*Journal of Statistical Physics, Vol. 5, No. 1/2, 1972*

# Generalization of the Gibbsian Relation for Dilute Systems

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*Received November 2, 1970; revised March 29, 1971*

The Gibbsian relation is of fundamental importance to the thermodynamics of nonequilibrium systems. In this paper, we shall present an analytical derivation and several generalizations of this relation for dilute, nonequilibrium and certain highly nonequilibrium, systems. Our analysis will be *independent* of the collision dynamics, because it will be based on the general kinetic equation with *arbitrary* collision integrals. Consequently, our analysis can provide a *thermodynamic* derivation and several generalizations of the Gibbsian relation. Our distribution functions can also admit some arbitrary, nonequilibrium and highly nonequilibrium, forms. With the help of the generalized Gibbsian relation and a fundamental axiom to be postulated, the entropy production rates and the generalized forces and fluxes will be studied for our highly nonequilibrium systems. The second law of thermodynamics will be postulated and verified in specific cases. Onsager's reciprocity relations will be discussed.

**KEY WORDS:** Nonequilibrium thermodynamics; kinetic theory; Gibbsian relation; dilute systems; analytical generalization; entropy production.

## 1. INTRODUCTION AND DEFINITIONS

The Gibbsian relation for a multispecies fluid system is

$$T\,Ds/Dt = (D\epsilon/Dt) + p[D(1/\rho)/Dt] - \sum_i \mu_i\,Dx_i/Dt \tag{1}$$

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Here, $D/Dt$ will denote a material-derivative; $s$, $\epsilon$, $p$, and $\rho$ will represent respectively the specific entropy, the specific internal energy, the pressure, and the density of the system; and $\mu_i$ and $x_i$ will denote the chemical potential and the concentration of the *i*th species.

This relation is of fundamental importance to the thermodynamics of nonequilibrium systems. Together with the first and the second laws of thermodynamics and Onsager's reciprocity relation it forms the foundation of this important area of thermodynamics.(1,2)

For nonequilibrium systems in general, the Gibbsian relation is usually assumed to be valid, since it is valid for equilibrium systems undergoing reversible processes. So far, the validity of this assumption, in the words of DeGroot and Mazur (Ref. 1, p. 23), "can only be justified by virtue of the validity of the conclusions derived from it." Therefore, an analytical and *thermodynamic* derivation of this relation is needed in order to substantiate this assumption and to define its region of validity for nonequilibrium systems, and then in order to discover the generalizations of this relation when the systems become highly nonequilibrium.

Analytical derivations of the Gibbsian relation have been presented by various investigators(1–5) for dilute nonequilibrium systems, based on the Boltzmann equation, which is valid only for binary and elastic collisions. Hence, these derivations are *not* thermodynamic derivations because they are *dependent* upon the collision dynamics. For example, their validity for inelastic and multibody collisions is yet to be established. The latter types of collisions are of prime importance in chemical reactions involving dilute systems; in such reactions, several particles may come together and experience a binary or a multibody inelastic collision.

Another derivation of the Gibbsian relation also has been presented by Coleman and co-workers(6,7) based on the continuum approach. This derivation is phenomenological, and not analytical, in nature; it is a thermodynamic one, however, since it is independent of the collision dynamics. It is also restricted to nonequilibrium systems.

Summarizing, we still do not have a derivation of the Gibbsian relation which is *both* analytical and thermodynamic, and which is valid for nonequilibrium as well as highly nonequilibrium systems, which are frequently encountered in practice. As a result, we do not know what should be the form of the Gibbsian relation when the systems become highly nonequilibrium.

Let us set forth the following definitions. By systems, we shall mean multispecies gaseous systems, where, for the *i*th species, we have the particle-velocity distribution function $f_i$, the local species temperature $T_i$, and the local species mean velocity $\mathbf{u}_i$. By equilibrium systems, we mean systems that are in their thermostatic equilibria and will not undergo any spontaneous changes. For a system in local thermodynamic equilibrium (LTE), its species are locally in equilibrium with each other such that both $T_i$ and $\mathbf{u}_i$ are locally the same for all species, and that every $f_i$ is locally Maxwellian. An important feature of an LTE system is, of course, that its $T_i$ and $\mathbf{u}_i$ can still change with time and space. Hence, at each instant, it is already not in thermostatic equilibrium.

Adopting usual terminology, we shall call a system nonequilibrium (highly nonequilibrium) if it is close to (far away from) its LTE. Two criteria may be employed for this classification: how far the species of the system are nonequilibrial to each other, and how the system as a whole deviates from its LTE; for example, if it has large spatial or temporal gradients.

Let us write

$$f_i = f_i^{(0)}(1 + \phi_i), \qquad \text{with} \quad | \phi_i | < 1 \tag{2}$$

Then, for a nonequilibrium system, its species should be nearly in local equilibrium with each other and its gradients should be small in magnitude. Thus, it is required that the $\phi_i$ are small quantities; the $f_i^{(0)}$ are *locally* Maxwellian; and *both* $T_i$ and $\mathbf{u}_i$ are *locally* the same for all species.

We emphasize that in a nonequilibrium system, *both* $T_i$ and $\mathbf{u}_i$ do not vary much from one species to the other, although they can change with time and space. If we introduce the local temperature $T$, velocity $\mathbf{u}$, and sonic velocity $a$ for the mean fluid system, then both

$$| \mathbf{u}_i - \mathbf{u} |/a \ll 1 \tag{3a}$$

and

$$| T_i - T |/T \ll 1 \tag{3b}$$

should be satisfied. Thus, every one of the diffusion velocities

$$\mathbf{w}_i = \mathbf{u}_i - \mathbf{u} \tag{4}$$

has to be subsonic even though $\mathbf{u}$ may become supersonic, indicating small effects of diffusion.

Having defined nonequilibrium systems according to the usual convention, we realize that there are many varieties of hightly nonequilibrium systems. In particular, there are systems for which it is not possible to define the species temperatures $T_i$ and/or the species entropies $s_i$. A new approach based on the continuum theory has been proposed recently by Meixner(8) for studying thermodynamics of systems without defining the entropy; his work is therefor not concerned with the Gibbsian relation. Another type of highly nonequilibrium system has been studied by Truesdell.(9) He has investigated, based on a continuum approach, nonequilibrium and highly nonequilibrium single-species solid systems which have fading memories.

We shall confine ourselves to two broad types of highly nonequilibrium gaseous systems where it is possible to define both $T_i$ and $s_i$. For both types, the species will be allowed to become highly nonequilibrial to each other, but, the gradients of the state variables will still be restricted to be small in magnitude.

For our first type, called Type I, the distribution functions $f_i$ are again restricted to be nearly locally Maxwellian, but with *no* restriction on $T_i$ or on $\mathbf{u}_i$ such that $T_i$ and $\mathbf{u}_i$ may vary greatly from one species to the other, and the system can become highly nonequilibrium. In other works, both conditions (3a) and (3b) can be relaxed. Consequently, the diffusion velocities $\mathbf{w}_i$ can become supersonic even when the fluid velocity $\mathbf{u}$ remains subsonic, as discussed by Yen,$^{(10)}$ indicating very large and generally nonlinear effects of diffusion. The dynamics and the kinetic theory of such systems have been studied by different authors, for example, Refs. 10–19. However, due to its nonlinearity, the thermodynamics of such systems have not been investigated so far. It is obvious that an analytical procedure which is independent of the collision dynamics is necessary for such investigations; the phenomenological and semi empirical procedures employed in the usual themodynamic studies are inadequate for our purpose.

The establishment of the desired analytical procedure will be carried out in Section 2. There, as an initial step, we shall consider only a particular kind of Type I system, by making the restriction that each system have negligible internal degrees of freedom and that the $\mathbf{u}_i$ be nearly the same for all of its species, although the $T_i$ can still vary greatly from one species to another, and the small deviations $\phi_i$ can still assume arbitrary forms.

For our second type, called Type II, to be treated in Section 3, the Maxwellian requirement is removed such that the $f_i^{(0)}$ can assume *arbitrary* forms. The small deviations $\phi_i$ can also admit arbitrary forms, to cover a large variety of highly nonequilibrium systems. In order to obtain detailed results, however, we need to adopt mathematically suitable non-Maxwellian forms, and we need to extend the analysis of Section 2. The dynamics and the kinetic theory, but not the thermodynamics, of some specific highly non-Maxwellian systems have been studied, for example, in Ref. 19.

Our analysis, to be presented in Sections 2 and 3, will be based on the *general kinetic equation*:

$$\mathscr{D}f_i \equiv (\partial f_i/\partial t) + \boldsymbol{\xi}_i \cdot (\partial f_i/\partial \mathbf{x}) + (\mathscr{F}_i/m_i) \cdot (\partial f_i/\partial \boldsymbol{\xi}_i) = \mathscr{C}_i \qquad (5)$$

The collision integral denoted by $\mathscr{C}_i$ is *entirely arbitrary* in form and will represent the sum of the rates of *all* kinds of collisions—elastic and inelastic, binary and multibody—occurring among all *i*-type particles, and between the *i*th species and all other species. We have employed standard notation in Eq. (5), with $\mathscr{F}_i$ denoting the force acting on an *i*-type particle having mass

$m_i$, velocity $\xi_i$, and velocity distribution function $f_i$. Since the collision integral is entirely arbitrary, the general kinetic equation (5) is *independent* of the collision dynamics; thus, our analysis can qualify as a thermodynamic analysis.

In order to derive the Gibbsian relation from the general kinetic equation (5), we need to relate the specific entropy $s_i$ to the distribution function $f_i$. For dilute systems, and based on the Boltzmann statistics, $s_i$ is defined to be(1,14,15)

$$\rho_i s_i = -k \int f_i(\ln f_i - 1)\, d\xi_i \tag{6}$$

where $k$ is the Boltzmann constant and $\rho_i$ the density of the $i$th species. For dense systems, the mutual potential of the particles will contribute to $s_i$; binary or multiparticle distribution functions will appear in the integral of Eq. (6). Then, the analysis becomes very complicated; in fact, the existing analytical derivation(1–5) is also based on Eq. (6) and is therefore also restricted to dilute systems.

By a dilute system, we mean that the particles do not interact with each other except during collisions; the mutal potential of the particles is important only during the time periods of these collisions; the latter periods are much shorter than the time between collisions. However, these collisions can be inelastic and multibody. These collisions are of prime importance in chemical reactions occurring within a dilute system, where several particles may come together and participate in a multibody inelastic collision resulting in a chemical reaction. Hence, such collisions should be included in any thermodynamic treatment of dilute systems. In our case, this is achieved through the general kinetic equation (5).

Since we shall analyze dilute systems with negligible internal degrees of freedom, the species temperatures $T_i$ will be defined as the species kinetic temperatures ($d\mathbf{c}_i = dc_{ix}\, dc_{iy}\, dc_{iz}$)

$$\begin{aligned} \tfrac{3}{2}kT_i &= n_i^{-1} \int \tfrac{1}{2}mc_i^2 f_i\, d\mathbf{c}_i \\ &= \langle \tfrac{1}{2}mc_i^2 \rangle \end{aligned} \tag{7}$$

which also defines the notation $\langle\ \rangle$. The number density $n_i$ and the peculiar velocity $\mathbf{c}_i$ of the $i$th species are defined by

$$n_i = \int f_i\, d\mathbf{c}_i \tag{8a}$$

and

$$\mathbf{c}_i = \xi_i - \mathbf{u} \tag{8b}$$

The fluid velocity $\mathbf{u}$, density $\rho$, and temperature $T$ are then defined by

$$\mathbf{u} = \rho^{-1} \sum_i \rho_i \mathbf{u}_i \tag{9a}$$

where

$$\mathbf{u}_i = \langle \boldsymbol{\xi}_i \rangle \tag{9b}$$

$$\rho = \sum_i \rho_i \tag{9c}$$

where

$$\rho_i = n_i m_i \tag{9d}$$

and

$$T = n^{-1} \sum n_i T_i \tag{9e}$$

where

$$n = \sum_i n_i \tag{9f}$$

From our analysis presented below, it is clear that the restriction on the internal degrees of freedom can be relaxed; we can study systems with highly nonequilibrium internal degrees of freedom, for example, if different species have different vibrational, rotational, and translational temperatures. A simpler case, where these three temperatures are different from each other for each species, but are the same for all species, has been analyzed by Reik.(4)

In Section 2, we also obtain for our highly nonequilibrium systems the First Law statement and its entropy production rate; the latter specifies the generalized forces and fluxes with the help of a fundamental axiom to be postulated. The Second Law is then postulated in the form that the entropy production rate is always nonnegative. Specific systems and specific kinetic equations are studied. For each case, we obtain linear or nonlinear relations between the generalized forces and fluxes, and also an analytical proof of the Second Law statement. Thus, we are provided with some analytical basis for postulating that the Second Law is valid in general. Some discussion regarding Onsager's reciprocity relations will be presented. Some interesting relations linking the generalized forces to the fluxes will also be obtained, when there are arbitrary inelastic collisions and chemical reactions.

## 2. ANALYSIS

We shall study a simple class of Type I highly nonequilibrium dilute systems which has been specified in Section 1. Hence, we shall allow the species temperatures $T_i$ to vary greatly from one species to another, while the small deviations $\phi_i$ can still assume arbitrary forms.

If the $T_i$ become close to each other, then our highly nonequilibrium dilute system become the usual nonequilibrium dilute system; the latter is the system studied in the existing analytical derivations$^{(1-5)}$ of the Gibbsian relation (1). We have also emphasized in Section 1 that these existing derivations are restricted to binary and elastic collisions since they are based on the Boltzmann equation

$$\mathscr{D}f_i = \sum_j \int\int (f_i'f_j' - f_if_j)gb\; db\; d\epsilon\; d\xi_j \tag{10}$$

It seems that one cannot remove the dependence on the Boltzmann collision integrals from these derivations, due to the amount of complexities involved. This kind of attitude may be unwarranted. Moreover, since the Gibbsian relation is a thermodynamic one, we should raise the question of *why* we cannot completely remove such dependence and obtain a derivation that is *both* analytical and thermodynamic. We shall demonstrate that this aim can be achieved. Indeed, we shall work directly with our highly nonequilibrium systems with multiple species temperatures; once we can generalize the Gibbsian relation (1) for such systems based on the general kinetic equation (5), the desired derivation of the Gibbsian relation (1) itself will readily follow.

Apart from the fact that we shall deal with multiple species temperatures, the details of our analysis will be similar to those of the existing analyses.$^{(1-5)}$ We should point out that in the latter analyses (see Ref. 1, p. 177), the small deviation $\phi_i$ is further divided into various orders $\phi_i^{(1)}$, $\phi_i^{(2)}$, etc.; these also define the different orders of their analyses. Moreover, $\phi_i^{(1)}$ is linear in the spatial gradients, but otherwise *arbitrary* in form. We shall retain $\phi_i$ as a whole in our analysis without any subdivision; hence our $\phi_i$ should also be *arbitrary* in form. Moreover, the different orders of our analysis will correspond to the different powers of $\phi_i$; in other words, those terms scaled by $\phi_i^m$ will be called $m$th order terms.

Also, we shall adopt the following expansions:

$$f_i = f_i^{(0)}(1 + \phi_i) \qquad \text{with} \quad |\phi_i| < 1 \tag{11a}$$

$$f_i(\ln f_i - 1) = -f_i^{(0)} + f_i \ln f_i^{(0)} + f_i^{(0)}\phi_i^2 g_1(\phi_i) \tag{11b}$$

$$\ln f_i = \ln f_i^{(0)} + \phi_i - \phi_i^2 g_2(\phi_i) \tag{11c}$$

with

$$g_1(\phi_i) = \sum_{m=0}^{\infty} [(-1)^m/(m+1)(m+2)]\, \phi_i^m \tag{11d}$$

and

$$g_2(\phi_i) = \sum_{m=0}^{\infty} [(-1)^m/(m+2)]\, \phi_i^{\,m} \tag{11e}$$

Equations (11b) and (11c) represent new groupings of terms, different from the usual grouping; the latter is illustrated by Eqs. (68)–(70), p. 178 of Ref. 1.

Since we allow multiple species temperatures, i.e., $T_i \neq T$, but nearly the same species velocities, i.e., $\mathbf{u}_i \approx \mathbf{u}$, the locally Maxwellian zeroth-order distribution function of the $i$th species should be based on $T_i$ and $\mathbf{u}$. Thus

$$f_i^{(0)} = \exp(m_i/kT_i)[\tilde{\mu}_i - \tfrac{1}{2}(\boldsymbol{\xi}_i - \mathbf{u})^2] \tag{12a}$$

where

$$\tilde{\mu}_i = (kT_i/m_i)[\ln n_i - \tfrac{3}{2}\ln(2\pi kT_i/m_i)] \tag{12b}$$

which will be shown as a part of the usual chemical potential $\mu_i$.

Now, each particle of the $i$th species may also have a chemical energy $\psi_i$, such as the heat of formation or the ionization potential. To consider the energy balance for each species, we take the $\frac{1}{2}mc_i^2 + \psi_i$ moment of the general kinetic equation (5) and obtain

$$\begin{aligned}
&(\partial/\partial t)(\tfrac{3}{2}n_i kT_i + n_i\psi_i) \\
&\quad + \nabla \cdot (\tfrac{3}{2}n_i kT_i\mathbf{u} + n_i\psi_i\mathbf{u}) \\
&\quad + \rho_i\mathbf{w}_i \cdot [(D\mathbf{u}/Dt) - (\mathbf{F}_i/m_i)] + \nabla \cdot (\mathbf{q}_i + n_i\mathbf{w}_i\psi_i) \\
&\quad + p_i\nabla \cdot \mathbf{u} + \mathbf{P}_i : \nabla\mathbf{u} \\
&= \int (\tfrac{1}{2}m_i c_i^2 + \psi_i)\, \mathscr{C}_i\, d\boldsymbol{\xi}_i
\end{aligned} \tag{13}$$

where

$$\mathbf{w}_i = \mathbf{u}_i - \mathbf{u} \tag{14a}$$

$$D/Dt = \partial/\partial t + \mathbf{u} \cdot \nabla \tag{14b}$$

$$p_i = n_i kT_i = n_i\langle \tfrac{1}{3}m_i c_i^2\rangle \tag{14c}$$

$$P_i = n_i\langle m_i\mathbf{c}_i\mathbf{c}_i\rangle - p_i\mathbf{I} \tag{14d}$$

and

$$\mathbf{q}_i = n_i\langle \tfrac{1}{2}m_i c_i^2\mathbf{c}_i\rangle \tag{14e}$$

These equations have given us, with the help of the unit tensor $\mathbf{I}$, the definitions of the diffusion velocity $\mathbf{w}_i$, the partial pressure $p_i$, the stress tensor $\mathbf{P}_i$ and the heat flux vector $\mathbf{q}_i$, for the $i$th species.

The body force $\mathbf{F}_i$ appearing in Eq. (13) is defined by $\mathbf{F}_i = \langle \mathscr{F}_i \rangle$ where $\mathscr{F}_i$ appeared in Eq. (5). The usual assumption that $\mathscr{F}_i$ is independent of $\xi_i$ has been made in Eq. (13). If $\mathscr{F}_i$ does depend on $\xi_i$, such as the Lorentzian or the nonconservative forces, then in Eq. (13), the term containing $\mathbf{F}_i$ should be written as the sum of two integrals,

$$\int (\mathscr{F}_i \cdot \mathbf{c}_i) f_i \, d\xi_i$$

and

$$\int (\tfrac{1}{2} c_i^2 + \psi_i/m_i)(\partial \mathscr{F}_i/\partial \xi_i) f_i \, d\xi_i$$

Notice that the same remark also applies to the corresponding terms of Eqs. (16a) and (16d); on the other hand, only the first integral is needed for Eqs. (22), (25), and (27). For Eq. (17), we need to add only

$$-(k/m_i) \int f_i (\ln f_i - 1)(\partial \mathscr{F}_i/\partial \xi_i) \, d\xi_i$$

and, for Eqs. (23), (24), and (34), a sum of all three integrals, with $f_i$ changed to $f_i^{(0)}$ in the first integral, which is frequently the only nonvanishing contribution.

Next, we take the species mass moment and obtain the species continuity equation as

$$\partial \rho_i/\partial t + \nabla \cdot (\rho_i \mathbf{u}_i) = \int m_i \mathscr{C}_i \, d\mathbf{c}_i \tag{15a}$$

or

$$\rho \, Dx_i/Dt = -\nabla \cdot (\rho_i \mathbf{w}_i) + \int m_i \mathscr{C}_i \, d\mathbf{c}_i \tag{15b}$$

where $x_i$ is the concentration of the $i$th species,

$$x_i = \rho_i/\rho \tag{15c}$$

From these, we obtain for the mean fluid

$$\rho (D/Dt)(1/\rho) = \nabla \cdot \mathbf{u} \tag{15d}$$

and, for any property $Q_i$ of the $i$th species,

$$(\partial/\partial t)(\rho Q_i) + \nabla \cdot (\rho_i Q_i \mathbf{u}) = \rho (D/Dt)(x_i Q_i) \tag{15e}$$

Thus, a First Law statement for each species follows directly from Eqs. (13), (15d), and (15e). It reads, by employing the specific internal energies $\epsilon_i = (\frac{3}{2}kT_i + \psi_i)/m_i$ and by emphasizing that the total energy of each species is *not* necessarily conserved,

$$\begin{aligned}-(1/\rho)\,\nabla\cdot\mathbf{q}_i = {} & (D/Dt)\,x_i\epsilon_i + p_i(D/Dt)(x_i/\rho_i) + (1/\rho)\,\nabla\cdot(n_i\mathbf{w}_i\psi_i)\\ & +(1/\rho)\,\mathbf{P}_i : \nabla\mathbf{u} + x_i\mathbf{w}_i\cdot[(D\mathbf{u}/Dt) - (\mathbf{F}_i/m_i)]\\ & -\,(1/\rho)\int(\tfrac{1}{2}m_ic_i^2 + \psi_i)\,\mathscr{C}_i\,d\mathbf{c}_i \qquad (16\text{a})\end{aligned}$$

For the mean fluid, the total energy is conserved when we consider all elastic and inelastic collisions; thus,

$$\sum_i\int(\tfrac{1}{2}m_i\mathbf{c}_i^2 + \psi_i)\,\mathscr{C}_i\,d\mathbf{c}_i = 0 \qquad (16\text{b})$$

Also,

$$\sum_i \rho_i\mathbf{w}_i = 0 \qquad (16\text{c})$$

Hence, the First Law states for the mean fluid,

$$\begin{aligned}&-(1/\rho)\,\nabla\cdot(\mathbf{q} + \sum_i n_i\mathbf{w}_i\psi_i)\\ &\quad= (D\epsilon/Dt) + p(D/Dt)(1/\rho) + (1/\rho)\,\mathbf{P} : \nabla\mathbf{u} - \sum_i(x_i/m_i)\,\mathbf{w}_i\cdot\mathbf{F}_i \qquad (16\text{d})\end{aligned}$$

Here, $\epsilon = \sum_i x_i\epsilon_i$ and $p$, $\mathbf{P}$, and $\mathbf{q}$ equal, respectively, to the sums of $p_i$, $\mathbf{P}_i$ and $\mathbf{q}_i$. When the chemical energy $\psi_i$ is neglected, then Eq. (16d) reduces to the First Law statement of Ref. 1 [see their Eq. (36), p. 18].

Now, the specific entropy $s_i$ of our dilute system has been defined in Eq. (6). Combining with the general kinetic equation (5) yields the *entropy balance equation*:

$$(\partial/\partial t)\,\rho_is_i = -\nabla\cdot(\rho_is_i\mathbf{u}_i + \mathbf{J}_{si}) + \sigma_i \qquad (17)$$

with

$$\mathbf{J}_{si} = -k\int\mathbf{c}_if_i(\ln f_i - 1)\,d\mathbf{c}_i \qquad (17\text{a})$$

and

$$\sigma_i = -k\int\mathscr{C}_i\ln f_i\,d\mathbf{c}_i \qquad (17\text{b})$$

representing, respectively, the entropy flow vector and the entropy production rate per unit volume due to the $i$th species.

By adopting the expansions (11) and the definitions (12), we find that

$$\mathbf{J}_{si} = [(\mathbf{q}_i - \rho_i\mathbf{w}_i\tilde{\mu}_i)/T_i] + \delta\mathbf{J}_{si}\,. \qquad (18)$$

with

$$\delta \mathbf{J}_{si} = -k \int \mathbf{c}_i \phi_i^2 g_1(\phi_i) f_i^{(0)}\, d\mathbf{c}_i$$

and

$$\sigma_i = (1/T_i) \int (\tfrac{1}{2} m_i c_i^2 - m_i \tilde{\mu}_i - kT_i \phi_i)\, \mathscr{C}_i\, d\mathbf{c}_i + \delta_1 \sigma_i \tag{19}$$

where

$$\delta_1 \sigma_i = k \int \phi_i^2 g_2(\phi_i)\, \mathscr{C}_i\, d\mathbf{c}_i$$

We proceed to show that when Eqs. (13) and (17) are combined with the help of (18) and (19), all terms involving the arbitrary collision integrals will vanish in the first order. First, Eq. (15b) leads to

$$\begin{aligned} -(1/T_i) \int m_i \mu_i \mathscr{C}_i\, d\mathbf{c}_i \\ &= -(\mu_i/T_i)\, \rho (Dx_i/Dt) - \nabla \cdot (\rho_i \mathbf{w}_i \mu_i / T_i) \\ &\quad + (\rho_i \mathbf{w}_i \cdot \nabla \mu_i)/T_i + \rho_i \mu_i \mathbf{w}_i \cdot \nabla\, (1/T_i) \end{aligned} \tag{20}$$

where $\mu_i = \tilde{\mu}_i + \psi_i / m_i$ is the usual chemical potential, which can be used to define the free energy and the chemical affinity. Next, $f_i^{(0)}$ demands, upon invoking the definitions of (12) and (14), that

$$\begin{aligned} \int (f_i^{(0)} \phi_i)\, d\mathbf{c}_i &= 0 \\ \int m_i \mathbf{c}_i (f_i^{(0)} \phi_i)\, d\mathbf{c}_i &= \rho_i \mathbf{w}_i \\ \int \tfrac{1}{2} m_i c_i^2 (f_i^{(0)} \phi_i)\, d\mathbf{c}_i &= 0 \\ \int m_i \mathbf{c}_i \mathbf{c}_i (f_i^{(0)} \phi_i)\, d\mathbf{c}_i &= \mathbf{P}_i \\ \int \tfrac{1}{2} m_i c_i^2 \mathbf{c}_i (f_i^{(0)} \phi_i)\, d\mathbf{c}_i &= q_i \end{aligned} \tag{21}$$

Consequently, utilizing the operator $\mathscr{D}$ of Eq. (5) and the definition (11a), we get

$$\begin{aligned} kT_i \int \phi_i \mathscr{D} f_i^{(0)}\, d\mathbf{c}_i &= \rho_i \mathbf{w}_i \cdot [(D\mathbf{u}/Dt) - (\mathbf{F}_i/m_i) + \nabla \tilde{\mu}_i - (\tilde{\mu}_i/T_i)\, \nabla T_i] \\ &\quad + T_i^{-1} \mathbf{q}_i \cdot \nabla T_i + \mathbf{P}_i : \nabla \mathbf{u} \end{aligned} \tag{22a}$$

and

$$kT_i \int \phi_i \mathscr{C}_i\, d\mathbf{c}_i = kT_i \int \phi_i \mathscr{D} f_i^{(0)}\, d\mathbf{c}_i - T_i\, \delta_2 \sigma_i \tag{22b}$$

where

$$\begin{aligned}\delta_2\sigma_i &= -k \int \phi_i \mathscr{D}(f_i^{(0)}\phi_i)\, d\mathbf{c}_i \\ &= -k \int [\phi_i/(1+\phi_i)](\phi_i \mathscr{C}_i + f_i^{(0)}\mathscr{D}\phi_i)\, d\mathbf{c}_i \qquad (22c)\end{aligned}$$

Summarizing and combining Eqs. (13) and (17) with (18)–(22) yield, upon invoking Eq. (15e),

$$\begin{aligned}T_i(D/Dt)\, x_i s_i &= (D/Dt)\, x_i \epsilon_i + p_i(D/Dt)(x_i/\rho_i) - \mu_i(Dx_i/Dt) \\ &\quad + (T_i/\rho)[-\nabla \cdot \delta\mathbf{J}_{si} + \delta_1\sigma_i + \delta_2\sigma_i] \qquad (23)\end{aligned}$$

which is our desired entropy equation. It clearly shows that all terms involving the arbitrary collision integrals $\mathscr{C}_i$ have cancelled out each other in the first order; every term inside the bracket is connected with the $\phi_i^2$ or higher-order terms in our expansion.

For the mean fluid, Eq. (23) gives the following entropy equation, up to the first order,

$$\sum_i T_i(D/Dt)\, x_i s_i = (D\epsilon/Dt) + p(D/Dt)(1/\rho) - \sum_i \mu_i\, Dx_i/Dt \qquad (24)$$

Equation (24) is a desired extension of the Gibbsian relation (1). We have analytically derived this extension, based on the general kinetic equation (5) and for our highly nonequilibrium multispecies systems specified in Section 1.

When the systems become nonequilibrium, such that the species temperatures $T_i$ become close to each other, then Eq. (24) reduces to Eq. (1). In this way, we have obtained the desired analytical derivation of the Gibbsian relation (1) from the general kinetic equation (5). We emphasize again that only such a derivation can qualify as a thermodynamic derivation, as we have discussed in Section 1.

## 3. ENTROPY PRODUCTION RATE; RELATION BETWEEN GENERALIZED FORCES AND GENERALIZED FLUXES

Returning to our highly nonequilibrium systems, we obtain the desired expression for the entropy production rate by combining Eq. (19) with (20) and (21) to yield

$$\begin{aligned}\sigma_i &= (1/T_i)[\mathscr{T}(\epsilon_i) - \mu_i \mathscr{T}(m_i)] - (1/T_i)\, \mathbf{w}_i \cdot (\mathbf{d}_i - \rho_i\rho^{-1}\, \nabla \cdot \mathbf{P}) \\ &\quad + \mathbf{q}_i^* \cdot \nabla(1/T_i) - (1/T_i)\, \mathbf{P}_i : \nabla\mathbf{u} \qquad (25)\end{aligned}$$

where

$$\begin{aligned}\mathbf{d}_i &= \nabla p_i - \rho_i\rho^{-1}\nabla p - \rho_i(\mathbf{F}_i/m_i) + \rho_i\rho^{-1} \sum_j (\rho_j \mathbf{F}_j/m_j) \\ \mathbf{q}_i^* &= \mathbf{q}_i - \tfrac{5}{2}\,(kT_i/m_i)\, \rho_i \mathbf{w}_i\end{aligned}$$

and

$$\mathscr{T}(\epsilon_i) = \int \tfrac{1}{2} m_i c_i^2 \mathscr{C}_i \, d\mathbf{c}_i \tag{25a}$$

$$\mathscr{T}(m_i) = \int m_i \mathscr{C}_i \, d\mathbf{c}_i \tag{25b}$$

Eqs. (25a) and (25b) define, respectively, the net rate of gain or loss of the energy and the mass of the $i$th species by collisions; $\mathbf{P}$ is the negative of the usual viscous shear stress, and $\mathbf{d}_i$ is the driving force for diffusion, used in Ref. 16 but differing by a factor $p$, since $T_i = T$ in Ref. 16. Notice that in deriving Eq. (25), we have utilized the equation of motion for the mean fluid, which reads

$$\rho \, D\mathbf{u}/Dt = -\nabla p - \nabla \cdot \mathbf{P} + \sum_j \rho_j F_j/m_j \tag{26}$$

By virtue of Eq. (25), the local entropy production rate per unit volume of our highly nonequilibrium system is given by

$$\begin{aligned} \sigma &= \sum_i \sigma_i \\ &= \sum_i (1/T_i)[\mathscr{T}(\epsilon_i) - \mu_i \mathscr{T}(m_i)] \\ &\quad -\sum_i (1/T_i)\mathbf{w}_i \cdot (\mathbf{d}_i - \rho_i \rho^{-1} \nabla \cdot \mathbf{P}) \\ &\quad + \sum_i \mathbf{q}_i^* \cdot \nabla(1/T_i) - \sum_i (1/T_i)\mathbf{P}_i : \nabla\mathbf{u} \end{aligned} \tag{27}$$

With the help of Eq. (16b) and definitions (25a) and (25b), Eq. (27) will reduce to the usual form [see, for example, Eq. (21), *p.* 24 of Ref. 1] when the system becomes simply nonequilibrium with the $T_i$ nearly equal to each other.

Here, we want to emphasize that in inelastic collisions, particles can be liberated or absorbed, and radiation and transfer of energies can also be involved. Hence, we no longer can guarantee the time-reversal invariance or the microscopic reversibility from the particle equations of motion. These equations of motion may now include nonconservative forces (Ref. 17, pp. 70–72), and may depend on the past history of the particles and the energies involved in the collisions. They may become integrodifferential equations, lose the simple uniqueness property of the usual first-order differential equations, and fail to establish the microscopic reversibility. The latter property is essential (Ref. 1, p. 186) for deriving Onsager's reciprocity relations from the Boltzmann kinetic equation, and possibly, also from other kinetic equations.

Next, we want to utilize Eqs. (25) and (27) to achieve two aims: (A) we want to establish some analytical basis upon which we can postulate the general validity of the Second Law statement in the form that

$$\sigma \geqslant 0 \tag{28}$$

and (B) we want to establish relations (33), to be presented later, which will link the generalized forces to the generalized fluxes of our highly nonequilibrium systems specified in Section 1.

Here, we want to point out that our highly nonequilibrium systems are nearly *locally isotropic* in their center-of-mass reference frame, i.e., as viewed by an observer traveling with the local fluid-mean velocity **u**. This is the case because any nearly Maxwellian distribution function $f_i$ is nearly isotropic in the velocity space, and, all of our $f_i$ are nearly centered at the fluid-mean velocity **u**, as evidenced by definitions (12).

This locally isotropic property will be emphasized in our study of both Case B and Case G defined below. In both cases, we shall be concerned with our highly nonequilibrium systems, but we shall distinguish the two cases by admitting different kinds of collisions among the particles of our systems:

*Case G*: based on the *general* kinetic equation (5), i.e., admitting *arbitrary* collisions.

*Case B*: based on the *Boltzmann* equation, i.e., restricted to binary and elastic collisions.

Let us first study Case B with the aid of the results of Burgers,(13) Hirshfelder *et al.*,(16) Chapman and Cowling,(11) and Yen.(10) From the results of Burgers,(13) the stress and the heat flux equations can be written as

$$\begin{aligned}\sum_j \left(A_{ij}\mathbf{P}_i + \tilde{A}_{ij}\mathbf{P}_j\right) = p_i\{\nabla\mathbf{u}\} \\ + [(D/Dt)\,\mathbf{P}_i + \mathbf{P}_i\nabla\cdot\mathbf{u} + \nabla\cdot(\langle\rho_i\mathbf{c}_i\mathbf{c}_i\mathbf{c}_i\rangle - \tfrac{2}{3}\mathbf{q}_i\mathbf{I}) \\ + \{\mathbf{P}_i\cdot\nabla\mathbf{u}\} + \rho_i\{\mathbf{w}_i\,D\mathbf{u}/Dt\} - N_i\langle\mathbf{c}_i\mathscr{F}_i\rangle]\end{aligned} \tag{29a}$$

where

$$\{\mathbf{ab}\} = \mathbf{ab} + \mathbf{ba} - \tfrac{2}{3}\mathbf{a}\cdot\mathbf{bI}$$

and

$$\begin{aligned}&\sum_j \left[B_{ij}\mathbf{q}_i{}^* + \tilde{B}_{ij}\mathbf{q}_j{}^* + C_{ij}(\mathbf{w}_i - \mathbf{w}_j)\right] \\ &= \tfrac{5}{2}p_i\rho_i^{-1}(\mathbf{d}_i - \rho_i\rho^{-1}\nabla\cdot\mathbf{P}) + \tfrac{5}{2}(n_ik^2T_i/m_i)\,\nabla T_i \\ &\quad + \{(D/Dt)\,\mathbf{q}_i + \mathbf{q}_i\nabla\cdot\mathbf{u} + \mathbf{q}_i\cdot\nabla\mathbf{u} + \mathbf{P}_i\cdot[(D\mathbf{u}/Dt) - (\mathbf{F}_i/m_i)] \\ &\quad + \nabla\cdot(\langle\tfrac{1}{2}\rho_ic_i{}^2\mathbf{c}_i\mathbf{c}_i\rangle - \tfrac{5}{2}n_ik^2T_i{}^2/m_i) \\ &\quad + \langle\rho_i\mathbf{c}_i\mathbf{c}_i\mathbf{c}_i\rangle : \nabla\mathbf{u} - n_i\langle(\mathscr{F}_i - \mathbf{F}_i)\cdot(\mathbf{c}_i\mathbf{c}_i + \tfrac{1}{2}\mathbf{c}_i{}^2\mathbf{I})\rangle\}\end{aligned} \tag{29b}$$

Equation (29b) is the heat flux equation in its complete form; Burgers has subtracted from this equation terms equal to $\frac{5}{2}p_i/\rho_i$ times the species momentum equation. Here, $A_{ij}$, $\tilde{A}_{ij}$, etc. represent different coefficients given by Burgers. The terms inside the curly brackets are negligible, because they involve second-order quantities.(13) We proceed to prove the Second Law statement (28) for Case B.

Equation (29b) can be solved algebraically to yield the linear relations for Case B, up to the first order,

$$\mathbf{w}_i = -\alpha_i(1/T_i)[\mathbf{d}_i - (\rho_i/\rho)\,\nabla\cdot\mathbf{P}] + \sum_j \alpha_{ij}\,\nabla(1/T_j) \tag{30a}$$

and

$$\mathbf{q}_i{}^* = \sum_j \beta_{ij}(1/T_j)[\mathbf{d}_j - (\rho_j/\rho)\,\nabla\cdot\mathbf{P}] + \beta_i\nabla(1/T_i) \tag{30b}$$

They are identical to Eqs. (8.5-7) and (4.41-3) of Ref. 16 for the simpler case of binary mixtures with $\mathbf{d}_{12} = \mathbf{d}_1 - \mathbf{d}_2$ and $T_1 = T_2$. In this simpler case, the terms involving $\nabla\cdot\mathbf{P}$ should be dropped from Eqs. (30a) and (30b) since they will disappear from Eq. (25); these terms have been anticipated for Case B in general, by Eq. (7.5-12) of Ref. 16. Next, from other numerical results of Refs. 11 and 13, we also establish that $\alpha_i$ and $\beta_i$ are nonnegative, and that for case B,

$$\alpha_{ij} = \beta_{ji} \tag{31}$$

which represents a reciprocity relation of Onsager.(1) Moreover, from the results of Burgers(13) and Yen,(10) the species energy moment yields, for case B,

$$\mathscr{T}(\epsilon_i) = \sum_j \gamma_{ij}[(1/T_i) - (1/T_j)] \tag{32}$$

where $\gamma_{ij}$ is always nonnegative and has been given by Burgers and Yen. This relation is compatible with Eq. (27) and the fundamental axiom to be stated later.

Combining Eqs. (29) and (30)–(32) with Eq. (27) yields an analytical proof of the Second Law statement (28) for Case B. It is clear that the same proof works also if Case B is further restricted such that the system becomes simply nonequilibrium, or if the system contains only a simple species. Consequently, we are provided with some analytical basis for postulating that the Second Law is valid in general. We remark that this procedure does not yield a definitive statement on $\sigma_i$ for each species.

Summarizing, the above results exhibited as Eqs. (29), (30a), (30b), and (32) indicate that for Case B, each generalized flux does not depend on all of the generalized forces, and, moreover, is related only to those forces of the same tensorial rank as the flux in question. This is precisely the statement of Curie's principle (Ref. 1, p. 33), which is usually postulated to be valid for isotropic systems. The above results prove that the Curie's principle is indeed valid for the nearly locally isotropic and highly nonequilibrium systems of our Case B. Hence, we can set forth a fundamental axiom in order to study more general cases such as Case G.

*Fundamental Axiom*: The entropy production rate $\sigma$ defined by Eq. (17b) specifies the generalized forces and the generalized fluxes by admitting only *scalar* products, linear or nonlinear, of these forces with these fluxes. If the system under consideration is nearly locally isotropic, then Curie's principle will be valid; otherwise, nonlinear relations linking these forces to these fluxes will be determined through specific collision integrals.

Let us study Case G. In contrast to Case B, no such detailed result is available for Case G. We have to rely on the Fundamental Axiom, which, when applied to Eq. (27), implies that for Case G

$$\mathscr{T}(\epsilon_i) = \sum_j \alpha'_{ij}[(1/T_i) - (1/T_j)] + \mu_i \mathscr{T}(m_i) \tag{33a}$$

$$\mathbf{w}_i = \sum_j \beta'_{ij}(1/T_j)[\mathbf{d}_j - (\rho_j/\rho)\,\nabla \cdot \mathbf{P}] + \sum_j \beta''_{ij}\nabla(1/T_j) \tag{33b}$$

$$\mathbf{q}_i{}^* = \sum_j \gamma'_{ij}(1/T_j)[\mathbf{d}_j - (\rho_j/\rho)\,\nabla \cdot \mathbf{P}] + \sum_j \gamma''_{ij}\nabla(1/T_j) \tag{33c}$$

$$\mathbf{P}_i = \sum_j \delta'_{ij} p_i \{\nabla \mathbf{u}\} \tag{33d}$$

where $\alpha'_{ij}$, $\beta'_{ij}$, $\beta''_{ij}$, etc. denote unknown coefficients.

Equation (33a) displays an interesting result: The net rate of energy gain or loss by the $i$th species due to all elastic and inelastic collisions is proportional to the inverse temperature differences $(1/T_i) - (1/T_j)$, and, includes the net rate of change in the chemical potential by the liberation or absorption of $i$-type particles during inelastic collisions. So far in the literature, Eq. (33a) has not been derived for Case G from a thermodynamic consideration, although it can be deduced from a postulated model,$^{(18)}$ and it has been used in many analyses.

If both $T_i \neq T$ and $\mathbf{u}_i \neq \mathbf{u}$ for all species of our system, then the above-mentioned isotropy within the center-of-mass reference frame is destroyed. Nonlinear relations will be needed to correlate the generalized forces and fluxes. A new entropy equation as another extention of the Gibbsian relation will be derived. These will be presented in a subsequent paper.

## 4. ARBITRARY ZEROTH-ORDER DISTRIBUTION FUNCTIONS

General expressions will be obtained in this section based on entirely arbitrary zeroth-order distribution functions which can be isotropic or nonisotropic. We start from the general definitions (2), (7)–(9), and (14). In other words, we define the pressure $p_i$ as one-third of the trace of its pressure tensor. $p_i$ or $T_i$ will denote the averages of the "parallel" and the "perpendicular" pressures or temperatures if $f_i^{(0)}$ is nonisotropic.

We now extend Maxwell's iteration$^{(20)}$ as substantiated by Ikenberry and Truesdell$^{(21)}$ to multispecies systems by assuming that the diffusional effects do not appear at the zeroth order, i.e.,

$$\int (\boldsymbol{\xi}_i - \mathbf{u}) f_i^{(0)}\, d\boldsymbol{\xi}_i = 0$$

Otherwise, $p_i$ is still considered as of zeroth order while $\mathbf{P}_i$ and $\mathbf{q}_i$ are still higher-order quantities. These considerations directly establish Eqs. (21) independently of $f_i^{(0)}$. Now, the distribution functions $f_i^{(e)}$ for species at their local thermodynamic equilibrium are well-established from statistical machanics: (We use the superscript "$e$" to denote "locally thermodynamic equilibrium states"):

$$f_i^{(e)} = [\exp(m_i/kT)][\tilde{\mu}_i^{(e)} - \tfrac{1}{2}(\boldsymbol{\xi}_i - \mathbf{u})^2]$$

with

$$\begin{aligned}\tilde{\mu}_i^{(e)} &= (kT/m_i)[\ln n_i - \tfrac{3}{2}\ln(2\pi kT/m_i)]\\ &= \mu_i^{(e)} - (\psi_i/m_i)\end{aligned}$$

Following the analysis of Section 2, we obtain the general entropy equation for each species

$$\begin{aligned}T_i(D/Dt)\, x_i s_i = {} & (D/Dt)\, x_i \epsilon_i + p_i(D/Dt)(x_i/\rho_i) - \mu_i^{(e)}(Dx_i/Dt)\\ & + (kT/\rho)\, \nabla \cdot \int (\boldsymbol{\xi}_i - \mathbf{u}) f_i \ln(f_i^{(0)}/f_i^{(e)})\, d\boldsymbol{\xi}_i\\ & - (kT/\rho) \int \phi_i f_i \mathscr{D} \ln(f_i^{(0)}/f_i^{(e)})\, d\boldsymbol{\xi}_i\\ & - (kT/\rho) \int \ln(f_i^{(0)}/f_i^{(e)})\, \mathscr{C}_i\, d\boldsymbol{\xi}_i\\ & + (T/\rho)(-\nabla \cdot \delta \mathbf{J}_{si} + \delta_1 \sigma_i + \delta_2 \sigma_i) \qquad (34)\end{aligned}$$

The last line involves three higher-order terms which have been defined in Eqs. (18), (19), and (22). Equation (34) reduces to Eq. (23) when Eqs. (12) are employed to define $f_i^{(0)}$. The summation of Eq. (34) over all species gives another analytical extension of the Gibbsian relation (1).

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