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# Phenomenological Equations for Multicomponent Fluids

Osamu Aono[1]

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A hydrodynamic equation of motion for each component of a multicomponent fluid is derived on the basis of nonequilibrium thermodynamics. Special care has been directed to the choice of state variables. In some limiting cases, this equation leads to customary phenomenological equations, such as the equation for diffusion and the Navier–Stokes equation. The viscosity is a consequence of nonlocal coupling of forces and fluxes. The reciprocity between the linear coefficients is examined closely.

**KEY WORDS:** Nonequilibrium thermodynamics; electrolyte solution; high-temperature plasma; state variable; forces and fluxes; nonlocal linear relation; Onsager reciprocity; hydrodynamic equation of motion for component; Navier–Stokes equation; diffusion; viscosity.

## 1. INTRODUCTION

Though the thermodynamics of irreversible processes has been developed conspicuously,$^{(1-7)}$ there still remain unsatisfactory features when it is applied to continuous systems—namely deficiencies or redundancies exist at every step leading to phenomenological equations for irreversible processes. The present paper reveals and removes such unsatisfactory features. The system to be considered is isolated and composed of charged and neutral particles. Electrolyte solutions and high-temperature plasmas are typical examples of such systems. It is assumed that all components have a common temperature, and that no chemical reaction occurs.

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[1] Department of Physics, Faculty of Science, University of Tokyo, Tokyo, Japan.

Customary theories of irreversible processes in a continuous system are constructed as follows. On the basis of the first and second laws of thermodynamics, an expression for the entropy production is obtained in the form of a sum of several terms. Each term is regarded as a product of two quantities; one of the two is defined as the flux, and the other as the conjugate force. Linear relations, namely phenomenological equations, are assumed between the forces and the fluxes thus defined. Then, Onsager(1) reciprocity is applied to the phenomenological coefficients occurring in these equations.

However, the above-mentioned forces and fluxes are generally different from those defined by Onsager; consequently, the corresponding phenomenological coefficients do not necessarily obey(8) Onsager reciprocity. In the present paper, the forces and fluxes will be defined in connection with thermodynamical variables of state in order that the reciprocity between the linear coefficients may be clear. Most of previous work lacks due consideration of the variables which determine the state of the system.

In particular, the internal energy per unit volume or per unit mass is selected customarily as one of such state variables. However, the internal energy is not a useful quantity for the purpose of obtaining phenomenological equations in continuous systems, because its time derivative is complicated and obscure. On the other hand, the total energy density makes a simple change because of the conservation law, as shown in the next section. A complete set of state variables is given in Section 3.

The forces and fluxes are defined in Section 4. The linear relation between them is nonlocal: that is, the flux at a position of the system is related to the forces at other positions as well as at the same position. There is no reason to avoid this nonlocal relation, which is a kind of cross-phenomenon. In fact, the viscosity is a consequence of this nonlocal cross-effect.

Section 5 treats the reciprocal relation between the linear coefficients occurring in the nonlocal phenomenological equations given in Section 4. The last section is devoted to transforming these nonlocal equations. A hydrodynamic equation of motion for the individual component is obtained instead of the customary equation for diffusion; the former includes the latter and the Navier–Stokes equation.

## 2. THE FIRST LAW OF THERMODYNAMICS

The isolated system under consideration is a multicomponent fluid; each component makes a mass motion, and may have electric charge. According to the principle of conservation of energy, the total energy content within an arbitrary volume in the system can change only if some energy flows into the volume considered through its boundary. The total energy includes all forms of energy in the system, such as the electrostatic potential energy, the macroscopic kinetic energy of the mass motion of every component, and the internal energy. A local form of the first law of thermodynamics can be written as (Ref. 3, p. 17)

$$\dot{u}^* = -\operatorname{div} \mathbf{q}^* \tag{1}$$

where $u^*$ is the total energy per unit volume, the dot denotes partial differentiation with respect to time, and $\mathbf{q}^*$ is the total energy flux per unit surface and unit time.

The total energy flux $\mathbf{q}^*$ consists of the "heat flux" $\mathbf{q}$ and the fluxes associated with the mass motions of the individual components:

$$\mathbf{q}^* = \mathbf{q} + \sum n_i \mathbf{v}_i u_i^* \tag{2}$$

where $n_i$, $\mathbf{v}_i$, and $u_i^*$ are the number density, the velocity of the mass motion, and the energy per particle, of the component $i$, respectively. The energy $u_i^*$ per particle comprises the internal energy $u_i$, the kinetic energy $\frac{1}{2}m_i v_i^2$, and the electrostatic potential energy $e_i\phi$:

$$u_i^* = u_i + \tfrac{1}{2}m_i v_i^2 + e_i\phi \tag{3}$$

where $m_i$ is the mass, $e_i$ is the charge, and $\phi$ is the electrostatic potential. It should be noted that the heat flux itself is not a physically observable quantity: Only its divergence has a physical meaning. Equation (1) together with Eq. (2) defines the observable part of the heat flux.

If conservative forces other than the electrostatic force are present, their potential energies should also be included in $u_i^*$ and in $u^*$. Nonconservative forces, if any, merely convert the kinetic energy of mass motion into heat; such forces need not be taken into account explicitly. The presence of a stress tensor results in a momentum flux; a transfer of momentum always involves a transfer of energy (Ref. 7, p. 53). The energy flux due to the stress is customarily separated from the heat flux $\mathbf{q}$, but such separation is unnecessary; instead, another heat flux will be defined in Section 4.

## 3. ENTROPY AND STATE VARIABLES

The Gibbs equation for the continuous system can be expressed as

$$du = T\,ds + \sum \mu_i\,dn_i \tag{4}$$

where $u$ is the internal energy per unit volume, $T$ is the absolute temperature common to all components, $s$ is the entropy density, and $\mu_i$ is the chemical potential of component $i$. The rate of change of the entropy density is thus given by

$$\dot{s} = \left(\dot{u} - \sum \mu_i \dot{n}_i\right)\Big/T \tag{5}$$

upon which customary theories are based, the dotted quantities being the partial derivatives with respect to time. The expression for $\dot{u}$ is complicated, because the internal energy does not conserve; it is desired to express $\dot{s}$ in terms of $\dot{u}^*$, namely the derivative of the total energy density discussed in the preceding section.

Since the total energy includes the potential and kinetic energies in addition to the internal energy, the differential of the total energy density is given by

$$\begin{aligned} du^* &= du + \sum \phi e_i \, dn_i + \sum d(\tfrac{1}{2} n_i m_i v_i^2) \\ &= T\,ds + \sum \mu_i^* \, dn_i + \sum n_i m_i \mathbf{v}_i \cdot d\mathbf{v}_i \qquad (6) \end{aligned}$$

where $\mu_i^*$ has been defined by

$$\mu_i^* = \mu_i + e_i \phi + \tfrac{1}{2} m_i v_i^2 \qquad (7)$$

Therefore, the entropy density $s$ may be regarded as a function of $u^*$, $n_i$, and $\mathbf{v}_i$; and its time derivative may be written as

$$\dot{s} = \left(\dot{u}^* - \sum \mu_i^* \dot{n}_i - \sum n_i m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i\right) \Big/ T \qquad (8)$$

which is more tractable than (5).

The macroscopic state of the system under consideration is determined by the total energy density $u^*$, the particle number densitites $n_i$, and the flow velocities $\mathbf{v}_i$ of the mass motions; therfore, these quantities make a complete set of state variables. Since the state variable in a continuum is a function of space coordinate and time, the entropy $S$ of the whole system is a functional of these state variables, that is, a space integral of the entropy density $s$ as a function of these variables. There is a choice in selecting a complete set of state variables. For example, the internal energy density $u$ can be substituted for the total energy density $u^*$, although it yields complication, as mentioned above. The flow velocities $\mathbf{v}_i$ are often replaced by the velocity of the local center of mass; however, such replacement causes the set of state variables to be incomplete.

The fluxes of irreversible processes are defined in the sense of Onsager as the time derivatives of the state variables: that is,

$$\dot{u}^*, \quad \dot{n}_i, \quad \text{and} \quad \dot{\mathbf{v}}_i \qquad (9)$$

The conjugate forces are the functional derivatives of the entropy $S$ with respect to the corresponding state variables: that is,

$$1/T, \quad -\mu_i^*/T, \quad \text{and} \quad -n_i m_i \mathbf{v}_i / T \qquad (10)$$

Strictly speaking, it is the deviations of the quantities (9) and (10) from their equilibrium values that may be considered as the fluxes or the forces. Without regard to this definition, other forces and fluxes are defined in the next section for convenience of comparison with customary results.

## 4. LINEAR RELATION

Equation (8) for the entropy density can be transformed into the form

$$\begin{aligned}\dot{s} = {} & -\mathrm{div}\left(\mathbf{q}'T^{-1} + \sum n_i\mathbf{v}_i s_i\right) + \mathbf{q}' \cdot \mathrm{grad}\, T^{-1} \\ & - \sum n_i\mathbf{v}_i T^{-1} \cdot [(\mathrm{grad}\, \bar{\mu}_i)_T + m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i \cdot \mathrm{grad}\, \mathbf{v}_i)] \qquad (11)\end{aligned}$$

Here, $\mathbf{q}'$ is a kind of heat flux defined by

$$\mathbf{q}' = \mathbf{q} + \sum n_i\mathbf{v}_i(u_i{}^* - \mu_i{}^* - Ts_i) \qquad (12)$$

$s_i$ being the entropy per particle of the component $i$;

$$\bar{\mu}_i \equiv \mu_i{}^* - \tfrac{1}{2}m_i v_i{}^2 \qquad (13)$$

$$(\mathrm{grad}\, \bar{\mu}_i)_T \equiv \mathrm{grad}\, \bar{\mu}_i + s_i\, \mathrm{grad}\, T \qquad (14)$$

where $\bar{\mu}_i$ is sometimes called the electrochemical potential, and use has been made of the energy equation (1) and the equation of continuity

$$\dot{n}_i + \mathrm{div}\, n_i\mathbf{v}_i = 0 \qquad (15)$$

The difference between $\mathbf{q}'$ and $\mathbf{q}$ is related to the work associated with the volume increment produced by diffusion and convection of the various components (Ref. 5, p. 29).

When all $\mathbf{v}_i$ in the square brackets on the right side of (11) are replaced by the velocity $\mathbf{v}$ of the local center of mass, the expression (11) is equivalent to that given by Kihara.(9) If the Navier–Stokes equation is further assumed, a customary expression for the entropy production will be obtained. However, such replacement cannot be permitted, because the entropy production is a second-order quantity with respect to the small deviations of the state variables from their equilibrium values: The difference between $\mathbf{v}_i$ and $\mathbf{v}$ has to be retained up to the second order.

Since the system under consideration is isolated, the entropy $S$ of the whole system takes its maximum value when there is equilibrium. In other words, the first derivatives of $S$ with respect to the state variables vanish under certain restrictions due to the laws of conservation of energy, particle number, and so on. As proved in the appendix, this extremum condition leads to

$$\operatorname{grad} T \to 0 \tag{16a}$$

$$\mathbf{v}_i \to \mathbf{v}_0 + \boldsymbol{\omega} \times (\mathbf{r} - \mathbf{r}_0), \qquad \dot{\mathbf{r}}_0 = \mathbf{v}_0 \tag{16b}$$

$$m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i \cdot \operatorname{grad} \mathbf{v}_i) + \operatorname{grad} \bar{\mu}_i \to 0 \tag{16c}$$

$$\mathbf{q}' \to 0 \tag{16d}$$

Here, the arrow denotes that the left side reduces to the right at equilibrium; $\mathbf{v}_0$ and $\boldsymbol{\omega}$ are respectively the linear and angular velocities of the system as a whole; and $\mathbf{r}_0$ gives the center of mass of the system.

Hereafter, the frame of reference is taken to translate and rotate with the system. The quantities appearing up to this point may be considered to be defined in this frame. In particular, the substantial derivative $m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i \cdot \operatorname{grad} \mathbf{v}_i)$ in the inertial frame is transformed into

$$m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i \cdot \operatorname{grad} \mathbf{v}_i) - 2m_i\mathbf{v}_i \times \boldsymbol{\omega} - m_i(\boldsymbol{\omega} \times \mathbf{r}) \times \boldsymbol{\omega} \tag{17}$$

where the subtrahends are the Coriolis and the centrifugal forces, respectively, $\mathbf{r}$ being the distance from the origin of the frame.

The integration of (11) over the whole system gives the entropy production in the form

$$\dot{S} = \int \left(\mathbf{J}_0 \cdot \mathbf{X}_0 - \sum \mathbf{J}_i \cdot \mathbf{X}_i\right) d\mathbf{r} \tag{18}$$

Here, the "forces" are defined by

$$\mathbf{X}_0 = \operatorname{grad} T^{-1} \tag{19a}$$

$$\mathbf{X}_i = n_i\mathbf{v}_iT^{-1} \tag{19b}$$

and the "fluxes" by

$$\mathbf{J}_0 = \mathbf{q}' \tag{20a}$$

$$\mathbf{J}_i = (\operatorname{grad} \bar{\mu}_i)_T + 2m_i\boldsymbol{\omega} \times \mathbf{v}_i + m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i \cdot \operatorname{grad} \mathbf{v}_i) \tag{20b}$$

where $\bar{\mu}_i$ includes the centrifugal potential energy. Though the term $\mathbf{v}_i \cdot \operatorname{grad} \mathbf{v}_i$ is small in the frame moving with the system, it may become large in other frames. The force could be defined as $-\mathbf{X}_i$; however, the present definition will simplify the reciprocity between linear coefficients.

When the system is in thermal equilibrium, all the fluxes and forces vanish. Therefore, the fluxes may be related to the forces by the linear equation

$$\mathbf{J}_a(\mathbf{r}_1) = \sum_{b=0,i} \int l_{ab}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{X}_b(\mathbf{r}_2)\, d\mathbf{r}_2, \qquad a = 0, i \tag{21}$$

The flux at the position $\mathbf{r}_1$ depends on the forces at a different position $\mathbf{r}_2$, which is a kind of cross-phenomenon. Since the linear coefficients vanish rapidly as the distance $|\mathbf{r}_2 - \mathbf{r}_1|$ increases, the relation (21) is usually approximated by the local relation

$$\mathbf{J}_a(\mathbf{r}_1) = \sum \left[\int l_{ab}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2\right] \cdot \mathbf{X}_b(\mathbf{r}_1) \tag{22}$$

Nevertheless, this approximation cannot apply to viscous fluids; a better approximation will be given in Section 6.

## 5. RECIPROCITY BETWEEN LINEAR COEFFICIENTS

The linear coefficients appearing in (21) obey the symmetric relation

$$l_{ab}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = l_{ba}^{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1) \tag{23}$$

which is to be proved in this section, the Greek indices denoting the tensorial component. The direction of the angular velocity $\boldsymbol{\omega}$ of the system as a whole is considered to be reversed where necessary: The quantities on the left and the right sides are defined in the systems with $\boldsymbol{\omega}$ and with $-\boldsymbol{\omega}$, respectively. The reciprocity (23) comprises the three relations

$$l_{ij}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = l_{ji}^{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1) \tag{23a}$$

$$l_{i0}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = l_{0i}^{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1) \tag{23b}$$

$$l_{00}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = l_{00}^{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1) \tag{23c}$$

where the suffixes $i$ and $j$ refer to substances, and 0 to heat.

In order to prove the above reciprocity, several expressions should be mentioned. As a result of the fact that the equations of motion for individual particles are invariant under time inversion, the correlations between state variables and Onsager's fluxes (9) satisfy the relations[1,10,11]

$$\langle v_i^{\alpha}(\mathbf{r}_1)\, \dot{v}_j^{\beta}(\mathbf{r}_2)\rangle = \langle v_j^{\beta}(\mathbf{r}_2)\, \dot{v}_i^{\alpha}(\mathbf{r}_1)\rangle \tag{24a}$$

$$\langle u^*(\mathbf{r}_1)\, \dot{v}_i^{\alpha}(\mathbf{r}_2)\rangle = -\langle v_i^{\alpha}(\mathbf{r}_2)\, \dot{u}^*(\mathbf{r}_1)\rangle \tag{24b}$$

$$\langle u^*(\mathbf{r}_1)\, \dot{u}^*(\mathbf{r}_2)\rangle = \langle u^*(\mathbf{r}_2)\, \dot{u}^*(\mathbf{r}_1)\rangle \tag{24c}$$

Here, the bracket notation means the statistical average, and the state variables are to be considered as the deviations from their equilibrium values.

The correlations between state variables and Onsager's forces (10) can be expressed as[10,11]

$$\langle v_i^\alpha(\mathbf{r}_1)\, m_j X_j^\beta(\mathbf{r}_2)\rangle = \kappa\delta_{ij}\,\delta_{\alpha\beta}\,\delta(\mathbf{r}_1 - \mathbf{r}_2) \tag{25a}$$

$$\langle u^*(\mathbf{r}_1)/T(\mathbf{r}_2)\rangle = -\kappa\delta(\mathbf{r}_1 - \mathbf{r}_2) \tag{25b}$$

$$\langle v_i^\alpha(\mathbf{r}_1)\,\mu_j^*(\mathbf{r}_2)/T(\mathbf{r}_2)\rangle = 0 \tag{25c}$$

$$\langle u^*(\mathbf{r}_1)\,\mu_j^*(\mathbf{r}_2)/T(\mathbf{r}_2)\rangle = 0 \tag{25d}$$

$$\langle v_i^\alpha(\mathbf{r}_1)/T(\mathbf{r}_2)\rangle = 0 \tag{25e}$$

$$\langle u^*(\mathbf{r}_1)\, m_i X_i^\alpha(\mathbf{r}_2)\rangle = 0 \tag{25f}$$

where $\kappa$ is the Boltzmann constant.

First, it is to be proved that the correlations between the flow velocities and the fluxes given by (20b) satisfy the relation

$$\langle m_i v_i^\alpha(\mathbf{r}_1)\, J_j^\beta(\mathbf{r}_2)\rangle = \langle m_j v_j^\beta(\mathbf{r}_2)\, J_i^\alpha(\mathbf{r}_1)\rangle \tag{26}$$

Since the flow velocities are small, their third-order terms are negligible. Equation (25c), therefore, reduces to

$$\langle \mathbf{v}_i(\mathbf{r}_1)[\operatorname{grad}\mu_j(\mathbf{r}_2)]_T\rangle = 0 \tag{27}$$

where (25e) has been used. Consequently, the relation (26) turns out to be the same as (24a). The substitution of (21) into (26) gives (23a), through (25a) and (25e).

Similarly, it can be proven that

$$\langle m_i v_i^\alpha(\mathbf{r}_1)\operatorname{div}\mathbf{J}_0(\mathbf{r}_2)\rangle = \langle u^*(\mathbf{r}_2)\, J_i^\alpha(\mathbf{r}_1)\rangle \tag{28}$$

$$\langle u^*(\mathbf{r}_1)\operatorname{div}\mathbf{J}_0(\mathbf{r}_2)\rangle = \langle u^*(\mathbf{r}_2)\operatorname{div}\mathbf{J}_0(\mathbf{r}_1)\rangle \tag{29}$$

These equations lead, respectively, to

$$(\partial/\partial x_2^\beta)\, l_{i0}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = (\partial/\partial x_2^\beta)\, l_{0i}^{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1) \tag{30}$$

$$(\partial/\partial x_1^\alpha)(\partial/\partial x_2^\beta)\, l_{00}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = (\partial/\partial x_1^\alpha)(\partial/\partial x_2^\beta)\, l_{00}^{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1) \tag{31}$$

where $x_1^\alpha$ and $x_2^\beta$ are the components of the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. These complicated relations are a reflection of the fact that only the divergence of the heat flux has a physical meaning. The above equations can be integrated under the boundary condition that the linear coefficients are independent of the shape of the system, and vahish if $\mathbf{r}_1$ or $\mathbf{r}_2$ is outside the system. Hence (23b) and (23c). Though it would be fatuous not to accept this convention, it is interesting to note that Onsager's relation itself does not imply (23b) or (23c).[10]

## 6. PHENOMENOLOGICAL EQUATION

The local approximation (22) cannot apply to the integral of the form

$$I_{ij} = \int [n_i(\mathbf{r}_1)\, l_{ij}(\mathbf{r}_1 , \mathbf{r}_2)\, n_j(\mathbf{r}_2)/T(\mathbf{r}_2)] \cdot \mathbf{v}_j(\mathbf{r}_2)\, d\mathbf{r}_2 \tag{32}$$

which appears in (21). Here, the integrand has been multiplied by $n_i(\mathbf{r}_1)$, for convenience. The quantity in the square brackets may be regarded as a function of $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ ; this function is to be denoted by $l(\mathbf{R}, \mathbf{r})$. As $r$ increases, $l(\mathbf{R}, \mathbf{r})$ should vanish rapidly; the dependence on $\mathbf{R}$ is weak.

The linear coefficient $l(\mathbf{R}, \mathbf{r})$ is assumed to be an even function with respect to $\mathbf{r}$, which is valid for isotropic system, for example. The integral (32) can be written as

$$I_{ij} = \int l(\mathbf{r}_1 + \tfrac{1}{2}\mathbf{r}, \mathbf{r}) \cdot \mathbf{v}_j(\mathbf{r}_1 + \mathbf{r})\, d\mathbf{r} \tag{33}$$

because $\mathbf{R} = \mathbf{r}_1 + \frac{1}{2}\mathbf{r}$ and $\mathbf{r}_2 = \mathbf{r}_1 + \mathbf{r}$; with respect to these $\mathbf{r}$, the integrand can be expanded. Since the third- and higher-order terms may be neglected, this integral reduces to

$$I_{ij}^{\alpha\beta} = L_{ij}^{\alpha\beta}(\mathbf{r}_1)\, v_j{}^{\beta}(\mathbf{r}_1) + (\partial/\partial x_1{}^{\gamma})\, K_{ij}^{\alpha\beta\gamma\delta}(\mathbf{r}_1)(\partial/\partial x_1{}^{\delta})\, v_j{}^{\beta}(\mathbf{r}_1) \tag{34}$$

Here, $L_{ij}$ is a tensor of the second rank,

$$L_{ij}^{\alpha\beta}(\mathbf{r}_1) = \int l^{\alpha\beta}(\mathbf{r}_1 + \tfrac{1}{2}\mathbf{r}, \mathbf{r})\, d\mathbf{r} \tag{35}$$

and $K_{ij}$ is a tensor of the fourth rank,

$$K_{ij}^{\alpha\beta\gamma\delta}(\mathbf{r}_1) = \tfrac{1}{2} \int l^{\alpha\beta}(\mathbf{r}_1 , \mathbf{r})\, x^{\gamma} x^{\delta}\, d\mathbf{r} \tag{36}$$

where $x^{\gamma}$ and $x^{\delta}$ are the $\gamma$ and $\delta$ components of the vector $\mathbf{r}$, repectively.

By means of the approximations (22) and (34), the linear relation (21) reduces to more familiar equations

$$\mathbf{q}' = -L_{00} \cdot \operatorname{grad} \ln T + \sum L_{0i} \cdot \mathbf{v}_i \tag{37}$$

$$\begin{aligned} n_i m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i \cdot \operatorname{grad} \mathbf{v}_i) + n_i(\operatorname{grad} \bar{\mu}_i)_T + 2n_i m_i \boldsymbol{\omega} \times \mathbf{v}_i \\ = -L_{i0} \cdot \operatorname{grad} \ln T + \sum L_{ij} \cdot \mathbf{v}_j + \sum \operatorname{Div}(K_{ij} : \operatorname{grad} \mathbf{v}_j) \end{aligned} \tag{38}$$

The reciprocal relations between the phenomenological coefficients are obtained from (23) as

$$L_{ab}^{\alpha\beta} = L_{ba}^{\beta\alpha} \tag{39}$$

$$K_{ij}^{\alpha\beta\gamma\delta} = K_{ji}^{\beta\alpha\gamma\delta} = K_{ij}^{\alpha\beta\delta\gamma} \tag{40}$$

The symmetric property with respect to the exchange of $\gamma$ and $\delta$ is irrelevant to the microscopic reversibility.

Equation (38) is a hydrodynamic equation of motion for component $i$. The terms on the right side can be interpreted as the force related to the thermal diffusion, frictional forces between the components, and the viscous force, respectively. A similar equation has been obtained by Bearman and Kirkwood$^{(12)}$ on the basis of the classical kinetic theory. The viscosity term of their equation depends not on $\mathbf{v}_j$, but on the velocity of local center of mass. The kinetic theory could give the dependence of the viscosity term on $\mathbf{v}_j$; however, it is an overgeneralized theory for the purpose of knowing what the term depends on.

The customary equation for diffusion holds true only in the case where the inertial and the viscosity terms may be neglected. The reason why the previous theory of irreversible processes failed to obtain the inertial term is that the set of state variables was incomplete: The velocity of the local center of mass was substituted for the velocities of the individual components. The omission of the viscosity term is due to the local approximation, and to the careless application of the so-called Curie theorem that vectorial phenomena are not coupled with tensorial forces in isotropic systems. For a solute in aqueous solutions, the inertial and viscous terms of (38) are generally small;$^{(13)}$ in high-temperature plasmas, however, the inertial term is even more important than the friction term which governs the diffusion.

Apart from the relations (39) and (40), some restrictions are imposed on the linear coefficients. The summation of the both sides of (38) over the components gives

$$\begin{aligned}\partial\Big(\sum n_i m_i \mathbf{v}_i\Big)/\partial t + \operatorname{Div}\sum n_i m_i \mathbf{v}_i \mathbf{v}_i + 2\boldsymbol{\omega} \times \sum n_i m_i \mathbf{v}_i + \operatorname{grad} P - \mathbf{F} \\ = -\sum L_{io} \cdot \operatorname{grad} \ln T + \sum\sum L_{ij} \cdot \mathbf{v}_j + \sum\sum \operatorname{Div}(K_{ij} : \operatorname{grad} \mathbf{v}_j) \qquad (41)\end{aligned}$$

where $P$ is the pressure, $\mathbf{F}$ is the sum of all the conservative forces, and use has been made of the formula

$$\sum n_i (\operatorname{grad} \bar{\mu}_i)_T = \operatorname{grad} P - \mathbf{F} \qquad (42)$$

The left side of (41) vanishes after the integration over the whole system, because it represents the equation of motion for the center of mass of the system. This means that the integral of the right side also vanishes; the last term does not contribute to the integral. Since grad ln $T$ and $\mathbf{v}_j$ are arbitrary, their coefficients must vanish: that is,

$$\sum L_{io} = \sum L_{0i} = 0 \qquad (43)$$

$$\sum_i L_{ij} = \sum_i L_{ji} = 0 \qquad (44)$$

where (39) has been applied. In isotropic systems, the fourth-rank tensor $K_{ij}$ has only two independent components corresponding to the shear and bulk viscosities, because the linear coefficients $l(\mathbf{r}_1, \mathbf{r})$ of (36) can be written as

$$l^{\alpha\beta} = l'\delta_{\alpha\beta} + l''x^{\alpha}x^{\beta} \tag{45}$$

where $l'$ and $l''$ are scalars.

If all the flow velocities are the same, or if no diffusion occurs, (41) reduces to the Navier–Stokes equation

$$\begin{aligned}\left(\sum n_i m_i\right)(\dot{\mathbf{v}} + \mathbf{v}\cdot\operatorname{grad}\mathbf{v})\\ = 2\left(\sum n_i m_i\right)\mathbf{v}\times\boldsymbol{\omega} - \operatorname{grad}P + \mathbf{F} + \operatorname{Div}(K:\operatorname{grad}\mathbf{v})\end{aligned} \tag{46}$$

where $\mathbf{v}$ is the velocity of local center of mass, and $K$ is the viscosity coefficient given by

$$K = \sum\sum K_{ij} \tag{47}$$

In customary theories, on the contrary, (46) is assumed at the beginning in order to obtain an equation for the internal energy density; in this connection, it is necessary to substitute $\mathbf{v}$ for $\mathbf{v}_i$. It should be mentioned in conclusion that the imprudent use of the internal energy density necessitated such a superfluous assumption, which caused the defects in the customary theory.

## APPENDIX. EQUILIBRIUM CONDITION

The entropy $S$ of the whole system is a functional of the state variables $u^*(\mathbf{r})$, $n_i(\mathbf{r})$, and $\mathbf{v}_i(\mathbf{r})$, which are not independent of each other. The variables satisfy the equations for conservation of

| | |
|---|---|
| energy | $\int u^*(\mathbf{r})\,d\mathbf{r} = U^*$ |
| particle number | $\int n_i(\mathbf{r})\,d\mathbf{r} = N_i$ |
| momentum | $\sum\int m_i n_i(\mathbf{r})\,\mathbf{v}_i(\mathbf{r})\,d\mathbf{r} = \mathbf{P}$ |
| angular momentum | $\sum\int (\mathbf{r}-\mathbf{r}_0)\times m_i n_i(\mathbf{r})\,\mathbf{v}_i(\mathbf{r})\,d\mathbf{r} = \mathbf{M}$ |

where the right sides are all constant, and $\mathbf{r}_0$ is the center of mass of the system:

$$\mathbf{r}_0 = \int\sum m_i n_i \mathbf{r}\,d\mathbf{r}\Big/\int\sum m_j n_j\,d\mathbf{r}$$

Under these restrictions, the first functional derivatives of $S$ at equilibrium vanish.

Lagrange's multiplier method gives the equilibrium conditions as follows:

$$\begin{aligned}
\delta S/\delta u^* &= (1/T) - (1/T_0) = 0 \\
\delta S/\delta n_i &= -(\mu_i{}^*/T) + \lambda_i + (m_i\mathbf{v}_i \cdot \mathbf{v}_0/T_0) + \{m_i\mathbf{v}_i \cdot [\boldsymbol{\omega} \times (\mathbf{r} - \mathbf{r}_0)]/T_0\} \\
&\qquad + \Big[m_i\boldsymbol{\omega} \times \mathbf{P} \cdot (\mathbf{r} - \mathbf{r}_0)\Big/\Big(T_0 \textstyle\sum m_jN_j\Big)\Big] = 0 \\
\delta S/\delta \mathbf{v}_i &= -m_in_i\{(\mathbf{v}_i/T) - (\mathbf{v}_0/T_0) - [\boldsymbol{\omega} \times (\mathbf{r} - \mathbf{r}_0)/T_0]\} = 0
\end{aligned}$$

which lead to (16a)–(16c). Here, $1/T_0$, $\lambda_i$, $\mathbf{v}_0/T_0$, and $\boldsymbol{\omega}/T_0$ are the Lagrange multipliers, and use has been made of the formula

$$\delta \mathbf{r}_0/\delta n_i = m_i(\mathbf{r} - \mathbf{r}_0)/\textstyle\sum m_jN_j$$

The multipliers have the following meanings: $T_0$ is the equilibrium temperature; $\mathbf{v}_0$ and $\boldsymbol{\omega}$ are respectively the velocity and the angular velocity of the system as a whole; and $\lambda_iT_0 + \frac{1}{2}m_iv_i{}^2$ is the equilibrium value of the electrochemical potential at the center of mass. From the continuity equation (15) there follows $\dot{\mathbf{r}}_0 = \mathbf{v}_0$.

Equilibrium thermodynamics gives the entropy $s_i$ per particle in the form

$$s_i = \partial\mu_i/\partial T$$

where $\mu_i$ is regarded as a function of the pressure, temperature, and particle densities. From this equation and the differentiation of both sides of $\delta S/\delta n_i = 0$ with respect to the equilibrium temperature, and the position or the time, it follows that

$$\operatorname{grad} s_i = 0 \qquad \text{and} \qquad \dot{s}_i = 0$$

Since $\mathbf{X}_0$ and $\mathbf{J}_i$ vanish at equilibrium, (11) reduces to

$$\dot{s} = -\operatorname{div}\Big(\mathbf{q}'T^{-1} + \textstyle\sum n_i\mathbf{v}_is_i\Big)$$

which gives, by virtue of $s = \sum n_is_i$,

$$\operatorname{div} \mathbf{q}' = 0$$

As mentioned in Section 2, the divergence-free part of the heat flux has no physical effect. Therefore, the heat flux itself at equilibrium may be taken to vanish. Notwithstanding this, the heat flux $\mathbf{q}$ based on the first law may not vanish.

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## REFERENCES

1. L. Onsager, *Phys. Rev.* **37**:405 (1931); **38**:2265 (1931).
2. S. R. de Groot, *Thermodynamics of Irreversible Processes*, North-Holland, Amsterdam (1952).
3. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam (1962).
4. I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, Thomas, Springfield, Ill. (1955).
5. D. D. Fitts, *Nonequilibrium Thermodynamics*, McGraw-Hill, New York (1962).
6. A. Katchalsky and P. F. Curran, *Nonequilibrium Thermodynamics in Biophysics*, Harvard University, Cambridge (1965).
7. L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (English translation), Pergamon, New York (1959).
8. B. D. Coleman and C. Truesdell, *J. Chem. Phys.* **33**:28 (1960).
9. T. Kihara, *J. Phys. Soc. Japan* **14**:128 (1959).
10. H. B. G. Casimir, *Rev. Mod. Phys.* **17**:343 (1945).
11. S. R. de Groot and P. Mazur, *Phys. Rev.* **94**:218 (1954).
12. R. J. Bearman and J. G. Kirkwood, *J. Chem. Phys.* **28**:136 (1958).
13. R. J. Bearman, *J. Chem. Phys.* **31**:751 (1959).