Variational Principles and Entropy Production

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We have found a variational principle which is valid for irreversible processes, whether microscopic reversibility is obeyed or not, and beyond the region of linear response. A convenient general expression for entropy production is also found and the relation of entropy production to the solution of transport problems is discussed.

I

THE solution of transport equations always requires approximations. One of the most useful methods is the variational principle (V.P.) and many authors have developed such principles for transport theory in the absence of a magnetic field. The presence of a magnetic field or time variation has frustrated previous attempts to establish a V.P. which actually has a maximum (or minimum) for the correct distribution function. The primary purpose of this paper is to present such a principle, which in addition will be valid for nonlinear problems, but we will also discuss other V.P.'s and their physical interpretation, in particular, their relation to entropy production.

II

In discussing irreversible processes, we will write as our basic equation

$$Df = Lf, \qquad (II.1)$$

where Df will be called the drift term and will be equal to

$$Df = \frac{\partial f}{\partial t} + \frac{i}{\hbar} [f, H], \qquad (II.2)$$

f being the density matrix which is also subject to the requirement that its trace be at all times one. H represents the entire Hamiltonian except for terms which are attributed to "collisions," the latter being included in Lf. The split is to some extent arbitrary, a point which will be somewhat clarified shortly. For intuitive purposes it suffices to think of H as containing the terms one can handle dynamically, such as kinetic energy, and electric or magnetic fields which vary slowly in space or time. In particular problems either H or L may be neglected. In many problems, the commutator in (II.2) may be replaced by a Poisson bracket (P.B.) and the density matrix by a distribution function.

In many classical problems one assumes for Lf the following definite form:

$$Lf(\{\mathbf{p}\},\{\mathbf{x}\},t) = \int d\mathbf{p}'(P(\{p\},\{\mathbf{p}'\})f(\{\mathbf{p}'\})$$
$$-P(\{\mathbf{p}'\},\{\mathbf{p}\})f(\{\mathbf{p}\})), \quad (II.3)$$

but this is not essential. Here, $\{\mathbf{p}\}$, $\{\mathbf{x}\}$ represent the momenta and positions of all particles in the problem. We shall assume a very general form for L

$$Lf_n = \sum_{n'} L_{nn'} f_{n'}, \qquad (II.3a)$$

where now n represents the totality of dynamical variables for the system *as well as the time*. In a quantum-mechanical problem f will be a density matrix $f(\{l\},\{l'\},t)$, where $\{l\}$ is a set of values for a complete set of commuting observables for the problem. In such a case n will represent the totality of indices $(\{l\},\{l'\},t)$.

In general, it is essential that n refer to states of the entire system, because we wish to make use of the linearity of Eq. (II.1). If we were to use single-particle density matrices, the collision terms at least would be nonlinear for collisions involving more than one particle, and additional nonlinearities would be introduced by the use of Bose or Fermi statistics. In cases where we are interested in small deviations from equilibrium and are content to neglect terms of higher order than first in this deviation, it is possible to obtain linear equations for the deviations, and in such cases it would be possible to use single-particle density matrices or distribution functions. On the other hand, once we have obtained a general variational principle it will be possible to use trial functions containing no correlations, if desired, and thus obtain equations for single-particle distributions. On the other hand, we also have the freedom to retain such correlations, something we could not do if we tried to use one-particle functions from the beginning.

Having considered L and D as linear operators it is now natural to view f as a vector in a space defined by the components f_n. There is the difference that whereas in quantum mechanics we deal with normalized vectors $\int |\psi|^2 = 1$, here we have instead the restriction

$$\text{Tr} f = 1$$

or

$$\int d\{\mathbf{p}\} d\{\mathbf{x}\} f = 1,$$

expressing the fact that the probability is normalized to 1.

As in quantum mechanics there are potential difficulties when the variables have infinite ranges, and we must restrict ourselves to certain classes of f's if we

wish to avoid them. Fortunately, these restrictions cause no serious limitation. A sufficient restriction is that the f's or their deviation from some suitably chosen f_0 be square integrable and have a sufficient number of moments $\int p^l x^m t^n |f|^2$ for the problem at hand. This merely restricts us to the kind of situation which can be physically realized. Having said these pious words, we will merely keep them in the back of our mind from now on.

We define for arbitrary operator, O, the objects

$$(f,Og) = \sum_{n,n'} f_n^* O_{nn'} g_{n'} \qquad (II.4)$$

for arbitrary density matrices or distribution functions f and g. (Recall that the sum over n includes integration over time.) f^* is the complex conjugate of f, which for the quantum-mechanical density matrix implies its transpose. We also define $(f,Og)_t$ in which the time integration implied in (II.4) is not carried out, the quantity being evaluated at time t. Substituting D from (II.2) for O, we can write

$$(f,Dg)_t = \mathrm{QTr}(f,i[g,H]) + \left(f\frac{\partial g}{\partial t}\right)_t, \qquad (II.5)$$

where QTr means the trace of the operator in parentheses, considered as a quantum-mechanical entity which we shall call the Q trace. Integration over t then yields

$$(f,Dg) = -(g,Df). \qquad (II.5a)$$

Thus, D is antisymmetric, and since the Q trace of an Hermitian operator is real, D is anti-Hermitian. In steady-state problems, the t integration is omitted, and t is omitted from the index n.

If we set $f=g$, we obtain from (II.5a)

$$(f,Df) = 0;$$

therefore,

$$(f,Lf) = 0$$

for any f which is the solution to any problem with this L for arbitrary D. On the other hand, L is not, in general, antisymmetric. This fact is its most important property, for without some symmetric part of L, irreversible behavior would be impossible, as will be seen below. As an illustration we may consider a case where L actually represents elastic collisions of electrons with impurities; then if detailed balance applies P in (II.3) is real symmetric as is L. This is indeed true for all internal scattering which obeys detailed balance. In the case of scattering with external objects, the symmetry may be broken, as it may if detailed balance is violated. If L has an antisymmetric part, it is rather arbitrary whether it is included in L or D, but the symmetric part will be kept in L.

III

Before proceeding to the consideration of V.P.'s it will be useful to discuss entropy production, for it will turn out that some of the V.P.'s are related to this quantity.

The change in entropy during a process is given by

$$\Delta S = -(k \ln f,(df/dt)) + \Delta S_e,$$
$$\Delta S_e = \sum_{n,n'} S_{nn'} L_{nn'} f_{n'} \qquad (III.1)$$

where the first term is the change in entropy of the system and the second term represents the increase in entropy of the external scatterers. Here, $S_{nn'}$ is simply a two-index symbol containing sufficient freedom to make this form correct. For a steady-state process we eliminate the integration over time and consider the rate of entropy increase.

It will now be helpful to consider a concrete situation. Frequently we think of scattering as being pretty well localized in space and time so that if the n's are the sets $\{p_i,x_i,t\}$ a particle is scattered from p_i to p_i' at fixed x_i and t. Furthermore, life is simpler if the scatterer is a temperature bath (possibly moving) so that $L(p_i,p_i',x)f_0(p_i',x) = 0$, that is if the particles at x_i are in a Maxwellian distribution f_0, this is not changed by the scattering. Then, if we write

$$f_0(\mathbf{p}_i,\mathbf{x},t)$$
$$= \exp\{-[(\epsilon_i + \mathbf{p}_i \cdot \mathbf{u}(\mathbf{x},t) - \zeta(\mathbf{x},t)]/kT(\mathbf{x},t)\}, (III.2)$$

where ζ is the chemical potential and $\mathbf{u}$ the velocity, we find for the entropy change of the scatterer

$$S_{p,p'} = k(\ln f_{0p} - \ln f_{0p'})$$
$$= \frac{1}{T}[\epsilon_{p'} - \epsilon_p + (\mathbf{p}' - \mathbf{p}) \cdot \mathbf{u}]. \qquad (III.3)$$

Integration over $\mathbf{p}$, $\mathbf{p}'$ and $\mathbf{x}$ of the second term in (III.1) then yields the familiar result that for the external scatterers the entropy increase is given by the integral of heat change divided by the temperature where the heat change is the energy increase minus the work done.

Let us then substitute this quantity in (III.1)

$$\Delta S = -\left(k \ln f,\frac{df}{dt}\right) + (k \ln f_0, Lf). \qquad (III.4)$$

For the true f then, defining

$$f \equiv f_0 + g \equiv f_0 + f_0 \varphi,$$

we have

$$\Delta S = -\left(k \ln f,\frac{df}{dt}\right) + (k \ln f_0, Df) \qquad (III.5)$$

$$= -(g,kD \ln f_0) - \left(k \ln f,\frac{df}{dt}\right) + (k \ln f_0, Df_0). \qquad (III.6)$$

Now we can write the last two terms

$$-\left(k\ln f,\frac{df}{dt}\right)+\left(k\ln f_0,\frac{df_0}{dt}\right)+(k\ln f_0,D'f_0),\quad\text{(III.6a)}$$

where $D'=D-d/dt$. If the system starts from equilibrium and is allowed to return at the end to equilibrium, then $f=f_0$ at large positive and negative times so the first two terms of (III.6a) cancel, while if the system is in a steady state, they separately vanish. If the system is of finite extent, or uniform in space, the last term vanishes. The first term of (III.6) can now be written

$$S_p=k(\varphi,f_0D\ln f_0)$$
$$=(\varphi,X)=-(\varphi,\Re\varphi),\quad\text{(III.7)}$$

where

$$X=-Df_0=-f_0Dk\ln f_0\quad\text{(III.8a)}$$

and $\Re$ is so defined that for arbitrary g or φ

$$(L-D)g=\Re\varphi.\quad\text{(III.8b)}$$

Thus, φ satisfies the equation

$$\Re\varphi=-X.\quad\text{(III.9)}$$

The last line of (III.8a) is valid when D is a first-order differential operator like $\partial/\partial t$ or P.B. The point of this derivation has been to obtain the entropy production in a quadratic form, rather than a form involving logarithms even for nonlinear problems.

To investigate more closely the validity of these expressions, we consider the instantaneous rate of change of entropy

$$dS/dt=-(k\ln f,(L-D')f)_t+dS_e/dt,\quad\text{(III.10)}$$

where $D'=D-d/dt$. The term involving D' actually yields zero if D' is a P.B. or a commutator but it is convenient to leave it in. Let us now write $f=f_0+g$, where f_0 is not yet determined, and expand about f_0. We will for the rest of this section assume that the coupling between the system and the external scatterers is so weak that only the first-order term in g need be kept. This is not essential but it simplifies (III.13) and may be valid for a considerably wider class of scatterers than thermal baths. More strongly coupled scatterers could be included in the system.

$$dS/dt=-(k\ln f_0,(L-D')f_0)_t+(dS_e/dt)(f_0)$$
$$-(k\ln f_0,(L-D')g)_t+(\sigma,g)_t$$
$$-k(f_0(\tilde{L}-\tilde{D}'),f_0^{-1}g)_t+k/2(g^2f_0^{-2},(L-D')f_0)_t$$
$$-k(gf_0^{-1},(L-D')g)_t+\cdots.\quad\text{(III.11)}$$

The term $(\sigma,g)_t$ is due to external scatterers as just discussed. (This is valid for the classical case.) The quantum-mechanical problem involves more manipulation but leads to the same result (III.14), as shown in the Appendix.

Now if we require f_0 to be a state of minimum instantaneous entropy production at all times, subject to the condition that the Q trace of f_0 be one at all times, we obtain, by requiring the terms linear in g in (III.11) to vanish, the equation

$$\sigma_n=\lambda'(t)\delta_{n'}+[k(\tilde{L}-\tilde{D}')\ln f_0]_{n'}$$
$$+[(L-D')f_0]_{n'}f_{0n'}^{-1},\quad\text{(III.12)}$$

where λ' is a Lagrangian multiplier. Since, as we remarked previously D' could be omitted from (III.10), an alternative equation is

$$\sigma_n=\lambda'(t)\delta_{n'}-[k\ln(f_0L)]_{n'}-[Lf_0]_{n'}f_{0n'}^{-1}.\quad\text{(III.12a)}$$

$\delta_{n'}$ is defined to be one for the classical problem, but in the quantum-mechanical case, it is one if n' refers to a diagonal density matrix element and zero otherwise. Substituted into (III.11) this yields for the zero-order terms

$$(dS/dt)_0=\lambda(t)=\lambda'(t)+(dS_e/dt)(f_0).$$

If we now substitute (III.12) in (III.1), we find

$$\Delta S=-\left(k\ln f,\frac{df}{dt}\right)+(k\ln f_0,(L-D')f)$$

$$+(f_0,(\tilde{L}-\tilde{D}')f_0^{-1}g)+\int\lambda(t)dt$$

$$=-\left(k\ln f,\frac{df}{dt}\right)+\left(k\ln f_0,\frac{df}{dt}\right)$$

$$+(f_0,(\tilde{L}-\tilde{D}')f_0^{-1}g)+\int\lambda dt$$

$$=-k(\ln f,f)\Big|_{-\infty}^{\infty}+k(\ln f_0,f_0)\Big|_{-\infty}^{\infty}$$

$$+(f_0(\tilde{L}-\tilde{D}),f_0^{-1}g)+\int\lambda dt.\quad\text{(III.13)}$$

The first two terms cancel each other if $f=f_0$ at large positive and negative times. Therefore, in such cases,

$$\Delta S-\int\lambda dt=(X,\varphi)=-(\varphi\Re\varphi),\quad\text{(III.14)}$$

where we now and hereafter define

$$X\equiv(L-D)f_0,\quad\text{(III.8c)}$$

while the definition of φ is unchanged and φ still satisfies

$$\Re\varphi=-X.\quad\text{(III.9)}$$

[These definitions and Eq. (III.9) are valid for arbitrary f_0.] We will always assume that $\text{QTr}f_0=1$ at all times. φ is then subject to the restriction $(f_0,\varphi)=\text{QTr}g=0$.

Equation (III.14) is always true [for steady-state processes the integrals involving $\partial/\partial t$ in (III.13) are

identically zero] but it can be used only if an f_0 can actually be found for which dS/dt is at least a local minimum. We will not attempt to determine just when this can be done, but shall describe a wide class of important cases where it is easy and which encompasses, so far as we know, practically all problems whose solution has been attempted. If all scattering is either internal or with one or more external temperature reservoirs, possibly in motion and such that no two different reservoirs have elements of L with the same n or n', (III.12a) can be satisfied with $\lambda=0$. For then, we can break the matrix L into one or more blocks $L^{(i)}$ along the diagonal; the corresponding $f_0^{(i)}$ are then independent. Each $f^{(i)}$ can be chosen to satisfy $Lf^{(i)}=0$ and be in equilibrium with its own reservoir, so that the instantaneous rate of entropy increase is zero. If the individual reservoirs are not identical and if the sub-spaces are connected by the action of D, the entropy will soon increase, but that does not affect our argument which is based on the instantaneous dS/dt. As an example, in metals we sometimes idealize the problem of electronic heat conduction by supposing that the phonons are maintained in local equilibrium at temperature $T(\mathbf{x})$ and scatter the electrons. Then the electrons see at each point (or small region) a thermal scatterer. We can choose f_0 to be at each $\mathbf{x}$ locally Maxwellian with the local temperature and (III.12) will be satisfied with $\lambda=0$. True equilibrium is not reached in this way because $Df_0\neq0$, which means that electrons drift from one temperature to another, so that in a very short time the distribution is no longer locally Maxwellian and entropy is then produced, because φ is not zero and neither is $(\varphi\Re\varphi)$. Basically, the situations which provide the easy evaluation of f_0 are those for which under the action of scattering alone, equilibrium could be reached. Actually our argument can be expanded to cover cases where equilibrium can be reached under the combined action of L and all or any part of D' since the addition (or subtraction) of any part of D' in (III.10) does not affect the value of dS/dt. By "any part of D'" we mean (II.2) with any part of H, and without $\partial f/\partial t$.

The f_0 we have described are indeed not even unique in cases where L breaks up into more than one block, for then if L conserves number, each $f^{(i)}$ can be chosen to correspond to an arbitrary density of particles. In the heat-conduction example, we could have chosen f_0 so that the density of electrons varied widely from point to point. In the case where the scattering also conserves energy or momentum, additional arbitrariness appears. This can be resolved if desired. In problems like the heat-conduction example, one can require that when the f_0 is substituted into the Boltzmann equation and the first few moments are taken, the resulting equations are satisfied. These give conditions like the equation of continuity and the hydrodynamical equation. An alternative, more general, procedure might be to minimize (X,X). On the other hand, it may be more convenient to choose an arbitrary f_0 within the requirement (III.12a), rather than to expend too much effort in optimization.

Our emphasis on the above class of cases where $\lambda=0$ should not be taken to imply that only such cases are important. In some problems this choice is not possible. One of these will be discussed later.

The important point is that when the proper choice of f_0 is made, the entropy production is a quadratic form in φ plus $\int\lambda dt$ which may be viewed as an irreducible entropy production due usually to departure from equilibrium even in a small neighborhood.

[In problems where we can treat the "particles" independently and they obey Fermi or Bose statistics, it is easily shown that it is possible to obtain (III.14), but we must redefine $\Re$ and φ

$$f=f_0+g=f_0+kT(\partial f_0/\partial E)\varphi,$$
$$\Re\varphi=(L-D)g. \tag{III.15}$$

We also define $\mathcal{L}$ and $\mathfrak{D}$ as the parts of $\Re$ arising from L and D, respectively.]

Finally, from (III.11) we find to second order

$$dS/dt=\lambda-(\varphi\mathcal{S}\varphi)_t, \tag{III.16}$$

$$\mathcal{S}\equiv\tfrac{1}{2}(\Re+\Re^T-\mathcal{X}), \tag{III.17}$$

$$\mathcal{X}_{nn'}\equiv[(L-D')f_0]_n\delta_{nn'}. \tag{III.18}$$

In $\mathcal{S}$ the contributions of D are readily seen to cancel. If f_0 is a state of minimum entropy production, then $\mathcal{S}$ must be negative semidefinite. If $Lf_0=0$, then $\mathcal{L}+\mathcal{L}^T$ must be negative semidefinite.

In some problems it is possible to sharpen this up considerably. For example, we may be able to require that dS/dt be a minimum and that $(L-D_0)f_0=0$ where D_0 represents the part of D due to an "unperturbed" Hamiltonian, frequently the kinetic energy alone or in a crystal the energy in the absence of electric fields or thermal gradients. In such cases, we can include D_0 in (III.11) but omit the rest of D'. If then the solution f_0 is the unique state of minimum entropy production, or in particular, the unique equilibrium state under the unperturbed Hamiltonian, $\Re_0+\Re_0^T$ is negative definite not semidefinite where $\Re_0=(\mathcal{L}-\mathfrak{D}_0)$. [$\mathfrak{D}$ is defined after (III.15).] This is a very common occurrence.

We have imposed the requirement that $f=f_0$ at large positive and negative times. For real systems this will normally be satisfied, since a system is usually set up in termal equilibrium and is allowed to return to it, possibly at another temperature. In such cases, one will want to require that f_0 be the equilibrium state at beginning and end. In cases where these conditions are not true, and which are not steady-state problems, we might have a system starting in one steady-state regime and ending in another neither being a state of minimum entropy production. We can then do the time integration between fixed limits in these two regions. These end points will then contribute an additional term to

ΔS which, however, will not depend on the intervening process, which is our primary concern.

IV

In many problems of the type just discussed, we can, in addition, choose f_0 so that $D_0 f_0 = 0$ and require that $\mathfrak{D}_0 \varphi = 0$; this will normally arise from the translational invariance of the system, including scatterers and perturbations. If we are, in addition, content with the linear response of the system, we can ignore the remainder of $\mathfrak{D}$ and write

$$\mathcal{L}\varphi = -X. \qquad (IV.1)$$

Furthermore, $\mathcal{L}$ is negative definite, and in an important category of problems, symmetric. These are the problems in which detailed balance holds for all scattering, and the external scattering is thermal. For then,

$$L_{nn'} = L_{n'n} e^{(\epsilon_{n'} - \epsilon_{n'})/kT}, \qquad (IV.2)$$

$$f_{0n} = e^{-\epsilon_n/kT}. \qquad (IV.3)$$

In such cases, then, we can obtain (IV.1) from a V.P. which will have a maximum at the correct solution φ. A number of essentially equivalent forms are possible, such as:

(a) Maximize $(\varphi, X) + (X, \varphi) + (\varphi \mathcal{L} \varphi)$.

(b) Maximize $-(\varphi, X)(X, \varphi)/(\varphi \mathcal{L} \varphi)$.

(c) Maximize $-(\varphi \mathcal{L} \varphi)$ subject to
$$-2(\varphi \mathcal{L} \varphi) = (\varphi X) + (X \varphi).$$

This type of V.P. was first proposed by Onsager[1] and has been discussed also by Kohler[2] and Ziman.[3] In all cases the limiting value is $-(X \mathcal{L}^{-1} X) = -(\varphi \mathcal{L} \varphi) = (\varphi, X)$, which in this approximation is equal to the entropy production (III.14).

The next simplest situation is that $\mathcal{L}$ still be definite but not necessarily symmetric, $\mathcal{L} f_0 = 0$, and X small but not necessarily $\mathfrak{D}$ small. This last is, for example, true when a large magnetic field is present. $\mathfrak{D}$ then contains a term $(\mathbf{H} \times \mathbf{v}) \cdot \partial/\partial \mathbf{k}$ which acting on f_0 gives zero, assuming that f_0 is a function only of energy. $\mathfrak{D}\varphi$ is not necessarily small compared to $\mathcal{L}\varphi$ however. Another example occurs when H contains the time explicitly, so that though f_0 may be time-independent, X is not. Then $\partial/\partial t$ cannot be neglected. In such situations we have

$$\mathfrak{R}_0 \varphi \equiv (\mathcal{L} - \mathfrak{D}_0) \varphi = -X, \qquad (IV.4)$$

where we are again satisfied with the linear solution, and $(\mathcal{L} - \mathfrak{D}_0)$ is negative definite, but not Hermitian. $\mathfrak{D}_0$ contains the parts of $\mathfrak{D}$ which we do not consider small.

Now we can try to use a V.P. similar to (IV.3a):

$$W = (\psi, X) + (X, \varphi) + (\psi \mathfrak{R}_0 \varphi). \qquad (IV.5)$$

Varying φ and ψ independently yields a stationary point when

$$\mathfrak{R}_0 \varphi = -X, \qquad (IV.6)$$

$$\mathfrak{R}_0^T \psi = -X.$$

Thus, if $\mathfrak{R} \neq \mathfrak{R}^T$, ψ will not equal φ and there is no particular meaning to the equation for ψ in general, except that there exists a problem for which it is a solution. Nevertheless, when (IV.6) is satisfied,

$$W = W_0 = (X, \varphi) = -(\varphi \mathfrak{R}_0 \varphi) = -(\psi \mathfrak{R}_0 \psi), \qquad (IV.7)$$

as before. Again this is equal to the entropy production to the accuracy desired.

The important point right now is that W does not have a maximum or minimum when (IV.6) is satisfied, but a saddle point. To see this, we write $2X_1 = \delta\varphi + \delta\psi$, $2X_2 = \delta\varphi - \delta\psi$, where $\delta\varphi$ and $\delta\psi$ are the deviations from the equilibrium values and we find

$$W = W_0 - (X_1 \mathfrak{R}_0 X_1) + (X_2 \mathfrak{R}_2 \mathfrak{R}_0 X_2) - (X_1 \mathfrak{R}_0 X_2) + (X_2 \mathfrak{R}_0 X_1). \qquad (IV.8)$$

Thus, W has a maximum as a function of X_1 and a minimum as a function of X_2 at W_0.

A different V.P. can be obtained by multiplying (IV.4) by A where A is the antisymmetric part of $\mathfrak{R}_0$

$$A \mathfrak{R}_0 \varphi = -AX. \qquad (IV.9)$$

This equation can be obtained from the V.P.,

$$W' = (\psi, AX) - (XA\varphi) - (\psi A \mathfrak{R}_0 \varphi), \qquad (IV.10)$$

whose equilibrium value is

$$W_0' = -(XA\varphi) = (\varphi \mathfrak{R}_0^T A \varphi). \qquad (IV.11)$$

The physical significance of W_0' will be considered in Sec. V.

We have commented that, in general, the second equation of (IV.6) has no simple meaning. There are, however, a number of important physical problems in which $\mathfrak{R}^T$ is the $\mathfrak{R}$ for a closely related problem. Thus, if $\mathfrak{D}_0$ contains $\partial/\partial t$, its Hermitian conjugate is also its time-inverse. If $\mathfrak{D}_0$ contains $(\mathbf{B} \times \mathbf{v}) \cdot \partial/\partial \mathbf{p}$, its transpose is also its value for reversed field. In such cases, ψ is the solution of a closely related problem. Indeed, previous derivations of (IV.5) have explicitly used the field-reversal properties in their arguments. We see that this is quite unnecessary. (IV.5) is essentially the V.P. used by Ziman and his associates[3] for the magnetic-field case. Robinson and Bernstein[4] have used much more complicated V.P.'s which are equivalent to (IV.5) and (IV.10), so far as we can tell. Like their λ_2, W' gives the components of the conduc-

[1] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

[2] M. Kohler, Physik **124**, 772 (1948); **125**, 679 (1949); Ann. Physik **6**, 18 (1949).

[3] J. Ziman, Can. J. Phys. **34**, 1256 (1956); F. Garcia-Moliner and S. Simons, Proc. Cambridge Phil. Soc. **53**, 848 (1957); F. Garcia-Moliner, Proc. Roy. Soc. (London) **249**, 73 (1959).

[4] B. Robinson and I. Bernstein, Ann. Phys. (N. Y.) **18**, 110 (1962).

tivity tensor which are odd in the magnetic field and in the ac conductivity problem, the components odd in frequency, that is, the reactive components (see Sec. V).

The great deficiency of the methods based on W or W' is that they do not have a maximum for the correct value. This leads to a number of disadvantages. First, nothing guarantees that the variational solution for a given class of trial functions is in any way better than some other member of the class. In particular, there will always be functions which give the *correct* values of W or W' since the range of values is unbounded. Second, unless one chooses functions linear in the parameters, the determination of the saddle point is not so easy as the determination of a minimum or maximum. Finally, they are not applicable to nonlinear problems. Therefore, we conclude that there is good reason to seek a V.P. which does have a minimum or maximum for the correct solution.

Such a V.P. is, in fact, easy to obtain. Rewrite (III.9) in the form

$$\mathcal{R}^T T \mathcal{R} \varphi = -\mathcal{R}^T T X, \qquad (\text{IV.12})$$

where T is for the time being an arbitrary real symmetric positive definite operator. Obviously, if φ_0 is the solution of (III.9) it also solves (IV.12). Similarly, if φ_1 is another solution of (IV.12), then

$$\mathcal{R}^T T \mathcal{R} (\varphi_1 - \varphi_0) = 0.$$

Since T is definite $\mathcal{R}(\varphi_1 - \varphi_0) = 0$ and φ_1 is a solution of (III.9). Thus, the solution of (IV.2) is precisely as unique as that of (III.9) or (II.1). Since $\mathcal{R}^T T \mathcal{R}$ is also Hermitian, we can obtain V.P.'s in forms analogous to (IV.3). For definiteness, consider the form

$$V = (\varphi \mathcal{R}^T T X) + (X T \mathcal{R} \varphi) + (\varphi \mathcal{R}^T T \mathcal{R} \varphi), \quad (\text{IV.13})$$

which has the maximum value (XTX).

V can also be written in terms of φ_0 as

$$V = ([\varphi - \varphi_0], \mathcal{R}^T T \mathcal{R}[\varphi - \varphi_0]) - \varphi_0 \mathcal{R}^T T \mathcal{R} \varphi_0, \quad (\text{IV.13a})$$

and $\mathcal{R}^T T \mathcal{R}$ can then be replaced by $\mathcal{T}$. A particularly interesting special case is then provided by $\mathcal{T} = \frac{1}{2}(\mathcal{R} + \mathcal{R}^T - \mathcal{X})$ which yields

$$V_s = -(\varphi_0 \tfrac{1}{2}[\mathcal{R} + \mathcal{R}^T - \mathcal{X}] \varphi_0) \\ + ([\varphi - \varphi_0] \tfrac{1}{2}[\mathcal{R} + \mathcal{R}^T - \mathcal{X}][\varphi - \varphi_0]).$$

If we add $-(\varphi_0 \tfrac{1}{2} \mathcal{X} \varphi_0)$, we obtain

$$V_s' = \tfrac{1}{2}(\varphi[\mathcal{R} + \mathcal{R}^T - \mathcal{X}] \varphi) - \tfrac{1}{2}(\varphi_0[\mathcal{R} + \mathcal{R}^T - \mathcal{X}] \varphi) \\ - \tfrac{1}{2}(\varphi[\mathcal{R} + \mathcal{R}^T - \mathcal{X}] \varphi_0) - \tfrac{1}{2}(\varphi_0 \mathcal{X} \varphi_0), \quad (\text{IV.14})$$

and the maximum value is

$$V_{s0}' = -(\varphi_0 \mathcal{R} \varphi_0)$$

$$= \Delta S - \int \lambda dt,$$

which again is equal to the entropy production if f_0 has been chosen to be a state of minimum entropy production, and $\lambda = 0$. Whether the state of minimum entropy production is unique depends on whether $\mathcal{R} + \mathcal{R}^T - \mathcal{X}$ is definite or semidefinite as discussed at the end of the last section. If $L f_0 = 0$, we can omit $\mathcal{X}$ and replace $\mathcal{R}$ by $\mathcal{L}$ in (IV.14). We will discuss the interpretation of entropy production in a later section. Now we must point out that this V.P., which for the case of linear galvanomagnetic effects is basically equivalent to that of Tsuji,[5] suffers from the drawback for computational purposes that it requires at least partial knowledge of φ_0, whose determination is the object of the whole problem.

For computational purposes, we would want to use known forms for T and the simplest, of course, is $T = 1$.[6] This may not always be the most useful, however. We want to emphasize also that it may frequently be useful to use more than one T and compare the results. This will have the following advantages:

(1) If the φ's found for different T's differ a great deal, we would not have much confidence in any of them. Conversely, we would be encouraged by obtaining similar g's from rather different T's.

(2) It may be possible to extrapolate in a loose sort of way from known values T to an unknown one with more physical significance. Thus, in may cases, $\mathcal{L}^{-1}$ will not be very different from $\mathcal{R}^{-1} + \mathcal{R}^{T-1}$. Then $T = 1$, $\mathcal{L}$, $\mathcal{L}^2, \cdots$, constitute a sequence which could hopefully suggest the value to be obtained for $T = \mathcal{L}^{-1}$ and, thus, for $T = \frac{1}{2}(\mathcal{R} + \mathcal{R}^{T-1})$.

Another feature of (IV.13) is that $(XTX) - V$ yields a limit on $(g - g_0)$

$$(XTX) - V = ((g - g_0)(\mathcal{R}^T T \mathcal{R})(g - g_0)) \\ \geq |g - g_0|^2 (\mathcal{R}^T T \mathcal{R})_{\min}, \quad (\text{IV.15})$$

where $(\mathcal{R}^T T \mathcal{R})_{\min}$ is the minimum eigenvalue of $\mathcal{R}^T T \mathcal{R}$.

On the other hand,

$$|(g - g_0, X)|^2 \leq |g - g_0|^2 |X|^2$$

$$\leq \frac{[(XTX) - V]|X|^2}{(\mathcal{R}^T T \mathcal{R})_{\min}}. \quad (\text{IV.16})$$

Thus, although we cannot, in general, find a useful V.P. for the entropy production, we may be able to obtain explicit limits on our error which is not possible when the V.P. is an unknown quantity.

This last class of V.P.'s could have been deduced without selecting an f_0, which is most useful for making problems linear. Thus, we need only start from (II.1) in the form

$$(L - D)f = 0.$$

[5] M. Tsuji, J. Phys. Soc. Japan **13**, 979 (1958).

[6] C. Herring has also discovered this form in unpublished work on the linear magnetic field problem.

Its solution minimizes the quantity

$$V = (f[\tilde{L}-\tilde{D}]T[L-D]f) \qquad \text{(IV.17)}$$

for arbitrary positive definite Hermitian T. If we compare V' with V, we see that

$$V' = (XTX) - V.$$

We have pointed out that the fact that certain other V.P.'s do not have maxima or minima at the saddle points is a disadvantage relative to the class of V.P.'s we have proposed. Candor requires that we point out that Robinson and Bernstein[4] have, in fact, obtained excellent results in a case which could be compared with a rigorous solution. It would be very difficult to judge how much this example says about the general relative utility of the different procedures for linear problems.

V

In this section we shall consider an illustrative example, concerning electrons in a magnetic field subject to weak electric fields as in cyclotron resonance. We assume the scattering relaxes the electron toward f_0 a Fermi distribution. We consider only the linear response. In this case, it is shown in Wilson's book[7] that we can write Lf in the form

$$Lf = \mathcal{L}\varphi, \qquad \text{(V.1)}$$

where $\mathcal{L}$ is symmetric and $f = f_0 + f_0'\varphi$ and $f_0 = f_0((E-\zeta)/kT)$. Then (II.1) reads

$$\mathcal{L}\varphi - i\Omega\varphi = X$$

$$-i\Omega \equiv f_0'\left(\frac{\partial}{\partial t} + \mathbf{B}\times\mathbf{v}\cdot\frac{\partial}{\partial \mathbf{p}}\right)$$

$$X = \mathbf{E}\cdot\mathbf{v}\frac{f_0'}{kT},$$

where E is the electric force and B is e/c times the magnetic induction. It is easy to verify that in this case the entropy production is

$$\Delta S = -(\varphi, \mathcal{L}\varphi).$$

We now take the Fourier transform with respect to time, obtaining

$$-i\Omega = -f_0'\left(i\omega + \mathbf{B}\times\mathbf{v}\cdot\frac{\partial}{\partial \mathbf{p}}\right).$$

Now consider ions or electrons whose energy is $p^2/2m$ and whose differential scattering cross section is a function only of the angle between the incoming and outgoing momenta, and the initial and final energies.

Then, if we expand φ in spherical harmonics,

$$\varphi = \sum \varphi_{lm}(E)Y_{lm}(\theta, \chi),$$

$\mathcal{L}\varphi$ takes the form

$$\mathcal{L}\varphi_{lm}(E) = \int \nu_l(E, E')\varphi_{lm}(E')dE'$$

and $-i\Omega$ takes the form

$$-i\Omega = f_0'(-i\omega + B\partial/\partial\chi)\varphi,$$
$$-i\Omega\varphi_{lm}(E) = f_0'i(-\omega + m\omega_c)\varphi_{lm}(E).$$

Thus, in this case, the equations for the individual φ_{lm} are completely separate, each being driven by the corresponding part of X. In the common problems where only temperature gradients and electric fields are involved, the only X's correspond to $l = 1$.

An advantage of this procedure is that Ω is broken into groups of single, positive- or negative-definite operators. A separate V.P. can be used for each component. A similar procedure has been used by Robinson and Bernstein with their variational principle.

In solid-state problems, Ω can be diagonalized, but, in general, $\mathcal{L}$ will not be so simple. On the other hand, the work involved will not be an order of magnitude greater than that required for a nonmagnetic static problem.

In Eq. (IV.2) we found that the V.P., W', had an equilibrium value

$$W_0' = -(XA\varphi) = (\varphi AX).$$

In the present problems, this quantity can be given a simply physical meaning. In a problem of electric conduction in a magnetic field, $X = Evf_0'$ and $A = \mathbf{B}\times\mathbf{v}\cdot\partial/\partial\mathbf{p}$. Thus,

$$AX = \mathbf{B}\times\mathbf{v}\cdot\boldsymbol{\alpha}\cdot\mathbf{E}f_0',$$

where $\boldsymbol{\alpha}$ is the inverse effective mass tensor and may be a function of at least p. In case $\boldsymbol{\alpha}$ is an isotropic constant, m^{-1}

$$W_0' = (\varphi, AX) = \frac{\mathbf{E}\times\mathbf{H}}{m}\cdot(\varphi, vf_0') = \frac{\mathbf{E}\times\mathbf{H}}{m}\cdot\mathbf{J},$$

where J is the total current. Thus, W_0' gives the Hall component of the current in this special case. If A arises from time dependence, it will for each frequency component have the form $i\omega$, and W_0' then gives simply the imaginary part of the conductivity as W gives the real part.

In problems of this type, like that discussed in Sec. IV, we can also find maximum principles which yield the same quantities. This is done by separating the equation for different ω and m. Then if $T = AO^{-1} - O^{-1}A$, the maximum value of V is φAX for each component.

[7] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), p. 194.

VI

We found in Sec. III a convenient form for the increase in entropy of a system

$$\Delta S = \int \lambda dt - (\varphi_0 \Re \varphi_0). \qquad (VI.1)$$

In Sec. IV we found that the last term is the value of a number of V.P.'s. In the case of (IV.3) the connection is even more intimate for in that case $(\varphi \mathcal{L} \varphi)_t$ is actually the instantaneous value of entropy increase, to second order, since $\mathfrak{X}$ can be neglected to that order in (III.17). For the other V.P.'s, we can only say that W and V' are equal to the correct value of $(\varphi_0 \Re \varphi_0)$ when φ_0 substituted into them for φ.

We have then in a restricted sense a "principle of maximum entropy production." The question arises whether any deeper significance is to be attributed to it. We feel that this is really a matter of taste. In the case of the linear problem, (IV.3), Ziman has suggested that the V.P. is really a basic physical principle. If this is to be maintained, it should be true not only for linear processes, but in general. Our feeling is that the link between V.P. and entropy production in the general case is not sufficiently close to justify such an interpretation. We have seen that, in fact, there are a great variety of possible V.P.'s to maximize and that it really takes a fair amount of artificiality to get one in the form of entropy production. Even so, what we obtained is a quadratic form which agrees with the entropy production or any part of it only for the true distribution function except in the small perturbation limit. Unless $Lf_0 = 0$ we even have to add an extra term to the V_s to make it equal the entropy production. Thus, our point of view is that not too much significance should be attributed to the maximum entropy production, but we would not strongly dispute those whose taste differs from ours in this regard. V_s can be viewed somewhat differently as follows: Maximize $-\frac{1}{2}(\varphi[\Re + \Re^T - \mathfrak{X}]\varphi)$ subject to the restriction that it equal $\frac{1}{2}(\varphi[\Re + \Re^T - \mathfrak{X}]\varphi_0)$. The quadratic term is equal to the quadratic form for the second-order entropy increase (III.11) so that while it is not exactly equal to the excess of entropy increase over the minimum it is intimately related. On the other hand, the term $+\frac{1}{2}(\varphi_0 \mathfrak{X} \varphi_0)$ certainly is an obstacle to any glib interpretation, except in lowest order when it vanishes, being at least third order in $\mathfrak{X}$. The best we can say is that it appears here in much the same way that the right side of (III.14) differs by the same term from the quadratic term of (III.11).

Entropy production has been a favorite topic of irreversible phenomena for a long time and a principle of minimum entropy production has been enunciated by Prigogine[8] and discussed by a number of authors.[9]

Two different such principles have, in fact, been proposed, though their difference seems to have been largely overlooked.

The first is based on the theorem due to Prigogine[8] that if a system is operating in a state of minimum entropy production and the forces acting on it are then changed the currents will change in such a way as to counteract the change in forces. The meaning of "a state of minimum entropy production" is different from ours, for it envisions a system subject to a certain number of "forces," X_{0i} such as electrical potential differences or concentration gradients, some of which are fixed, while the others are not. The rate of entropy production is defined by the quantity $\frac{1}{2}L_{il}J_iJ_l$, where L is the matrix relating the currents J_i to the forces $X_i: L_{il}J_l = X_i$. The state of minimum entropy production is then a state in which $L_{ik}J_iJ_k$ is minimized subject to the condition that the fixed forces X_i be equal to the corresponding $L_{il}J_l$. The theorem as stated is true, but there has been a tendency to go beyond it and assume that whenever some forces are fixed and others are free, the steady state of the system will actually be the state of minimum entropy production. This would amount to obtaining a complete solution to an incompletely specified problem. This is not true unless there are boundary conditions requiring the J_i corresponding to the unspecified forces to be zero. The misinterpretation of the theorem rests in trying to obtain the currents in a situation in which not all the forces are specified. In fact, while not all the forces need be specified it is essential that an equivalent number of conditions be given. These will frequently appear as boundary conditions. As a simple example, consider a thermocouple with junctions at temperatures T and $T + \delta T$, and a voltage V across a pair of leads. Then the entropy production can be written in the form, $2\sigma = K\delta T^2 + \rho J^2$. If we set $\delta T = X_1$ the state of minimum entropy production is attained when $J = 0$. This is the actual solution, however, only if open circuit boundary conditions are imposed. If the two leads are shorted, the current is not zero but is determined by the thermoelectric power and resistivity. If intermediate conditions are imposed such as $V = IR$, due to a load resistance, intermediate currents will flow. The actual current is determined by the applied temperature difference and the boundary condition.

The logical gap between Prigogine's theorem and the "principle of minimum entropy production" is that the "tendency to counteract the change in forces" will be, in fact, consumated only when the open circuit boundary conditions apply. In our example, if this boundary condition applies and the voltage should fluctuate the

[8] I. Prigogine, *Étude Thermodynamique des Phenomines Irreversibles* (Maison Desoer, Liége, 1947), Chap. V; S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951), Chap. X.

[9] M. J. Klein and P. H. E. Meijer, Phys. Rev. **96**, 250 (1954); M. J. Klein, *ibid.* **98**, 1736 (1955); P. H. E. Meijer, *ibid.* **103**, 839 (1956); M. J. Klein, in *Transport Processes in Statistical Mechanics* (edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958), p. 311.

current would change and charge would build up at the boundaries in such a way as to restore the original voltage and current; but if the boundary condition is a short circuit or leak, the tendency will not be consummated and the minimum entropy production state will not be stable.

Inspired apparently by Prigogine's theorem, Klein and Meijer[9] have investigated what is really a different principle of minimum entropy production, stating that the steady state is the state in which the distribution function or density matrix adjusts itself to produce minimum entropy production. This is much more closely related to what we have done earlier in this paper. Klein and Meijer conclude that this principle is not always valid, but claim that it is approximately valid in the models they study in the neighborhood of equilibrium. Klein has emphasized, in addition, that the temperature must be much larger than the energy level spacing in the two-level system he considers. We can investigate the realm of validity of this principle on a much broader front. From (III.12) we find that the necessary requirement for the entropy production minimum to occur when Eq. (II.1) is obeyed is

$$(L-D)f_n=0,$$
$$(\tilde{L}-\tilde{D}')k\ln f_n=\sigma_n-\lambda\delta_n. \qquad (VI.2)$$

Obviously we cannot absolutely rule out the simultaneous solution of these two equations, at least until we make some hypotheses as to $L_{nn'}$ and σ_n. On the other hand, we can certainly say that there is no reason to expect such solutions in general; for assuming $L-D$ to have a unique solution for given initial conditions, the second equation constitutes a set of conditions which must be satisfied by f and their sum determines λ:

$$(\sigma,f)=\lambda.$$

Since completely general statements would be very difficult we restrict ourselves to problems where the deviation from equilibrium is small. Any general results should also be true for this special case. The equilibrium distribution $f^{(0)}$ is the solution of the equation

$$L^{(0)}f^{(0)}=0. \qquad (VI.3)$$

Our Eqs. (VI.2) now read, after adding and subtracting:

$$(\mathcal{L}^{(0)}+\mathcal{L}^{T(0)})\varphi_n=-L^{(1)}f_n^{(0)}-\mathcal{L}^{T(1)}\ln f_n^{(0)}$$
$$+\frac{1}{k}\sigma_n^{(1)}-\lambda\delta_n, \qquad (VI.4)$$

$$(\mathcal{L}^{(0)}-\mathcal{L}^{T(0)})\varphi_n=2Df_n^{(0)}-L^{(1)}f_n^{(0)}+\mathcal{L}^{T(1)}\ln f_n^{(0)}$$
$$-\frac{1}{k}\sigma_n^{(1)}+\lambda\delta_n,$$

where $L^{(1)}$ is a perturbation on $L^{(0)}$ and $\sigma^{(1)}$ is the associated external entropy production. For simplicity we make the (nonessential) assumption that $\mathcal{L}^{(0)}$ is symmetric. Then

$$2Df_n^{(0)}=L^{(1)}f_n^{(0)}-\mathcal{L}^{T(1)}\ln f_n^{(0)}$$
$$+\frac{1}{k}\sigma^{(1)}_n-\lambda\delta_n f_n^{(0)}, \qquad (VI.5)$$

and

$$2(f^{(0)},Df^{(0)})=0=(f^{(0)},L^{(1)}f^{(0)})-(f^{(0)},\mathcal{L}^{T(1)}\ln f^{(0)})$$
$$+\frac{1}{k}(\sigma^{(1)},f^{(0)})-\lambda. \qquad (VI.6)$$

Thus, λ and $Df^{(0)}$ are completely determined by $L^{(1)}$ and $\sigma^{(1)}$. Clearly then for general $Df^{(0)}$, the state of minimum entropy production is not a solution of (II.1). A special case of importance occurs when the scattering is adequately described by $L^{(0)}$, so that $L^{(1)}=\sigma^{(1)}=0$. This leads to $\lambda=Df^{(0)}=0$. Thus, all the usual transport problems are ruled out.

So far as we can see the only situation in which (VI.5) can even approximately be satisfied, aside from complete happenstance, is the following: We assume that there is scattering only between n's with nearly equal f. Thus, we write $f_{n'}=C_n(\delta_{n'}+\psi_{n',n})$. Then (VI.5) reads to lowest order

$$2Df_n^{(0)}=C_n\sum_{n'}L_{nn'}^{(1)}\delta_{n'}+\frac{1}{k}\sigma_n^{(1)}C_n(\delta_n+\psi_{nn})$$
$$-\lambda\delta_nC_n(1+\psi_{nn})+C_n\sum_{n'}L_{nn'}^{(1)}\psi_{n'n}$$
$$-C_n(\delta_n+\psi_{nn})\sum_{n'}\tilde{L}_{nn'}^{(1)}\delta_{n'}\ln C_n$$
$$-C_n\delta_n\tilde{L}_{nn'}^{(1)}\psi_{n'n}. \qquad (VI.7)$$

Again because of the independence of D, $L^{(1)}$ and $f^{(0)}$, we can expect a solution only for a class of cases in which f does not enter. We can achieve this by restricting ourselves to $D=\sigma^{(1)}=0$. We also divide by C_n and obtain

$$\sum_{n'}L_{nn'}^{(1)}\delta_{n'}+\sum_{n'}(L_{nn'}^{(1)}-\delta_n\tilde{L}_{nn'}^{(1)})\psi_{n'n}$$
$$=\lambda\delta_n(1+\psi_{nn}). \qquad (VI.8)$$

Now if $L_{nn'}^{(1)}=L_{n'n}^{(1)}\delta_n$, $\sum_{n'}L_{nn'}^{(1)}\delta_{n'}=\delta_n\sum\delta_{n'}L_{n'n}^{(1)}$ $=0$ because this is a condition L must obey to conserve probability, and on taking the trace, $\lambda=0$. Also if $L_{nn'}^{(1)}=L_{n'n}^{(1)}\delta_n$, then further it equals $L_{nn'}^{(1)}\delta_{n'}\delta_n$ $=L_{n'n}^{(1)}\delta_{n'}\delta_n$. That is, $L^{(1)}$ is symmetric and connects only diagonal density matrix elements in the quantum-mechanical case. This description, along with $\sigma^{(1)}=0$ fits transitions due to radiation of effectively infinite temperature. This then fits the essential features of the models considered by Klein and Meijer. We do not

see that any other physical realizable situations will even so approximately fit the requirements.

Our discussion of Sec. III indicates that the true role of the state of minimum entropy production is to provide a particularly convenient "base." The additional entropy production has a particularly simple quadratic form and is given by a variational principle, though this V.P. is not particularly useful for computation.

One can make an analogy to the relation between quantum mechanics and classical mechanics. In the latter the motion is determined by the minimization of the action, but when quantum effects are taken into account, this no longer holds. The analogy is that if kT, the analog of $\hbar^{-1}$, is very large, minimum entropy production is a good approximation. (In a sense this is true even if $Df_0 \neq 0$. In this case, if f_0 is Maxwellian, Df_0 becomes small at high temperature and the deviation from equilibrium becomes small. Unfortunately, only the deviation is interesting in most cases.) The analogy is not very interesting, in most cases, however, because "large" must mean large compared to the width of the spectrum, which again limits us to spectra of finite width.

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APPENDIX

To discuss entropy production in the quantum-mechanical case, we consider $S(f)$, the entropy considered as a functional of f. For the internal part of dS/dt we write

$$\left(\frac{dS}{dt}\right)_{\text{int}} = \lim_{\tau \to 0} \frac{d}{d\tau} S\left(f + \tau \frac{df}{dt}\right) \qquad (A1)$$

$$= \lim_{\tau \to 0} \frac{d}{d\tau} S(f + \tau(L-D')f). \qquad (A2)$$

To investigate the behavior near a minimum we write

$$\frac{dS}{dt} = \lim_{\tau \to 0} \frac{d}{d\tau} S(f_0 + g + \tau(L-D')(f_0+g))$$
$$+ \sum_{nn'} S_{n'n} L_{n'n}(f_{0n}+g_n). \qquad (A3)$$

This leads us to an equation for f_0

$$\lim_{\tau \to 0, \mu \to 0} \frac{\delta}{\delta g_n} \frac{d}{d\tau}\left(\frac{1}{\mu}\right) S(f_0 + \mu g + \tau(L-D')(f_0+\mu g))$$
$$+ \sum_{n'} S_{n'n} L_{n'n} = \lambda \delta_n. \qquad (A4)$$

Thus, we can substitute into (III.1)

$$\frac{dS}{dt} = \lim_{\tau \to 0} \frac{d}{d\tau} S\left(f + \tau \frac{df}{dt}\right)$$

$$- \lim_{\tau \to 0, \mu \to 0} \frac{d}{d\mu} \frac{d}{d\tau} S(f_0 + \mu f + \tau(L-D')(f_0+\mu f)) + \lambda$$
$$\qquad (A5)$$

$$= \frac{dS(f)}{dt} - \lim_{\tau \to 0, \mu \to 0} \frac{d}{d\mu} \frac{d}{d\tau} S\left(f_0 + \mu f_0 + \mu g + \tau(L-D)f_0\right.$$

$$\left. + \tau(1+\mu)\frac{df_0}{dt} + \tau\mu\frac{dg}{dt}\right) + \lambda, \qquad (A6)$$

where we have used $(L-Df=0$. We can now rewrite this as follows:

$$\Delta S = \int \left\{ \frac{dS(f)}{dt} - \lim_{\tau \to 0, \mu \to 0} \frac{d}{d\mu} \frac{d}{d\tau}\left[S\left(f_0 + \mu f_0 + \tau(L-D)f_0 + \tau\frac{df_0}{dt}\right) + S(f_0 + \mu g + \tau(L-D)f_0) \right.\right.$$

$$\left.\left. + S\left(f_0 + \mu g + \tau\frac{d}{dt}(f_0+\mu g)\right) + S\left(f_0 + \tau\mu\frac{df_0}{dt}\right)\right]\right\} dt + \int \lambda \, dt. \qquad (A7)$$

Since $S(f) = QTr(f \ln f)$, $\lim_{\tau \to 0}(d/d\tau)S((1+\mu)f_0 + \tau Y)$ is for arbitrary Y equal to

$$QTr([\ln(1+\mu) + \ln f_0]Y)$$

and

$$\lim_{\mu \to 0, \tau \to 0} \frac{d}{d\mu} \frac{d}{d\tau} S((1+\mu)f_0 + \tau Y) = QTr Y. \qquad (A8)$$

Thus, the first term in square brackets in (A7) vanishes. The third term is

$$\lim_{\mu \to 0} \frac{d}{dt} \frac{d}{d\mu} S(f_0 + \mu g).$$

The fourth term is $(d/dt)S(f_0)$. These two combine with $dS(f)/dt$ to yield $(d/dt) QTr(\ln f_0 - \ln f, f)$ which vanishes on integration if $f = f_0$ at beginning and end.

We are then left with

$$\Delta S - \int \lambda dt$$

$$= \int dt \lim_{\tau \to 0, \mu \to 0} \frac{d}{d\tau} \frac{d}{d\mu} S(f_0 + \mu g + \tau(L-D)f_0). \quad (A9)$$

We now introduce φ such that $g = f_0\varphi$, and X such that for arbitrary φ

$$(\varphi, X) \equiv \int dt \lim_{\tau \to 0, \mu \to 0} \frac{d}{d\tau} \frac{d}{d\mu}$$

$$\times S(f_0 + \mu f_0\varphi + \tau(L-D)f_0), \quad (A10)$$

as well as $\mathfrak{R}$ such that

$$(\varphi \mathfrak{R} \varphi') = \int dt \lim_{\tau \to 0, \mu \to 0} \frac{d}{d\tau} \frac{d}{d\mu}$$

$$\times S(f_0 + \mu f_0\varphi + \tau(L-D)f_0\varphi'). \quad (A11)$$

With these definitions of X and $\mathfrak{R}$, (III.14) and other formulas following it remain valid. In (III.18), we use for $\mathfrak{X}$

$$(\varphi \mathfrak{X} \varphi) = \lim_{\tau \to 0, \mu \to 0} \frac{1}{2} \frac{d^2}{d\mu^2} \frac{d}{d\tau}$$

$$\times S(f_0 + \mu f_0\varphi + \tau(L-D')f_0). \quad (A12)$$

Broken Symmetries and Massless Particles*

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The following generalization of a theorem conjectured by Goldstone is proven: In a theory admitting a continuous group of transformations, suppose a set of operators $\phi_i(x)$, transforming under an irreducible representation of the group, has the property that in the vacuum some expectation values $\langle \phi_i(x) \rangle \neq 0$ for $i = i'$. The theorem then asserts that $\bar{D}_{ij}(p)$, the Fourier transform of the propagator of $\phi_i(x)$, is singular at $p^2 = 0$ for some $i \neq i'$. (The maximum number of $\langle \phi_i \rangle \neq 0$ is a property of the group representation. The further identification of the singularities as poles and their interpretation as massless particles depends on the usual apparatus of quantum field theory.)

The appropriate choice to be made for the field ϕ_i when it describes a boson excitation and when the Lagrangian contains only direct fermion-fermion coupling is discussed. It is suggested that such Fermi interaction theories may be renormalizable when expanded in terms of the coupling between fermions and the collective boson field.

The theorem is illustrated by the following models: (A) γ_5 gauge group (Nambu and Jona-Lasinio), where a massless pseudoscalar meson is predicted; (B) isospin group (Nambu and Jona-Lasinio) where massless charged mesons are predicted; (C) $SU(3)$ octet model (Baker and Glashow) where six or four massless mesons are predicted; (D) Lorentz group (Bjorken) where the massless photon is predicted. The limitations of the theorem are also discussed.

I. INTRODUCTION

A WIDESPREAD feature of many-body systems is the existence of collective modes of excitation for which the energy vanishes in the long-wavelength limit, these modes constituting the only low-energy excitations. Well-known examples are the spin waves in the Heisenberg model of ferromagnetism,[1] the phonons of superfluid helium,[2] and the phonons which presumably would be exhibited by a superconductor in the absence of Coulomb interactions.[3] The common feature of these systems is the appearance of a condensation or coopera-

tive phenomenon; the theoretical description then requires, or at least is facilitated by, the introduction of a degenerate or symmetry-breaking ground state.

Thus, in ferromagnetism, where the Hamiltonian is invariant under spatial rotations, the ground state has a macroscopic spin proportional to the size of the system. For an infinite system, at least, the ground state is then not rotationally invariant. In this sense, the ground state is nonsymmetric or degenerate; the spin points in some direction which, because of the symmetry of the Hamiltonian, is arbitrary. Each particular choice of spin direction, however, defines a representation of the Hilbert space inequivalent to all the other possible choices.

The BCS model of superconductivity[4] can be formu-

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