Table II. Theoretical and experimental full widths for various proportional counter pressures.

Proportional counter thickness cm argon	Mean energy loss	% full width due to Landau-Symon effect	
		Theoretical	Experimental
12.0	220 kev	34±3	32.5±3
5.0	85 kev	40±3	45 ±3
2.0	34 kev	45±3	50 ±4

was found to be 13%. Since a part of this is due to the energy spread of the nonuniform thickness α source, the inherent resolution of the counter is better than 13%, and certainly adequate to investigate the observed distributions.

The highest pressure proportional counter measurement was equivalent in terms of absorber thickness to the 0.005-in. plastic scintillator. This affords a check on the shape of the distribution in this region. Figures 4 and 5 show the distribution of pulses produced in the proportional counter in the Landau region and symmetrical region, respectively. Also shown are the theoretical curves calculated from the formulas of Symon, and a Poisson distribution appropriate to the statistical fluctuations in the number of ion pairs formed in the absorber. The Poisson distribution is arbitrarily normalized to the same maximum value as the Landau distribution. Table II shows theoretical and experimental full widths for three proportional counter pressures. The errors quoted in this table for the measured percent full widths were estimated graphically from the accuracy of drawing a smooth curve through the experimental points.

CONCLUSIONS

The frequency distribution of energy losses of 37-Mev protons was found to be in good agreement, both in shape and full width, with the predictions of Landau and Symon, for absorber thicknesses from 34 kev to 2 Mev.

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Principle of Minimum Entropy Production*

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Prigogine has shown that in the steady state in which certain macroscopic affinities $F_1, F_2, \cdots F_k$ are fixed and other macroscopic affinities $F_{k+1}, F_{k+2}, \cdots F_r$ are unconstrained, the values assumed by the unconstrained affinities are such as to minimize the rate of production of entropy. We here show that the complete *microscopic* density matrix of the system is that which minimizes the rate of entropy production subject to the imposed constraints. All magnetic fields are assumed to be zero.

It is shown that the kinetic coefficients connecting Casimer's α-type and β-type variables always vanish. The validity of the minimum entropy production theorem in the absence of a magnetic field depends on this fact. The limitations on the validity of the minimum entropy production theorem in the presence of a magnetic field are briefly discussed.

Calculations on particular models by Klein and Meijer and by Klein corroborate the theorem here proved. An analysis of magnetic resonance by Wangsness suggests certain modifications necessary in this case of a nonzero, nonstationary, magnetic field.

INTRODUCTION

THE essential foundation of the theory of irreversible thermodynamics is the Onsager reciprocity theorem.[1] This theorem establishes a symmetry in the mutual interference between two simultaneous, linear, irreversible processes. In particular, if $\{J_k\}$ is a set of "fluxes," and if $\{F_k\}$ is a set of associated affinities so defined that the rate of entropy production $\dot{S}$ is

$$\dot{S}=\sum_k F_k J_k, \tag{1}$$

and if the phenomenological equations between fluxes and affinities are linear

$$J_k=\sum_i L_{ik} F_i, \tag{2}$$

then the Onsager theorem states that

$$L_{ik}(H)=L_{ki}(-H). \tag{3}$$

Here H signifies a magnetic field.

Attempts have been made to rephrase the Onsager

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[1] For general references see S. R. deGroot, *Thermodynamics of Irreversible Processes* (Interscience Publishers Inc., New York, 1951).

theorem, in the hope that a statement with a greater appearance of generality might fortunately prove also to have a greater content of generality, or might at least suggest directions of possible generalizations of the theory. Thus Onsager himself showed that in the absence of a magnetic field the reciprocity relations follow from the statement that the entropy production function $\dot{S}(\cdots J_k)$, considered as a function of the fluxes, is a "potential" for the affinities. That is

$$F_k = \left.\frac{\partial \dot{S}}{\partial J_k}\right]_{J_1,\, J_2 \cdots}. \tag{4}$$

The strong analogy with equilibrium thermostatics is evident; the entropy S, considered as a function of the extensive parameters X_k, is a potential for the intensive parameters $\mathfrak{F}_k$.

$$\mathfrak{F}_k = \left.\frac{\partial S}{\partial X_k}\right]_{X_1,\, X_2 \cdots}. \tag{5}$$

Another restatement of the Onsager theorem is that the entropy production function, considered as a function of the affinities, is a potential for the fluxes. That is,

$$J_k = \left.\frac{\partial \dot{S}}{\partial F_k}\right]_{F_1,\, F_2 \cdots}. \tag{6}$$

The thermostatic analogy is that the Massieu function $S[\cdots \mathfrak{F}_k \cdots]$ (the Legendre transform of the entropy),[2] considered as a function of the intensive parameters, is a potential for the extensive parameters

$$X_k = \left.\frac{\partial S[\cdots \mathfrak{F}_k \cdots]}{\partial \mathfrak{F}_k}\right]_{\mathfrak{F}_1,\, \mathfrak{F}_2 \cdots}. \tag{7}$$

As we anticipated, these reformulations of the Onsager theorem, by their analogy with thermostatics, suggest a further extension of the theorem. In particular it is suggestive that the entropy production function may, like the entropy itself, be subject to an extremum principle. Accordingly Prigogine showed that in the steady state which is reached when certain affinities are constrained to have definite values, all unconstrained affinities assume the values which minimize the entropy production function.[3] This theorem is easily seen from Eqs. (1), (2), and (3) which yield

$$\dot{S} = \textstyle\sum_{i,k} L_{ik} F_i F_k. \tag{8}$$

If F_k is unconstrained, we tentatively compute its value by minimizing $\dot{S}$; that is, we write

$$\partial \dot{S} / \partial F_k = 2 \textstyle\sum_i L_{ik} F_i = 0. \tag{9}$$

To corroborate that this equation does yield the correct value of the unconstrained affinities we note that Eq. (9) implies, by Eq. (2), that $J_k = 0$, and this is the obviously correct condition in the steady state. We consequently have checked Prigogine's theorem.

Again Prigogine's theorem naturally suggested in turn a further generalization, although this conjectured further generalization does not appear to have been formulated explicitly in the literature.

It was conjectured that in the steady state in which one or more affinities are constrained, not only do the several remaining affinities assume values which minimize $\dot{S}$, but that every detailed element of the microscopic density matrix also assumes a value which minimizes $\dot{S}$. The investigation of this conjecture was the underlying motivation of Klein and Meijer's[4] study of the flow of a gas between two pressure reservoirs, and of Klein's[5] study of the Overhauser effect. Setting up a specific and tractable model, they were able to compute explicitly the density matrix in the steady state, and thence to show that in these special cases the density matrix does indeed minimize the rate of entropy production.

Subsequently, Wangsness[6] carried out a similar analysis of the steady state in magnetic resonance. His results suggest that a related theorem (with certain modifications proposed by Wangsness) may apply even in the case of a nonzero, nonstationary, magnetic field. We shall restrict our attention to the zero-field case.

Finally, we note that the conjectured generalization of the minimum entropy production theorem is in agreement with the thermostatic equilibrium principle for that steady state in which the number of constrained affinities is zero. For then the "steady state" is just the equilibrium state, and the density matrix both maximizes S and minimizes $\dot{S}$, giving the latter its minimum possible value of zero.

With these special cases in which the extended principle of minimum entropy production is corroborated, the validity of the conjecture is strongly suggested. We, therefore, shall prove, in this paper, that in the steady state of an irreversible process the density matrix is such as to minimize the rate of entropy production.

1. DENSITY OPERATORS

The interaction of a system with the irreducible fluctuations of the walls and of the vacuum induces an ergodic behavior and makes the wave function of the system a stochastic rather than a definite function. If the set of functions $\{\psi_n\}$ constitutes a complete orthonormal set spanning the Hilbert space of the system, and if we write the wave function of the system as

$$\Psi = \textstyle\sum_n a_n \psi_n, \tag{10}$$

then the coefficients a_n are stochastic variables, with random moduli and random phases. The density matrix

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[2] See E. A. Guggenheim, *Thermodynamics* (North Holland Publishing Company, Amsterdam, 1949), p. 19.

[3] Reference 1, Chap. 10 and I. Prigogine, *Etude Thermodynamique des Phénomènes Irreversibles* (Ed. Desoer, Liège 1947).

[4] M. J. Klein and P. H. E. Meijer, Phys. Rev. **96**, 250 (1954).

[5] M. J. Klein, Phys. Rev. **98** 1736 (1955).

[6] R. K. Wangsness, Phys. Rev. **101**, 1 (1956).

$\mathfrak{R}$ has elements ρ_{nm} which are the statistical averages of all pairs of coefficients[7]:

$$\rho_{nm}\equiv\langle a_n{}^*a_m\rangle. \tag{11}$$

The average value of any operator can be computed in terms of the density matrix. Thus for an operator β: $\langle\beta\rangle=\langle(\psi|\beta|\psi)\rangle=\langle\sum_{n,m} a_n{}^*a_m(n|\beta|m)\rangle$

$$=\sum_{n,m}\rho_{nm}\beta_{nm}=\text{trace}\mathfrak{R}^t\cdot\mathfrak{B}. \tag{12}$$

The $\langle\ \ \rangle$ brackets here signify a statistical average, the $(\ \ )$ parentheses signify a quantum-mechanical matrix element, and the definition of the matrix $\mathfrak{B}$ is the evident, standard definition.

The entropy of the system is also defined in terms of the density matrix, by the definition[8]

$$S=-k\ \text{trace}[\mathfrak{R}\cdot\ln\mathfrak{R}]. \tag{13}$$

Although in equilibrium the quantities ρ_{nm} are time-independent, in the course of an irreversible process they may depend explicitly on the time. We shall now show that the complete set of variables $\dot{\rho}_{nm}$ can be treated analogously with the macroscopic fluxes J_k, with a set of linear kinetic equations analogous to Eqs. (2), subject to the symmetry of Eq. (3), and consequently subject to the theorem of minimum entropy production.

We first note that the elements of the density matrix, like the extensive parameters of thermostatics, can be considered as average values of appropriate operators. Let the set of operators $\{\tilde{\rho}_{nm}\}$ be the idempotent (if $n=m$) and nilpotent (if $n\neq m$) operators for the set of functions $\{\psi_n\}$. That is, define the operators $\tilde{\rho}_{nm}$ so that

$$(n'|\tilde{\rho}_{nm}|m')=\delta_{nn'}\delta_{mm'}. \tag{14}$$

Then the average value of $\tilde{\rho}_{nm}$ is

$$\langle(\tilde{\rho}_{nm})\rangle=\rho_{nm}, \tag{15}$$

where $(\ \ )$ indicates a quantum-mechanical and $\langle\ \ \rangle$ a statistical averaging process.

The operators $\tilde{\rho}_{nm}$ are not Hermitian but the operators

$$\tilde{\rho}_{nm}{}^+=\tfrac{1}{2}[\tilde{\rho}_{nm}+\tilde{\rho}_{mn}] \tag{16}$$

and

$$\tilde{\rho}_{nm}{}^-=\tfrac{1}{2}[\tilde{\rho}_{nm}-\tilde{\rho}_{mn}] \tag{17}$$

are Hermitian. Then

$$\rho_{nm}=\langle(\tilde{\rho}_{nm}{}^+)\rangle+i\langle(\tilde{\rho}_{nm}{}^-)\rangle. \tag{18}$$

The density matrix is a Hermitian matrix. Its elements are complex, but both the real and imaginary parts are average values of Hermitian operators.

The fact that $\mathfrak{R}$ is a Hermitian matrix implies that the entropy, as defined by Eq. (13), is real. For the matrix $\mathfrak{R}\ln\mathfrak{R}$ is defined by its series expansion and consequently is the sum of terms of the form $\mathfrak{R}^n$. But $\mathfrak{R}^n$ is Hermitian if $\mathfrak{R}$ is Hermitian, and therefore $\mathfrak{R}\ln\mathfrak{R}$ is Hermitian. The trace of a Hermitian matrix is real (the trace is the sum of the eigenvalues, all of which are real), so that the entropy is real.

The elements of the density matrix are not all independent; we have the necessary restriction

$$\text{trace}\mathfrak{R}=1. \tag{19}$$

Throughout the following, all variations of the ρ_{nm} are assumed to be subject to the condition (19).

By Eq. (13), the entropy is a function of the parameter ρ_{nm}. Associated with each matrix element ρ_{nm} we define an affinity F_{nm}:

$$F_{nm}=\partial S/\partial\rho_{nm}. \tag{20}$$

Then, since the equilibrium value of the density matrix is that which maximizes the entropy, the condition of equilibrium is that

$$F_{nm}=0. \tag{21}$$

2. KINETIC EQUATIONS

If a system is not in equilibrium the density matrix elements will change with time, tending toward the equilibrium values determined by equations (21). We define a set of fluxes by

$$J_{nm}\equiv\dot{\rho}_{nm}, \tag{22}$$

and we note that the fluxes are functions of the affinities, such that the fluxes vanish if the affinities all vanish. For sufficiently small values of the affinities the fluxes are therefore linear homogeneous functions of the affinities, and we can therefore write

$$J_{nm}=\sum_{r,s}L_{rs,nm}F_{rs}. \tag{23}$$

We now seek to show that the Onsager symmetry applies to the kinetic coefficients $L_{rs,nm}$.

The Onsager theorem follows from a consideration of the statistics of the spontaneous fluctuations in the equilibrium state. We therefore consider the appropriate distribution function governing the statistics of the density matrix elements.

The "instantaneous density matrix elements" $(\tilde{\rho}_{nm})$ are defined as

$$(\tilde{\rho}_{nm})\equiv(\Psi|\tilde{\rho}_{nm}{}^++i\tilde{\rho}_{nm}{}^-|\Psi)=a_n{}^*a_m. \tag{24}$$

The density matrix elements ρ_{nm} are statistical averages of the $(\tilde{\rho}_{nm})$, by Eq. (15). A corresponding "instantaneous entropy" s is defined in analogy with Eq. (13):

$$s=-k\ \text{trace}[(\mathfrak{R})\ln(\mathfrak{R})]. \tag{25}$$

Now the probability of a given set of instantaneous density matrix elements is[9]

$$Pd(\tilde{\rho}_{11})d(\tilde{\rho}_{12})\cdots=Ae^{s/k}d(\tilde{\rho}_{11})d(\tilde{\rho}_{12})\cdots. \tag{26}$$

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[7] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, New York, 1938), Chap. 9.

[8] J. von Neumann, *Mathematische Grundlagen der Quantenmechanik* (Dover Publications, New York, 1943), p. 202 and L. Landau and E. Lifshitz, *Statistical Physics* (Oxford University Press, New York, 1938).

[9] R. F. Greene and H. B. Callen, Phys. Rev. **83**, 1231 (1950).

In passing, we note that the wave functions ψ_n of Eq. (10) span the Hilbert space of a system with a definite energy, volume and composition. The system can be considered to be composed of a small subsystem and a reservoir; the reservoir being merely that portion of the system other than the small subsystem. The probability distribution (26) for the total system then implies a probability distribution for the subsystem. The resultant "generalized canonical distribution" has the form[9]

$$P = A \exp\{[s - \sum F_k x_k]/k\}. \tag{27}$$

Here the quantities x_k are the thermodynamic extensive parameters, defined as certain linear combinations of the instantaneous density matrix elements, and the F_k are appropriate linear combinations of the reservoir affinities. Thus if x_0 is, in particular, the energy, we have

$$x_0 \equiv \epsilon = \sum\nolimits_{n,m} \epsilon_n \rho_{nm} \delta_{nm}. \tag{28}$$

Although we shall not use Eqs. (27) or (28) we cite these to indicate the point of contact between our formulation in terms of the density matrix elements and the usual formulation in terms of certain linear combinations of them—the thermodynamic extensive parameters.

Returning now to Eq. (26) we note that the equilibrium state is that which maximizes P, and consequently is that which maximizes s. Expanding s around the equilibrium state in powers of the deviations

$$\Delta(\tilde{\rho}_{nm}) = (\tilde{\rho}_{nm}) - \rho_{nm}{}^0 \tag{29}$$

from the equilibrium values, there are no linear terms. For small deviations from equilibrium, $s - S$ is then a homogeneous quadratic function of the deviations $\Delta(\tilde{\rho}_{nm})$, and P is a multidimensional Gaussian distribution. It is this form of the distribution function which underlies the statistical considerations leading to the Onsager reciprocity relations.

Having established the Gaussian form of the distribution function for the instantaneous density matrix elements we are almost ready to take over verbatim Casimir's demonstration of the reciprocity relations.[10] One further observation is necessary; we must consider the behavior of the density matrix elements under the operation in which all the particle momenta are reversed.

3. MOMENTUM REVERSAL SYMMETRY

As Casimir has carefully pointed out,[10] the symmetry or antisymmetry of the fluctuating parameters under the momentum reversal operation is important in the Onsager proof. Whereas Casimir's observation is not usually of importance, because thermodynamic extensive parameters are always automatically symmetric under momentum inversion, our density matrix elements do not automatically have simple symmetry, and the Casimir observation now assumes a real significance. We therefore must so arrange our choice of basis functions $\{\psi_n\}$ as to insure a simple symmetry behavior in the density matrix elements.

All of the basis functions $\{\psi_n\}$ of Eq. (10) may be chosen as eigenfunctions of the system Hamiltonian, with energy eigenvalues lying in an extremely narrow range of energy, in accordance with the microcanonical constraint on the energy. For convenience in discussion, we shall assume that all the eigenvalues are nondegenerate. If wave functions are actually degenerate, it is nevertheless possible to choose proper linear combinations so as to obtain the same symmetry properties as those obtained in the nondegenerate case, so that our assumption of nondegeneracy is purely a matter of analytic convenience.

The Hamiltonian which generates the basis functions $\{\psi_n\}$ is necessarily invariant under a reversal of all particle momenta, because the system is contained within fixed rigid walls. Since all the basis-functions are nondegenerate, it follows that each basis function is either symmetric or antisymmetric under the momentum-reversal operator. We shall say that each basis function ψ_n has either even or odd "momentum-parity."

The effect of the momentum-reversal operator on the total wave function Ψ of Eq. (10) is to change the signs of the a_n corresponding to odd parity, and to leave unaltered the a_n corresponding to even parity. The parity of the product $a_n{}^* a_m$ is then the product of the parities of ψ_n and ψ_m. It therefore follows that the parity of the density matrix element ρ_{nm} is the product of the parities of ψ_n and ψ_m. The diagonal elements of the density matrix all have even momentum parity, whereas the nondiagonal elements may have either even or odd momentum parity.

We may now identify each density matrix element of even parity as an "α-type variable" in Casimir's nomenclature, whereas each density matrix element of odd parity is a "β-type variable." We may now merely adopt Casimir's derivation to conclude that (in the absence of a magnetic field) the coefficients $L_{rs,nm}$ of Eq. (23) are subject to the following symmetry.

$$\begin{aligned} L_{rs,nm} &= L_{nm,rs} \text{ if parity of } \rho_{nm} = \text{parity of } \rho_{rs}, \\ L_{rs,nm} &= -L_{nm,rs} \text{ if parity of } \rho_{nm} \neq \text{parity of } \rho_{rs}. \end{aligned} \tag{30}$$

4. CASIMIR ANTISYMMETRY

We have now shown that in the absence of a magnetic field the kinetic coefficients are either symmetric or antisymmetric according to the parities of the associated density matrix elements. But the minimum-entropy production theorem, as proved in Eqs. (8) and (9) depends upon the kinetic coefficients being symmetric. We consequently wish to show that those kinetic coefficients which, by Casimir's argument, are ostensibly antisymmetric are actually zero.

The argument which we use is essentially that which is ordinarily employed to show that those kinetic

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[10] H. B. G. Casimir, Revs. Modern Phys. 17, 343 (1945).

coefficients connecting fluxes of different vectorial character must vanish. Thus if J_1 corresponds to a (scalar) flux of energy from the electron "gas" to the lattice vibrations and if J_2 is an x-directed (vectorial) electrical current, then the kinetic coefficient L_{12} vanishes. This is true because all nonzero terms in the equation

$$J_1=L_{11}F_1+L_{12}F_2+\cdots \tag{31}$$

must behave in the same way under the coordinate transformation $x\rightarrow -x$, $y\rightarrow -y$, $z\rightarrow -z$; both F_1 and J_1 are invariant under this transformation whereas F_2 is odd.

In our case we consider an equation of the form (23), and we assume that J_{nm} is of even momentum parity. We consider for the moment that the basis functions in Eq. (10) are expressed in the momentum representation. Then the momentum inversion operator is equivalent to the coordinate transformation $x\rightarrow -x$, $y\rightarrow -y$, and $z\rightarrow -z$. The requirement that all terms in Eq. (10) behave in the same way under this coordinate transformation now implies that $L_{rs,\,nm}=0$ if ρ_{nm} and ρ_{rs} have different parity. We thus conclude that Casimir's antisymmetry is not real, and that the matrix of the kinetic coefficients is necessarily symmetric in the absence of a magnetic field.

5. GENERALIZED MINIMUM ENTROPY PRODUCTION THEOREM

We now have the linear kinetic equations

$$J_{nm}=\sum L_{rs,\,nm}F_{rs}, \tag{32}$$

with the symmetry conditions, in the absence of a magnetic field;

$$L_{nm,\,rs}=L_{rs,\,nm}. \tag{33}$$

Furthermore the entropy is a function of the density matrix elements, so that

$$\frac{dS}{dt}=\sum_{n,m}\frac{\partial S}{\partial\rho_{nm}}\frac{d\rho_{nm}}{dt}, \tag{34}$$

or

$$\dot{S}=\sum\nolimits_{n,m}F_{nm}J_{nm}. \tag{35}$$

Inserting (32) into (35) gives

$$\dot{S}=\sum_{nm,rs}L_{nm,\,rs}F_{nm}F_{rs}. \tag{36}$$

The entropy is a quadratic function of the density matrix element deviations, and consequently the affinities are linear functions of the density matrix element deviations:

$$F_{nm}=\sum\nolimits_{rs}S_{rs,\,nm}\Delta\rho_{rs}, \tag{37}$$

where

$$S_{rs,\,nm}=\partial^2 S/\partial\Delta\rho_{rs}\partial\Delta\rho_{nm}. \tag{38}$$

We now assume a set of κ imposed constraints of the form

$$\sum\nolimits_{n,m}b_{nm}{}^{(k)}F_{nm}=1,\quad k=1,2,\cdots\kappa. \tag{39}$$

As a typical case we have a macroscopic affinity (such as a gradient of the inverse temperature) constrained to some constant value; as the macroscopic affinities are linear combinations of our density affinities such a constraint is of the form (39).

In the steady state consistent with the constraints (39) and (19), we wish to show that the elements of the density matrix are such as to minimize $\dot{S}$.

In order to carry out the analysis conveniently, we adopt a concise notation. We consider the various density matrix element deviations $\Delta\rho_{nm}$ to be components of a "vector" $\boldsymbol{\rho}$. The affinity vector $\mathbf{F}$ is related to the density vector $\boldsymbol{\rho}$ by the entropy matrix $\mathfrak{S}$, in accordance with Eq. (37):

$$\mathbf{F}=\mathfrak{S}\cdot\boldsymbol{\rho} \tag{40}$$

and $\mathfrak{S}$ is symmetric:

$$\mathfrak{S}=\mathfrak{S}^t. \tag{41}$$

The scalar entropy is, accordingly

$$\Delta S=\tfrac{1}{2}\mathbf{F}\cdot\boldsymbol{\rho}=\tfrac{1}{2}\boldsymbol{\rho}\cdot\mathfrak{S}\cdot\boldsymbol{\rho}. \tag{42}$$

The flux vector $\mathbf{J}$ is related to the affinity vector $\mathbf{F}$ by the kinetic matrix $\mathfrak{L}$:

$$\mathbf{J}\equiv\dot{\boldsymbol{\rho}}=\mathfrak{L}\cdot\mathbf{F}=\mathfrak{L}\cdot\mathfrak{S}\cdot\boldsymbol{\rho}, \tag{43}$$

and

$$\mathfrak{L}=\mathfrak{L}^t. \tag{44}$$

Finally, the scalar entropy production function is defined by

$$\dot{S}=\mathbf{J}\cdot\mathbf{F}=\mathbf{F}\cdot\mathfrak{L}\cdot\mathbf{F} \tag{45}$$

$$=\boldsymbol{\rho}\cdot\mathfrak{S}\cdot\mathfrak{L}\cdot\mathfrak{S}\cdot\boldsymbol{\rho}. \tag{46}$$

The constraints (39) can now be written in the form

$$\mathbf{b}^{(k)}\cdot\mathbf{F}=1,\quad k=1,2\cdots\kappa. \tag{47}$$

The additional constraint (19) can be written in the form

$$\mathfrak{E}\cdot\boldsymbol{\rho}=0, \tag{48}$$

where $\mathfrak{E}$ is a diagonal unit matrix. When we invert Eq. (40) to express $\boldsymbol{\rho}$ in terms of $\mathbf{F}$, this constraint can be written as

$$\mathbf{b}^{(\kappa+1)}\cdot\mathbf{F}=0 \tag{49}$$

where $b^{\kappa+1}$ is simply $\mathfrak{E}\cdot\mathfrak{S}^{-1}$.

Our problem now is to be phrased as follows. We are given a set of constraints of the form (47) and (49) and we wish to show that $\boldsymbol{\rho}$ assumes a value which minimizes $\dot{S}$.

We first note that it is always possible to replace the set of $(\kappa+1)$ equations (47) and (49) with an equivalent set

$$\mathbf{a}^{(k)}\cdot\mathbf{F}=A^{(k)},\quad k=1,2,\cdots\kappa+1 \tag{50}$$

where the $\mathbf{a}^{(k)}$ are orthogonal, the $A^{(k)}$ are constants, and $A^{\kappa+1}$ is zero. That is, the $\mathbf{b}^{(k)}$ can be written in terms of a set of $(\kappa+1)$ orthonormal vectors $\mathbf{a}^{(k)}$, spanning the $(\kappa+1)$-dimensional subspace defined by the vectors $\mathbf{b}^{(k)}$, and with $\mathbf{a}^{(\kappa+1)}=\mathbf{b}^{(\kappa+1)}$.

$$\mathbf{a}^{(k)}\cdot\mathbf{a}^{(j)}=\delta_{jk}. \tag{51}$$

It is natural now to augment the orthonormal set of vectors $\mathbf{a}^{(k)}$ $(k\leq\kappa+1)$ by a complete orthonormal set $\mathbf{a}^{(k)}$ spanning the complete space of the $\boldsymbol{\rho}$. We consider the coordinate transformation to this new set of axes, with the matrix $\mathfrak{a}$ as the transformation matrix. We define a transformed density vector

$$\boldsymbol{\rho}'=\mathfrak{a}^{-1}\cdot\boldsymbol{\rho}. \tag{52}$$

Inserting this into Eq. (42), we compute the entropy scalar

$$\Delta S=\tfrac{1}{2}\boldsymbol{\rho}\cdot\mathfrak{S}\cdot\boldsymbol{\rho}=\tfrac{1}{2}\boldsymbol{\rho}'\cdot\mathfrak{a}\cdot\mathfrak{S}\cdot\mathfrak{a}\cdot\boldsymbol{\rho}'. \tag{53}$$

From this we can compute the transformed affinity vector, defined by

$$\Delta S=\tfrac{1}{2}\mathbf{F}'\cdot\boldsymbol{\rho}', \tag{54}$$

whence

$$\mathbf{F}'=\mathfrak{a}\cdot\mathfrak{S}\cdot\mathfrak{a}\cdot\boldsymbol{\rho}', \tag{55}$$

or

$$\mathbf{F}'=\mathfrak{a}\cdot\mathbf{F}. \tag{56}$$

The transformed flux vector follows from Eq. (52):

$$\dot{\boldsymbol{\rho}}'=\mathfrak{a}^{-1}\cdot\dot{\boldsymbol{\rho}}, \tag{57}$$

whence

$$\mathbf{J}'=\mathfrak{a}^{-1}\cdot\mathbf{J}, \tag{58}$$

and we easily find

$$\mathbf{J}'=\mathfrak{a}^{-1}\cdot\mathfrak{L}\cdot\mathfrak{a}^{-1}\cdot\mathbf{F}'. \tag{59}$$

Finally, the entropy production is

$$\dot{S}=\mathbf{J}\cdot\mathbf{F}=(\mathfrak{a}\cdot\mathbf{J}')\cdot(\mathfrak{a}^{-1}\cdot\mathbf{F}')=\mathbf{J}'\cdot\mathbf{F}' \tag{60}$$

$$=\mathbf{F}'\cdot\mathfrak{a}^{-1}\cdot\mathfrak{L}\cdot\mathfrak{a}^{-1}\cdot\mathbf{F}' \tag{61}$$

$$=\boldsymbol{\rho}'\cdot\mathfrak{a}\cdot\mathfrak{S}\cdot\mathfrak{L}\cdot\mathfrak{S}\cdot\mathfrak{a}\cdot\boldsymbol{\rho}', \tag{62}$$

If we choose a coordinate transformation in agreement with Eq. (52), our conditions of constraint now become

$$\mathbf{F}'\cdot\mathfrak{d}_k=A^{(k)},\quad k=1,2,\cdots\kappa+1 \tag{63}$$

where $\mathfrak{d}_k$ is a unit vector along the kth axis of the primed coordinate system.

The actual steady state which will be realized with the constraints (63) is now trivial to compute. It is determined by the equations

$$\mathbf{J}'\cdot\mathfrak{d}_k=0,\quad k>\kappa. \tag{64}$$

Equations (63) and (64) determine the solution. Writing each of these equations in terms of the $\boldsymbol{\rho}'$ vector, we find

$$\boldsymbol{\rho}'\cdot\mathfrak{a}\cdot\mathfrak{S}\cdot\mathfrak{a}\cdot\mathfrak{d}_k=A^{(k)},\quad k\leq\kappa, \tag{65}$$

$$\boldsymbol{\rho}'\cdot\mathfrak{a}\cdot\mathfrak{S}\cdot\mathfrak{L}\cdot\mathfrak{a}^{-1}\cdot\mathfrak{d}_k=0,\quad k>\kappa. \tag{66}$$

This set of simultaneous equations determines $\boldsymbol{\rho}'$ and hence $\boldsymbol{\rho}$ in the steady state.

We now show that this solution can also be obtained by minimizing $\dot{S}$. From Eq. (61) we find

$$\delta\dot{S}=2\mathbf{F}'\cdot\mathfrak{a}^{-1}\cdot\mathfrak{L}\cdot\mathfrak{a}^{-1}\cdot\delta\mathbf{F}'=0, \tag{67}$$

where the variation $\delta\mathbf{F}'$ is to be taken subject to the constraint (63). But the only restriction implied by Eq. (63) is that $\delta\mathbf{F}'$ must be zero in the subspace $\leq\kappa$, and is completely arbitrary in the subspace $>\kappa$. Thus Eq. (67) implies that the coefficient of $\delta\mathbf{F}'$ have no components in the subspace $>\kappa$. That is,

$$\mathbf{F}'\cdot\mathfrak{a}^{-1}\cdot\mathfrak{L}\cdot\mathfrak{a}^{-1}\cdot\mathfrak{d}_k=0,\quad k>\kappa. \tag{68}$$

Expressing $\mathbf{F}'$ in terms of $\boldsymbol{\rho}'$ by Eq. (55) gives

$$\boldsymbol{\rho}'\cdot\mathfrak{a}\cdot\mathfrak{S}\cdot\mathfrak{L}\cdot\mathfrak{a}^{-1}\cdot\mathfrak{d}_k=0,\quad k>\kappa. \tag{69}$$

The fact that this equation is identical with Eq. (66) proves the theorem that in the absence of a magnetic field, and subject to constraints of the form (39) and (19), the density matrix elements assume values which minimize the rate of entropy production.

6. ROLE OF THE MAGNETIC FIELD

In order that the minimum entropy production theorem be valid, we must have

$$\mathfrak{L}=\mathfrak{L}^t. \tag{70}$$

The Onsager theorem gives only

$$\mathfrak{L}(H)=\mathfrak{L}^t(-H). \tag{71}$$

In the absence of a magnetic field, (71) reduces to (70) and the minimum entropy production theorem is valid. In the presence of a magnetic field, the symmetry (71) must be augmented by geometrical considerations which determine the behavior of $\mathfrak{L}$ under the transformation $H\rightarrow -H$. If the geometry is such that $\mathfrak{L}(H)=\mathfrak{L}(-H)$, then (71) again implies (70), and the minimum-entropy production theorem is valid even in the presence of a magnetic field. If, however, the geometry is such that $\mathfrak{L}(H)=-\mathfrak{L}(-H)$, as in a typical Hall effect experiment, then the minimum-entropy production theorem is not valid in the form here proved.

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