

Equations for the Theory of Response and Transport in Statistical Mechanics*

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Taking the viewpoint that a *complete* solution of the Liouville equation contains much more information than is necessary in response theory (wherein one is concerned with a *particular* response), projection techniques are employed to introduce a shortcut in the problem. The treatment supplements and completes the formalism initiated in a previous publication and yields a general equation which is more relevant to response theory in the usual sense. The most natural application is to the theory of transport. The general transport equation is analyzed in the context of electrical conduction. Meaningful similarities to the simple classical Drude model of conduction are exhibited; the relationship of this exact formalism to the Kubo theory of linear response is shown, an exact solution for a step-function stimulus and approximation procedures which go beyond the linear regime are presented, and an expression for the electrical resistivity is explicitly calculated thus making contact with an earlier paper by Kenkre and Dresden. The response equation is also analyzed in the context of electric and magnetic polarization.

I. INTRODUCTION

In a previous publication¹ an integrodifferential equation was obtained for response theory in the context of statistical mechanics. Projection techniques were employed to avoid the complicated problem of the full dynamics of the system density matrix ρ and to select only that part of ρ which is relevant to the response r . The techniques achieved a formal elimination of the irrelevant part of ρ and yielded a general linear homogeneous equation for r . This equation (or one having its general character) has been used^{2,3} in several different ways to obtain various results. However it has a definite drawback: Its derivation entails the assumption that the value of the response at $t=0$ is *not* zero. Such an assumption is no doubt perfectly valid in situations like the ones treated in Refs. 2 and 3 wherein the response is a correlation function or a reduced distribution function. On the other hand, important situations also exist in which the response is indeed zero before the application of the external stimulus, the simplest example being the electric current which arises when (and not before) an external electric field is applied. The theory developed in Ref. 1 does not apply to these instances and the response formalism initiated in that paper must therefore be supplemented by more general considerations. These are the content of this paper.

The Liouville equation⁴ obeyed by the system density matrix $\rho(t)$ is

$$i \frac{\partial \rho(t)}{\partial t} = L(t)\rho(t), \quad (1)$$

where the Planck's constant has been equated to 2π , and the Liouville operator $L(t)$ is defined in terms of the Hamiltonian $H(t)$ through the relation⁵

$$L(t)\varrho = [H(t), \varrho] \text{ for any } \varrho. \quad (2)$$

The Hamiltonian $H(t)$ includes the stimulus applied to the system.

The conventional problem of response theory consists of the solution of (1) and the subsequent extraction of the response r from the ρ thus obtained by means of the prescription⁶

$$r(t) = \text{Tr} R \rho(t), \quad (3)$$

where R is the operator corresponding to the response. Clearly, if one's interest lies only in the response r , one requires only that part of ρ which figures in (3), and the complete solution of (1) contains too much information. A solution of (1) is therefore not really necessary in response theory and, as we have shown in Ref. 1, the two operations in (1) and (3) may be combined in a certain sense to obtain an evolution equation for the response:

$$\frac{\partial r(t)}{\partial t} = B(t)r(t) + \int_0^t ds K(t, s)r(s) + C_1(t) - r(0)C_2(t). \quad (4)$$

Whenever $r(0) \neq 0$, one may choose the projection operators involved in the derivation of (4) in such a way that the last two terms in (4) are eliminated, giving⁷

$$\frac{\partial r}{\partial t} = Yr, \quad (5)$$

with Y as a linear integrodifferential operator.

However, if one has zero initial response, it is not possible to get (5) from (4), and one must always have an inhomogeneous term added to the right-hand side of an equation like (5). Such a term is obviously necessary since if $r(0)=0$ in an equation like (5) with Y a linear operator, the re-

sponse will never "pick up" and will be forever destined to remain at its initial zero value. The approach of Ref. 1 may no doubt be extended trivially to cover these situations by merely putting $r(0)=0$ in Eq. (4) to obtain

$$\frac{\partial r}{\partial t} = Yr + C_1(t). \quad (6)$$

An examination of the term $C_1(t)$ reveals, however, that it has no important significance, and such an approach does not facilitate the analysis of response theory. The formalism developed in the present paper proceeds along quite different lines and will be found to be more natural and suggestive. While this analysis was begun merely to complete the arguments of Ref. 1, it is, in its final form, more general and more useful to the theory of response in general and the theory of transport in particular.

In Sec. II it will be shown that the condition $r(0)=0$ immediately suggests that one split the density matrix into two parts ρ_0 and ρ' and concentrate merely on the time evolution of one of them, viz., ρ' . This latter part of the system density matrix, which is the part that arises after and due to the application of the external stimulus, will be found to be described not by a homogeneous equation like (1) but by one containing an inhomogeneous term. The Zwanzig projection techniques⁸ (which must then be applied to this equation) have been most frequently used in conjunction with homogeneous equations. In Sec. II their use is extended to inhomogeneous equations and the projected equation (19) is obtained. This is quite complicated in structure but it is shown that by defining the projection operator in a certain way (which is different from the way it is defined in previous publications) a significant simplification results. In Sec. IV this equation is applied to the problem of response theory and Eq. (27), the principal result of this paper, is obtained. Some exact results connected with this equation are also derived. The problem of electrical conduction is studied in Sec. V with the help of the general transport equation which takes a form amazingly similar to the result one obtains from the simple classical Drude model. Remarks are made connecting the formalism to the Kubo theory and an explicit expression (in terms of the matrix elements of the scattering potential) is obtained in the linear approximation. Exact solutions and approximation procedures going beyond the linear regime are also discussed. In Sec. VI a difficulty that seems to arise in the application of the formalism to the study of phenomena like electric or magnetic polarization is pointed out. The difficulty is resolved by redefining the projection operators. General remarks are made in Sec. VII, where the formalism is also compared to other investigations which have used the method of projection techniques.

II. SPLITTING OF THE DENSITY MATRIX

The condition $r(0)=0$ (which has launched this analysis) naturally suggests that the density matrix be split into two parts ρ_0 and ρ' ,

$$\rho = \rho_0 + \rho', \quad (7)$$

where ρ_0 equals $\rho(0)$ and ρ' is the part that is initially zero and rises solely due to the application of the stimulus. Such a splitting is natural because Eqs. (3) and (7) and the condition $r(0)=0$ above show that

$$r(t) = \text{Tr} R \rho'(t). \quad (8)$$

For such responses therefore, it is only ρ' that is of immediate relevance. Carrying out the corresponding splitting for the Hamiltonian and the Liouville operators

$$H = H_0 + H', \quad (9)$$

$$L = L_0 + L', \quad (10)$$

where H' and L' contain the external stimulus and H_0 and L_0 do not, it is possible to put (7) and (10) in (1); note that

$$i \frac{\partial \rho_0}{\partial t} = L_0 \rho_0, \quad (11)$$

and obtain the equation governing the time evolution of ρ' :

$$i \frac{\partial \rho'}{\partial t} = L_0 \rho' + L' \rho, \quad (12a)$$

$$i \frac{\partial \rho'}{\partial t} = L \rho' + L' \rho_0. \quad (12b)$$

The two forms of Eq. (12) are equivalent to each other. A certain separation of the causes which bring about the change in ρ' seems to have occurred in (12a). The first term represents the contribution of the stimulusless system alone, the stimulus being entirely placed in the second term.⁹ A further advantage of (12a) over (12b) appears to be inherent in the terms linear in ρ' . In (12a) it is $L_0 \rho'$, while in (12b) it is $L \rho'$. The operator L_0 is always simpler than L and is often time independent (in most, if not all, applications). It will become clear later on in the discussion that such a lack of dependence on t is highly advantageous for it gives rise to time-independent terms and difference kernels in the final projected equation, making possible such techniques as Laplace transforms to be applied toward its solution. In spite of all these advantages of (12a) over (12b), it turns out that it is not practical to use (12a) in subsequent calculations, and the simpler character of the last term in (12b) makes it preferable to (12a) as the point of departure.

The conventional problem of response theory may therefore be reworded as the solution of ρ' from (12) followed by the extraction of the response by

means of (8). In order to combine Eqs. (8) and (12) in a manner parallel to that of Ref. 1, projections must be applied to Eqs. (12). These equations, however, possess an additional feature not present in (1). Unlike the latter they contain an inhomogeneous term. In (12a) it is $L'\rho$ while in (12b) it is $L'\rho_0$. Projection techniques, which have been applied most frequently in conjunction with linear homogeneous equations, must therefore be generalized in the context of inhomogeneous equations. This is done in Sec. III.

III. PROJECTION TECHNIQUES

Consider the inhomogeneous equation for a quantity $x(t)$ ¹⁰:

$$i \frac{\partial x}{\partial t} = \mathcal{L}(t)x(t) + \alpha(t). \tag{13}$$

Defining x' , x'' , α' , and α'' through

$$x' = Px, \tag{14a}$$

$$x'' = (1 - P)x, \tag{14b}$$

$$\alpha' = P\alpha, \tag{15a}$$

$$\alpha'' = (1 - P)\alpha, \tag{15b}$$

where P is a linear time-independent operator, it is noted that the respective application of P and $(1 - P)$ to (13) gives

$$i \frac{\partial x'}{\partial t} = P\mathcal{L}(t)x' + P\mathcal{L}(t)x'' + \alpha', \tag{16a}$$

$$i \frac{\partial x''}{\partial t} = (1 - P)\mathcal{L}(t)x'' + (1 - P)\mathcal{L}(t)x' + \alpha''. \tag{16b}$$

Since an equation like

$$\frac{\partial y}{\partial t} = Dy + C(t) \tag{17}$$

may be solved¹⁰ as

$$y(t) = \int_0^t ds \mathcal{G}(t, s)C(s) + \mathcal{G}(t, 0)y(0), \tag{18}$$

$$\mathcal{G}(t, s) = \exp\left[\int_s^t dt' D(t')\right], \tag{18a}$$

the solution x'' of (16b) may be substituted in (16a) to obtain

$$i \frac{\partial x'}{\partial t} = P\mathcal{L}x' + \alpha' + P\mathcal{L}G(t, 0)x''(0) - iP\mathcal{L}(t) \int_0^t ds G(t, s)(1 - P)\mathcal{L}(s)x'(s) - iP\mathcal{L}(t) \int_0^t ds G(t, s)\alpha''(s), \tag{19}$$

$$G(t, s) = \exp\left(\int_s^t dt' (1 - P)\mathcal{L}(t')\right). \tag{19'}$$

Equation (19) is horrendously complicated, and one

might naturally wonder whether it is at all possible for anything nice and simple to emerge from the frightening depths of this complicated result. However, it will now be shown that a significant simplification is indeed possible. If Eq. (13) is used always with the condition that $x(0) = 0$ (as is the case for the particular case $x = \rho'$) and if $(1 - P)$ does not disturb this zero value, i. e., if $(1 - P)x(0) = 0$, the third term on the right-hand side of (19) disappears. It will now be assumed that the inhomogeneous term $\alpha(t)$ in (13) is of the form

$$\alpha(t) = \alpha f(t), \tag{20}$$

where α is a time-independent operator (if x is an operator) and $f(t)$ is a c number. Note that this is the form used by Kubo¹¹ in his theory of linear response, and it is the form most frequently met with. It is perhaps in order to remark at this stage that projection techniques make a real contribution to the solution of a problem only when a carefully selected projection operator is defined and that without the proper choice the techniques can hardly achieve anything of value. A search must therefore be made for such a projection operator as will allow a simplification of Eq. (19).

The choice

$$P\theta \equiv (\text{Tr}M\alpha)^{-1}\alpha \text{Tr}M\theta \text{ for any } \theta, \tag{21}$$

M being some operator satisfying $\text{Tr}M\alpha \neq 0$, shows that P is linear, time independent, and idempotent. Its most important property, however, is that it projects the inhomogeneous term $\alpha(t)$ at any time t onto itself:

$$\alpha'(t) \equiv P\alpha(t) = \alpha(t). \tag{22}$$

Since P must be time independent, it is the particular form (20) of $\alpha(t)$ that makes (22) possible. A corollary of (22) is that

$$\alpha''(t) \equiv (1 - P)\alpha(t) = 0 \text{ for all } t. \tag{23}$$

The last term in (19) is then suddenly eliminated on account of (23) and the equation is enormously simplified to

$$i \frac{\partial x'(t)}{\partial t} = P\mathcal{L}(t)x'(t) - i \int_0^t ds P\mathcal{L}(t)G(t, s) \times (1 - P)\mathcal{L}(s)x'(s) + \alpha(t), \tag{24}$$

which may be written in the manner of Eq. (6) as

$$i \frac{\partial x'}{\partial t} = Y_1 x' + c(t). \tag{25}$$

Note, however, that unlike the $C_1(t)$ of Eq. (6) the $c(t)$ in Eq. (25) is highly significant: It is the inhomogeneous or "driving" term appearing in Eq. (13).

The foregoing analysis has thus succeeded in

yielding from Eq. (13) a projected equation [Eq. (25)] which is relatively simple and suggestive. This equation will be put to use in Secs. IV-VII in the context of response theory.

IV. GENERAL RESPONSE EQUATION

The external Hamiltonian H' appearing in (9) will now be assumed to have the time dependence of Eq. (20), i. e., it will be taken as $Af(t)$, where A is a time-independent operator and $f(t)$ is a c number. As remarked earlier, H' covers a very large part of stimuli one encounters in practice and is also the choice made by Kubo.¹¹ It will be noticed that such an H' throws the inhomogeneous term in (12b) [but not the one in (12a)]¹² into the form of Eq. (20) if the stimulusless density matrix ρ_0 is taken to be time independent. This will of course be true unless the initial state of the system is a highly complicated nonequilibrium one. The following correspondence between (12b) and (13) is therefore established:

$$\begin{aligned} x &\rightarrow \rho', & \mathcal{L}(t) &\rightarrow L(t), \\ \alpha &\rightarrow L_A \rho_0, & f(t) &\rightarrow f(t). \end{aligned} \quad (26)$$

The results of Sec. III, the correspondence (26), and the choice $M \equiv R$ give

$$\frac{\partial r(t)}{\partial t} = \alpha(t)r(t) + \int_0^t ds Q(t, s)r(s) - i\eta f(t), \quad (27a)$$

which may be rewritten differently as

$$\frac{\partial r(t)}{\partial t} = \int_0^t ds \mathcal{Q}(t, s)r(s) - i\eta f(t), \quad (27b)$$

or cast into the by now familiar form

$$\frac{\partial r}{\partial t} = Yr - i\eta f(t). \quad (27c)$$

The various quantities appearing in Eq. (27) are given by

$$\alpha(t) = (1/i\eta) \text{Tr}[RL(t)L_A \rho_0], \quad (28a)$$

$$Q(t, s) = - (1/\eta) \text{Tr}RL(t)G(t, s)(1-P)L(s)L_A \rho_0, \quad (28b)$$

$$G(t, s) = \exp - [i \int_s^t dt' (1-P)L(t')], \quad (28c)$$

$$\mathcal{Q}(t, s) = Q(t, s) + \alpha(t)\delta(t-s), \quad (28d)$$

$$P\theta = (1/\eta)L_A \rho_0 \text{Tr}R\theta \quad \text{for any } \theta, \quad (28e)$$

$$\eta = \text{Tr}RL_A \rho_0. \quad (28f)$$

Equations (27) and (28) constitute the principal result of this paper. Given any response of interest, one may immediately write down Eq. (27) for its time evolution. The tedious and partially irrelevant problem of the solution of ρ from the original Liouville equation or Eqs. (12) is thus formally avoided. Surely whether or not a really signifi-

cant advantage has been gained will be decided only by the actual form of the response and the operator $G(t, s)$. However, the formal simplification introduced may be (dramatically) appreciated by considering a particular instance wherein the response operator R has nonzero elements only in an extremely limited part of its matrix. Solving for a highly complicated ρ with zillions of nonzero matrix elements and then applying the simple operator R to the ρ through (3) throwing out in the process all but a highly limited number of the matrix elements of ρ (because they are irrelevant to the response), knowledge about which has been gained at the cost of enormous effort, is then seen to be a ridiculous way of tackling the response problem. Equation (27) achieves this elimination of the irrelevant information automatically through the means of the projection techniques and thus recommends itself to be taken as the point of departure in all response calculations. Unlike the matrix equation (1), (27) is a c -number equation and is therefore (at least formally) much more simple. Also, the equation is exact and highly suggestive. What is meant by the term "suggestive" will become clear in our discussion of electrical conduction. Qualitative considerations, approximation procedures, or even exact calculations could profitably proceed with (27) as the starting point. Examples of approximation procedures will be provided below. Exact calculations of a function like $Q(t, s)$ have also been carried out¹³ in a different context and similar considerations may be immediately applied to the general $Q(t, s)$ in Eq. (27). Note also that linear response emerges trivially from our equation.¹⁴ One merely replaces Y by Y_0 where by the latter we mean the expression for Y wherein the external stimulus has been put equal to zero. When this is done a beautiful separation occurs in the right-hand side of (27): the effect of the external stimulus and that of the interaction of the system components (collisions, for instance) are neatly separated, the former residing only in the last term in the right-hand side of Eq. (27) and the latter only in the first. In the general nonlinear case the last term still denotes the sole effect of the external stimulus, but the system interactions and the stimulus get mixed in the first term. It is easy to show that in the linear case, $\alpha(t)$ sheds its time dependence, $Q(t, s)$ turns into a pure difference kernel, and a solution of Eq. (27) with the aid of Laplace transforms (see e.g., Ref. 1) is made possible. It should be borne in mind that the latter device may be employed not only in the linear approximation but whenever α and Q become, respectively, time independent and a difference kernel.¹⁵ Since Eq. (27) will probably be used most frequently in its linear approximation, it is exhibited explicitly in that form:

$$\frac{\partial r(t)}{\partial t} = \alpha_0 r(t) + \int_0^t ds Q_0(t-s)r(s) - i\eta f(t), \quad (29)$$

with the solution for its Laplace transform

$$\tilde{r}(\epsilon) = \tilde{\phi}(\epsilon)\tilde{f}(\epsilon), \quad (30)$$

where the Laplace transform of any function $g(t)$ is written as $\tilde{g}(\epsilon)$ and where the "linear response coefficient" $\tilde{\phi}(\epsilon)$, given by

$$\tilde{\phi}(\epsilon) = -i\eta/[\epsilon - \alpha_0 - \tilde{Q}_0(\epsilon)], \quad (31)$$

depends only on the system components and is independent of the stimulus. Equation (30) may be inverse Laplace transformed into the well-known form

$$r(t) = \int_0^t ds \phi(t-s)f(s). \quad (32)$$

This makes contact with the Kubo theory¹¹ which is thus contained in, and is obtained effortlessly from, our formalism. It is further possible to show that ϕ is indeed a correlation function and thus to establish the fluctuation dissipation theorem.^{11,16} The quantities α_0 and Q_0 in (29) are given by

$$\alpha_0 = (1/i\eta) \text{Tr} R L_0 L_A \rho_0, \quad (33a)$$

$$Q_0(t-s) = - (1/\eta) \text{Tr} R L_0 e^{-i(t-s)(1-P)L_0} (1-P)L_0 L_A \rho_0. \quad (33b)$$

I shall end this section with some exact reductions of Eqs. (27) and (28) that are possible in particular instances when certain relations exist between the stimulus and the response operators. Some of these will be used in the subsequent discussion.

Suppose that the stimulus operator A and the response operator R have a c -number commutator:

$$L_A R = [A, R] = a \text{ } c \text{ number}. \quad (34)$$

Since $\text{Tr} R L_A L_A \rho_0 = -\text{Tr} (L_A R) L_A \rho_0$ and the trace of a commutator must equal zero, (34) makes the above trace equal zero and yields in Eq. (28a) a purely time-independent $\alpha(t)$:

$$\alpha(t) = (1/i\eta) \text{Tr} R L_0 L_A \rho_0. \quad (35)$$

It should go without saying that the η in (28f) equals, in this case, the negative of the c -number commutator in (34).

On the other hand, if A and R are conjugate operators, in the sense that

$$R = (\text{const}) \times [A, H_0], \quad (36)$$

one may write out the full commutator for L_A in the expression for $\text{Tr} R L_0 L_A \rho_0$, use the fact that $L_0 \rho_0 = 0$ and obtain

$$\text{Tr} R L_0 L_A \rho_0 = \text{Tr} [R(L_0 A) \rho_0 - R \rho_0 L_0 A]. \quad (37)$$

Using (36) to substitute for R in (37), the trace in (37) is found to be zero, giving for the $\alpha(t)$ of (28a),

$$\alpha(t) = (1/i\eta) f(t) \text{Tr} R L_A^2 \rho_0. \quad (38)$$

Note that (35) and (38) are the two parts of $\alpha(t)$ in general and if the conditions of (34) and (36) are simultaneously satisfied, the $\alpha(t)$ drops out completely. This will be seen to happen in the case of electrical conduction.

V. ELECTRICAL CONDUCTION

To better understand and appreciate the formalism developed in the preceding sections, we shall now study, with its help, the phenomenon of electrical conduction. Striking formal similarities with the simple classical Drude approach¹⁷ will be noticed, and a usable result in terms of the matrix elements of the scattering potential will be derived.

Consider a spatially constant, time-dependent electric field $\mathcal{E}(t)$ applied to a system containing N electrons of charge $-e$. If the position and velocity operators for the k th electron are denoted by x_k and v_k , respectively, the operators A and R in (27) are found to be

$$A = -e \sum_k x_k, \quad (39a)$$

$$R = -e \sum_k v_k. \quad (39b)$$

Since the position and the velocity are related to each other through $v_k = iL_0 x_k$, and $[x_k, v_l] = (i/m)\delta_{k,l}$, where m is the electron mass and δ the Kronecker δ the following relations between A and R are obtained:

$$R = iL_0 A, \quad (40)$$

$$L_A R = iNe^2/m. \quad (41)$$

An immediate simplification of Eq. (27) is obtained through the use of the exact reductions described at the end of Sec. IV. Equations (40) and (41) are cases of (36) and (34), respectively, and the term $\alpha(t)$ is therefore completely eliminated from Eq. (27). The equation obeyed by the electric current

$$j(t) \equiv -e \text{Tr} \left\{ \sum_k v_k \rho(t) \right\}$$

is then

$$\frac{\partial j(t)}{\partial t} = \int_0^t ds Q(t, s) j(s) + \frac{Ne^2}{m} \mathcal{E}(t). \quad (42)$$

The result used here, viz.,

$$\eta = -iNe^2/m \quad (43)$$

can be easily obtained from (28e) and (41).

Equation (42) is the exact equation governing the phenomenon of electrical conduction. The first term on the right-hand side represents a generalized friction or resistance to the growth of the current, and the second term is simply the electric field (with the correct multiplicative factor). The equation is remarkably similar to the result one

might get from the simple Drude model¹⁷ wherein one writes Newton's equation

$$m\ddot{x} = -\alpha' \dot{x} + e\mathcal{E}(t), \quad (44)$$

giving in our notation

$$\frac{\partial j(t)}{\partial t} = -\frac{\alpha'}{m} j(t) + \frac{Ne^2}{m} \mathcal{E}(t). \quad (45)$$

The only difference in (45) and (42) is the appearance (in the latter) of a non-Markoffian friction constant instead of $-\alpha'/m$. Needless to say, this is not a shortcoming of our theory. Nature does indeed behave quite often in a non-Markoffian manner. In fact, the most general form of the friction term would be $\int_0^\infty ds Q(t, s)j(s)$ and the upper limit of integration is stopped at $s=t$ in (39) only due to the cutoff introduced for $s>t$ by the principle of causality (our firm belief that future events cannot influence the present). A Markoffian behavior would demand the opposite cutoff, i. e., for $s<t$, and is by no means a necessary *a priori* feature of a theory. If memory were not present in the friction term, an exponential behavior would always be assured for $j(t)$, and surely not all systems have such a universal and simple behavior. The characteristics of each individual system under consideration will make themselves felt through the particular details of the structure of the memory term $Q(t, s)$. Note, however, that the results of the Drude model are easily recovered by making $Q(t, s)$ proportional to a Dirac δ function in time: $Q(t, s) = (-\alpha'/m)\delta(t-s)$.

Before proceeding with an analysis of the transport equation (42) in its linear approximation, we shall make a few remarks about other possible attacks on (42). As noted in Sec. IV, any set of conditions which permits one to write $Q(t, s)$ in the difference form $Q(t-s)$, allows a solution through Laplace transforms. An example is a step-function stimulus. If a constant electric field is applied suddenly at $t=0$,

$$\mathcal{E}(t) = \mathcal{E}\theta(t), \quad (46)$$

where $\theta(t)$ is the Heaviside step function and \mathcal{E} is time independent, the Liouville operator takes the form

$$\begin{aligned} L(t) &= L_0, & t < 0 \\ &= L_0 + \mathcal{E}L_A, & t > 0 \end{aligned} \quad (47)$$

and therefore one obtains a time-independent $L(t)$ all times after the application of the field. This makes $Q(t, s)$ a difference kernel and allows an exact solution of (42):

$$\tilde{j}(\epsilon) = (Ne^2 \mathcal{E}/m)[\epsilon^2 - \epsilon\tilde{Q}(\epsilon)]^{-1}. \quad (48)$$

It should be clear that such a treatment for the case of a step-function stimulus is possible not only for

(42) but also for the general response equation (27), since (46) or its equivalent

$$f(t) = f\theta(t) \quad (46')$$

allows $Q(t, s)$ to be written as $Q(t-s)$ and $\alpha(t)$ as a time-independent α , the exact solution for the response then being

$$\tilde{r}(\epsilon) = (-i\eta f)/[\epsilon^2 - \epsilon\alpha - \epsilon\tilde{Q}(\epsilon)]. \quad (49)$$

In situations wherein $\mathcal{E}(t)$ has an arbitrary time dependence but $Q(t, s)$ is a difference kernel $Q(t-s)$, a nonlinear conductivity $\tilde{j}(\epsilon)/\tilde{\mathcal{E}}(\epsilon)$ similar to the one defined by Tani^{18,19} may be obtained as

$$\tilde{j}(\epsilon)/\tilde{\mathcal{E}}(\epsilon) = (Ne^2/m)[\epsilon - \tilde{Q}(\epsilon)]^{-1}. \quad (50)$$

It should not be forgotten that (50) is not a linear approximation (although if the latter is invoked, Laplace transforms may be employed towards the solution of the equation in a manner identical to the above analysis). Similar remarks obviously apply to the solution of the general response equation (27).

From the linear form of the transport equation (42) an explicit expression in terms of the matrix elements of the scattering interaction will now be obtained for the dc resistivity of a system. Such formulas have been given by Greenwood,²⁰ Chester and Thellung,²¹ Verboven,²² and Kenkre and Dresden.³ The expression we derive here will be almost identical (although obtained from different considerations) to the one in Ref. 3 and different from the ones in Refs. 20-22.

Defining the frequency-dependent resistivity $\gamma(\epsilon)$ as equal to $\tilde{\mathcal{E}}(\epsilon)/\tilde{j}(\epsilon)$, one obtains from the linearized version of (42),

$$\gamma(\epsilon) = (m/Ne^2)[\epsilon - \tilde{Q}_0(\epsilon)], \quad (51)$$

where $\tilde{Q}_0(\epsilon)$, the zero-field limit $\tilde{Q}(\epsilon)$, appears as the Laplace transform of the difference function $Q_0(t-s)$. Taking the limit as $\epsilon \rightarrow 0$ one obtains from (51) the dc resistivity $\gamma(0)$:

$$\gamma(0) = (m/Ne^2) \int_0^\infty dt Q_0(t). \quad (52)$$

It is now possible to express the system Hamiltonian H_0 as a sum of two parts, a scattering interaction V and a "free" part H_0^0 whose only assumed property is that it commutes with the current operator R in (39b), write correspondingly

$$L_0 = L_0^0 + L_V; \quad (53)$$

note that

$$PL_0^0\theta = 0 \text{ for any } \theta \quad (54)$$

make the "weak-coupling approximation"^{3,6} in (33b), approximate the equilibrium density matrix as

$$\rho_0 \approx \rho_0^0 + \rho_V, \quad (55)$$

where ρ_V is the linear term in a suitable expansion of ρ_0 in orders of the scattering V , and finally obtain

$$\gamma(0) = \frac{m}{Ne^2} \frac{\pi}{NmkT} \int dE e^{-\beta E} \sum_{\xi\mu} |\langle \xi | V | \mu \rangle|^2 \times (F_\mu - F_\xi)^2 \delta(E - E_\xi) \delta(E - E_\mu) / \int dE e^{-\beta E} \sum_{\xi} \delta(E - E_\xi), \quad (56)$$

where F is the operator for the total momentum component along the direction of the applied field and the current (only the diagonal elements of the resistivity tensor have been considered here) and is related to R through $F = -(m/e)R$; F_ξ , F_μ are its diagonal elements $\langle \mu | F | \mu \rangle$, $\langle \xi | F | \xi \rangle$, etc. in the representation of the many-body eigenstates μ , ξ of the "free" Hamiltonian H_0^0 ; k is the Boltzmann constant, T is the temperature, and $\beta = 1/kT$; and E is the quasicontinuous energy variable (completely continuous in the thermodynamic limit that we have used here) denoting the eigenvalues of H_0^0 . The equilibrium matrix has been taken to be canonical in the above argument.

Further details of the derivation of (56) may be found in Ref. 3 where a parallel calculation has been carried out. The difference in the derivation above and the one in Ref. 3 lies in the meaning of the projection operator. The difference is not trivial and the derivation in the present paper allows one to avoid considerable work involving extraneous expansions of the quantity $J(0)$ appearing in Ref. 3. Remarks showing the connection of the development in Ref. 3 and the present theory are perhaps in order. Defining $\gamma(\epsilon)$ through $\tilde{J}(\epsilon) = \gamma(\epsilon)\tilde{j}(\epsilon)$, where $\tilde{j}(\epsilon)$ is the Laplace transform of the linear current, the Kubo theory¹¹ or the fluctuation dissipation theorem^{11,16} exhibits the relationship between γ and the equilibrium correlation function $J(t)$ through

$$\gamma(\epsilon) = 1/\tilde{J}(\epsilon). \quad (57)$$

The work in Ref. 3 proceeds to show, with the help of projection techniques, that

$$\tilde{J}(\epsilon) = [\epsilon - \tilde{Q}'(\epsilon)]^{-1}, \quad (58)$$

where $Q'(t)$ is very similar to the $Q_0(t)$ of (51). Projection techniques are therefore used in Ref. 3 to "invert" $\tilde{J}(\epsilon)$ and thereby remove the divergence difficulties in the expression for $\tilde{J}(0)$. In the present paper they are used in the very beginning for the totally different purpose of obtaining the general equation (27) or (42). The starting point of the considerations in Ref. 3 was the Kubo correlation expression for $1/\gamma$, whereas our present formalism does not involve the Kubo theory. In spite of this, the calculations can be shown to be

almost equivalent.

It is possible to obtain simple Boltzmann results from (56). For this and other discussions concerning the resistivity formula, we refer the reader to Ref. 3. It is also possible to analyze the transport equation (42) in other ways leading to expressions for nondiagonal elements of the resistivity tensor, magnetoresistance, an analysis of the validity of Matthiessen's rule,²³ and such other discussions in transport theory. These will form the content of a future publication. A scheme for obtaining higher-order contributions to the resistivity similar to those of Refs. 21 and 22 has been constructed and will also be presented in that paper.

VI. POLARIZATION

For the phenomenon of polarization or magnetization, the response and the stimulus operators (R and A) turn out to be identical or proportional to each other. For instance, in the case of electric polarization

$$A = R = -e \sum_k x_k, \quad (59)$$

where $-e$ and x_k are the charge and the position (the displacement of the electron from its "original position") of the k th electron. This may at first sight appear to pose a serious problem in the application of the present formalism because from (28f)

$$\eta = 0, \quad (60)$$

and the projection operator P cannot even be defined since in (28e) it carries a factor $(1/\eta)$ in its expression. The entire formalism then seems to break down, and one might conclude that in these cases it is not possible to define a suitable operator D in

$$P\Theta = (\text{Tr}DR)^{-1}D \text{Tr}R\Theta \text{ for any } \Theta, \quad (61)$$

such that it simultaneously satisfies $\text{Tr}DR \neq 0$ and eliminates the complicated last term appearing in the projected equation (19).

However, closer inspection reveals that this seeming breakdown of the formalism is only apparent and arises only from a habitual (but unnecessary) ingredient in the definition of P . This habitual ingredient probably owes its existence to the nomenclature used to describe P , in particular the term *projection* operator. Every single application of the Zwanzig projection techniques known to the author uses P 's which are idempotent, i. e., which obey

$$P^2 = P. \quad (62)$$

It is this property that requires the factor $(\text{Tr}DR)^{-1}$ to appear in (61). It is, however, a property that is entirely unnecessary for the present development.

Linearity and lack of dependence on t are all that is required of P for the discussion in Sec. III. Equation (62) need not, therefore, be obeyed, and one may define instead of (28e),

$$P\theta = L_A \rho_0 \text{ Tr} R \theta \quad \text{for any } \theta. \quad (28e')$$

We may, if we wish, imagine a factor of value 1 and of appropriate dimensions multiplying the right-hand side. The entire formalism then applies as developed earlier with the modifications

$$\alpha(t) = -i \text{Tr} R L(t) L_A \rho_0, \quad (28a')$$

$$Q(t, s) = -\text{Tr} R L(t) G(t, s) (1 - P) L(s) L_A \rho_0, \quad (28b')$$

and (28e').

For cases when

$$A = aR, \quad (63)$$

a being a c number, one obtains with the help of (34)

$$\alpha(t) = -ia \text{Tr} A L_0 L_A \rho_0 = a \text{Tr} \dot{A} L_A \rho_0, \quad (64)$$

where $\dot{A} = i \text{Tr} L_0 A$ is the Heisenberg equation of motion for A . Note thus that $\alpha(t)$ is exactly time independent and equals $-iNe^2/m$ in the particular case of polarization. Also (28b') reduces *exactly* to

$$Q(t, s) = -a \text{Tr} A L_0 G(t, s) (1 - P) L(s) L_A \rho_0, \quad (65)$$

with the understanding that

$$PL(s) L_A \rho_0 = PL_0 L_A \rho_0 = -a \text{Tr} \dot{A} L_A \rho_0. \quad (66)$$

Approximation techniques and detailed results may be obtained for these cases but will not be exhibited here.

VII. CONCLUSION

A formalism has thus been presented for the theory of response in the context of statistical mechanics, which is exact, suggestive, and, I believe useful. One begins with the Liouville equation and first shows that for responses that are initially zero, the density matrix should be separated into two parts, only one of which is directly relevant to the calculation of the response. One then notes that this part obeys an inhomogeneous equation, finds it, therefore, necessary to extend the use of projection techniques to such equations, selects a particular projection operator to bring about a very significant simplification, and finally obtains the response equation (27). Whereas it was the desire to complete the arguments of Ref. 1 [valid for cases with $r(0) \neq 0$] that led to the present development, the latter is truly general from the point of view of usual response theory. Thus, even if $r(0) \neq 0$, if one focuses one's attention on the change in the response $\Delta r(t) \equiv r(t) - r(0)$ and renames this $\Delta r(t)$ as *the* response, one will find that it satisfies

the zero-initial-value condition used in this paper. In most instances of response theory $\Delta r(t)$ is indeed what one is interested in. Thus, while it is not to be denied that important applications of the formalism based on $r(0) \neq 0$ do exist,²⁴ the theory in the present paper is perfectly general from the customary viewpoint of response theory.

Needless to say, the validity of the response equation (27) or the transport equation (42) is dependent on nothing more than the validity of the Liouville equation, since projection techniques do not, in themselves, introduce any approximations. For the same reason, (27) and (42) are reversible like the Liouville equation, and irreversibility is made to enter (in applications of the equations) artificially by replacing a quasicontinuous sum over states by an integral, introducing Dirac δ functions in the place of time integrals of imaginary exponentials, or with the help of such other artifices. Like the Kubo theory, this formalism does not (and is not supposed to or expected to) yield irreversibility because it is a direct consequence of the microscopic equations. The development here is not aimed at the problem of irreversibility, and for applications of projection techniques to the latter, the reader is referred to the works of Zwanzig,⁸ Jones,²⁵ and Muriel and Dresden.²⁶

The exact response equation derived in this paper is simple on two counts: It is a c -number equation as opposed to the matrix equations one is faced with in the Liouville problem, and it has a built-in elimination of the parts of the density matrix not relevant to the particular response of interest. The form of the equation is quite simple and in transport theory [Eq. (42)] it takes on an especially suggestive aspect. The $Q(t, s)$ [or in the general response equation the $\mathcal{Q}(t, s)$] plays the part of a generalized friction and, in the case of electrical conduction, is very closely related to the resistance. Several simplifications arising from manipulations with the projection operators are already seen to occur in my formal discussion. Further reductions will be made possible when one uses a concrete Hamiltonian in the expressions of (27), (28), and (42). To establish the usefulness of the formalism and to show the details of how it makes contact with usable expressions involving scattering matrix elements, free eigenfunctions, the temperature, etc., I have derived a formula for electrical resistivity [Eq. (56)]. Such results involving exact considerations or approximation techniques can be obtained for other situations in response theory.

It is seen that in more senses than one the response equation (27) is nonlinear. Linearity is obtained by expelling the stimulus from $\mathcal{Q}(t, s)$. Some remarks must be made in connection with this linearized version of (27) and (5) which is exact but derived only for $r(0) \neq 0$. There are two meanings

to linearity. Thus, one may state that

$$\frac{\partial y}{\partial t} = \Omega y \quad (67)$$

is linear, meaning that the operator Ω is such that the principle of superposition applies: $(y_1 + y_2)$ is a solution if y_1 and y_2 are solutions. Such a linearity is clearly absent from

$$\frac{\partial y}{\partial t} = \Omega y + c(t), \quad (68)$$

since $(y_1 + y_2)$ will not satisfy (68) if y_1 and y_2 do unless $c(t) = 0$. However, there may be another kind of linearity to Eq. (68). Calling the $c(t)$'s the inputs and the $y(t)$'s the outputs, Ω may be such that if inputs c_1 and c_2 cause outputs y_1 and y_2 , respectively, input $c_1 + c_2$ causes output $y_1 + y_2$. We then say that (68) describes a linear system. The former kind of linearity is associated with the superposition principle, the Schrödinger equation in quantum mechanics, the Liouville equation, etc. It exists also in Eq. (5) which was derived in Ref. 1. It is absent in the equations developed in the present paper. However, these, in the approximate form (29), possess the input-output type of linearity discussed above. The latter is typical to response theory and is encountered in the literature on control systems and related electrical-engineering matters.

Finally I shall compare the present formalism to the theory developed by Mori.²⁷ This work, of which I was unaware during most of the period of preparation of the present paper, proceeds to provide a justification to the Langevin equation used in the theory of Brownian motion. Projection techniques are used for this purpose and equations resembling some presented here are derived. A brief comparison of Mori's formalism and the present approach will be found at the end of Ref. 3 and I shall mainly repeat some of those comments. Some of the equations derived by Mori bear a resemblance to some obtained in this paper, but very significant differences exist both in the results and the spirit of the investigation. The Heisenberg equa-

tion of motion for an operator (with no statistical mechanics in it) serves as the starting point for Mori's investigations and the result obtained is an equation obeyed by the *same operator* whose Heisenberg equation is the point of departure. The present development begins with the Liouville equation containing the statistical element through the density matrix ρ and ends with the response equation for a c number, viz., r . A "random force" term appears in Mori's results and is indeed relevant to the theory of Brownian motion that he treats. No such term appears in the results in this paper. The real differences between two treatments using projection techniques lie in the definition of the projection operators. These are totally different in Mori's approach and the present formalism. His bear a greater resemblance to the ordinary projection operators in quantum mechanics²⁸ and are chosen specifically to eliminate the first term in a projected equation like (19) and to retain an initial value term [like the third term in (19)] which is to play the role of the random force. My projections, however, are chosen for the particular purpose of eliminating the last term in (19) and obtaining an equation which (almost) separates the effect of the stimulus and the system and is therefore particularly suited to response investigations. The theory of Brownian motion is ideally discussed in the context of Mori's work while my formalism aims specifically at response theory. Another author whose work involves projections, is Argyres. In a lucid and detailed exposition²⁹ he has described the use of projection techniques to obtain kinetic equations. A splitting of the density matrix ρ (as in Sec. II) occurs in his treatment, and he also applies projections to an inhomogeneous equation. However, he (approximately) separates ρ into an equilibrium part and a *linear* part, and his projection operators are quite different from the ones employed here. Also, his aim in the use of projections is to obtain kinetic equations for reduced density matrices, and is therefore entirely different from the one in this paper.

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⁴This equation is also referred to in the literature as the Von Neumann, the Liouville-Von Neumann, and, in some cases, the Bloch equation.

⁵The Liouville operator L_Z corresponding to an operator Z will be always defined through $L_Z \Theta \equiv [Z, \Theta]$, except where it is stated otherwise. Also, all our con-

siderations apply to the classical case if L is redefined in the well-known classical manner.

⁶Throughout this paper we refrain from exhibiting explicitly the normalizing factors such as $[\text{Tr} \rho(t)]^{-1}$ which should multiply expressions like the right-hand side of (3).

⁷Equations (4) and (5) are identical to Eqs. (11a) and (12) of Ref. 1, which should be consulted for the details and the meaning of the various terms.

⁸R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Downs and J. Down (Interscience, Boulder, Colo., 1961), Vol. III.

⁹This separation is not however clearcut, since the second term *does* contain the effect of the stimulusless system through ρ which has ρ_0 in it.

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¹¹R. Kubo, *J. Phys. Soc. Japan* **12**, 570 (1957).

¹²This is due to the fact that ρ has a complicated time dependence which definitely cannot be expressed in the form of Eq. (20).

¹³A. Muriel and M. Dresden (unpublished).

¹⁴This should be contrasted with the discussion in Ref. 1.

¹⁵If the time dependence of the external stimulus is such that it eventually steadies itself, $\alpha(t)$ becomes time independent for large times. If the situation, therefore, allows the simultaneous approximation of $Q(t, s)$ by $Q(t - s)$, one has an example where Laplace transforms can be used for the solution of the problem.

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²⁹P. N. Argyres, in *Lectures in Theoretical Physics* (Interscience, Boulder, Colo., 1966), Vol. VIII A.

Ambipolar-to-Free Diffusion: The Temporal Behavior of the Electrons and Ions*

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Simultaneous measurements of the time dependence of the electron number density and the ion wall current in a helium afterglow are reported. The transition from ambipolar-to-free diffusion is investigated as a function of gas pressure and discharge-tube size. The onset of the transition regime occurs when $\Lambda / \langle \lambda_D \rangle = 86$, where $\langle \lambda_D \rangle$ is the Debye length corresponding to the average electron or ion density, and Λ is the characteristic diffusion length of the vessel. The time dependence of the transition regime was found to depend only on $\Lambda / \langle \lambda_D \rangle$ if times are scaled as tD_+ / Λ^2 . This latter result is in agreement with high-pressure theories which assume mean free paths short with respect to experimental dimensions. The ion current changed by a factor of $(1.2 \pm 0.5) \times 10^5$ during the transition. The ions diffuse free by space-charge effects when $\Lambda / \langle \lambda_D \rangle < 0.25$, where $\langle \lambda_D \rangle$ is the Debye length corresponding to the average ion density.

I. INTRODUCTION

The space charge in a plasma inhibits the diffusion of electrons while enhancing the ion diffusion. At sufficiently high values of charged-particle densities the electrons and positive ions diffuse at the same rate (ambipolar diffusion) and for isothermal conditions the ambipolar-diffusion coefficient is exactly twice the ion-free diffusion coefficient. For very low densities, space-charge effects become negligible; electrons and ions diffuse independently of each other and this is known as free diffusion. The density range between these two extremes is called the transition regime. This regime is of primary interest in this paper.

The transition from ambipolar-to-free diffusion has been studied both theoretically¹⁻⁴ and experimentally⁵⁻⁷ for many years. Allis and Rose¹ laid the groundwork for these studies by calculating the

behavior of the electrons in a steady-state discharge. Their calculations were for a gas in which $D_e / D_+ = 32$, where D_e and D_+ are the electron and ion diffusion coefficients, respectively. Although their results give a qualitative understanding of the transition regime, an exact comparison between experiment and their calculations cannot be made because D_e / D_+ is much greater than 32 for most gases. Cohen and Kruskal² extended the steady-state calculations of Ref. 1 by using a somewhat different approach. Since both of these analyses are for a steady-state discharge, some question arises concerning their applicability to an afterglow. In neither case do the authors discuss the temporal behavior of the ions during the transition from ambipolar-to-free diffusion although the decay of the free-electron density is easily inferred from the solutions. Measurements^{5,6} of the electron density in the range from 10^{11} to 2×10^4 cm⁻³ in a