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Evolution of a subsystem in a heat bath with no initial factorized state assumption

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HIGHLIGHTS

- Homogeneous evolution equations retaining subsystem–heat bath initial correlations.
- Initial subsystem–heat bath correlations influence a subsystem evolution process.
- Initial electron–phonon correlations contribute to polaron mobility.

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ABSTRACT

A problem of the realistic initial conditions for the evolution equation of the statistical operator of a subsystem in interaction with a heat bath is addressed. Starting from the canonical equilibrium distribution for a full subsystem–heat bath system, the evolution of a subsystem driven by an external force is considered. The exact new homogeneous time-convolution and time-convolutionless (time-local) generalized master equations for a subsystem statistical operator are obtained. They include initial (conventionally ignored) correlations on an equal footing with collisions in the kernel governing their evolution. No conventional initial factorized state assumption is used. In the second-order approximation on the subsystem–heat bath interaction, when both equations become identical, time-local and essentially simpler, they are applied to the electron–phonon system in an external electric field. It is shown, that, in general, the initial correlations influence the subsystem's evolution in time. It is also explicitly demonstrated (in the linear response regime), that on the large timescale (actually at $t \to \infty$) initial correlations cease to influence the electron evolution in time, the time-reversal symmetry breaks and the subsystem enters the kinetic irreversible regime. At the same time, the initial correlations contribute to kinetic coefficients like the electron mobility. As an application, the low-temperature mobility for weak coupling (Fröhlich) polaron and arbitrary coupling (Feynman) polaron, which was under debate for a long time, is obtained. It shows the corrections to polaron mobility due to initial correlations.

1. Introduction

Since the introduction of the famous Boltzmann equation, the concept of chaos is a central topic in kinetic theory. The principal questions are: How to rigorously derive the irreversible kinetic equations from underlying microscopic (reversible) classical or quantum dynamic equations and what is the reason for the emergence of irreversibility. Boltzmann replied to the criticism of H theorem, revealing an irreversible evolution to an equilibrium state, that his equation has a statistical

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meaning. Several approaches are usually used to address these problems, commonly starting with the linear Liouville–von-Neumann equation for a distribution function (statistical operator) of the N-particle ($N \gg 1$) system under consideration. This equation, however, is not practically useful due to enormous number of variables, but fortunately, we need only the reduced distribution functions (statistical operators) for calculation of the measurable values (statistical expectations) characterizing a nonequilibrium state of a many-particle system. Looking for an equation describing the evolution of a one-particle distribution function (statistical operator), we arrive at the chain of coupled first-order differential equations for s-particle distribution functions $F_s(x_1, \ldots, x_s, t)$ ($1 \leq s \leq N$) known as the BBGKY hierarchy [1], where x_i stands for a particle (with number i) coordinate and momentum (in case of classical mechanics) and in the case of quantum mechanics x_i is a particle coordinate or momentum. Thus, the equation for a one particle distribution function $F_1(x_1, t)$ contains a two-particle function $F_2(x_1, x_2, t)$, etc. Therefore, in order to obtain the Boltzmann equation for a one particle distribution function $F_1(x_1, t)$, we need to decouple the first BBGKY equation by setting

$$F_2(x_1, x_2, t) = F_1(x_1, t)F_1(x_2, t), t \geq t_0, \tag{1}$$

which means that the tagged particles 1 and 2 are statistically independent. Of course, Eq. (1) is wrong from the mechanics point of view, even if assumed at the initial time t_0, because the inter-particle interaction creates correlations at $t > t_0$. However, it can be expected that the property (1) will be realized in some asymptotic situation at a suitable scaling limit.

Thus, one of the possibilities to obtain the closed nonlinear Boltzmann equation for $F_1(x_1, t)$ is to find the conditions at which the *propagation of chaos* expressed by Eq. (1) holds (Boltzmann's "*Stosszahlanzatz*"). Indeed, Grad [2] postulated the validity of the Boltzmann equation (and thus of the propagation of chaos (1)) for very rarefied gas of the hard spheres in the so-called Boltzmann–Grad limit, when $N \to \infty$, $\varepsilon \to 0$ (N is a number of particles per unit volume, ε is a particle diameter). After that Lanford [3] succeeded in deriving rigorously the Boltzmann equation, though for a short time interval, using Cercignani's [4] hierarchy of equations for the hard-sphere system.

Another approach to dealing with the BBGKY hierarchy was suggested by Bogoliubov [1]. He introduced several characteristic timescales for a gas of particles and postulated the principle of weakening of initial correlations which implies that at a sufficiently large time $t - t_0 \gg t_{cor}$ (t_{cor} is the correlation time due to interparticle interaction), all initial correlations (existing at the initial instant t_0) are damped and the time-dependence of multiparticle distribution functions is completely determined by the time-dependence of a one-particle distribution function (Bogoliubov's ansatz). This assumes the existence of the time interval (time scale)

$$t_{cor} \ll t - t_0 \ll t_{rel} \tag{2}$$

(where t_{rel} is the relaxation time for a one-particle distribution function) and leads to an approximate conversion (valid only on the large time scale indicated above) of the inhomogeneous equation (including two-particle correlations) for a one-particle distribution function (of the BBGKY hierarchy) into a homogeneous nonlinear equation. Thus, if we even do not assume a chaos at initial moment of time t_0, the Bogoliubov principle implies that on every time interval (2) the correlation between particles vanishes, i.e. the factorization condition for the BBGKY chain can be conventionally used from the very beginning, and the propagation of chaos (1) is (presumably) justified. Actually, the Bogoliubov principle of weakening of initial correlations is introduced as the boundary (initial) condition for the BBGKY chain. For example, it can be written as the following asymptotic ($t_0 \to -\infty$)

$$\lim_{t-t_0\to\infty} U(t, t_0)\left[F_N(x_1, \ldots, x_N, t_0) - \prod_{i=1}^{N} F_1(x_i, t_0)\right] = 0, \tag{3}$$

where $F_N(x_1, \ldots, x_N, t_0)$ is an N-particle distribution function at $t = t_0$ and $U(t, t_0)$ is the operator determining the evolution of all x_i in time. Using this approach, Bogoliubov successfully derived, in particular, the classical and quantum Boltzmann equations, which describe the time-evolution with the characteristic time t_{rel} but are unsuitable for taking the initial evolution stage $t_0 \leq t \leq t_{cor}$ into account.

However, the factorizing initial condition approximation is in many cases doubtful, as it has been clearly pointed out by van Kampen [5]. Thus, it would be desirable to avoid the randomness approximation by, e.g., including the initial correlations into consideration, and to obtain the equations which describe the system evolution on an arbitrary timescale. It would, in particular, enable studying the influence of initial correlations on the relaxation process and the transition from reversible (short timescale) dynamics to a kinetic (large timescale) regime. The method which allows to include initial correlations into the kernel governing the evolution of the relevant part of the statistical operator of the many-body system (like gas or liquid) and obtain homogeneous generalized master equations (GMEs) valid on any timescale was developed in works [6–9].

The same situation is in another important case of a subsystem S of the total system interacting with the remaining part of a full system Σ in an equilibrium state (a thermal bath). The standard approach here is the projection operator method leading to the time-convolution [10–12] and time-convolutionless [13–15] Generalized Master Equations (GMEs) for the relevant part of statistical operator. These equations are the inhomogeneous ones and contain the irrelevant initial condition term comprising all subsystem–heat bath correlations. A proper accounting for these initial correlations is an important (and generally not easy) problem to deal with (see, e.g., [13]). Thus, in this case, the factorizing initial condition for the statistical operator of the whole system $\rho(t)$

$$\rho(t_0) = \rho_S(t_0)\rho_\Sigma \tag{4}$$