Markovian kinetic equations in a nonequilibrium statistical ensemble formalism

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The nonlinear quantum kinetic theory for many-body systems either near or far from equilibrium that a nonequilibrium ensemble formalism provides is revisited. In this communication we consider an important limit of such transport equations, consisting of the memoryless approximation, which leads to the so-called Markovian kinetic equations. They are derived in Zubarev's approach to the method, and next applied to a particular model of a spin system in interaction with a thermal bath of lattice vibrations. The limitations of the approach, as well as some criticism it has received, are discussed. [S1063-651X(98)10203-9]

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A physical question of quite large interest is the one related to the evolution of the macroscopic state of dissipative systems. Earlier attempts to tackle this problem go back to the fundamental work of Maxwell and Boltzmann in the nineteenth century. They were followed in the present century by a vast number of contributions by many authors, particularly the nonequilibrium statistical operator method (NESOM) [1], which provides for a nonlinear kinetic theory [1–3] of large relevance for dealing with a large class of experimental situations in dissipative systems arbitrarily away from equilibrium. Among the different approaches to NESOM, the one due to Zubarev [1] (the renowned Russian scientist deceased a few years ago [4]) appears to be soundly based, and provides a most concise and practical method. In this theory the so-called *Markovian limit* plays an important role, which is valid in the weak coupling limit of interaction between subsystems, when one can retain terms only up to second order in the interaction strength. We carry an analysis and discussion of it, and we introduce as an illustration the case of a spin system in interaction with the lattice.

The first, and fundamental, step in NESOM is the choice of the basic set of variables deemed appropriate for the characterization of the macroscopic state of the system. This involves a description in terms of, say, the mechanical quantities $\{\hat{P}_j(\mathbf{r})\}$, $j=1,2,\ldots$, with the upper circumflex indicating Hermitian operators, and the dependence on the space coordinate $\mathbf{r}$ indicates the local density of the corresponding dynamical quantity $\hat{P}_j$. The NESOM nonequilibrium statistical operator will be denoted by $\rho_\epsilon(t)$, and Zubarev's approach is consistently used. The thermodynamic state is characterized by a point in Gibbs—or thermodynamic state—space given, at time t, by the set of macrovariables $\{Q_j(\mathbf{r},t)\}$, $j=1,2,\ldots$, which are the averages of the $\hat{P}_j(\mathbf{r})$, i.e., $Q_j(\mathbf{r},t)=\mathrm{Tr}\{\hat{P}_j(\mathbf{r})\rho_\epsilon(t)\}$. The choice of the basic variables is assisted by the fundamental Bogoliubov procedure of the contraction of the description based on a hierarchy of relaxation times [1,5], introducing a separation of the total Hamiltonian into two parts, namely,

$$\hat{H}=\hat{H}_0+\hat{H}', \tag{1}$$

where $\hat{H}_0$ is the ''relevant'' part composed of the Hamiltonian for the free subsystems and the strong interactions leading to processes with very short relaxation times. The other term, $\hat{H}'$, contains the interactions related to long-time relaxation mechanisms. Assuming that the basic set $\{\hat{P}_j(\mathbf{r})\}$ has been chosen, the nonequilibrium statistical operator is built in NESOM, using the principle of maximization of the statistical-informational entropy, with fading memory and an *ad hoc* hypothesis that introduce from the outset irreversible evolution from an initial condition of preparation of the system [1].

Let us consider the construction of the NESOM nonlinear quantum kinetic theory. First, it should be noticed that the equations of evolution for the basic variables are given by

$$\frac{\partial}{\partial t}Q_j(\mathbf{r},t)=\mathrm{Tr}\left\{\frac{1}{i\hbar}[\hat{P}_j(\mathbf{r}),\hat{H}]\;\rho_\epsilon(t)\right\}, \tag{2}$$

that is to say, they are the average over the nonequilibrium ensemble of the corresponding Heisenberg equation of motion for quantities $\hat{P}_j(\mathbf{r})$. Equation (2) can be rewritten in the form of equations of evolution of the type

$$\frac{\partial}{\partial t}Q_j(\mathbf{r},t)=\sum_{m=0}^{\infty}\Omega_j^{(m)}(\mathbf{r},t), \tag{3}$$

where the partial collision operators $\Omega_j^{(m)}$, which are of order m and higher in the interaction strengths, are given in [3]. We stress that Eq. (3), which is highly nonlinear, contains contributions nonlocal in space (space correlations) and memory (time correlations), and can be considered as far-reaching generalizations of Mori's equations [6]. Let us retain only terms up to $m=2$, and take the *Markovian limit* consisting of neglecting contributions of order higher than two, when the kinetic equations become [1–3]

$$\frac{\partial}{\partial t}Q_j(\mathbf{r},t)=J_j^{(0)}(\mathbf{r},t)+J_j^{(1)}(\mathbf{r},t)+J_j^{(2)}(\mathbf{r},t), \tag{4}$$

where

$$J_j^{(0)}(\mathbf{r},t)=\mathrm{Tr}\left\{\frac{1}{i\hbar}[\hat{P}_j(\mathbf{r}),\hat{H}_0]\overline{\rho(t,0)}\right\};$$

$$J_j^{(1)}(\mathbf{r},t)=\mathrm{Tr}\left\{\frac{1}{i\hbar}[\hat{P}_j(\mathbf{r}),\hat{H}']\overline{\rho(t,0)}\right\} \tag{5}$$

and

$$J_j^{(2)}(\mathbf{r},t)=\left(\frac{1}{i\hbar}\right)^2\int_{-\infty}^{t}dt' e^{\epsilon(t'-t)}\mathrm{Tr}\{[\hat{H}'(t'-t)_0,[\hat{H}',\hat{P}_j(\mathbf{r})]]\overline{\rho(t,0)}\}, \tag{6}$$

the lower-right index nought in $\hat{H}'(t'-t)_0$ stands for evolution in the interaction representation (i.e., the evolution due to H_0 alone), and $\overline{\rho(t,0)}$ is the so-called coarse-graining part of the statistical operator $\rho_\epsilon(t)$ [1–3].

Let us next consider in particular a system of N spins in interaction with a lattice, the latter composed of a phonon gas at temperature T_0 and to be taken as an ideal reservoir, and in the presence of a magnetic field $\mathbf{B}=(B_x,B_y,B_z)$. Spin-lattice relaxation is of fundamental relevance in the area of eletronic paramagnetic resonance, the first studies dating back to the work of Waller in 1932. Two types of processes were proposed, a direct one with absorption or emission of a phonon, and a so-called Raman process with scattering of phonons. The theory was extended by van Vleck on the basis of the study of the effect arising out of the modulation of the crystalline electrostatic potential [7]. We are considering here an ideal model involving only the direct process mentioned above. In this case the Hamiltonian is of the form of Eq. (1), where now (third part of Ref. [7])

$$\hat{H}_0=\hat{H}_S+\hat{H}_R=\sum_{j=1}^{N}(\hbar\omega_x\hat{S}_{jx}+\hbar\omega_y\hat{S}_{jy}+\hbar\omega_z\hat{S}_{jz})+\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}\left(a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+\frac{1}{2}\right) \tag{7}$$

and

$$\hat{H}'=i\sqrt{\lambda}\hbar\sum_{j=1}^{N}\sum_{m}\hat{S}_{jm}\sum_{\mathbf{k}}g_m(\mathbf{k})(a_{\mathbf{k}}-a_{-\mathbf{k}}^{\dagger}). \tag{8}$$

In Eq. (7), $\omega_{x,y,z}$ are the Larmor frequencies of the spins in the magnetic field, $\hat{H}_S$ accounts for the precession of the spin around the magnetic field, and H_R the Hamiltonian of the free phonons with frequency dispersion relation $\omega_{\mathbf{k}}$. Moreover, $\hat{S}_x,\hat{S}_y,\hat{S}_z$ are the spin-half operators, a ($a^\dagger$) boson annihilation (creation) operators. In Eq. (8), $m=x,y,z$, λ is a coupling constant, $g_m(\mathbf{k})$ the matrix elements of the interaction between spin and thermal bath. The choice $\omega_y=0$, $g_x=g_y=0$, corresponds to the model Hamiltonian used in the theory of paraeletric resonance and relaxation, where $\hat{S}_m$ stands for isospin [8], and in what follows, for simplicity, we take an isotropic, $g_x=g_y=g_z=g$, model.

The chosen set of basic dynamical variables for the spin system is composed of $3N$ spin operators, namely, $\{\hat{S}_{jx},\hat{S}_{jy},\hat{S}_{jz},j=1,2,\ldots,N\}$, we call $\langle\hat{S}_{jm}|t\rangle$ the corresponding macrovariables, and $F_{jm}(t)$ the associated Lagrange multipliers, with the Zubarev-Peletminskii closure condition of Eq. (2) being satisfied. For the thermal bath, the basic variable is the Hamiltonian $\hat{H}_R$ and, since it is assumed to constantly remain in equilibrium, it is statistically characterized by a canonical distribution in which the associated Lagrange multiplier is $\beta_0=1/k_BT_0$. On the other hand, the contribution to the spin dynamics due to the interaction is

$$\frac{1}{i\hbar}[\hat{S}_{jm},\hat{H}']=i\sqrt{\lambda}\sum_{\mathbf{k}}\epsilon_{mm'mm''}g(\mathbf{k})(a_{\mathbf{k}}-a_{\mathbf{k}}^{\dagger})(\hat{S}_{jm''}-\hat{S}_{jm'}), \tag{9}$$

for each $j=1,2,\ldots,N$, and where $m\neq m'\neq m''$, $m,m',m''=x,y,z$; $\epsilon_{mm'm''}=1$ if $mm'm''$ is a cyclic permutation of xyz (i.e., xyz, zxy, and yzx) and null otherwise. For such a choice of basic variables the auxiliary NESOM nonequilibrium statistical operator is

$$\overline{\rho(t,0)}=\exp\left\{-\phi(t)-\sum_{j=1}^{N}\sum_{m}F_{jm}(t)\hat{S}_{jm}\right\}\times\exp\{-\phi_R-\beta_0\hat{H}_R\}. \tag{10}$$

This operator is the direct product of the auxiliary statistical operator for the spin system times the one for the thermal bath, the latter being the equilibrium canonical distribution as already noticed. We recall that ϕ and ϕ_R ensure the normalization of each one, respectively, and $F_{jm}(t)$ are the Lagrange multipliers that the variational method introduces.

Applying the memoryless approximation of Eq. (4), once it is verified that all four contributions of the type $J^{(1)}$ are null, it follows in a matrix form, which is the same for each spin ($j=1,2,\ldots,N$), that

$$\frac{d}{dt}\mathbf{M}(t)=\mathbb{A}\mathbf{M}(t)+\boldsymbol{\alpha}, \tag{11}$$

where $\mathbf{M}(t)$ is the column vector with components $\langle\hat{S}_x|t\rangle$, $\langle\hat{S}_y|t\rangle$, and $\langle\hat{S}_y|t\rangle$; $\boldsymbol{\alpha}$ is the nonhomogeneous term in this equation, namely, the column vector of components

$$\alpha_m=\frac{\pi}{4\Omega}\int_0^{\omega_D}d\omega G(\omega)\left\{\frac{2\Omega\omega_S\epsilon_{mm'm''}(\omega_{m''}-\omega_{m'})}{\pi\omega(\omega^2-\Omega^2)}+\sum_{m'}(\omega_{m'}-\omega_m)\delta(\omega-\Omega)\right\}, \tag{12}$$

where $\omega_s=\omega_x+\omega_y+\omega_z$, $\Omega^2=\omega_x^2+\omega_y^2+\omega_z^2$, ω_D is Debye cut-off frequency, and $G(\omega)=\lambda|g(\omega)|^2D(\omega)$ where $D(\omega)$ is the density of phonon states, and $g(\omega)$ the matrix element $g(\mathbf{k})$ in frequency space in this isotropic model. The square matrix $\mathbb{A}$ is

$$\mathbb{A}=\begin{bmatrix} -\gamma_x & -\omega_z+a_x & \omega_y+a_x \\ \omega_z+a_y & -\gamma_y & -\omega_x+a_y \\ -\omega_y+a_z & \omega_x+a_z & -\gamma_z \end{bmatrix}, \tag{13}$$

where the quantities γ_m and a_m are given by (we recall that $m'\neq m''$)

$$\gamma_m=\frac{\pi}{2\Omega^2}\int_0^{\omega_D} d\omega G(\omega)[2n(\omega)+1]\Bigg\{\frac{2\Omega^2}{\pi}\epsilon_{mm'm''}(\omega_{m'}-\omega_{m''})(\omega^2-\Omega^2)^{-1} + \Bigg[(\omega_{m''}-\omega_{m'})^2+\sum_{m'}\omega_m(\omega_m-\omega_{m'})\Bigg]\delta(\omega-\Omega)\Bigg\}, \tag{14a}$$

$$a_m=\frac{\pi}{2\Omega^2}\int_0^{\omega_D} d\omega G(\omega)[2n(\omega)+1]\Bigg\{\frac{2\Omega^2}{\pi}\epsilon_{mm'm''}(\omega_{m''}-\omega_{m'})(\omega^2-\Omega^2)^{-1}+\sum_{m'}\omega_{m'}(\omega_{m'}-\omega_m)\delta(\omega-\Omega)\Bigg\}. \tag{14b}$$

Finally, $n(\omega)=[\exp\{\beta_0\hbar\omega\}-1]^{-1}$ is the population of the phonon modes.

Consider now the steady state, which is the final state of equilibrium with the lattice. After some lengthy, but straightforward algebra, we find that the components of the magnetization in the steady state are

$$M_m^{ss}=\langle\hat{S}_m\rangle_{ss}=-\frac{\tilde{\omega}_m}{2\Omega}\tanh\left(\frac{\beta_0\hbar\Omega}{2}\right), \tag{15}$$

where

$$\tilde{\omega}_m=\omega_m\chi_m, \quad \chi_m=(1-q_m)(1-p)^{-1}, \tag{16}$$

$$q_m=\lambda\int_0^{\omega_D} d\omega D(\omega)|g(\omega)|^2(\omega^2-\Omega^2)^{-1}\Bigg\{\sum_{m'}(\omega_m-\omega_{m'})\omega_m^{-1}(2n(\omega)+1)+\Bigg[-2\omega_x\omega_y\omega_z+\sum_{m'\neq m}\omega_{m'}(\Omega^2-\omega_m^2)\Bigg] \times(\Omega\omega\omega_m)^{-1}(2n(\Omega)+1)\Bigg\}, \tag{17a}$$

$$p=\frac{2\lambda}{\Omega^2}\int_0^{\omega_D} d\omega D(\omega)|g(\omega)|^2(\omega^2-\Omega^2)^{-1}(2n(\omega)+1)\eta, \tag{17b}$$

where $\eta=\Omega^2-(\omega_x\omega_y+\omega_x\omega_z+\omega_y\omega_z)$. To be consistent with the fact that the Markovian limit is valid only in first order in λ (second order in the interaction strengths), we expand $(1-p)^{-1}$ in a series of powers of λ around $\lambda=0$ and take only terms up to first order, to obtain $1+p+O(\lambda^2)$. Consequently, up to first order in λ, $\chi_m=1+p-q_m$ and then the renormalized Larmor frequencies are $\tilde{\omega}_m=\omega_m+\Delta\omega_m$ where $\Delta\omega_m=\omega_m(p-q_m)$.

Moreover, taking into account Eqs. (15), (16), and (17) we find that

$$|\mathbf{M}_{ss}|^2=\sum_m|\langle\hat{S}_m\rangle_{ss}|^2=\left[\sum_m\frac{\tilde{\omega}_m^2}{4\Omega^2}\right]\left[\tanh\left(\frac{\beta_0\hbar\Omega}{2}\right)\right]^2=\frac{1}{4}\left[\tanh\left(\frac{\beta_0\hbar\Omega}{2}\right)\right]^2\leqslant\frac{1}{4}, \tag{18}$$

as it should. This is so because we have neglected contributions of type $O(\lambda^2)$ to be consistent with the Markovian approximation. The contribution linear in λ (second order in the interaction strength), in $\tilde{\omega}_x^2+\tilde{\omega}_y^2+\tilde{\omega}_z^2$, that is, $\omega_x\,\Delta\omega_x+\omega_y\,\Delta\omega_y+\omega_z\,\Delta\omega_z$ cancels out, while those of order $O(\lambda^2)$ do not. Overlooking this point led Luczka [9] to the wrong conclusion that the Markovian limit in Zubarev's NESOM has not been properly derived. He claims that Eq. (4) is incorrect, because from it there follow unphysical results, that is, the Lagrange parameters F_m (β_n in his nomenclature) cannot in all circumstances be real numbers as they should. In other words, according to Luczka the Markovianization process in Zubarev's approach does not, in this case, satisfy that the sum of the squares of the steady state values of the spin variables is smaller or at most equal to one-fourth. An alternative Markovianization procedure is attempted by Luczka resorting to a modified version of Davies' technique [10]. Equations of the form of Eq. (11) are obtained but with a modified matrix $\mathbb{A}$ and vector $\boldsymbol{\alpha}$, which apparently corrects the above mentioned claimed incorrectness of the Markovianization procedure described in the previous section. However, the modified terms lead to new equations of evolution for the magnetization which are not Heisenberg equations of motion for the spins averaged over the nonequilibrium ensemble as it should, which are our Eq. (11), but contain additional (spurious) terms. This evidently points to some mistake in Luczka's treatment of the problem, which, as noticed, resides in that a failure of consistency in the calculation has been introduced, consisting in the fact that he obtains the value of $|\mathbf{M}_{ss}|^2$ larger than 1/4, but as a consequence of the presence of terms $O(\lambda^2)$.

Let us now look into the relevant question of analyzing the Lagrange multipliers $F_m(t)$. A straightforward calculation leads to the result that

$$M_m(t)=\langle \hat{S}_m|t\rangle = \mathrm{Tr}\{\hat{S}_m\overline{\rho(t,0)}\}=-\frac{1}{2}\frac{F_m(t)}{F(t)}\tanh\left(\frac{F(t)}{2}\right), \tag{19}$$

where

$$F(t)=[F_x^2(t)+F_y^2(t)+F_z^2(t)]^{1/2}. \tag{20}$$

Using Eqs. (19) and (20), it follows that the Lagrange multipliers can be expressed in the form

$$F_m(t)=-\frac{M_m(t)}{|\mathbf{M}(t)|}\ln\left(\frac{1+2|\mathbf{M}(t)|}{1-2|\mathbf{M}(t)|}\right), \tag{21}$$

where $\mathbf{M}(t)$ is the solution of the equations of evolution for the magnetization, Eq. (11), and $|\mathbf{M}(t)|^2=M_x^2(t)+M_y^2(t)+M_z^2(t)$. In the steady state regime it follows, up to first order in λ (second order in the interaction strengths), that $F_m^{ss}=\beta_0\hbar\tilde{\omega}_m$. This suggests rewriting the Lagrange multipliers as $F_m^{ss}=\beta_m\hbar\omega_m$ where now β_m plays the role of a kind of inverse temperature for the m component of magnetization, which we write as

$$\beta_m=\beta_0+\Delta\beta_m\,;\quad \Delta\beta_m=\beta_0\frac{\Delta\tilde{\omega}_m}{\omega_m}=\beta_0(p-q_m). \tag{22}$$

Finally, we note that using the Lagrange multipliers as defined above, i.e., $F_m^{ss}=\beta_m\hbar\omega_m$, in Eq. (10) and introducing the latter in the expression that defines Zubarev's statistical operator in the steady state, ρ_ϵ^{ss}, we obtain a ''fine-grained'' statistical operator that coincides with the canonical distribution in equilibrium at temperature T_0.

In conclusion, we have considered the particular case of the Markovian limit, showing that the equations of evolution are composed, in this memoryless limit, of a contribution that can be interpreted as the ''golden rule'' of quantum mechanics (involving two-particle collisions) averaged over the nonequilibrium ensemble plus a contribution arising out of the change in time of the macroscopic variables that characterize the macroscopic state of the system. Moreover, we have applied the theory to a specific model for a spin system in interaction with a thermal reservoir composed of the lattice vibrations in the material. The equations of evolution for the variables corresponding to the average of the spin dynamical variables are derived in the memoryless limit. The complete solution for the evolution of the magnetization is obtained, as well as the correct final state of equilibrium of the spin system and the lattice at temperature T_0. In this process we have compared our results, for such system, with those of Luczka [9], who mantained that the Markovian approach as derived by Zubarev, Peletminskii, and us is incorrect. We have shown that such consideration is invalid, and the result of a failure of consistency in the order of the approximations he introduced.

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