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Non-Markovian Quantum Kinetics and Conservation Laws

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A link between memory effects in quantum kinetic equations and nonequilibrium correlations associated with the energy conservation is investigated. In order that the energy be conserved by an approximate collision integral, the one-particle distribution function and the mean interaction energy are treated as independent nonequilibrium state parameters. The density operator method is used to derive a kinetic equation in second-order non-Markovian Born approximation and an evolution equation for the nonequilibrium quasi-temperature which is thermodynamically conjugated to the mean interaction energy. The kinetic equation contains a correlation contribution which exactly cancels the collision term in thermal equilibrium and ensures the energy conservation in non-equilibrium states. Explicit expressions for the entropy production in the non-Markovian regime and the time-dependent correlation energy are obtained.

KEY WORDS: Nonequilibrium statistical mechanics; quantum kinetic theory; non-Markovian kinetic equations; nonequilibrium correlations.

1. INTRODUCTION

Experimental studies of fast relaxation processes caused by the interaction of short laser pulses with matter$^{(1, 2)}$ have inspired a renewed interest in non-Markovian kinetics. Although this subject has been under development for many years, recent investigations have shown that the inclusion of memory effects in collision integrals leads to some serious problems, which did not receive proper attention previously.

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Since in many cases of experimental interest the system can be described in terms of weakly interacting quasiparticles, the most-used non-Markovian quantum kinetic equations are in fact modifications of the so-called *Levinson equation*(3) in which the collision integral is taken in second-order Born approximation and the energy-conserving delta function is replaced by an oscillating memory kernel (see, e.g., ref. 2). It should be noted, however, that such kinetic equations have some grave disadvantages. (i) The Levinson-like kinetic equations have unstable solutions and even produce negative distribution functions. (ii) If the initial state of the system is already thermal equilibrium, the collision integrals do not vanish, giving rise to nonphysical time evolution. The first defect can be overcome by using certain decaying memory kernels(2, 4, 5) which take account of the quasiparticle damping. However, in such approaches, the problem of the equilibrium solution still persists because all "improved" memory kernels lead to collision integrals which do not conserve the total energy of the system. As a consequence, in the long-time (Boltzmann) limit the "improved" non-Markovian quantum kinetic equations do not describe the relaxation to thermal equilibrium, leading to an overpopulation of high-energy states.

To summarize, it appears that the quasiparticle damping alone cannot be responsible for the long-time asymptotic behavior of non-Markovian quantum kinetic equations; there must be another physical mechanism which provides the exact cancellation of collision effects in thermal equilibrium and does not violate the energy conservation. The origin of such a mechanism can be deduced from consideration of kinetic processes in the presence of initial correlations. As early as 1970 Lee *et al.*(6) studied the evolution of a weakly interacting low-density classical gas with a correlated initial state and showed that in equilibrium the changes in the one-particle distribution function due to collisions (including memory effects) and initial correlations exactly cancel each other. Recently the same result was obtained for quantum systems.(7) It therefore would appear reasonable that the interplay between collisions and *nonequilibrium* correlations would be the mechanism which provides the correct long-time behavior of non-Markovian quantum kinetic equations.

This paper presents an approach in which the time evolution of the one-particle distribution function is coupled with the evolution of long-lived correlations associated with conservation laws. The basic idea is to treat conserved quantities, most notably the energy, as independent state parameters in addition to the one-particle distribution function. Although this is not to say that all many-particle correlations can be incorporated in this way, the advantage of the above idea, originally suggested in the context of a generalization of the Enskog theory to dense classical gases with "soft" inter-particle potentials(8, 9) and then applied to quantum systems,$^{(10, 11)}$ lies in the fact that now, due to microscopic equations of motion, the energy is an exactly conserved quantity in any approximation for the collision integral. Moreover, the energy conservation leads to the appearance of additional correlation terms in the kinetic equation, which substantially compensate the collision contribution. In this paper, within second-order non-Markovian Born approximation, we derive a collision integral involving the collision and correlation terms. It is shown that the kinetic equation is consistent with the energy conservation and has the correct equilibrium solution.

The paper is organized as follows. In Section 2 we consider a generalized Gibbs ensemble in which the energy and the one-particle distribution function play the role of given nonequilibrium state parameters. The corresponding *relevant statistical operator* is used to define the thermodynamic quantities: nonequilibrium entropy, the quasi-temperature, and the quasi-chemical potential. We also derive the evolution equations for the thermodynamic quantities in terms of the collision integral. Section 3 is concerned with construction of the nonequilibrium statistical operator describing non-Markovian kinetic processes in a spatially homogeneous system. The nonequilibrium statistical operator is found in terms of the relevant statistical operator for quantum systems with a weak interaction by employing iterative solution of the von Neumann equation. In Section 4 the nonequilibrium statistical operator is used to calculate the non-Markovian collision integral. In Section 5 we derive the entropy production in the non-Markovian regime and an expression for the time-dependent correlation energy of the system. Section 6 sketches a generalization of the theory to spatially non-homogeneous systems. Finally, Section 7 contains the final conclusions and comments on further applications of the theory.

2. NONEQUILIBRIUM CORRELATIONS ASSOCIATED WITH CONSERVATION LAWS

To put our discussion into a straightforward language, we shall consider a system of fermions or bosons with the Hamiltonian $\hat{H}=\hat{H}_0+\hat{H}'$, where $\hat{H}_0$ is the kinetic energy operator and the term $\hat{H}'$ describes a pairwise interaction between particles. In second quantized form, these operators are given by

$$\hat{H}_0=\sum_1 \varepsilon_{11'} a_1^\dagger a_{1'}, \qquad \hat{H}'=\frac{1}{2}\sum_{121'2'} \langle 1'2'|\, V\, |12\rangle\, a_{2'}^\dagger a_{1'}^\dagger a_1 a_2 \tag{2.1}$$

where the label k denotes a complete set of single-particle quantum numbers, $\varepsilon_{11'}$ is a hermitian single-particle energy matrix, a_k and $a_k^\dagger$ are

Fermi or Bose annihilation and creation operators. Generally speaking, the Hamiltonian can also contain additional terms describing interaction of the system with external fields. For simplicity, we will not consider this interaction explicitly and restrict ourselves to relaxation processes in the system just after the initial excitation by the external field. However, the theory can easily be generalized to the case where the field effects are taken into consideration (see Section 7 for a discussion).

In what follows the system is assumed to be spatially homogeneous, which is adequate for most experimental situations where memory effects are of crucial importance.[(2)] Some aspects of the following analysis may also be of interest for transport processes in nonhomogeneous systems, so that we shall return to this point in Section 6. In the spatially homogeneous case, it is convenient to take $(k)=(\mathbf{p}_k,\sigma_k)$, where $\mathbf{p}$ is the momentum and σ is the spin index. Then the kinetic energy operator in Eq. (2.1) becomes

$$\hat{H}_0=\sum_1 \varepsilon_1 a_1^\dagger a_1 \tag{2.2}$$

where $\varepsilon_1=\varepsilon_p$ are single-particle energies.

Within the kinetic description of the system, the main objective is to derive a kinetic equation for the one-particle distribution function

$$f_1(t)=\langle a_1^\dagger a_1\rangle^t\equiv\langle \hat{f}_1\rangle^t, \tag{2.3}$$

where the symbol $\langle\cdots\rangle^t$ stands for the average calculated with some nonequilibrium statistical operator $\varrho(t)$. Formally, the kinetic equation follows immediately from the von Neumann equation for the statistical operator

$$\frac{\partial\varrho(t)}{\partial t}+\frac{1}{i\hbar}[\varrho(t),\hat{H}]=0 \tag{2.4}$$

Taking the product of this equation with $\hat{f}_1$ and then calculating the trace, we get

$$\frac{\partial f_1(t)}{\partial t}=I_1(t) \tag{2.5}$$

where

$$I_1(t)=\frac{1}{i\hbar}\langle[\hat{f}_1,\hat{H}']\rangle^t=\frac{1}{i\hbar}\mathrm{Tr}\{[\hat{f}_1,\hat{H}']\,\varrho(t)\} \tag{2.6}$$

is the collision integral. In order that Eq. (2.5) be a closed kinetic equation, the collision integral must be expressed in terms of the one-particle distribution function—which is equivalent to requiring that the statistical operator $\varrho(t)$ is represented as a functional of the one-particle distribution function. A common technique for obtaining such a representation is based on the condition of complete weakening of initial correlations for the quantum BBGKY hierarchy in combination with some truncation procedure. A limitation of this standard scheme is the very strong assumption that the one-particle distribution function is the only nonequilibrium state variable describing the system. However, there exist long-lived correlations which cannot be expressed *exactly* in terms of the one-particle distribution function. For example, many-particle correlations arise due to formation of bound states. Another origin of long-lived correlations lies in local conservation laws. The conservation of energy is of special importance because the density of the interaction energy is determined by the two-particle distribution function. Thus, strictly speaking, kinetic processes must always be considered together with the evolution of locally conserved quantities, i.e., with hydrodynamic processes. A consistent description of kinetics and hydrodynamics can be developed by treating the one-particle distribution function (for quantum systems, the Wigner function) and the energy density as independent state parameters, which means that the statistical operator $\varrho(t)$ is represented as a functional of the corresponding dynamical variables (see, e.g., refs. 11–13 and references therein). Here we will follow this approach to study non-Markovian kinetic processes in a spatially homogeneous system. In this case the correlation effects arise due to the fact that the total energy is an integral of motion. Modifications of the theory needed for the spatially non-homogeneous case will be discussed in Section 6.

2.1. The Relevant Statistical Operator

We begin by considering the statistical thermodynamics description of nonequilibrium states with correlations caused by conservation laws. For a one-component spatially homogeneous system, the conserved quantities of interest are the total number of particles, N, the total momentum, $\mathbf{P}$, and the total energy, $\mathscr{E}$. They can be expressed as the mean values of the dynamical variables $\hat{N}=\sum_1 \hat{f}_1$, $\hat{\mathbf{P}}=\sum_1 \mathbf{p}_1 \hat{f}_1$, and $\hat{H}$, i.e.,

$$N=\langle \hat{N} \rangle^t = \sum_1 f_1(t), \qquad \mathbf{P}=\langle \hat{\mathbf{P}} \rangle^t = \sum_1 \mathbf{p}_1 f_1(t), \qquad \mathscr{E}=\langle \hat{H} \rangle^t \tag{2.7}$$

For simplicity, we shall assume the total momentum to be zero. Then the only integrals of motion that must be considered are the energy and the number of particles.

To see how the statistical thermodynamics description of nonequilibrium correlations can be developed, we recall the well-known grand canonical statistical operator

$$\varrho_{\text{eq}} = \exp\{-\beta(\hat{H}-\mu\hat{N})\}/\text{Tr}\exp\{-\beta(\hat{H}-\mu\hat{N})\} \tag{2.8}$$

where the equilibrium inverse temperature, $\beta = 1/T$, and the chemical potential, μ, are related to N and $\mathscr{E}$ by the equations of state

$$N = \text{Tr}\{\hat{N}\varrho_{\text{eq}}\}, \qquad \mathscr{E} = \text{Tr}\{\hat{H}\varrho_{\text{eq}}\} \tag{2.9}$$

The grand canonical operator (2.8) describes the equilibrium Gibbs ensemble and is a stationary solution of the von Neumann equation (2.4). Suppose now that we want to construct a statistical operator which describes a generalized Gibbs ensemble characterized by a *nonequilibrium* one-particle distribution function $f_1(t)$ and by given values of the conserved quantities. This is a special case of a more general situation where the state of the system is described by a set of parameters $P_m(t)$ which can be represented as the mean values, $P_m(t) = \text{Tr}\{\hat{P}_m \varrho(t)\}$, of some dynamical variables $\hat{P}_m$. As argued by Jaynes,(14) the corresponding *relevant statistical operator* can be derived by maximizing the entropy functional for given $P_m(t)$. The extremum condition for the entropy gives(12)

$$\varrho_{\text{rel}}(t) = \exp\left\{-\sum_m \lambda_m(t)\,\hat{P}_m\right\}\Big/\text{Tr}\exp\left\{-\sum_m \lambda_m(t)\,\hat{P}_m\right\} \tag{2.10}$$

The Lagrange multipliers $\lambda_m(t)$ are to be expressed in terms of the $P_n(t)$ from the self-consistency conditions

$$P_m(t) = \text{Tr}\{\hat{P}_m \varrho_{\text{rel}}(t)\} \tag{2.11}$$

which can also be interpreted as nonequilibrium equations of state. Following the above line of reasoning, it is easy to derive the relevant statistical operator which describes the generalized Gibbs ensemble with given values of the total energy, the total number of particles, and the one-particle distribution function. We write it in the form

$$\varrho_{\text{rel}}(t) = \frac{1}{Z_{\text{rel}}(t)} \exp\left\{-\beta^*(t)(\hat{H}-\mu^*(t)\,\hat{N}) - \sum_1 \lambda_1(t)\,\hat{f}_1\right\} \tag{2.12}$$

where the partition function is determined by the normalization condition,

$$Z_{\text{rel}}(t) = \text{Tr}\exp\left\{-\beta^*(t)(\hat{H}-\mu^*(t)\,\hat{N}) - \sum_1 \lambda_1(t)\,\hat{f}_1\right\} \tag{2.13}$$

and the Lagrange multipliers $\beta^*(t), \mu^*(t)$, and $\lambda_1(t)$ are to be calculated from the self-consistency conditions (nonequilibrium equations of state)

$$f_1(t) = \mathrm{Tr}\{\hat{f}_1 \varrho_{\mathrm{rel}}(t)\}, \qquad N = \mathrm{Tr}\{\hat{N} \varrho_{\mathrm{rel}}(t)\}, \qquad \mathscr{E} = \mathrm{Tr}\{\hat{H} \varrho_{\mathrm{rel}}(t)\} \tag{2.14}$$

Note that the grand canonical operator (2.8) is a special case of the relevant statistical operator (2.12), where the state parameters are integrals of motion.

2.2. Alternative Representations for the Relevant Statistical Operator

By analogy with Eq. (2.8), the quantities $T^*(t) = 1/\beta^*(t)$ and $\mu^*(t)$ may be called the *quasi-temperature* and the *quasi-chemical potential*, respectively. Here one comment is in order. The important difference between the state parameters N and $\mathscr{E}$ is that the former is a linear combination of the one-particle distribution functions, $f_1(t)$, whereas $\mathscr{E}$ involves the mean interaction energy

$$\mathscr{E}_{\mathrm{int}}(t) = \langle \hat{H}' \rangle^t \tag{2.15}$$

which, in general, cannot be expressed in terms of $f_1(t)$ only. Thus, in fact, the set of independent state parameters consists of $f_1(t)$ and $\mathscr{E}_{\mathrm{int}}(t)$. This also is seen from Eq. (2.12) where the terms coming from the kinetic energy operator and the particle number operator can be combined with the last term by introducing new Lagrange multipliers $\Lambda_1(t)$ through the relation

$$\Lambda_1(t) = \beta^*(t)[\varepsilon_1 - \mu^*(t)] + \lambda_1(t) \tag{2.16}$$

Then Eq. (2.12) reduces to

$$\varrho_{\mathrm{rel}}(t) = \frac{1}{Z_{\mathrm{rel}}(t)} \exp\left\{ -\beta^*(t)\, \hat{H}' - \sum_1 \Lambda_1(t)\, \hat{f}_1 \right\} \tag{2.17}$$

with the partition function given by

$$Z_{\mathrm{rel}}(t) = \mathrm{Tr}\exp\left\{ -\beta^*(t)\, \hat{H}' - \sum_1 \Lambda_1(t)\, \hat{f}_1 \right\} \tag{2.18}$$

The self-consistency conditions for the Lagrange multipliers $\beta^*(t)$ and $\Lambda_1(t)$ can now be taken in the form

$$f_1(t) = \mathrm{Tr}\{\hat{f}_1 \varrho_{\mathrm{rel}}(t)\}, \qquad \mathscr{E}_{\mathrm{int}}(t) = \mathrm{Tr}\{\hat{H}' \varrho_{\mathrm{rel}}(t)\} \tag{2.19}$$

since the mean kinetic energy is exactly expressed in terms of the one-particle distribution function. Summarizing, the quasi-chemical potential, $\mu^*(t)$, can, in principle, be excluded from the set of Lagrange parameters since the second of the conditions (2.14) follows from the first one. Nevertheless, the expression (2.12) has two advantages. First, it goes over explicitly to the equilibrium statistical operator, if $\beta^*(t)=1/T$, $\mu^*(t)=\mu$, and $\lambda_1(t)=0$. Second, some formulas to be derived in the following have a more clear physical interpretation when written in terms of the quasi-chemical potential. For these reasons, we will consider Eq. (2.12) as a representation for $\varrho_{\mathrm{rel}}(t)$ which is equivalent to Eq. (2.17) by virtue of Eq. (2.16). Note, however, that Eq. (2.16) determines only $\lambda_1(t)-\beta^*(t)\,\mu^*(t)$, but not the quasi-chemical potential itself. Since no physical quantity depends on the special choice of the quasi-chemical potential, the function $\mu^*(t)$ may be chosen arbitrarily provided that $\mu^*(t)=\mu$ in thermal equilibrium. For our purposes, it will be convenient to define the quasi-chemical potential through the condition

$$N=\mathrm{Tr}\{\hat{N}\varrho_{\mathrm{rel}}(t)\} \tag{2.20}$$

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

$$\varrho_{\mathrm{q}}(t)=\exp\{-\beta^*(t)(\hat{H}-\mu^*(t)\,\hat{N})\}/\mathrm{Tr}\exp\{-\beta^*(t)(\hat{H}-\mu^*(t)\,\hat{N})\} \tag{2.21}$$

which describes the state characterized by the quasi-temperature $T^*(t)=1/\beta^*(t)$ and the total number of particles N. Equation (2.20) ensures that, in the equilibrium limit, $\mu^*(t)$ goes to the chemical potential μ since $\beta^*(t)$ goes to the equilibrium inverse temperature.

For completeness, we give one more representation for the relevant statistical operator, which is obtained from Eq. (2.12) by the formal decomposition of the Hamiltonian

$$\hat{H}=\hat{\mathscr{H}}_0(t)+\hat{\mathscr{H}}'(t) \tag{2.22}$$

where

$$\hat{\mathscr{H}}_0(t)=\sum_1 E_1(t)\,a_1^\dagger a_1, \qquad \hat{\mathscr{H}}'(t)=\hat{H}'-\sum_1 \Sigma_1^{\mathrm{HF}}(t)\,a_1^\dagger a_1 \tag{2.23}$$

and the re-normalized single-particle energies,

$$E_1(t)=\varepsilon_1+\Sigma_1^{\mathrm{HF}}(t) \tag{2.24}$$

involve the exchange Hartree–Fock term

$$\Sigma_1^{\mathrm{HF}}(t)=\sum_2 \langle 12|\,V\,|12\rangle_{\mathrm{ex}}\,f_2(t) \tag{2.25}$$

Here and in what follows the subscript "ex" indicates the symmetrized (antisymmetrized) interaction amplitude

$$\begin{aligned}\langle 12|\, V\, |1'2'\rangle_{\text{ex}} &= \langle 12|\, V\, |1'2'\rangle \mp \langle 12|\, V\, |2'1'\rangle \\ &= \langle 12|\, V\, |1'2'\rangle \mp \langle 21|\, V\, |1'2'\rangle \end{aligned} \tag{2.26}$$

with the upper sign for fermions and the lower sign for bosons. Insertion of Eq. (2.22) into Eqs. (2.12) and (2.13) gives

$$\varrho_{\text{rel}}(t) = \frac{1}{Z_{\text{rel}}(t)} \exp\left\{ -\beta^*(t)\, \hat{\mathscr{H}}'(t) - \sum_1 \tilde{\Lambda}_1(t)\, \hat{f}_1 \right\} \tag{2.27}$$

$$Z_{\text{rel}}(t) = \text{Tr} \exp\left\{ -\beta^*(t)\, \hat{\mathscr{H}}'(t) - \sum_1 \tilde{\Lambda}_1(t)\, \hat{f}_1 \right\} \tag{2.28}$$

The new Lagrange multipliers, $\tilde{\Lambda}_1(t)$, are related to $\Lambda_1(t)$ and $\lambda_1(t)$ by

$$\tilde{\Lambda}_1(t) = \Lambda_1(t) + \beta^*(t)\, \Sigma_1^{\text{HF}}(t) = \beta^*(t)[E_1(t) - \mu^*(t)] + \lambda_1(t) \tag{2.29}$$

We emphasize once again that the representations for the relevant statistical operator given by Eqs. (2.12), (2.17), and (2.27), are equivalent to each other and differ only in the definition of the Lagrange multipliers conjugated to the one-particle distribution function.

C. Thermodynamic Relations

It is important to note that the relevant statistical operator allows to extend thermodynamic relations to nonequilibrium systems (see, e.g., ref. 12). The key quantities are the Massieu–Planck function

$$\Phi(t) = \ln Z_{\text{rel}}(t) = \ln \text{Tr} \exp\left\{ -\sum_m \lambda_m(t)\, \hat{P}_m \right\} \tag{2.30}$$

and the nonequilibrium entropy

$$S(t) = -\text{Tr}\{\varrho_{\text{rel}}(t) \ln \varrho_{\text{rel}}(t)\} = \Phi(t) + \sum_m \lambda_m(t)\, P_m(t) \tag{2.31}$$

which play the role of thermodynamic potentials in the variables $\{\lambda_m(t)\}$ and $\{P_m(t)\}$, respectively. In the case under consideration, using the above given representations for the partition function, we obtain formally different but equivalent thermodynamic relations. Taking, for instance, the partition function in the form (2.13), we see that the Massieu–Planck function can be interpreted as a nonequilibrium thermodynamic potential in the variables $\beta^*(t)$, $\mu^*(t)$, and $\lambda_1(t)$. Calculation of its variation gives

$$\delta\Phi(t) = -[\mathscr{E} - \mu^*(t)\, N]\, \delta\beta^*(t) + \beta^*(t)\, N\delta\mu^*(t) - \sum_1 f_1(t)\, \delta\lambda_1(t) \tag{2.32}$$

In the same representation, the entropy (2.31) can be written as

$$S(t) = \Phi(t) + \beta^*(t)[\mathscr{E} - \mu^*(t)\, N] + \sum_1 \lambda_1(t)\, f_1(t) \tag{2.33}$$

where the self-consistency conditions (2.14) have been used. Varying both sides of Eq. (2.33) and recalling Eq. (2.32), we find

$$\begin{aligned} \delta S(t) &= \beta^*(t)[\delta\mathscr{E} - \mu^*(t)\, \delta N] + \sum_1 \lambda_1(t)\, \delta f_1(t) \\ &= \beta^*(t)\, \delta\mathscr{E} + \sum_1 [\lambda_1(t) - \beta^*(t)\, \mu^*(t)]\, \delta f_1(t) \end{aligned} \tag{2.34}$$

In the last line we have taken into account that $\delta N = \sum_1 \delta f_1$. The entropy may thus be considered as a nonequilibrium thermodynamic potential in the variables $\mathscr{E}$ and $f_1(t)$ or, what is the same—in the variables $\mathscr{E}_{\text{int}}(t)$ and $f_1(t)$. From Eqs. (2.34) it follows that

$$\beta^*(t) = \left(\frac{\partial S(t)}{\partial \mathscr{E}}\right)_f = \left(\frac{\partial S(t)}{\partial \mathscr{E}_{\text{int}}(t)}\right)_f, \qquad \lambda_1(t) - \beta^*(t)\, \mu^*(t) = \left(\frac{\partial S(t)}{\partial f_1(t)}\right)_{\mathscr{E}} \tag{2.35}$$

The second equation confirms the fact that thermodynamics determines only the combination of the Lagrange multiplier $\lambda_1(t)$ and the quasi-chemical potential.

2.4. Evolution Equations for Thermodynamic Quantities

As already discussed, in the approach presented here the total energy is regarded as an independent state parameter in addition to the one-particle function. The evolution equation for the total energy is trivial: $d\mathscr{E}/dt = 0$. We shall see, however, that the correlation contribution to the kinetic equation is related to the time dependence of other thermodynamic quantities, such as the quasi-temperature and the interaction energy. We will now show that the evolution equations for the thermodynamic quantities of interest can be expressed in terms of the collision integral (2.6).

2.4.1. Energy Balance

We start with equation for the interaction energy, Eq. (2.15). Since the total energy is conserved and

$$\mathscr{E} = \langle \hat{H} \rangle^t = \sum_1 \varepsilon_1 f_1(t) + \mathscr{E}_{\mathrm{int}}(t) \tag{2.36}$$

we immediately obtain the balance equation

$$\frac{d\mathscr{E}_{\mathrm{int}}(t)}{dt} = -\sum_1 \varepsilon_1 I_1(t) \tag{2.37}$$

In dealing with nonequilibrium many-particle correlations, it is convenient to introduce the *correlation energy*, $\mathscr{E}_{\mathrm{corr}}(t)$, which is defined as

$$\mathscr{E}_{\mathrm{corr}}(t) = \mathscr{E}_{\mathrm{int}}(t) - \mathscr{E}_{\mathrm{HF}}(t) = \mathscr{E} - \sum_1 \varepsilon_1 f_1(t) - \mathscr{E}_{\mathrm{HF}}(t) \tag{2.38}$$

where

$$\mathscr{E}_{\mathrm{HF}}(t) = \tfrac{1}{2} \sum_{12} \langle 12|\, V \,|12\rangle_{\mathrm{ex}}\, f_1(t)\, f_2(t) = \tfrac{1}{2} \sum_1 \Sigma_1^{\mathrm{HF}}(t)\, f_1(t) \tag{2.39}$$

is the Hartree–Fock contribution to the total energy. From Eqs. (2.37) and (2.38) follows the balance equation

$$\frac{d\mathscr{E}_{\mathrm{corr}}(t)}{dt} = -\sum_1 E_1(t)\, I_1(t) \tag{2.40}$$

which differs from Eq. (2.37) in that now the single-particle energies are given by Eq. (2.24), i.e., they involve the exchange Hartree–Fock term.

2.4.2. Equation for the Quasi-Temperature

In principle, the evolution equation for $\beta^*(t)$ may be derived from the equation of state, $\beta^*(t) = \beta^*(\mathscr{E}, \{f(t)\})$, where the second argument indicates that β^* is a functional of $f_1(t)$. This way, however, is not appropriate because we have to calculate the functional derivative of $\beta^*(t)$ with respect to the one-particle distribution function. It is more convenient to make use of the self-consistency conditions (2.19) by differentiating them with respect to time. This gives

$$\mathrm{Tr}\left\{\frac{\partial \varrho_{\mathrm{rel}}(t)}{\partial t}\, \hat{f}_1\right\} = I_1(t), \qquad \mathrm{Tr}\left\{\frac{\partial \varrho_{\mathrm{rel}}(t)}{\partial t}\, \hat{H}'\right\} = \frac{d\mathscr{E}_{\mathrm{int}}(t)}{dt} \tag{2.41}$$

Since the relevant statistical operator, when taken in the form (2.17), depends on time through the Lagrange multipliers $\beta^*(t)$ and $\Lambda_1(t)$, we may write

$$\frac{\partial \varrho_{\text{rel}}(t)}{\partial t}=\frac{\delta \varrho_{\text{rel}}(t)}{\delta \beta^*(t)}\frac{d\beta^*(t)}{dt}+\sum_1 \frac{\delta \varrho_{\text{rel}}(t)}{\delta \Lambda_1(t)}\frac{\partial \Lambda_1(t)}{\partial t} \tag{2.42}$$

With the aid of Eqs. (2.17) and (2.18), the variations of $\varrho_{\text{rel}}(t)$ can easily be calculated and then Eqs. (2.41) are transformed to (for brevity, the argument t is omitted)

$$(\hat{f}_1, \hat{H}')\frac{d\beta^*}{dt}+\sum_{1'}(\hat{f}_1, \hat{f}_{1'})\frac{\partial \Lambda_{1'}}{\partial t}=-I_1 \tag{2.43}$$

$$(\hat{H}', \hat{H}')\frac{d\beta^*}{dt}+\sum_{1}(\hat{H}', \hat{f}_1)\frac{\partial \Lambda_1}{\partial t}=-\frac{d\mathscr{E}_{\text{int}}}{dt} \tag{2.44}$$

where we have introduced the correlation function of two dynamical variables:

$$(\hat{A}, \hat{B})=\int_0^1 dx \langle \Delta\hat{A}\varrho_{\text{rel}}^{x}\, \Delta\hat{B}\varrho_{\text{rel}}^{-x}\rangle_{\text{rel}} \tag{2.45}$$

with $\Delta\hat{A}=\hat{A}-\langle\hat{A}\rangle_{\text{rel}}$. Equation (2.43) can formally be solved for $\partial\Lambda_1/\partial T$ to give

$$\frac{\partial \Lambda_1}{\partial t}=-\sum_{1'}\chi^{-1}_{11'}\left\{(\hat{f}_{1'}, \hat{H}')\frac{d\beta^*}{dt}+I_{1'}\right\} \tag{2.46}$$

where χ^{-1} is inverse to the correlation matrix

$$\chi_{11'}=(\hat{f}_1, \hat{f}_{1'}) \tag{2.47}$$

Substituting the expression (2.46) into Eq. (2.44) and recalling the balance equation (2.37), we obtain

$$\frac{d\beta^*(t)}{dt}=\frac{1}{C}\sum_{11'}(\hat{H}, \hat{f}_1)\,\chi^{-1}_{11'}I_{1'} \tag{2.48}$$

with the following notation:

$$C=(\hat{H}', \hat{H}')-\sum_{11'}(\hat{H}', \hat{f}_1)\,\chi^{-1}_{11'}(\hat{f}_{1'}, \hat{H}') \tag{2.49}$$

It is easy to check that C in invariant under transformations $\hat{H}' \to \hat{H}' + \sum_1 \alpha_1 \hat{f}_1$ with arbitrary coefficients α_k. This property allows one, for instance, to replace $\hat{H}'$ in Eq. (2.49) by the operator $\hat{\mathscr{H}}'(t)$ [cf. Eqs. (2.23)].

2.4.3. The Entropy Production

We finally derive the entropy balance equation. Recalling Eq. (2.34), we write

$$\frac{dS(t)}{dt} = \beta^*(t)\,\frac{d\mathscr{E}(t)}{dt} + \sum_1 \left[\lambda_1(t) - \beta^*(t)\,\mu^*(t)\right] \frac{\partial f_1(t)}{\partial t}$$

The first term on the right-hand side is zero since the total energy is conserved. Taking also into account that $\partial f_1/\partial t = I_1$ and $\sum_1 I_1 = dN/dt = 0$, we arrive at the equation

$$\frac{dS(t)}{dt} = \sum_1 \lambda_1(t)\, I_1(t) \tag{2.50}$$

which determines the entropy production in the system. We have already noted that, in thermal equilibrium, the Lagrange multipliers $\lambda_1(t)$ are equal to zero. In addition, the collision integral is also zero in thermal equilibrium. Consequently, the entropy production given by Eq. (2.50) is at least of second order in the deviations from equilibrium, as it should be.

3. THE NONEQUILIBRIUM STATISTICAL OPERATOR

To proceed beyond the formal thermodynamic relations, we have to calculate the collision integral (2.6). In other words, we have to find a solution of the von Neumann equation (2.4) for the statistical operator $\varrho(t)$ in terms of the state parameters. Since Eq. (2.4) is a differential equation with respect to time, one has to give the statistical operator at some initial time t_0 or require the $\varrho(t)$ to satisfy some boundary condition for $t \to -\infty$. An appropriate choice of the initial or boundary condition depends on the physical situation under consideration. Formally, one may consider the initial statistical operator $\varrho(t_0)$ or the limiting statistical operator in a distant past to be arbitrary. We will, however, use the initial condition $\varrho(t_0) = \varrho_{\mathrm{rel}}(t_0)$ at some time t_0 and the boundary condition that the true statistical operator coincides with the relevant statistical operator in a distant past. The choice of these special conditions, however, is taken only for simplicity since it is of little consequence for the long-time behavior of the kinetic equation, which is of interest to us here.

Assuming that

$$\varrho(t_0) = \varrho_{\text{rel}}(t_0) \tag{3.1}$$

and using the decomposition (2.22) of the Hamiltonian, it can easily be verified that the von Neumann equation (2.4) is equivalent to the integral equation

$$\begin{aligned}\varrho(t) = \varrho_{\text{rel}}(t) - \int_{t_0}^{t} dt'\, U_0(t,t') \left\{ \frac{\partial \varrho_{\text{rel}}(t')}{\partial t'} + \frac{1}{i\hbar} [\varrho_{\text{rel}}(t'), \hat{\mathscr{H}}_0(t')] \right\} U_0^{\dagger}(t,t') \\ - \int_{t_0}^{t} dt'\, U_0(t,t') \frac{1}{i\hbar} [\varrho(t'), \hat{\mathscr{H}}'(t')]\, U_0^{\dagger}(t,t')\end{aligned} \tag{3.2}$$

where

$$U_0(t,t') = \exp_{+} \left\{ -\frac{i}{\hbar} \int_{t'}^{t} \hat{\mathscr{H}}_0(t'')\, dt'' \right\} \tag{3.3}$$

is the unperturbed evolution operator; the symbol $\exp_{+}\{\cdots\}$ stands for the time-ordered exponent. Equation (3.2) is still exact. If $\hat{\mathscr{H}}'(t)$ is treated as a small perturbation, an approximate solution of Eq. (3.2) can be found by an iterative procedure. We shall restrict our discussion to the second-order non-Markovian Born approximation in the collision integral, which leads, in the standard approach,$^{(2)}$ to the Levinson kinetic equation.

To calculate the second-order collision integral (2.6), we need the statistical operator $\varrho(t)$, correct to first order in the perturbation $\hat{\mathscr{H}}'$. We shall show later than the time derivative $\partial\varrho_{\text{rel}}(t')/\partial t'$ in Eq. (3.2) is at least of second order in $\hat{\mathscr{H}}'$ and, consequently, can be omitted. We next note that the interaction term enters explicitly into the relevant statistical operator [see, e.g., (2.27)]. Therefore the leading interaction contribution to the commutator $[\varrho_{\text{rel}}(t'), \hat{\mathscr{H}}_0(t')]$ is at least linear in $\hat{\mathscr{H}}'$; this term must be retained. Finally, since the last term in Eq. (3.2) is already of first order in the interaction, we may replace $\varrho(t')$ in this term by $\varrho_{\text{rel}}(t')$. Thus, the nonequilibrium statistical operator, correct to first order in $\hat{\mathscr{H}}'$, is given by

$$\begin{aligned}\varrho(t) = \varrho_{\text{rel}}(t) - \int_{t_0}^{t} dt'\, U_0(t,t') \frac{1}{i\hbar} [\varrho_{\text{rel}}(t'), \hat{\mathscr{H}}_0(t')]\, U_0^{\dagger}(t,t') \\ - \int_{t_0}^{t} dt'\, U_0(t,t') \frac{1}{i\hbar} [\varrho_{\text{rel}}(t'), \hat{\mathscr{H}}'(t')]\, U_0^{\dagger}(t,t')\end{aligned} \tag{3.4}$$

Another solution of the von Neumann equation can be obtained by imposing the boundary condition that the true nonequilibrium statistical operator coincides with the relevant statistical operator in a distant past. This solution follows easily by adding to Eq. (2.4) an infinitesimally small source:(12)

$$\frac{\partial \varrho(t)}{\partial t}+\frac{1}{i\hbar}\left[\varrho(t), \hat{\mathscr{H}}_0(t)+\hat{\mathscr{H}}'(t)\right]=-\varepsilon\{\varrho(t)-\varrho_{\mathrm{rel}}(t)\} \tag{3.5}$$

where $\varepsilon \to +0$ after the calculation of averages with $\varrho(t)$. It is important to note that the inclusion of the source term into the von Neumann equation does not violate the energy conservation. This can be seen by taking the product of Eq. (3.5) with $\hat{H}$ and calculating the trace. Then we obtain

$$\frac{d\mathscr{E}(t)}{dt}=-\varepsilon\{\mathscr{E}(t)-\mathrm{Tr}(\hat{H}\varrho_{\mathrm{rel}}(t))\} \tag{3.6}$$

The right-hand side of this equation is zero due to the self-consistency condition for the total energy in the relevant ensemble.

Analogously to the derivation of Eq. (3.4), we use Eq. (3.5) to derive the first-order statistical operator in the form

$$\begin{aligned}\varrho(t)=\varrho_{\mathrm{rel}}(t)&-\int_{-\infty}^{t} dt'\, \mathrm{e}^{-\varepsilon(t-t')} U_0(t,t')\frac{1}{i\hbar}\left[\varrho_{\mathrm{rel}}(t'), \hat{\mathscr{H}}_0(t')\right] U_0^{\dagger}(t,t')\\ &-\int_{-\infty}^{t} dt'\, \mathrm{e}^{-\varepsilon(t-t')} U_0(t,t')\frac{1}{i\hbar}\left[\varrho_{\mathrm{rel}}(t'), \hat{\mathscr{H}}'(t')\right] U_0^{\dagger}(t,t')\end{aligned} \tag{3.7}$$

This expression can also be interpreted as a rule for passing to the limit $t_0 \to -\infty$ in Eq. (3.4) since the factor $\exp\{-\varepsilon(t-t')\}$ provides the regularization of the integral.

4. THE NON-MARKOVIAN COLLISION INTEGRAL

We now turn to the calculation of the collision integral (2.6) using the explicit expression (3.4) for the statistical operator. First we will show that the term $\varrho_{\mathrm{rel}}(t)$ in Eq. (3.4) does not contribute to the collision integral. Note that the obvious identity $\langle[\hat{f}_1, \ln \varrho_{\mathrm{rel}}(t)]\rangle_{\mathrm{rel}}^{t}=0$ and Eq. (2.17) give

$$\beta^*(t)\langle[\hat{f}_1, \hat{H}']\rangle_{\mathrm{rel}}^{t}+\sum_{1'} \Lambda_{1'}(t)\langle[\hat{f}_1, \hat{f}_{1'}]\rangle_{\mathrm{rel}}^{t}=0$$

Since $[\hat{f}_1, \hat{f}_{1'}]=0$, we find that $\langle[\hat{f}_1, \hat{H}']\rangle_{\mathrm{rel}}^{t}=0$. Thus the collision integral (2.6) is at least of second order in the interaction. This allows us to show that the time derivative $\partial\varrho(t')/\partial t'$ in Eq. (3.2) is also of second order in $\mathscr{H}'$ and, consequently, it does not contribute to the first-order expressions (3.4) and (3.7). We use the fact that the relevant statistical operator depends on time through the state parameters or through the conjugated Lagrange multipliers. For instance, we may assume that $\varrho_{\rm rel}(t') = \varrho_{\rm rel}(\mathscr{E}, \{f(t')\})$. Then, since the total energy is conserved,

$$\frac{\partial\varrho_{\rm rel}(t')}{\partial t'} = \sum_{1} \frac{\delta\varrho_{\rm rel}(t')}{\partial f_1(t')} \frac{\partial f_1(t')}{\partial t'} = \sum_{1} \frac{\delta\varrho_{\rm rel}(t')}{\delta f_1(t')} I_1(t')$$

whence it follows that $\partial\varrho_{\rm rel}(t')/\partial t'$ is at least of second order in the perturbation, as was to be proved.

The last two terms in the expression (3.4), when substituted into Eq. (2.6), lead to the decomposition of the collision integral

$$I_1(t) = I_1^L(t) + I_1^C(t) \tag{4.1}$$

where

$$I_1^L(t) = -\frac{1}{\hbar^2} \int_{t_0}^{t} dt' \, \mathrm{Tr}\{[U_0^\dagger(t,t')[\hat{f}_1, \hat{H}'] \, U_0(t,t'), \hat{\mathscr{H}}'(t')] \, \varrho_{\rm rel}(t')\} \tag{4.2}$$

$$I_1^C(t) = \frac{1}{\hbar^2} \int_{t_0}^{t} dt' \, \mathrm{Tr}\{[U_0^\dagger(t,t')[\hat{f}_1, \hat{H}'] \, U_0(t,t')[\varrho_{\rm rel}(t'), \hat{\mathscr{H}}_0(t')]\} \tag{4.3}$$

We shall see later that the term $I_1^L(t)$ is nothing but the Levinson collision integral. The new term, $I_1^C(t)$, is due to many-particle correlations in the ensemble described by the relevant statistical operator. If the one-particle distribution function $f_1(t)$ is taken as the only state parameter, the relevant statistical operator (2.17) does not involve the term with $\hat{H}'$; hence, $\varrho_{\rm rel}(t')$ commutes with $\hat{\mathscr{H}}_0(t')$ and $I_1^C(t) = 0$.

4.1. The Collision Contribution

We now calculate the term $I_1^L(t)$, Eq. (4.2), in the non-Markovian Born approximation. Since this term is explicitly of second order in the interaction, the relevant statistical operator, Eq. (2.27), can be approximated by

$$\varrho^0_{\rm rel}(t) = \exp\left\{-\sum_1 \tilde{\Lambda}_1(t)\, a_1^\dagger a_1\right\} \Big/ \mathrm{Tr} \exp\left\{-\sum_1 \tilde{\Lambda}_1(t)\, a_1^\dagger a_1\right\} \tag{4.4}$$

Formally, this statistical operator describes a nonequilibrium ideal quantum gas, so that the self-consistency condition for the Lagrange multipliers $\widetilde{\Lambda}_1(t)$ reads

$$f_1(t) = \mathrm{Tr}\{a_1^\dagger a_1 \varrho_{\mathrm{rel}}^0(t)\} = \frac{1}{\exp\{\widetilde{\Lambda}_1(t)\} \pm 1} \tag{4.5}$$

whence it follows that

$$\widetilde{\Lambda}_1(t) = \ln\left(\frac{1 \mp f_1(t)}{f_1(t)}\right) \tag{4.6}$$

The time dependence of the operators in Eq. (4.2) can be worked out by using the following properties of the evolution operator (3.3):

$$U_0^\dagger(t,t')\, a_1\, U_0(t,t') = \mathrm{e}^{-i\omega_1(t,t')} a_1, \qquad U_0^\dagger(t,t')\, a_1^\dagger\, U_0(t,t') = \mathrm{e}^{i\omega_1(t,t')} a_1^\dagger \tag{4.7}$$

where

$$\omega_1(t,t') = \frac{1}{\hbar}\int_{t'}^{t} dt''\, E_1(t'') = \frac{\varepsilon_1}{\hbar}(t-t') + \frac{1}{\hbar}\int_{t'}^{t} dt''\, \Sigma_1^{\mathrm{HF}}(t'') \tag{4.8}$$

Taking into account that the statistical operator (4.4) admits Wick's decomposition of the averages, a simple algebra gives

$$\begin{aligned} I_1^L(t) = {} & -\frac{1}{\hbar^2} \sum_{21'2'} |\langle 12|\, V\, |1'2'\rangle_{\mathrm{ex}}|^2 \\ & \times \int_{t_0}^{t} dt' \cos[\Delta\omega_{12,1'2'}(t,t')]\, \mathscr{F}_{12,1'2'}(\{f(t')\}) \end{aligned} \tag{4.9}$$

where

$$\Delta\omega_{12,1'2'}(t,t') = \omega_1(t,t') + \omega_2(t,t') - \omega_{1'}(t,t') - \omega_{2'}(t,t') \tag{4.10}$$

and the functional $\mathscr{F}_{12,1'2'}(\{\varphi\})$ is defined for any set of single-particle functions φ_1 as

$$\mathscr{F}_{12,1'2'}(\{\varphi\}) = \varphi_1\varphi_2\bar{\varphi}_{1'}\bar{\varphi}_{2'} - \bar{\varphi}_1\bar{\varphi}_2\varphi_{1'}\varphi_{2'}, \qquad \bar{\varphi}_1 = 1 \pm \varphi_1 \tag{4.11}$$

In the context of Eq. (4.9), the functional $\mathscr{F}_{12,1'2'}(\{f(t')\})$ is nothing but the gain-loss term which appears in quantum collision integrals. Expression (4.9) only differs from the original Levinson collision integral$^{(3)}$ in that the quantities $\omega_k(t,t')$ in Eq. (4.10) involve the exchange Hartree–Fock term.

4.2. The Correlation Contribution

To calculate the second-order correlation contribution to the collision integral, Eq. (4.3), we expand the relevant statistical operator (2.27) in $\hat{\mathscr{H}}'$, keeping only the first-order terms. This gives

$$\varrho_{\mathrm{rel}}(t)=\left\{1-\beta^*(t)\int_0^1 dx[\varrho^0_{\mathrm{rel}}(t)]^x\,(\hat{\mathscr{H}}'(t)-\langle\hat{\mathscr{H}}'\rangle^t_0)[\varrho^0_{\mathrm{rel}}(t)]^{-x}\right\}\varrho^0_{\mathrm{rel}}(t) \tag{4.12}$$

Here the symbol $\langle\hat{\mathscr{H}}'\rangle^t_0$ stands for the average with the statistical operator (4.4). Having the above expression, we calculate the commutator appearing in Eq. (4.3) (for brevity the time argument t' is omitted):

$$\begin{aligned}[\varrho_{\mathrm{rel}},\hat{\mathscr{H}}_0]=-\frac{1}{2}\beta^*\sum_{121'2'}\langle 1'2'|\,V\,|12\rangle\,\frac{\Delta E_{12,\,1'2'}}{\Delta\tilde{\Lambda}_{12,\,1'2'}}&\\ \times\{\mathrm{e}^{\Delta\tilde{\Lambda}_{12,\,1'2'}}-1\}\;a^\dagger_{2'}a^\dagger_{1'}a_1a_2\varrho^0_{\mathrm{rel}}&\end{aligned} \tag{4.13}$$

where

$$\Delta E_{12,\,1'2'}(t)=E_1(t)+E_1(t)-E_{1'}(t)-E_{2'}(t) \tag{4.14}$$

$$\Delta\tilde{\Lambda}_{12,\,1'2'}(t)=\tilde{\Lambda}_1(t)+\tilde{\Lambda}_2(t)-\tilde{\Lambda}_{1'}(t)-\tilde{\Lambda}_{2'}(t) \tag{4.15}$$

We next substitute Eq. (4.13) into Eq. (4.3) and use Wick's theorem to calculate the average. In the final result it is convenient to eliminate $\Delta\tilde{\Lambda}_{12,\,1'2'}$. To this end, we introduce a functional

$$\mathscr{K}_{12,\,1'2'}(\{\varphi\})=\frac{\varphi_1\varphi_2\bar{\varphi}_{1'}\bar{\varphi}_{2'}}{\bar{\varphi}_1\bar{\varphi}_2\varphi_{1'}\varphi_{2'}} \tag{4.16}$$

Then, recalling Eq. (4.6), it can easily be verified that

$$\Delta\tilde{\Lambda}_{12,\,1'2'}(t)=-\ln\mathscr{K}_{12,\,1'2'}(\{f(t)\}) \tag{4.17}$$

Omitting a simple algebra, we present the final expression for the correlation term in the collision integral:

$$\begin{aligned}I^C_1(t)=-\frac{1}{\hbar^2}\sum_{21'2'}|\langle 12|\,V\,|1'2'\rangle_{\mathrm{ex}}|^2\int_{t_0}^t dt'\cos[\Delta\omega_{12,\,1'2'}(t,t')]&\\ \times\frac{\beta^*(t')\,\Delta E_{12,\,1'2'}(t')}{\ln\mathscr{K}_{12,\,1'2'}(\{f(t')\})}\,\mathscr{F}_{12,\,1'2'}(\{f(t')\})&\end{aligned} \tag{4.18}$$

It is similar to the collision term (4.9) but contains the additional factor in the integrand.

C. The Full Collision Integral and Its Properties

Due to the similarity in structure, the two contributions, Eqs. (4.9) and (4.18), are conveniently combined into a single expression

$$I_1(t) = -\frac{1}{\hbar^2} \sum_{21'2'} |\langle 12| V |1'2'\rangle_{\text{ex}}|^2 \int_{t_0}^{t} dt' \cos[\varDelta\omega_{12,1'2'}(t,t')] \times \left\{ 1 + \frac{\beta^*(t')\, \varDelta E_{12,1'2'}(t')}{\ln \mathscr{K}_{12,1'2'}(\{f(t')\})} \right\} \mathscr{F}_{12,1'2'}(\{f(t')\}) \tag{4.19}$$

which can be written in a more elegant form by using the relation

$$\beta^*(t)\, \varDelta E_{12,1'2'}(t) = -\ln \mathscr{K}_{12,1'2'}(\{F(t)\}) \tag{4.20}$$

where

$$F_1(t) = \frac{1}{\exp\{\beta^*(t)[E_1(t) - \mu^*(t)]\} \pm 1} \tag{4.21}$$

is the one-particle distribution function in the quasi-equilibrium ensemble [cf. Eq. (2.21)]. With Eq. (4.20), the expression (4.19) becomes

$$I_1(t) = -\frac{1}{\hbar^2} \sum_{21'2'} |\langle 12| V |1'2'\rangle_{\text{ex}}|^2 \int_{t_0}^{t} dt' \cos[\varDelta\omega_{12,1'2'}(t,t')] \times \left\{ 1 - \frac{\ln \mathscr{K}_{12,1'2'}(\{F(t')\})}{\ln \mathscr{K}_{12,1'2'}(\{f(t')\})} \right\} \mathscr{F}_{12,1'2'}(\{f(t')\}) \tag{4.22}$$

This collision integral has some remarkable properties. First, it vanishes in the quasi-equilibrium state where $f_1(t) = F_1(t)$. In this case the collision contribution and the correlation contribution cancel each other. In particular, $I_1 = 0$ in complete equilibrium since $F_1(t)$ goes over to the equilibrium distribution function as $\beta^*(t) \to 1/T$ and $\mu^*(t) \to \mu$, where T and μ are the equilibrium temperature and the equilibrium chemical potential, respectively. It should be emphasized that the collision term (4.9) alone does not vanish in thermal equilibrium, which is the grave disadvantage of the Levinson-type kinetic equations. Another important property of the collision integral is its asymptotic behavior as $t - t_0 \to \infty$. This stage of the evolution can be described on a large time scale, so that we may pass to the Markovian limit. To analyze this case, it is convenient to return to the expression (4.19). Putting there $f(t') \approx f(t)$, $F(t') \approx F(t)$, and then performing the limit $t_0 \to \infty$ with the regularization factor $\exp\{-\varepsilon(t-t')\}$, we find that the correlation contribution vanishes due to the fact that now the cosine term is replaced by the delta function $\delta(\Delta E_{12,1'2'}(t)/\hbar)$. As a result, we get the well-known Uehling–Uhlenbeck collision integral

$$I_1(t) = -\frac{\pi}{\hbar^2} \sum_{21'2} |\langle 12| V |1'2'\rangle_{\text{ex}}|^2 \, \delta\left(\frac{\Delta E_{12,1'2'}(t)}{\hbar}\right)(f_1 f_2 \bar{f}_{1'} \bar{f}_{2'} - \bar{f}_1 \bar{f}_2 f_{1'} f_{2'})_t \tag{4.23}$$

where we have used the definition of $\mathscr{F}_{12,1'2'}$, Eq. (4.11). We would like to draw attention to the role of the correlation term in the collision integral. Although this term goes to zero in the long-time limit, the non-Markovian expression (4.19) is constructed such that the interplay between collisions and correlations is precisely the reason why the Markovian regime arises. It should be noted, however, that beyond Born approximation, for instance, in the T-approximation for the collision integral, the correlation term does not go to zero in the Markovian limit.(11)

4.4. A Simplified Version of the Non-Markovian Collision Integral

Because of the presence of the $\mathscr{K}$-functional, the full collision integral (4.19) has a more complicated structure than the Levinson term (4.9). Having in mind practical applications of the scheme developed here, it makes sense to formulate a simplified version of the non-Markovian collision integral which, nevertheless, retains the main properties of the full expression (4.19). Let us approximate the correlation term (4.18) by its value in the quasi-equilibrium state described by the statistical operator (2.21). In the case of weak interaction, this approximation means that we put $f(t') \approx F(t')$. Then, recalling Eq. (4.20), we obtain

$$I_1^C(t) = \frac{1}{\hbar^2} \sum_{21'2'} |\langle 12| V |1'2'\rangle_{\text{ex}}|^2 \int_{t_0}^{t} dt' \cos[\Delta\omega_{12,1'2'}(t,t')] \, \mathscr{F}_{12,1'2'}(\{F(t')\}) \tag{2.24}$$

Now the expression (4.19) takes a simpler form

$$\begin{aligned} I_1(t) = -\frac{1}{\hbar^2} \sum_{21'2'} |\langle 12| V |1'2'\rangle_{\text{ex}}|^2 \int_{t_0}^{t} dt' \cos[\Delta\omega_{12,1'2'}(t,t')] \\ \times [\mathscr{F}_{12,1'2'}(\{f(t')\}) - \mathscr{F}_{12,1'2'}(\{F(t')\})] \end{aligned} \tag{4.25}$$

Obviously this collision integral vanishes in the quasi-equilibrium state and, consequently, in complete equilibrium. Another important point is that, in the Markovian limit, Eq. (4.25) reduces to the Uehling–Uhlenbeck collision integral (4.23) since, in this limit, the contribution from $\mathscr{F}_{12,\,1'2'}(\{F(t')\})$ vanishes, as can easily be verified with the aid of Eqs. (4.11) and (4.21). Recently, an "improved" version of the Levinson collision integral was proposed in the Green's function method on the basis of approximate solution of a Dyson equation with initial correlations.$^{(7)}$ It differs from Eq. (4.25) in that the single-particle energies did not involve the Hartree–Fock corrections and the correlation term was approximated by $\mathscr{F}_{12,\,1'2'}(\{f^{(\mathrm{eq})}\})$, where $f_1^{(\mathrm{eq})}$ is the distribution function in complete equilibrium. Physically, the drug of choice for a simplified non-Markovian collision integral is the expression (4.25) which involves effects of *running* correlations, whereas replacing the quasi-equilibrium distribution function $F_1(t')$ by $f_1^{(\mathrm{eq})}$ implies that the state of the system is close to complete equilibrium.

5. BALANCE EQUATIONS IN THE NON-MARKOVIAN REGIME

Having the explicit expression (4.19). for the collision integral, it is of interest to analyze in more detail the balance equations derived in Section 2.

5.1. Energy Balance. The Nonequilibrium Correlation Energy

We have already shown that the non-Markovian kinetic equation with the collision integral (4.19) has the correct equilibrium solution. Now we want to demonstrate that the right-hand side of Eq. (2.40) can be represented as a time derivative, i.e., the non-Markovian kinetic equation is consistent with the energy conservation.

First we will prove that any collision integral of the form

$$I_1(t) = -\sum_{21'2'} \int_{t_0}^{t} dt' \cos[\Delta\omega_{12,\,1'2'}(t,t')]\, G_{12,\,1'2'}(t') \tag{5.1}$$

conserves the total energy, if the function $G_{12,\,1'2'}(t)$ has the symmetry properties

$$G_{12,\,1'2'}(t) = G_{21,\,1'2'}(t) = G_{12,\,2'1'}(t), \qquad G_{12,\,1'2'}(t) = -G_{1'2',\,12}(t) \tag{5.2}$$

and the function $\Delta\omega_{12,\,1'2'}(t,t')$ satisfies the conditions

$$\hbar\frac{\partial}{\partial t}\omega_{12,\,1'2'}(t,t') = \Delta E_{12,\,1'2'}(t), \qquad \Delta\omega_{12,\,1'2'}(t,t) = 0 \tag{5.3}$$

where $\Delta E_{12,\,1'2'}(t)$ is given by Eq. (4.14). The proof is as follows. Multiplying Eq. (5.1) by $E_1(t)$ and then summing over the quantum numbers 1, we obtain

$$\begin{aligned}\sum_{1} E_1(t)\, I_1(t) &= -\frac{1}{4} \sum_{121'2'} \Delta E_{12,\,1'2'}(t) \int_{t_0}^{t} dt' \cos[\Delta\omega_{12,\,1'2'}(t,t')]\, G_{12,\,1'2'}(t') \\ &= \frac{d}{dt}\left(-\frac{\hbar}{4} \sum_{121'2'} \int_{t_0}^{t} dt' \sin[\Delta\omega_{12,\,1'2'}(t,t')]\, G_{12,\,1'2'}(t') \right) \qquad (5.4)\end{aligned}$$

where use has been made of Eqs. (5.2) and (5.3). Comparison of Eqs. (2.40) and (5.4) shows that the non-Markovian collision integral (5.1) indeed conserves the total energy. As a byproduct of the proof, we have the following expression for the nonequilibrium correlation energy:

$$\mathscr{E}_{\text{corr}}(t) = \mathscr{E}_{\text{corr}}(t_0) + \frac{\hbar}{4} \sum_{121'2'} \int_{t_0}^{t} dt' \sin[\Delta\omega_{12,\,1'2'}(t,t')]\, G_{12,\,1'2'}(t') \qquad (5.5)$$

where $\mathscr{E}_{\text{corr}}(t_0)$ is an initial value of the correlation energy at $t = t_0$.

Turning now to the collision integral (4.19) and recalling the definition of the functionals $\mathscr{F}$ and $\mathscr{K}$, it is easy to check that the symmetry conditions (5.2) are satisfied. Thus, the collision integral (4.19) conserves the total energy. In our case Eq. (5.5) reads

$$\mathscr{E}_{\text{corr}}(t) = \mathscr{E}_{\text{corr}}(t_0) + \Delta\mathscr{E}'_{\text{corr}}(t) + \Delta\mathscr{E}''_{\text{corr}}(t) \qquad (5.6)$$

where

$$\begin{aligned}\Delta\mathscr{E}'_{\text{corr}}(t) = \frac{1}{4\hbar} &\sum_{121'2'} |\langle 12|\, V\, |1'2'\rangle_{\text{ex}}|^2 \\ &\times \int_{t_0}^{t} dt' \sin[\Delta\omega_{12,\,1'2'}(t,t')]\, \mathscr{F}_{12,\,1'2'}(\{f(t')\}) \qquad (5.7)\end{aligned}$$

$$\begin{aligned}\Delta\mathscr{E}''_{\text{corr}}(t) = \frac{1}{4\hbar} &\sum_{121'2'} |\langle 12|\, V\, |1'2'\rangle_{\text{ex}}|^2 \int_{t_0}^{t} dt' \sin[\Delta\omega_{12,\,1'2'}(t,t')] \\ &\times \frac{\beta^*(t')\, \Delta E_{12,\,1'2'}(t')}{\ln \mathscr{K}_{12,\,1'2'}(\{f(t')\})}\, \mathscr{F}_{12,\,1'2'}(\{f(t')\}) \qquad (5.8)\end{aligned}$$

We have separated the time-dependent contribution to the correlation energy into two parts which have different physical interpretation. The term (5.7) can be regarded as the collision contribution to the correlation energy. An analogous term was derived previously from the Levinson kinetic equation$^{(15, 16)}$ and by the Green's function method.$^{(7)}$ The term (5.8) arises due to collective (correlation) effects. In thermal equilibrium these two terms cancel each other so that the correlation energy does not depend on time.

It is interesting to note that the simplified non-Markovian collision integral (4.25) has the form (5.1), where $G_{12,\,1'2'}$ is the difference of two $\mathscr{F}$-functionals, each of which satisfies the symmetry conditions (5.2). We may thus conclude that the collision integral (4.25) conserves the total energy. The approximate correlation energy is given by

$$\Delta\mathscr{E}_{\text{corr}}(t)=\frac{1}{4\hbar}\sum_{121'2'}|\langle 12|\,V\,|1'2'\rangle_{\text{ex}}|^2\int_{t_0}^{t}dt'\,\sin[\Delta\omega_{12,\,1'2'}(t,t')] \\ \times\{\mathscr{F}_{12,\,1'2'}(\{f(t')\})-\mathscr{F}_{12,\,1'2'}(\{F(t')\})\} \tag{5.9}$$

Exactly the same expression follows from Eq. (5.6) if the term (5.8) is replaced by its value in the quasi-equilibrium state.

5.2. Non-Markovian Equation for the Quasi-Temperature

In general, the quasi-temperature evolves in time according to Eq. (2.48). Within the framework of non-Markovian Born approximation, the correlation function $(\hat{H}, \hat{f}_1)$ in this equation can be replaced by $(\hat{\mathscr{H}}_0(t), \hat{f}_1)$ since the collision integral is already of second order in the interaction. Then a little algebra shows that Eq. (2.48) reduces to

$$\frac{d\beta^*(t)}{dt}=\frac{1}{C(t)}\sum_{1}E_1(t)\,I_1(t) \tag{5.10}$$

With Eq. (4.19), this is written in the expanded form as

$$\frac{d\beta^*(t)}{dt}=-\frac{1}{4\hbar^2C(t)}\sum_{121'2'}\Delta E_{12,\,1'2'}(t)\,|\langle 12|\,V\,|1'2'\rangle_{\text{ex}}|^2 \\ \times\int_{t_0}^{t}dt'\,\cos[\Delta\omega_{12,\,1'2'}(t,t')] \\ \times\left\{1+\frac{\beta^*(t')\,\Delta E_{12,\,1'2'}(t')}{\ln\mathscr{K}_{12,\,1'2'}(\{f(t')\})}\right\}\mathscr{F}_{12,\,1'2'}(\{f(t')\}) \tag{5.11}$$

The correlation function $C(t)$ is given by Eq. (2.49) and can be calculated, in the leading approximation, by using the statistical operator (4.4) which admits Wick's decomposition of averages. The Lagrange multipliers $\tilde{\Lambda}_1(t)$

can then be expressed in terms of the one-particle distribution function by means of Eq. (4.6). After some algebra, one obtains

$$C(t)=\frac{1}{4}\sum_{121'2'}|\langle 12|\,V\,|1'2'\rangle_{\mathrm{ex}}|^2\,\bar{f}_1(t)\,\bar{f}_2(t)\,f_{1'}(t)\,f_{2'}(t)\,\frac{\mathscr{K}_{12,\,1'2'}(\{f(t)\})-1}{\ln\mathscr{K}_{12,\,1'2'}(\{f(t)\})} \tag{5.12}$$

whence it follows that $C(t)>0$. Now the kinetic equation (2.5), together with the expression (4.19) for the collision integral and the evolution equation (5.11) for the quasi-temperature, form a closed set of equations describing non-Markovian relaxation processes in the system.

5.2. Entropy Production in the Non-Markovian Regime

Of special physical interest is the entropy equation (2.50). To second order in the interaction, the Lagrange multipliers $\lambda_1(t)$ can be expressed in terms of the one-particle distribution functions, $f_1(t)$ and $F_1(t)$, with the aid of Eqs. (2.29), (4.6), and (4.21). Eliminating $\tilde{\Lambda}_1$ and $\beta^*(E_1-\mu^*)$, we obtain

$$\lambda_1(t)=\ln\left[\frac{\bar{f}_1(t)\,F_1(t)}{f_1(t)\,\bar{F}_1(t)}\right] \tag{5.13}$$

Substituting this expression, together with Eq. (4.22), into Eq. (2.50) and then making use of the symmetry of the collision integral under permutations of the single-particle quantum numbers, the entropy production takes the form

$$\begin{aligned}\frac{dS(t)}{dt}=\frac{1}{4\hbar^2}\sum_{121'2'}&|\langle 12|\,V\,|1'2'\rangle_{\mathrm{ex}}|^2\ln\left[\frac{\mathscr{K}_{12,\,1'2'}(\{f(t)\})}{\mathscr{K}_{12,\,1'2'}(\{F(t)\})}\right]\\&\times\int_{t_0}^{t}dt'\,\cos[\Delta\omega_{12,\,1'2'}(t,t')]\\&\times\left\{1-\frac{\ln\mathscr{K}_{12,\,1'2'}(\{F(t')\})}{\ln\mathscr{K}_{12,\,1'2'}(\{f(t')\})}\right\}\mathscr{F}_{12,\,1'2'}(\{f'(t)\})\end{aligned} \tag{5.14}$$

Although the right-hand side of his equation involves memory effects, the entropy production is identically zero in thermal equilibrium, as it must be. To understand the behavior of the entropy production in the Markovian limit, we put $f(t')\approx f(t)$, $F(t')\approx F(t)$, and then pass to the limit $t_0\to-\infty$ inserting the factor $\exp\{-\varepsilon(t-t')\}$. As we have already noted, such a procedure leads to the appearance of the delta function $\delta(\Delta E_{12,\,1'2'}(t)/\hbar)$ in place of the oscillating cosine term. Due to Eq. (4.20), we may then put

$\mathscr{K}_{12,\,1'2'}(\{F(t)\})=1$. Finally, it is convenient to eliminate the $\mathscr{F}$-functional be means of the relation

$$\mathscr{F}_{12,\,1'2'}(\{f\})=\bar{f}_1\bar{f}_2 f_{1'} f_{2'}(\mathscr{K}_{12,\,1'2'}(\{f\})-1) \tag{5.15}$$

which follows from Eqs. (4.11) and (4.16). As a result of these manipulations, we find the entropy production in the Markovian limit:

$$\begin{aligned}\frac{dS(t)}{dt}=\frac{\pi}{4h^2}\sum_{121'2'}|\langle 12|\,V\,|1'2'\rangle_{\text{ex}}|^2\,\delta\left(\frac{\varDelta E_{12,\,1'2'}(t)}{\hbar}\right)[\mathscr{K}_{12,\,1'2'}(\{f(t)\})-1]\\ \times\ln\mathscr{K}_{12,\,1'2'}(\{f(t)\})(\bar{f}_1\bar{f}_2 f_{1'} f_{2'})_t\end{aligned} \tag{5.16}$$

It depends only on the one-particle distribution function and is positive, since $(x-1)\ln x\geqslant 0$ for $x>0$. The result (5.16) agrees with the well-known expression for the entropy production in a weakly interacting quantum system described by a Markovian kinetic equation (see, e.g., ref. 17).

6. GENERALIZATION TO SPATIALLY NON-HOMOGENEOUS SYSTEMS

Here we shall briefly touch upon the extension of the foregoing treatment to spatially non-homogeneous systems. In such cases, many-particle correlations associated with the energy conservation can be incorporated by taking mean energy density $\mathscr{E}(\mathbf{r},t)=\langle\hat{H}(\mathbf{r})\rangle^t$ as a state variable, together with the one-particle Wigner function $f_\alpha(\mathbf{r},\mathbf{p},t)=\langle\hat{f}_\alpha(\mathbf{r},\mathbf{p})\rangle^t$. The energy density operator, $\hat{H}(\mathbf{r})$, is defined through the relation

$$\hat{H}=\int d\mathbf{r}\,\hat{H}(\mathbf{r}) \tag{6.1}$$

and the operator corresponding to the Wigner function is given by

$$\hat{f}_\alpha(\mathbf{r},\mathbf{p})=\int d\mathbf{x}\,\mathrm{e}^{-\mathbf{p}\cdot\mathbf{r}/\hbar}\psi^\dagger_\alpha(\mathbf{r}-\mathbf{x}/2)\,\psi_\alpha(\mathbf{r}+\mathbf{x}/2) \tag{6.2}$$

where $\psi_\alpha(\mathbf{r})$ and $\psi^\dagger_\alpha(\mathbf{r})$ are the second-quantized field operators; the Greek indices $\alpha=(i,\sigma)$ specify the type of particles (i) and the spin state (u). Now the relevant statistical operator takes the form [cf. Eq. (2.12)]

$$\begin{aligned}\varrho_{\text{rel}}(t)=\frac{1}{Z_{\text{rel}}(t)}\exp\bigg\{-\int d\mathbf{r}\,\beta^*(\mathbf{r},t)\bigg[\hat{H}(\mathbf{r})-\sum_i\mu^*_i(\mathbf{r},t)\,\hat{n}_i(\mathbf{r})\bigg]\\ -\sum_\alpha\int\frac{d\mathbf{p}}{(2\pi\hbar)^3}\,\lambda_\alpha(\mathbf{r},\mathbf{p},t)\,\hat{f}_\alpha(\mathbf{r},\mathbf{p})\bigg\}\end{aligned} \tag{6.3}$$

where $\hat{n}_i(\mathbf{r}) = \sum_\sigma \psi^\dagger_\alpha(\mathbf{r})\,\psi_\alpha(\mathbf{r})$ are the particle-number density operators for the species. The local inverse quasi-temperature $\beta^*(\mathbf{r}, t)$ and the Lagrange multipliers $\lambda_\alpha(\mathbf{r}, \mathbf{p}, t)$ are to be determined from the local equations of state

$$\mathscr{E}(\mathbf{r}, t) = \mathrm{Tr}\{\hat{H}(\mathbf{r})\,\varrho_{\mathrm{rel}}(t)\}, \qquad f_\alpha(\mathbf{r}, \mathbf{p}) = \mathrm{Tr}\{\hat{f}_\alpha(\mathbf{r}, \mathbf{p})\,\varrho_{\mathrm{rel}}(t)\} \tag{6.4}$$

Just as in the spatially homogeneous case, the local quasi-chemical potentials $\mu_i^*(\mathbf{r}, t)$ in Eq. (6.3) can be eliminated by re-defining the Lagrange multipliers $\lambda_\alpha(\mathbf{r}, \mathbf{p}, t)$. Another possible way is to define the $\mu_i^*(\mathbf{r}, t)$ in the local-equilibrium state described by the statistical operator

$$\varrho_{\mathrm{loc}}(t) = \frac{1}{Z_{\mathrm{loc}}(t)} \exp\left\{ -\int d\mathbf{r}\,\beta^*(\mathbf{r}, t)\left[\hat{H}(\mathbf{r}) - \sum_i \mu_i^*(\mathbf{r}, t)\,\hat{n}_i(\mathbf{r}) \right]\right\} \tag{6.5}$$

Then the quasi-chemical potentials are to be determined from the local equations of state

$$n_i(\mathbf{r}, t) = \mathrm{Tr}\{\hat{n}_i(\mathbf{r})\,\varrho_{\mathrm{loc}}(t)\} \tag{6.6}$$

where $n_i(\mathbf{r}, t) = \langle \hat{n}_i(\mathbf{r}) \rangle^t$ are the mean particle-number densities for the species. The latter definition of the quasi-chemical potentials is typical for the hydrodynamic description of transport processes.

In the spatially non-homogeneous case, the basic evolution equations are the kinetic equation for the Wigner function

$$\frac{\partial}{\partial t} f_\alpha(\mathbf{r}, \mathbf{p}, t) = \frac{1}{i\hbar} \langle [\hat{f}_\alpha(\mathbf{r}, \mathbf{p}), \hat{H}] \rangle^t \tag{6.7}$$

and the local conservation law for the mean energy density

$$\frac{\partial}{\partial t} \mathscr{E}(\mathbf{r}, t) = \frac{1}{i\hbar} \langle [\hat{H}(\mathbf{r}), \hat{H}] \rangle^t = -\nabla \cdot \langle \hat{\mathbf{J}}(\mathbf{r}) \rangle^t \tag{6.8}$$

where $\hat{\mathbf{J}}(\mathbf{r})$ is the energy flux operator. To calculate the averages appearing in Eqs. (6.7) and (6.8), the nonequilibrium statistical operator has to be found as a functional of the state variables. This can be done by solving Eq. (3.2) in some approximation with the relevant statistical operator given by Eq. (6.3). If, for instance, the interaction term in the Hamiltonian can be regarded as a small perturbation, then Eq. (3.2) can be solved by an iterative method which is similar to the procedure used in Section 3. There are, however, some new features which are specific to spatially non-homogeneous systems. First, now the average on the right-hand side of

Eq. (6.7), when calculated with the relevant statistical operator, is not zero and the kinetic equation for the Wigner function has the form

$$\frac{\partial}{\partial t} f_\alpha(\mathbf{r}, \mathbf{p}, t) + D_\alpha(\mathbf{r}, \mathbf{p}, t) = I_\alpha(\mathbf{r}, \mathbf{p}, t) \tag{6.9}$$

where

$$D_\alpha(\mathbf{r}, \mathbf{p}, t) = \frac{i}{\hbar} \langle [\hat{f}_\alpha(\mathbf{r}, \mathbf{p}), \hat{H}] \rangle^t_{\mathbf{rel}} \tag{6.10}$$

is a generalized drift term which involves the correlation contributions.(11) The collision integrals $I_\alpha(\mathbf{r}, \mathbf{p}, t)$ are determined by the integral terms in Eq. (3.2). The second important point is that, in the spatially non-homogeneous case, the right-hand side of Eq. (3.2) contains terms with gradients of the Lagrange multipliers, $\beta^*(\mathbf{r}, t), \mu_i^*(\mathbf{r}, t)$, and $\lambda_\alpha^*(\mathbf{r}, \mathbf{p}, t)$. Finally, the collision integrals $I_\alpha(\mathbf{r}, \mathbf{p}, t)$ are, in general, non-local functionals of the Wigner function. If the state parameters vary little over the range of the interaction potential and the mean de Broglie wavelength, which is typical for real situations, then the non-locality effects can be incorporated by using an expansion of averages in Eqs. (6.7) and (6.8) in powers of spatial gradients. Within this scheme, the evolution equations derived in this paper may be interpreted as transport equations in the local approximation, where all the gradient terms are neglected.

7. CONCLUSIONS AND OUTLOOK

We now summarize the main implications of the above analysis. The first point is that a non-Markovian kinetic equation conserves the total energy and has the correct equilibrium solution only, if the collision, and correlation effects are incorporated in a self-consistent way, for instance, within the same approximation in the interaction between particles. We have also seen that it is precisely the interplay between correlations and collisions that is responsible for the long-time behavior of the non-Markovian collision integral.

Another important feature of the outlined approach is that the kinetic equation for the one-particle distribution function is supplemented by the equation for the quasi-temperature, Eq. (5.10), which describes the "slow" evolution of the system. This representation for non-Markovian kinetics differs from standard schemes, say the Green's function method,(18–20) where the goal is to derive a closed kinetic equation, so that the collision and correlation effects have to be described in terms of single-particle quantities. The inclusion of long-lived many-particle correlations into the Green's function formalism is a rather difficult problem and there are only first steps in this way.(21–23) On the other hand, the Green's function technique provides a powerful tool for calculating the collision contribution to a kinetic equation beyond the Born approximation. Thus an interesting point would be a unification of the Green's function method and the density operator method to develop the self-consistent non-Markovian quantum kinetic theory involving the correlation effects and the quasiparticle damping.

It is significant that the approach outlined in this paper is non-perturbative in external fields. If the external field does not directly affect interactions between particles, then the nonequilibrium statistical operator will have the form (3.4), but the evolution operator $U_0(t, t')$ will now involve the field effects which can be taken into account exactly (not in terms of perturbation theory). It should also be noted that, in the presence of an external field, the energy of the system is not conserved and the trivial equation $d\mathscr{E}/dt=0$ has therefore to be replaced by a balance equation including the work produced by the field.

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