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Identity for memory operators in classical kinetic theory*

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Kinetic equations for classical time-dependent correlation functions of arbitrary phase-space variables are discussed. An operator identity is obtained that relates two previously derived forms of the memory operator. The Zwanzig-Mori projection-operator formalism expresses the memory operator in terms of projected dynamics, while the Mazenko form contains only unprojected, or Hamiltonian dynamics. With the single-particle correlation function as an example, the formal kinetic theory of Mazenko is simply derived and its relationship to the results of Gross and Boley exhibited.

The use of projection operators in classical kinetic theory has been successful in systematizing and generalizing linear kinetic equations for time-dependent correlation functions.[1,2] Following the procedure of Mori[3] and Zwanzig,[4] the full N-body dynamics is projected onto an appropriate subspace. A formally exact generalized Langevin kinetic equation results with a mean field or static term that may be calculated from the equilibrium properties of the system, and a time-dependent memory operator. The memory operator is typically expressed in terms of another correlation function whose time dependence, however, is generated by the projection of the Hamiltonian dynamics orthogonal to the chosen subspace. For a properly chosen subspace, the mean-field term incorporates long-lived collective excitations and hence the memory operator will decay on a shorter time scale than that of the original correlation function, and is expected to be less sensitive to approximation.

However, mathematical analysis of this modified dynamics is difficult and it may be advantageous to have an alternate form for the memory operator expressed entirely in terms of ordinary time-correlation functions. The purpose of this note is to present a general operator identity which provides this latter form, independent of the particular subspace defining the projection operator.

The motivation for this analysis stems from recent studies of formally exact linear kinetic equations for the single-particle phase-space density, $|\delta N_1(1,t)\rangle$, defined by Eq. (15) below. Akcasu and Duderstadt[1] project onto this subspace and the memory function of their single-particle kinetic equation depends on a two particle correlation function with projected dynamics. Gross[5] and Boley[6] apply projection operators to this two-particle correlation function. A formally exact two-particle kinetic equation is derived, whose memory function is characterized by a three-particle correlation function with different projected dynamics. Continuing this procedure, a hierarchy of non-Markoffian kinetic equations results. At each level, the time-propagation operators are modified and the memory function contains another correlation function involving the dynamics of one more particle.

Mazenko[7,8] has obtained what appears to be the first two equations of a similar hierarchy. However, all time propagation in his theory is generated by unprojected, or Hamiltonian dynamics. As the Mazenko form contains no reference to projection operators, it is reasonable to expect that the Mazenko theory may be derived without projection-operator methods.

As an application of the above mentioned operator identity, this derivation will be carried out. A hierarchy of kinetic equations for the correlation functions of the memory operators is rederived. At each level the memory operator will contain another correlation function involving the dynamics of one more particle and may be expressed in Gross and Boley's, or Mazenko's form. The derivation of Mazenko's results is especially simplified and extended to infinite order. Other applications of the general operator identity are implicit in the literature. For example, the generalized transport coefficients of linear hydrodynamics[9] may be expressed in either projected or unprojected forms.

It is notationally convenient to work in terms of the Laplace transformed time development operator. In the notation of Gross,[10] consider the equation for the resolvent operator, $G=(s+L)^{-1}$,

$$(s+L)G=\mathbb{1}_N, \quad \operatorname{Re} s>0, \tag{1}$$

where s is a Laplace transform variable, $\mathbb{1}_N$ the symmetric, normalized identity operator in N body space, and L the Liouville operator for an N-particle system interacting with a continuous, central, two-body potential, V,

$$L=\sum_{\alpha=1}^{N}\frac{\vec{p}_\alpha}{m}\cdot\frac{\partial}{\partial\vec{q}_\alpha}-\sum_{\alpha\neq\beta}^{N}\frac{\partial V(|\vec{q}_\alpha-\vec{q}_\beta|)}{\partial\vec{q}_\alpha}\cdot\frac{\partial}{\partial\vec{p}_\alpha}, \quad (2)$$

where the αth particle has the phase-space coordinates $(\vec{q}_\alpha,\vec{p}_\alpha)$. An idempotent projection operator, P, is defined through a phase function R as

$$P=|R\rangle\langle RR\rangle^{-1}\langle R|=P^2=\mathbb{1}_N-Q\,. \quad (3)$$

Generalizations of R to vectors and continuous parameters, with implied summation and integration in P, are readily made. The brackets indicate the grand canonical ensemble average.

Operating on (1) by P and Q results, after some rearrangement, in a kinetic equation for PGP,[10] which is proportional to the correlation function, $\langle RGR\rangle$,

$$(s+PLP+M)PGP=P\,, \quad (4)$$

where PLP contains the static term and

$$M=-PLQ(s+QLQ)^{-1}QLP \quad (5)$$

is the memory operator.

Several methods have been applied to relate the modified resolvent operator, $(s+QLQ)^{-1}$, to the more common resolvent of (1). The expansion,

$$(s+LQ)^{-1}=(s+L)^{-1}+(s+LQ)^{-1}LP(s+L)^{-1}\,, \quad (6)$$

with the identity

$$M(PGP)=PLQGP\,, \quad (7)$$

implies

$$M=M^0+M(PGQLP)\,, \quad (8)$$

where $M^0=-PLQGQLP$.[11] Combining (7) and (8) yields a formula due to Mori,[3]

$$M=M^0+M(PGP)M\,. \quad (9)$$

The Mazenko form of (5) may be derived without explicit reference to projection operators by considering

$$s\langle RGR\rangle+\langle RLR\rangle\langle RR\rangle^{-1}\langle RGR\rangle+\langle RMR\rangle\langle RR\rangle^{-1}\langle RGR\rangle=\langle RR\rangle \quad (10)$$

as an ansatz for

$$s\langle RGR\rangle+\langle RLGR\rangle=\langle RR\rangle\,. \quad (11)$$

From (10) and (11), this is equivalent to

$$(\langle RLR\rangle+\langle RMR\rangle)\langle RR\rangle^{-1}s\langle RGR\rangle=s\langle RLGR\rangle\,. \quad (12)$$

Substituting (11) for $s\langle RGR\rangle$ on the left of (12) and $sG=\mathbb{1}_N-GL$ on the right, one finds,

$$\langle R|M|R\rangle=-\langle RLGLR\rangle+\langle RLGR\rangle\langle RGR\rangle^{-1}\langle RLGR\rangle\,. \quad (13)$$

It is also possible to derive (13) by solving (7) for M, substituting in (9) and using (3). Equation (13) may also be written as

$$M=-PL\hat{Q}GLP\,,$$
$$\hat{Q}=\mathbb{1}_N-\hat{P}=\mathbb{1}_N-G|R\rangle\langle RGR\rangle^{-1}\langle R|\,, \quad (14)$$

where $\hat{Q}$ projects G onto the modified dynamics.

The equivalence of Eqs. (5) and (13) is the principal result of this note. The correlation functions associated with M (i.e., $\langle R|M|R\rangle$) may be expressed in terms of G, or $(s+QLQ)^{-1}$. Because of the optional insertion of Q in front of $L|R\rangle$ in (13), only the part of $L|R\rangle$ surviving when operated on by Q need be retained. Since there is now no reference to a projection operator in $\langle R|M|R\rangle$, the memory function will contain no equilibrium correlation functions, only time-dependent ones. These results are valid for arbitrary phase functions, $|R\rangle$.

The formalism developed above will now be applied to the singlet distribution,

$$|\delta N_1(1)\rangle=\Bigg|\sum_{\alpha=1}^{N}\delta(\vec{x}_1-\vec{q}_\alpha)\delta(\vec{p}_1-\vec{p}_\alpha)-\Big\langle\sum_{\alpha=1}^{N}\delta(\vec{x}_1-\vec{q}_\alpha)\delta(\vec{p}_1-\vec{p}_\alpha)\Big\rangle\Bigg\rangle\,, \quad (15)$$

and shown to generate Mazenko's result.

Likewise, the n-body distribution is given by

$$|N_n(1\ldots n)\rangle=\Bigg|\sum_{\alpha_1\neq\alpha_2\ldots\neq\alpha_n}^{N}\delta(\vec{x}_1-\vec{q}_{\alpha_1})\delta(\vec{p}_1-\vec{p}_{\alpha_1})\ldots\times\delta(\vec{x}_n-\vec{q}_{\alpha_n})\delta(\vec{p}_n-\vec{p}_{\alpha_n})\Bigg\rangle\,,$$

$$|\delta N_n(1\ldots n)\rangle=|N_n(1\ldots n)-\langle N_n(1\ldots n)\rangle\rangle\,. \quad (16)$$

A sequence of phase functions is recursively defined as

$$|A_1(1)\rangle=|\delta N_1(1)\rangle\,,$$
$$|A_2(12)\rangle=Q_1|\delta N_2(12)\rangle\,,$$
$$\cdots$$
$$\cdots$$
$$\cdots$$
$$|A_n(1\ldots n)\rangle=Q_{n-1}\ldots Q_1|\delta N_n(1\ldots n)\rangle\,, \quad (17)$$

in conjunction with a sequence of projection operators,

$$P_1=|A_1(\bar{1})\rangle\langle A_1(\bar{1})A_1(\bar{2})\rangle^{-1}\langle A_1(\bar{2})|\,,$$
$$P_n=|A_n(\bar{1}\ldots\bar{n})\rangle\langle A_n(\bar{1}\ldots\bar{n})A_n(\bar{1}'\ldots\bar{n}')\rangle^{-1}\langle A_n(\bar{1}'\ldots\bar{n}')|\,, \quad (18)$$

$$P_nP_m=\delta_{nm}P_n\,, \quad (19)$$

where inverses are defined by

$$\langle A_n(1\ldots n)A_n(\bar{1}''\ldots\bar{n}'')\rangle^{-1}\langle A_n(\bar{1}''\ldots\bar{n}'')A_n(1'\ldots n')\rangle = \frac{1}{n!}\sum_P{}^{(n)}(\delta(1-1')\ldots\delta(n-n')) \tag{20}$$

Bars over variables indicate integration and $\sum_P^{(n)}$ produces a sum of $n!$ terms with permuted unprimed variables.

A hierarchy of Laplace transformed time-dependent correlation functions is introduced,

$$C_1(1\ldots l, 1'\ldots m') = \langle\delta N(1\ldots l)G\delta N(1'\ldots m')\rangle,$$

$$\cdots$$

$$\cdots$$

$$\cdots$$

$$C_n(1\ldots l,1'\ldots m') = C_{n-1}(1\ldots l,1'\ldots m') - C_{n-1}[1\ldots l,\bar{1}''\ldots(\bar{n}-\bar{1})'']C_{n-1}^{-1}(\bar{1}''\ldots(\bar{n}-\bar{1})'',\bar{1}'''\ldots(\bar{n}-\bar{1})''')$$
$$\times C_{n-1}(\bar{1}'''\ldots(\bar{n}-\bar{1})''',1'\ldots m'),\quad l,m\geq n\geq 2, \tag{21}$$

$$C_n^{-1}(1\ldots n,\bar{1}''\ldots\bar{n}'')\,C_n(\bar{1}''\ldots\bar{n}'',1'\ldots n') = \frac{1}{n!}\sum_P{}^{(n)}[\delta(1-1')\ldots\delta(n-n')]. \tag{22}$$

An analogous chain exists for an equilibrium version setting $G=1$, and will be denoted by $\tilde{C}_n$. The square $C_n(1\ldots n, 1'\ldots n')$'s in both the equilibrium and nonequilibrium cases are cumulants since they vanish if any one particle is statistically independent of all the others.

At this point, the kinetic theories may be simply derived. Let $P=P_1$ in (4). A kinetic equation for $C_1(1,2)=\int_0^\infty dt\, e^{-st}\langle\delta N(1,t)\delta N(2,0)\rangle$ results in the form,

$$sC_1(1,2)+\sum_1{}^{(s)}(1,\bar{3})C_1(\bar{3},2)+\sum_1{}^{(c)}(1,\bar{3})C_1(\bar{3},2)=\tilde{C}_1(1,2), \tag{23}$$

where $\sum_1^{(s)}$ is the static term, calculable in terms of the equilibrium pair correlation function, and $\sum_1^{(c)}$ is the collisional memory function,

$$\begin{aligned}\sum_1{}^{(s)}(1,\bar{3})\tilde{C}_1(\bar{3},2) &= \langle\delta N_1(1)L\,\delta N_1(2)\rangle,\\ \sum_1{}^{(c)}(1,\bar{3})\tilde{C}_1(\bar{3},2) &= -\langle\delta N_1(1)\,|\,LQ_1(s+Q_1LQ_1)^{-1}Q_1L\,|\,\delta N_1(2)\rangle\\ &= L_I(1\bar{1}')L_I(2\bar{2}')\langle\delta N_2(1\bar{1}')\,|\,Q_1(s+Q_1LQ_1)^{-1}Q_1\,|\,\delta N_2(2\bar{2}')\rangle,\end{aligned} \tag{24}$$

where the external variable interaction operators are defined by

$$L_I(1\ldots n) = -\sum_{i=1}^{n-1}\frac{\partial V(|\vec{x}_i-\vec{x}_n|)}{\partial\vec{x}_i}\cdot\frac{\partial}{\partial\vec{p}_i}. \tag{25}$$

Using (13), the expression for the memory kernel, (24), may be immediately rewritten as

$$\begin{aligned}\sum_1{}^{(c)}(1,\bar{3})\tilde{C}_1(\bar{3},2) &= L_I(1\bar{1}')L_I(2\bar{2}')C_2(1\bar{1}',2\bar{2}'),\\ C_2(11',22') &= C_1(11',22')-C_1(11',\bar{3})C_1^{-1}(\bar{3},\bar{4})C_1(\bar{4},22'),\end{aligned} \tag{26}$$

and C_2 is identical to Mazenko's G.[12]

At the next level, (24) may be considered as the integral of another time-correlation function with the identifications,

$$P=P_2,\quad L\to Q_1LQ_1,\quad G\to(s+Q_1LQ_1)^{-1}\equiv G_1, \tag{27}$$

and a kinetic equation,

$$(s+P_2LP_2+M_2)P_2G_1P_2=P_2,\qquad M_2=-P_2LQ_1Q_2(s+Q_2Q_1LQ_1Q_2)^{-1}Q_2Q_1LP_2. \tag{28}$$

In M_2, two applications of (12) remove the Q operators in the modified resolvent operator and yields Mazenko's result for $\sum_2^{(c)}$.

This series of steps may be repeated indefinitely. At the nth level of the chain a kinetic equation results

$$sC_n(1\ldots n,1'\ldots n')+\sum_n^{(s)}(1\ldots n,\bar{1}''\ldots\bar{n}'')C_n(\bar{1}''\ldots\bar{n}'',1'\ldots n')+\sum_n^{(c)}(1\ldots n,\bar{1}''\ldots\bar{n}'')C_n(\bar{1}''\ldots\bar{n}'',1'\ldots n')=\tilde{C}_n(1\ldots n,1'\ldots n'),$$

$$\sum_n^{(s)}(1\ldots n,\bar{1}''\ldots\bar{n}'')\tilde{C}_n(\bar{1}''\ldots\bar{n}'',1'\ldots n')=\langle A_n(1\ldots n)LA_n(1'\ldots n')\rangle, \tag{29}$$

$$\sum_n^{(c)}(1\ldots n,\bar{1}''\ldots\bar{n}'')\tilde{C}_n(\bar{1}''\ldots\bar{n}'',1'\ldots n')=L_I(1\ldots n,\bar{n}+\bar{1})L_I[1'\ldots n',(\bar{n}+\bar{1})']\langle A_{n+1}(1\ldots\bar{n}+\bar{1})|(s+Q_n\ldots Q_1LQ_1\ldots Q_n)^{-1}|A_{n+1}(1'\ldots(1'\ldots(\bar{n}+\bar{1})')\rangle.$$

The static term is the n-body additive or projection-operator theory of Gross[5] and Boley.[6] The Liouville operator, and the explicit dependence of $\sum_n^{(s)}$ on the two-body force, may be eliminated by partial integration. By induction, it follows that

$$\sum_n^{(c)}(1\ldots n,\bar{1}''\ldots\bar{n}'')\tilde{C}_n(\bar{1}''\ldots\bar{n}'',1'\ldots n')=L_I(1\ldots n,\bar{n}+\bar{1})L_I(1'\ldots n',(\bar{n}+\bar{1})')C_{n+1}(1\ldots n,\bar{n}+\bar{1},1'\ldots n',(\bar{n}+\bar{1})'), \tag{30}$$

providing the link between different levels of the chain.

This technique appears to be the most transparent method of deriving Mazenko's results. A similar analysis also holds for the test-particle problem.[7] The method facilitates the comparison of approximations, which are usually on equilibrium correlation functions in the Gross and Boley formalism, and on time-dependent correlation functions for the Mazenko theory.

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[12]Reference 8, Eq. (3.17).