value of Θ_0, obtained by the "semi-analytic" method described by de Launay,[18] is 24.5°K, again in fairly good agreement with the values in Table II.

III. CONCLUSION

In summary, our data indicate that bcc He^4 is probably not much different from the other forms of solid helium. This is based upon the following results discussed in detail above:

(a) The compressibility κ and the expansion coefficient α are well behaved. The expansion coefficient is positive and agrees with the Gruneisen equation with a Gruneisen constant $\gamma = 2.6$, which is the value found for the other low-pressure forms of solid helium and which is not inconsistent with the variation of the Debye Θ with volume in the present measurements. As was illustrated in Fig. 10, the V-T data available at present are not precise enough to use dV/dT to obtain either κ or α, so that earlier calculations which gave negative values of α are unreliable.

(b) The entropy of bcc He^4 when plotted as S/C_v versus T/Θ (Fig. 8) is found to be consistent with the values for the other low-pressure, crystalline forms of He^4 and He^3, indicating that the temperature dependence of Θ and the lattice spectra are very similar.

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[18] J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. II, p. 285.

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Equations of Motion in Nonequilibrium Statistical Mechanics*†

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Exact equations of motion for the space- and time-dependent thermodynamic coordinates of a many-body system are derived directly from the Liouville equation. This is done by definining a generalized canonical density operator depending only upon present values of the thermodynamic coordinates. This operator is used no matter how far the system is from equilibrium. An explicit expression for the entropy of a system possibly not in equilibrium is given in terms of this operator. The equation of motion for the operator is derived, and the coupled, nonlinear, integrodifferential equations of motion for the thermodynamic coordinates follow immediately.

INTRODUCTION

EQUATIONS of motion for the thermodynamic coordinates of a many-body system have been remarkably successful in describing the results of nonequilibrium experiments. The equations of hydrodynamics, London's equations for superconductors, and Bloch's equations for nuclear magnetism are well-known examples. Originally, these equations were not derived from microscopic considerations, but were obtained by more or less qualitative physical reasoning and contained adjustable parameters whose values were determined empirically. Since the assumptions made in order to obtain these phenomenological equations limited their applicability, it would be desirable to generalize these equations and thus extend their usefulness.

Unfortunately, it is not easy to just guess phenomenological improvements for these equations by using qualitative physical reasoning alone. Furthermore, it would be desirable to be able to calculate the values of the parameters appearing in the equations. Thus we are led to derive these equations from the Liouville equation and thereby obtain formal expressions for the parameters.

Once we have derived the equations, they may be solved as if they were classical equations, and in this manner many problems in nonequilibrium statistical mechanics can be solved. This equation of motion approach yields more general results than the perturbation-theory approach used in the linear theory of irreversible processes. In particular, we will be able to describe systems that may be arbitrarily far from equilibrium, and this is not possible with the linear theory.

The characteristic feature of our method is that no matter how far the system is from equilibrium we use a generalized canonical density operator $\sigma(t)$ that is a

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functional of the present values of the thermodynamic coordinates $\langle F_n(\mathbf{r})\rangle_t$, which are functions of both space and time. By using this operator, we obtain an explicit expression for the entropy of a system that may be arbitrarily far from equilibrium as well as an expression for the temperature of a system in thermodynamic equilibrium.

This generalized canonical density operator does not satisfy the Liouville equation as does the statistical density operator $\rho(t)$, but it does satisfy another equation of motion, which we derive. Given the initial condition for $\rho(t)$, we need no statistical argument for this derivation. We start by rewriting the Liouville equation using the Liouville operator $L(t)$. Then, once we have defined $\sigma(t)$, we define another operator $P(t)$ that converts the time derivative of $\rho(t)$ into the time derivative of $\sigma(t)$. These operators, along with another operator $T(t,t')$ that is an integrating factor, appear in the equation of motion for $\sigma(t)$. From this equation, we immediately get a set of coupled, nonlinear, integrodifferential equations of motion for the thermodynamic coordinates.

DEFINITIONS

It is necessary to use our intuition and experience to decide upon the thermodynamic coordinates that adequately describe the system and the experiment whose results we wish to predict. The pertinent thermodynamic coordinates are not determined merely by specifying the system or its Hamiltonian; they also depend upon what quantities are controlled or measured in the experiment considered. For systems not in equilibrium, it may be that the thermodynamic coordinates are not uniform throughout the system and hence have a spatial dependence. In general, the number of coordinates used will be quite small compared with the immense number of microscopic coordinates of the system. Usually it will be immediately apparent which coordinates should be used in our theory.

Once the thermodynamic coordinates have been chosen, we choose a set of time-independent, macroscopic, quantum-mechanical (i.e., Hermitian, linear, and possibly noncommuting) operators corresponding to some of these thermodynamic coordinates (e.g., energy density, particle density, magnetization per unit volume, etc.). These operators are denoted by $F_n(\mathbf{r})$, where n takes the values $1, 2, \cdots, m$. If the thermodynamic coordinates are not uniform throughout the sample, the corresponding operators may be expressed in a representation in the second quantized description where they will depend explicitly upon position $\mathbf{r}$ in space, as indicated. This functional notation is superfluous if the thermodynamic coordinates do not depend upon $\mathbf{r}$; then the operators may be expressed in a representation where they do not depend upon $\mathbf{r}$. In that case read F_n in place of $F_n(\mathbf{r})$ and simplify the following formalism accordingly.

Not all thermodynamic coordinates have corresponding quantum-mechanical operators. In particular, it appears that temperature and entropy are uniquely thermodynamic variables and are not at all mechanical. Furthermore, if there is an external electric or magnetic field and if that field is not quantized, then the field must be treated as a parameter. The thermodynamic coordinates that have no corresponding operators must be treated in a different way from the ones that do. As the theory develops, the entropy and the other remaining coordinates (e.g., temperature, chemical potential, magnetic field, etc., all as a function of position $\mathbf{r}$) will be defined so that they may be calculated from the values of the thermodynamic coordinates corresponding to the $F_n(\mathbf{r})$. We then will have a complete scheme for describing the thermodynamics of a quantum-mechanical system.

The thermodynamic coordinates corresponding to the operators $F_n(\mathbf{r})$ are the quantum-mechanical and statistical expectations of these operators

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

where the trace, indicated by the symbol Tr, is the sum of the diagonal elements of a matrix representation of the operator in the brackets. These expectations depend upon $\mathbf{r}$ since the operators $F_n(\mathbf{r})$ in the second quantized description themselves depend upon $\mathbf{r}$. They also depend upon time t, as indicated by the t on the left side of the equation, since the statistical density operator $\rho(t)$ depends upon t.

The statistical density operator $\rho(t)$ satisfies the equation of motion

$$i\hbar\dot{\rho}(t) = [\mathcal{H}(t),\rho(t)] \tag{2}$$

first derived by Dirac[1] from Schrödinger's equation. Since this equation is the quantum-mechanical analog of the classical Liouville theorem and since another equation is already called the Dirac equation, it is reasonable to call it the Liouville-Dirac equation or more simply the Liouville equation. The operator $\mathcal{H}(t)$ is the total Hamiltonian whose time dependence is what causes the deviations from equilibrium that we intend to study. Because of the invariance of the trace of a product of operators to cyclic permutations of the operators, the normalization

$$\mathrm{Tr}[\rho(t)] = 1 \tag{3}$$

is consistent with this equation of motion.

The Liouville equation (2) may be written

$$\dot{\rho}(t) = -iL(t)\rho(t), \tag{4}$$

where $L(t)$ is the Liouville operator,[2,3] which, when operating to the right on any operator A, yields the

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

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

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

commutator of the Hamiltonian with A:

$$L(t)A = \hbar^{-1}[\mathcal{H}(t), A]. \tag{5}$$

The Liouville operator is not a quantum-mechanical operator since it does not operate on states and its expectation is not defined. It operates only on other operators, turning them into new operators in a way analogous to a quantum-mechanical operator changing one state into a new one. All of the operators to the right of $L(t)$ must be included within the commutator.

The Liouville operator is a linear operator. This means that when it operates on the sum of any two operators A and B, the result is

$$L(t)(A+B) = L(t)A + L(t)B.$$

The dimensionality of the Hilbert space in which $L(t)$ is defined is the square of the dimensionality of the Hilbert space in which $\mathcal{H}(t)$, $\rho(t)$, and the $F_n(\mathbf{r})$ are defined. Since the operators A on which $L(t)$ operates will always have the same dimensionality as $\rho(t)$, then $L(t)A$ will also have that same dimensionality.

This formalism can be understood most easily if we write the operators in a matrix representation. A matrix representation of Eq. (4) is

$$\dot{\rho}_{nm}(t) = -i \sum L_{nm,kl}(t) \rho_{kl}(t),$$

where, from Eq. (5), the matrix representation of the Liouville operator is

$$L_{nm,kl}(t) = \hbar^{-1}[\mathcal{H}_{nk}(t)\delta_{lm} - \delta_{nk}\mathcal{H}_{lm}(t)].$$

Here $\mathcal{H}_{nk}(t)$ is the matrix element of the Hamiltonian, and δ_{lm} is the Kronecker delta. By using a matrix representation, we have been able to give an explicit expression for the Liouville operator. However, in order to keep our equations from becoming burdened with indices, we will use operator notation instead of matrix notation.

If $\mathcal{H}(t)$ and therefore $L(t)$ were independent of time, the formal solution to Eq. (2) would be

$$\rho(t) = \exp(-it\mathcal{H}/\hbar)\rho(0)\exp(it\mathcal{H}/\hbar),$$

whereas the formal solution to Eq. (4) would be

$$\rho(t) = \exp(-itL)\rho(0).$$

By comparing these two expressions, we can see the effect of the operator $\exp(-itL)$ when operating on a quantum-mechanical operator such as $\rho(0)$. We may also see that the two expressions are equal by expanding them both in powers of t and using Eq. (5). Neither formal solution is of much use since it is not easy to calculate explicitly all of the terms of the infinite series. Furthermore, even the formal solution to Eq. (4) is usually more complicated than here since $L(t)$ is usually a function of time.

In addition to the Liouville equation (4) and (5) and the expression for the expectation of an operator (1), we need the initial condition for $\rho(t)$, and it is only here that statistical methods enter. In the following section, we will state the initial condition for $\rho(t)$. Then, once the Hamiltonian is explicitly specified, we will have a complete formulation of quantum-statistical mechanics. The Pauli exclusion principle and the resulting Fermi statistics will automatically be included if anticommuting creation and annihilation operators are used. On the other hand, Bose statistics will automatically result if commuting creation and annihilation operators are used. No additional physical principles will be required for calculating the expectations (1) or for obtaining their equations of motion.

QUANTUM-STATISTICAL THERMODYNAMICS

In this paper we will derive the equation of motion of the generalized canonical density operator, which is defined to be

$$\sigma(t) = \exp\left[-\lambda_0(t) - \sum \int d^3r\, \lambda_n(\mathbf{r},t) F_n(\mathbf{r})\right], \tag{6}$$

where $\lambda_0(t)$ and the $\lambda_n(\mathbf{r},t)$ are to be calculated from the $m+1$ equations

$$\langle F_n(\mathbf{r})\rangle_t = \mathrm{Tr}[F_n(\mathbf{r})\sigma(t)], \quad n = 1,2,\cdots,m, \tag{7}$$

$$\mathrm{Tr}[\sigma(t)] = 1, \tag{8}$$

by solving them simultaneously with Eq. (6). This section will be devoted to discussing some of the properties of $\sigma(t)$, to using $\sigma(t)$ for concisely expressing the initial condition for $\rho(t)$, and to identifying $\lambda_0(t)$ and the $\lambda_n(\mathbf{r},t)$.

Calculating the $\lambda_n(\mathbf{r},t)$ involves the simultaneous solution of $m+1$ coupled, nonlinear, integral equations, which we can at least consider formally. The $\lambda_n(\mathbf{r},t)$ are functions of $\mathbf{r}$ and t since the expectations (7) themselves are functions of $\mathbf{r}$ and t. As a result, $\sigma(t)$ depends upon t, but it does not depend upon $\mathbf{r}$ since only the integral $\int d^3r\, \lambda_n(\mathbf{r},t)F_n(\mathbf{r})$ appears in Eq. (6).

As can be seen from Eq. (6), the generalized canonical density operator $\sigma(t)$ is defined in the same Hilbert space as the operators $F_n(\mathbf{r})$ and therefore in the same space as the total Hamiltonian $\mathcal{H}(t)$ and the statistical density operator $\rho(t)$. Hence, in constructing a theory around $\sigma(t)$, we are looking at the problem from Gibbs' point of view and considering the system as a whole instead of using the single-particle model for our many-body system. Such a point of view is necessary for systems of strongly interacting microscopic subsystems.

Equations (7) and (8) may be rewritten in terms of the partition functional

$$Z[\lambda_1(\mathbf{r},t), \lambda_2(\mathbf{r},t), \cdots, \lambda_m(\mathbf{r},t)]$$
$$= \mathrm{Tr}\left\{\exp\left[-\sum \int d^3r\, \lambda_n(\mathbf{r},t) F_n(\mathbf{r})\right]\right\} \tag{9}$$

as follows. The normalization condition (8) gives

$$\lambda_0(t) = \ln Z \tag{10}$$

and the $\lambda_n(\mathbf{r},t)$ are obtained from

$$\langle F_n(\mathbf{r})\rangle_t = -\delta\lambda_0(t)/\delta\lambda_n(\mathbf{r},t), \quad n=1,2,\cdots,m, \tag{11}$$

where δ denotes a functional derivative. We can understand this operation by considering the limit of the discrete case as follows. Corresponding to each of the possible values of $\mathbf{r}$ and t, there is a value of $\lambda_n(\mathbf{r},t)$. In performing the functional derivative, consider each of these values of $\lambda_n(\mathbf{r},t)$ to be an independent variable and perform an ordinary derivative. Care must be taken since the operators $F_n(\mathbf{r})$ may not commute with each other although the results are the same as if they did. This equivalence can be seen by using the trace of Eq. (A2) from Appendix A and observing that the trace of a product of operators is not changed when the operators are permuted cyclically.

The generalized canonical density operator defined by Eqs. (6)–(8) is the operator that renders

$$S(t) = -k\,\mathrm{Tr}[\sigma(t)\ln\sigma(t)] \tag{12}$$

a maximum subject to the constraints (7) and (8).[4] By use of Eqs. (6)–(8) and (12), we may write

$$S(t) = k\lambda_0(t) + k\sum\int d^3r\,\lambda_n(\mathbf{r},t)\langle F_n(\mathbf{r})\rangle_t. \tag{13}$$

Since the $\lambda_n(\mathbf{r},t)$ are functions of the $\langle F_n(\mathbf{r})\rangle_t$, it follows that $\lambda_0(t)$ and $S(t)$ as defined by Eqs. (13), (10), and (9) can be considered to be functions of the $\langle F_n(\mathbf{r})\rangle_t$ only. By calculating the total functional derivative of Eq. (13) with respect to the $\langle F_n(\mathbf{r})\rangle_t$ and applying Eq. (11), is is easy to show that

$$k\lambda_n(\mathbf{r},t) = \delta S(t)/\delta\langle F_n(\mathbf{r})\rangle_t, \quad n=1,2,\cdots,m. \tag{14}$$

To perform this functional derivative, again consider the $\langle F_n(\mathbf{r})\rangle_t$ for each of the values of $\mathbf{r}$ and t to be independent variables.

Gibbs' canonical and grand-canonical densities are special cases of our $\sigma(t)$. Our $\sigma(t)$ reduces to a grand-canonical density operator when F_1 is the total Hamiltonian $\mathcal{H}$ and F_2 is the total particle number operator N and there are no other operators $F_n(\mathbf{r})$. However, in general $\sigma(t)$ will be a functional of all the operators $F_n(\mathbf{r})$ corresponding to all of the observed variables and not just $\mathcal{H}$ and N, and we will use it whether or not the system is in equilibrium.

A system in thermodynamic equilibrium, however, is described by a canonical or grand-canonical density operator or, more generally, a generalized canonical density operator containing only operators that are macroscopic constants of the motion. Examples of such operators are the total energy, the total particle number, the total momentum, the total angular momentum, etc. Since most systems on which nonequilibrium experiments are performed are in thermodynamic equilibrium at one time or another, we may without loss of generality choose the initial condition for our system to be one of thermodynamic equilibrium. The initial condition for the statistical density operator $\rho(t)$, then, will be that at $t=0$ it equals a generalized canonical density operator containing only macroscopic constants of the motion.

We may express this initial condition in a convenient and concise form provided the generalized canonical density operator (6)–(8) is at least as general as the statistical density operator $\rho(0)$. It will be—provided there are enough operators in the set $\{F_n(\mathbf{r}),\ n=1, 2, \cdots, m\}$ so that all of the macroscopic constants of the motion can be written as linear combinations of the $F_n(\mathbf{r})$. If there are enough operators $F_n(\mathbf{r})$, then, for special values of the $\lambda_n(\mathbf{r},t)$, the $\sum\int d^3r\,\lambda_n(\mathbf{r},t)F_n(\mathbf{r})$ appearing in Eq. (6) will reduce to a nontrivial linear combination of the macroscopic constants of the motion. The initial condition for $\rho(t)$ then may be written as

$$\rho(0) = \sigma(0), \tag{15}$$

as can be seen by the following consideration. Since the the $\lambda_n(\mathbf{r},0)$ in Eq. (6) are determined by the $\langle F_n(\mathbf{r})\rangle_0$, which for systems in thermodynamic equilibrium are given by Eq. (1) with $\rho(0)$ being a generalized canonical density operator containing only macroscopic constants of the motion, it follows that the $\lambda_n(\mathbf{r},0)$ will have just the values so that Eq. (15) will be true. All systems initially in thermodynamic equilibrium at $t=0$ will have a statistical density operator $\rho(t)$ satisfying Eq. (15), but it is also possible for Eq. (15) to be true even if the system is not in thermodynamic equilibrium at $t=0$.

The experimenter may object to our including so many operators in the set $\{F_n(\mathbf{r}),\ n=1, 2, \cdots, m\}$ on the grounds that he does not intend to observe all of the corresponding dynamical variables. The objection may be answered as follows. Because of the simplicity of the initial condition (15) for the density operator $\rho(t)$, the equations of motion for the $\langle F_n(\mathbf{r})\rangle_t$ will be much simpler. If there were fewer operators in the set $\{F_n(\mathbf{r}),\ n=1, 2, \cdots, m\}$ so that Eq. (15) could not be true, then the equations of motion for the $\langle F_n(\mathbf{r})\rangle_t$ would be so complicated as to make it very difficult to use them. For the macroscopic equations of motion to be simple, they must state explicitly that, for example, the total energy, the total particle number, etc., of an isolated system are conserved.

If the experimenter insists on not observing all of the necessary dynamical variables, then he takes the risk of not completely controlling the experimental conditions. If he performs the experiment carefully so that he can be confident that he knows the values of the dynamical variables he does not observe, then we should include this information in the theory. We may do so, for example, by stating that the unobserved

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[4] E. T. Jaynes, Phys. Rev. **106**, 620 (1957); **108**, 171 (1957); *Statistical Physics, 1962 Brandeis Lectures* (W. A. Benjamin, Inc., New York, 1963), Vol. 3, p. 181; Am. J. Phys. **33**, 391 (1965).

dynamical variables are constant and then by dropping the corresponding equations of motion, keeping only enough equations to describe the remaining dynamical variables.

We now direct our attention to identifying the temperature and thermodynamic entropy. In doing so, we will see that some of the equations already written are familiar equations of equilibrium thermodynamics. We will use them whether or not the system is in thermodynamic equilibrium.

If the system undergoes a nonequilibrium process for $t>0$ and then settles down to thermodynamic equilibrium, the equilibrium thermodynamic entropy will be larger than before. But, $-k\,\mathrm{Tr}[\rho(t)\ln\rho(t)]$ is independent of time. This can be proved using the Liouville equation (2), the trace of Eq. (A2) with $A=\ln\rho(t)$, and the cyclic invariance of the trace. Hence, even though $-k\,\mathrm{Tr}[\rho(t)\ln\rho(t)]$ is identical with the equilibrium thermodynamic entropy for $t<0$, it cannot agree with the new value of the equilibrium thermodynamic entropy after the system has undergone a nonequilibrium process. Therefore, we must seek another quantity to identify as the thermodynamic entropy of a system possibly not in equilibrium.

In thermodynamics, the entropy is defined only for systems in thermodynamic equilibrium, and so it depends upon only present values of the thermodynamic coordinates and has no memory of past values. The function $S(t)$ in Eq. (13) is such a function and furthermore is equal to the thermodynamic entropy whenever the system is in thermodynamic equilibrium, as we now show. Consider an infinitesimal change in the thermodynamic state of the system for any instant t. Suppose the thermodynamic coordinates $\langle F_n(\mathbf{r})\rangle_t$ are changed by $\Delta\langle F_n(\mathbf{r})\rangle_t$; there will be no change in the operators $F_n(\mathbf{r})$ themselves since we do not change what coordinates we observe. Denote the resulting change in $\lambda_n(\mathbf{r},t)$ by $\Delta\lambda_n(\mathbf{r},t)$. Then, as a result of the change, $\lambda_0(t)$ will change by

$$\Delta\lambda_0(t)=-k\sum\int d^3r\,\Delta\lambda_n(\mathbf{r},t)\langle F_n(\mathbf{r})\rangle_t,\tag{16}$$

which may be derived from Eq. (11) and the usual expression for a total derivative. Therefore, for each instant of time t, the function $S(t)$ will change by

$$\Delta S(t)=k\sum\int d^3r\,\lambda_n(\mathbf{r},t)\Delta\langle F_n(\mathbf{r})\rangle_t,\tag{17}$$

which follows from Eq. (13). This equation is valid whether or not the system is in thermodynamic equilibrium at time t.

In order to identify $S(t)$ and the $\lambda_n(\mathbf{r},t)$, consider, for example, a system of nuclear spins interacting with each other and with an external magnetic field H. If the system is in thermodynamic equilibrium, we need consider only the total energy U of interaction between the spins and the total magnetic moment M instead of the local internal energy and the magnetization per unit volume. Thus we may simplify our theory by using operators that do not depend upon position in space. For this example, then, two macroscopic operators are used: F_1 is the total internal energy operator, and F_2 is the total magnetic moment operator. While the system is in thermodynamic equilibrium, we may compare Eq. (17) with equations from equilibrium thermodynamics as follows. The term for $n=1$ is $k\lambda_1\Delta U$, and the term for $n=2$ is $k\lambda_2\Delta M$; so when we compare Eq. (17) with the thermodynamic expression for changes in the entropy

$$\Delta S=\Delta Q/T$$

and the first law of thermodynamics

$$\Delta Q=\Delta U-H\Delta M,$$

we see that $S(t)$ is the thermodynamic entropy, λ_1 is $1/kT$, and λ_2 is $-H/kT$, where T is the temperature.

We now recognize Eqs. (11), (14), (16), and (17), which have been obtained from our definition of $\sigma(t)$, as equations of thermodynamics. Whenever the system is in thermodynamic equilibrium, $S(t)$ is the thermodynamic entropy, and the $\lambda_n(\mathbf{r},t)$ are simple functions of some of the remaining thermodynamic coordinates. Even when the system is not in equilibrium, $S(t)$ is the same function of the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r},t)$ as when the system is in thermodynamic equilibrium.

During a nonequilibrium process, $S(t)$ may be calculated as follows. Although the system is isolated so that no heat can flow in or out, we can imagine the original irreversible change to be replaced by an equivalent reversible change during which we let heat enter or leave. We construct this imaginary reversible change so that the final values of the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r},t)$ for the imaginary final thermodynamic state are the same as the values of the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r},t)$ for the original nonequilibrium state at time t. In order to do this, we must imagine a Hamiltonian whose time-dependent parameters change slowly enough for the system to remain in thermodynamic equilibrium. At the end of the imaginary reversible change, these parameters, of course, will have values different from the values of the parameters in the Hamiltonian of the real system—provided the real system is not already in thermodynamic equilibrium at time t. Whether or not the system is in thermodynamic equilibrium at time t, then, we get

$$S(t)=S(0)+\int_{REV} đQ/T,\tag{18}$$

where $đQ$ is the heat we imagine to enter the system while it undergoes the equivalent reversible change.

We are now ready to define the entropy of a system not in thermodynamic equilibrium. In thermodynamics, entropy is not defined for systems not in thermodynamic equilibrium. However, since $S(t)$ reduces to the equilibrium thermodynamic entropy whenever the system is in thermodynamic equilibrium and since it is always the same functional of the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r},t)$ whether or not the system is in thermodynamic equilibrium, we define it to be the thermodynamic entropy also for systems that are not in thermodynamic equilibrium. It may always be calculated since it is a function only of measured quantities, and it satisfies a form of the second law of thermodynamics.

For completeness, we list without proof several properties of the entropy $S(t)$. It turns out that $S(t)$ is not always a nondecreasing function of time; if the system approaches equilibrium in an oscillatory manner, the entropy can also approach its equilibrium value in an oscillatory manner. Although $dS(t)/dt \geq 0$ is not always true, $S(t)$ always has a lower bound. If the system is in thermodynamic equilibrium for $t<0$, then

$$S(t) \geq S(0) \quad \text{for} \quad t \geq 0. \tag{19}$$

The thermodynamic entropy of an isolated system can never be less than its initial value during an initial period of thermodynamic equilibrium. This is a form of the second law of thermodynamics.

Furthermore, it is easy to show that

$$\dot{S}(0)=0. \tag{20}$$

At the start of a nonequilibrium process, the entropy as a function of time always has zero slope.

Finally, if the Hamiltonian of our system is time-dependent only during the interval of time $0<t<t'$ and becomes independent of time for $t>t'$ and if the system does settle down to thermodynamic equilibrium for $t \gg t'$, then

$$S(t) \leq S(\infty) \quad \text{for} \quad t>t'. \tag{21}$$

That is, when the system settles down to equilibrium after being disturbed, the entropy will equal the maximum value it attained while with a time-independent Hamiltonian the system was approaching equilibrium.

DERIVATION OF THE EQUATIONS OF MOTION

Our present task is to construct equations that describe the time and space dependence of the thermodynamic coordinates $\langle F_n(\mathbf{r})\rangle_t$. Although we will use quantum mechanics to derive these equations of motion, they will be classical in form. Our hope is not only to use first principles to derive some useful phenomenological equations, such as Bloch's equations for magnetic resonance, but to obtain generalizations of these equations that can describe more complicated phenomena. Although we have had much success in this program, unfortunately we have not yet been able to completely calculate the functional form of all the expressions appearing in these equations. In applying a linear approximation of this formalism in another paper, we will make some phenomenological assumptions for the functional form of these expressions. The calculation in this paper, however, will be strictly deductive starting with the Liouville equation.

We will derive the equations of motion for the $\langle F_n(\mathbf{r})\rangle_t$ by first deriving the equation of motion for the generalized canonical density operator $\sigma(t)$.

Although either $\rho(t)$ or $\sigma(t)$ can be used to calculate the expectations $\langle F_n(\mathbf{r})\rangle_t$, the two density operators have important differences. Since $\rho(t)$ satisfies a first-order differential equation, it need be known at only one instant for it to be determined for all later (or earlier) instants. Thus memory is contained in the operator $\rho(t)$. On the other hand, since the $\lambda_n(\mathbf{r},t)$ depend upon only the present values of the expectations $\langle F_n(\mathbf{r})\rangle_t$, it follows that $\sigma(t)$ depends upon only those present values. But the values of the $\langle F_n(\mathbf{r})\rangle_t$ at only one instant do not in general completely determine their values for later (or earlier) instants. Thus $\sigma(t)$ does not satisfy a first-order differential equation; it does not satisfy a differential equation of any order. Since $\sigma(t)$ contains no memory of past values of the expectations $\langle F_n(\mathbf{r})\rangle_t$, that memory must be supplied by the equation of motion for $\sigma(t)$. In this equation, an integral of $\sigma(t)$ over the time interval 0 to t is used to determine how $\sigma(t)$ changes in time.

The form of the Liouville equation (4) suggests that an attempt to obtain an equation of motion for $\sigma(t)$ should begin with the calculation of the time derivative $\dot{\sigma}(t)$. Now Eqs. (6)–(8) state that $\sigma(t)$ is a functional of the $\langle F_n(\mathbf{r})\rangle_t$, which themselves are functions of time. So, we need to calculate the total derivative of $\sigma(t)$ with respect to the time. This total derivative can be expressed in the concise form

$$\dot{\sigma}(t)=P(t)\dot{\rho}(t) \tag{22}$$

by use of the time-dependent linear operator $P(t)$ defined by

$$P(t)A=\sum_{n=1}^{m}\int d^3r \frac{\delta\sigma(t)}{\delta\langle F_n(\mathbf{r})\rangle_t}\mathrm{Tr}[F_n(\mathbf{r})A], \tag{23}$$

where δ denotes a functional derivative. Here A may be any operator defined in the same space as the $F_n(\mathbf{r})$ and thus as $\sigma(t)$ and $\rho(t)$. The operator $P(t)A$ will then be defined in that same space while $P(t)$ itself is defined in the same space that $L(t)$ is. All operators to the right of $P(t)$ must be included in the trace.

A matrix representation of $P(t)A$ is

$$[P(t)A]_{ij}=\sum P(t)_{ij,kl}A_{kl},$$

where

$$P(t)_{ij,kl}=\sum_{n=1}^{m}\int d^3r\left[\frac{\delta\sigma(t)}{\delta\langle F_n(\mathbf{r})\rangle_t}\right]_{ij}[F_n(\mathbf{r})]_{lk}.$$

However, as we have already said, we will use operator notation instead of matrix notation. We have written the last two equations only to clarify the definition of the operator $P(t)$.

It follows from the definition (23), Eq. (7), and the definition of the functional derivative that

$$\mathrm{Tr}[F_n(\mathbf{r})P(t)A]=\mathrm{Tr}[F_n(\mathbf{r})A] \tag{24}$$

so that

$$P(t)P(t')A=P(t)A\,, \tag{25}$$

where t' need not equal t. Although the last equation with $t=t'$ appears to suggest otherwise, $P(t)$ is not a projection operator[3,5] in the usual sense. For an operator P to be a projection operator, it must not only be linear and satisfy $P^2=P$, but it must also be Hermitian. Our operator $P(t)$ is not Hermitian in general.

The dependence of $P(t)$ upon time arises because $P(t)$ depends upon $\sigma(t)$ or equivalently the $\langle F_n(\mathbf{r})\rangle_t$. That $P(t)$ depends upon only $\sigma(t)$ can be seen as follows. Considering the definition (6)–(8) of $\sigma(t)$, we can view $\sigma(t)$ as depending only upon the $\langle F_n(\mathbf{r})\rangle_t$ so that the $\delta\sigma(t)/\delta\langle F_n(\mathbf{r})\rangle_t$ and hence $P(t)$ depend only upon the $\langle F_n(\mathbf{r})\rangle_t$. But, Eq. (7) states that the $\langle F_n(\mathbf{r})\rangle_t$ themselves depend only upon $\sigma(t)$. Therefore, $P(t)$ depends only upon $\sigma(t)$.

We proceed with the derivation of an equation of motion for $\sigma(t)$ by using the Liouville equation (4) to evaluate $\rho(t)$ in Eq. (22). As a result, the right side of Eq. (22) will contain $\rho(t)$ whose time dependence is not known. However, $\rho(t)$ may be written as the sum of the desired $\sigma(t)$ and another unknown, $\rho(t)-\sigma(t)$, so that Eq. (22) becomes

$$\dot{\sigma}(t)=-iP(t)L(t)\sigma(t)-iP(t)L(t)[\rho(t)-\sigma(t)]\,.$$

Now an equation for $\rho(t)-\sigma(t)$ can be formed by calculating the time derivative $d[\rho(t)-\sigma(t)]/dt$ using Eq. (4) and the previous equation, and again separating $\rho(t)$ into $\sigma(t)$ plus $\rho(t)-\sigma(t)$ to get

$$d[\rho(t)-\sigma(t)]/dt+i[1-P(t)]L(t)[\rho(t)-\sigma(t)] =-i[1-P(t)]L(t)\sigma(t)\,.$$

No additional unknowns appear in this equation so that there are as many coupled equations (two) as there are unknowns (two). Thus these two differential equations are sufficient to determine the time dependence of both $\sigma(t)$ and $\rho(t)-\sigma(t)$. The equation of motion for $\sigma(t)$ is formed by solving the second equation above for $\rho(t)-\sigma(t)$ as a function of $\sigma(t)$ and using that solution to eliminate $\rho(t)-\sigma(t)$ in the first equation.

Since the second equation has only one time derivative and is linear in $\rho(t)-\sigma(t)$, it can be solved by a method analogous to the usual method of solving ordinary first-order linear differential equations. The integrating factor for the second equation is a linear operator $T(t,t')$ that satisfies the differential equation

$$\partial T(t,t')/\partial t'=iT(t,t')[1-P(t')]L(t') \tag{26}$$

and has the initial condition

$$T(t,t)=1\,. \tag{27}$$

Since $P(t)$ depends upon $\sigma(t)$, the operator $T(t,t')$ depends upon $\sigma(t'')$ over the time interval between t' and t. If $[1-P(t)]L(t)$ were independent of time, the solution to Eq. (26) would be $T(t,t')=\exp[-i(t-t')\times(1-P)L]$. In general, however, both $P(t)$ and $L(t)$ depend upon time so that the solution cannot be written in closed form without the use of time ordering operators or the equivalent. Nevertheless, it is not necessary that we have an explicit expression for $T(t,t')$ in order to proceed with the formal derivation of the equation of motion for $\sigma(t)$. We will have to face that problem eventually, however.

Now replace t by t' in the second of the coupled equations, multiply the result by the integrating factor $T(t,t')$, and use Eq. (26) and the linearity of $T(t,t')$ to get

$$\partial\{T(t,t')[\rho(t')-\sigma(t')]\}/\partial t' =-iT(t,t')[1-P(t')]L(t')\sigma(t')\,.$$

Of course, this equation can also be verified directly by using Eqs. (4), (22), and (26). When the equation is integrated from 0 to t, it becomes

$$\rho(t)-\sigma(t)=-i\int_0^t dt'\,T(t,t')[1-P(t')]L(t')\sigma(t')\,,$$

where we have used the initial conditions (15) and (27). When this is inserted into the first of the coupled equations, the result is[6]

$$\dot{\sigma}(t)=-iP(t)L(t)\sigma(t) -\int_0^t dt'\,P(t)L(t)T(t,t')[1-P(t')]L(t')\sigma(t')\,, \tag{28}$$

which is the desired equation of motion. The only unknown in this equation is $\sigma(t)$ so that in principle this equation along with Eqs. (5)–(8), (23), (26), and (27) determines the time and space dependence of the thermodynamic coordinates $\langle F_n(\mathbf{r})\rangle_t$. Although Eq. (28) appears to be linear in $\sigma(t)$, it is not since the operators $P(t)$ and $T(t,t')$ depend upon $\sigma(t)$.

Since $\sigma(t)$ depends upon the $\langle F_n(\mathbf{r})\rangle_t$, Eq. (28) may be written as a set of m coupled, nonlinear, integro-differential equations for the m unknowns $\langle F_n(\mathbf{r})\rangle_t$. These equations are obtained by multiplying Eq. (28) by the $F_n(\mathbf{r})$, taking the trace of both sides, and using

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

[6] A derivation that appears to be similar to this has been given by Nakajima (Ref. 3) and in more detail by Zwanzig (Ref. 5). Although our derivation was partly motivated by Zwanzig's, it necessarily is different since $\sigma(t)$ is not a linear function of $\rho(t)$. Hence, although Eq. (28) appears to resemble an equation of his, it is not the same equation, the most important difference being in the definition (23) of the operator $P(t)$. Our $P(t)$ depends upon the unknown $\sigma(t)$, is not a projection operator, and does not give the relevant part of $\rho(t)$, but instead satisfies Eq. (22).

Eqs. (7) and (24) to get

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t = -i\,\mathrm{Tr}[F_n(\mathbf{r})L(t)\sigma(t)] - \int_0^t dt'\,\mathrm{Tr}\{F_n(\mathbf{r})L(t)T(t,t')[1-P(t')]L(t')\sigma(t')\},\qquad n=1,2,\cdots,m. \quad (29)$$

In principle, to use these equations, one must first calculate $T(t,t')$ from Eqs. (26) and (27), where $L(t)$ is defined by Eq. (5) and $P(t)$ is defined by Eq. (23) and then use Eqs. (6)–(8) to express $T(t,t')$, $P(t)$, and $\sigma(t)$ in terms of the $\langle F_n(\mathbf{r})\rangle_t$.

Instead of viewing the $\langle F_n(\mathbf{r})\rangle_t$ as being the only unknowns, it is easier to consider the $\lambda_n(\mathbf{r},t)$ as also being unknowns that are to be calculated simultaneously with $\langle F_n(\mathbf{r})\rangle_t$. Then, when Eqs. (6) and (10) are inserted into Eqs. (7) and (29), the latter equations become $2m$ coupled, nonlinear, integral and integrodifferential equations in the $2m$ unknowns $\langle F_n(\mathbf{r})\rangle_t$ and $\lambda_n(\mathbf{r},t)$. These equations are coupled algebraic and integrodifferential equations for the time dependence of the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r},t)$. Furthermore, they are coupled integral equations for the space dependence of the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r},t)$. Thus the theory is memory-retaining and nonlocal.

Finally, we rewrite the last term of Eq. (29) to make some of its dependence on the $\lambda_n(\mathbf{r},t)$ more explicit. By using the definition (5) of $L(t)$, we may prove the identity[2]

$$L(t)A = -\hbar^{-1}\int_0^1 dx\, d[A^x\mathcal{H}(t)A^{1-x}]/dx, \quad (30)$$

which along with Eq. (6) gives

$$L(t)\sigma(t) = -\sum_n \int d^3r \int_0^1 dx\,\sigma(t)^x \times[L(t)F_n(\mathbf{r})]\sigma(t)^{1-x}\lambda_n(\mathbf{r},t). \quad (31)$$

By using this and the identity

$$\mathrm{Tr}\{A[B,C]\} = \mathrm{Tr}\{[A,B]C\}, \quad (32)$$

we may write Eqs. (29) as

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t = \mathrm{Tr}\{[iL(t)F_n(\mathbf{r})]\sigma(t)\} + \int_0^t dt' \sum_{n'} \int d^3r'\, K_{nn'}(\mathbf{r},\mathbf{r}',t,t')\lambda_{n'}(\mathbf{r}',t'),\qquad n=1,2,\cdots,m, \quad (33)$$

where

$$K_{nn'}(\mathbf{r},\mathbf{r}',t,t') = -\int_0^1 dx\,\mathrm{Tr}\{[iL(t)F_n(\mathbf{r})]T(t,t') \times[1-P(t')]\sigma(t')^x[iL(t')F_n(\mathbf{r}')]\sigma(t')^{1-x}\}. \quad (34)$$

These equations are all exact and have no restrictions to their generality. In Appendix B we show that $K_{nn'}(\mathbf{r},\mathbf{r}',t,t')$ is real. Furthermore, in a linear approximation, $K_{nn'}(\mathbf{r},\mathbf{r}',t,t')$ will satisfy a reciprocity relation and a time-reversal symmetry relation,[2] which we prove in Appendix C. In general, $K_{nn'}(\mathbf{r},\mathbf{r}',t,t')$ depends upon the unknown $\lambda_n(\mathbf{r},t)$ in a complicated way. For the examples of the application of Eqs. (33) so far worked out, the first term on the right reduces to easily recognized kinematic terms, and the integral term causes relaxation.

CONCLUSION

Regardless of the complexity of a system or of the experiment performed on that system, it is always possible to describe the results of the experiment with a set of exact equations of motion whose only unknowns are quantities that are directly observed, i.e., the $\langle F_n(\mathbf{r})\rangle_t$ and the $\lambda_n(\mathbf{r},t)$. In our notation these equations are Eqs. (7) and (29), which are to be used with Eqs. (5), (6), (9), (10), (23), (26), and (27).

That these equations are exact and have been derived from quantum-statistical mechanics without assumption or restriction of generality is the most important feature that distinguishes our work. However, these equations do contain expressions that in general may be evaluated only approximately, a difficulty that appears to be inherent to the subject. In the following we will compare our work in detail with a few recent papers in order to illustrate the advantages of our method.

By making several assumptions, Zwanzig[7] has obtained approximate equations for the thermodynamic coordinates $\alpha_n(t)$ and $F_n[\alpha(t)]$, which correspond to our $\langle F_n\rangle_t$ and $\lambda_n(t)$. To do this, he uses a probability distribution in classical statistical mechanics that does not correspond to any expression in our formalism. In his notation, our generalized canonical density operator $\sigma(t)$ corresponds to the generalized microcanonical density $\delta[A(x)-\alpha(t)]/\int dx'\,\delta[A(x')-\alpha(t)]$, which he does not consider. In obtaining his approximate Eq. (40) which corresponds to our exact Eq. (33), he restricts the Hamiltonian to be independent of time and assumes what in our notation is equivalent to assuming that $P(t)$ may be set equal to zero in the equation for $T(t,t')$. The latter assumption precludes a description of many systems exhibiting interesting memory effects.

Mori[8] obtains approximate equations for his $A(t)$, whose expectation corresponds to our $\langle F_n\rangle_t$, by applying the method of Ref. 5 to Heisenberg's equations of motion instead of to the Liouville equation. His operator $\mathcal{P}$, however, is not Hermitian and hence is not a projection operator. Nevertheless, the method still works since his $\mathcal{P}$ is independent of time. But he does not obtain an exact equation of motion for his $A(t)$ with that $A(t)$ as the only unknown. He uses a high-tempera-

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

[8] H. Mori, Progr. Theoret. Phys. (Kyoto) **33**, 423 (1965).

ture approximation to his initial density operator. In Appendix C, we restrict our Hamiltonian to be independent of time and make a linear approximation. If we furthermore restrict our system to be uniform in space, our formalism reduces to Mori's once we eliminate the $\mu_n(t)$ between Eqs. (C4) and (C8). Our operator $P(t)$ then is independent of $\sigma(t)$ and furthermore is independent of time and reduces to the Hermitian conjugate of his $\mathcal{P}$. An advantage still remains in our formalism even after being so restricted and approximated: Our operators F_n are the directly observed dynamical variables, and we need not remove their invariant part, i.e., the part that is diagonal in a representation in which the Hamiltonian is diagonal. This is important since removing the invariant part of an operator is as difficult as solving the entire many-body problem itself. A further advantage of our formalism even in this linear approximation is that we use the $\mu_n(\mathbf{r},t)$, which together with the $\langle F_n(\mathbf{r})\rangle_t$ comprise all of the thermodynamic coordinates at least when the system is in thermodynamic equilibrium. The simple physical interpretation of the $\mu_n(\mathbf{r},t)$ and the simplification of the formalism resulting from their use makes it desirable to keep them in the formalism and not eliminate them as has Mori. Like his formalism and that of Ref. 5, our formalism in general takes the same form in classical as in quantum-statistical mechanics.

In a study of relaxation in a gas, Fano[9] has applied the method of Ref. 5 in the frequency domain instead of the time domain and so restricts his discussion to Hamiltonians that are independent of time. In a study of relaxation in a solid, Lax[10] has used an improved Hartree procedure in a density matrix formulation. Both authors consider a system of interest interacting with a thermal bath, a point of view that we did not find necessary to take. Neither author obtains exact equations of motion whose only unknowns are the thermodynamic coordinates of an arbitrary system.

A survey of the theory of irreversible processes has been made by Chester,[11] and a comparison between the Nakajima-Zwanzig master equation and other master equations has been made by Zwanzig.[12]

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APPENDIX A

If A and B are any two operators that possibly do not commute with each other and that do not operate on or depend upon a parameter x', then

$$(d/dx')\exp[x'(A+B)]\exp[-x'A]=\exp[x'(A+B)]B\exp[-x'A],$$

which may be verified by direct differentiation. Now integrate this over x' from 0 to x, multiply both sides on the right by $\exp(xA)$, and transpose the lower limit on the left side to the right side of the equation to get

$$\exp[x(A+B)]=\exp[xA]+\int_0^x dx'\exp[x'(A+B)]B\exp[(x-x')A].$$

This integral equation may be solved approximately for the unknown $\exp[x(A+B)]$ by iteration giving

$$\begin{aligned}\exp[x(A+B)]&=\exp[xA]+\int_0^x dx_1\exp[x_1A]B\\&\times\exp[(x-x_1)A]+\int_0^x dx_1\int_0^{x_1}dx_2\exp[x_2A]B\\&\times\exp[(x_1-x_2)A]B\exp[(x-x_1)A]+\cdots.\end{aligned}\tag{A1}$$

Finally, let $B=\delta A$ and keep only first-order terms to show that

$$\begin{aligned}\delta\exp[xA]&\equiv\exp[x(A+\delta A)]-\exp[xA]\\&=\int_0^x dx'\exp[x'A](\delta A)\exp[(x-x')A],\end{aligned}\tag{A2}$$

which is valid for any operator A.

APPENDIX B

The proof that $K_{nn'}(\mathbf{r},\mathbf{r}',t,t')$ defined by Eq. (34) is real is as follows. Equation (26) may be integrated using Eq. (27) to form a linear integral equation with $T(t,t')$ as the unknown. This integral equation may be solved by iteration giving

$$\begin{aligned}T(t,t')=1-\mathrm{i}\int_{t'}^t dt_1[1-P(t_1)]L(t_1)\\-\int_{t'}^t dt_1\int_{t1}^t dt_2[1-P(t_2)]L(t_2)[1-P(t_1)]L(t_1)+\cdots.\end{aligned}\tag{B1}$$

Now since $[A,B]^\dagger=-[A^\dagger,B^\dagger]$ for any linear operators A and B, where the dagger indicates a Hermitian conjugate, we have

$$[iL(t)A^\dagger]=iL(t)A^\dagger,\tag{B2}$$

where $L(t)$ is defined by Eq. (5) with $\mathcal{H}(t)^\dagger=\mathcal{H}(t)$. Furthermore, because of the definition (23) of $P(t)$, we have

$$[P(t)A]^\dagger=P(t)A.\tag{B3}$$

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[9] U. Fano, Phys. Rev. **131**, 259 (1963); *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic Press Inc., New York, 1964), Vol. 2, p. 217.

[10] M. Lax, J. Phys. Chem. Solids **25**, 487 (1964).

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

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

As a result,

$$[T(t,t')A]^\dagger = T(t,t')A^\dagger. \tag{B4}$$

Finally, we need

$$\left[\int_0^1 dx\, \sigma(t)^x A \sigma(t)^{1-x}\right]^\dagger = \int_0^1 dx\, \sigma(t)^x A^\dagger \sigma(t)^{1-x}, \tag{B5}$$

which follows from $\sigma(t)^\dagger = \sigma(t)$. Now, since the complex conjugate of the trace of a product of two operators is the trace of the product of the Hermitian conjugates of the operators, and since the $F_n(\mathbf{r})$ are Hermitian, it follows from these equations that $K_{nn'}(\mathbf{r},\mathbf{r}',t,t')$ is real.

APPENDIX C

In this Appendix we restrict ourselves to a Hamiltonian that for $t>0$ is independent of time and consider a linear approximation to our formalism in order to prove some reciprocity relations and time-reversal relations. Such a restriction is not always necessary in order to obtain a useful theory. This Appendix is the only place in this paper any approximations or restrictions to generality are made.

Let $\mathcal{H} = \mathcal{H}(0+)$ represent the Hamiltonian for $t>0$ where $\mathcal{H}(0+)$ is different from the initial Hamiltonian $\mathcal{H}(0-)$ so that at $t=0$ the system is disturbed from its initial state of thermodynamic equilibrium. Because of our requirement that the operators $F_n(\mathbf{r})$ be sufficiently general that all of the macroscopic constants of the motion may be written as linear combinations of the $F_n(\mathbf{r})$, we are always able to write

$$\mathcal{H} = \sum \int d^3r\, \eta(\mathbf{r}) F_n(\mathbf{r}), \tag{C1}$$

$$N = \sum \int d^3r\, \nu_n(\mathbf{r}) F_n(\mathbf{r}), \tag{C2}$$

where $\eta_n(\mathbf{r})$ and $\nu_n(\mathbf{r})$ are suitable functions of $\mathbf{r}$. If $\mathcal{H}$ and N are the only macroscopic constants of the motion, a useful approximation will be to consider

$$\mu_n(\mathbf{r},t) = \lambda_n(\mathbf{r},t) - \alpha\, \nu_n(\mathbf{r}) - \beta \eta_n(\mathbf{r}) \tag{C3}$$

as being small, where $1/k\beta$ is the temperature and α/β is the chemical potential. Then to first order in $\mu_n(\mathbf{r},t)$, the definition (6), (10), and (9) of $\sigma(t)$ becomes

$$\sigma(t) = \sigma_0 - \sum \int d^3r\, \mu_n(\mathbf{r},t)[\bar{F}_n(\mathbf{r}) - \langle F_n(\mathbf{r})\rangle]\sigma_0, \tag{C4}$$

where

$$\sigma_0 \equiv \exp(-\alpha N - \beta\mathcal{H}) / \mathrm{Tr}[\exp(-\alpha N - \beta\mathcal{H})] \tag{C5}$$

and where

$$\langle A\rangle \equiv \mathrm{Tr}(A\sigma_0), \tag{C6}$$

$$\bar{A} \equiv \int_0^1 dx\, \sigma_0{}^x A \sigma_0 \delta^{-x}, \tag{C7}$$

for any operator A. As in Eqs. (7), the $\mu_n(\mathbf{r},t)$ are to be determined in terms of the $\langle F_n(\mathbf{r})\rangle_t$ by solving the coupled equations

$$\langle F_n(\mathbf{r})\rangle_t = \langle F_n(\mathbf{r})\rangle - \sum\nolimits_{n'} \int d^3r'\, [\langle F_n(\mathbf{r})\bar{F}_{n'}(\mathbf{r}')\rangle$$
$$- \langle F_n(\mathbf{r})\rangle\langle F_{n'}(\mathbf{r}')\rangle]\mu_{n'}(\mathbf{r}'),\ n=1,2,\cdots,m. \tag{C8}$$

In this linear approximation, the definition (23) of the operator $P(t)$ becomes

$$PA = -\sum_{nn'} \int d^3r\, d^3r' \frac{\delta\mu_{n'}(\mathbf{r}',t)}{\delta\langle F_n(\mathbf{r})\rangle_t}$$
$$\times[\bar{F}_{n'}(\mathbf{r}') - \langle F_{n'}(\mathbf{r}')\rangle]\sigma_0\, \mathrm{Tr}[F_n(\mathbf{r})A]. \tag{C9}$$

We have written P for $P(t)$ since that operator is independent of time as may be seen by observing that the $\delta\mu_{n'}(\mathbf{r}',t)/\delta\langle F_n(\mathbf{r})\rangle_t$ are the solutions to the coupled equations

$$-\sum_{n'} \int d^3r'\, [\langle F_{n''}(\mathbf{r}'')\bar{F}_{n'})\rangle - \langle F_{n''}(\mathbf{r}'')\rangle\langle F_{n'}(\mathbf{r}')\rangle]$$
$$\times \frac{\delta\mu_{n'}(\mathbf{r}',t)}{\delta\langle F_n(\mathbf{r})\rangle_t} = \delta_{nn''}\delta(\mathbf{r}-\mathbf{r}''), \tag{C10}$$

which are obtained by taking the functional derivative of Eqs. (C8) with respect to $\langle F_n(\mathbf{r})\rangle_t$. From now on we will consider the $\delta\mu_{n'}(\mathbf{r}',t)/\delta\langle F_n(\mathbf{r})\rangle_t$ as having been eliminated between Eqs. (C9) and (C10).

The kernel (34) may now be considerably simplified by solving Eqs. (26) and (27) for $T(t,t')$ and inserting the solution into Eq. (34) to get

$$K_{nn'}(\mathbf{r},\mathbf{r}',t-t') = -\langle[iLF_n(\mathbf{r})]\exp[-i(t-t')(1-P)L]$$
$$\times(1-P)[iL\bar{F}_{n'}(\mathbf{r}')]\rangle, \tag{C11}$$

where we have written L for $L(0+)$. Finally, Eqs. (33) become

$$\partial\langle F_n(\mathbf{r})\rangle_t/\partial t = -\sum\nolimits_{n'} \int d^3r'\, \langle[iLF_n(\mathbf{r})]\bar{F}_{n'}(\mathbf{r}')\rangle\mu_{n'}(\mathbf{r}',t)$$
$$+\int_0^t dt' \sum\nolimits_{n'} \int d^3r'\, K_{nn'}(\mathbf{r},\mathbf{r}',t-t')\mu_n(\mathbf{r}',t'),$$
$$n=1,2,\cdots,m. \tag{C12}$$

The kernels in Eqs. (C8) and (C12) are now independent of the unknown $\sigma(t)$ or equivalently the $\mu_n(\mathbf{r},t)$ or the $\langle F_n(\mathbf{r})\rangle_t$. The first two kernels may usually be calculated at least approximately, but the third kernel (C11) is more difficult to calculate. However, our theory becomes immediately useful phenomenologically if a convenient functional form is assumed for the kernel (C11). The kernel should decrease to zero for increasing $|\mathbf{r}-\mathbf{r}'|$ and for increasing $(t-t')$ although not necessarily monotonically. This will be assumed in another paper in which our formalism will be applied to a paramagnetic system with a time-dependent

Hamiltonian that drives the system far from equilibrium.

The reciprocity relations may now be derived as follows: Equations (C6) and (C7) give

$$\langle A\bar{B}\rangle = \langle B\bar{A}\rangle \tag{C13}$$

for any operators A and B. The reciprocity relation

$$\langle F_n(\mathbf{r})\bar{F}_{n'}(\mathbf{r}')\rangle = \langle F_{n'}(\mathbf{r}')\bar{F}_n(\mathbf{r})\rangle \tag{C14}$$

follows immediately. Since the matrix

$$-[\langle F_{n''}(\mathbf{r}'')F_{n'}(\mathbf{r}')\rangle - \langle F_{n''}(\mathbf{r}'')\rangle\langle F_{n'}(\mathbf{r}')\rangle]$$

is symmetrical in $n'\mathbf{r}'$ and $n''\mathbf{r}''$, then its inverse (C10) is symmetrical also

$$\delta\mu_{n'}(\mathbf{r}',t)/\delta\langle F_n(\mathbf{r})\rangle_t = \delta\mu_n(\mathbf{r},t)/\delta\langle F_{n'}(\mathbf{r}')\rangle_t. \tag{C15}$$

Now Eqs. (5), (C5), and (C6) give

$$\langle(iLA)\rangle = 0 \tag{C16}$$

for any operator A. Also, Eqs. (5), (C9), (C13), (C15), and (C16) give

$$\langle(iLA)P(iL\bar{B})\rangle = \langle(iLB)P(iL\bar{A})\rangle \tag{C17}$$

and Eqs. (5), (32), and (C13) give

$$\langle A(iL\bar{B})\rangle = -\langle B(iL\bar{A})\rangle \tag{C18}$$

for any operators A and B. The reciprocity relation

$$\langle[iLF_n(\mathbf{r})]\bar{F}_{n'}(\mathbf{r}')\rangle = -\langle[iLF_{n'}(\mathbf{r}')]\bar{F}_n(\mathbf{r})\rangle \tag{C19}$$

follows immediately from Eqs. (32) and (C18). Furthermore, by using a method similar to the method used to prove Eqs. (C17) and (C18), we may prove

$$\begin{aligned}&\langle(iLA)[i(1-P)L]^k(1-P)(iL\bar{B})\rangle\\ &\quad=\langle(iLB)[-i(1-P)L]^k(1-P)(iL\bar{A})\rangle\end{aligned} \tag{C20}$$

by induction for any operators A and B and for k being a non-negative integer. The reciprocity relation

$$K_{nn'}(\mathbf{r},\mathbf{r}',t-t') = K_{n'n}(\mathbf{r}',\mathbf{r},t'-t) \tag{C21}$$

follows immediately by Taylor expanding the right side of Eq. (C11) and using Eq. (C20) term by term.

Next we derive the time-reversal symmetry relations. Under time reversal given[13] by the similarity transformation $R(\ \ )R^{-1}$, the Hamiltonian $\mathcal{H}_\mathbf{H}$ becomes

$$R\mathcal{H}_\mathbf{H}R^{-1} = \mathcal{H}_{-\mathbf{H}}, \tag{C22}$$

where the subscript indicates the sign of the external magnetic field $\mathbf{H}$ appearing in the Hamiltonian. Under time reversal and simultaneous reversal of the external magnetic field, then, $\mathcal{H}_\mathbf{H}$ is unchanged. Also, since $RNR^{-1}=N$, Eqs. (C5) and (C22) give

$$R(\sigma_0)_\mathbf{H}R^{-1} = (\sigma_0)_{-\mathbf{H}}. \tag{C23}$$

Furthermore, since $RiR^{-1}=-i$, Eqs. (5) and (C22) give

$$R(iL_\mathbf{H}A)R^{-1} = -iL_{-\mathbf{H}}RAR^{-1} \tag{C24}$$

for any operator A. Now, without loss of generality, we may define the operators $F_n(\mathbf{r})$ so that

$$RF_n(\mathbf{r})R^{-1} = \epsilon_nF_n(\mathbf{r}),\quad \epsilon_n=\pm1,\quad n=1,2,\cdots,m, \tag{C25}$$

i.e., under time reversal $F_n(\mathbf{r})$ changes at most in sign only. Then, by introducting $1=R^{-1}R$ into the trace in Eq. (C6) and by using Eqs. (C7), (C23), and (C25) and the invariance of the trace of a product of operators to cyclic permutations of the operators, we may prove the time-reversal symmetry relation

$$\langle F_n(\mathbf{r})\bar{F}_{n'}(\mathbf{r}')\rangle_\mathbf{H} = \epsilon_n\epsilon_{n'}\langle F_n(\mathbf{r})\bar{F}_{n'}(\mathbf{r}')\rangle_{-\mathbf{H}}, \tag{C26}$$

where ϵ_n is the same as in Eq. (C25) and the subscript indicates that $\mathbf{H}$ is changed in sign in σ_0. Also, by introducing $1=R^{-1}R$ into the trace in the first term on the right of Eq. (C12) and by using Eqs. (C6), (C7), and (C23)–(C25) and the cyclic invariance of the trace, we may prove the time-reversal symmetry relation

$$\langle[iLF_n(\mathbf{r})]\bar{F}_{n'}(\mathbf{r}')\rangle_\mathbf{H} = \epsilon_n\epsilon_{n'}\langle[iLF_n(\mathbf{r})]\bar{F}_{n'}(\mathbf{r}')\rangle_{-\mathbf{H}}, \tag{C27}$$

where ϵ_n is the same as in Eq. (C25) and the subscript indicates that $\mathbf{H}$ is changed in sign in both L and σ_0. Furthermore, by introducing $1=R^{-1}R$ into the trace in Eq. (C6) with A replaced by $F_n(\mathbf{r})$ and by using Eqs. (C23) and (C25) and the cyclic invariance of the trace, we may prove the time-reversal symmetry relation

$$\langle F_n(\mathbf{r})\rangle_\mathbf{H} = \epsilon_n\langle F_n(\mathbf{r})\rangle_{-\mathbf{H}},\quad n=1,2,\cdots,m, \tag{C28}$$

where ϵ_n is the same as in Eq. (C25). By applying Eqs. (C22), (C25), and (C28) to Eqs. (C7) and (C9), we get

$$R(P_\mathbf{H}A)R^{-1} = P_{-\mathbf{H}}RAR^{-1}. \tag{C29}$$

Finally, introduce $1=R^{-1}R$ into the trace in Eq. (C11) and use Eqs. (C24), (C25), and (C29), $RtR^{-1}=t$, and the cyclic invariance of the trace to get the time-reversal symmetry relation

$$K_{nn'}(\mathbf{r},\mathbf{r}',t-t')_\mathbf{H} = \epsilon_n\epsilon_{n'}K_{nn'}(\mathbf{r},\mathbf{r}',t'-t)_{-\mathbf{H}}, \tag{C30}$$

where the subscript indicates that $\mathbf{H}$ is changed in sign everywhere it appears.

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[13] R. R. Bliss, Rept. Progr. Phys. **26**, 307 (1963).