Equations of Motion in Nonequilibrium Statistical Mechanics. II. Energy Transport

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The exact equations of motion for the space- and time-dependent coordinates of an arbitrary many-body system have been derived previously. These equations are partial integro-differential equations whose kernels are generalizations of time-correlation functions. In this paper the equations are rewritten using flux operators satisfying conservation equations, and the memory-retaining nonlocal generalizations of the equations of nonequilibrium thermodynamics are obtained. The formalism is applied to energy transport, and the usual expression for heat conductivity is derived without making the usual assumptions. Finally, a simple function is assumed for the kernel, and the equation then reduces to a well-known heat-conduction and -wave equation.

I. INTRODUCTION AND SUMMARY OF PREVIOUS RESULTS

IN the first paper[1] of this series, the exact equations of motion for the space- and time-dependent coordinates of an arbitrary, isolated, many-body system are derived using a method similar to the method of Nakajima[2] and Zwanzig.[3] This general formalism has been applied in a high-temperature approximation to the derivation of the linear equations of motion of nuclear magnetism.[4] In this paper we obtain exact equations that are generalizations of the phenomenological equations of nonequilibrium thermodynamics, and then we apply the formalism to energy transport.

In this section we summarize the main results of the previous paper[1] and compare that work with the work of Richardson,[5] Zwanzig,[6] Mori,[7] and others. In Sec. II we use flux operators satisfying conservation equations to rewrite the general equations of motion and obtain memory-retaining nonlocal generalizations of the equations of nonequilibrium thermodynamics. In Sec. III we apply the general formalism to energy transport and derive the usual expression for the heat conductivity without making the usual assumptions, which are reviewed in detail by Zwanzig.[8] Finally, in order to make contact with the previous work of others, a simple function is assumed for the time-correlation function appearing in the equation of motion, and the equation immediately reduces to a well-known heat-conduction and -wave equation. In Appendix A we derive some formulas useful for simplifying the equations of motion in applications. In Appendix B we discuss a projection operator related to an operator $P(t)$ defined below, and we discuss how this operator is related to an operator introduced by Mori.[7] In Appendix C we show how our formalism can be modified so that it will be more similar to Zwanzig's.[3] Appendix C may be read independently of Appendix B, and both may be read independently of Secs. II and III.

Let $F_n(\mathbf{r})$ denote the quantum-mechanical (i.e., Hermitian, linear, and possibly noncommuting) operators whose expectations we wish to describe as functions of position and time. Here n takes the values 1, 2, $\cdots$, m labeling the different operators, and these operators depend explicitly upon position $\mathbf{r}$. The quantum-mechanical and statistical expectation of $F_n(\mathbf{r})$ is

$$\langle F_n(\mathbf{r})\rangle_t = \mathrm{Tr}[F_n(\mathbf{r})\rho(t)], \tag{1}$$

where $\rho(t)$ satisfies the Liouville equation.[9] The equations of motion that we will discuss are equations for the space and time dependence of the expectations $\langle F_n(\mathbf{r})\rangle_t$.

In order to simplify the derivation of the equations of motion of the $\langle F_n(\mathbf{r})\rangle_t$ from the Liouville equation, it is convenient to introduce additional variables $\lambda_n(\mathbf{r}, t)$ defined to be functionals of the $\langle F_n(\mathbf{r})\rangle_t$ as follows. The $\lambda_n(\mathbf{r}, t)$ are obtained from the $\langle F_n(\mathbf{r})\rangle_t$ by solving the m simultaneous, nonlinear, integral equations

$$\langle F_n(\mathbf{r})\rangle_t = \frac{\mathrm{Tr}\left\{F_n(\mathbf{r})\exp\left[-\sum_{n'}\int d^3r'\lambda_{n'}(\mathbf{r}', t)F_{n'}(\mathbf{r}')\right]\right\}}{\mathrm{Tr}\left\{\exp\left[-\sum_{n'}\int d^3r'\lambda_{n'}(\mathbf{r}', t)F_{n'}(\mathbf{r}')\right]\right\}}, \quad n=1, 2, \cdots, m, \tag{2}$$

where the $\lambda_n(\mathbf{r}, t)$ are the unknowns and where for the moment the $\langle F_n(\mathbf{r})\rangle_t$ are taken to be known functions

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[1] B. Robertson, Phys. Rev. **144**, 151 (1966). Equation (2) of this reference will be denoted in the present paper by Eq. (1–2), etc. Notice the sign error in Eqs. (34) and (C11) and the misprints in Eqs. (34), (B2), (B3), (C1), (C7), and (C8), and in the expression following Eq. (C14). Most of the work in this reference was first presented in a dissertation submitted to Stanford University, 1964. See also B. Robertson, Bull. Am. Phys. Soc. **9**, 733 (1964).

[2] S. Nakajima, Progr. Theoret. Phys. (Kyoto) **20**, 948 (1958).

[3] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).

[4] B. Robertson, Phys. Rev. **153**, 391 (1967).

[5] J. M. Richardson, J. Math. Anal. Appl. **1**, 12 (1960).

[6] R. Zwanzig, Phys. Rev. **124**, 983 (1961).

[7] H. Mori, Progr. Theoret. Phys. (Kyoto) **33**, 423 (1965); **34**, 399 (1965).

[8] R. Zwanzig, Ann. Phys. Chem. **16**, 67 (1965).

[9] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **25**, 62 (1928).

of $\mathbf{r}$ for each value of t.[10] It follows from the form of Eq. (2) that the $\lambda_n(\mathbf{r}, t)$ are the same functionals of the $\langle F_n(\mathbf{r})\rangle_t$ regardless of the value of t. Nevertheless, since the dependence of the $\langle F_n(\mathbf{r})\rangle_t$ upon $\mathbf{r}$ will be different for each value of t, we have written the $\lambda_n(\mathbf{r}, t)$ as functions of t as well as of $\mathbf{r}$.

Equation (2) is a generalization of the usual formula for calculating the expectation of $F_n(\mathbf{r})$ in equilibrium statistical mechanics. It is not the same as the usual formula since the $F_{n'}(\mathbf{r}')$ in the exponential are not constants of the motion in general. The use of Eq. (2) does not involve an assumption that the system is in any sense close to equilibrium at time t. It does not involve any assumption. Equation (2) is just the definition of the $\lambda_n(\mathbf{r}, t)$.

The $\lambda_n(\mathbf{r}, t)$ are called the thermodynamic conjugates of the $\langle F_n(\mathbf{r})\rangle_t$. In the preceding paper,[1] an expression for the entropy and other thermodynamic equations involving the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r}, t)$ are written down for systems arbitrarily far from equilibrium. This use of equilibriumlike formulas on systems not in equilibrium is implicit in Jaynes's publications,[11] which motivated the preceding work.[1] Jaynes's ideas have also been expanded in this direction by Schwegler.[12] Much earlier, the same use of equilibriumlike formulas was made by Bergmann and Thompson[13] and Richardson,[5] although they started from a different point of view than Jaynes. However, this use of equilibriumlike formulas on systems not in equilibrium, although elegant, commands attention only because the $\lambda_n(\mathbf{r}, t)$ also appear in the equations of motion for the $\langle F_n(\mathbf{r})\rangle_t$.

The exact equations of motion derived in the previous paper[1] are

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t = \langle \dot{F}_n(\mathbf{r}, t)\rangle_t + \int_0^t dt' \sum_{n'} \int d^3r' K_{nn'}(\mathbf{r}, t, \mathbf{r}', t')\lambda_{n'}(\mathbf{r}', t'), \quad n = 1, 2, \cdots, m, \tag{3}$$

where the kernel, which is a generalization of a correlation function, is given by

$$K_{nn'}(\mathbf{r}, t, \mathbf{r}', t') = \langle \dot{F}_n(\mathbf{r}, t) T(t, t')[1-P(t')]\bar{\dot{F}}_{n'}(\mathbf{r}', t')\rangle_{t'}, \tag{4}$$

and the symbols used here have the following definitions.

The angular brackets on the right of Eqs. (3) and (4) are defined by

$$\langle A\rangle_t \equiv \mathrm{Tr}[A\sigma(t)], \tag{5}$$

and the bar over an operator is defined by[14]

$$\bar{A} \equiv \int_0^1 \sigma(t)^x A \sigma(t)^{-x}\, dx - \langle A\rangle_t, \tag{6}$$

where A may be any operator and where

$$\sigma(t) \equiv \frac{\exp\left[-\sum_n \int d^3r\, \lambda_n(\mathbf{r}, t) F_n(\mathbf{r})\right]}{\mathrm{Tr}\left\{\exp\left[-\sum_n \int d^3r\, \lambda_n(\mathbf{r}, t) F_n(\mathbf{r})\right]\right\}}. \tag{7}$$

Equation (6) defines an operator average of the operator A at time t. This time must be the relevant time, which is t' in Eq. (4). A bar over an operator has been used by Jaynes to represent a Kubo-Tomita[15] operator average with $\exp(-\beta\mathcal{H})$ instead of $\sigma(t)$ and without subtraction of the expectation (5). The operator average (6) is a generalization of the Kubo-Tomita average. In classical statistical mechanics, $\sigma(t)$ will commute with A so that the integral may be performed, and $\bar{A}$ reduces to simply $A - \langle A\rangle_t$.

The operator $\dot{F}_n(\mathbf{r}, t)$ is a Schrödinger operator defined by

$$\dot{F}_n(\mathbf{r}, t) \equiv i\hbar^{-1}[\mathcal{H}(t), F_n(\mathbf{r})], \tag{8}$$

where $\mathcal{H}(t)$ is the total Hamiltonian whose time dependence causes the deviations from equilibrium that interest us.

The operator $P(t)$ is defined by

$$P(t)A \equiv \sum_n \int d^3r \frac{\delta\sigma(t)}{\delta\langle F_n(\mathbf{r})\rangle_t} \mathrm{Tr}[F_n(\mathbf{r})A], \tag{9}$$

where A may be any operator and must include all operators following $P(t)$.[16] Finally, the operator $T(t, t')$ is defined to be the solution to the differential equation

$$\partial T(t, t')/\partial t' = T(t, t')[1-P(t')]iL(t') \tag{10}$$

with the initial condition $T(t, t) = 1$. Here $L(t)$ is the

[10] It is easy to see how this solution can be accomplished approximately by Fourier transformation if the exponentials are expanded about $\exp(-\beta\mathcal{H})$, for example, and only linear terms are kept, and if

$$\int_0^\beta d\beta' \,\mathrm{Tr}\{F_n(\mathbf{r})\exp(-\beta'\mathcal{H})F_{n'}(\mathbf{r}')\exp[-(\beta-\beta')\mathcal{H}]\}$$

is a function of $\mathbf{r}-\mathbf{r}'$ only. In practice either this or some other approximation usually must be made eventually. In the present paper we consider formally the exact solution and assume that a unique solution exists. (See Appendix C.)

[11] E. T. Jaynes, in *Lectures in Theoretical Physics, Brandeis, 1962, Statistical Physics* (W. A. Benjamin, Inc., New York, 1963), Vol. 3, p. 181; Phys. Rev. **106**, 620 (1957); **108**, 171 (1957).

[12] H. Schwegler, Z. Naturforsch. **20a**, 1543 (1965).

[13] P. G. Bergmann and A. C. Thompson, Phys. Rev. **91**, 180 (1953).

[14] Although Eqs. (4) and (6) are not identical to Eq. (1-34), they give the same result when used in Eq. (3) or (1-33) because of the identity

$$\sum_n \int d^3r \langle \dot{F}_n(\mathbf{r}, t)\rangle_t \lambda_n(\mathbf{r}, t) = 0.$$

This identity follows from Eqs. (5), (7), (8), and (1-32).

[15] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[16] For example, the $P(t')$ appearing explicitly in Eq. (4) operates also on the $\sigma(t')$ which is to the right of $P(t')$, as implied by Eq. (5).

Liouville operator defined by[17]

$$L(t)A \equiv \hbar^{-1}[\mathcal{H}(t), A], \tag{11}$$

where again A may be any operator and must include all operators to the right of $L(t)$. The operator $T(t, t')$ advances quantum-mechanical operators on the right from time t' to time t while subtracting out a part at each step.

As may be seen from Eqs. (4)–(11), both $\langle \dot{F}_n(\mathbf{r}, t) \rangle_t$ and $K_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ in Eq. (3) depend upon the $\lambda_n(\mathbf{r}, t)$ or equivalently the $\langle F_n(\mathbf{r}) \rangle_t$. Because this dependence is nonlinear, it is convenient to take a slightly different point of view. Instead of considering the $\lambda_n(\mathbf{r}, t)$ as having been eliminated in favor of the $\langle F_n(\mathbf{r}) \rangle_t$, consider Eqs. (2) and (3) as being $2m$ coupled equations to be solved simultaneously for the $2m$ unknowns $\langle F_n(\mathbf{r}) \rangle_t$ and $\lambda_n(\mathbf{r}, t)$.

Sometimes it is convenient to consider a linear approximation to this formalism. We can obtain one by expanding $\sigma(t)$ in Eq. (7) about

$$\exp(-\beta\mathcal{H})/\mathrm{Tr}[\exp(-\beta\mathcal{H})]$$

and keeping corrections to first order only. Then $P(t)$ and $K_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ become independent of the $\lambda_n(\mathbf{r}, t)$ or the $\langle F_n(\mathbf{r}) \rangle_t$ and depend only upon β, and then $K_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ reduces to a correlation function. If the correlation time is short, P may often be neglected in Eq. (10), and Eq. (4) reduces to the usual expression for a correlation function.[8] However, our main interest is in problems for which the correlation time is not short and memory effects are important and therefore for which the operator P is essential. Furthermore, it frequently is necessary to make an approximation different from the above linear approximation. For these reasons we postpone approximations until they are absolutely necessary. Our present development will be exact; we mentioned the above approximation only to make contact with well-known concepts.

The first term on the right of Eq. (3) does not directly change the entropy[18] and hence is called the reversible term. On the other hand, the integral term will cause relaxation and will change the entropy in general and hence is called the irreversible term. In applications of these equations so far worked out, the reversible terms are either zero or can be calculated exactly in terms of recognizable quantities such as the $\langle F_n(\mathbf{r}) \rangle_t$ and the $\lambda_n(\mathbf{r}, t)$. The kernel $K_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ usually cannot be calculated exactly, but its approximate functional form can sometimes be guessed, as we will illustrate in Sec. III.

The idea of deriving equations such as Eq. (3) is an old one and recently has attracted much interest. By using a qualitative argument, Richardson[5] wrote down an equation identical to Eq. (3), but did not derive it and did not write down an expression for

$$K_{nn'}(\mathbf{r}, t, \mathbf{r}', t').$$

By making several plausible assumptions, Zwanzig[6] derived approximate equations similar to Eqs. (3) and (4), but only for classical statistical mechanics. By making several additional plausible assumptions, Sewell[19] derived an approximate quantum-mechanical generalization of Zwanzig's formalism. Zwanzig introduced a density defined in the m-dimensional space spanned only by the expectations of the macroscopic observables and hence defined in a space of much smaller dimensionality than the phase space of the entire system. This density is initially microcanonical. The exact formalism of Eqs. (2)–(11), on the other hand, always uses a generalized canonical density operator (7) defined in the space of the entire system. This generalized canonical formalism is superior because carrying out explicit calculations in applications is much easier with it. Furthermore, only one assumption is necessary for its derivation from Hamiltonian mechanics, and that assumption is that the initial condition for the density operator $\rho(t)$ at $t=0$ be Gibbs's canonical density or the like.

We may express this initial condition in a convenient and concise form by using the following formal device. We require that the set of operators $F_n(\mathbf{r})$, $n = 1, 2, \cdots, m$ include operators that can be combined in a linear combination that equals the total Hamiltonian $\mathcal{H}(0)$. Then, for suitable values of $\lambda_n(\mathbf{r}, 0)$, the exponents in Eq. (2) will reduce to $-\beta\mathcal{H}(0)$ where $1/k\beta$ is the temperature, in which case Eq. (2) becomes the usual equilibrium statistical-mechanical expression for the expectation of $F_n(\mathbf{r})$. It follows that, for systems in equilibrium at temperature $1/k\beta$, the $\lambda_n(\mathbf{r}, 0)$ will take just those values. Then the exponents in Eq. (7) will also reduce to $-\beta\mathcal{H}(0)$, and therefore

$$\rho(0) = \sigma(0). \tag{12}$$

Equation (12) can also be true even if the system is not in equilibrium at $t=0$. In the derivation of the equations of motion (3), only the initial condition (12) need be assumed; it is not necessary to assume that the system is in equilibrium at $t=0$.

Since Eq. (12) is the only assumption necessary for deriving Eqs. (3) from Hamiltonian mechanics and since Eq. (12) or the like is always assumed in statistical mechanics, there is no restriction to the generality of Eqs. (3). They apply to any system regardless of its complexity or of the experiment performed on it.

By making an assumption different from Eq. (12), Mori has also derived equations of motion for the expectations of macroscopic observables using Zwanzig's method.[3] Mori's initial condition is a linear approximation to ours and is obtained by expanding $\sigma(0)$ about $\exp(-\beta\mathcal{H})/\mathrm{Tr}[\exp(-\beta\mathcal{H})]$ and keeping the corrections to first order only. This linear approximation applies either if the temperature is large compared with certain energies, as in Ref. 4, or if the system is only slightly disturbed from equilibrium. In his derivation, Mori restricts the Hamiltonian to be time-independent

[17] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[18] Proof: Combine Eqs. (3) and (8) and the identity in Footnote 14 with an expression for $dS(t)/dt$ similar to Eq. (1–17).

[19] G. L. Sewell, Physica **31**, 1520 (1965).

and assumes that the invariant part of the observables, i.e., the part that is diagonal in a representation in which the Hamiltonian is diagonal, has been removed. Furthermore, his formalism does not include anything corresponding to our $\lambda_n(\mathbf{r}, t)$ and so cannot yield the equations in Sec. III, for example. We have discussed the limitations to Mori's work in greater detail previously.[20] In Appendix B, we discuss some similarities between his work and ours.

The following authors have also used Zwanzig's method.[3] Fano[21] has given a general discussion of relaxation and applied it to a system interacting with a thermal bath, a concept we did not need to consider. Zwanzig has given a simplified derivation of the master equation[22] and demonstrated the identity of three versions of this equation.[23] Emch[24] and Mathews[25] have also derived generalized master equations.

II. THE EQUATIONS REWRITTEN USING FLUX OPERATORS

The flux operator $\mathbf{J}_n(\mathbf{r}, t)$ corresponding to the operator $F_n(\mathbf{r})$ is defined to be the solution to

$$\nabla\cdot\mathbf{J}_n(\mathbf{r}, t)=-\dot{F}_n(\mathbf{r}, t), \qquad \mathbf{r} \text{ inside } \mathfrak{R}, \quad (13)$$

and is defined to be

$$\mathbf{J}_n(\mathbf{r}, t)=0, \qquad \mathbf{r} \text{ outside } \mathfrak{R}, \quad (14)$$

where $\mathfrak{R}$ is the region of space occupied by the system.

Equations (13) and (14) do not determine $\mathbf{J}_n(\mathbf{r}, t)$ unambiguously. To obtain a solution different from a given solution to Eqs. (13) and (14), add $\nabla\times\mathbf{A}_n(\mathbf{r}, t)$, where $\mathbf{A}_n(\mathbf{r}, t)$ may be any operator such that $\nabla\times\mathbf{A}_n(\mathbf{r}, t)$ is zero for $\mathbf{r}$ outside $\mathfrak{R}$. Fortunately, this ambiguity does not appear in the exact equations of motion that we will derive although it does appear in the expression for the time-correlation function.

Solutions to Eqs. (13) and (14) for the momentum density, the stress tensor, and the energy flux have been known for a long time for a system of noninteracting particles. For interacting particles, approximate solutions for the stress tensor and the energy flux have been obtained by Irving and Kirkwood[26] and for the energy flux of a lattice by Hardy.[27] Of course exact formal solutions can easily be written down.[28,29] An exact solution will be necessary whenever higher-order gradients are important.

Equation (13) is the operator version of the conservation equation

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t=-\nabla\cdot\,\mathrm{Tr}[\mathbf{J}_n(\mathbf{r}, t)\rho(t)], \quad (15)$$

which follows from Eqs. (1), (8), and (13) and the Liouville equation. We now rewrite the equations of motion using Eq. (13) and obtain an expression for the trace on the right of Eq. (15).

By inserting Eq. (13) into Eqs. (3) and (4) and performing an integration by parts, we get

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t=-\nabla\cdot\langle\mathbf{J}_n(\mathbf{r}, t)\rangle_t-\nabla\cdot\int_0^t dt'\sum_{n'}\int d^3r'\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')\cdot\nabla'\lambda_{n'}(\mathbf{r}', t'), \qquad n=1, 2, \cdots, m, \quad (16)$$

where the kernel is a dyadic given by

$$\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')=\langle\mathbf{J}_n(\mathbf{r}, t)T(t, t')[1-P(t')]\bar{\mathbf{J}}_{n'}(\mathbf{r}', t')\rangle_{t'}. \quad (17)$$

The surface term is zero since $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ is zero outside the system, as may be seen from Eqs. (17) and (14). Notice that Eqs. (16) follow from Eq. (15) and the expressions

$$\mathrm{Tr}[\mathbf{J}_n(\mathbf{r}, t)\rho(t)]=\langle\mathbf{J}_n(\mathbf{r}, t)\rangle_t+\int_0^t dt'\sum_{n'}\int d^3r'\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')\cdot\nabla'\lambda_{n'}(\mathbf{r}', t'), \qquad n=1, 2, \cdots, m, \quad (18)$$

[20] See the Conclusion and Appendix C of Ref. 1.

[21] U. Fano, in *Lectures on the Many-Body Problem, International School of Physics, Ravello, 1963* (Academic Press Inc., New York, 1964), Vol. 2, p. 217; Phys. Rev. **131**, 259 (1963).

[22] R. W. Zwanzig, in *Lectures in Theoretical Physics, Boulder, 1960* (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106.

[23] R. Zwanzig, Physica **30**, 1109 (1964).

[24] G. Emch, Helv. Phys. Acta **37**, 532 (1964).

[25] P. M. Mathews, Physica **32**, 2007 (1966).

[26] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).

[27] R. J. Hardy, Phys. Rev. **132**, 168 (1963).

[28] For example,

$$\mathbf{J}_n(\mathbf{r}, t)=\int_{\mathfrak{R}}\mathbf{G}(\mathbf{r}, \mathbf{r}')\dot{F}_n(\mathbf{r}', t)d^3r',$$

where $\mathbf{G}(\mathbf{r}, \mathbf{r}')$ is not an operator but is an ordinary Green's function defined to be the solution to

$$\nabla\cdot\mathbf{G}(\mathbf{r}, \mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}')$$

for $\mathbf{r}'$ and $\mathbf{r}$ inside $\mathfrak{R}$ and defined to be zero for $\mathbf{r}'$ inside $\mathfrak{R}$ and $\mathbf{r}$ outside $\mathfrak{R}$. This expression for $\mathbf{J}_n(\mathbf{r}, t)$ satisfies Eqs. (13) and (14) exactly. However, $\mathbf{G}(\mathbf{r}, \mathbf{r}')$ has not been defined unambiguously here.

For an infinite region $\mathfrak{R}$, the solution to the above equation with $\nabla\times\mathbf{G}(\mathbf{r}, \mathbf{r}')=0$ is easily shown to be $\mathbf{G}(\mathbf{r}, \mathbf{r}')=\nabla(1/4\pi\,|\,\mathbf{r}-\mathbf{r}'\,|)$. However, this Green's function cannot be used for a finite region $\mathfrak{R}$ because then $\mathbf{J}_n(\mathbf{r}, t)$ and $\mathrm{Tr}[\mathbf{J}_n(\mathbf{r}, t)\rho(t)]$ would not be zero for $\mathbf{r}$ outside $\mathfrak{R}$.

This exact solution (see Ref. 29) with $\nabla\times\mathbf{J}_n(\mathbf{r}, t)=0$ does not reduce to the usual approximate solutions (see Refs. 26 and 27) with $\nabla\times\mathbf{J}_n(\mathbf{r}, t)\neq0$. An exact solution that does reduce to the usual approximate solutions when $\delta(\mathbf{r}-\mathbf{r}_j)$ is Taylor-expanded about $\delta(\mathbf{r}-\mathbf{r}_i)$ can be obtained by using

$$\delta(\mathbf{r}-\mathbf{r}_j)=\delta(\mathbf{r}-\mathbf{r}_i)-\nabla\cdot\int_{\mathbf{r}_i}^{\mathbf{r}_j}\delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}'$$

instead of the usual Taylor expansion. Here the path of integration may be along any contour entirely within the system. This formula can often also be used on expressions involving quantized field operators since the expressions are often antisymmetric functions of two spatial arguments one of which is integrated over all space.

[29] A. Kugler, Z. Physik **198**, 236 (1967).

whose derivation is similar to the derivation of Eqs. (16).

Equations (16) are the desired equations of motion. Equations (18) are the memory-retaining nonlocal generalizations of the equations of nonequilibrium thermodynamics. Here the $\mathrm{Tr}[\mathbf{J}_n(\mathbf{r}, t)\rho(t)]$ are the fluxes, the $\langle \mathbf{J}_n(\mathbf{r}, t)\rangle_t$ are their reversible parts, the $\nabla\lambda_n(\mathbf{r}, t)$ are the thermodynamic forces, and in a linear approximation the $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ satisfy reciprocity relations.[1] The above equations are all exact and have no restriction to their generality, although Eqs. (3) and (4) or a combination of these equations may be more convenient to use, as we shall discuss later.

Notice that the ambiguity arising because only $\nabla\cdot\mathbf{J}_n(\mathbf{r}, t)$ is specified does not appear in Eq. (16). This follows because the $\nabla\cdot$ in the last term cancels to zero the ambiguous part of $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$, arising from the ambiguous part of $\mathbf{J}_n(\mathbf{r}, t)$. Also the $\cdot\nabla$, after an integration by parts, cancels the ambiguous part of $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ arising from the ambiguous part of $\mathbf{J}_{n'}(\mathbf{r}', t')$. Of course, the ambiguity does appear in Eqs. (17) and (18).

We now list some identities useful in simplifying the application of Eq. (16). We may easily prove[30]

$$P(t)T(t, t')[1-P(t')]=0. \tag{19}$$

Equation (9) gives

$$\mathrm{Tr}[F_n(\mathbf{r})P(t)A]=\mathrm{Tr}[F_n(\mathbf{r})A]. \tag{20}$$

Finally, in Appendix A, we prove that

$$P(t)\bar{F}_n(\mathbf{r})\sigma(t)=\bar{F}_n(\mathbf{r})\sigma(t). \tag{21}$$

These identities are applied as follows.

Because of Eq. (21), the $[1-P(t')]$ in Eq. (17) frequently simplifies that expression for $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$. If $\mathbf{J}_{n'}(\mathbf{r}', t')$ is equal to a linear combination of $F_1(\mathbf{r}')$, $F_2(\mathbf{r}'), \cdots, F_m(\mathbf{r}')$, then $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')=0$ for all n and $\mathbf{r}$. As a result some of the integral terms in Eq. (16) will be identically zero. For the remaining integral terms, the $[1-P(t')]$ automatically accomplishes a subtraction of an average flux. Such a subtraction has been discussed by Green[31] and McLennan.[32]

Because of Eq. (19), a $[1-P(t)]$ can also be introduced to the left of the operator $T(t\ t')$ in Eq. (17). This also simplifies the expression for $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$. If $\mathbf{J}_n(\mathbf{r}, t)$ is equal to a linear combination of $F_1(\mathbf{r})$, $F_2(\mathbf{r}), \cdots, F_m(\mathbf{r})$, then Eq. (20) gives $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')=0$ for all n' and $\mathbf{r}'$. As a result, some of the equations of motion (16) reduce to conservation equations

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t=-\nabla\cdot\langle \mathbf{J}_n(\mathbf{r}, t)\rangle_t, \tag{22}$$

which of course also follow directly from Eqs. (13) and (1) and the Liouville equation.

Frequently $\mathbf{J}_n(\mathbf{r}, t)$ is a sum of two or more terms not all of which are linear combinations of the $F_n(\mathbf{r})$. Then only the part that cannot be written as a linear combination of the $F_n(\mathbf{r})$ survives. This can considerably simplify the expressions for the $\mathsf{K}_{nn'}(\mathbf{r}, t, \mathbf{r}', t')$ that are not zero. There are also other ways of simplifying the kernels, as illustrated, for example, in Ref. 4.

For some applications of the general formalism, it is convenient to write $\dot{F}_n(\mathbf{r}, t)$ as the sum of two terms, one of which is easily recognized as it stands and the other of which is put into Eq. (13). Then the equations of motion will have some terms as in Eq. (3) and others as in Eq. (16).

Combinations of Eqs. (3) and (16), such as these, are, in general notation, the memory-retaining nonlocal generalizations of the equations of quantum hydrodynamics. The equations of quantum hydrodynamics were first derived by Irving and Zwanzig,[33] using the Wigner distribution function. Green,[34] Richardson,[5] and Kadanoff and Martin,[35] have also discussed hydrodynamics extensively. In the present paper, we will not consider hydrodynamics further, but instead will discuss just energy transport.

III. THE MEMORY-RETAINING NONLOCAL EQUATIONS OF ENERGY TRANSPORT

In this section we apply the previous general formalism to one of the formally simplest situations—energy transport. We derive the equation of motion and the well known expression for the heat conductivity.

If the only observable we consider is the energy density, then the only operator $F_n(\mathbf{r})$ is the Hamiltonian density $\mathcal{H}(\mathbf{r})$, and Eqs. (2) reduce to

$$\langle\mathcal{H}(\mathbf{r})\rangle_t=\frac{\mathrm{Tr}\left\{\mathcal{H}(\mathbf{r})\exp\left[-\int d^3r'\beta(\mathbf{r}', t)\mathcal{H}(\mathbf{r}')\right]\right\}}{\mathrm{Tr}\left\{\exp\left[-\int d^3r'\beta(\mathbf{r}', t)\mathcal{H}(\mathbf{r}')\right]\right\}}, \tag{23}$$

where we have written $\beta(\mathbf{r}, t)$ for the thermodynamic conjugate to $\langle\mathcal{H}(\mathbf{r})\rangle_t$. As before, this equation involves no assumption but serves merely to define $\beta(\mathbf{r}, t)$ as a functional of $\langle\mathcal{H}(\mathbf{r})\rangle_t$.

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[30] Proof: Every term but the first in the infinite series in Eq. (1–B1) has a factor $[1-P(\ )]$ to the left. So, if we multiply the series on the left by $P(t)$ and apply Eq. (1–25), only the first terms will survive, and we get $P(t)T(t, t')=P(t)$.

[31] M. S. Green, Phys. Rev. **119**, 829 (1960).

[32] J. A. McLennan, Progr. Theoret. Phys. (Kyoto) **30**, 408 (1963).

[33] J. H. Irving and R. W. Zwanzig, J. Chem. Phys. **19**, 1173 (1951).

[34] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954).

[35] L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) **24**, 419 (1963); P. C. Martin, in *Lectures on the Many-Body Problem, International School of Physics, Ravello, 1963* (Academic Press Inc., New York, 1964), Vol. 2, p. 247; in *Statistical Mechanics of Equilibrium and Nonequilibrium, International Symposium on Statistical Mechanics and Thermodynamics, Aachen, 1964* (North-Holland Publishing Company, Amsterdam, 1965), p. 100.

Although in this example the generalized canonical density (7) takes a form identical to Mori's local equilibrium density,[36] we use it in a way other than does Mori. For us, $\sigma(t)$ is just a convenient operator we have defined, and its use involves no assumption that $\rho(t)$ is at all like $\sigma(t)$. In order to simplify the equations of motion, however, we do assume the initial condition (12) for $\rho(t)$, but this assumption is fundamental to statistical mechanics.

In the example considered in this section, the total Hamiltonian is

$$\mathcal{H}=\int \mathcal{H}(\mathbf{r})\, d^3r, \tag{24}$$

and the energy-flux operator $\mathbf{J}_e(\mathbf{r})$ is the solution to

$$\nabla\cdot\mathbf{J}_e(\mathbf{r})=-\dot{\mathcal{H}}(\mathbf{r}). \tag{25}$$

These operators are time-independent because the system we consider has a time-independent Hamiltonian density $\mathcal{H}(\mathbf{r})$.

In this example, Eqs. (16) and (17) reduce to

$$\frac{\partial\langle\mathcal{H}(\mathbf{r})\rangle_t}{\partial t}=-\nabla\cdot\int_0^t dt'\int d^3r'\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')\cdot\nabla'\beta(\mathbf{r}',t'), \tag{26}$$

$$\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')=\langle\mathbf{J}_e(\mathbf{r})T(t,t')\mathbf{J}_e(\mathbf{r}')\rangle_{t'}, \tag{27}$$

where a term does not appear in Eq. (26) because $\langle\mathbf{J}_e(\mathbf{r})\rangle_t$ is zero.

The proof that $\langle\mathbf{J}_e(\mathbf{r})\rangle_t$, defined by Eqs. (5) and (25), is zero is as follows. The trace, if it is real, of an operator is invariant under time reversal of that operator. Now $\mathcal{H}(\mathbf{r})$ and therefore $\mathcal{H}$ are unchanged under time reversal. But $\mathbf{J}_e(\mathbf{r})$, which includes a factor i, changes sign under time reversal. Therefore, $\langle\mathbf{J}_e(\mathbf{r})\rangle_t=-\langle\mathbf{J}_e(\mathbf{r})\rangle_t$ must be zero.

A similar argument shows that the $P(t')$ appearing explicitly in Eq. (17) does not survive in Eq. (27) although $P(t')$ remains in Eq. (10).

We have not proved that the expectation of the energy flux $\mathrm{Tr}[\mathbf{J}_e(\mathbf{r})\rho(t)]$ is zero. That quantity is given by the right side of Eq. (26) without the divergence operator.

Equation (26) can be written with $\beta(\mathbf{r},t)$ as the only unknown by use of Eq. (A6) and Eq. (A5), which for the present problem becomes

$$\frac{\partial\langle\mathcal{H}(\mathbf{r})\rangle_t}{\partial t}=-\int d^3r'\langle\mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle_t\frac{\partial\beta(\mathbf{r}',t)}{\partial t}. \tag{28}$$

Equation (26), when combined with Eq. (28), is a generalization of the heat-conduction equation, but because of the time integral does not predict an infinite velocity. Equations (26) and (28), which are to be used with Eqs. (5)–(11), (23)–(25), (27), and (A6), are the memory-retaining nonlocal equations of energy transport. These equations are all exact and apply to any system and to any experiment that can be described with a Hamiltonian that is time-independent for $t>0$.

Of course, the more complicated the experiment, the more complicated the kernel (27). If phenomena other than energy transport occur, it would be better to include more observables in our formalism than just the energy density. Then there would be more equations of motion and more kernels in each equation, but each kernel would be simpler than if we did not include more observables. For the present example, the kernel (27) will be simplest if we restrict our discussion to experiments in which no mass, momentum, or charge transport occurs, no electric or magnetic fields are applied, and no phase transition occurs. The experiment is to be such that only energy transport will occur. Furthermore we restrict our discussion to systems approximately in local equilibrium, and we consider small deviations from that state. Then the dependence of the kernel on its position and time arguments will be simplified.

These restrictions will not only make the kernel simple, but they will also permit identification of $1/k\beta(\mathbf{r},t)$ as the temperature read by a thermometer at position $\mathbf{r}$ at time t. We can see this by supposing $\mathcal{H}(\mathbf{r})$, when integrated over a small region containing a particular position $\mathbf{r}_0$, to be the Hamiltonian of a thermometer located at $\mathbf{r}_0$. We also suppose this thermometer has a large heat conductivity, has a small heat capacity, interacts weakly with its surroundings, and is smaller than distances over which $\beta(\mathbf{r}',t)$ changes appreciably. Then the thermometer will be nearly in equilibrium, and $1/k\beta(\mathbf{r}_0,t)$ will be its temperature as may easily be proven by an argument similar to one given previously.[1] Finally, provided the interaction between the thermometer and its surroundings is not too weak compared with the heat capacity of the thermometer, the temperature of the thermometer will be the same as the temperature of its surroundings, and $\beta(\mathbf{r}',t)$ for $\mathbf{r}'$ near the thermometer will equal $\beta(\mathbf{r}_0,t)$. This completes our identification of $1/k\beta(\mathbf{r},t)$ as the temperature. A discussion of the definition of temperature has been given by Garcia-Colin and Green.[37]

In order to simplify discussion of some of the features of Eqs. (26) and (28), we now make the near-equilibrium approximation discussed in Sec. I and described in detail in Appendix C of Ref. 1. In this linear approximation, $\beta(\mathbf{r},t)$ is a constant, β, plus a small correction term, which we keep in the equations to first order only. As a result, both $\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')$ and $\langle\mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle$ are now independent of the correction term and depend only upon the constant β, and hence $\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')$ becomes a function of $t-t'$ only.

Next we make the long-wavelength approximation.

[36] H. Mori, J. Phys. Soc. Japan **11**, 1029 (1956); Phys. Rev. **112**, 1829 (1958); **115**, 298 (1959); H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 271.

[37] L. S. Garcia-Colin and M. S. Green, Phys. Rev. **150**, 153 (1966).

Then $\langle \mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle$ is nearly zero for $|\mathbf{r}-\mathbf{r}'|$ much larger than a correlation length that is short compared with the distance over which $\partial\beta(\mathbf{r},t)/\partial t$ changes appreciably. So $\partial\beta(\mathbf{r}',t)/\partial t$ can be replaced with $\partial\beta(\mathbf{r},t)/\partial t$ and taken outside of the integral in Eq. (28). The coefficient of $\partial\beta(\mathbf{r},t)/\partial t$ in Eq. (28) then is $C/k\beta^2$, where

$$C=k\beta^2\int d^3r'\langle \mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle \tag{29}$$

is the heat capacity per unit volume. Also in this approximation the wavelength of variations in $\beta(\mathbf{r},t)$ is much longer than the distance $|\mathbf{r}-\mathbf{r}'|$ for $\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')$ to be nearly zero. So $\nabla'\beta(\mathbf{r}',t')$ can be replaced with $\nabla\beta(\mathbf{r},t')$ and taken outside of the space integral in Eq. (26).

We also make the short-correlation-time approximation. Then $\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')$ is nearly zero for $t-t'$ much larger than a correlation time short compared with the time required for $\nabla\beta(\mathbf{r},t)$ to change appreciably. So $\nabla\beta(\mathbf{r},t')$ can be replaced with $\nabla\beta(\mathbf{r},t)$ and taken also outside of the time integral in Eq. (26). The $\nabla\beta(\mathbf{r},t)$ in Eq. (26) then is dot-multiplied by $-\nabla\cdot\boldsymbol{\kappa}/k\beta^2$, where

$$\boldsymbol{\kappa}=k\beta^2\int_0^\infty dt''\int d^3r'\langle \mathbf{J}_e(\mathbf{r})\exp(-iLt'')\bar{\mathbf{J}}_e(\mathbf{r}')\rangle \tag{30}$$

is the usual expression for the heat-conductivity dyadic first derived by Green.[31] Here we have used $t''=t-t'$ and replaced the upper limit by infinity, since after a short time the integrand quickly approaches zero. The operator $T(t,t')$ in Eq. (27) has been simplified in this short-correlation-time approximation by dropping the P from Eq. (10).

Apart from the near-equilibrium approximation, which can be removed, the only approximations and restrictions that we have made in deriving Eqs. (30) and (31) are just the conditions required in the definition of the heat capacity C and the heat conductivity $\boldsymbol{\kappa}$. We have derived the usual expression for $\boldsymbol{\kappa}$ without making any of the usual assumptions described in the reviews by Chester[38] and Zwanzig.[8]

Finally, in order to compare our exact Eqs. (26) and (28) with the previous work of others, we assume a simple function for the time dependence of $\mathsf{K}(\mathbf{r},t-t',\mathbf{r}',0)$. This assumption replaces the short-correlation-time approximation although we do continue to make the long-wavelength approximation.

Now the long-wavelength approximation to $\langle \mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle$ can be conveniently expressed formally by means of

$$\langle \mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle\approx(C/k\beta^2)\delta(\mathbf{r}-\mathbf{r}'), \tag{31}$$

where the coefficient is chosen to satisfy Eq. (29). The $\delta(\mathbf{r}-\mathbf{r}')$ here is meant to be just a concise formal way of stating that $\langle \mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle$ approaches zero in a distance short compared with the distance over which $\partial\beta(\mathbf{r},t)/\partial t$ changes appreciably. Of course $\langle \mathcal{H}(\mathbf{r})\bar{\mathcal{H}}(\mathbf{r}')\rangle$ is not really infinitely sharp. We express the long-wavelength approximation to $\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')$ in a similar way below.

We assume the time dependence of $\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')$ to be a simple exponential with time constant τ. This assumption and the long-wavelength approximation can be conveniently expressed by

$$\mathsf{K}(\mathbf{r},t,\mathbf{r}',t')\approx\frac{\boldsymbol{\kappa}}{k\beta^2}\delta(\mathbf{r}-\mathbf{r}')\frac{1}{\tau}\exp\left(-\frac{t-t'}{\tau}\right), \tag{32}$$

where the coefficient $\boldsymbol{\kappa}/k\beta^2$ is chosen to satisfy Eq. (30). As τ approaches zero, the function to the right of $\delta(\mathbf{r}-\mathbf{r}')$ in Eq. (32) approaches $\delta(t-t')$, and we recover the short-correlation-time approximation.

When the assumption (32) is inserted into Eq. (26) and the result combined with Eqs. (28) and (31), we get

$$\frac{\partial\beta(\mathbf{r},t)}{\partial t}=\nabla\cdot\int_0^t dt'\frac{\boldsymbol{\kappa}}{C\tau}\exp\left(-\frac{t-t'}{\tau}\right)\cdot\nabla\beta(\mathbf{r},t'), \tag{33}$$

which when differentiated once with respect to t becomes

$$(\partial^2\beta/\partial t^2)+\tau^{-1}(\partial\beta/\partial t)=\nabla\cdot(\boldsymbol{\kappa}/C\tau)\cdot\nabla\beta. \tag{34}$$

If deviations from equilibrium are small, $\beta(\mathbf{r},t)^{-1}$ will satisfy the same equation. If $\boldsymbol{\kappa}$ is diagonal, we get ∇^2 on the right, and the equation approaches the Fourier heat-conduction equation as τ approaches zero. However, unlike the Fourier equation, Eq. (34), which includes a second time derivative, predicts a finite velocity of propagation of disturbances from equilibrium where $\mathbf{v}^2\equiv\boldsymbol{\kappa}/C\tau$ is the velocity dyadic.

The constant τ may be eliminated from the expression for $\mathbf{v}^2$ by equating Eqs. (32) and (27), integrating over $\mathbf{r}'$, and setting $t'=t$ to get

$$\mathbf{v}^2=\frac{k\beta^2}{C}\int d^3r'\langle \mathbf{J}_e(\mathbf{r})\bar{\mathbf{J}}_e(\mathbf{r}')\rangle. \tag{35}$$

A phenomenological derivation of Eq. (34) with $\boldsymbol{\kappa}$ diagonal has been given for superfluid helium by Vernotte[39] and Ulbrich[40] and for dielectric solids by Chester.[41] The equation has also been derived for solids by Guyer and Krumhansl[42] from the linearized phonon Boltzmann equation by introducing adjustable parameters equivalent ultimately to $\boldsymbol{\kappa}/C$ and $1/\tau$. However, our assumption (32) is too simple to yield their correction to the phenomenological equation. A solution to the one-dimensional version of this equation has

[38] G. V. Chester, Rept. Progr. Phys. **26**, 411 (1963).

[39] D. Vernotte, Compt. Rend. **246**, 3154 (1958).

[40] C. W. Ulbrich, Phys. Rev. **123**, 2001 (1961).

[41] M. Chester, Phys. Rev. **131**, 2013 (1963).

[42] R. A. Guyer and J. A. Krumhansl, Phys. Rev. **133**, A1411 (1964); **148**, 766 (1966).

been compared by Brown, Chung, and Matthews[43] with experiments on superfluid helium and crystalline Al_2O_3 and found to give better agreement than the solution to the Fourier equation.

Of course the assumption (32) and the resulting Eq. (34) are too simple to be correct except under very special circumstances. In general, the exact Eqs. (26) and (28) must be used, and $\mathsf{K}(\mathbf{r}, t, \mathbf{r}', t')$ will be more complicated than in Eq. (32).

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APPENDIX A: USEFUL IDENTITIES

In this appendix we derive some identities used in Secs. II and III and in Appendices B and C.

In order to simplify notation,[7] let F denote the column vector whose elements are the operators $F_1(\mathbf{r})$, $F_2(\mathbf{r})$, $\cdots$, $F_m(\mathbf{r})$, and let $\lambda(t)$ denote the row vector whose elements are $\lambda_1(\mathbf{r}, t)$, $\lambda_2(\mathbf{r}, t)$, $\cdots$, $\lambda_m(\mathbf{r}, t)$. Furthermore, let a dot between $\lambda(t)$ and F represent the sum and integral

$$\lambda(t)\cdot F\equiv \sum_n \int d^3r\lambda_n(\mathbf{r}, t)F_n(\mathbf{r}). \tag{A1}$$

This vector notation (used in the Appendices only) permits concise expression of the functional derivative

$$\delta\sigma(t)/\delta\lambda(t) = -\bar{F}\sigma(t), \tag{A2}$$

which follows from Eqs. (7), (1–A2), and (6). By calculating the trace of F times Eq. (A2) and then using Eq. (5), we get

$$\delta\langle F\rangle_t/\delta\lambda(t) = -\langle F\bar{F}\rangle_t. \tag{A3}$$

This matrix will be useful below.

Now the identity

$$\langle A\bar{B}\rangle_t = \langle B\bar{A}\rangle_t \tag{A4}$$

may be verified directly from the definitions (5) and (6) where A and B may be any operators (but not column vectors of operators, just the elements). It follows that $\langle F\bar{F}\rangle_t$ is a symmetric matrix, and therefore so is $\delta\langle F\rangle_t/\delta\lambda(t)$.

Finally, we use these equations to derive some important identities. By viewing $\langle F\rangle_t$ as a functional of $\lambda(t)$ as in Eq. (2) and then calculating the total functional derivative of $\langle F\rangle_t$ with respect to time t, we get

$$\partial\langle F\rangle_t/\partial t = -\langle F\bar{F}\rangle_t^{-1}\cdot\partial\lambda(t)/\partial t, \tag{A5}$$

where we have used Eq. (A3). Also, by viewing $\sigma(t)$ in Eq. (7) as a functional of $\lambda(t)$, which in turn is a functional of $\langle F\rangle_t$, and by calculating the functional derivative in Eq. (9) as a total functional derivative, we may rewrite the definition of $P(t)$ as

$$P(t)A = \bar{F}\sigma(t)\cdot\langle F\bar{F}\rangle_t^{-1}\cdot \mathrm{Tr}(FA), \tag{A6}$$

where we have used Eqs. (A2) and (A3). Equation (21) follows immediately from Eqs. (A6) and (5). Furthermore, Eqs. (A6), (A4), (A2), and (A3) give

$$P(t)\bar{A}\sigma(t) = \bar{F}\sigma(t)\cdot[\delta\langle A\rangle_t/\delta\langle F\rangle_t], \tag{A7}$$

which is often very useful.

APPENDIX B: THE PROJECTION OPERATOR $\mathcal{P}(t)$

In this appendix we develop some expressions useful for comparing our general formalism with Mori's.[7]

The Hermitian conjugate (i.e., complex conjugate and transpose) of the operator $P(t)$ in Eq. (9) or in Eq. (A6) is an operator $\mathcal{P}(t)$ satisfying

$$\mathcal{P}(t)A = F\cdot\delta\langle A\rangle_t/\delta\langle F\rangle_t \tag{B1}$$

$$= F\cdot\langle F\bar{F}\rangle_t^{-1}\cdot\langle F\bar{A}\rangle_t, \tag{B2}$$

where as usual A may be any operator. Equations (9) and (B1) give

$$\mathrm{Tr}[AP(t)B] = \mathrm{Tr}[B\mathcal{P}(t)A], \tag{B3}$$

and Eqs. (A6) and (B2) give

$$P(t)\bar{A}\sigma(t) = \overline{[\mathcal{P}(t)A]}\sigma(t). \tag{B4}$$

When Eq. (B1) is inserted into Eq. (B4), the result is Eq. (A7).

Also, either Eq. (B1) or Eq. (B2) gives

$$\mathcal{P}(t)F = F, \tag{B5}$$

and therefore

$$\mathcal{P}(t')\mathcal{P}(t) = \mathcal{P}(t). \tag{B6}$$

Furthermore, since $\langle F\bar{F}\rangle_t^{-1}$ is a symmetric matrix, Eqs. (B2) and (A4) give

$$\langle[\mathcal{P}(t)A]\bar{B}\rangle_t = \langle A\overline{[\mathcal{P}(t)B]}\rangle_t. \tag{B7}$$

Now $\langle A\bar{B}\rangle_t$ satisfies the conditions of an inner product between A and B and with respect to the weight $\sigma(t)$. Furthermore, even though $\mathcal{P}(t)$ and its transpose complex conjugate $P(t)$ are not equal, Eq. (B7) states that $\mathcal{P}(t)$ is Hermitian with respect to this inner product, i.e., with respect to the weight $\sigma(t)$. Therefore, although $\mathcal{P}(t)$ is not a projection operator in the usual sense, it is a projection operator with respect to the weight $\sigma(t)$.

In the linear approximation discussed in Sec. I and described in detail in Appendix C of Ref. 1, $\mathcal{P}(t)$ reduces to Mori's[7] projection operator $\mathcal{P}$ which depends only upon β and not upon $\lambda(t)$ or $\langle F\rangle_t$.

[43] J. B. Brown, D. Y. Chung, and P. W. Matthews, Phys. Letters **21**, 241 (1966); D. Y. Chung, dissertation, University of British Columbia, 1966 (unpublished).

APPENDIX C: $\sigma(t)$ A HOMOGENEOUS FUNCTIONAL OF $\langle F\rangle_t$

In this Appendix we show how $\sigma(t)$ can be written as a homogeneous functional of $\langle F\rangle_t$ of degree 1. Then our formalism becomes more similar to Zwanzig's[3] than it was before.

In many applications, it turns out that a linear combination of the $F_n(\mathbf{r})$ equals 1. By letting ζ represent a column vector whose elements are the coefficients of this linear combination, we may express this equality as

$$\zeta\cdot F=1, \tag{C1}$$

where the dot represents a sum and integral similar to that in Eq. (A1). Equation (C1) would automatically be true if, for example, $F_1(\mathbf{r})$ were the particle density and if the total particle number N were constant. Then $\zeta_1(r)\equiv 1/N$ is the only nonzero element of ζ.

If F is such that there exists a ζ satisfying Eq. (C1), then Eq. (C2) will not define $\lambda(t)$ uniquely since to any solution of Eq. (2) for $\lambda(t)$ may be added ζ times any functional of $\langle F\rangle_t$ in order to obtain another solution. This ambiguity, which can arise even though $\sigma(t)$ is always a unique functional of $\langle F\rangle_t$,[11] could lead to an ambiguity in $P(t)$ if $P(t)$ were calculated using $\delta\lambda(t)/\delta\langle F\rangle_t$ instead of $-\langle F\bar{F}\rangle_t^{-1}$. But if we have Eq. (C1), then $\lambda(t)$ may be defined in a different way, one which not only eliminates this possibility of ambiguity but also leads to a simpler and more elegant formalism. This formalism is always available since an additional operator $F_0\equiv 1$ can always be included in the set of operators $\{F_n(\mathbf{r})\}$, so that there will exist a ζ satisfying Eq. (C1).

Given Eq. (C1), we may replace the definitions (2) and (7) with

$$\langle F\rangle_t=\mathrm{Tr}\{F\exp[-\lambda(t)\cdot F]\}, \tag{C2}$$

$$\sigma(t)\equiv\exp[-\lambda(t)\cdot F] \tag{C3}$$

and still have $\sigma(t)$ normalized to unity.[5] This happens because $\langle 1\rangle_t=1$, which follows from the Liouville equation and Eq. (1) since $\rho(0)$ is normalized. If we use Eqs. (C2) and (C3), then we must replace the definition (6) with

$$\bar{A}\equiv\int_0^1\sigma(t)^x A\sigma(t)^{-x}\,dx. \tag{C4}$$

Then all of the other equations in this paper except those in Sec. III may be used without change.

For the following, $\langle 1\rangle_t$ is to be free to take any value and is not to be restricted to satisfy $\langle 1\rangle_t=1$. This last equality follows only from the Liouville equation, which is to be used only after the functional derivatives in the definition of $P(t)$ have been carried out.

We assume that Eq. (C2) uniquely defines $\lambda(t)$ as a functional of $\langle F\rangle_t$. We may denote this functional dependence by $\lambda[\langle F\rangle_t]$. Then Eqs. (C2) and (C1) give

$$\lambda[a\langle F\rangle_t]=\lambda[\langle F\rangle_t]-\zeta\ln a, \tag{C5}$$

where a may be any real positive number. Also, Eq. (C3) defines $\sigma(t)$ as a functional of $\lambda(t)$, which is a functional of $\langle F\rangle_t$. We may denote this functional dependence by $\sigma[\langle F\rangle_t]$. Then Eqs. (C3), (C5), and (C1) give

$$\sigma[a\langle F\rangle_t]=a\sigma[\langle F\rangle_t], \tag{C6}$$

where a is real and positive. This states that $\sigma[\langle F\rangle_t]$ is a homogeneous functional of $\langle F\rangle_t$ of degree 1.

By differentiating Eq. (C6) with respect to a and then letting $a=1$, we get

$$[\delta\sigma(t)/\delta\langle F\rangle_t]\cdot\langle F\rangle_t=\sigma(t). \tag{C7}$$

Combining Eqs. (9), (2), and (C7), we get

$$P(t)\rho(t)=\sigma(t). \tag{C8}$$

Many other interesting identities can be similarly obtained.[44] But Eq. (C8), which was not true with the previous definitions,[1] is what interests us here.

Equation (C8) states that when $P(t)$ operates on $\rho(t)$, it gives $\sigma(t)$, which is the relevant part of $\rho(t)$. Even though $P(t)$ is nontrivially time-dependent, both Eq. (C8) and Eqs. (1–22) are true since $P(t)$ is a homogeneous functional of $\langle F\rangle_t$ of degree zero. Now that Eqs. (C8) and (1–22) are both true, our formalism more closely parallels Zwanzig's.[3] The important difference that remains is in the dependence of $P(t)$ on $\langle F\rangle_t$.

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[44] Differentiate Eq. (C5) to get

$$[\delta\lambda(t)/\delta\langle F\rangle_t]\cdot\langle F\rangle_t=-\zeta,$$

which when combined with Eqs. (A3) and (C1) gives

$$F\cdot\langle F\bar{F}\rangle_t^{-1}\cdot\langle F\rangle_t=1$$

or when combined with Eq. (A3) gives

$$\langle F\rangle_t=\langle F\bar{F}\rangle_t\cdot\zeta.$$

This equation also follows from Eqs. (C1) and (C4).