamma^2\left[1 - i\,(C\,B/2\,\Gamma^2)\right]}\,x\,.$$

Defining Y'_{n_1+2} and Y''_{n_1+2} for some large odd number n_1 from equation (A12) we may break the chain of equations (A11) and use the obtained system of n_1+1 equations for the numerical calculation of $Q(\omega) = Y'_1$ in a computer.

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