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Non-Markovian electron-phonon relaxation

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Kinetic equations describing short-time evolution of the electron-phonon system are derived in non-Markovian Born approximation by the density matrix method. The approach presented in the paper differs from earlier schemes in that the interaction energy is treated as an independent state parameter on the same footing as the electron and phonon distribution functions. This introduces new correlation terms into the kinetic equations, which ensure the energy conservation and the existence of the correct equilibrium solution. An explicit expression for the time-dependent correlation energy is obtained.

Key words: *quantum kinetic theory, non-Markovian kinetic equations, nonequilibrium correlations, electron-phonon interaction*

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1. Introduction

In recent years, much attention has been attached to the memory effects in quantum kinetics in connection with experimental studies of the effect of ultrafast optical pulses on the electrons in semiconductors [1]. Theoretically, the transient relaxation of excited electrons has to be described by non-Markovian kinetic equations which can, in principle, be derived within the Green's function formalism [2] or the density matrix method [3]. In Born approximation, the simplest versions of non-Markovian kinetic equations have the same structure as Boltzmann-like equations, but with the oscillating memory kernels replacing the energy-conserving delta functions. Unfortunately, such kinetic equations with a full memory have got unstable solutions and even produce nonphysical negative distribution functions. This defect can be overcome by including a quasiparticle damping into the memory kernels [2]. However, the trouble with the "improved" memory kernels is that the corresponding collision integrals do not conserve the total energy of the system and, besides, in the Markovian limit the kinetic equation does not describe the relaxation of the electron subsystem toward the equilibrium Fermi distribution leading to an overpopulation of high-energy states. Within the Green's function approach, Haug and Bányai [4] proposed an interpolation formula for the memory kernel which to a large degree eliminates the nonphysical long-time properties of the electron-phonon collision integral. The asymptotic form of the electron distribution function was found to be close (but not equal) to the Fermi distribution. It should be noted, however, that attempts to construct more and more complicated memory kernels cannot completely solve the problem of self-consistency in non-Markovian kinetics because *any* memory kernel with a non-zero quasiparticle damping violates the energy conservation.

Another way toward resolving the difficulties of non-Markovian quantum kinetics was outlined in our recent paper [5]. The main idea is to treat the total energy (or, which is the same, the interaction energy) and the one-particle distribution as independent state parameters. This leads to new "correlation" terms in a non-Markovian kinetic equation. The essential point is that the "collision" term can be substantially compensated by these "correlation" terms, which is important to ensure the correct long-time behaviour of the one-particle distribution function. In thermal equilibrium, the "collision" and "correlation" terms *exactly cancel each other*. In this paper the approach of [5] is applied to the electron scattering by longitudinal optical phonons in semiconductors. Our aim will be to derive explicit non-Markovian kinetic equations for the electron and phonon distribution functions, which conserve the total energy of the system and have the correct equilibrium solution.

The structure of the paper is as follows. Section 2 dwells on the choice of nonequilibrium state parameters describing collisions and long-lived correlations associated with the energy conservation. In section 3 we introduce a generalized "Gibbsian" ensemble with given values of the nonequilibrium state parameters and construct the corresponding relevant statistical operator which gives a thermodynamic description of the system. We introduce the nonequilibrium *quasi-temperature* which is thermodynamically conjugated to the total energy of the system and plays a crucial role in our approach. In section 4 the von Neumann equation is solved by an iterative procedure and the nonequilibrium statistical operator is found as a functional of the state parameters. In section 5 we use this statistical operator to find explicit expressions for the non-Markovian collision integrals, correct to second order in the interaction. Section 6 is concerned with the evolution equation for the quasi-temperature. In section 7 we discuss some properties of the electron and phonon kinetic equations and the equation for the quasi-temperature. In particular, we show that these equations have the correct equilibrium solution and conserve the total energy of the system. We conclude the paper with a few remarks concerning our results.

2. Nonequilibrium state parameters

The second-quantized Hamiltonian for electrons with band dispersion ε_k and longitudinal optical (LO) phonons with energies $\hbar\omega_q$ has the form

$$\begin{aligned}\hat{H} &= \hat{H}_{\mathrm{e}} + \hat{H}_{\mathrm{ph}} + \hat{H}_{\mathrm{int}} \\ &= \sum_k \varepsilon_k\, a_k^\dagger a_k + \sum_q \hbar\omega_q \left(b_q^\dagger b_q + \frac{1}{2}\right) + \sum_{k,q} D_q \left(b_q a_k^\dagger a_{k-q} + b_q^\dagger a_{k-q}^\dagger a_k\right), \end{aligned} \quad (2.1)$$

where D_q is the coupling constant. In order to have a compact notation, the symbol k stands for the set of one-electron quantum numbers including the wave vector $\mathbf{k}$ and the spin variable σ. From now on we also denote $\mathbf{k} \pm \mathbf{q}$ by $k \pm q$.

Assuming for simplicity the system to be spatially homogeneous and introducing the occupation-number operators, $\hat{f}_k = a_k^\dagger a_k$ and $\hat{n}_q = b_q^\dagger b_q$, the basic quantities of interest are the electron and phonon distribution functions

$$f_k(t) = \langle \hat{f}_k \rangle^t \equiv \mathrm{Tr}\left\{\hat{f}_k\, \varrho(t)\right\}, \qquad n_q(t) = \langle \hat{n}_q \rangle^t \equiv \mathrm{Tr}\left\{\hat{n}_q\, \varrho(t)\right\}, \quad (2.2)$$

where $\varrho(t)$ is a nonequilibrium statistical operator which obeys the von Neumann equation

$$\frac{\partial \varrho(t)}{\partial t} + \frac{1}{\mathrm{i}\hbar}\left[\varrho(t), \hat{H}\right] = 0. \quad (2.3)$$

It should be emphasized that, writing the von Neumann equation in this form, we consider relaxation processes in the electron-phonon system just after the initial excitation by the laser field. In other words, at some time t_0 the statistical operator $\varrho(t_0)$ should be constructed in such a way that it gives an appropriate description of the initial state of the system. In a more general formulation, the interaction between electrons and the laser field is taken into account explicitly by an additional term $\hat{H}_{\text{field}}(t)$ in the Hamiltonian, so that the statistical operator $\varrho(t_0)$ can be found by solving the von Neumann equation for times $t < t_0$. The scheme presented below can easily be extended to take account of the field effects (see section 8 for a discussion).

Formal kinetic equations for $f_k(t)$ and $n_q(t)$ follow immediately from the von Neumann equation:

$$\frac{\partial f_k(t)}{\partial t} = I_k^{(\mathrm{e})}(t), \qquad \frac{\partial n_q(t)}{\partial t} = I_q^{(\mathrm{ph})}(t), \quad (2.4)$$

where the collision integrals are given by

$$I_k^{(\mathrm{e})}(t) = \frac{1}{\mathrm{i}\hbar}\,\mathrm{Tr}\left\{[\hat{f}_k, \hat{H}_{\mathrm{int}}]\varrho(t)\right\}, \qquad I_q^{(\mathrm{ph})}(t) = \frac{1}{\mathrm{i}\hbar}\,\mathrm{Tr}\left\{[\hat{n}_q, \hat{H}_{\mathrm{int}}]\varrho(t)\right\}. \quad (2.5)$$

In order that (2.4) be a closed set of kinetic equations, it is desirable to find a solution of the von Neumann equation, which is a functional of the electron and phonon distributions. If memory effects are of importance, the functional in question has the form $\varrho(t) = \varrho[\{f(t')\}, \{n(t')\}]$, where $t_0 < t' < t$. We have already noted, however, that in this standard approach one faces difficulties with the energy conservation and the long-time behaviour of collision integrals. The origin of these difficulties lies in the fact that, generally speaking, the one-particle distributions are not the only independent variables which give an accurate description of the system on the kinetic time scale. In many cases, proper allowance must be made for the dynamics of long-lived correlations. Systems with bound states are an obvious example supporting this statement. Conservation laws represent another source of relevant many-particle correlations. Of special interest in kinetic theory is the energy conservation. To illustrate this point, we note that the time change of the kinetic energy

$$\mathcal{E}_{\text{kin}}(t) = \sum_k \varepsilon_k \, f_k(t) + \sum_q \hbar\omega_q \, n_q(t) \tag{2.6}$$

is determined completely by the collision integrals (2.5) since

$$\frac{\mathrm{d}\mathcal{E}_{\text{kin}}(t)}{\mathrm{d}t} = \sum_k \varepsilon_k \, I_k^{(\text{e})}(t) + \sum_q \hbar\omega_q \, I_q^{(\text{ph})}(t). \tag{2.7}$$

On the other hand, the energy conservation requires that $\mathrm{d}\mathcal{E}_{\text{kin}}(t)/\mathrm{d}t = -\mathrm{d}\mathcal{E}_{\text{int}}(t)/\mathrm{d}t$, where the interaction energy

$$\mathcal{E}_{\text{int}}(t) = \langle \hat{H}_{\text{int}} \rangle^t \tag{2.8}$$

depends on the correlation functions $T_{k,q}(t) = \langle b_q a_k^\dagger a_{k-q} \rangle^t$ as seen from equation (2.1). Thus, for the total energy to be conserved, an approximation for the collision integrals must be consistent with the time change of the correlation functions. An approach based on kinetic equations for one-particle distributions coupled with equations of motion for the correlation functions would thus be expected to overcome difficulties with the behaviour of the one-electron distribution function in the non-Markovian regime. Recent attempts along these lines [6] show that, indeed, the time behaviour of the one-electron distribution agrees with experiment much better than the results obtained within Born approximation in non-Markovian kinetic equations. A shortcoming of this approach is that it deals with a hierarchy of equations for correlation functions and even one step beyond Born approximation leads to a very complicated set of evolution equations. We also would like to point out that it is crucial to construct truncations of the hierarchy, which do not violate the conservation of the total energy. However, the conserving properties of a truncation procedure are very difficult to ensure because of a large number of the evolution equations.

We follow another way in going beyond the standard version of non-Markovian quantum kinetics. To incorporate nonequilibrium many-particle correlations caused by the energy conservation, the interaction energy (2.8) will be regarded as an independent state parameter in addition to the electron and phonon distribution functions (2.2). In this scheme, the kinetic equations for $f_k(t)$ and $n_q(t)$ are coupled to the balance equation for $\mathcal{E}_{\text{int}}(t)$. Here one remark is in order. Since the kinetic energy is exactly expressed in terms of one-particle distributions, we can take the total energy $\mathcal{E} = \mathcal{E}_{\text{kin}}(t) + \mathcal{E}_{\text{int}}(t)$ as a state parameter instead of the $\mathcal{E}_{\text{int}}(t)$. In this case, the balance equation is trivial: $\mathrm{d}\mathcal{E}/\mathrm{d}t = 0$. Nevertheless, we shall see that this equation leads to additional (correlation) terms in the collision integrals.

3. The relevant statistical operator

Now the main objective is to find a solution of the von Neumann equation (2.3) as a functional $\varrho(t)=\varrho[\mathcal{E}_{\rm int}(t'),\{f(t')\},\{n(t')\}]$ or $\varrho(t)=\varrho[\mathcal{E},\{f(t')\},\{n(t')\}]$, where $t_0<t'<t$. We first construct an auxiliary *relevant statistical operator*, $\varrho_{\rm rel}(t)$, which describes a generalized "Gibbsian" ensemble characterized by given values of $f_k(t)$, $n_q(t)$, and $\mathcal{E}_{\rm int}(t)$. This statistical operator can be derived from the maximum of the information entropy for given averages $\langle\hat{f}_k\rangle$, $\langle\hat{n}_q\rangle$, and $\langle\hat{H}_{\rm int}\rangle$. Following the standard procedure (see, e.g., [7]), we obtain

$$\varrho_{\rm rel}(t)=\frac{1}{Z_{\rm rel}(t)}\,\exp\left\{-\beta^*(t)\,\hat{H}_{\rm int}-\sum_k\Lambda_k^{(\rm e)}(t)\,\hat{f}_k-\sum_q\Lambda_q^{(\rm ph)}(t)\,\hat{n}_q\right\},\tag{3.1}$$

where the partition function

$$Z_{\rm rel}(t)={\rm Tr}\,\exp\left\{-\beta^*(t)\,\hat{H}_{\rm int}-\sum_k\Lambda_k^{(\rm e)}(t)\,\hat{f}_k-\sum_q\Lambda_q^{(\rm ph)}(t)\,\hat{n}_q\right\}\tag{3.2}$$

is determined by the normalization condition, and the Lagrange multipliers $\beta^*(t)$, $\Lambda_k^{(\rm e)}(t)$, and $\Lambda_q^{(\rm ph)}(t)$ are to be calculated from the self-consistency conditions

$$f_k(t)={\rm Tr}\left\{\hat{f}_k\,\varrho_{\rm rel}(t)\right\},\qquad n_q(t)={\rm Tr}\left\{\hat{n}_q\,\varrho_{\rm rel}(t)\right\},\qquad \mathcal{E}_{\rm int}(t)={\rm Tr}\left\{\hat{H}_{\rm int}\,\varrho_{\rm rel}(t)\right\},\tag{3.3}$$

which play the role of nonequilibrium equations of state. In what follows, for some purposes it will be convenient to write the relevant statistical operator (3.1) in a somewhat different form by re-defining the Lagrange multipliers conjugated to the electron and phonon distributions. Let us introduce new multipliers $\lambda_k^{(\rm e)}(t)$ and $\lambda_q^{(\rm ph)}(t)$ through the relations

$$\Lambda_k^{(\rm e)}(t)=\beta^*(t)\,[\varepsilon_k-\mu^*(t)]+\lambda_k^{(\rm e)}(t),\qquad \Lambda_q^{(\rm ph)}(t)=\beta^*(t)\,\hbar\omega_q+\lambda_q^{(\rm ph)}(t),\tag{3.4}$$

where $\mu^*(t)$ will be defined below. Substitution of these expressions into equation (3.1) gives

$$\varrho_{\rm rel}(t)=\frac{1}{Z_{\rm rel}(t)}\,\exp\left\{-\beta^*(t)\left(\hat{H}-\mu^*(t)\,\hat{N}^{(\rm e)}\right)-\sum_k\lambda_k^{(\rm e)}(t)\,\hat{f}_k-\sum_q\lambda_q^{(\rm ph)}(t)\,\hat{n}_q\right\},\tag{3.5}$$

where $\hat{N}^{(\rm e)}=\sum_k\hat{f}_k$ is the electron number operator. Obviously the partition function (3.2) can be written as

$$Z_{\rm rel}(t)={\rm Tr}\,\exp\left\{-\beta^*(t)\left(\hat{H}-\mu^*(t)\,\hat{N}^{(\rm e)}\right)-\sum_k\lambda_k^{(\rm e)}(t)\,\hat{f}_k-\sum_q\lambda_q^{(\rm ph)}(t)\,\hat{n}_q\right\}.\tag{3.6}$$

Formula (3.5) shows clearly that the relevant statistical operator describes thermal equilibrium as a special case, if $\beta^*=1/T$, $\mu^*=\mu$, and $\lambda_k^{(\rm e)}=\lambda_q^{(\rm ph)}=0$, where T and μ are the equilibrium temperature and the chemical potential, respectively. Based on this property, it is natural to interpret $\beta^*(t)$ as the inverse *quasi-temperature* of the system and $\mu^*(t)$ may be called the *quasi-chemical potential*. When using the expression (3.5) for the relevant statistical operator, it is convenient to assume that the Lagrange multipliers are determined by the conditions

$$f_k(t) = \mathrm{Tr}\left\{\hat{f}_k \varrho_{\mathrm{rel}}(t)\right\}, \qquad n_q(t) = \mathrm{Tr}\left\{\hat{n}_q \varrho_{\mathrm{rel}}(t)\right\}, \qquad \mathcal{E} = \mathrm{Tr}\left\{\hat{H} \varrho_{\mathrm{rel}}(t)\right\}, \quad (3.7)$$

which are equivalent to equations (3.3).

Finally, we briefly touch upon the definition of the quasi-chemical potential $\mu^*(t)$. There is some freedom in choosing this parameter, as seen from the first of equations (3.4) which defines only the difference $\lambda_k^{(e)} - \beta^*\mu^*$. The usual case is to define the chemical potential in a grand ensemble by the condition that the average number of particles is a given quantity. In our case, however, this condition follows from the first of equations (3.7) and the relation $N^{(e)} = \sum_k f_k(t)$. Then, assuming that the kinetic equation conserves the total number of electrons, the value of $N^{(e)}$ is determined by the initial distribution $f_k(t_0)$. Since no physical quantity depends on the special choice of $\mu^*(t)$, this parameter may be chosen arbitrarily provided that $\mu^* = \mu$ in thermal equilibrium. It will be convenient to define $\mu^*(t)$ by the condition

$$N^{(e)} = \mathrm{Tr}\left\{\hat{N}^{(e)} \varrho_{\mathrm{q}}(t)\right\}, \quad (3.8)$$

where $\varrho_{\mathrm{q}}(t)$ is the *quasi-equilibrium statistical operator*

$$\varrho_{\mathrm{q}}(t) = \frac{1}{Z_{\mathrm{q}}(t)} \exp\left\{-\beta^*(t)\left(\hat{H} - \mu^*(t)\,\hat{N}^{(e)}\right)\right\} \quad (3.9)$$

and

$$Z_{\mathrm{q}}(t) = \mathrm{Tr}\,\exp\left\{-\beta^*(t)\left(\hat{H} - \mu^*(t)\,\hat{N}^{(e)}\right)\right\} \quad (3.10)$$

is the corresponding partition function. Clearly equation (3.8) determines the quasi-chemical potential as a function $\mu^*(t) = \mu^*(N^{(e)}, \beta^*(t))$ and ensures that $\mu^* = \mu$ in thermal equilibrium.

4. Iterative solution of the von-Neumann equation

We now want to find the nonequilibrium statistical operator, $\varrho(t)$, as a functional of the controlled observables $f_k(t)$, $n_q(t)$, and $\langle \hat{H}_{\mathrm{int}} \rangle^t$. At present there exists a number of formally different but, in fact, equivalent schemes for constructing solutions of the von Neumann equation, which are functionals of controlled averages. We follow the method in which the relevant statistical operator is used as an auxiliary operator determining the desired structure of $\varrho(t)$. This method is detailed, e.g., in the book [7].

As pointed out above, our approach is based on the assumption that the main part of relevant many-particle correlations are incorporated through the description of the system including the interaction energy as an independent state parameter.

Following this line of reasoning, we shall look for a solution of the von Neumann equation that satisfies the initial condition

$$\varrho(t_0) = \varrho_{\rm rel}(t_0). \tag{4.1}$$

It should be emphasized, however, that the scheme presented in this paper can be generalized to the case where $\varrho(t_0)$ is an arbitrary initial statistical operator. Since our main interest here lies in the long-time behaviour of the collision integrals, the detailed structure of $\varrho(t_0)$ is of little consequence and the condition (4.1) is taken only for simplicity.

Assuming that the electron-phonon interaction is weak, it is convenient to split the Hamiltonian (2.1) into the main part

$$\hat{H}_0 = \hat{H}_{\rm e} + \hat{H}_{\rm ph} \tag{4.2}$$

and the perturbation $\hat{H}_{\rm int}$. It can easily be verified that the von Neumann equation (2.3) with the initial condition (4.1) is equivalent to the integral equation

$$\begin{aligned} \varrho(t) \;=\; & \varrho_{\rm rel}(t) - \int\limits_{t_0}^{t} {\rm d}t'\, U_0(t,t') \left\{ \frac{\partial \varrho_{\rm rel}(t')}{\partial t'} + \frac{1}{{\rm i}\hbar}[\varrho_{\rm rel}(t'), \hat{H}_0] \right\} U_0^{\dagger}(t,t') \\ & - \int\limits_{t_0}^{t} {\rm d}t'\, U_0(t,t')\, \frac{1}{{\rm i}\hbar}[\varrho(t'), \hat{H}_{\rm int}]\, U_0^{\dagger}(t,t'), \end{aligned} \tag{4.3}$$

where

$$U_0(t,t') = {\rm e}^{-{\rm i}(t-t')\hat{H}_0/\hbar} \tag{4.4}$$

is the unperturbed evolution operator. Equation (4.3) is still exact. In the case that $\hat{H}_{\rm int}$ corresponds to a weak interaction, the statistical operator $\varrho(t)$ can be found by an iterative procedure. We will restrict our consideration to the second-order non-Markovian Born approximation in which the electron and phonon collision integrals are explicitly proportional to D_q^2. Then, since $I_k^{\rm (e)}$ and $I_q^{\rm (ph)}$ given by equations (2.5) are already proportional to the interaction amplitude, we need a solution of equation (4.3), correct to the first order in the interaction.

Let us show that, within the Born approximation, the derivative $\partial\varrho_{\rm rel}(t')/\partial t'$ in equation (4.3) can be neglected. We recall that the relevant statistical operator depends on time through the Lagrange multipliers or, which is the same, through the controlled averages. Assuming, for instance, that $\varrho_{\rm rel}(t') = \varrho_{\rm rel}(\mathcal{E}, \{f(t')\}, \{n(t')\})$ and taking into account that the total energy is conserved, we have

$$\frac{\partial \varrho_{\rm rel}(t')}{\partial t'} = \sum_k \frac{\delta \varrho_{\rm rel}(t')}{\delta f_k(t')}\, I_k^{\rm (e)}(t') + \sum_q \frac{\delta \varrho_{\rm rel}(t')}{\delta n_q(t')}\, I_q^{\rm (ph)}(t'). \tag{4.5}$$

This derivative may thus be neglected if the collision integrals do not contain terms of the first order in the interaction. Such terms could appear only from the relevant statistical operator $\varrho_{\rm rel}(t)$ in the right-hand side of equation (4.5). Let us show, however, that the collision integrals (2.5) vanish if $\varrho(t) = \varrho_{\mathrm{rel}}(t)$. This property of the collision integrals follows from the obvious identity

$$\langle [\hat{A}, \ln \varrho_{\mathrm{rel}}(t)] \rangle^{t}_{\mathrm{rel}} = 0, \tag{4.6}$$

where $\hat{A}$ is an arbitrary operator (hereafter, the symbol $\langle \ldots \rangle_{\mathrm{rel}}$ stands for the averages calculated with the relevant statistical operator). Taking $\hat{A} = \hat{f}_k$, $\hat{A} = \hat{n}_q$, and recalling the explicit form of the relevant statistical operator, equation (3.1), we find that $\langle [\hat{f}_k, \hat{H}_{\mathrm{int}}] \rangle^{t}_{\mathrm{rel}} = \langle [\hat{n}_q, \hat{H}_{\mathrm{int}}] \rangle^{t}_{\mathrm{rel}} = 0$. Thus the collision integrals are zero in the relevant ensemble, whence it follows that the derivative (4.5) is at least of the second order in the interaction.

Turning back to equation (4.3), we conclude that the nonequilibrium statistical operator, correct to the first order in the interaction, is

$$\begin{aligned} \varrho(t) \;&=\; \varrho_{\mathrm{rel}}(t) - \int\limits_{t_0}^{t} \mathrm{d}t'\, U_0(t,t')\, \frac{1}{\mathrm{i}\hbar} [\varrho_{\mathrm{rel}}(t'), \hat{H}_0]\, U_0^{\dagger}(t,t') \\ &\quad - \int\limits_{t_0}^{t} \mathrm{d}t'\, U_0(t,t')\, \frac{1}{\mathrm{i}\hbar} [\varrho_{\mathrm{rel}}(t'), \hat{H}_{\mathrm{int}}]\, U_0^{\dagger}(t,t'). \end{aligned} \tag{4.7}$$

The integral terms can be combined into a single expression, but it is more convenient to analyze these terms separately because they have a different physical interpretation. We would like to emphasize that the first integral term in equation (4.7) contributes to $\varrho(t)$ due to the fact that the relevant statistical operator (3.1) does not commute with the operator of the kinetic energy. If the distributions $f_k(t)$ and $n_q(t)$ are the only controlled quantities, the relevant statistical operator does not contain $\hat{H}_{\mathrm{int}}$ and, consequently, the first integral term in equation (4.7) vanishes. In thermal equilibrium $\varrho_{\mathrm{rel}} = \varrho_{\mathrm{eq}}$, where ϱ_{eq} is the grand canonical distribution. In this case equation (4.7) gives $\varrho = \varrho_{\mathrm{eq}}$, as it should be.

5. Collision integrals in non-Markovian Born approximation

With the expression (4.7) for the statistical operator, the electron and phonon collision integrals (2.5) can be written in the form

$$\begin{aligned} I^{(\mathrm{e})}_k(t) \;&=\; -\frac{1}{\hbar^2} \int\limits_{t_0}^{t} \mathrm{d}t'\, \mathrm{Tr} \left\{ \left[U_0^{\dagger}(t,t') [\hat{f}_k, \hat{H}_{\mathrm{int}}] U_0(t,t'), \hat{H}_{\mathrm{int}} \right] \varrho_{\mathrm{rel}}(t') \right\} \\ &\quad + \frac{1}{\hbar^2} \int\limits_{t_0}^{t} \mathrm{d}t'\, \mathrm{Tr} \left\{ U_0^{\dagger}(t,t') [\hat{f}_k, \hat{H}_{\mathrm{int}}] U_0(t,t') [\varrho_{\mathrm{rel}}(t'), \hat{H}_0] \right\}, \end{aligned} \tag{5.1}$$

$$I^{(\mathrm{ph})}_q(t) \;=\; -\frac{1}{\hbar^2} \int\limits_{t_0}^{t} \mathrm{d}t'\, \mathrm{Tr} \left\{ \left[U_0^{\dagger}(t,t') [\hat{n}_q, \hat{H}_{\mathrm{int}}] U_0(t,t'), \hat{H}_{\mathrm{int}} \right] \varrho_{\mathrm{rel}}(t') \right\}$$

$$+\frac{1}{\hbar^2}\int_{t_0}^{t} \mathrm{d}t' \,\mathrm{Tr}\left\{U_0^{\dagger}(t,t')[\hat{n}_q,\hat{H}_{\mathrm{int}}]U_0(t,t')[\varrho_{\mathrm{rel}}(t'),\hat{H}_0]\right\}. \tag{5.2}$$

The first terms in these expressions are well known from the quantum kinetic theory (see, e.g., [7]). In the Markovian limit, they coincide with the Bloch collision integrals which are commonly used in the theory of metals and semiconductors. The last terms in equations (5.1) and (5.2) may be identified as the correlation contributions to the collision integrals.

Explicit calculations of $I_k^{(\mathrm{e})}(t)$ and $I_q^{(\mathrm{ph})}(t)$ are detailed in appendix A. Here we write out the results, correct to the second order in the interaction:

$$\begin{aligned}
I_k^{(\mathrm{e})}(t) \;=\; & -\frac{2}{\hbar^2}\sum_q D_q^2 \int_{t_0}^{t} \mathrm{d}t' \,\cos\left[\Omega_{k,k-q,q}(t-t')\right] \\
& \times\left(1-\beta^*(t')\,\frac{\hbar\Omega_{k,k-q,q}}{\ln\mathcal{K}_{k,k-q,q}(\{f(t'),n(t')\})}\right)\left(f_k\bar{f}_{k-q}\bar{n}_q-\bar{f}_kf_{k-q}n_q\right)_{t'} \\
& -\frac{2}{\hbar^2}\sum_q D_q^2 \int_{t_0}^{t} \mathrm{d}t' \,\cos\left[\Omega_{k+q,k,q}(t-t')\right] \\
& \times\left(1-\beta^*(t')\,\frac{\hbar\Omega_{k+q,k,q}}{\ln\mathcal{K}_{k+q,k,q}(\{f(t'),n(t')\})}\right)\left(f_k\bar{f}_{k+q}n_q-\bar{f}_kf_{k+q}\bar{n}_q\right)_{t'}, \qquad (5.3)\\
I_q^{(\mathrm{ph})}(t) \;=\; & -\frac{2D_q^2}{\hbar^2}\sum_k \int_{t_0}^{t} \mathrm{d}t' \,\cos\left[\Omega_{k,k-q,q}(t-t')\right] \\
& \times\left(1-\beta^*(t')\,\frac{\hbar\Omega_{k,k-q,q}}{\ln\mathcal{K}_{k,k-q,q}(\{f(t'),n(t')\})}\right)\left(n_qf_{k-q}\bar{f}_k-\bar{n}_qf_k\bar{f}_{k-q}\right)_{t'}, \qquad (5.4)
\end{aligned}$$

where we have introduced the designations:

$$\Omega_{k_1,k_2,q}=\frac{1}{\hbar}\left(\varepsilon_{k_1}-\varepsilon_{k_2}-\hbar\omega_q\right), \tag{5.5}$$

$$\mathcal{K}_{k_1,k_2,q}(\{f,n\})=\frac{\bar{f}_{k_1}f_{k_2}n_q}{f_{k_1}\bar{f}_{k_2}\bar{n}_q}\equiv\frac{(1-f_{k_1})f_{k_2}n_q}{f_{k_1}(1-f_{k_2})(1+n_q)}. \tag{5.6}$$

The correlation contributions to the collision integrals are represented by the terms with the time-dependent quasi-temperature. Thus, to have a closed scheme, we need an evolution equation for $\beta^*(t)$.

6. Equation for the quasi-temperature

To derive the equation for the quasi-temperature, we start from the balance equation for the interaction energy

$$\frac{\mathrm{d}\mathcal{E}_{\mathrm{int}}(t)}{\mathrm{d}t}=-\sum_k\varepsilon_k\,I_k^{(\mathrm{e})}(t)-\sum_q\hbar\omega_q\,I_q^{(\mathrm{ph})}(t), \tag{6.1}$$

which follows from the balance equation (2.7) for the kinetic energy and the conservation of the total energy, $\mathrm{d}\mathcal{E}/\mathrm{d}t = 0$. We next differentiate the conditions (3.3) with respect to time. Making use of equations (2.4) and (6.1), we get

$$\mathrm{Tr}\left\{\hat{f}_k\,\frac{\partial\varrho_{\mathrm{rel}}}{\partial t}\right\} = I_k^{(\mathrm{e})}, \qquad \mathrm{Tr}\left\{\hat{n}_q\,\frac{\partial\varrho_{\mathrm{rel}}}{\partial t}\right\} = I_q^{(\mathrm{ph})},$$

$$\mathrm{Tr}\left\{\hat{H}_{\mathrm{int}}\,\frac{\partial\varrho_{\mathrm{rel}}}{\partial t}\right\} = -\sum_k \varepsilon_k\,I_k^{(\mathrm{e})} - \sum_q \hbar\omega_q\,I_q^{(\mathrm{ph})}. \tag{6.2}$$

Since the relevant statistical operator (3.1) depends on time only through the Lagrange multipliers, the derivative $\partial\varrho_{\mathrm{rel}}(t)/\partial t$ can easily be calculated and equations (6.2) become

$$(\hat{f}_k,\hat{H}_{\mathrm{int}})\,\frac{\mathrm{d}\beta^*}{\mathrm{d}t} + \sum_{k'}(\hat{f}_k,\hat{f}_{k'})\,\frac{\partial\Lambda_{k'}^{(\mathrm{e})}}{\partial t} + \sum_q(\hat{f}_k,\hat{n}_q)\,\frac{\partial\Lambda_q^{(\mathrm{ph})}}{\partial t} = -I_k^{(\mathrm{e})}, \tag{6.3}$$

$$(\hat{n}_q,\hat{H}_{\mathrm{int}})\,\frac{\mathrm{d}\beta^*}{\mathrm{d}t} + \sum_{k}(\hat{n}_q,\hat{f}_{k})\,\frac{\partial\Lambda_{k}^{(\mathrm{e})}}{\partial t} + \sum_{q'}(\hat{n}_q,\hat{n}_{q'})\,\frac{\partial\Lambda_{q'}^{(\mathrm{ph})}}{\partial t} = -I_k^{(\mathrm{e})}, \tag{6.4}$$

$$(\hat{H}_{\mathrm{int}},\hat{H}_{\mathrm{int}})\,\frac{\mathrm{d}\beta^*}{\mathrm{d}t} + \sum_{k}(\hat{H}_{\mathrm{int}},\hat{f}_{k})\,\frac{\partial\Lambda_{k}^{(\mathrm{e})}}{\partial t} + \sum_{q}(\hat{H}_{\mathrm{int}},\hat{n}_{q})\,\frac{\partial\Lambda_{q}^{(\mathrm{ph})}}{\partial t} = $$
$$= \sum_k \varepsilon_k\,I_k^{(\mathrm{e})} + \sum_q \hbar\omega_q\,I_q^{(\mathrm{ph})}. \tag{6.5}$$

Here we have introduced the correlation function of dynamical variables in the relevant ensemble (for brevity, the fixed argument t is omitted):

$$(\hat{A},\hat{B}) = \int_0^1 \mathrm{d}x\,\langle \Delta\hat{A}\,\varrho_{\mathrm{rel}}^{x}\,\Delta\hat{B}\,\varrho_{\mathrm{rel}}^{-x}\rangle_{\mathrm{rel}}, \tag{6.6}$$

where $\Delta\hat{A} = \hat{A} - \langle\hat{A}\rangle_{\mathrm{rel}}$. Equations (6.3) – (6.5) can be solved for the time derivatives of the Lagrange multipliers (see appendix B). Our interest is only with the time derivative of the quasi-temperature, which is given by

$$\frac{\mathrm{d}\beta^*(t)}{\mathrm{d}t} = \frac{1}{C(t)}\left\{\sum_k\left(\varepsilon_k + R_k^{(\mathrm{e})}(t)\right)I_k^{(\mathrm{e})}(t) + \sum_q\left(\hbar\omega_q + R_q^{(\mathrm{ph})}(t)\right)I_q^{(\mathrm{ph})}(t)\right\}, \tag{6.7}$$

where C, $R_k^{(\mathrm{e})}$, and $R_q^{(\mathrm{ph})}$ are some combinations of the correlation functions. Explicit expressions for these quantities are given in appendix B.

Equation (6.7) is still exact. For a weak electron-phonon interaction, the quantities $R_k^{(\mathrm{e})}$ and $R_q^{(\mathrm{ph})}$ can be neglected, while the C can be expressed explicitly in terms of the nonequilibrium electron and phonon distribution functions (see appendix B):

$$C(t) = 2\sum_{kq} D_q^2\,\frac{n_q\bar{f}_k f_{k-q} - \bar{n}_q f_k\bar{f}_{k-q}}{\ln\left[\dfrac{n_q\bar{f}_k f_{k-q}}{\bar{n}_q f_k\bar{f}_{k-q}}\right]}, \tag{6.8}$$

where the following designations are used:

$$\bar{f}_k(t) = 1 - f_k(t), \qquad \bar{n}_q(t) = 1 + n_q(t). \tag{6.9}$$

Since $\{(x-1)/\ln x\} > 0$, we see from equation (6.8) that $C > 0$.

Thus, in the case of a weak electron-phonon interaction the quasi-temperature evolves in time according to the equation

$$\frac{\mathrm{d}\beta^*(t)}{\mathrm{d}t} = \frac{1}{C(t)} \left\{ \sum_k \varepsilon_k\, I_k^{(\mathrm{e})}(t) + \sum_q \hbar\omega_q\, I_q^{(\mathrm{ph})}(t) \right\} \tag{6.10}$$

with $C(t)$ given by equation (6.8). It is interesting to note that the expression in braces is just the time derivative of the kinetic energy, $\mathrm{d}\mathcal{E}_{\mathrm{kin}}(t)/\mathrm{d}t$.

After inserting expressions (5.3) and (5.4) into equation (6.10) we obtain the equation for the quasi-temperature in the explicit form:

$$\begin{aligned} \frac{\mathrm{d}\beta^*(t)}{\mathrm{d}t} = &- \frac{2}{\hbar C(t)} \sum_{kq} D_q^2\, \Omega_{k,k-q,q} \int\limits_{t_0}^{t} \mathrm{d}t'\, \cos\left[\Omega_{k,k-q,q}(t-t')\right] \\ &\times \left(1 - \beta^*(t')\, \frac{\hbar\Omega_{k,k-q,q}}{\ln \mathcal{K}_{k,k-q,q}(\{f(t')\},\{n(t')\})}\right) \left(f_k \bar{f}_{k-q} \bar{n}_q - \bar{f}_k f_{k-q} n_q\right)_{t'}. \end{aligned} \tag{6.11}$$

Now kinetic equations (2.4), together with equation (6.11), form a closed set of equations describing non-Markovian relaxation processes in the electron-phonon system.

7. Some properties of the evolution equations

We recall that the analysis in this paper seeks to overcome some difficulties in non-Markovian quantum kinetics, which were mentioned in the introduction. Therefore, it make sense to look at the evolution equations (2.4) and (6.11) from this point of view.

7.1. The equilibrium solution

First we will show that the equilibrium electron and phonon distributions

$$f_k^{(\mathrm{eq})} = \frac{1}{\exp\{\beta\,(\varepsilon_k - \mu)\} + 1}, \qquad n_q^{(\mathrm{eq})} = \frac{1}{\exp\{\beta\hbar\omega_q\} - 1} \tag{7.1}$$

are a stationary solution of equations (2.4) and (6.11). For this purpose it is convenient to express the collision integrals (5.3) and (5.4) in a slightly different form by introducing the quasi-equilibrium distributions

$$f_k^0(t) = \frac{1}{\exp\{\beta^*(t)\,(\varepsilon_k - \mu^*(t))\} + 1}, \qquad n_q^0(t) = \frac{1}{\exp\{\beta^*(t)\hbar\omega_q\} - 1}. \tag{7.2}$$

These distributions correspond to the state described by the quasi-equilibrium statistical operator (3.9) in the absence of the electron-phonon interaction. Obviously the equilibrium distributions (7.1) are a special case of the quasi-equilibrium distributions (7.2).

It can easily be checked that

$$\beta^*(t)\hbar\Omega_{k_1,k_2,q} = \mathcal{K}_{k_1,k_2,q}(\{f^0(t), n^0(t)\}), \tag{7.3}$$

where the $\mathcal{K}$-function in the right-hand side is obtained from the function (5.6) by replacing $f_k(t) \to f_k^0(t)$ and $n_q(t) \to n_q^0(t)$. Using equation (7.3), we see that the collision integrals (5.3) and (5.4) are equal to zero if $f_k(t') = f_k^0(t')$ and $n_q(t') = n_q^0(t')$. Note that in this case the right-hand side of equation (6.11) is also zero. Suppose now that at the initial time t_0

$$f_k(t_0) = f_k^0(t_0) = f_k^{(\mathrm{eq})}, \qquad n_q(t_0) = n_q^0(t_0) = n_q^{(\mathrm{eq})}. \tag{7.4}$$

These conditions imply that $\beta^*(t_0) = \beta$ and $\mu^*(t_0) = \mu$, i.e., the evolution of the system starts from thermal equilibrium. Then the above considerations show that the state of the system will remain unchanged for all times $t > t_0$. Physically, this property of the evolution equations reflects the fact that in thermal equilibrium the collision and correlation effects exactly cancel each other. The same result was obtained previously within the Green's function formalism [8].

7.2. The Markovian limit

The Markovian approximation implies that the collision integrals (5.3), (5.4), and the right-hand side of equation (6.11) depend on the distribution functions and the quasi-temperature taken at time t. The Markovian approximation is inadequate for the initial stage of evolution because of initial correlations and, strictly speaking, describes the limiting long-time regime where $\partial f_k/\partial t \to 0$, $\partial n_q/\partial t \to 0$, and $\partial\beta^*/\partial t \to 0$. Thus, on passage to the Markovian limit in the collision integrals (5.3), (5.4), and in equation (6.11) for the quasi-temperature, we put $f_k(t') \approx f_k(t)$, $n_q(t') \approx n_q(t)$, and then pass to the limit $t - t_0 \to \infty$. The remainder integrals over t' are calculated in the standard way:

$$\lim_{t-t_0\to\infty} \int_{t_0}^{t} \mathrm{d}t' \, \cos\left[\Omega(t-t')\right] = \lim_{\varepsilon\to+0} \int_{-\infty}^{0} \mathrm{d}\tau \, \mathrm{e}^{\varepsilon\tau} \, \cos\left(\Omega\tau\right) = \pi\delta(\Omega). \tag{7.5}$$

As a result we obtain the collision integrals (5.3) and (5.4) in the Markovian limit:

$$\begin{aligned} I_k^{(\mathrm{e})}(t) &= \frac{2\pi}{\hbar}\sum_q D_q^2\,\delta\left(\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q\right)\left(f_k\bar{f}_{k-q}\bar{n}_q - \bar{f}_k f_{k-q} n_q\right)_t \\ &\quad - \frac{2\pi}{\hbar}\sum_q D_q^2\,\delta\left(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q\right)\left(f_k\bar{f}_{k+q} n_q - \bar{f}_k f_{k+q}\bar{n}_q\right)_t, \end{aligned} \tag{7.6}$$

$$I_q^{(\mathrm{ph})}(t) = -\frac{2\pi}{\hbar}D_q^2\sum_k \delta\left(\varepsilon_k - \varepsilon_{k-q} - \hbar\omega_q\right)\left(n_q f_{k-q}\bar{f}_k - \bar{n}_q f_k\bar{f}_{k-q}\right)_t. \tag{7.7}$$

These expressions coincide with the well-known collision integrals for the electron-phonon system [9]. We also note that the right-hand side of equation (6.11) tends to zero in the Markovian limit and, consequently, the equation for the quasi-temperature becomes $\mathrm{d}\beta^*/\mathrm{d}t = 0$. We see that the correlation contributions to the collision integrals vanish in the Markovian limit, but this is true only in the Born approximation. In higher-order approximations, say, in the T-matrix approximation, the correlation terms do not vanish in the Markovian limit [10].

It is also interesting to observe that the time derivative of the quasi-temperature is zero in the Markovian regime, whereas the collision integrals remain finite. Physically, this result shows that the characteristic time scale for the quasi-temperature is larger than the relaxation time for the distribution functions. In a sense, the time change of the quasi-temperature describes the evolution of long-lived correlations associated with the energy conservation.

7.3. Energy conservation

To demonstrate that the evolution equations (2.4) and (6.11) conserve the total energy of the system, we calculate the time derivative of the kinetic energy, equation (2.6), with the collision integrals (5.3) and (5.4). A little algebra shows that

$$\frac{\mathrm{d}\mathcal{E}_{\mathrm{kin}}(t)}{\mathrm{d}t} = -\frac{2}{\hbar}\int_{t_0}^{t} \mathrm{d}t' \sum_{kq} D_q^2\, \Omega_{k,k-q,q} \cos\left[\Omega_{k,k-q,q}(t-t')\right]$$

$$\times \left(1 - \beta^*(t')\,\frac{\hbar\Omega_{k,k-q,q}}{\ln \mathcal{K}_{k,k-q,q}(\{f(t')\},\{n(t')\})}\right)\left(f_k \bar{f}_{k-q}\bar{n}_q - \bar{f}_k f_{k-q} n_q\right)_{t'} . \quad (7.8)$$

This equation can be written as the conservation law

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{\mathcal{E}_{\mathrm{kin}}(t) + \mathcal{E}_{\mathrm{int}}(t)\right\} = 0 \quad (7.9)$$

with the time-dependent correlation energy

$$\mathcal{E}_{\mathrm{int}}(t) = \mathcal{E}_{\mathrm{int}}(t_0) + \frac{2}{\hbar}\int_{t_0}^{t} \mathrm{d}t' \sum_{kq} D_q^2 \sin\left[\Omega_{k,k-q,q}(t-t')\right]$$

$$\times \left(1 - \beta^*(t')\,\frac{\hbar\Omega_{k,k-q,q}}{\ln \mathcal{K}_{k,k-q,q}(\{f(t')\},\{n(t')\})}\right)\left(f_k \bar{f}_{k-q}\bar{n}_q - \bar{f}_k f_{k-q} n_q\right)_{t'} . \quad (7.10)$$

Applying the arguments of subsection 7.1 to equation (7.8), we see that the kinetic energy and, consequently, the interaction energy do not depend on time in thermal equilibrium, as it should be. In the Markovian limit equation (7.8) also gives $\mathrm{d}\mathcal{E}_{\mathrm{kin}}(t)/\mathrm{d}t = 0$. This, of course, accords with the fact that the Markovian collision integrals (7.6) and (7.7) conserve the total kinetic energy of the quasiparticles.

8. Conclusions and outlook

The major points covered in this paper may be summarized as follows. First, we have seen that the correlation effects associated with the energy conservation contribute to the collision integrals even in the second-order non-Markovian Born approximation and play a very important role in kinetic processes. For example, it is just the interplay between collisions and correlations which is responsible for the existence of the correct equilibrium solution of kinetic equations with memory. The second point is that memory effects, correlation effects, and conservation laws are intimately related. Therefore it is not surprising that in many existing approaches, where the above effects are not taken into account self-consistently, the correct long-time behaviour of the one-particle distribution function cannot be combined with the energy conservation. Finally, in non-Markovian kinetics we deal with quite different time scales even for spatially homogeneous systems. The short time scale corresponds to collisions and is of the same order as in the Markovian limit. Another, larger, time scale is involved in the evolution of long-lived correlations. Within our scheme the slow evolution of correlations is described by equation (6.11) for the quasi-temperature.

In closing we would like to dwell on some open problems in non-Markovian quantum kinetics. The most important one is the inclusion of quasiparticle damping in such a way as to circumvent problems with the energy conservation. The quasi-particle effects appear naturally in the Green's function formalism and are rather difficult to describe in the density matrix method. On the other hand, the Green's function technique meets serious difficulties in attempting to describe long-lived many-particle correlations which play a crucial role in the energy conservation. The origin of these difficulties is that the correlation contributions to self-energies can only be calculated by summing up divergent secular terms, which is a very complicated problem. Thus, it would be of great importance to develop a workable Green's function formalism involving dynamics of running correlations. Another interesting aspect of non-Markovian quantum kinetics is the interplay between collisions, correlations and the field effects. In the scheme presented here, one has to consider explicitly the interaction of electrons with a time-dependent optical excitation pulse. In this case the evolution operator (4.4) involves the corresponding field Hamiltonian. Note also that in the presence of an external field the energy of the electron-phonon system is not conserved and, consequently, the quasi-temperature changes in time according to an energy balance equation in which the work produced by the field is to be included.

A. Calculation of collision integrals (5.1) and (5.2)

Let us write the electron and phonon collision integrals as

$$I_k^{(\mathrm{e})}(t) = \mathcal{I}_k^{(\mathrm{e})}(t) + \mathcal{J}_k^{(\mathrm{e})}(t), \qquad I_q^{(\mathrm{ph})}(t) = \mathcal{I}_q^{(\mathrm{ph})}(t) + \mathcal{J}_q^{(\mathrm{ph})}(t), \tag{A.1}$$

where $\mathcal{I}_k^{(\mathrm{e})}(t)$ and $\mathcal{I}_q^{(\mathrm{ph})}(t)$, given by the first terms in equations (5.1) and (5.2), may be called the "collision" contributions, while $\mathcal{J}_k^{(\mathrm{e})}(t)$ and $\mathcal{J}_q^{(\mathrm{ph})}(t)$ are the "correlation" contributions; they are represented by the last terms in equations (5.1), (5.2) and come from the interaction Hamiltonian in the relevant statistical operator (3.1).

Since the collision contributions are explicitly of the second order in the interaction, they can be approximated as

$$\begin{aligned}
\mathcal{I}_k^{(\mathrm{e})}(t) &= -\frac{1}{\hbar^2}\int\limits_{t_0}^{t} \mathrm{d}t'\,\mathrm{Tr}\left\{\left[U_0^\dagger(t,t')[\hat{f}_k,\hat{H}_{\mathrm{int}}]U_0(t,t'),\hat{H}_{\mathrm{int}}\right]\tilde{\varrho}_{\mathrm{rel}}(t')\right\},\\
\mathcal{I}_q^{(\mathrm{ph})}(t) &= -\frac{1}{\hbar^2}\int\limits_{t_0}^{t} \mathrm{d}t'\,\mathrm{Tr}\left\{\left[U_0^\dagger(t,t')[\hat{n}_q,\hat{H}_{\mathrm{int}}]U_0(t,t'),\hat{H}_{\mathrm{int}}\right]\tilde{\varrho}_{\mathrm{rel}}(t')\right\},
\end{aligned}\tag{A.2}$$

where the statistical operator

$$\tilde{\varrho}_{\mathrm{rel}}(t) = \frac{1}{\tilde{Z}_{\mathrm{rel}}(t)}\exp\left\{-\sum_k \Lambda_k^{(\mathrm{e})}(t)\,\hat{f}_k - \sum_q \Lambda_q^{(\mathrm{ph})}(t)\,\hat{n}_q\right\}\tag{A.3}$$

describes a system of non-interacting quasiparticles. In the same approximation, the Lagrange multipliers $\Lambda_k^{(\mathrm{e})}(t)$ and $\Lambda_q^{(\mathrm{ph})}(t)$ are determined by the self-consistency conditions

$$f_k(t) = \mathrm{Tr}\left\{\hat{f}_k\tilde{\varrho}_{\mathrm{rel}}(t)\right\},\qquad n_q(t) = \mathrm{Tr}\left\{\hat{n}_q\tilde{\varrho}_{\mathrm{rel}}(t)\right\}.\tag{A.4}$$

Now (A.2) can easily be evaluated by using the expression for the interaction Hamiltonian [see equation (2.1)], the relations

$$\begin{aligned}
&U_0^\dagger(t,t')\,a_k U_0(t,t') = \mathrm{e}^{-\mathrm{i}\varepsilon_k(t-t')/\hbar}\,a_k, &&U_0^\dagger(t,t')\,a_k^\dagger U_0(t,t') = \mathrm{e}^{\mathrm{i}\varepsilon_k(t-t')/\hbar}\,a_k^\dagger,\\
&U_0^\dagger(t,t')\,b_q U_0(t,t') = \mathrm{e}^{-\mathrm{i}\omega_q(t-t')}\,b_q, &&U_0^\dagger(t,t')\,b_q^\dagger U_0(t,t') = \mathrm{e}^{\mathrm{i}\omega_q(t-t')}\,b_q^\dagger,
\end{aligned}\tag{A.5}$$

and Wick's decomposition of the averages. A straightforward algebra leads to

$$\begin{aligned}
\mathcal{I}_k^{(\mathrm{e})}(t) &= -\frac{2}{\hbar^2}\sum_q D_q^2\int\limits_{t_0}^{t}\mathrm{d}t'\left\{\cos\left[\Omega_{k+q,k,q}(t-t')\right]\left(f_k\bar{f}_{k+q}n_q - \bar{f}_k f_{k+q}\bar{n}_q\right)_{t'}\right.\\
&\qquad\left. +\cos\left[\Omega_{k,k-q,q}(t-t')\right]\left(f_k\bar{f}_{k-q}\bar{n}_q - \bar{f}_k f_{k-q}n_q\right)_{t'}\right\},\\
\mathcal{I}_q^{(\mathrm{ph})}(t) &= -\frac{2}{\hbar^2}D_q^2\sum_k\int\limits_{t_0}^{t}\mathrm{d}t'\cos\left[\Omega_{k,k-q,q}(t-t')\right]\left(\bar{f}_k f_{k-q}n_q - f_k\bar{f}_{k-q}\bar{n}_q\right)_{t'}
\end{aligned}\tag{A.6}$$

with $\Omega_{k_1,k_2,q}$ given by equation (5.5).

Let us now turn to the correlation terms in the collision integrals (5.1) and (5.2). In Born approximation, we have to calculate the commutator $[\varrho_{\mathrm{rel}}(t'),\hat{H}_0]$, correct to the first order in the coupling constant D_q. To do this, we make use of the Kubo identity [7]

$$\left[\mathrm{e}^{\hat{A}}, \hat{B}\right] = \int_0^1 \mathrm{d}x\, \mathrm{e}^{x\hat{A}}\, [\hat{A}, \hat{B}]\, \mathrm{e}^{-x\hat{A}}\, \mathrm{e}^{\hat{A}}. \tag{A.7}$$

Recalling the expression (3.1) for the relevant statistical operator, we obtain

$$\left[\varrho_{\mathrm{rel}}(t'), \hat{H}_0\right] = \beta^*(t') \int_0^1 \mathrm{d}x\, \tilde{\varrho}^{\,x}_{\mathrm{rel}}(t') \left[\hat{H}_0, \hat{H}_{\mathrm{int}}\right] \tilde{\varrho}^{\,-x}_{\mathrm{rel}}(t')\, \tilde{\varrho}_{\mathrm{rel}}(t'), \tag{A.8}$$

where higher-order terms have been omitted. Further manipulations are straightforward and require only a few comments. The x integration is easily performed with the aid of relations

$$\begin{aligned} \tilde{\varrho}^{\,x}_{\mathrm{rel}}\, a_k\, \tilde{\varrho}^{\,-x}_{\mathrm{rel}} &= \mathrm{e}^{x\Lambda^{(\mathrm{e})}_k}\, a_k, & \tilde{\varrho}^{\,x}_{\mathrm{rel}}\, a^\dagger_k\, \tilde{\varrho}^{\,-x}_{\mathrm{rel}} &= \mathrm{e}^{-x\Lambda^{(\mathrm{e})}_k}\, a^\dagger_k, \\ \tilde{\varrho}^{\,x}_{\mathrm{rel}}\, b_q\, \tilde{\varrho}^{\,-x}_{\mathrm{rel}} &= \mathrm{e}^{x\Lambda^{(\mathrm{ph})}_q}\, b_q, & \tilde{\varrho}^{\,x}_{\mathrm{rel}}\, b^\dagger_q\, \tilde{\varrho}^{\,-x}_{\mathrm{rel}} &= \mathrm{e}^{-x\Lambda^{(\mathrm{ph})}_q}\, b^\dagger_q. \end{aligned} \tag{A.9}$$

At the end of calculations the Lagrange multipliers can be eliminated by means of equations (A.4) which give

$$\Lambda^{(\mathrm{e})}_k(t) = \ln\left(\frac{1 - f_k(t)}{f_k(t)}\right), \qquad \Lambda^{(\mathrm{ph})}_q(t) = \ln\left(\frac{1 + n_q(t)}{n_q(t)}\right). \tag{A.10}$$

Then, substituting (A.8) into the last terms in equations (5.1) and (5.2), and using Wick's theorem to evaluate the averages, we obtain the correlation contributions to the collision integrals in non-Markovian Born approximation:

$$\begin{aligned} \mathcal{J}^{(\mathrm{e})}_k(t) &= \frac{2}{\hbar^2} \sum_q D^2_q \int_{t_0}^{t} \mathrm{d}t'\, \beta^*(t') \\ &\times \left\{ \frac{\hbar\Omega_{k,k-q,q}}{\ln \mathcal{K}_{k,k-q,q}(\{f(t'), n(t')\})} \left(f_k \bar{f}_{k-q} \bar{n}_q - \bar{f}_k f_{k-q} n_q\right)_{t'} \cos\left[\Omega_{k,k-q,q}(t-t')\right] \right. \\ &\quad \left. + \frac{\hbar\Omega_{k+q,k,q}}{\ln \mathcal{K}_{k+q,k,q}(\{f(t'), n(t')\})} \left(f_k \bar{f}_{k+q} n_q - \bar{f}_k f_{k+q} \bar{n}_q\right)_{t'} \cos\left[\Omega_{k+q,k,q}(t-t')\right] \right\}, \end{aligned}$$

$$\begin{aligned} \mathcal{J}^{(\mathrm{ph})}_q(t) &= \frac{2}{\hbar^2} D^2_q \sum_k \int_{t_0}^{t} \mathrm{d}t'\, \beta^*(t') \\ &\times \frac{\hbar\Omega_{k,k-q,q}}{\ln \mathcal{K}_{k,k-q,q}(\{f(t'), n(t')\})} \cos\left[\Omega_{k,k-q,q}(t-t')\right] \left(\bar{f}_k f_{k-q} n_q - f_k \bar{f}_{k-q} \bar{n}_q\right)_{t'} \end{aligned} \tag{A.11}$$

with $\mathcal{K}_{k_1,k_2,q}$ given by equation (5.6). Combining equations (A.6) and (A.11) yields the final results (5.3) and (5.4) for the collision integrals.

B. Derivation of equation (6.7)

A formal solution of equations (6.3) and (6.4) for the time derivatives $\partial\Lambda^{(e)}_k/\partial t$ and $\partial\Lambda^{(ph)}_q/\partial t$ reads

$$\frac{\partial\Lambda^{(e)}_k}{\partial t} = -\sum_{k'}\left(\chi^{(e)}\right)^{-1}_{kk'}\left\{I^{(e)}_{k'} + (\mathcal{P}^{(e)}\hat{f}_{k'},\hat{H}_{\rm int})\,\frac{{\rm d}\beta^*}{{\rm d}t} - \sum_{qq'}(\hat{f}_{k'},\hat{n}_q)\,(\hat{n},\hat{n})^{-1}_{qq'}\,I^{(ph)}_{q'}\right\},$$
$$\frac{\partial\Lambda^{(ph)}_q}{\partial t} = -\sum_{q'}\left(\chi^{(ph)}\right)^{-1}_{qq'}\left\{I^{(ph)}_{q'} + (\mathcal{P}^{(ph)}\hat{n}_{q'},\hat{H}_{\rm int})\,\frac{{\rm d}\beta^*}{{\rm d}t} - \sum_{kk'}(\hat{n}_{q'},\hat{f}_k)\,(\hat{f},\hat{f})^{-1}_{kk'}\,I^{(e)}_{k'}\right\}, \tag{B.1}$$

where $(\hat{f},\hat{f})^{-1}_{kk'}$ is the inverse to the electron correlation matrix $(\hat{f}_k,\hat{f}_{k'})$ and $(\hat{n},\hat{n})^{-1}_{qq'}$ is the inverse to the phonon correlation matrix $(\hat{n}_q,\hat{n}_{q'})$. We also have introduced the matrices

$$\chi^{(e)}_{kk'} = (\hat{f}_k,\hat{f}_{k'}) - \sum_{qq'}(\hat{f}_k,\hat{n}_q)(\hat{n},\hat{n})^{-1}_{qq'}(\hat{n}_{q'},\hat{f}_{k'}),$$
$$\chi^{(ph)}_{qq'} = (\hat{n}_q,\hat{n}_{q'}) - \sum_{kk'}(\hat{n}_q,\hat{f}_k)(\hat{f},\hat{f})^{-1}_{kk'}(\hat{f}_{q'},\hat{n}_{q'}) \tag{B.2}$$

and the projectors $\mathcal{P}^{(e)}$, $\mathcal{P}^{(ph)}$, which act on quantum-mechanical operators $\hat{A}$ according to the rules

$$\mathcal{P}^{(e)}\hat{A} = \hat{A} - \sum_{qq'}(\hat{A},\hat{n}_q)\,(\hat{n},\hat{n})^{-1}_{qq'}\,\hat{n}_{q'}, \qquad \mathcal{P}^{(ph)}\hat{A} = \hat{A} - \sum_{kk'}(\hat{A},\hat{f}_k)\,(\hat{f},\hat{f})^{-1}_{kk'}\,\hat{f}_{k'}. \tag{B.3}$$

Note that $\mathcal{P}^{(e)}\hat{n}_q = 0$ and $\mathcal{P}^{(ph)}\hat{f}_k = 0$.

Insertion of equations (B.1) into equation (6.5) leads to the evolution equation for the quasi-temperature, which can be written in the form (6.7), where

$$R^{(e)}_k = \sum_{k'}(\hat{H}_{\rm int},\hat{f}_{k'})\left(\chi^{(e)}\right)^{-1}_{k'k} - \sum_{k'qq'}(\hat{H}_{\rm int},\hat{n}_q)\left(\chi^{(ph)}\right)^{-1}_{qq'}(\hat{n}_{q'},\hat{f}_{k'})\,(\hat{f},\hat{f})^{-1}_{k'k},$$
$$R^{(ph)}_q = \sum_{q'}(\hat{H}_{\rm int},\hat{n}_{q'})\left(\chi^{(ph)}\right)^{-1}_{q'q} - \sum_{q'kk'}(\hat{H}_{\rm int},\hat{f}_k)\left(\chi^{(e)}\right)^{-1}_{kk'}(\hat{f}_{k'},\hat{n}_{q'})\,(\hat{n},\hat{n})^{-1}_{q'q}, \tag{B.4}$$

and the correlation function $C(t)$ is given by

$$C = (\hat{H}_{\rm int},\hat{H}_{\rm int}) - \sum_{kk'}(\hat{H}_{\rm int},\hat{f}_k)\left(\chi^{(e)}\right)^{-1}_{kk'}(\mathcal{P}^{(e)}\hat{f}_{k'},\hat{H}_{\rm int})$$
$$- \sum_{qq'}(\hat{H}_{\rm int},\hat{n}_q)\left(\chi^{(ph)}\right)^{-1}_{qq'}(\mathcal{P}^{(ph)}\hat{n}_{q'},\hat{H}_{\rm int}). \tag{B.5}$$

So far we have not made any approximations. We now assume that the electron-phonon interaction is weak and keep in equation (6.7) the terms of the leading order in the interaction. In this case the correlation functions appearing in equations (B.4) and (B.5) can be evaluated with the relevant statistical operator (A.3) for a non-interacting electron-phonon system. Then we obtain the relations

$$(\hat{f}_k, \hat{n}_q) = (\hat{H}_{\rm int}, \hat{f}_k) = (\hat{H}_{\rm int}, \hat{n}_q) = 0, \tag{B.6}$$

which show that $R_k^{(\rm e)}$ and $R_q^{(\rm ph)}$ can be neglected in equation (6.7), and the correlation function C can be taken in the form

$$C = (\hat{H}_{\rm int}, \hat{H}_{\rm int}) = \int\limits_0^1 {\rm d}x\, {\rm Tr}\left\{\hat{H}_{\rm int}\, \tilde{\varrho}_{\rm rel}^{x}\, \hat{H}_{\rm int}\, \tilde{\varrho}_{\rm rel}^{-x}\, \tilde{\varrho}_{\rm rel}\right\}. \tag{B.7}$$

Making use of equations (A.9) and taking into account that the relevant statistical operator $\tilde{\varrho}_{\rm rel}$ admits Wick's decomposition of averages, the correlation function (B.7) can easily be evaluated. Finally, eliminating the Lagrange multipliers with the aid of equations (A.10), we obtain the expression (6.8).

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Немарковське електрон-фононне загасання

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За допомогою методу матриці густини в немарковському борнівському наближенні отримано кінетичні рівняння, що описують короткочасову еволюцію електрон-фононної системи. Запропонований у цій статті підхід відрізняється від попередніх схем тим, що енергія взаємодії вважається незалежним параметром стану нарівні з електронною та фононною функціями розподілу. За рахунок цього у кінетичних рівнняннях виникають нові кореляційні члени, що забезпечують збереження енергії та існування правильного рівноважного розв’язку. Отримано явний вираз для залежної від часу кореляційної енергії.

Ключові слова: *квантова кінетична теорія, немарковські кінетичні рівняння, нерівноважні кореляції, електрон-фононна взаємодія*

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