

## Short-time dynamics of correlated many-particle systems: Molecular dynamics versus quantum kinetics

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Ultrafast relaxation and correlation buildup in an  $N$ -particle system can be described theoretically using two completely different methods: mechanical equations of motion (molecular dynamics) and quantum-statistical models (Kadanoff-Baym equations). We propose to perform detailed quantitative comparisons of the two methods to obtain a powerful and unbiased tool for testing different approximations. Results of such comparison are presented for a weakly coupled electron gas, which show remarkable agreement.  
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Ultrafast relaxation phenomena, which are related to the buildup of correlations, are currently of great interest in a variety of fields, ranging from plasmas to semiconductors and nuclear matter; see, e.g., [1]. This has been stimulated mainly by the development of femtosecond lasers, which allow one both to excite the nonequilibrium particle ensemble and to probe it with high accuracy. At the same time, this created the need for precise theoretical modeling of these phenomena.

The conventional description of relaxation processes is based upon irreversible kinetic equations of the Boltzmann type. However, these equations are not suitable for the situations that are of interest here because they are valid only for times longer than the correlation time  $\tau_{cor}$ , they do not include initial correlations, and they conserve only kinetic energy instead of total energy [2,3]. Thus, for the theoretical description of ultrafast relaxation phenomena, generalized kinetic equations are necessary. Such equations have been extensively studied in recent years, with the help of nonequilibrium Green's functions (see, e.g., [4,5]) and density operator techniques, (e.g. [2,3], and references therein). However, due to the complex form of these equations, so far only the Born approximation, i.e., the limit of small coupling parameters  $\Gamma \ll 1$ , where  $\Gamma$  is the ratio of the potential and the kinetic energy in the system, is feasible for systematic numerical studies.

On the other hand, the time evolution of a system of  $N$  interacting particles is completely determined by the fundamental equations of classical or quantum mechanics:  $N$  coupled Newton's equations or, in the quantum case, the  $N$ -particle Schrödinger equation, supplemented with initial conditions for the particle coordinates and momenta  $\mathbf{r}_i(t_0), \mathbf{p}_i(t_0)$ , or the wave function  $\Psi_{1\dots N}(t_0)$ , respectively. The principal problem that only limited information on the initial state may be available is successfully overcome by performing multiple runs for different initial conditions (microstates) with a subsequent ensemble averaging. This is the well-known idea of molecular-dynamics simulations that have been very successful in modeling a large variety of relaxation processes in classical many-particle systems both weakly and strongly coupled. However, for quantum systems

with finite degeneracy parameter  $\eta = n\Lambda^3/(2s+1) \geq 1$  (where  $n$  is the density,  $s$  the spin projection, and  $\Lambda = h/\sqrt{2\pi mk_B T}$  the thermal de Broglie wavelength), the mechanical treatment has to be based on the  $N$ -particle Schrödinger equation (nonrelativistic case), which becomes very complicated if the particle number is growing. Therefore, other concepts of quantum molecular dynamics have been proposed (see, e.g., [7]), which are based upon an approximate calculation of the wave function and already achieved remarkable results (some recent results are presented in [1]). Yet these methods are only emerging and we will not discuss them here.

Due to the mentioned limitations of kinetic theory and classical molecular dynamics (MD), comparisons of their results are of great interest. Such comparisons have been performed previously, but only for thermodynamic or kinetic properties. It is now well established that (reversible) mechanical dynamics is able to reproduce (irreversible) relaxation results of kinetic theory on sufficiently long time scales. However, no comparisons have been made of the short-time behavior ( $t_0 \leq t < \tau_{cor}$ ) of correlated systems. This is not trivial, since one first has to clarify what kind of kinetic theory is equivalent to the MD approach in this regime. It is the purpose of our paper to answer this question. We compare the underlying concepts of both approaches and show that only kinetic equations that are defined as an initial-value problem may be equivalent to MD. The best candidate for this task is found to be the quantum kinetic equations of Kadanoff and Baym [8], which, however, have to be generalized to allow for arbitrary initial correlations. Finally, we present a numerical comparison between MD and Kadanoff-Baym calculations for the case of a weakly coupled and weakly degenerate electron gas, which show remarkable agreement.

Let us consider in detail the concepts of the two approaches.

(i) Both MD and kinetic theory are based on the fundamental equations of motion of classical or quantum mechanics (see above).

(ii) Both approaches differ only in the treatment of these equations: While MD works with microstates, kinetic theory

uses ensemble-averaged quantities, such as the  $N$ -particle density operator  $\rho_{1\dots N}$ . The time evolution of this averaged quantity is the von Neumann equation. If it is supplemented with an initial condition  $\rho_{1\dots N}(t=t_0)=\rho_{1\dots N}^0$ , it is fully equivalent to the  $N$ -particle Schrödinger equation: Both are mechanical equations that are time reversible and conserve energy.

(iii) Thus, both approaches use ensemble averages, only in different places: In the kinetic case, the ensemble average is performed *before* solving the equations of motion, while in the case of MD, it is performed *afterward*, on the solutions (realizations) of the microscopic equations.

(iv) Therefore, the theories must lead to the same results for all ensemble averages (observables).

(v) The reduction of the  $N$ -particle problem is, in the MD case, performed by simply taking only a small piece  $N_{MD}\ll N$  of the system and including *all interactions*, while the kinetic approach takes *all particles* but includes only a subset of the interactions.

The main conclusion of points (i)–(iv) is that, in fact, agreement between both concepts is possible. If the relaxation starts from the same initial state, the two concepts must give the same result for ensemble averages for all times.

Of course, the practical question arises as to whether this agreement can be achieved also for approximations, since the approximation schemes [point (v)] are completely different. Thus we have to find formulations of kinetic theory that (a) are given as an initial-value problem and allow for arbitrary initial correlations and (b) preserve the conservation properties of the full  $N$ -particle case (ii). Furthermore, (c) the theory should be straightforwardly extendable to all situations of interest, including arbitrary values of the coupling and the degeneracy parameters  $\Gamma$  and  $\eta$ .

The most general equations for the time evolution of quantum ensemble averages are generalized Kadanoff-Baym equations

$$\begin{aligned} & \left( i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2 \nabla_1^2}{2m} \right) g^{\cong}(1,1') - \int d\bar{r}_1 \Sigma^{HF}(1,\bar{1}) g^{\cong}(\bar{1},1') \\ & = F^+(1,1') + \int_{t_0}^t d\bar{t} \bar{t}_1 \{ \Sigma^>(1,\bar{1}) - \Sigma^<(1,\bar{1}) \} g^{\cong}(\bar{1},1') \\ & \quad - \int_{t_0}^{t'} d\bar{t} \bar{t} \Sigma^{\cong}(1,\bar{1}) \{ g^>(\bar{1},1') - g^<(\bar{1},1') \}, \end{aligned} \quad (1)$$

where  $t_0$  is a *finite* initial time and  $F^+$  contains arbitrary initial binary correlations

$$\begin{aligned} & F^+(1,1') \\ & = \int d\mathbf{r}_2 \{ V(r_1-r_2) \pm V(r'_1-r_2) \} \int d\bar{r}_1 d\bar{r}_2 d\tilde{r}_1 d\tilde{r}_2 \\ & \quad \times g_{12}^R(r_1 r_2 t, \bar{r}_1 \bar{r}_2 t_0) g_{12}^<(\bar{r}_1 \bar{r}_2 t_0, \tilde{r}_1 \tilde{r}_2, t_0) \\ & \quad \times g_{12}^A(\tilde{r}_1 \tilde{r}_2 t_0, r'_1 r_2 t'). \end{aligned} \quad (2)$$

Here  $\mathbf{l}=(\mathbf{r}_1 s_3 t_1)$ ,  $V$  is the interaction potential,  $\Sigma^{HF}$  the Hartree-Fock self-energy, and  $g^{R(A)}$  are retarded (advanced)

Green's functions. The introduction of initial correlations is discussed in some detail in [5] and [9]; see also [10].

The Kadanoff-Baym equations are equations of motion for special ensemble averages, the two-time correlation functions  $g^{\cong}$ , which allow for the calculation of all averages, such as the Wigner distribution and mean potential energy ( $\mathcal{V}$  is the volume),

$$f(\mathbf{p},t) = -i\hbar g^<(\mathbf{p},t,t), \quad (3)$$

$$\begin{aligned} \langle V \rangle(t) &= \frac{1}{4} \mathcal{V} \hbar \int \frac{d\mathbf{p}}{(2\pi\hbar)^3} \left\{ \left( i\hbar \frac{\partial}{\partial t} - i\hbar \frac{\partial}{\partial t'} \right) - \frac{p^2}{m} \right\} \\ & \quad \times (\mp i) g^<(\mathbf{p},t,t')|_{t=t'}. \end{aligned} \quad (4)$$

The Kadanoff-Baym equations (1) have a number of remarkable properties. They trivially include quantum effects (arbitrary degeneracy). There are no consistency problems: The structure of approximations is completely determined by the approximation for the self-energies  $\Sigma^{\cong}$  alone. Moreover, the conservation properties of Eqs. (1) depend on simple well-known symmetry properties of the self-energies [8]. Due to this consistency, the equations yield the correct asymptotic state of a correlated many-particle system. Furthermore, for the self-energies there exist powerful nonperturbative methods based on diagrammatic expansions [8], which allow for a systematic derivation of approximations, including strong coupling and many-body effects. In the generalized form (1), the Kadanoff-Baym equations are time reversible and allow one to include arbitrary binary correlations at a finite initial time  $t_0$ . Thus Eqs. (1) satisfy the above requirements (a)–(c). In this form, statistical mechanics and molecular dynamics are equivalent [12].

Let us discuss now what kind of comparisons between the two approaches are possible. As pointed out in (iv), comparable quantities are ensemble averages. Quantities that are sensitive to the short-time dynamics, which we are concerned with, have been found to be the kinetic and the correlation energy [6,2,11]. They reflect very well the decay of the initial correlation and the buildup of correlations due to the interaction. Typically, at the initial stage  $t_0 \leq t \leq \tau_{cor}$ , the potential energy changes until it saturates around  $t \sim \tau_{cor}$ . For larger times, the potential and kinetic energies each remain approximately constant, indicating that the kinetic regime has been reached. The amount of potential-energy change is a measure for the strength of the interaction, while the time scale of this change yields an estimate for the correlation time itself and thus for the characteristic times of the relevant relaxation mechanisms in the system. Therefore, we will use the time evolution of kinetic energy for comparison below.

The next question is the appropriate choice of system to study and its parameters. Interestingly, the advantages of one method overlap with the weak points of the other: Quantum effects, which are problematic in the MD approach, are trivially included in the Kadanoff-Baym equations. Conversely, strong-coupling effects, which are difficult to handle in the latter, are no problem for the former. This creates a great potential for a systematic combination of both approaches proposed here. Advances to different approximations in one

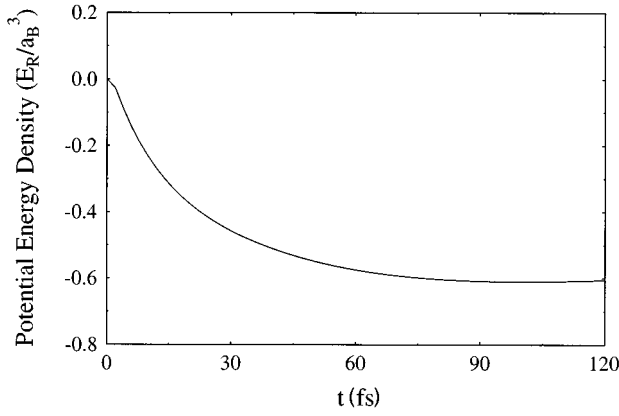


FIG. 1. Potential-energy density from the Kadanoff-Baym calculation. The electron density and initial kinetic-energy density are  $1.228a_B^{-3}$  and  $64.2E_Ra_B^{-3}$ ; the Rydberg energy and the Bohr radius are  $E_R=4.2$  meV and  $a_B=132$  Å.

field can be checked quantitatively on well-established results of the other. Deviations from one another can provide valuable indications for possible inconsistencies of the underlying theoretical concepts.

The starting point for this kind of combination has to be a simple situation where quantitative agreement is expected. We therefore consider an electron gas and neglect initial correlations. Since the parameter ranges where both methods give reliable results overlap in the corner of small coupling and weak degeneracy, we chose  $\Gamma=0.1$  and  $\eta=0.1$ . For the comparison, we use results of Zwicknagel *et al.* [11], who performed classical MD simulations for these parameters. They used periodic boundary conditions with  $N_{MD}=500$  particles. We performed Kadanoff-Baym calculations for the same parameters.

The MD simulation used a microstate with initial coordinates and velocities  $\mathbf{r}_i(t_0), \mathbf{v}_i(t_0)$ , which were distributed homogeneously in coordinate space and isotropically in momentum space, according to the initial one-particle distribution  $f(\mathbf{r}, \mathbf{v}, t_0) = f(v, t_0) \sim \exp[-64(v-1)^2]$ . The initial state was uncorrelated, i.e., the initial potential energy was  $\langle V \rangle(t_0) = 0$ . The initial value of the coupling parameter was  $\Gamma_0 = 0.1$ , which was calculated using the initial kinetic energy instead of temperature  $\Gamma_0 = (4\pi n/3)^{1/3} e^2 / (kT_0)$ , with  $3/2kT_0 = E_{kin}(t_0)$ .

The Kadanoff-Baym equations were solved as in Ref. [6]. For the weak-coupling–weak-degeneracy limit that we are concerned with, the self-energy has to be calculated in the second-order Born approximation

$$\begin{aligned} \Sigma^{\cong}(\mathbf{p}_1, t, t') &= 2\hbar^2 \mathcal{V}^2 \int \frac{d\mathbf{p}_2}{(2\pi\hbar)^3} \int \frac{d\mathbf{q}}{(2\pi\hbar)^3} V\left(\frac{\mathbf{q}}{\hbar}, t\right) V\left(\frac{\mathbf{q}}{\hbar}, t'\right) \\ &\times g^{\cong}(\mathbf{p}_1 + \mathbf{q}, t, t') g^{\cong}(\mathbf{p}_2 - \mathbf{q}, t, t') g^{\cong}(\mathbf{p}_2, t', t). \end{aligned} \quad (5)$$

For the matrix element of the interaction potential  $V(q)$ , we used the static long-wavelength limit of the screened potential in the random-phase approximation, where the inverse

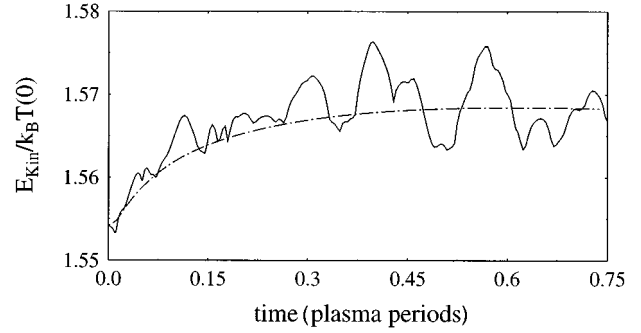


FIG. 2. Comparison of the kinetic-energy relaxation: molecular dynamics vs Kadanoff-Baym equations. The latter result was shifted to match the starting point of the MD curve.

screening length  $\kappa(t)$  was calculated self-consistently from the current nonequilibrium distribution  $f(p, t)$ ,

$$V(q, t) = \frac{4\pi e^2 / \epsilon_r}{q^2 + \kappa^2(t)}, \quad \kappa^2(t) = \frac{4m}{\pi} \int_0^\infty dp f(p, t). \quad (6)$$

For our calculations, we chose typical semiconductor parameters (bulk GaAs)  $\epsilon_r = 13.99$  and  $m/m_r = 1.284$  and took exactly the same initial distribution as above. But the kinetic approach contains an additional length parameter, the screening length  $\kappa^{-1}$ , allowing one to reproduce the MD conditions using different distributions (e.g., different peak positions in units of  $\kappa$ ). Our choice was dictated by the requirement of weak degeneracy  $\eta = 0.1$  and negligible Pauli blocking effects.

In Fig. 1 the Kadanoff-Baym result for the evolution of potential-energy density during the initial period is given; cf. Eq. (4). As one can see, the potential-energy change saturates after about 120 fs. One readily verifies that this time is close to the plasma period  $\tau_p = \sqrt{\pi m \epsilon_r / n e^2} \approx 160$  fs, which is the correlation time in this system. Due to energy conservation, at the same time kinetic energy increases; see Fig. 2.

To compare the Kadanoff-Baym calculation with the MD data of Zwicknagel *et al.*, we had to rescale our results for the kinetic energy in their units (units of  $kT_0$ ). The results of both calculations are shown in Fig. 2. Notice that the MD data in Ref. [11] were given for a single realization and therefore contain fluctuations around the ensemble average, which are not present in the Kadanoff-Baym run. Nevertheless, the agreement between both calculations is obvious.

In summary, we have discussed two theoretical methods for the investigation of ultrafast relaxation phenomena: molecular dynamics and the generalized Kadanoff-Baym equations (1). Both constitute mechanical models (reversible initial-value problems) of the  $N$ -particle problem that conserve the total energy and yield the correct asymptotic state and are therefore expected to yield identical results for ensemble averages for identical initial data (including initial correlations). Such quantitative agreement was demonstrated for a weakly coupled, weakly degenerate electron gas by a comparison of the evolution of kinetic energy.

Future comparisons can also use other quantities, including two-time correlation functions, and consider larger values of the coupling and degeneracy parameters, yielding

valuable information on the influence of strong coupling and quantum effects. Developments in statistical physics such as strong-coupling approximations for the Kadanoff-Baym equations and also quantum molecular-dynamics concepts will benefit from the proposed comparison.

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- [11] G. Zwicknagel, C. Toepffer, and P.-G. Reinhard, in *Physics of Strongly Coupled Plasmas* (Ref. [1]), p. 45.
- [12] This does not rule out other generalized kinetic equations, such as non-Markovian equations for the Wigner distribution, which can be derived from Eq. (1), e.g., [4,5], but our choice is the most general one.