STATISTICAL MECHANICS OF IRREVERSIBILITY*

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Introduction

These lectures have two objectives. One is to explain in an elementary way some recent advances in the theory of irreversibility. The other is to describe several mathematical ideas and devices that are useful in this subject.

The recent advances to which we refer are due mainly to Van Hove[1, 2] and to Prigogine and his co-workers.[3, 4] Van Hove and Prigogine have developed an elaborate mathematical technique for following the temporal evolution of initial states of many-body systems. They use an infinite order perturbation theory, along with various prescriptions, based on physical arguments, for keeping specific terms in the perturbation expansion, and leaving out the rest.

The idea of starting out with a precisely, (although not necessarily completely), defined initial state is useful and attractive. It distinguishes the work of Van Hove and the Prigogine school from most earlier work in this field. (Kubo's theory of linear transport processes,[5] discussed in this volume by Montroll (p. 221), is in the same spirit.)

However, the infinite order, many-body perturbation theory often seems to be more complicated than is really needed. One has to pay close attention to the details of tedious combinatorial and topological (or "diagrammatic") arguments; this can obscure fundamental questions of a more physical kind.

We shall show in these lectures that much of the combinatorial topology can be avoided entirely by analytic methods that are at least as clear, and considerably more compact. These methods are presented in Sections II, III and IV.

A significant difference between the work of Prigogine and that of Van Hove is that Prigogine studied mainly the classical ensemble distribution function and the classical Liouville equation, while Van Hove was concerned with the quantum mechanical wave function and the Schroedinger equation. Van Hove had to deal with the additional formal complication, not occurring in classical statistical mechanics, that average values of observables are bilinear in the wave function.

In these lectures we show how this extra complication can be

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avoided by using the density matrix. We thereby display a striking formal similarity between weak-coupling problems in classical and quantum statistical mechanics.

Section VI contains two examples of our general method. The first is a new derivation of the Pauli equation, and the second is a derivation of a classical analogue, due originally to Prigogine and Brout.

Some new material on the evaluation of time correlation functions is presented in Section VII.

From the point of view of fundamental theory of irreversibility, Section V is perhaps the most important in these lectures. This section has to do with the time dependence of physical quantities, and with some mathematical methods that are pertinent. We work out a special prototype example in great detail, with emphasis on asymptotic time dependence, and on the effect of the finite size of a real physical system.

I. The Dynamical Problem

In both classical and quantum mechanics, dynamical problems can be formulated in terms of operators in Hilbert space. Because this is a powerful method, and because it has universal applicability, we shall discuss it first.

The Hilbert space formulation of quantum mechanics has been common knowledge for a long time; the corresponding formulation of classical mechanics has existed almost as long, but is not nearly so widely known. In this section I shall mention also the relatively unfamiliar formulation of quantum mechanics in terms of the Hilbert space of operators (rather than of states); this should be quite useful in quantum statistical mechanics.

In all cases we shall find that equations of motion can be written in the simple form

$$i\frac{dx}{dt} = Lx, \tag{I.1}$$

where x is a vector in Hilbert space and L is a Hermitian operator.

In classical mechanics the equation of motion of any dynamical quantity $a(R, p)$, depending on coordinates R and momenta p, but not explicitly on time, can be written in Poisson bracket form:

$$\frac{da}{dt} = -\{H, a\}_{P.B.} . \tag{I.2}$$

Here H is the Hamiltonian function and $\{\ \}_{P.B.}$ denotes the Poisson bracket. Let us define the Liouville operator L by

$$i\frac{da}{dt} = -La = -i\{H, a\}_{P.B.} . \tag{I.3}$$

More specifically, L is

$$L = i \frac{\partial H}{\partial R} \frac{\partial}{\partial p} - i \frac{\partial H}{\partial p} \frac{\partial}{\partial R} . \qquad (I.4)$$

The operator L was first introduced by Koopman[6]. Note that L is Hermitian in the Hilbert space of phase functions.

Liouville's equation for the time dependence of the phase space ensemble density f(R, p; t) is

$$i \frac{\partial f}{\partial t} = Lf. \qquad (I.5)$$

The change in sign from Eq. (3) to Eq. (5) is important.

The classical equations of motion possess formal solutions as initial value problems. These solutions are given by exponential operators,

$$a(t) = \exp(itL) \cdot a(0), \qquad (I.6)$$

$$f(t) = \exp(-itL) \cdot f(0). \qquad (I.7)$$

The operator $\exp(\pm itL)$ is unitary in Hilbert space. It is often referred to as a Green's function or a propagator. Its Laplace transform with respect to time,

$$\int_0^\infty dt\, e^{-pt}\, e^{itL} = \frac{1}{p - iL} , \qquad (I.8)$$

is also called a Green's function, propagator and, more often, a resolvent operator.

Equations (6) and (7) illustrate a kind of Heisenberg picture in classical mechanics. The expectation value of a variable $a(R, p)$, weighted according to the ensemble density f(R, p; t), is

$$\langle a;\ f(t) \rangle = \iint dR\, dp\ a(R, p)\, f(R, p; t). \qquad (I.9)$$

The integration covers all of phase space. But this average is also

$$\langle a;\ f(t) \rangle = \langle a;\ e^{-itL} f(0) \rangle$$

$$= \langle e^{+itL} a\ ;\ f(0) \rangle$$

$$= \langle a(t);\ f(0) \rangle . \qquad (I.10)$$

The expectation at t can be calculated in two ways: by following the evolution of either the ensemble density or the dynamical variable. It is a matter of convenience which is preferred.

In quantum mechanics, an observable a is represented by a matrix or an operator in Hilbert space. The evolution of a is determined by Heisenberg's equation of motion,

$$i \frac{da}{dt} = -\frac{1}{\hbar} [H, a] = -\frac{1}{\hbar} (Ha - aH). \qquad (I.11)$$

We can define a linear Hermitian operator L by

$$La = \frac{1}{\hbar} [H, a] ; \qquad (I.12)$$

then Eq. (11) becomes

$$i \frac{da}{dt} = -La. \qquad (I.13)$$

This L is an operator that works in the Hilbert space of operators rather than the space of states.

The quantum mechanical L has been mentioned by Kubo,[7] and Fano[8] has shown how to calculate it explicitly in, for example, spin problems.

Liouville's equation for the density matrix $\rho(t)$ is

$$i \frac{d\rho}{dt} = \frac{1}{\hbar} [H, \rho] = L\rho . \qquad (I.14)$$

Again note the change in sign from Eq. (13), which reflects the Heisenberg-Schroedinger duality.

The quantum mechanical equations of motion also have formal operator solutions, which can be written in the familiar Hamiltonian or the unfamiliar Liouville form,

$$a(t) = e^{iHt/\hbar}\, a(0)\, e^{-iHt/\hbar} = e^{itL}\, a(0), \qquad (I.15)$$

$$\rho(t) = e^{-iHt/\hbar}\, \rho(0)\, e^{iHt/\hbar} = e^{-itL}\, \rho(0). \qquad (I.16)$$

The expectation of a, weighted according to $\rho(t)$, is

$$\langle a;\ \rho(t) \rangle = \text{Trace}\ \{ a\, \rho(t) \} . \qquad (I.17)$$

It is easy to verify the quantum form of Eq. (10).

This shows that all equations of motion can be written in the general form

$$i \frac{dx}{dt} = Lx ,$$

where L is Hermitian. We have introduced the formal, abstract operator solution

$$\chi(t) = G(t)\, \chi(0), \qquad (I.18)$$

$$G(t) = \exp(-itL). \qquad (I.19)$$

Much of the current work in statistical mechanics consists of finding useful approximations for G(t).*

II. The Diagonal Part of G(t)

On many occasions one is not interested in full knowledge of G(t), but only in its diagonal matrix elements. We shall give an example later; for the present let us just assume that this is so.

There is an obvious, though hard, way of calculating G(t). This is to solve the Liouville equation, or, the same thing, to evaluate exp(-itL). But there is another more devious way of proceeding, and this is the subject of the present section. The idea is to replace Eq. (I.1), which involves all matrix elements of G, by a new equation containing only the diagonal part of G.

The procedure followed here is completely equivalent to what has been done in the past by diagrams and perturbation theory. However, the present method is more direct and does not involve expansions.

We introduce an operator D, which selects the diagonal part of the entire matrix on which it operates, and which discards the off-diagonal part. Then

$$(DA)_{jk} = A_{jj}\,\delta_{jk} \,. \tag{II.1}$$

Note that when D operates on a product it sees both factors, not only the nearest one:

$$(DAB)_{jk} = \sum_{\ell} A_{j\ell}\,B_{\ell j}\,\delta_{jk} \,. \tag{II.2}$$

Furthermore, D is a projection operator:

$$D^2 = D, \qquad D(1-D) = 0. \tag{II.3}$$

It is possible to write D as a tetradic operator. The (ij) component of DA is

$$(DA)_{ij} = \sum_{k}\sum_{\ell} D_{ijk\ell}\,A_{k\ell} \,. \tag{II.4}$$

In order to recover Eq. (1), we require that

$$D_{ijk\ell} = \delta_{ij}\,\delta_{ik}\,\delta_{j\ell} \,. \tag{II.5}$$

Since the combination (1-D) occurs also, we need the unit tetradic; this is just

$$1_{ijk\ell} = \delta_{ik}\,\delta_{j\ell} \,.$$

* As long as the density matrix is represented as a two-index matrix, the quantum mechanical L cannot be represented in the same way. In fact, L is a tetradic operator, with four indices. Because of this, classical and quantum mechanical treatments in matrix notation must be made independently.

Using D, the Green's function can be divided into diagonal and non-diagonal parts:

$$G_d = D\cdot G, \qquad G_{o.d.} = (1-D)\cdot G, \tag{II.6}$$

and

$$G = G_d + G_{o.d.} \,. \tag{II.7}$$

In the same way the kinetic equation for G,

$$i\,\frac{dG}{dt} = LG, \tag{II.8}$$

can be divided into two equations. First we multiply by D:

$$D\,i\,\frac{dG}{dt} = i\,\frac{dG_d}{dt} = DLG = DLG_d + DLG_{o.d.} \,. \tag{II.9}$$

Then we do the same with (1-D):

$$(1-D)\,i\,\frac{dG}{dt} = i\,\frac{dG_{o.d.}}{dt} = (1-D)LG = (1-D)LG_d + (1-D)LG_{o.d.} \tag{II.10}$$

Now we formally solve the second of these, Eq. (10), for $G_{o.d.}$ In doing this a modified Green's function appears:

$$\mathcal{G}(t) \equiv \exp[\,-it(1-D)L\,] \,. \tag{II.11}$$

This function can be defined either by its series expansion or by its use in solving the equation for matrix A,

$$i\,\frac{dA}{dt} = (1-D)LA, \tag{II.12}$$

with the initial condition A = A(0). The solution is then

$$A(t) = e^{-it(1-D)L}\,A(0) \equiv \mathcal{G}(t)\cdot A(0). \tag{II.13}$$

The operator (1-D) in the exponent of $\mathcal{G}(t)$ sees not only the L that follows it directly, but everything to its right, including the matrix on which $\mathcal{G}$ operates.

Returning to the solution of Eq. (10), one can verify by substitution that

$$G_{o.d.}(t) = -i\int_0^t ds\;\; \mathcal{G}(t-s)(1-D)L\,G_d(s)$$

$$= -i\int_0^t ds\;\; \mathcal{G}(s)\,(1-D)L\,G_d(t-s). \tag{II.14}$$

The initial condition $G_{o.d.}(0) = 0$ was used.

When Eq. (14) is substituted in Eq. (9), we obtain the desired result,

$$i\frac{dG_d}{dt} = DLG_d(t) - i\int_0^t ds\ DL\mathcal{G}(s)(1-D)LG_d(t-s). \qquad (II.15)$$

After this equation has been solved for $G_d(t)$, Eq. (14) may be used to calculate $G_{o.d.}$.

The same equations can be written out in matrix form. (The following statements are not correct when L is the quantum mechanical Liouville operator; then, as we shall see, the commutator definition of L leads to more complicated results.) A diagonal element of G is denoted by G_{kk} and its kinetic equation is

$$i\frac{dG_{kk}(t)}{dt} = L_{kk}G_{kk}(t) - i\int_0^t ds[L\mathcal{G}(s)(1-D)L]_{kk}G_{kk}(t-s). \qquad (II.16)$$

The various diagonal elements of G are not coupled. Similarly, the off-diagonal elements ($j \neq k$) are

$$G_{jk}(t) = -i\int_0^t ds\ [\mathcal{G}(s)(1-D)L]_{jk}G_{kk}(t-s). \qquad (II.17)$$

In a later section the perturbation expansion of Eq. (15) will be presented. It will then become clear that the results of this section are entirely equivalent to those found by "diagram" methods.

III. Generalization

In the last section we considered only the diagonal part of a Green's function. While this is useful and important, one may be interested in other more complicated situations. We shall consider several variations on the "diagonal part" theme in this section.

It is instructive to begin by checking over the preceding derivation to see just where the diagonal property of D was used. In fact, it appeared explicitly only in the assertion that G is initially diagonal, or $DG(0) = G(0)$. Otherwise D could have been quite arbitrary.

Suppose that we want to find the diagonal part of the density matrix ρ, which satisfies the equation

$$i\frac{d\rho}{dt} = L\rho\ . \qquad (III.1)$$

The procedure used before cannot work here exactly, because the initial density matrix may have off-diagonal elements. This means that the initial value $\rho_{o.d.}(0)$ must appear. We shall just give the general result; the method of derivation will be obvious. We find

$$i\frac{d\rho_d(t)}{dt} = DL\rho_d(t) - i\int_0^t ds\ DL\mathcal{G}(s)(1-D)L\rho_d(t-s) + DL\mathcal{G}(t)\rho_{o.d.}(0) \qquad (III.2)$$

and

$$\rho_{o.d.}(t) = -i\int_0^t ds\ \mathcal{G}(s)(1-D)L\rho_d(t-s) + \mathcal{G}(t)\rho_{o.d.}(0). \qquad (III.3)$$

These equations may be used as the starting point for the derivation of the Pauli equation (weakly-coupled master equation) of quantum statistical mechanics. We shall go through the derivation later.

If ρ is initially diagonal, Eqs. (2) and (3) reduce to the same formal structure as the equations we have already found for the diagonal part of a Green's function. But the difference in interpretation is important. In the case of the density matrix, we are not solving for a Green's function in the same sense as in the preceding section. The Green's function that goes with the density matrix has the property

$$\rho_{jk}(t) = \sum_\ell \sum_m G_{jk,\,\ell m}(t)\,\rho_{\ell m}(0), \qquad (III.4)$$

and its diagonal part, $G_{jk,\,jk}(t)$, connects an element of ρ at time t with the initial value of the same element:

$$\rho_{jk}(t) = G_{jk,\,jk}(t)\,\rho_{jk}(0) + \text{off-diagonal terms}, \qquad (III.5)$$

while Eq. (2) refers to the quantities $\rho_{jj}(t)$ only.

The use that one makes of the diagonalization device depends on what kind of information is desired, and what kind of information is available initially.

Finally we describe one more generalization. Let us consider the abstract problem

$$i\frac{dx}{dt} = Lx\ , \qquad (III.6)$$

where x and L are, respectively, a vector and an operator in some Hilbert space. Let P denote a projection operator in this space; it defines a subspace of Hilbert space, and Px is the part of the vector

x that lies in the subspace. One can easily verify that Eqs. (2) and (3) remain correct if one makes the following changes:

$$\begin{aligned} D &\to P, \\ \rho_d &\to Px, \\ \rho_{o.d.} &\to (1-P)x, \\ \mathcal{G}(s) &\to \exp[-is(1-P)L]. \end{aligned} \tag{III.7}$$

This is the most general result of its kind; it includes the D-operator as a special case.

IV. Perturbation Theory

A. Weak Perturbations.

When L can be represented conveniently as a diagonal matrix, there are no dynamical problems, because the equation of motion can be integrated immediately. If L has a small off-diagonal part, then a perturbation theory is useful. Many problems can be reduced to this situation. Later we shall discuss in particular the master equations for classical and quantum mechanical weakly-coupled systems--the Prigogine-Brout and the Pauli equations. But in this section we consider for simplicity only a special case, the perturbation theory of the diagonal part of a matrix Green's function.

Suppose that L can be separated into two parts,

$$L = L^o + \lambda L', \tag{IV.1}$$

where L^o is diagonal (and hence commutes with D: $L^oD = DL^o$), and L' has no diagonal elements. The parameter λ measures the strength of the perturbation L'.

We want to see the form taken by the exact equation (II.15),

$$i\frac{dG_d(t)}{dt} = DLG_d(t) - i\int_0^t ds\, DL\,\mathcal{G}(s)(1-D)LG_d(t-s), \tag{IV.2}$$

in the limit of weak perturbation or small λ. The first term is easy:

$$DLG_d = L^o G_d, \tag{IV.3}$$

because we take the diagonal part of L times a diagonal matrix G_d:

$$(DLG_d)_{jj} = (LG_d)_{jj} = \sum_k L_{jk}(G_d)_{kj} = L_{jj}(G_d)_{jj} = (L^oG_d)_{jj}. \tag{IV.4}$$

The contribution from the integral in Eq. (2) is a bit harder to work out. The (1-D) on the right operates on L times a diagonal matrix G_d, so the L^o part drops out:

$$DL\mathcal{G}(1-D)LG_d = DL\mathcal{G}(1-D)\lambda L'G_d. \tag{IV.5}$$

Next we observe that $\mathcal{G}(1-D)\lambda L'G_d$ has no diagonal elements. This is most easily seen by the pedestrian method of expanding; for any arbitrary matrix M,

$$\begin{aligned} \mathcal{G}(1-D)M &= \exp[-it(1-D)L](1-D)M \\ &= [1 - it(1-D)L + (1/2)(it)^2(1-D)L(1-D)L - \ldots](1-D)M \\ &= (1-D)M - it(1-D)L(1-D)M \\ &\quad + (1/2)(it)^2(1-D)L(1-D)L(1-D)M + \ldots \end{aligned} \tag{IV.6}$$

Each term in the expansion begins with a (1-D). This is in fact the same as the expansion

$$\mathcal{G}(1-D)M = (1-D)\exp[-itL(1-D)]M \tag{IV.7}$$

and the whole quantity has only off-diagonal elements. Now the first D on the left of the integral in Eq. (2) operates on L times a non-diagonal matrix of the form of Eq. (7), so that L can be replaced by $\lambda L'$.

In this way Eq. (2) becomes, exactly,

$$i\frac{dG_d(t)}{dt} = L^oG_d(t) - i\lambda^2\int_0^t ds\, DL'\mathcal{G}(s)(1-D)L'G_d(t-s). \tag{IV.8}$$

A factor λ^2 appears explicitly, and $\mathcal{G}(s)$ depends on λ:

$$\mathcal{G}(s) = \exp[-is(1-D)(L^o + \lambda L')]. \tag{IV.9}$$

(It should be noted that one may not simplify $\mathcal{G}(s)$ in the following apparently obvious way:

$$\mathcal{G}(s) \to \exp[-is(1-D)\lambda L'], \tag{IV.10}$$

even though L^o is diagonal and $(1-D)L^o$ appears to vanish. The reason is that (1-D) operates on everything to its right. See the expansion in Eq. (6) and the equivalent Eq. (7).)

If we want only the weak coupling limit, we can replace the general $\mathcal{G}(s;\lambda)$ by its limit $\mathcal{G}(s;0)$, given by

$$\mathcal{G}(s;0) = \exp[-is(1-D)L^o]; \tag{IV.11}$$

and, for example by expansion, one can see that

$$\mathcal{G}(s;0)(1-D) = \exp[-is(1-D)L^o](1-D) = e^{-isL^o}(1-D), \tag{IV.12}$$

so only the unperturbed Green's function $\exp(-isL^o)$ appears.

Thus Eq. (8) becomes

$$i\frac{dG_d(t)}{dt} = L^oG_d(t) - i\lambda^2\int_0^t ds\ DL'\,e^{-isL^o}(1-D)L'G_d(t-s) + O(\lambda^3 G_d). \quad \text{(IV.13)}$$

If one writes this out with subscripts, the result is

$$i\frac{dG_{kk}(t)}{dt} = L^o_{kk}G_{kk}(t) - i\lambda^2\int_0^t ds\sum_{j\neq k}L'_{kj}\,e^{-isL^o_{jj}}L'_{jk}G_{kk}(t-s) + O(\lambda^3 G). \quad \text{(IV. 14)}$$

The assumptions that went into the derivation of Eqs. (13) and (14) are purely mathematical and have nothing to do with physical ideas. They are:

1) G is initially diagonal,

2) L^o is diagonal, L' is non-diagonal,

3) The lowest order in λ only is kept.

B. Perturbation Theory to Higher Order.

In order to demonstrate the relation of our results to other more familiar ones, and to provide a convenient way of going to higher orders in λ, we introduce Laplace transforms.

Let

$$\varphi(p) = \int_0^\infty dt\ e^{-pt}\,G_d(t) \quad \text{(IV.15)}$$

be the Laplace transform of $G_d(t)$. The transform of $\mathcal{G}$ is

$$\int_0^\infty dt\ e^{-pt}\ \mathcal{G}(t) = \frac{1}{p+i(1-D)L} \quad \text{(IV.16)}$$

and the transform of the (exact) Eq. (8) is

$$ip\varphi(p) - iG_d(0) = L^o\varphi(p) - i\lambda^2\,DL'\frac{1}{p+i(1-D)L} \times (1-D)L'\varphi(p). \quad \text{(IV.17)}$$

We have used the property that the transform of a convolution is the product of the transforms.

Solving Eq. (17) for $\varphi(p)$, we find

$$\varphi(p) = \left[\, p+iL^o + \lambda^2 DL'\left(\frac{1}{p+i(1-D)L}\right)(1-D)L'\,\right]^{-1} G_d(0). \quad \text{(IV.18)}$$

The standard formula for inverting a Laplace transform is

$$G_d(t) = \frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty} dp\ e^{pt}\,\varphi(p)\ ; \quad \text{(IV.19)}$$

the real constant ϵ must be chosen so that (for positive t) the path of integration lies to the right of all singularities of $\varphi(p)$.

The perturbation theory now comes in through the expansion in powers of λ of $\kappa(p;\lambda)$,

$$\kappa(p;\lambda) = DL'\frac{1}{p+i(1-D)(L^o+\lambda L')}(1-D)L'. \quad \text{(IV. 20)}$$

First we expand the middle factor:

$$\frac{1}{p+i(1-D)(L^o+\lambda L')} = \frac{1}{p+i(1-D)L^o} - \frac{1}{p+i(1-D)L^o}\,i(1-D)\lambda L' \times \frac{1}{p+i(1-D)L^o} + \frac{1}{p+i(1-D)L^o}\,i(1-D)\lambda L'\,\frac{1}{p+i(1-D)L^o} \times i(1-D)\lambda L'\,\frac{1}{p+i(1-D)L^o} + \ldots\ . \quad \text{(IV.21)}$$

Taking the Laplace transform of Eq. (12), we find that

$$\frac{1}{p+i(1-D)L^o}\ (1-D) = \frac{1}{p+iL^o}(1-D). \quad \text{(IV.22)}$$

Let

$$\gamma^o = \frac{1}{p+iL^o} \quad \text{(IV.23)}$$

be the transform of the unperturbed Green's function. Then

$$\kappa(p;\lambda) = DL'\gamma^o(1-D)L' - i\lambda\,DL'\gamma^o(1-D)L'\gamma^o(1-D)L' + (i\lambda)^2 DL'\gamma^o(1-D)L'\gamma^o(1-D)L'\gamma^o(1-D)L' - \ldots\ . \quad \text{(IV.24)}$$

Since κ is to operate on the identity $G_d(0) = 1$, and since each term begins with D, we need only the diagonal part of κ itself. Each factor γ^o is diagonal, and the only non-diagonal contributions come from L'. If we write the general term of κ as a matrix product, each L' forming a separate factor, the effect of the (1-D) is that no matrix subscript in the interior of the product can equal the initial or final subscript on the product. In the language of the diagram method, the matrix products are connected.

Incidentally, this provides a method of calculating partition functions in quantum mechanics. If we want

$$Q = \text{Trace } e^{-\beta H} = \sum_j (e^{-\beta H})_{jj}, \tag{IV.25}$$

where H is the Hamiltonian operator and $\beta = 1/kT$, then we want the sum of the diagonal elements of the matrix

$$G = e^{-\beta H}. \tag{IV.26}$$

But G satisfies the Bloch equation,

$$\frac{\partial G}{\partial \beta} = -HG, \tag{IV.27}$$

with the initial condition $G(0) = 1$. This is a natural setup for the preceding perturbation theory. We replace (iL) by H, and write, as with L,

$$H = H^o + \lambda H'. \tag{IV.28}$$

We replace t by β, take the Laplace transform of $Q(\beta)$, and find that (as in Eq. (18)),

$$\int_0^\infty d\beta\, e^{-\beta z}\, Q(\beta) = \text{Trace } \frac{1}{z+H}$$

$$= \sum_j \left(z + H^o_{jj} - \left[H \frac{1}{z+(1-D)H} (1-D) H \right]_{jj} \right)^{-1}$$

$$= \sum_j \left(z + H^o_{jj} - \lambda^2 \left[H' \frac{1}{z+(1-D)H} H' \right]_{jj} \right)^{-1}. \tag{IV.29}$$

All matrices are expressed in the representation where H^o is diagonal. Equation (29) is a suitable starting point for the investigation of various kinds of approximation schemes in the calculation of partition functions.

Perturbation expansions are only natural when λ is actually small and when all pertinent quantities exist (mathematically speaking). At this point the advantage of our general method becomes evident. Most of our results are independent of whether or not a perturbation expansion exists or converges, and other methods of evaluating the memory operator $\kappa(p;\lambda)$ may be sought in case perturbation theory does not work.

V. Time Dependence

The ultimate objective of this work is to find the time dependence of various quantities of interest in statistical mechanics. In order to avoid excessive detail, we shall consider only a very special prototype example.

We shall look for the solution of

$$\frac{dG(t)}{dt} = -\lambda^2 \int_0^t ds\, K(s;\lambda)\, G(t-s) \tag{V.1}$$

with the initial condition $G(0)=1$. Here $G(t)$ and $K(s;\lambda)$ are just functions, not operators or matrices, and we assume that $K(s;\lambda)$ is regular for small λ. In particular we are interested in the solution for small λ.

Equation (1) has the form of Eq. (IV.8) without the L^o.

In the weak coupling limit (small λ) one can proceed in several ways. Perhaps the most elementary argument is that when λ is small, then dG/dt is small and $G(t-s)$ can be replaced by the term $G(t) + O(\lambda^2)$. In this way Eq. (1) becomes

$$\frac{dG(t)}{dt} = -\lambda^2 \int_0^t ds\, K(s;\lambda)\, G(t) + O(\lambda^4). \tag{V.2}$$

This is now a simple differential equation rather than an integral equation. Its solution is

$$G(t) = \exp\left[-\lambda^2 \int_0^t ds \int_0^s ds'\, K(s';\lambda) + O(\lambda^4) \right]. \tag{V.3}$$

We assume that K is integrable from zero to infinity, so that there is some time τ_m beyond which

$$\int_0^t ds\, K(s;\lambda) \simeq \int_0^{\tau_m} ds\, K(s;\lambda) \tag{V.4}$$

to sufficient accuracy. Then for t much larger than τ_m,

$$\int_0^t ds \int_0^s ds' K(s';\lambda) \simeq t \int_0^{\tau_m} ds\, K(s;\lambda) , \qquad (V.5)$$

and for such large times, G decays exponentially:

$$G(t) \cong \exp\left[-\lambda^2 t \int_0^{\tau_m} ds\, K(s;\lambda) + O(\lambda^4)\right]. \qquad (V.6)$$

Note that small λ is required in this argument.

The preceding "derivation" is not rigorous, and the result is not quite correct. In this paragraph we give a more rigorous but less informative derivation. This is based on the substitutions

$$x = \lambda^2 t, \qquad (V.7)$$

$$g(x) = G(t) . \qquad (V.8)$$

Now Eq. (1) can be written

$$\frac{dg(x)}{dx} = -\int_0^{x/\lambda^2} ds\, K(s;\lambda)\, g(x-\lambda^2 s). \qquad (V.9)$$

We take the limit

$$\lambda \to 0, \qquad t \to \infty , \qquad x \text{ fixed}. \qquad (V.10)$$

Then in the limit,

$$\frac{dg(x)}{dx} = -\int_0^{\infty} ds\, K(s;0)\, g(x), \qquad (V.11)$$

or

$$g(x) = \exp\left[-x \int_0^{\infty} ds\, K(s;0)\right], \qquad (V.12)$$

which is equivalent to

$$G(t) = \exp\left[-\lambda^2 t \int_0^{\infty} ds\, K(s;0)\right] . \qquad (V.13)$$

Again we find an exponential decay, with the same sort of rate constant as before, but only in the double limit $\lambda \to 0$, $t \to \infty$, $\lambda^2 t$ fixed. This limiting process, introduced by Van Hove, is elegant and easy to apply, but tends to obscure an important feature of the time dependence when λ does not go to zero, but remains finite.

To see that all may not be well, let us assume that as $t \to \infty$, G decays exponentially:

$$G(t) \sim \exp(-\alpha t). \qquad (V.14)$$

When this is put into Eq. (1) we get

$$\alpha\, e^{-\alpha t} \sim \lambda^2 \int_0^t ds\, K(s;\lambda)\, e^{-\alpha(t-s)} \qquad (V.15)$$

as $t \to \infty$. The factor $\exp(-\alpha t)$ can be cancelled out, leaving

$$\alpha = \lambda^2 \int_0^{\infty} ds\, K(s;\lambda)\, e^{+\alpha s} \qquad (V.16)$$

in the limit $t \to \infty$. This equation determines the rate constant for the assumed decay.

If there is actually a decay, then α is positive and $\exp(\alpha s)$ increases exponentially in s. For α to exist, the memory $K(s;\lambda)$ must decrease exponentially at least as fast as $\exp(-\alpha s)$. The Laplace transform

$$\kappa(p;\lambda) = \int_0^{\infty} ds\, e^{-ps}\, K(s;\lambda), \qquad (V.17)$$

in particular, must be analytic on the imaginary p-axis.

But this cannot be so, in the weak coupling limit anyhow. There the form of $K(s;\lambda)$ is known; it is typically, as in Eq. (IV.14),

$$K(s;\lambda) = \sum_{k \neq j} L'_{kj}\, e^{-is L^0_{jj}} L'_{jk} \qquad (V.18)$$

and the Laplace transform is

$$\kappa(p;\lambda) = \kappa(p) = \sum_{k \neq j} L'_{kj}\, \frac{1}{p + iL^0_{jj}}\, L'_{jk}. \qquad (V.19)$$

Since L^0 is Hermitian, $\kappa(p)$ has poles on the imaginary axis. We are forced to conclude that G(t) will not decrease exponentially as $t \to \infty$.

What is the trouble here? It is that $K(s;\lambda)$, according to Eq. (18), is a periodic or almost periodic function and is not integrable. This is connected with the problem of recurrences. Again,

by taking a special example we can see what is going on in general.

Let us assume that

$$K(s;\lambda) = \sum_{\substack{j=-N \\ j\neq 0}}^{+N} \frac{1}{2N} \exp(-isj/N)$$

$$= \frac{1}{N} \sum_{1}^{N} \cos(sj/N). \qquad (V.20)$$

This corresponds to Eq. (18) with

$$j = 0, \qquad L'_{k0} = L'_{0k} = 1/\sqrt{2N}, \quad \text{if } k \neq 0,$$
$$L^{o}_{kk} = k/N, \qquad \text{for } -N \leq k \leq +N, \qquad (V.21)$$

where N is supposed to be very large. In the limit $N \to \infty$, we can replace the sum by an integral, and we find

$$K(s;\lambda) \to \frac{\sin s}{s}, \qquad (V.22)$$

which is certainly not periodic or even almost periodic.

But why should we take the limit $N \to \infty$? We may be dealing with a finite system, so N is not infinite. It is important to see what limitations are imposed by finite N. In the case of Eq. (22), for example, the approximation $(\sin s)/s$ is valid only for certain s. We note first that by its definition $K(s;\lambda)$ is periodic:

$$K(s + 2\pi N;\lambda) = K(s;\lambda), \qquad (V.23)$$

although the period is very large. Next we observe that the sum in Eq. (20) can be calculated exactly, since it is a geometric series. We find

$$K(s;\lambda) = \frac{1}{2N}(\cos s - 1) + \frac{s}{2N}\cot(s/2N)\frac{\sin s}{s}, \qquad (V.24)$$

which shows what is left out in Eq. (22). Only when s is much smaller than N, and only if terms of order $1/N$ are neglected, will Eq. (22) be valid (in the first period anyhow).

Now we observe that G(t) is determined only by values of K(s) for $s < t$; this follows from Eq. (1). Use of the approximation in Eq. (22) is valid only for $s << N$, and only if microscopic "noise" in K, of order $1/N$, is of no interest. The G(t) calculated using Eq. (22) is valid only under the same restrictions. In particular,

the behavior of G(t), as $t \to \infty$ but N remains finite, is not correctly calculated in this way.

If we want only the "early behavior, $s << N$, then we can find it by the following procedure.

We shall solve Eq. (1) by Laplace transforms. Let

$$\varphi(p) = \int_0^\infty dt\, e^{-pt} G(t). \qquad (V.25)$$

Then Eq. (1) becomes

$$p\,\varphi(p) - 1 = -\lambda^2 \kappa(p)\,\varphi(p), \qquad (V.26)$$

where $\kappa(p)$ is the transform of K,

$$\kappa(p) = \frac{1}{2i}\log\frac{p+i}{p-i}. \qquad (V.27)$$

Note that $\kappa(p)$ has branch points on the imaginary axis at $p = \pm i$. So even with the approximate K, G does not decay exponentially for long t.

Solving for $\varphi(p)$ we find

$$\varphi(p) = \frac{1}{p + \lambda^2\kappa(p)}. \qquad (V.28)$$

The standard formula for the inverse Laplace transform gives

$$G(t) = \frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty} dp\, \frac{e^{pt}}{p + \lambda^2\kappa(p)}, \qquad (V.29)$$

where ϵ is any positive real number. The calculation of G(t) has thus been reduced to quadratures.

The Laplace transform $\kappa(p)$ was defined only for $\mathrm{Re}(p) > 0$. If we want to use the methods of theory of complex variables, deforming contours, evaluating residues, etc., we have to find the analytic continuation of $\kappa(p)$ to the negative half plane, $\mathrm{Re}(p) < 0$. Because the singularities of $\kappa(p)$ are branch points, we must cut the plane, and this may be done in any way that is convenient. The choice that seems easiest to use is indicated by the heavy line in Fig. 1, p. 124.

With this choice of analytic continuation of $\kappa(p)$, it turns out that κ is analytic near the origin:

$$\kappa(p) = \frac{\pi}{2} + O(p), \qquad (V.30)$$

so that $\varphi(p)$ has a pole at the root of

$$p + \lambda^2\kappa(p) = 0, \qquad (V.31)$$

namely,

$$p = -\lambda^2 \frac{\pi}{2} + O(\lambda^4) . \qquad (V.32)$$

The presence of the pole at this point is due entirely to the particular choice of cut. If the plane were cut instead from p = -i to p = +i, there would be no pole in the cut plane.

Now the contour in Eq. (29) may be deformed as shown in Fig. 1. Then G(t) falls into two parts, a term from the residue at

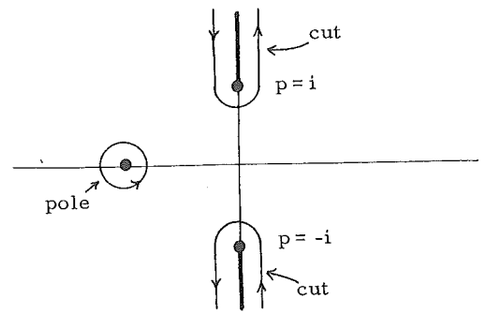

Fig. 1

the pole and the integrals around the cuts. We shall not evaluate the latter integrals here; they are tedious, but easy to find when λ is small. We determine that

$$G(t, \text{ from cuts}) = -\lambda^2 \int_1^\infty d\omega \frac{\cos \omega t}{\omega^2} + O(\lambda^4) \qquad (V.33)$$

in the limit of small λ. The pole gives a contribution that decays exponentially:

$$G(t, \text{from pole}) = [1 + \lambda^2 + O(\lambda^4)] \exp[-(\lambda^2\pi/2)t + O(\lambda^4 t)] . \qquad (V.34)$$

The sum has the structure

$$G(t) = \exp[-(\lambda^2 \pi/2)t + O(\lambda^4 t)] + \lambda^2 \times (\text{a function bounded in t, but not exponentially decaying}) . \qquad (V.35)$$

The most instructive feature of this result is that the exponential decay represented by the first term is ultimately submerged in the non-exponential decay of the second term. In the Van Hove

limit $\lambda \to 0$, $t \to \infty$, $\lambda^2 t$ fixed, the second term drops out and one gets simple exponential behavior:

$$G(t) \xrightarrow{\text{V.H.}} \exp(-\lambda^2 \pi t/2). \qquad (V.36)$$

But for finite λ and t, the exponential decay persists only for times

$$t << O\left(\frac{1}{\lambda^2} \log(1/\lambda^2)\right) . \qquad (V.37)$$

If we had cut the p-plane from p = -i to p = +i instead, we would not have been able to analytically continue $K(p)$ through the origin, and the contour integral would not see a pole. The function G(t) must be the same no matter how it is evaluated; but in this way the separation into an exponential decay and a small remainder would not have been so obvious.

If the parameter λ is not small, it is no longer clear that G will show exponential behavior for any significant time interval. Much more study of solutions of Eq. (1), with various λ and K(s), is needed.

We have considered in this section only a rather special example of the general problem of finding time dependence. However, several general conclusions are suggested. First, exponential decay is not universal, and if it appears, it may ultimately be hidden in some other kind of time dependence. Second, when one takes advantage of the approximations that can be made on a system with a large number of degrees of freedom, the resulting G(t) may be valid only for a limited time interval, and only if small scale "noise" is ignored.

VI. Examples of Weak Perturbation Theory

In this section we shall study two specific examples of the preceding formalism. The first example is the Pauli equation, the second is a classical analogue.

It must be emphasized that entirely satisfactory derivations of both equations are known. In particular, Van Hove's derivation of the Pauli equation is responsible, to a large extent, for much of the work going on these days in the theory of irreversibility, especially that in which diagram and perturbation techniques are used. We shall discuss new derivations here just to illustrate the convenience and directness of the preceding formalism.

A. The Pauli Equation.

Let us consider the Pauli equation first. The system is described by a Hamiltonian

$$H = H^o + \lambda H' ; \qquad (VI.1)$$

we write all operators as matrices in the representation where H^o is diagonal. We require further that H' has no diagonal elements. Now suppose that we are interested only in averages of operators that commute with H^o, or are diagonal in the unperturbed representation. Since the average of any observable a is given by

$$< a > = \text{Trace}\{a\,\rho(t)\}, \tag{VI.2}$$

where $\rho(t)$ is the density matrix, it is evident that we need to know only the diagonal elements of $\rho(t)$. Because of this limitation the theory we have just discussed is immediately applicable.

We make one further restriction. Instead of the most general initial condition, we shall use only ensembles whose density matrices are initially diagonal. This corresponds to initially making the phases random.

So we want to find the small-λ approximation of the following exact equation (see Eq. (III. 2)) for the diagonal part ρ_d of the density matrix (assuming $\rho_{o.d.}(0) = 0$):

$$i\frac{d\rho_d(t)}{dt} = DL\rho_d(t) - i\int_0^t ds\; DL\mathcal{G}(s)(1-D)L\rho_d(t-s), \tag{VI.3}$$

where

$$L = L^o + \lambda L' \tag{VI.4}$$

and

$$\mathcal{G}(s) = \exp[-is(1-D)L]\ . \tag{VI.5}$$

Taking the (kk) element of ρ_d, we have

$$i\frac{d\rho_{kk}(t)}{dt} = [L\rho_d(t)]_{kk} - i\int_0^t ds[L\mathcal{G}(s)(1-D)L\rho_d(t-s)]_{kk}. \tag{VI.6}$$

Consider the first term on the right; this is

$$(L\rho_d)_{kk} = \frac{1}{\hbar}[H, \rho_d]_{kk} = \frac{1}{\hbar}\,(H\rho_d - \rho_d H)_{kk}. \tag{VI.7}$$

But because ρ_d is diagonal, the diagonal elements of $(H\rho_d - \rho_d H)$ vanish, and we find

$$DL\rho_d = 0. \tag{VI.8}$$

Now consider the " memory" term; this begins with

$$[L\cdot\mathcal{G}\cdot(1-D)\cdot L\rho_d]_{kk} = \frac{1}{\hbar}[H, \mathcal{G}\cdot(1-D)\cdot L\rho_d]_{kk}, \tag{VI.9}$$

and because $H = H^o + \lambda H'$ with H^o diagonal, we obtain

$$\frac{1}{\hbar}[\lambda H', \mathcal{G}\cdot(1-D)\cdot L\rho_d]_{kk}\ . \tag{VI.10}$$

Next we note that

$$\mathcal{G}(s)\cdot(1-D) = [e^{-isL^o} + O(\lambda)]\ (1-D), \tag{VI.11}$$

just as in our earlier discussions of perturbation theory. The term of order λ in Eq. (11) gives rise to a term of order λ^3 in the result, so we neglect it here. According to Eq. (I.16),

$$e^{-isL^o}(1-D)L\rho_d = e^{-iH^o s/\hbar}\,[(1-D)L\rho_d]\,e^{iH^o s/\hbar}\ , \tag{VI.12}$$

so the memory term becomes

$$\frac{1}{\hbar}[\lambda H',\ e^{-iH^o s/\hbar}\left((1-D)L\rho_d(t-s)\right)e^{iH^o s/\hbar}]_{kk}. \tag{VI.13}$$

Next we put in

$$(1-D)L\rho_d = \frac{1}{\hbar}(1-D)[H, \rho_d] = \frac{1}{\hbar}[\lambda H', \rho_d]\ ; \tag{VI.14}$$

the H^o term drops out. In terms of conventional matrices, the memory is

$$\frac{\lambda^2}{\hbar^2}\left[H',\ e^{-iH^o s/\hbar}[H', \rho_d(t-s)]\ e^{iH^o s/\hbar}\right]_{kk}. \tag{VI.15}$$

Incidentally this is just the same as

$$\lambda^2\, D\, L'\, e^{-isL^o}\, L'\, \rho_d\ , \tag{VI.16}$$

which illustrates clearly the formal similarity of the quantum mechanical theory to the simpler result given in Eqs. (IV.13) and (IV.14).

In order to write out the result completely in matrix form, we need the eigenvalues E_k of the unperturbed Hamiltonian H^o. Then it is easy to work out the commutators in Eq. (15); we get

$$\frac{\lambda^2}{\hbar^2}\sum_{\ell\neq k}|H'_{k\ell}|^2\cdot 2\cos\left(\frac{E_k - E_\ell}{\hbar}s\right)\{\rho_{kk}(t-s) - \rho_{\ell\ell}(t-s)\}. \tag{VI.17}$$

Let us define

$$\omega_{k\ell}(s) = \omega_{\ell k}(s) = \frac{2}{\hbar^2} \left| H'_{k\ell} \right|^2 \cos\left(\frac{E_k - E_\ell}{\hbar} s \right) . \quad \text{(VI.18)}$$

Then the equation for $\rho_{kk}(t)$ is

$$\frac{d\rho_{kk}(t)}{dt} = \lambda^2 \sum_{\ell \neq k} \int_0^t ds \; \omega_{k\ell}(s) \left[\rho_{\ell\ell}(t-s) - \rho_{kk}(t-s) \right] + O(\lambda^3 \rho). \quad \text{(VI.19)}$$

This is <u>almost</u> the Pauli equation. We still have to take care of the time convolution, and we have not yet introduced the simplifications that are possible with a large system.

We follow the first solution method described in Section V. Although it is not as neat as the Laplace transform method, it is much easier to use. In this scheme $\rho(t-s)$ is replaced by $\rho(t)$, terms of order $(\lambda^2 \rho)$ are neglected, and we get

$$\frac{d\rho_{kk}(t)}{dt} = \lambda^2 \sum_{\ell \neq k} \int_0^t ds \; \omega_{k\ell}(s) \left[\rho_{\ell\ell}(t) - \rho_{kk}(t) \right] + O(\lambda^3 \rho). \quad \text{(VI.20)}$$

The integration of ω is trivial:

$$\int_0^t ds \; \omega_{k\ell}(s) = \frac{2}{\hbar^2} \left| H'_{k\ell} \right|^2 \frac{\hbar}{E_k - E_\ell} \sin\left(\frac{E_k - E_\ell}{\hbar} t \right) . \quad \text{(VI.21)}$$

In the limit of large t, the final factor goes over into a delta function:

$$\frac{\hbar}{E_k - E_\ell} \sin\left(\frac{E_k - E_\ell}{\hbar} t \right) \rightarrow \pi \hbar \delta(E_k - E_\ell). \quad \text{(VI.22)}$$

But we shall not yet take this limit.

So far the unperturbed states have been labelled with single subscripts. However, in a many-body system each <u>unperturbed</u> state can generally be labelled with many quantum numbers. We choose the total energy E and we let α denote the eigenvalues of all operators that commute with H^0. Then each state is marked by (E, α). The matrix elements of the perturbation are

$$H'_{k\ell} \rightarrow H(E\alpha; E'\alpha') \quad \text{(VI.23)}$$

and the diagonal elements of the density matrix will be called

$$\rho_{kk}(t) \rightarrow \rho(E\alpha; t). \quad \text{(VI.24)}$$

In this notation Eq. (20) is

$$\frac{d\rho(E\alpha; t)}{dt} = \lambda^2 \sum_{E'} \sum_{\alpha'} \frac{2}{\hbar^2} \left| H(E\alpha; E'\alpha') \right|^2 \frac{\hbar}{E - E'} \sin\left(\frac{E - E'}{\hbar} t \right)$$

$$\times \left\{ \rho(E'\alpha'; t) - \rho(E\alpha; t) \right\} . \quad \text{(VI.25)}$$

In order to take advantage of the δ-function limit in Eq. (22), we should like to be able to replace the sum over E' by an integral. Let us investigate the conditions under which this is allowed.

When t is large, the sum over E' is limited, because of the sine factor, to those states for which

$$\left| E - E' \right| = O(\hbar / t). \quad \text{(VI.26)}$$

When the system is large, the energy levels will be closely spaced, and we can introduce a density function N(E) such that $N(E)\Delta E$ is the number of states whose energies lie between E and $E + \Delta E$. The number of states that are included in the sum in Eq. (25) is roughly

$$N(E) \times O(\hbar / t). \quad \text{(VI.27)}$$

In order to be able to convert the sum to an integral, this number of states must be considerably larger than one:

$$N(E) \times O(\hbar / t) >> 1, \quad \text{(VI.28)}$$

or

$$\frac{t}{N(E)\hbar} << O(1). \quad \text{(VI.29)}$$

But the density of states in a large system is proportional to the number of degrees of freedom. This means that the time interval for which the Pauli equation is valid is limited by the size of the system. (This is the same kind of limitation that we have discussed in Section V.)

We should also be prepared to find that for any finite λ the Pauli equation will only be valid for a finite time interval. This is connected with the possibility of branch points, as we have remarked in Section V.

In the limits used by Van Hove: (1) the size of the system goes to infinity first, (2) $\lambda \rightarrow 0$, and (3) $t \rightarrow \infty$ with $\lambda^2 t$ fixed. Then the Pauli equation is valid. The various corrections to be made, when these limits are not taken, must be based on a much more careful

analysis of Eq. (19).

In the limiting case we can replace the sum by an integral:

$$\sum_{E'} \rightarrow \int dE' N(E'), \tag{VI.30}$$

and we can use Eq. (22). Then Eq. (25) becomes

$$\frac{d\rho(Ea;t)}{dt} = \lambda^2 \sum_{a'} \int dE' N(E') \frac{2\pi}{\hbar} \delta(E-E') \left| H(Ea;E'a') \right|^2 \times \{\rho(E'a';t) - \rho(Ea;t)\} . \tag{VI.31}$$

Performing the integration, and using the abbreviation

$$W(a',a) = \frac{2\pi}{\hbar} \left| H(Ea';Ea) \right|^2 N(E) = W(a,a'), \tag{VI.32}$$

we find that Eq. (31) is

$$\frac{d\rho(Ea;t)}{dt} = \lambda^2 \sum_{a'} \{W(a,a')\, \rho(Ea';t) - W(a',a)\, \rho(Ea;t)\} . \tag{VI.33}$$

This is the Pauli equation

We have had to make various assumptions to get the desired result:

1) the density matrix is initially diagonal,
2) λ is small,
3) the system has many degrees of freedom,
4) t is large (of order $1/\lambda^2$), and
5) matrix elements are "smooth" functions of E.

The fifth assumption was made tacitly. The first and second assumptions are needed to arrive at Eq. (19); the others are needed to go the rest of the way to Eq. (33). If the third through fifth are not satisfied, one can always use Eq. (19), which is a kind of extension of the Pauli equation.

B. The Prigogine-Brout Equation.

As our second example of perturbation theory, we shall consider a system in classical mechanics where the unperturbed motion is that of free particles, and the perturbation is due to (weak) forces between the particles. We shall derive a "master" equation which was obtained first by Prigogine and Brout. Another derivation, based on diagram techniques, is given in this volume by Balescu (see p. 382).

The Hamiltonian for our system is

$$H = \sum_{j=1}^{N} \frac{1}{2m} p_j^2 + \frac{1}{2} \lambda \sum_{\substack{j \neq k \\ = 1}}^{N} \sum V(|r_j - r_k|). \tag{VI.34}$$

In this equation, p_j is the momentum of the j-th particle, m is its mass and $V(|r_j - r_k^j|)$ is the spherically symmetric potential energy of interaction of the particles situated at r_j and r_k. The Liouville operator is (as in Eq. (I.14))

$$L = L^o + \lambda L , \tag{VI.35}$$

$$L^o = -i \sum_{j=1}^{N} \frac{1}{m} p_j \frac{\partial}{\partial r_j} , \tag{VI.36}$$

$$L = +i \frac{1}{2} \sum_{j \neq k}^{N} \sum \frac{\partial V(|r_j - r_k|)}{\partial r_j} \left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_k} \right). \tag{VI.37}$$

The "vector" in Hilbert space is the phase space distribution function f(p, r; t). We use p and r to denote collectively all momenta and positions whenever convenient.

We can approach the derivation of the desired kinetic equation in two different but equivalent ways. The method used by Balescu, for example, is to expand f as a Fourier series in positions, keeping the momenta in the Fourier coefficients. Then the Liouville equation becomes a hybrid matrix (in Fourier components of position) and differential operator (in momentum space) equation. The Prigogine-Brout master equation is connected with a particular diagonal element of the Green's function exp(-itL) in this representation. It is instructive to carry through the derivation in this way, but we shall not do so here.

Instead we use the idea of a projection operator. Suppose that we are concerned with calculating averages of functions of momenta only. For this purpose we do not have to know all of f(p, r; t); we need only its projection on the subspace of functions of momenta. Let P be the operator that removes positions by integrating over the volume Ω of the system:

$$P = \frac{1}{\Omega^N} \int_{\Omega} dr_1 \cdots \int_{\Omega} dr_N . \tag{VI.38}$$

When P operates on a function that is already independent of positions, it gives back the same function, since the volume integrals then cancel out the factor Ω^{-N}. This means that $P^2 = P$, or P is a projection operator.

The projected distribution function

$$f_1(p;t) = P \cdot f(p, r; t) \tag{VI.39}$$

is all we need to know for calculating averages of functions of momenta. We shall now find the kinetic equation for f_1.

The starting point is Eq. (III. 2), translated, according to the prescription at the end of Section III, into

$$i \frac{\partial f_1(t)}{\partial t} = PL f_1(t) - i \int_0^t ds\, PL e^{-is(1-P)L} (1-P)L f_1(t-s) + PL e^{-it(1-P)L}(1-P) f(p, r; 0). \tag{VI.40}$$

The initial value of the position-dependent part of f, namely

$$(1-P) f(p, r; 0) = f(p, r; 0) - f_1(p; 0),$$

appears in this equation.

Once a suitable solution of Eq. (40) has been found, the remaining part, $(1-P)f(p, r; t)$, can be calculated by the translation of Eq. (III. 3).

Consider first the term

$$PLf_1 = PL^o f_1 + \lambda PL' f_1. \tag{VI. 41}$$

Because f_1 does not depend on position (by definition) and because L^o contains derivatives with respect to position, the term $PL^o f_1$ vanishes. The other part, $PL'f_1$, vanishes also, but for a different reason. The only position dependence of $L'f_1$ is contained in factors like $\partial V(r_{jk}) / \partial r_{jk}$. When the integrations required by P are performed, they see only such factors. The integral over all space of the force vanishes; so

$$P L' f_1 = 0.$$

Now let us consider the memory term. We note first that whenever PL^o operates on something it gives a vanishing result. This is because L^o differentiates with respect to position and P integrates these derivatives over all space. (We assume that the resulting surface integrals all vanish.) So the memory term begins with $\lambda PL'$. The final $Lf_1(t-s)$ in the memory term can be replaced by $\lambda L'f_1(t-s)$ because L^o differentiates with respect to position and f_1 has no position dependence. The memory term is thus

$$PLe^{-is(1-P)L}(1-P)Lf_1(t-s) = \lambda^2 PL'e^{-is(1-P)L}(1-P)L'f_1(t-s). \tag{VI. 42}$$

Just as in our previous examples of weak perturbation theory, we can now make the approximation

$$e^{-is(1-P)L}(1-P) = e^{-isL^o}(1-P) + O(\lambda), \tag{VI.43}$$

leading to

$$PLe^{-is(1-P)L}(1-P)Lf_1(t-s) = \lambda^2 PL' e^{-isL^o}(1-P)L'f_1(t-s) + O(\lambda^3). \tag{VI.44}$$

We have already shown that $PL'f_1 = 0$, so that

$$(1-P)L'f_1 = L'f_1;$$

we can therefore drop the (1-P) from the right-hand side of Eq. (44).

To the same order of approximation, the contribution from the initial (1-P)f is

$$\lambda PL' e^{-isL^o}(1-P) f(p, r; 0) + O(\lambda^2(1-P)f). \tag{VI.45}$$

Let us assume that f(0) has only a macroscopic variation in space, or that it is essentially constant over the range of intermolecular forces. Then the integration required by the P on the left sees essentially only the position dependence of the force in L', and the integral is negligibly small.

Furthermore, let us accept the argument of Prigogine and Balescu that the quantity (1-P) f(0) is to be regarded formally as being itself of order λ. Their reasoning is based on the idea that the spatial variation of a distribution function will generally be of the same order of magnitude as if the system were in thermal equilibrium. Since the spatial dependence of the equilibrium distribution is proportional to

$$\exp\left(-\lambda \sum_{j<k}\sum V(|r_j - r_k|)/kT \right),$$

in lowest order of λ the equilibrium distribution looks like

$$\begin{aligned} f(\text{equilibrium}) = {} & (\text{function of momenta}) \\ & + \lambda \times (\text{function of momenta and positions}) \\ & + O(\lambda^2). \end{aligned} \tag{VI. 46}$$

Then (1-P) f(equilibrium) is of order λ. This argument appears to be sensible as long as the nonequilibrium f does not deviate much from its equilibrium limit; otherwise it does not appear to be valid.

Anyhow, if we accept their argument, the extra term

$$O(\lambda^2(1-P)f)$$

in Eq. (45) is formally of order λ^3 and can be omitted.

The result of the preceding discussion is

$$\frac{\partial f_1(p;t)}{\partial t} = -\lambda^2 \int_0^t ds\, PL' e^{-isL^o} L' f_1(p;t-s) + O(\lambda^3). \qquad (VI.47)$$

We shall conclude the derivation by showing that in the limit of large time and small λ (with $\lambda^2 t$ held constant), Eq. (47) reduces to the Prigogine-Brout equation.

It will be clear, just as in our previous discussions, that the $\lambda^2 t$ limit gives

$$\frac{\partial f_1(p;t)}{\partial t} = -\lambda^2 \int_0^\infty ds\, PL' e^{-isL^o} L' f_1(p;t). \qquad (VI.48)$$

Putting in the definition of L', we obtain

$$PL' e^{-isL^o} L' = \frac{1}{2}\sum_{j\neq k}\sum \frac{1}{2}\sum_{\mu\neq\nu}\sum \left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_k}\right) \times \frac{1}{\Omega^N}\int_\Omega dr_1 \cdots \int_\Omega dr_N \frac{\partial V(|r_j - r_k|)}{\partial r_j} e^{-isL^o} \times \frac{\partial V(|r_\mu - r_\nu|)}{\partial r_\mu}\left(\frac{\partial}{\partial p_\mu} - \frac{\partial}{\partial p_\nu}\right). \qquad (VI.49)$$

From here on we will use Balescu's notation. The Fourier expansion of V is

$$V(r) = \frac{1}{\Omega}\sum_{\vec{\ell}} V_{\vec{\ell}}\, e^{i\vec{\ell}\cdot\vec{r}}. \qquad (VI.50)$$

The volume integral in Eq. (49) becomes

$$\frac{1}{\Omega^2}\sum_{\ell}\sum_{\ell'}(i\vec{\ell}V_{\vec{\ell}})(i\vec{\ell}' V_{\vec{\ell}'})\frac{1}{\Omega^N}\int_\Omega dr_1 \cdots \int_\Omega dr_N\, e^{i\ell(r_j - r_k)} \times e^{-isL^o} e^{i\ell'(r_\mu - r_\nu)}. \qquad (VI.51)$$

According to the definition of L^o,

$$\exp(-isL^o) = \exp\left(-s\sum_j \frac{1}{m} p_j \frac{\partial}{\partial r_j}\right), \qquad (VI.52)$$

so that

$$e^{-isL^o} e^{i\ell'(r_\mu - r_\nu)} = e^{i\ell'(r_\mu - r_\nu)} e^{-is\ell'(p_\mu - p_\nu)/m}. \qquad (VI.53)$$

It is now easy to do the volume integrals; the only nonvanishing contributions come from ($j=\mu$, $k=\nu$) or ($j=\nu$, $k=\mu$), and Kronecker deltas in ℓ and ℓ' appear. We get, after some rearrangement,

$$PL' e^{-isL^o} L' = -\frac{1}{2}\sum_{j\neq k}\sum\left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_k}\right)\frac{1}{\Omega}\sum_\ell \vec{\ell}\vec{\ell}\,|V_\ell|^2 \times \exp[-is\ell\cdot(p_j - p_k)/m]\left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_k}\right). \qquad (VI.54)$$

The time integral in Eq. (48) sees only the factor

$$\exp[-is\ell(p_j - p_k)/m],$$

and

$$\int_0^\infty ds\, e^{-is\ell(p_j - p_k)/m} = \pi\delta_-\left(\ell\cdot\frac{p_j - p_k}{m}\right) \qquad (VI.55)$$

in terms of the δ_- function.

The final equation is

$$\frac{\partial f_1(p;t)}{\partial t} = \frac{\lambda^2}{2}\sum_{j\neq k}\sum\left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_k}\right)\cdot\frac{\pi}{\Omega}\sum_\ell \vec{\ell}\vec{\ell}\,|V_\ell|^2\,\delta_-\left(\ell\cdot\frac{p_j - p_k}{m}\right) \times \left(\frac{\partial}{\partial p_j} - \frac{\partial}{\partial p_k}\right) f_1(p;t). \qquad (VI.56)$$

This is the result of our derivation, in a form and notation that agree entirely with Balescu's.

VII. Time-Correlation Functions

In a lot of recent work in the theory of irreversibility (see, for example, Montroll's lectures, this volume, p. 221) the evaluation of

time-correlation functions is of decisive importance. In this section we shall show that such functions (at least in classical statistical mechanics) obey Volterra equations of the sort that were discussed in Section V.

Consider some dynamical quantity U(p, q), and some equilibrium ensemble density f(p, q) such that

$$< U > = \int\int dp\, dq\, U(p, q)\, f(p, q) = 0 ,$$
$$< U^2 > = \int\int dp\, dq\, U^2(p, q)\, f(p, q) = 1. \qquad \text{(VII. 1)}$$

There is no loss of generality in restricting $< U >$ and $< U^2 >$ to the values zero and one; this can always be arranged.

Let p(t), q(t) be the momenta and positions at time t in terms of initial momenta and positions, and write

$$U(t) = U\Big(p(t),\ q(t)\Big) .$$

We want to find the time dependence of

$$A(t) = < U(0)\, U(t) > . \qquad \text{(VII. 2)}$$

Note that A(0) = 1 because of the normalization of U.

We shall demonstrate that

$$\frac{dA(t)}{dt} = -\int_0^t ds\, K(s)\, A(t-s) \qquad \text{(VII. 3)}$$

with K(s) suitably defined. We use the method of projection operators.

The time-correlation function will be rewritten in the suggestive way:

$$A(t) = \int\int dp\, dq\, U(p, q)\, \mathcal{7}(p, q; t) , \qquad \text{(VII. 4)}$$

where the quasi-distribution function $\mathcal{7}$ is

$$\mathcal{7}(p, q; t) = U\Big(p(t),\ q(t)\Big) f(p, q) \qquad \text{(VII. 5)}$$
$$= [e^{itL}\, U(p, q)]\ f(p,q) \qquad \text{(VII. 6)}$$
$$= e^{itL}\, [U(p, q)\, f(p, qP)] . \qquad \text{(VII. 7)}$$

In going from Eq. (5) to (6) we have used Eq. (I. 6). To get from (6) to (7) we took advantage of the assumption that f is an equilibrium

distribution, and therefore independent of time. Also, it is clear that

$$\mathcal{7}(p, q; t) = e^{itL}\ \mathcal{7}(p, q; 0)$$
$$\mathcal{7}(p, q; 0) = U(p, q)\, f(p, q) \ ; \qquad \text{(VII. 8)}$$

or

$$i\frac{\partial \mathcal{7}}{\partial t} = -L\mathcal{7} \qquad \text{(VII. 9)}$$

with the initial condition given by Eq. (8).

The basic point of the rest of this calculation is that we do not want the general properties of the Green's function exp(itL). We need only its effect on a special "initial state" U f , and we want only as much of $\mathcal{7}(p, q; t)$ as is needed for the averaging of U (Eq. (4)). One way of putting this is that we want the diagonal element of exp(itL) between "unit vectors" $U f^{1/2}$ in Hilbert space. However, we can also more conveniently use the projection operator formalism.

Let us introduce a projection operator P, and its associated subspace in Hilbert space. The subspace is supposed to include functions of the form U f, and it should allow the following :

$$\int\int dp\, dq\, U\mathcal{7} = \int\int dp\, dq\, U\, P\, \mathcal{7} . \qquad \text{(VII.10)}$$

The simplest projection that does this is the following one, defined by its effect on some arbitrary function G:

$$PG = U(p, q)\, f(p, q) \int\int dp'\, dq'\, U(p', q')\, G(p', q'). \qquad \text{(VII. 11)}$$

This P selects only the component of G in the direction of U. Because

$$P^2G = P(PG) = PG$$

(as a result of $< U^2 > = 1$), P is clearly a projection. This is the reason why we originally normalized U to unity.

With this P, the requirements that we set up may be shown to be satisfied. For example,

$$PUf = Uf \int\int dp'\, dq'\, U \cdot Uf = Uf , \qquad \text{(VII. 12)}$$

and

$$\int\int dp\, dq\, UP\mathcal{7} = \int\int dp\, dq\, U \cdot Uf \iint dp'dq'U\mathcal{7}$$
$$= \int\int dp'\, dq'\, U\mathcal{7} . \qquad \text{(VII. 13)}$$

Since we want only $P\mathcal{F}$, since $P\mathcal{F}(p, q; 0) = \mathcal{F}(p, q; 0)$ from Eq. (12), and since $\mathcal{F}$ satisfies Liouville's equation, we have exactly the situation discussed in Section III. The methods of that section can be used directly to find a kinetic equation for $P\mathcal{F}$:

$$i\frac{\partial P\mathcal{F}(t)}{\partial t} = -PLP\mathcal{F}(t) - i\int_0^t ds\, PL\, e^{is(1-P)L}(1-P)LP\mathcal{F}(t-s). \quad \text{(VII.14)}$$

(There is a change in sign from the equations of Section III. This is because Eq. (9) has a (-L) instead of a (+L).)

Now we multiply through by U and integrate over phase space. The left-hand side becomes

$$\int\int dp\, dq\, U\, i\frac{\partial P\mathcal{F}(t)}{\partial t} = i\frac{\partial A(t)}{\partial t}. \quad \text{(VII.15)}$$

On the right-hand side we note that

$$\int\int dp\, dq\, UPLP\mathcal{F} = \int\int dp\, dq\, ULP\mathcal{F}, \quad \text{(VII.16)}$$

because of the definition of P. Next we put in

$$P\mathcal{F} = Uf \int U\mathcal{F}\, dp'\, dq', \quad \text{(VII.17)}$$

so that

$$\int\int dp\, dq\, UPLP\mathcal{F} = \int\int dp\, dq\, ULUf \int\int dp'\, dq'\, U\mathcal{F}. \quad \text{(VII.18)}$$

But in general

$$\int\int dp\, dq\, ULUf = \langle ULU \rangle = 0. \quad \text{(VII.19)}$$

This is because LU is, aside from factors, just $\dot{U}$. Then ULU is proportional to $U\dot{U}$, or proportional to dU^2/dt. The equilibrium average of a time derivative vanishes; q.e.d. The first term on the right of Eq. (14) does not contribute.

In exactly the same way one can easily show that the second term on the right is

$$PL\, e^{is(1-P)L}(1-P)LP\mathcal{F}(t-s)$$
$$= \left\{ \iint dp\, dq\, ULe^{is(1-P)L} LUf \right\} \times \iint dp'\, dq'\, U(p', q')\, \mathcal{F}(p', q'; t)$$
$$= K(s)\, A(t-s), \quad \text{(VII.20)}$$

where the memory function K(s) is

$$K(s) = \int\int dp\, dq\, U\, L e^{is(1-P)L} LUf$$
$$= \langle U\, L e^{is(1-P)L} LU \rangle. \quad \text{(VII.21)}$$

Consequently, Eq. (14) is equivalent to

$$\frac{dA(t)}{dt} = -\int_0^t ds\, K(s)\, A(t-s), \quad \text{(VII.22)}$$

which is what we set out to show.

The memory can be expressed in a more suggestive way by using Eq. (I.3), or

$$LU = -i\dot{U}, \quad \text{(VII.23)}$$

and by taking advantage of the Hermitian character of L. Then we get

$$K(s) = \langle \dot{U}\, e^{is(1-P)L}\, \dot{U} \rangle. \quad \text{(VII.24)}$$

Thus K(s) is the time correlation of $\dot{U}$, but evaluated with a modified propagator.

We conclude this section with a few comments on the evaluation of transport coefficients with Eq. (22). As many authors have shown (see Montroll's lectures, this volume, for examples), transport coefficients can often be expressed in the form

$$\sigma = \lim_{\epsilon \to 0^+} \int_0^\infty dt\, e^{-\epsilon t} A(t). \quad \text{(VII.25)}$$

Let us define $\sigma(\epsilon)$ as the Laplace transform

$$\sigma(\epsilon) = \int_0^\infty dt\, e^{-\epsilon t} A(t). \quad \text{(VII.26)}$$

Equation (22) may be solved by Laplace transforms: see Section V for the method in some detail. The solution is

$$\sigma(\epsilon) = \left[\epsilon + \int_0^\infty dt\, e^{-\epsilon t} K(t) \right]^{-1}. \quad \text{(VII.27)}$$

If there are no peculiar divergence troubles, the limit σ is

$$\sigma = \lim_{\epsilon \to 0^+} \sigma(\epsilon) = \left[\lim_{\epsilon \to 0^+} \int_0^\infty dt\, e^{-\epsilon t} K(t) \right]^{-1}. \quad \text{(VII.28)}$$

All one needs is the limiting behavior of the transform of the memory function.

The preceding result has a close relationship to what one gets

from the Markoffian approximation

$$\frac{dA(t)}{dt} = -\int_0^\infty K(s)\, ds \cdot A(t) . \qquad \text{(VII. 29)}$$

This equation can be solved easily to give

$$A(t) = \exp\left[-t\int_0^\infty ds\, K(s)\right], \qquad \text{(VII. 30)}$$

and σ is given by

$$\sigma = \int_0^\infty dt\, A(t) = \left[\int_0^\infty ds\, K(s)\right]^{-1} \qquad \text{(VII. 31)}$$

It is interesting to see that if integrals and limits exist, etc., the Markoffian approximation actually gives correct results for transport coefficients.

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This list is not meant to be exhaustive.

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