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M Bonitz†, D Kremp†, D C Scott‡, R Binder‡, W D Kraeft§ and H S Köhler‖

† Universität Rostock, Fachbereich Physik, Universitätsplatz 3, Rostock 18151, Germany
‡ Optical Sciences Center, University of Arizona, Tucson, AZ 85721, USA
§ Ernst-Moritz-Arndt Universität Greifswald, Domstrasse 10a, 17489 Greifswald, Germany
‖ Physics Department, University of Arizona, Tucson, AZ 85721, USA

Abstract. The non-Markovian carrier–carrier scattering dynamics in a dense electron gas is investigated. Within the framework of quantum kinetic equations in the second Born approximation we study the relevance of retardation (memory) effects, energy broadening and correlation build-up for femtosecond relaxation processes. Furthermore, the important issue of total energy conservation, within various well-established approximation schemes, is analysed. The most important non-Markovian effect is shown to be the broadening of the energy delta function leading to an increase of kinetic energy with time. Our numerical analysis includes both the single-time kinetic equation and the full two-time Kadanoff–Baym equations. Our results are expected to correctly reproduce qualitative features of non-Markovian dynamics in plasmas, fluids, nuclear matter and in the intraband relaxation of semiconductors. The comparison of the exact solutions for different approximations allows suggestions for simplifications that make this kind of calculation and their extension, especially to realistic semiconductor situations, more feasible.

1. Introduction

Recent progress in the sub-picosecond spectroscopy of electron–hole (e–h) plasmas in semiconductors [1] increased the need for a theoretical description of charge-carrier scattering which goes beyond the well-studied Markov approximation regime (the Boltzmann, Landau or Lenard–Balescu equation); see, for example, [2, 3]. Generalized kinetic equations have been derived a long time ago—e.g., see [2–4]—and have been studied recently in application to semiconductors [5, 6, 7, 8]. These equations contain memory (or retardation) effects as well as the 'smearing out' of the kinetic energy conservation (or energy broadening) in two-particle collisions due to a generalized energy–time uncertainty. For example, studies of electron–phonon interactions in semiconductors have demonstrated the importance of non-Markovian (i.e., memory) effects in the initial stage of the thermalization of non-equilibrium e–h plasmas towards the lattice temperature [9–12]. Recently, oscillations of the transient four-wave-mixing signal in bulk GaAs have been successfully explained in terms of non-Markovian carrier–LO-phonon scattering, demonstrating the relevance of these generalized quantum kinetic equations [13]. A typical memory effect is temporal pulsations of the electron distribution [11].

Similar effects should occur in carrier–carrier scattering, but the more complex nature of the corresponding non-Markovian kinetic equations makes these processes significantly more difficult to investigate numerically, and previous numerical studies did not focus on the relaxation of the distribution function [7, 14]. We therefore study, amongst other issues, the temporal relaxation of the electron distribution. Our analysis reveals that temporal pulsations of the distribution are indeed intrinsically present, but that they are suppressed by both destructive interference and self-energy (damping) effects.

Another problem which, so far, has been investigated only rarely in recent solid-state studies [12, 17], is the issue of energy conservation. It is well known that conventional Markovian kinetic equations, besides being limited to time-scales large compared to the correlation time, conserve only kinetic (quasi-particle) energy. It was realized a long time ago [18, 4] that the problems of energy conservation and short-time behaviour are closely linked together. Presenting an explicit expression for the potential energy, we show that the non-Markovian kinetic equation does indeed conserve total (the sum of kinetic and potential) energy. As a consequence, kinetic energy may change during the thermalization, giving rise, for example, to a different temperature of the final state compared to that of Markovian approximations. Our numerical evaluation shows that this effect may be as large as 50% [19].

As a third issue, we study the effects of self-energy (damping) on the relaxation. In limiting the memory depth, these effects are essential for the correct long-time behaviour, including the transition to the Markovian regime. On the other hand, self-energy (damping) effects in the form in which they are often introduced into non-Markovian kinetic equations are shown to cause a violation of total energy conservation. This has recently been found also for carrier–phonon scattering [17]. Though this effect is of higher order (beyond the second Born approximation), this indicates a fundamental problem related to the generalized Kadanoff–Baym *ansatz*. We outline a solution to this problem. Furthermore, it is well known that the Kadanoff–Baym equations which treat the self-energy problem self-consistently do conserve total energy and should be regarded as an adequate theoretical model. We therefore present solutions of these equations too. The comparison of the results for the evolution of the distribution functions and the kinetic energy allows us to draw conclusions about the relevance of various general non-Markovian effects, such as retardation and collisional energy broadening. Furthermore, it allows us to suggest simplifications which render the numerical model for femtosecond carrier–carrier scattering numerically feasible yet physically appropriate. This should also allow one to treat more complex experimentally relevant situations, such as four-wave-mixing set-ups, more efficiently.

We want to underline that non-Markovian effects are very general phenomena in the short-time behaviour of interacting many-particle systems. These effects are related to the relaxation of binary correlations and will always be of importance for times shorter than the correlation time [26]. Besides semiconductor systems, these phenomena are of interest also for dense plasmas, fluids or nuclear matter. Therefore, we focus in this paper on phenomena which are common to all of these systems.

In our numerical analysis we consider a dense electron gas, choosing the parameters of an electron gas in the GaAs conduction band as an example. To focus on the issues outlined above, we consider the second Born approximation, assuming a static interaction potential. In real optical situations in semiconductors it is not always possible to separate excitation dynamics from carrier relaxation dynamics. However, in order to study non-Markovian effects on carrier relaxation in its pure form, we choose a simple model treating the optical excitation as a non-equilibrium initial condition. We also consider only the

electron component and its thermalization to intraband scattering alone. Of course for a quantitative theory–experiment comparison in semiconductor optics, the inclusion of the hole component would play an important role.

Numerical results will be presented for the following four approximations: the Markovian kinetic equation (a), the generalized kinetic equation (1) without damping in the limits of zero memory (b) and full memory (c), and the Kadanoff–Baym equations (12), (d).

2. A summary of the kinetic equations

2.1. The non-Markovian Landau equation

We would like to begin with a brief summary of the non-Markovian kinetic equations (for a derivation, see, for example, [6]). Neglecting contributions due to quantum mechanical exchange and from initial correlations [19], one can derive the kinetic equation for the one-particle distribution F, where one has to assume the existence of a neutralizing background (for the elimination of the contributions due to positive charge carriers from the system's Hamiltonian in the thermodynamic limit, see, e.g., [20]):

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} F_1(t) = \frac{2\mathcal{V}^2}{\hbar^2} \int_0^{t-t_0} \mathrm{d}\tau \int \frac{\mathrm{d}\boldsymbol{p}_2}{(2\pi\hbar)^3} \int \frac{\mathrm{d}\bar{\boldsymbol{p}}_1}{(2\pi\hbar)^3} \int \frac{\mathrm{d}\bar{\boldsymbol{p}}_2}{(2\pi\hbar)^3} (2\pi\hbar)^3 \delta(\boldsymbol{p}_{12} - \bar{\boldsymbol{p}}_{12}) \\
\times V^2\left(\frac{\bar{\boldsymbol{p}}_1 - \boldsymbol{p}_1}{\hbar}\right) \cos\left\{\frac{E_{12} - \bar{E}_{12}}{\hbar}\tau\right\} \mathrm{e}^{-(\gamma_{12} + \bar{\gamma}_{12})\tau/\hbar} \\
\times \left\{\bar{F}_1 \bar{F}_2 [1 - F_1][1 - F_2] - F_1 F_2 [1 - \bar{F}_1][1 - \bar{F}_2]\right\}\Big|_{t-\tau}
\end{aligned}
\tag{1}
$$

with $E_{12} = E_1 + E_2$, $\boldsymbol{p}_{12} = \boldsymbol{p}_1 + \boldsymbol{p}_2$, $\gamma_{12} = \gamma_1 + \gamma_2$, $F_1 = F(\boldsymbol{p}_1)$, $\bar{F} = F(\bar{\boldsymbol{p}})$ etc, where $\boldsymbol{p}$ denotes the momentum and $\mathcal{V}$ is the volume. F is the Wigner distribution function which is normalized to the particle number,

$$
\mathcal{V} \int \frac{\mathrm{d}\boldsymbol{p}}{(2\pi\hbar)^3} F(\boldsymbol{p}) = N.
$$

The binary interaction potential V contains the volume too, so it has the dimension of energy (see section 3.2). E_1 is the quasi-particle energy, and the damping coefficient is related to the imaginary part of the retarded self-energy by $\gamma_1 = \mathrm{Im}\,\Sigma^R(\boldsymbol{p}_1)$ [6]. Equation (1) contains memory or retardation effects (dependence on the distribution functions at all previous times) and energy broadening (the cosine of the energy difference instead of the δ-function appearing in Markovian kinetic equations). The memory depth is limited by the damping exponents which, in turn, are functionals of the distribution functions. The relaxation of the distribution function strongly depends on how these coefficients are calculated. To highlight this effect, we include in our numerical results (figures 1–4) solutions of equation (1) without damping, $\gamma = 0$, which are labelled 'approximation (c)'.

2.2. Total energy conservation

One can readily investigate the issue of total energy conservation for equation (1). For this one has to recall (cf., e.g., [4]), that the collision integral can be expressed in terms of a binary correlation operator g_{12}, i.e., the correlated part of the two-particle density operator

$g_{12} = \mathcal{F}_{12} - \mathcal{F}_1\mathcal{F}_2$, where $\mathcal{F}_1$ is the one-particle density operator. In operator notation we have [19]

$$i\hbar\frac{d\mathcal{F}_1}{dt} = n\,\mathrm{Tr}_2[V_{12}, g_{12}] \tag{2}$$

where square brackets denote the commutator, and n is density. Notice that the s-particle operator is normalized to $\mathcal{V}^s$.

We obtain an explicit expression for the potential energy of a homogeneous system using the definition $\langle V\rangle = (n^2/2)\mathrm{Tr}_{12}(V_{12}g_{12})$ and equation (2):

$$\langle V\rangle(t) = -\frac{\mathcal{V}^3 N}{2\hbar}\int_0^{t-t_0} d\tau \int\frac{dp_1}{(2\pi\hbar)^3}\int\frac{dp_2}{(2\pi\hbar)^3}\int\frac{d\bar{p}_1}{(2\pi\hbar)^3}\int\frac{d\bar{p}_2}{(2\pi\hbar)^3}\ V^2\left(\frac{\bar{p}_1 - p_1}{\hbar}\right)$$

$$\times\ (2\pi\hbar)^3\delta(p_{12} - \bar{p}_{12})e^{-(\gamma_{12}+\bar{\gamma}_{12})\tau/\hbar}\sin\left(\frac{E_{12} - \bar{E}_{12}}{\hbar}\tau\right)$$

$$\times\ \left\{2\bar{F}_1\bar{F}_2[1 - F_1][1 - F_2]\right\}\Big|_{t-\tau}. \tag{3}$$

The time derivative of equation (3) can be compared to the time derivative of the kinetic energy which follows immediately from the kinetic equation (1):

$$\frac{d}{dt}\langle T\rangle = \mathcal{V}\int\frac{dp_1}{(2\pi\hbar)^3}\frac{p^2}{2m}\frac{dF_1}{dt}$$

$$= \frac{\mathcal{V}^3 N}{2\hbar}\int\frac{dp_1}{(2\pi\hbar)^3}\int\frac{dp_2}{(2\pi\hbar)^3}\int\frac{d\bar{p}_1}{(2\pi\hbar)^3}\int\frac{d\bar{p}_2}{(2\pi\hbar)^3}$$

$$\times\ \left\{\frac{d}{dt} - \frac{\gamma_{12} + \bar{\gamma}_{12}}{\hbar}\right\}\int_0^{t-t_0} d\tau\ V^2\left(\frac{\bar{p}_1 - p_1}{\hbar}\right)$$

$$\times\ (2\pi\hbar)^3\delta(p_{12} - \bar{p}_{12})e^{-(\gamma_{12}+\bar{\gamma}_{12})\tau/\hbar}\sin\left(\frac{E_{12} - \bar{E}_{12}}{\hbar}\tau\right)$$

$$\times\ \left\{2\bar{F}_1\bar{F}_2[1 - F_1][1 - F_2]\right\}\Big|_{t-\tau} \tag{4}$$

where the last line is obtained after a symmetrization of the momenta yielding $(E_{12}-\bar{E}_{12})/4$. For the derivation of equation (4), the time dependence of the quasi-particle energy and the damping has been neglected. In most situations, this is justified, and our conclusions will not depend on that assumption. The general case is discussed in [27].

Summing equation (4) and the time derivative of equation (3) leaves us with the term containing $-V^2(\gamma_{12} + \bar{\gamma}_{12})/\hbar$; this means

$$\frac{d}{dt}\langle T + V\rangle \sim \frac{4\,\tilde{\gamma}_1}{\hbar}\,\langle V\rangle \tag{5}$$

where $\tilde{\gamma}_1$ is some value of the one-particle damping averaged over all momenta. We may, therefore, conclude that, if self-energy contributions are being neglected, total energy is exactly conserved. Otherwise, energy is conserved only approximately, with the error being of the order of the mean value of the damping constant itself, $\langle\tilde{\gamma}_1\rangle$. During the relaxation, the damping rate increases as a consequence of correlation build-up and reaches an almost time-independent value after the correlation time (e.g. the inverse plasma frequency, [26]). According to equation (5), the error to the total energy will accumulate in time, eventually giving rise to wrong predictions for the long-time behaviour of the system. This is indeed confirmed by numerical results. In calculations where we included damping but neglected the energy shift (related to $\mathrm{Re}\,\Sigma^R$), we found a constant almost linear increase of kinetic and total energy, with no tendency towards saturation (see the discussion in section 3.3).

Therefore, our result is important because it forces one to have a closer look at the non-Markovian kinetic equation (1), the appearance of the damping terms in it and the underlying theoretical assumptions.

There are several theoretical approaches on which the derivation of non-Markovian kinetic equations, such as equation (1), can be based—for example the method of Green's functions or the density operator formalism. Both approaches can be used to introduce energy renormalization, including damping. In the Green's functions approach, the starting point can be, for example, the two-time Kadanoff–Baym equation [21]; see section 2.4. Within the so-called generalized Kadanoff–Baym *ansatz* (GKBA), [23], the two-time correlation functions take the form

$$-\mathrm{i}g^{\gtrless}(\boldsymbol{p}, t_1, t_2) = \mp \mathrm{i} \left\{ g^R(\boldsymbol{p}, t_2, t_2) F^{\gtrless}(\boldsymbol{p}, t_2) - F^{\gtrless}(\boldsymbol{p}, t_1) g^A(\boldsymbol{p}, t_1, t_1) \right\} \tag{6}$$

which relates the two-time functions $g^{\gtrless}$ to the one-time distribution functions and thus allows one to derive non-Markovian kinetic equations from the two-time Kadanoff–Baym equations; see, e.g., [6]. In equation (6), $F^<(\boldsymbol{p}, t_1) = F(\boldsymbol{p}, t_1)$ and $F^>(\boldsymbol{p}, t_1) = 1 - F(\boldsymbol{p}, t_1)$. $g^{R/A}$ are the retarded/advanced Green's functions, respectively. In the local approximation, the retarded and advanced functions depend on the time difference:

$$g^R(\boldsymbol{p}, t_1, t_2) = -\mathrm{i}\hbar\Theta(t_1 - t_2)\exp\left(\left(-\mathrm{i}\frac{E(\boldsymbol{p})}{\hbar} - \frac{\gamma(\boldsymbol{p})}{\hbar}\right)(t_1 - t_2)\right) \tag{7}$$

$$g^A(\boldsymbol{p}, t_1, t_2) = \mathrm{i}\hbar\Theta(t_2 - t_1)\exp\left(\left(-\mathrm{i}\frac{E(\boldsymbol{p})}{\hbar} + \frac{\gamma(\boldsymbol{p})}{\hbar}\right)(t_1 - t_2)\right) \tag{8}$$

where the quasiparticle energy $E = E(\boldsymbol{p}, T)$ may depend on the macroscopic time T. $\gamma(\boldsymbol{p}, T)$ is the corresponding damping which gives rise to the damping terms in the kinetic equation (1). In principal, $E(\boldsymbol{p}, T)$ and $\gamma(\boldsymbol{p}, T)$ have to be calculated self-consistently from the retarded self-energy. For reasons of feasibility, this is usually avoided, and E is approximated by the free-particle energy, and for γ some phenomenological broadening is chosen. The result of equation (5) shows that this approximation violates total energy conservation in the sense discussed above. One can show that the main reason for this is the neglect of the energy shift (which is related to the real part of the retarded self-energy) which tends to reduce the error.

The problem of energy conservation in non-Markovian kinetic equations with energy renormalization can be studied conveniently within the density operator formalism; for a detailed discussion, see [27]. The main results of this analysis are that generalized kinetic equations with self-energy, such as equation (1), do conserve total energy up to higher orders in the interaction potential, if $E(\boldsymbol{p}, T)$ and $\gamma(\boldsymbol{p}, T)$ are calculated fully self-consistently from the retarded self-energy. Furthermore, additional simplifying approximations, such as retardation expansions (see section 2.3) can be developed which are also approximately energy conserving, providing that the self-consistent treatment between the retarded self-energy and collision integral is retained. This means that one has to use the same approximations for the collision integral and for the retarded self-energy.

Similar issues in the case of carrier–phonon scattering have been presented in [17].

2.3. The retardation expansion of the kinetic equation

The quite complex structure of the collision integral of the kinetic equation (1) makes simplifying approximations desirable, especially if the carrier dynamics is part of a more complex calculation. One systematic approach is a retardation expansion of the collision

integral. This means expanding the distribution function into a series with respect to the memory time τ, $F(t - \tau) = F(t) - \tau\, \mathrm{d}F(t)/\mathrm{d}\tau + \cdots$. The zeroth-order retardation term $(\sim\tau^0)$ is given by

$$I_{(0)}(t) = \frac{2\mathcal{V}^2}{\hbar^2} \int \frac{\mathrm{d}\boldsymbol{p}_2}{(2\pi\hbar)^3} \int \frac{\mathrm{d}\bar{\boldsymbol{p}}_1}{(2\pi\hbar)^3} \int \frac{\mathrm{d}\bar{\boldsymbol{p}}_2}{(2\pi\hbar)^3} \; (2\pi\hbar)^3 \delta(\boldsymbol{p}_{12} - \bar{\boldsymbol{p}}_{12})$$

$$\times\; V^2\left(\frac{\bar{\boldsymbol{p}}_1 - \boldsymbol{p}_1}{\hbar}\right) D_0(E_{12} - \bar{E}_{12}, \gamma_{12} + \bar{\gamma}_{12}, t - t_0)$$

$$\times\; \left\{ \bar{F}_1(t)\bar{F}_2(t)[1 - F_1(t)][1 - F_2(t)] - (F \leftrightarrow 1 - F) \right\} \tag{9}$$

with

$$D_0(\omega, \Gamma, t) = \frac{\hbar}{\omega^2 + \Gamma^2}\left\{ \left(\omega\sin\frac{\omega}{\hbar}t - \Gamma\cos\frac{\omega}{\hbar}t\right)\exp-\left(\frac{\Gamma}{\hbar}t\right) + \Gamma \right\}. \tag{10}$$

This approximation has been obtained in [6]. This expression is the exact short–time limit of equation (1), when the next terms of the retardation expansion ($\sim\tau, \tau^2, \cdots$) are still negligibly small. This approximation neglects the retardation (memory); however, it retains the energy broadening effect and, therefore, allows one to separate the influence of the two effects. Furthermore, at short times, self-energy effects are small, and approximation (9), (10) with $\gamma_{12} = 0$, i.e.

$$D_0(\omega, \Gamma, t - t_0) \longrightarrow D_0^0 = \frac{\sin((\omega/\hbar)(t - t_0))}{\omega/\hbar}$$

(below referred to as 'approximation (b)') can be expected to be a reasonable model. This will indeed be confirmed by our numerical results.

In the long–time limit,

$$\frac{\sin((\omega/\hbar)(t - t_0))}{\omega/\hbar} \longrightarrow \hbar\delta(\omega)$$

and approximation (b) yields just the Markovian collision integral in the second Born approximation. For comparison, below the solution of the Markovian kinetic equation ('approximation (a)') will be given too.

Of course, with increasing time, higher-order retardation contributions become important. However, there is a partial compensation due to the alternating sign of the successive terms. The relevant term at long times will be the first-order contribution $(\sim\tau^1)$, with the asymptotic form

$$\lim_{t \to \infty} D_1(\omega, \Gamma, t) = \frac{\hbar^2}{\omega^2 + \Gamma^2}\left(\frac{2\Gamma^2}{\omega^2 + \Gamma^2} - 1\right) \tag{11}$$

and the particular result for $\Gamma \longrightarrow 0$ equals $-\hbar(\mathrm{d}/\mathrm{d}\omega)(\mathcal{P}/\omega)$, with $\mathcal{P}$ denoting the principal value. Notice that an approximation that uses this first-order retardation integral plus the conventional Markovian Boltzmann integral (approximation (a)) gives a qualitative improvement of the theory. This gives a 'corrected' collision integral of Markov type which includes the main correlation effects correctly. Thermodynamic or transport properties calculated from this scattering term (correlation energy, virial coefficients, conductivity, optical properties and so on) will contain the proper correlation corrections which are essential for the description of interacting many-particle systems. In particular, this approximation is sufficient to conserve total energy, but already on the level of Markovian kinetic equations. This is just the result of [18, 4], which immediately follows from our more general analysis. A more detailed discussion will be given in [27].

2.4. Kadanoff–Baym equations in the second-order Born approximation

The fourth model which we consider in our numerical analysis is that of the full Kadanoff–Baym equations for the two-time correlation functions $g^{\gtrless}$ [21]:

$$
\left(i\hbar \frac{\partial}{\partial t} - \frac{p^2}{2m} \right) g^{\lessgtr}(\boldsymbol{p}, t, t') = \int_{t_0}^{t} d\bar{t} \, \left\{ \Sigma^{>}(\boldsymbol{p}, t, \bar{t}) - \Sigma^{<}(\boldsymbol{p}, t, \bar{t}) \right\} g^{\lessgtr}(\boldsymbol{p}, \bar{t}, t')
$$
$$
- \int_{t_0}^{t'} d\bar{t} \, \Sigma^{\lessgtr}(\boldsymbol{p}, t, \bar{t}) \left\{ g^{>}(\boldsymbol{p}, \bar{t}, t') - g^{<}(\boldsymbol{p}, \bar{t}, t') \right\} \tag{12}
$$

where the self-energy has to be calculated in the second-order Born approximation:

$$
\Sigma^{\lessgtr}(p_1, t, t') = 2\hbar^2 \mathcal{V}^2 \int \frac{d\boldsymbol{p}_2}{(2\pi\hbar)^3} \int \frac{d\bar{\boldsymbol{p}}_1}{(2\pi\hbar)^3} \int \frac{d\bar{\boldsymbol{p}}_2}{(2\pi\hbar)^3} \, V^2 \left(\frac{\boldsymbol{p}_1 - \bar{\boldsymbol{p}}_1}{\hbar} \right)
$$
$$
\times (2\pi\hbar)^3 \delta(\boldsymbol{p}_{12} - \bar{\boldsymbol{p}}_{12}) g^{\lessgtr}(\bar{\boldsymbol{p}}_1, t, t') g^{\lessgtr}(\bar{\boldsymbol{p}}_2, t, t') g^{\gtrless}(\boldsymbol{p}_2, t', t). \tag{13}
$$

Notice that in addition to equation (12), the functions $g^{\lessgtr}$ have to obey also the Hermitian conjugate equations, or, what is equivalent, the symmetry relation $g^{\lessgtr}(t', t) = -[g^{\lessgtr}(t, t')]^*$ [21].

Among the physical quantities of interest to us are the Wigner distribution function and the total energy, which are readily calculated from the two-time correlation functions [22]:

$$
F(\boldsymbol{p}, t) = -i\hbar g^{<}(\boldsymbol{p}, t, t) \tag{14}
$$

$$
\langle T + V \rangle(t) = \frac{1}{4} \mathcal{V}\hbar \int \frac{d\boldsymbol{p}}{(2\pi\hbar)^3} \left\{ \left(i\hbar \frac{\partial}{\partial t} - i\hbar \frac{\partial}{\partial t'} \right) + \frac{p^2}{m} \right\} (\mp i) g^{<}(\boldsymbol{p}, t, t')\big|_{t=t'}. \tag{15}
$$

Total energy is conserved by these equations [21]. The generalized kinetic equation (1) can be derived from equation (12) in a well-known manner, using the *ansatz* of Lipavski *et al*, equation (6) [23, 6].

Notice that the Kadanoff–Baym equations (12) were originally derived in the limit $t_0 \to -\infty$ [21], which leads to irreversible equations. Furthermore, in this limit correlations were assumed to vanish, which is equivalent to the neglect of all long-living correlations such as large-scale fluctuations and bound states. One can overcome this limitation in generalizing the derivation of the Kadanoff–Baym equations to include arbitrary initial correlations at a given finite initial moment t_0 [22, 28]. These modified equations are time-reversal invariant and their solution is uniquely defined by the initial values for the one-particle and two-particle correlation functions $g^{<}(t_0, t_0)$ and $g^{<}_{12}(t_0, t_0)$. For the specific situation of pulsed semiconductor excitation, the initial time may be chosen sufficiently long before the pulse that $g^{<}_{12}(t_0, t_0) = g^{<}(t_0, t_0) = 0$, and the evolution is driven by the laser-generated interband polarization. Such a complete simulation of the coupled-semiconductor–light-field dynamics is, however, beyond the scope of this paper. We, therefore, have to specify non-zero initial conditions. For simplicity and for consistency with the solution of the one-time kinetic equation (1), we used an alternative approach which uses the result of the excitation as an initial condition at the finite time t_0 and, furthermore, neglects initial two-particle correlations. So the only initial condition used with equations (12) is $-i\hbar g^{<}(t_0, t_0) = F(t_0)$ which determines the relaxation completely and in a unique way [22, 24, 31].

Notice that time-reversible equations, such as equations (1) with $\gamma = 0$ and (12), can be used successfully to model statistical processes of (irreversible) relaxation or transport phenomena. Examples are the solutions of the Vlassov equation, molecular dynamics approaches and the Jaynes–Cummings model for spontaneous emission and luminescence [30]. The main condition is the use of a macroscopically large particle number, so that

revival phenomena like the Poincaré revival occur on time-scales which are large compared to the characteristic times of all of the processes in the system. Note that for the derivation of equations (12) and (1), in fact, the thermodynamic limit is implied.
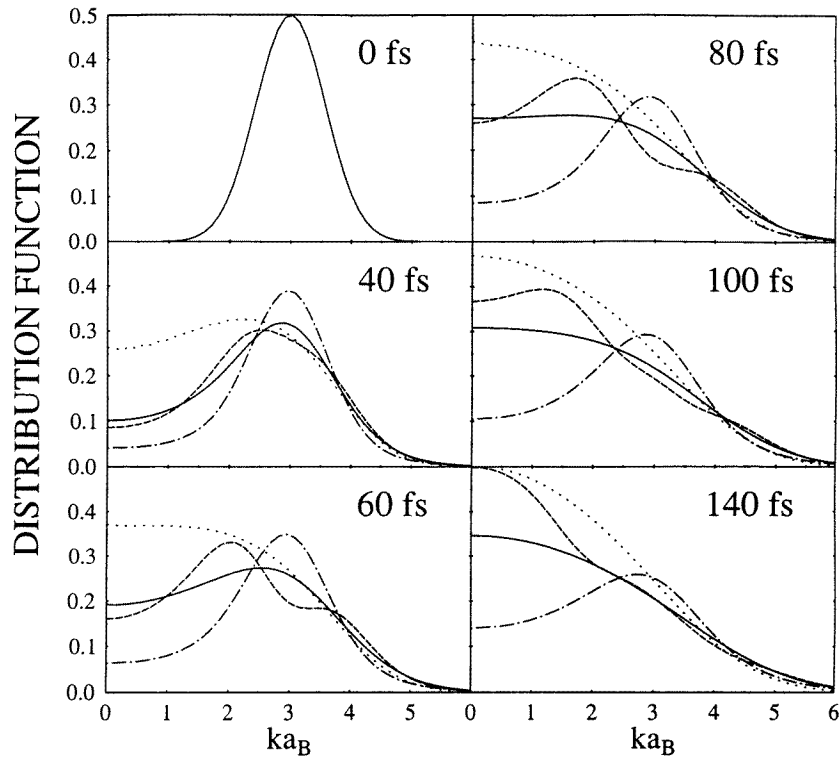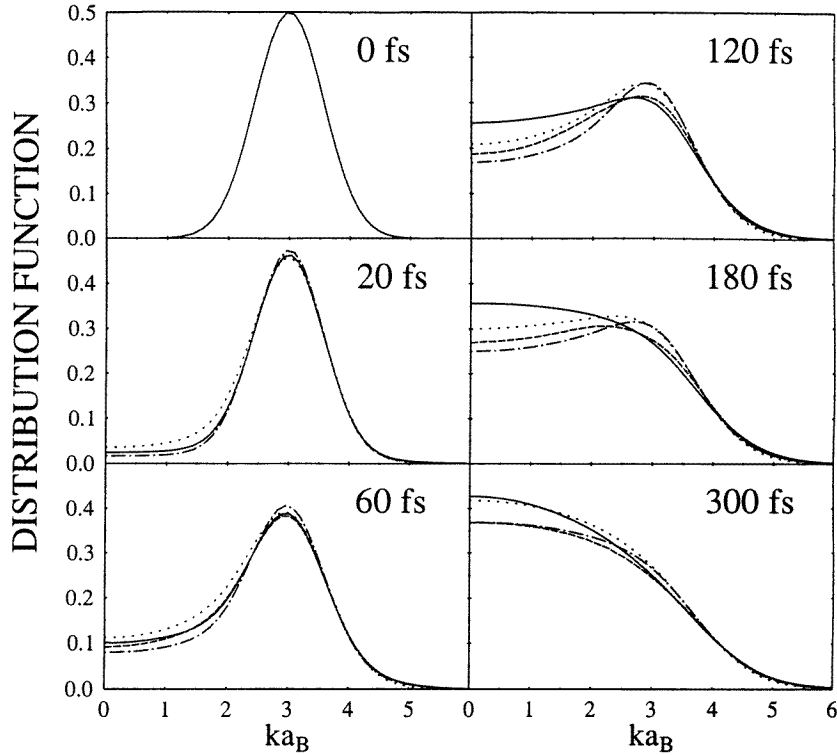

Figure 1. Relaxation of the distribution function for a strong long-range potential with $\kappa a_B = 0.2$. The figure parts correspond to different times. The relaxation corresponding to four different scattering approximations (denoted (a)–(d) in the text) is shown: the Markovian Landau equation (dotted line, (a)), the zeroth-order retardation approximation of equation (9) (full line, (b)), the non-Markovian equation (1) with full retardation but no self-energy (dashes, (c)), and the Kadanoff–Baym equations (dash–dotted line, (d)).

3. Numerical results

3.1. Description of the numerical methods

We perform our numerical studies for a one-component system. For detailed comparison of the different approximations, we solve (cf. above)
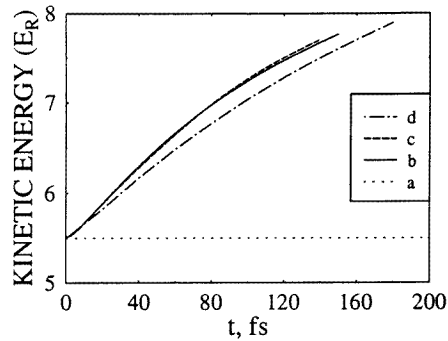
(a) the kinetic equation with the Markovian collision integral,

(b) the kinetic equation with the zeroth-order retardation integral of equation (9) with $\gamma_{12} = 0$, that includes energy broadening but neglects retardation effects,

(c) the kinetic equation with the collision integral of equation (1) including the retardation completely (full memory depth) but neglecting self-energy contributions, and

(d) the Kadanoff–Baym equations (12) in the second Born approximation which include self-energy self-consistently.

Figure 2. Relaxation of the distribution function for a weak short-range potential with $\kappa a_B = 1.16$. The figure parts correspond to different times. The relaxations corresponding to four different scattering approximations (denoted (a)–(d) in the text) are shown: the Markovian Landau equation (dotted line, (a)), the zeroth-order retardation approximation of equation (9) (full line, (b)), the non-Markovian equation (1) with full retardation but no self-energy (dashes, (c)), and the Kadanoff–Baym equations (dash–dotted line, (d)).

The Kadanoff–Baym equations and their Hermitian conjugate were solved as in [22, 24]. A particularly difficult part was the solution of the kinetic equation with full memory and no damping (c). (With damping included the solution simplifies substantially, since both the memory depth and the spread of the distribution in momentum space are cut off.) We therefore provide some numerical details. We solved the kinetic equation by direct integration, using a fourth-order adaptive-step-size Runge–Kutta scheme. In the isotropic case, the collision term of equation (1) contains a fivefold integral (over two momenta, two angles and time). The number of integration points was chosen in such a way that density and total energy are conserved within less than 1% during each simulation, and the oscillations of the integrands are well covered up to a time of about 300 fs. Typical numbers were 25 integration points and 100 points for the storage of the distribution. As an alternative integration scheme, we took advantage of the fact that the q-integration ($q = \bar{p}_1 - p_1$) over the potential can be performed analytically. Though this scheme is less stable and required more integration points (about 40), it saves one integration and, therefore, proved to be significantly faster. It is, however, not applicable to the collision integrals for the exchange terms. To verify the numerical results, we used as a third independent scheme the solution of the Kadanoff–Baym equations with the generalized Kadanoff–Baym *ansatz*

(6) without damping and found excellent agreement of all three approaches. The numerical complexity is drastically reduced in the zeroth-order retardation expansion (b) and in the Markov case (a).

Figure 3. Relaxation of the kinetic energy density for the four runs with $\kappa a_B = 0.2$ shown in figure 1: the Markovian Landau equation (dotted line, (a)), the zeroth-order retardation approximation of equation (9) (full line, (b)), the non-Markovian equation (1) with full retardation but no self-energy (dashes, (c)), and the Kadanoff—Baym equations (dash-dotted line, (d)).
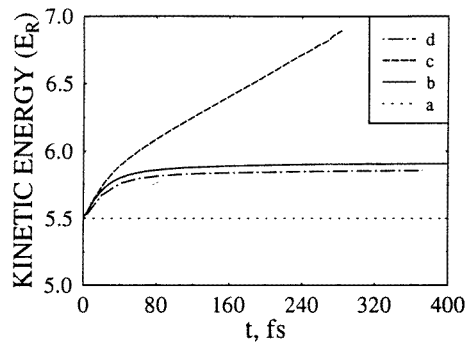
Figure 4. Relaxation of the kinetic energy density for the four runs with $\kappa a_B = 1.16$ shown in figure 2: the Markovian Landau equation (dotted line, (a)), the zeroth-order retardation approximation of equation (9) (full line, (b)), the non-Markovian equation (1) with full retardation but no self-energy (dashes, (c)), and the Kadanoff–Baym equations (dash–dotted line, (d)).

3.2. Parameters of the model

To be specific, we choose, as an example, electrons in a GaAs bulk semiconductor. The parameters are the effective mass $m = 0.067m_0$ (m_0 is the electron mass in vacuum), and the Rydberg energy $E_R = 4.2$ meV, corresponding to a background dielectric constant $\epsilon_b = 13.998$ and an exciton Bohr radius $a_B = 132$ Å. Our calculations are intended to be model calculations that reveal qualitative features of non-Markovian kinetics rather than quantitative predictions. Focusing on the Landau equation (the kinetic equation in the second Born approximation with statical interaction), we consider only static interaction potentials and do not consider screening dynamics. We use a Yukawa-type interaction potential with

the Fourier transform $V(q) = A/(q^2 + \kappa^2)$ for different amplitudes A and ranges κ^{-1}. This is a reasonable model for both neutral particles and for plasmas with constant carrier density. The following results are obtained for $A = 4\pi e_0^2/\mathcal{V}\epsilon_b$ (e_0 = free-electron charge). Modifying κ, we vary the strength and range of the potential.

We studied various types of initial non-equilibrium distribution. As a typical example, we present here a Gaussian centred around the momentum $p_0 = 3\hbar/a_B$, corresponding to a density of $n = 3.64 \times 10^{17}$ cm^{-3}. Figures 1 and 2 show the relaxation process for the models (a)–(d), for $\kappa = 0.2a_B^{-1}$ and $\kappa = 1.16a_B^{-1}$, respectively. The second number is close to the static long-wavelength limit of the equilibrium inverse screening length $\kappa = 1/r_{sc}$ in the random-phase approximation (RPA). This models the situation where in the initial state the screening cloud has already been formed. In principle the formation of a static screening cloud takes a time at least of the order of the inverse plasma frequency [15, 16], but for times beyond this initial stage, a quasi-static interaction should be reasonable. Taking κ to be the lower number, the situation is closer to that of a plasma without screening. This might model the initial stage of an optically excited plasma in semiconductors [14]. In this case, non-Markovian effects are expected to be most pronounced.

3.3. Results

Consider now the relaxations shown in figure 1. Comparison of the models (a) and (c) reveals that non-Markovian effects slow down the relaxation significantly. This is due do the fact that correlations have to be built up first ($\mathrm{d}F/\mathrm{d}t(t_0) = 0$). A true memory effect is seen in the relaxation (c). In place of the non-equilibrium peak of the initial distribution, the system tends to create a minimum (it still remembers the peak even after it has been destroyed). At the same time, the population of originally empty low-momentum states reveals a strong increase with an overshooting beyond the stationary value. These structures in the distribution show pulsations in time which increase with increasing amplitude A of the potential (they are more pronounced in the time evolution of the derivative $\mathrm{d}F/\mathrm{d}t$). This behaviour is natural, since in (c), the non-Markovian kinetic equation is equivalent to an equation which is local in time, but contains higher-order time derivatives. Since this approximation neglects self-energy, it leads to a time-reversible (dynamic) equation, where damping results only from destructive interference of the fast oscillations of the integrand. An unphysical by-product of this approximation is that there exist initial conditions for which the distribution functions become larger than 1 or negative. Therefore, here the inclusion of self-energy effects (Im Σ^R) is principally important for the correct long-time behaviour. The corresponding self-consistent result is shown in the relaxation (d). The evolution is completely smooth. At the same time, the reduction of the system's memory leads here to a further slowing down of the relaxation. A smooth relaxation is observed for the calculation (b) too, since it neglects the retardation completely.

Consider now figure 2. Due to the weaker amplitude and shorter range of the potential in this calculation ($\kappa = 1.16a_B^{-1}$), the interaction between the particles is much weaker compared to that for the run in figure 1. Now, even the full retardation approximation (c) is completely smooth. In this run, the deviations of all three non-Markovian runs (b)–(d) from the Markovian (a) are small. Differences are mainly pronounced in the high-momentum tail of the distributions (more pronounced in the momentum distribution of higher moments of the distribution function, such as the particle number or kinetic energy). The reason is that due to the broadening of the kinetic-energy-conserving delta function, scattering into high-momentum states becomes possible. An unexpected result is that the system relaxes faster with the weaker interaction for the Kadanoff–Baym equations. The reason is that

with increasing potential strength, the damping rates also increase. Since the damping rate appears in the exponent in the collision integral, its increase strongly reduces the memory depth and the energy range accessible for scattering processes. This point is further explored in [25].

Notice that all of the models yield a relaxation towards a stationary distribution. Models (a) and (b) relax towards a Fermi function, where model (b) gives a higher temperature due to the increase of the kinetic energy (see below). Models (c) and (d) do also show relaxation behaviour despite the time reversibility of the corresponding equations (see the discussion in section 2.4). However, due to correlation build-up, the stationary distribution in both cases deviates slightly from a Fermi function.

Since kinetic energy is not a constant in the non-Markovian models, it is interesting to consider its relaxation. The results for the approximations (a)–(d) are shown in figures 3 and 4. All non-Markovian models yield a monotonic increase. The reason is the correlation build-up in the system (in neglecting initial correlations, we assumed an initial state with zero potential energy). Since the asymptotic state of an interacting many-body system is characterized by binary correlations, during the relaxation, potential energy is accumulated in the system. The sign of the potential energy is negative (otherwise the system would be unstable); cf. equation (3). Despite the repulsion between electrons, the necessary account for a neutralizing background leads to an overall attractive interaction. The monotonic increase of (the absolute value of) the potential energy, via the conservation of total energy, transforms into the kinetic energy increase observed in figures 3 and 4. Naturally, particularly strong correlations are built up if the potential is strong (figures 1 and 3), and, therefore, the kinetic energy increases significantly. The increase with the weaker potential, is much smaller; cf. figure 4. Nevertheless, the asymptotic kinetic energy, i.e. the temperature established in the system, is significantly higher than predicted by the Markovian model (a).

After discussing the long-time behaviour of the system, let us consider now the initial stage of the relaxation. For this, it is instructive to compare the relaxation with the kinetic equation (c) and its short-time asymptotics, the zeroth-order retardation approximation (b). As expected, figure 4 shows good agreement between the kinetic energy evolution for the non-Markovian models (b) and (c) at the beginning (for the first 20 fs). After this time, the zeroth-order retardation term (b) starts to saturate whereas in (c) higher-order retardation terms become important, and kinetic energy increases further. The same tendency exists in the small-κ case (figure 3), but there the initial phase is much longer, and model (b) starts to saturate only after about 500 fs to a value of about $10E_R$. With saturation of the kinetic energy, the correlation build-up is finished, which yields a direct measure of the non-equilibrium correlation time in the system [26].

Notice that model (c) was shown to conserve total energy exactly; see section 2.2. Therefore, the long increase of the kinetic energy is merely related to a strong overestimation of the retardation. We also investigated the relevance of higher-order retardation contributions numerically. The first-order term contributes to the kinetic energy just after the saturation of model (b), but the effect is less by an order of magnitude. This indicates that for finite times the retardation expansion (beyond the zeroth-order term) is poorly converging, at least within the Born approximation and without taking into account self-energy effects.

Notice the surprisingly good agreement of the kinetic energy behaviour for models (b) and (d). This allows us to conclude that the actual memory depth (which is zero in model (b)) is rather small. On the other hand, in model (c), the memory depth has the maximum value (equal to the actual time t), which strongly overestimates retardation effects. To further investigate the effect of finite memory depth and of self-energy, we solved equation (1) with

non-zero damping, treating the self-energy approximately. The simplest approximation is to neglect the renormalization of the real part of the energy (related to Re Σ), but to include the damping coefficients $\gamma(p, t)$ and calculate them from the Markovian limit of the retarded self-energies Im $\Sigma^R(p, t, t)$. This means that we use as the damping coefficients the intraband dephasing rates calculated from the Markovian Boltzmann equation with the actual distribution function. The results show the same tendency as the Kadanoff–Baym equations: the relaxation is faster for the larger κ-value [26]. This is due to the fact that with decreasing κ, the dephasing rates γ grow rapidly, reducing at the same time the effective range of the τ-integration in equation (1) and, hence, the whole collision integral. However, the Markovian approximation for the self-energy turns out to be too large. As a result, with this approximation the relaxation of the distribution function is slowed down significantly in comparison to all other models. The reason is that in this approximation, the damping 'switched on' instantaneously rather than building up with the correlations. At the same time, the kinetic energy increases even more strongly than according to model (c), which here is a consequence of the violation of total energy conservation mentioned in the discussion of equation (4) above, caused by the neglect of the real part of the self-energy.

On the other hand, a self-consistent treatment of the retarded self-energy is possible. One can calculate the retarded self-energy in the second Born approximation from its full non-Markovian expression and keep both the real and the imaginary part. The collision integral calculated in this way shows good quantitative agreement with the results of the full two-time calculations (d). Results for various approximations for the self-energy will be given in [27].

4. Discussion

Despite their model character, our calculations allow a number of conclusions to be reached regarding the theoretical description of carrier–carrier scattering on short time-scales.

(i) In conserving total energy, the non-Markovian kinetic equation (1) provides a significant improvement over conventional kinetic equations. Without self-energy effects the conservation is exact. The inclusion of damping into the kinetic equation gives rise to additional contributions to the total energy. The commonly used phenomenological expressions for the damping violate energy conservation. Using total energy conservation as a criterion allows us to test the consistency of the approximations for the retarded self-energy, e.g. in the generalized Kadanoff–Baym *ansatz*. The physically correct conservation behaviour may be restored if also the real part of the renormalization (self-energy) is included and a self-consistent non-Markovian treatment of the self-energy is performed.

(ii) The most important non-Markovian effect turns out to be the kinetic energy increase. As a result, high-momentum states are more populated and the temperature of the final state is higher than predicted by Markovian models. This may significantly alter the thermodynamics and transport properties of the stationary state in comparison to those predicted by Markovian kinetic equations.

(iii) The inclusion of self-energy effects is essential for a correct description of the relaxation in the long-time limit. However, self-energy has to be treated well, balanced with the kinetic equation. This requires self-consistency, with respect to the actual distribution function, as to the level of approximation (e.g. Markovian versus non-Markovian). A fully self-consistent treatment is possible only on the basis of the full Kadanoff–Baym equations.

(iv) Good quantitative agreement with the results of the Kadanoff–Baym calculations can be achieved from a retardation expansion of the non-Markovian collision integral (1),

even from the first expansion term (approximation (b)). This means that the neglect of both the memory and the self-energy effects seems still to retain the main effects (energy broadening), at least within the Born approximation.

(v) As a consequence of point (ii), experimental tests of memory effects should be designed to probe directly the tail of the distribution. The best candidates are systems with strong carrier interaction, such as quantum-confined semiconductor structures, since the actual amount of kinetic energy increase directly depends on the strength of the interaction.

For the extension to femtosecond relaxation in semiconductors, the kinetic equation (1) has to be generalized to include the hole component(s) and the interband polarization dynamics, i.e. to the generalized semiconductor Bloch equations; see e.g., [7, 8]. Furthermore, the use of a static approximation which is mainly dictated by the numerical complexity is not always justified. In pre-excited or electrically pumped semiconductors (optical amplifiers and lasers), this approximation may safely be regarded as fully sufficient microscopic description. For optically excited semiconductors, a static model should be sufficient to describe processes after longer times. For the initial stage, the description of carrier generation has to include screening build-up [15, 16], for which (once a sufficient electron–hole density has been created) the appropriate approximation is the RPA [5, 6]. For the case of strong coupling (low density; the first few femtoseconds of the excitation), the Born approximation fails, and one has to use the ladder approximation (the T-matrix approximation), which, moreover, allows one to describe the formation of bound complexes, such as excitons and bi-excitons [29] .

Acknowledgments

References

[1] For a review, see, e.g.,
    Shah J 1989 *Solid State Electron.* **32** 1051
[2] Zwanzig R 1960 *J. Chem. Phys.* **33** 1338
[3] Prigogine I and Resibois I 1962 *Non-Equilibrium Statistical Mechanics* (New York: Interscience)
[4] Klimontovich Yu L 1982 *Kinetic Theory of Nonideal Gases and Nonideal Plasmas* (Oxford: Pergamon)
[5] Kuznetsov A V 1991 *Phys. Rev.* B **44** 8721
[6] Haug H and Ell C 1992 *Phys. Rev.* B **46** 2126
[7] Tran Thoai D B and Haug H 1993 *Z. Phys.* B **91** 199
[8] Binder R and Koch S W 1995 *Prog. Quantum Electron.* **19** 307
[9] Hartmann M and Schäfer W 1992 *Phys. Status Solidi* b **173** 165
[10] Banyai L, Tran Thoai D B, Remling C and Haug H 1992 *Phys. Status Solidi* b **173** 149
[11] Zimmermann R 1992 *J. Lumin.* **53** 187
[12] Schilp J, Kuhn T and Mahler G 1994 *Phys. Rev.* B **50** 5435
[13] Banyai L, Tran Thoai D B, Reitsamer E, Haug H, Steinbach D, Wehner M U, Wegener M, Marschner T and
    Stolz W 1995 *Phys. Rev. Lett.* **75** 2188
[14] El Sayed K, Banyai L and Haug H 1994 *Phys. Rev.* B **50** 1541
[15] El Sayed K, Schuster S, Haug H, Herzel F and Henneberger K 1994 *Phys. Rev.* B **49** 7337
[16] Manzke G, Henneberger K, Heeg J, El Sayed K, Schuster S and Haug H 1995 *Phys. Status Solidi* b **188** 395
[17] Schilp J, Kuhn T and Mahler G 1995 *Phys. Status Solidi* b **188** 417

Mahan G D 1986 *Many-Particle Physics* (New York: Plenum)

[18] Bärwinkel K 1969 *Z. Naturf.* a **24** 484

[19] A part of the results has been presented by the current authors at the *International Conference on Strongly Coupled Plasmas* and is published in the proceedings:
Kraeft W D, Schlanges M, Haberland H and Bornath T (ed) 1996 *Physics of Strongly Coupled Plasma* (Singapore: World Scientific)

[20] Fetter A L and Walecka J D 1971 *Quantum Theory of Many-Particle Systems* (New York: McGraw-Hill)

[21] Kadanoff L P and Baym G 1962 *Quantum Statistical Mechanics* (New York: Benjamin)

[22] Danielewicz P 1984 *Ann. Phys., NY* **152** 239, 305

[23] Lipavski P, Spicka V and Velicky B 1986 *Phys. Rev.* B **34** 6933

[24] Köhler H S 1995 *Phys. Rev.* C **51** 3232

[25] Köhler H S 1996 *Phys. Rev.* E **53** 3145

[26] Bonitz M and Kremp D 1996 *Phys. Lett.* **212A** 83

[27] Bonitz M, Kremp D, Binder R, Kraeft W D and Köhler H S 1996 to be published

[28] Kremp D, Bornath T, Bonitz M and Schlanges M 1996 to be published

[29] Kremp D, Bonitz M, Kraeft W D and Schlanges M 1996 submitted

[30] See, e.g.,
Meystre P and Sargent M III 1991 *Elements of Quantum Optics* 2nd edn (Berlin: Springer)

[31] In the case of non-zero initial correlations, the initial conditions are more complex. One can incorporate them either by using an additional collision term or the procedure of imaginary time stepping proposed by Danielewicz [22]. In the latter case, the one-particle correlation function has to be given initially over a whole area in the t–t' plane rather than at a single point.