Kinetic Theory and Irreversible Thermodynamics

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Entropy made its first appearance in the 1865 paper by Clausius[1] who obtained its explicit form by analyzing a reversible Carnot cycle of macroscopic transformations of an ideal gas. The conceptual predecessor of entropy, however, appeared in Clausius' early writings[2] in the guise of the term "disgregation". As a concept, disgregation is more molecular in nature than is the mathematical formula he obtained for the entropy change dS for a macroscopic heat transfer in a reversible cycle: $dS = dQ/T$. He thought, for example, that on evaporation from a liquid a vapor requires a larger value of "disgregation" than the liquid owing to an increased disorder. Clearly, one can discern in this idea a molecular concept not apparent in the expression $dS = dQ/T$. Nonetheless, a clear link between the macroscopic and microscopic pictures of entropy is missing in his theory.

Clausius also introduced the concept of *uncompensated heat*. It represents a kind of internal work performed by the system which is not compensated by an external source and thus tends to reduce the work done on the surroundings by the system. It is also positive but vanishes for reversible processes or at equilibrium. When it is taken into account, one can prove the Clausius inequality $dS \geq dQ/T$ where the heat absorbed by the system is reckoned positive. For an isolated system $dQ = 0$ and therefore $dS \geq 0$ from which originated the famous statement by Clausius that *the entropy of the universe tends to a maximum*. The precise nature of the uncompensated heat was not understood until the theory of linear irreversible thermodynamics was developed, and it remains a central topic in the study of irreversible thermodynamics.

Clausius's molecular concept of entropy was put on a firmer mathematical basis by Boltzmann[3] who introduced a statistical but formal expression for entropy in the form of his H-function. It is given in terms of the logarithm of the nonequilibrium distribution function obeying the Boltzmann equation. The Boltzmann equation, however, does not unequivocally indicate the macroscopic variable dependence of the distribution function. Therefore Boltzmann's expression for entropy is not illumunating as to its macroscopic variable dependence unless his equation is appropriately solved. Since it is a nonlinear integro–differential equation, its analytic solution is not generally possible, and as a consequence a perturbation theory is used. The Chapman–Enskog theory[4] is the most commonly used method and seeks the solution in a power series of thermodynamic forces (e.g., temperature gradients, etc.)

and their spatial gradients. It gives correct results for various transport processes occurring near equilibrium. It also gives, albeit approximate, a formula for the entropy production which is considered to be a local representation for uncompensated heat. Since the processes must occur near equilibrium for the first order results to be applicable the entropy production obtained must be also deemed valid near equilibrium. The first order Chapman–Enskog solution therefore yields only a theory of linear irreversible thermodynamics, and the equilibrium Gibbs relation (GR) is a result of it:[5,6]

$$TdS = dE + pdV - \sum_{i=1}^{r} \hat{\mu}_i dc_i \qquad (GR)$$

Most of natural phenomena, however, occur and are maintained at a state far removed from equilibrium in which the linear laws of macroscopic processes are no longer valid. Living systems are the most important examples. There are other natural phenomena in the domain of inanimate systems that are of interest and importance.

Prigogine and his co-workers[7] have used the local equilibrium hypothesis which uses (GR) to calculate the entropy change for systems far removed from equilibrium. In this hypothesis it is assumed that the entropy change accompanying a process occurring far from equilibrium can still be described by the equilibrium Gibbs relation (GR) in which variables are now made position- and time-dependent. This hypothesis obviously poses a dilemma in logic since the equilibrium Gibbs relation holds for systems at equilibrium yet it is supposed to describe their evolution far from equilibrium. One may then ask, how valid is the local equilibrium hypothesis and is there something beyond it? As a first step in an attempt at answering these questions, we initiated a series of investigations[8] on kinetic theory and irreversible thermodynamics of nonlinear transport processes, especially with their mutual connection in mind. The present account describes the salient results of the endeavor.

Modified Moment Method and Extended Gibbs Relation

The kinetic theory line of approach to irreversible thermodynamics can be taken with the Boltzmann equation[8a] or a generalized Boltzmann equation[8b,c] for

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(2) Clausius, R. *London, Edinburgh, Dublin Phil. Mag. J. Science* **1862**, *24*, 81, 201.
(3) Boltzmann, L. Lectures on Gas Theory, University of California, Berkeley, 1964.
(4) Chapman, S.; Cowling, T. G. *Mathematical Theory of Nonuniform Gases*, 3rd ed.; Cambridge: London, 1972.
(5) de Groot, S. R.; Mazur, P. *Nonequilibrium Thermodynamics*; North-Holland: Amsterdam, 1962.
(6) Prigogine, I. *Physica* **1949**, *15*, 272.
(7) Glansdorff, P.; Prigogine, I. *Thermodynamic Theory of Structure, Stability and Fluctuations*; Wiley: New York, 1971.

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dense fluids for both of which there exists a statistical entropy formula since both kinetic equations satisfy the H-theorem. We will call the Boltzmann and the generalized Boltzmann equation simply the kinetic equations in this account. The Chapman–Enskog and the moment method[9] may be used for approximate solutions of the kinetic equations, but the existing methods pay little attention to the entropy and the associated quantities, treating them on the same footing as the mechanical variables such as the internal energy, density, fluxes, etc. An unfortunate consequence is that the entropy and the associated quantities are not guaranteed to fulfill the inviolable requirements of the thermodynamic laws. The linear approximation in the Chapman–Enskog and the moment method fortunately meet the requirements, but higher order approximations encounter difficulty. The requirements are not generally met unless proper care is taken to satisfy them as is the case with the modified moment method described below.

Mechanical variables are defined in terms of particle velocities and positions whose time dependence can be obtained by solving the mechanical equations of motion such as Newton's. When their molecular expressions are suitably calculated by a rule of averaging over an ensemble of particles the mechanical variables are theoretically obtained. A similar procedure is used in molecular dynamics.[10] Unlike the mechanical variables the entropy, the entropy production, and the entropy flux are not averages of purely mechanical observables: They are inherently statistical and thus fundamentally different physical quantities from the mechanical variables. As well known, these statistical quantities are given in terms of the logarithm of the distribution function, but exact nonequilibrium distribution functions are impossible to find for physically realistic systems. As a consequence, we generally work with approximate solutions of one sort or another. If one ever hopes to acquire a theory of irreversible thermodynamics and a theory of transport processes consistent with the thermodynamic laws, *the approximate solutions, however, must be such that the entropy and its associated quantities rigorously satisfy the thermodynamic laws.* This is the tenet taken for the kinetic theory studies described in this account. The method of solving the kinetic equations under this tenet is called the modified moment method which is a modification of a method due to Maxwell.[11]

Consider a mixture of r chemically inert neutral and charged species contained in a volume and subject to an external electric field $\mathbf{E}(\vec{r},t)$ which changes slowly over the distance of molecular collision.[8d] The number density of particle i at a point in the phase space is given by the probability distribution function f_i obeying the kinetic equations. To see the significance of the kinetic equations let us take the Boltzmann equation. It may be looked upon as an equation describing the

change in population due to forward and reverse events of collisions and the net change in population due to the inflow and outflow of particles in the unit volume in the phase space. The Boltzmann equation states that these two factors are exactly balanced and is akin to a bimolecular reaction rate equation in chemical kinetics. A similar interpretation can be given to the generalized Boltzmann equation. We remark that the kinetic equations are not mechanical equations of motion like Newton's, but *equations of motion for statistical quantity f_i on the support of classical equations of motion.* As such, they are not as fundamental as the Newtonian equations of motion, but a fundamental postulate on the mesoscopic level, nevertheless.

The kinetic equations provide us with the molecular expressions for entropy density $\mathscr{S}$, entropy flux $\vec{J}_s$, and entropy production σ, which collectively form the entropy balance equation[6,8]

$$\rho(\mathrm{d}/\mathrm{d}t)\mathscr{S}(\vec{r},t) = -\vec{\nabla}\cdot\vec{J}_s(\vec{r},t) + \sigma(\vec{r},t) \qquad (1)$$

where $\mathrm{d}/\mathrm{d}t$ is the time derivative in the reference frame moving with the fluid velocity $\vec{u}$, ρ is the mass density, and $\vec{\nabla} = \partial/\partial\vec{r}$. The statistical expression for $\mathscr{S}$ consists of the mean values of the purely statistical quantities $(\ln f_i - 1)$ to which $\vec{J}_s$ and σ are also related. If we look upon the entropy as a kind of fluid, the entropy balance equation implies that the entropy change in a unit volume is equal to the sum of the entropy flowing into the volume from its surroundings and the entropy created within the volume. This source of entropy originates from the term accounting for molecular collisions in the kinetic equations. By Boltzmann's H-theorem,[3,4] the entropy production σ is always positive: $\sigma \geq 0$, the equality holding at equilibrium. This inequality has been generally taken, without proof, as a mathematical representation of the second law of thermodynamics, but recently it has been shown to be indeed the case.[12] Although (1) governs the evolution of entropy in space-time and it is important for thermodynamics, it does not indicate its connection with, e.g., the Gibbs relation (GR). The modified moment method[8] provides the connection for a nonequilibrium situation.

Since the mass and the energy must be conserved for a closed system, a kinetic equation must bear the conservation laws out. Indeed, the kinetic equations yield the conservation equations of mass density ρ (or specific volume $v = 1/\rho$), mass fraction c_i, momentum $\rho\vec{u}$ and internal energy density E:[8e]

$$\partial\rho(\vec{r},t)/\partial t = -\vec{\nabla}\cdot\rho\vec{u}(\vec{r},t) \text{ or } \rho(\mathrm{d}v/\mathrm{d}t) = \vec{\nabla}\cdot\vec{u} \qquad (2)$$

$$\rho(\mathrm{d}c_i/\mathrm{d}t) = -\vec{\nabla}\cdot\vec{J}_i \ (c_i = \rho_i/\rho) \qquad (3)$$

$$\rho(\mathrm{d}\vec{u}/\mathrm{d}t) = -\vec{\nabla}\cdot P + \rho z\mathbf{E} \ (z = \sum_i c_i z_i; \ z_i = \text{charge/mass}) \qquad (4)$$

$$\rho(\mathrm{d}E/\mathrm{d}t) = -\vec{\nabla}\cdot\vec{Q} - P{:}\vec{\nabla}\vec{u} + \vec{J}_e\cdot\mathbf{E} \qquad (5)$$

where $\vec{J}_i$ and ρ_i are the mass flux and the mass density of species i, respectively, $\vec{J}_e$ is the total mass current of charged species, $\vec{Q}$ is the heat flux carried by a fluid mass, and P is the stress tensor which is nothing but the momentum flux, or to put it differently, the force per unit area exerted on the fluid. It has the dimension

(8) Eu, B. C. (a) *J. Chem. Phys.* **1980**, *73*, 2958; (erratum) **1983**, *79*, 3607; (b) *Ann. Phys. (N.Y.)* **1979**, *118*, 187; (c) *J. Chem. Phys.* **1981**, *74*, 6362; (d) *Ibid.* **1985**, *82*, 4283; (e) *Ann. Phys. (N.Y.)* **1982**, *140*, 341; (f) In *Recent Developments in Nonequilibrium Thermodynamics*; J. Casas-Vazquez et al., Eds.; Springer: Berlin, 1984; pp 176–210; (g) J. Non-Equil. Thermodyn., in press.
(9) Grad, H. *Commun. Pure Appl. Math.* **1949**, *2*, 311.
(10) See, for example: Ashurst, W. T.; Hoover, W. G. *Phys. Rev. A* **1975**, *11*, 658.
(11) Maxwell, J. C. *The Scientific Papers of J. C. Maxwell*; Cambridge: Cambridge, 1890.

(12) Eu, B. C. *Carnot's Theorem and Existence of Entropy Balance Equation*, unpublished.

of pressure and indeed is related to the hydrostatic pressure. Equation 2 is the well known equation of continuity; (3) is the concentration balance equation; (4) is the equation of motion for the fluid where $\rho z \mathbf{E}$ is the external force term. It indeed becomes the Newtonian equation of motion when $\mathbf{P}$ is put equal to zero. Equation 5 is a local representation of the energy conservation law; $-\vec{\nabla} \cdot \vec{Q}$ gives the increase in energy due to an influx of heat from the surroundings; $-\mathbf{P} : \vec{\nabla} \vec{u}$ represents the work done on the system by the stress (force)(e.g., the pressure–volume work) and $\vec{J}_e \cdot \mathbf{E}$ gives the Coulomb heating due to the mass current of charged particles through the system under the external field.

The fluxes $\vec{J}_i$, $\vec{Q}$, and $\mathbf{P}$ in eq 2–5 are not determined by the conservation laws themselves. In the first order Chapman–Enskog theory[4] there hold linear algebraic relations between the fluxes and thermodynamic forces such as temperature, concentration, and velocity gradients. In general, the fluxes obey their own evolution equations which may be called the constitutive equations. It is convenient to introduce a new heat flux $\vec{Q}_i'$ for species i defined by $\vec{Q}_i' = \vec{Q}_i - \hat{h}_i \vec{J}_i$ where $\hat{h}_i$ is the enthalpy per unit mass of i. The $\vec{Q}$ is the sum of $\vec{Q}_i$'s. Since heat is also carried by mass flow, the new heat flux represents the net heat flow. The stress tensor (momentum flux) $\mathbf{P}$ may be written as the sum of its components $\mathbf{P}_i$ which in turn may be decomposed to hydrostatic pressure p_i of species i, the excess trace part Δ_i and the traceless symmetric part $\mathbf{P}_i^0$. The excess trace part is related to the dilatation of the fluid and therefore to the bulk viscosity and $\mathbf{P}_i^0$ is related to the shearing force and thus to the shear viscosity of the fluid. The constitutive equations for $\vec{J}_i$, $\vec{Q}_i'$, Δ_i, $\mathbf{P}_i^0$, etc. may be derived from the kinetic equations and we will express them collectively in the form

$$\rho(\mathrm{d}\hat{\Phi}_i^{(\alpha)}/\mathrm{d}t) = Z_i + \Lambda_i^{(\alpha)} \qquad (6)$$

where the fluxes $\Lambda_i^{(\alpha)}$ are ordered as follows: $\alpha = 1$ corresponds to $\mathbf{P}_i^0$; $\alpha = 2$ to Δ_i; $\alpha = 3$ to $\vec{Q}_i'$; $\alpha = 4$ to $\vec{J}_i$, etc. Equations 1–6 are the evolution equations for a set of macroscopic variables which we call (nonequilibrium) Gibbs variables: entropy, density, mass fractions, fluid velocity, internal energy, stress tensors, heat fluxes, and mass fluxes. Other macroscopic variables may be added to them if necessary for describing the fluid properties. The dissipative terms $\Lambda_i^{(\alpha)}$ are related to the collision term in the kinetic equations and thus have a feature in common with σ. They do not appear in the conservation eq 2–5, but do in the equations for fluxes since the latter are nonconserved variables. The terms $\Lambda_i^{(\alpha)}$ and $Z_i^{(\alpha)}$ are found to depend generally on the Gibbs variables. Their formulas are explicitly worked out in terms of Gibbs variables in ref 8. To the lowest order approximation, $Z_i^{(\alpha)}$ is proportional to the thermodynamic forces driving the flux corresponding to it.

Although (1)–(6) are derived from the kinetic equations, their mutual relationship is still obscure. In the modified moment method an exact relationship between them is sought, and we find it with the help of a pair of statements on the entropy production and the entropy flux. Before stating them, it is convenient to define the following derivatives:

$$T^{-1} = (\partial \mathscr{S}/\partial E); \quad pT^{-1} = (\partial \mathscr{S}/\partial v);$$
$$-\hat{\mu}_i T^{-1} = (\partial \mathscr{S}/\partial c_i); \quad X_i^{(\alpha)} T^{-1} = (\partial \mathscr{S}/\partial \hat{\Phi}_i^{(\alpha)}) \qquad (7)$$

where T will turn out to be the temperature, p the pressure, $\hat{\mu}_i$ the chemical potential per unit mass of i and $X_i^{(\alpha)}$ a generalized potential new to thermodynamics. They may be taken as shorthand notations for the derivatives for the moment.

We now assert that σ and $\vec{J}_s$ are respectively given by the expression

$$\sigma = T^{-1} \sum_{i\alpha} X_i^{(\alpha)} \odot \Lambda_i^{(\alpha)} \qquad (8)$$

$$\vec{J}_s = \sum_i (\vec{Q}_i - \hat{\mu}_i \vec{J}_i)/T + \vec{J}_{snc} \qquad (9)$$

where $\odot$ denotes a scalar product and $\vec{J}_{snc}$ is defined through the equation

$$\vec{\nabla} \cdot \vec{J}_{snc} = -T^{-1} \sum_{i\alpha} (Z_i^{(\alpha)} \odot X_i^{(\alpha)} + \Phi_i^{(\alpha)} \odot \chi_i^{(\alpha)}) \qquad (10)$$

Here $\chi_i^{(\alpha)}$ are the thermodynamic forces which are in fact spatial gradients of the fluid velocity, temperature, and chemical potentials as well as the external potential. These factors are the driving forces for viscous flow, dilatation, heat conduction, and diffusion. In the linear theory the fluxes are proportional to $\chi_i^{(\alpha)}$ subject to the Curie principle. The proportionality constants are the linear transport coefficients such as the viscosity, bulk viscosity, thermal conductivity, and diffusion coefficients. Noticing that $\Lambda_i^{(\alpha)}$ is the dissipative part of the constitutive equation for a nonconservative flux $\Phi_i^{(\alpha)}$, we may write the entropy production in the following more suggestive form:

$$\sigma = \sum_{i\alpha} (\partial \mathscr{S}/\partial \hat{\Phi}_i^{(\alpha)}) \odot \rho(\mathrm{d}\hat{\Phi}_i^{(\alpha)}/\mathrm{d}t)_{\text{dissipative}}$$

It implies that the entropy production is in essence the rate of change in entropy due to dissipative changes in the conservative fluxes. This interpretation is not afforded by the linear irreversible thermodynamics entropy production. Rayleigh[13] and Onsager[14] introduced, as a measure of energy dissipation in an irreversible process, a positive quadratic form of dissipative fluxes which is now called the Rayleigh–Onsager dissipation function (RODF). It is closely related to the entropy production. It can be shown that the entropy production (8) reduces to RODF when $\Lambda_i^{(\alpha)}$ are approximated with linear forms in $X_i^{(\alpha)}$ and if $X_i^{(\alpha)}$ are approximated by forms proportional to the fluxes. These approximations amount to the statements that the entropy surface is paraboloidal with respect to the fluxes and that the transport processes are linear. Since these approximations may be justified near equilibrium, they imply that the RODF is a representation of entropy production near equilibrium. Equation 8 is then judged to be a nonlinear generalization of the RODF. *It represents one of the most important results of the modified moment method and a cornerstone of the theory of irreversible thermodynamics presented here.*[8] The first term on the right of (9) has the same form as the classical form for the entropy flux, and the second term is new to thermodynamics and was introduced by Müller[15] in an approximate form different from the present.

On substitution of (8)–(10) into (1) and use of (2)–(6) we find an extension of the equilibrium Gibbs relation:

(13) Lord Rayleigh. *Theory of Sound*; Dover: New York, 1945.
(14) Onsager, L. *Phys. Rev.* **1931**, *37*, 405; **1931**, *38*, 2265.
(15) Müller, I. *Z. Phys.* **1967**, *198*, 329.

$$T \frac{d\mathscr{S}}{dt} = \frac{dE}{dt} + p \frac{dv}{dt} - \sum_i \hat{\mu}_i \frac{d}{dt} c_i + \sum_{i\alpha} X_i^{(\alpha)} \odot \frac{d}{dt} \hat{\Phi}_i^{(\alpha)}$$

$$= \frac{d}{dt} E_e + p \frac{dv}{dt} - z \frac{d\Psi}{dt} - \sum_i \hat{\mu}_{ei} \frac{d}{dt} c_i +$$

$$\sum_{i\alpha} X_i^{(\alpha)} \odot \frac{d}{dt} \hat{\Phi}_i^{(\alpha)} \quad (11)$$

where

$$E_e = E + z\Psi \quad \text{(electrochemical energy)}$$

$$\hat{\mu}_{ei} = \hat{\mu}_i + z_i\Psi \quad \text{(electrochemical potential)}$$

and Ψ is the potential of **E**: $\mathbf{E} = -(\partial\Psi/\partial\vec{r})$. This is called the *extended Gibbs relation* which reduces to (GR) if either $X_i^{(\alpha)} = 0$ or $d\hat{\Phi}_i^{(\alpha)}/dt = 0$. It is a generalization of the equilibrium Gibbs relation. Since there is no restriction whatsoever imposed on the extent of nonequilibrium, it holds away from equilibrium. *It is another of the most important results of the modified moment method from the thermodynamic foundations viewpoint.* Equations 7 and 11 together furnish the meanings for the entropy derivatives. For example, T is the temperature, but it must be emphasized that T^{-1} as a partial derivative of entropy depends on the values of the fluxes held constant during the differentiation. A similar comment applies to the other derivatives. The implication is that the temperature has an operational meaning even for a system away from equilibrium if the fluxes are held steady in the time span of measurement. For example, imagine a local volume in contact with the surroundings and there is a steady heat flux passing through the volume. Although the system is not in equilibrium, the temperature may be locally defined. This is exactly the situation we have in the case of Fourier heat conduction since one must then consider the temperature distribution.[16] The extended Gibbs relation thus suggests a way to generalize the concept of T, p, $\hat{\mu}_i$ to a situation where the fluxes are steady.

The local equilibrium hypothesis (GR) is recovered for the entropy change in the present theory, if the entropy derivatives $X_i^{(\alpha)}$ vanish or the fluxes are steady in the coordinate system moving with $\vec{u}$, i.e., $(d\hat{\Phi}_i^{(\alpha)}/dt) = 0$. Therefore, if a steady state experiment is performed for the fluxes involved, then the equilibrium Gibbs relation describes the entropy change, but the constitutive relations for the fluxes are not necessarily linear in thermodynamic forces unless $X_i^{(\alpha)}$ are linear in fluxes. The case where $X_i^{(\alpha)}$ all vanish corresponds to an equilibrium situation since $X_i^{(\alpha)} = 0$ means that there are no fluxes in the system. If one performs a nonsteady experiment as is in the case of dynamic shearing[21] or if the fluxes happen to oscillate as is the case of the current limit cycles (cf. the example with semiconductors discussed below), the local equilibrium hypothesis breaks down, and the extended Gibbs relation must be used for describing the entropy change. These examples indicate the limitations of the local equilibrium hypothesis for dissipative systems especially

(16) Biot, M. A. *Variational Principles in Heat Transfer*; Oxford: London, 1970.
(17) Eu, B. C. *J. Chem. Phys.* **1981**, *74*, 2998.
(18) Kirkwood, J. G.; Oppenheim, I. *Chemical Thermodynamics*; McGraw-Hill: New York, 1961.
(19) Eu, B. C. *Nonlinear Transport Coefficients and Boundary Layer*, unpublished.
(20) Batchelor, G. K. *Fluid Dynamics*; Cambridge: London, 1967.
(21) Eu, B. C.; Ohr, Y. G. *J. Chem. Phys.* **1984**, *81*, 2756.

when the processes are not steady in time.

Theory of Irreversible Thermodynamics

In the modified moment method we make a pair of assertions (8) and (9) on σ and $\vec{J}_s$ and then derive the extended Gibbs relation from the kinetic equations by using the entropy balance, the conservation, and the constitutive equations. Therefore the assertions may be considered to be the conditions for the validity of the extended Gibbs relation to hold. A theory of irreversible thermodynamics[8e,17] can be developed, on the phenomenological grounds, with the extended Gibbs relation in a manner similar to equilibrium thermodynamics. In such a theory the actual determination of the entropy production and the entropy flux is accomplished by developing a theory of transport processes. In the phenomenological approach the kinetic theory procedure leading to the extended Gibbs relation from the kinetic equation may be reversed. This procedure can be expressed with a set of axioms as follows:

Postulate I. There exists a set of Gibbs variables $Z \equiv \{E, v, \vec{u}, c_i, \hat{\Phi}_i^{(\alpha)}\}$ *by which the nonequilibrium (thermodynamic) state of a macroscopic system is specified. The Gibbs variables depend on time and position.*

Postulate II. There exists a piecewise differentiable function $S = \rho\mathscr{S}$ *called entropy which is extensive and depends on Z and which reaches a maximum, if the isolated system is brought to equilibrium.*

Postulate IIIa. The Gibbs variables obey the balance and evolution eq 2–6.

Postulate IIIb. The dissipative term $\Lambda_i^{(\alpha)}$ *in (6) are positive in the sense that* $\sum_{i\alpha} X_i^{(\alpha)} \odot \Lambda_i^{(\alpha)}/T \geq 0$ *where* $X_i^{(\alpha)}$ *is defined in (7).*

Postulate IV. There exists a quantity called entropy flux $\vec{J}_s$, *which is associated with transmission of heat, mechanical energy, and matter and also with intricate interplays of fluxes within the system. It is defined as in (9) and (10).*

The extended Gibbs relation follows from Postulates I and II with the help of (7) and, when combined with the rest of the postulates, yields the entropy balance equation (1). The result may be summarized by the following statement:

Theorem. The entropy density satisfies the balance eq 1 where the entropy production is given by (8) and the entropy flux by (9) and (10).

We may put the gist of the axiomatic theory in other terms: Instead of the entropy balance equation the extended Gibbs relation becomes the starting point and $(d\mathscr{S}/dt)$ is described by the conservation laws (2)–(5) and the constitutive equations (6), which are constructed such that σ as given by (8) is always positive. Then with the entropy flux consisting of the classical and nonclassical parts as in (9) it is possible to derive the entropy balance equation as a mathematical representation of the second law of thermodynamics.

In the phenomenological theory it is necessary to treat the derivatives defined in (7) as a set of empirical relations for the tangents touching the entropy surface in the space spanned by the Gibbs variables. By determining the empirical relations in terms of Gibbs variables, we find the shape of the entropy surface in the Gibbs space. Transport and thermodynamic data can be used to determine the derivatives in (7). Especially, since the derivatives $X_i^{(\alpha)}$ and $\Lambda_i^{(\alpha)}$ give the entropy production once $\Lambda_i^{(\alpha)}$ are chosen appropriately

for the constitutive equations, the formalism presents a well-defined theory of constructing the entropy, the entropy production, and the entropy flux from the data on transport processes and fluid properties. We will discuss this aspect in what follows.

Transport Processes and Irreversible Thermodynamics

In equilibrium thermodynamics[18] we measure heat capacity, compressibility, expansion coefficients, etc. from which the caloric equation of state, the equation of state, etc. can be constructed. This information in turn leads ultimately to the equilibrium entropy of the system or related quantities such as free energies, etc. It is then reasonable to say that the data gathering activity in equilibrium thermodynamics is just an effort to find the entropy as a *storage and generator of information* on matter in equilibrium. The entropy is a generator of information since thermodynamic quantities may be derived from it; see the derivatives in (7). The properties mentioned above are static. But a great deal of laboratory effort is also devoted to gathering information on nonstatic properties. Transport coefficients of fluids represent an important source of information on the nonstatic properties of fluids and solids. An important question for us to ask at this point is then, how do we understand transport processes in fluids and how do they fit in the framework of the theory described above? Answering these questions with some examples will help us better understand and use the theory for practical problems encountered in the laboratory. Before taking up some specific examples, we discuss the general concept and strategy that will guide us in carrying out the program.

Information on the fluid properties, either fluid dynamic or transport, is wholly contained in (2)-(6), the last of which can be constructed in the phenomenological theory with the help of (11) and (8)-(10) such that the second law is fully satisfied. Various terms appearing in the constitutive equations (6) can be estimated by means of the kinetic equations, and we find that the fluxes relax to their steady state value on a much faster time scale than the conserved variables that relax on the hydrodynamic time scale (10^{-9} s vs. 10^{-3} s or longer). This means that the conserved variables in the constitutive equations (6) remain constant over the time span in which the fluxes approach to their steady state value. The constitutive equations may then be in effect decoupled from (2)-(5) and solved before the latter are solved. This decoupling and solution of (6) subject to appropriate initial and boundary conditions yield algebraic constitutive relations between fluxes and the thermodynamic forces, and transport coefficients [$L_{ij}^{(\alpha\beta)}$ below], linear or nonlinear, can be identified from the relations:

$$\Phi_i^{(\alpha)} = \Phi_i^{(\alpha)}[\{\chi_j^{(\beta)}\},\{\Phi_j^{(\beta)} \ (t = 0)\}, \ \rho, \ E, \ c_1,...,c_r]$$

$$= \sum_{j\beta} L_{ij}^{(\alpha\beta)} \ [\{\chi_k^{(\gamma)}\}]\chi_j^{(\gamma)}. \qquad (12)$$

Here the transport coefficients generally depend on the thermodynamic forces. Substitution of this result into (3)-(5) yields a set of generalized hydrodynamic equations whose solution provides various flow properties of the system.[19] The Navier–Stokes and Fourier equations in hydrodynamics[20] can be obtained from the

generalized hydrodynamic equations when the constitutive relations are linear with respect to thermodynamic forces $\chi_j^{(\beta)}$. Therefore the usual hydrodynamic equations hold only near equilibrium.

The constitutive equations (6) can be constructed with the help of transport data as indicated below. The extended Gibbs relation indicates that $X_i^{(\alpha)}$ is the derivatives of $\mathcal{S}$ in the direction of $\hat{\Phi}_i^{(\alpha)}$. This derivative is now assumed to take a particular form as a function of $\hat{\Phi}_i^{(\alpha)}$. We also take a suitable form for $\Lambda_i^{(\alpha)}$ and $X_i^{(\alpha)}$ such that the entropy production (8) is positive and the transport data in question are reproduced. (Generally speaking, such choice is guided by kinetic theory considerations. Kinetic theory plays an invaluable role in irreversible thermodynamics in that sense.) Then (6) is solved under the adiabatic assumption, in which the conserved variables are kept constant, and we get (12). If the transport coefficients so determined are in agreement with experiment, then the choices made for $X_i^{(\alpha)}$, $Z_i^{(\alpha)}$, and $\Lambda_i^{(\alpha)}$ are judged reasonable. This in turn fixes the entropy production as well as the entropy surface itself, and we have gained information on the entropy and the associated quantities for the system at a nonequilibrium state. The solution of the generalized hydrodynamic equations then completes the task of finding the entropy when the velocity, temperature, and density profiles are obtained therefrom.

Non-Newtonian Viscosity and Normal Stress Coefficients

Knowledge of viscosity and normal stress coefficients is important for understanding the flow properties of a fluid. To obtain viscosity, etc., various components of the stress on the fluid are measured and analyzed. In general, there are nine components of a stress tensor. If the fluid is isotropic, the stress tensor is symmetric and the number of independent components is reduced to six. If the fluid is assumed to be incompressible, then the hydrostatic pressure is the same as the external pressure and the number becomes five. The problem can be further simplified if the geometry of flow is made simple. One typical example is a plane Couette flow. In this case the flow is occurring between two infinite parallel plates which may move in opposite directions (say, along the x-axis and the velocity gradient is in the y-direction). Then it can be shown[21] that the stress tensor has three nonvanishing independent components, P_{xy}, $P_{xx} - P_{yy}$, and $P_{yy} - P_{zz}$. The first component is related to the shearing and the last two to the extension or the compression along the direction normal to the surface. They are called the primary and the secondary normal stress difference.[22] Experiment shows that the shear viscosity and the normal stress coefficients decrease as the shear rate is increased and consequently the fluid becomes non-Newtonian. Such non-Newtonian behavior of fluids may be studied within the framework of the present theory.

For the purpose we first derive the constitutive equation (6) for the stress tensor from a kinetic equation. The constitutive equation contains the Newtonian viscosity η_0 and the zero shear-rate normal stress coefficients Ψ_k^0, $k = 1, 2$. When η_0 and Ψ_k^0 are treated as phenomenological parameters, the constitutive equation becomes empirical. With it we calculate the

(22) Erlich, F. R. *Rheology*; Academic: New York, 1967.

shear rate dependence of nonlinear transport coefficients (material functions) for non-Newtonian fluids.

In the case of the steady plane Couette flow mentioned, the steady state solution of the constitutive equation is sufficient. It is in the form of (12) from which the shear viscosity η and the normal stress coefficients Ψ_k, $k = 1, 2$, are found. They are defined through the relations:[21] $P_{xy} = 2\eta\gamma$, $P_{xx} - P_{yy} = -4\Psi_1\gamma^2$, $P_{yy} - P_{zz} = -4\Psi_2\gamma^2$ where γ is the shear rate $\gamma = -(\partial u_x/\partial y)/2$ with u_x denoting the velocity in the x-direction. The following simple formulas obtained from the constitutive equation (6) are found to give excellent agreement with experiment if η_0, Ψ_k^0 and the relaxation time τ are adjusted to experiment:[21,23]

$$\eta = \eta_0 \sinh^{-1} \tau\chi/\tau\chi; \quad \Psi_k = \Psi_k^0(\eta/\eta_0)^2, \quad k = 1, 2$$
$$(13a,b)$$

$$\tau = [2\eta_0(m_r k_B T/2)^{1/2}]^{1/2}/nk_B Td \qquad (13c)$$

with $\chi = (\gamma{:}\gamma)^{1/2}$, m_r and d denoting the reduced mass and the size parameter of the molecule, and n the number density. The formulas show that the viscometric functions η and Ψ_k not only satisfy the relation $\Psi_k/\Psi_k^0 = (\eta/\eta_0)^2 = (\sinh^{-1} \chi^*/\chi^*)^2$ where $\chi^* = \tau\gamma$, a dimensionless reduced shear rate, but also obey the corresponding state law[23] in the sense that there are reduced universal viscometric functions depending on χ^* only. This feature is tested in Figure 1. The corresponding state law is obeyed to a good accuracy for the materials examined. These viscometric functions satisfy the second law of thermodynamics since they are always positive. The theory along this line can be applied to study other aspects of the rheological behavior of fluids such as viscoelasticity[24] and thermoviscous effects.[25]

Rarefied Gases

Rarefied gas is another example for which the linear transport theory becomes impotent. For example, the viscosity decreases with the density in contradiction with the Chapman–Enskog viscosity which is independent of the gas density. By using the constitutive equation (6) for the stress tensor provided by the Boltzmann equation, we find a form similar to (13a) for the shear viscosity for rarefied gases. If we take a hard sphere model for the molecule, then it is possible to show that the relaxation time τ is proportional to the Knudsen number Kn which is the ratio of the mean free path of the molecule to the linear dimension of the container of the gas. Thus we find as Kn increases, the viscosity behaves asymptotically as $\eta \sim (\ln Kn)/Kn$. That is, η vanishes as the gas rarefies. This behavior is in agreement with experiment.[26] Indeed, if the viscosity formula (13a) is used to calculate the velocity profiles for a plane Couette flow in the rarefied gas, the boundary layer gets increasingly thinner,[19] vanishing like the inverse 2/3 power of the Reynolds number. This aspect appears to bear some important significance for rarefied gas dynamics.

The thermal conductivity of rarefied plasmas at high temperature is very interesting and useful in connection
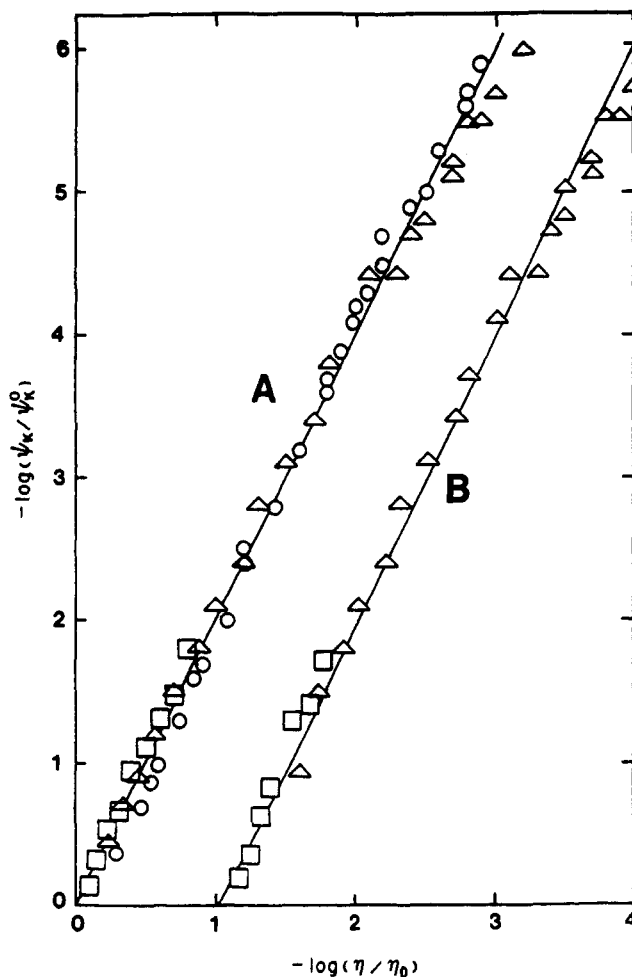

Figure 1. In this figure are tested the corresponding state law, the relation $\Psi_k/\Psi_k^0 = (\eta/\eta_0)^2$, $k = 1, 2$, and the viscometric functions in (12a,b). A is for the primary normal stress coefficient and B is for the secondary normal stress coefficient. In the case of B the origin is shifted to the right by one unit. The symbols are as follows: O = Separan AB 30; □ = Opanol B200; △ = 2.5% polyacrylamide in 50/50 water–glycerine solution.

with laser fusion and magnetic fusion. Basically the same theory as for rarefied neutral gases can be used for the purpose. By solving the heat flux evolution equations (6) derived from the Boltzmann equation, we can calculate the thermal conductivity of a plasma. It is found[27] that thermal conductivity becomes much smaller than the Chapman–Enskog thermal conductivity if the density is low and the temperature is high, the main determining factor being the Debye length. As the Debye length gets large, the collision frequency gets smaller and the thermal conductivity becomes smaller than the Chapman–Enskog prediction. The thermal conductivity thus calculated can be applied to study the heat injection into pellets in laser fusion experiments. A study[27b] shows an encouraging result for the heat flux inhibition factor.

Carrier Mobilities in Semiconductors

It is also possible to study the electric field dependence of charge carrier mobilities in semiconductors subject to an external electric field. The information is of utility in describing semiconductor oscillators.[28]

(23) Ohr, Y. G.; Eu, B. C. *Phys. Lett. A* 1984, *101*, 338.
(24) Eu, B. C. *J. Chem. Phys.* 1985, *82*, 4683.
(25) Eu, B. C.; Khayat, R.; Billing, G. D.; Nyeland, C., submitted for publication in *Phys. Fluids*.
(26) Kogan, M. N. *Rarefied Gas Dynamics*; Plenum: New York, 1969.

(27) (a) Eu, B. C. *Physica A* 1985, *133*, 120; (b) *Phys. Fluids* 1985, *28*, 222. (c) Clause, J. P.; Balescu, R. *Plasma Phys.* 1982, *24*, 1429.
(28) Shaw, M.; Grubin, H.; Solomon, P. *The Gunn–Hilsum Effect*; Academic: New York, 1979.

This example[29] is significant for the present theory of irreversible thermodynamics since it provides a non-trivial example for oscillating fluxes maintained by a steady external source of energy and *there is a reduction in the entropy production owing to the emergence (bifurcation) of a limit cycle.*

In the two-valley model[30] of conduction band in a semiconductor there are two valleys (subbands) of heavy and light effective electronic masses. The electrons of different effective masses are coupled through their interactions with phonons and through the collision between themselves. Through such interactions the electrons move in and out of the two valleys of different effective masses. As a result the charge carriers become alternatively faster and slower depending on which valley they are moving in, and the current consequently oscillates. This model can be translated into a pair of mass flux evolution equations for charge carriers. By solving these equations we can find the fluxes as a function of time and the field strength, and finally the mobilities of the carriers and the current–voltage characteristics.

As the electric field strength increases, the current–voltage characteristic begins to deviate from the Ohmic behavior and eventually becomes unstable, and there emerges (bifurcates) a limit cycle as the critical field strength is passed. In the course of a limit cycle the carriers pass through the regions of high and low entropy production in the mass flux space. *When the entropy production is averaged over a period, the average entropy production is found to be smaller than the entropy production that the system would have produced if it had remained at the unstable steady state from which the limit cycle has bifurcated.*

This phenomenon can be understood if we examine the geometrical shape of the entropy production surface in the flux space. Actual calculation shows that the entropy production surface has regions where the entropy production is lower than that of the unstable state and regions where it is higher than the latter, but the carriers spend most of a period in the low entropy production regions, the result being a lowered entropy production on the average; see Figure 2. This feature is potentially relevant as a possible paradigm for biological evolution since by evolving into an oscillatory motion a system can reduce the entropy production or the energy dissipation.[31] It also distinguishes the present example from those considered in the two previous examples since the entropy productions for the processes considered therein are basically paraboloidal in the flux space and thus without a structure that allows emergence of a limit cycle. On the other hand, the entropy production for a system exhibiting a limit cycle is nonmonotonic and contains more than one region of minimum. At least for the problem studied for this example there clearly is some correlation between the topology of the trajectory in the flux space and the entropy production surface. This feature is attractive and potentially significant, since such a correlation can be useful for devising evolution equations for fluxes on experimental and intuitive grounds.
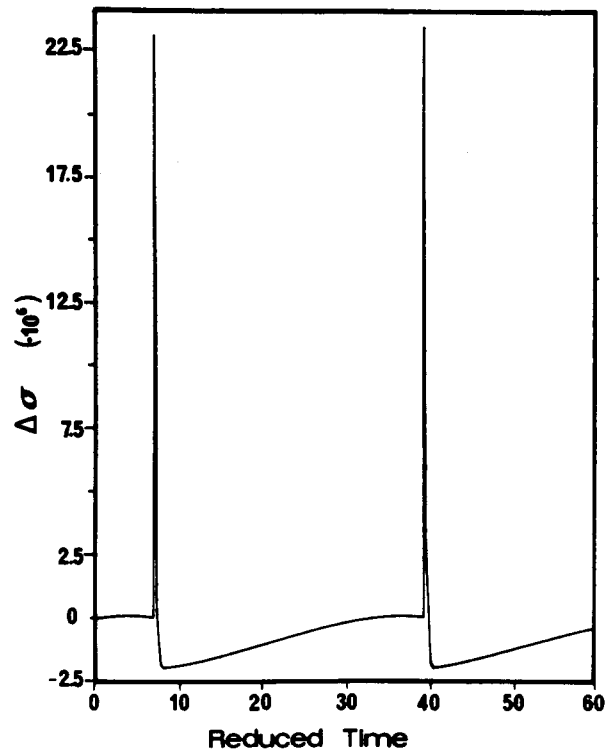

Figure 2. The relative entropy production over two periods of the limit cycle. The zero of the ordinate corresponds to the entropy production at the unstable steady state from which the limit cycle has bifurcated. The sharp peak corresponds to the impulsive energy dissipation required for the carrier to go over the mountain ridge in the entropy production surface that has two valleys and a mountain ridge in between.

Future Work and Conclusion

Most of interesting natural phenomena are in the domain of nonlinear processes, and the irreversible thermodynamic formalism described here offers an avenue of approach to them in a way fully consistent with the thermodynamic laws. Since the theory is general, it can be applied to any natural processes, the examples presented being only a few cases studied so far. The theory can be cast to deal with processes occurring in heterogeneous systems which possibly include cellular systems and mechanical engines. The present theory can be used to derive a set of global evolution equations for such systems.

When the solutions of constitutive equations 6 are substituted into the conservation equations (2)–(5), there follow generalized hydrodynamic equations, whose solutions are expected to yield various flow properties of the fluid under consideration. There are indications that the generalized hydrodynamic equations are capable of predicting the boundary layer profiles and the velocity and temperature profiles under steep thermodynamic gradients which often occur in rarefied gases, non-Newtonian fluids and fusion plasmas. The present theory can be used for studying such situations.

The extended Gibbs relation (11) can be a starting point for purely phenomenological approach to thermodynamics of irreversible processes,[17] but study in that direction has not been much pursued hitherto although it deserves more serious efforts and attention.

In this Account we have presented an extension of the equilibrium Gibbs relation together with a general expression for entropy production that gives a new interpretation for it, and an entropy flux formula similar

(29) Ali, J.; Eu, B. C. *J. Chem. Phys.* **1984**, *80*, 2063; **1985**, *81*, 4401.
(30) Butcher, P. H.; *Rep. Prog. Phys.* **1963**, *30*, 97.
(31) Richter, P. H.; Rehmus, P.; Ross, J. *Prog. Theoret. Phys.* **1981**, *66*, 385.

to Müller's. Measurements of transport properties are seen equivalent to those of thermodynamic properties such as heat capacities, compressibilities, etc., in the sense that they ultimately provide information on the entropy and the entropy production of the system. The measurements of thermodynamic and transport prop-

erties then may be regarded as efforts to construct the entropy, the entropy production, and the entropy flux, and especially *the entropy as a storage and a generator of information on matter*. The formalism described provides a theoretical framework and strategy by which to carry out such efforts.