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Compatibility of the Enskog-like kinetic theory with thermodynamics. II. Chemically reacting fluids

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An Enskog-like kinetic equation for chemically reacting fluids is introduced phenomenologically. It is proved that the suggested dynamical theory is compatible with thermodynamics (it includes the proof of an *H* theorem) provided one compatibility condition restricting the choice of the phenomenological quantities introduced by the proposed Enskog-like theory is satisfied. This work follows closely the similar discussion in Part I (preceding paper), where the inert fluids were discussed.

I. INTRODUCTION

The enormous success of kinetic theory for dilute systems as a result of the establishment of Boltzmann's equation has been now fully recognized.[1,2] Also, Enskog's empirical extension of this method to the case of hard sphere dense fluids has been largely accepted[3] as an adequate way of understanding the nonequilibrium properties of such systems although its mechanisitic foundations are even less understood than in Boltzmann's case. Kinetic theory, however, stands on its own and at a mesoscopic level it represents a structure from which one is able to obtain all the properties of a macroscopic system, both far away from equilibrium and in the equilibrium state, in terms of the microscopic information still contained in the first few particle distribution functions. It is almost unnecessary to emphasize that in the dilute gas case it gives a well-understood scheme of how the system evolves in time from an arbitrary initial state to its equilibrium one. The existence of this latter state can be indicated (*H* theorem), the entropy production equation is obtained as well as the features of the hydrodynamic regime and the equilibrium thermodynamics for the ideal gas is recovered. A similar study of the intrinsic consistency of the Enskog theory, that included, for example, an *H* theorem has been discussed only very recently.[4,12] Of course, one would also like to have some experimental evidence casting light on the validity of a kinetic equation. Although this may be partially accomplished by studying correlation functions of the single, pair, etc., particle distribution functions by light, neutron, and other types of scattering, direct experimental information on the particle distribution function themselves is almost too hard to obtain. Thus, the sought after validity of the theory is only evaluated via the results which are obtained, for instance, for the transport coefficients in the hydrodynamic regime, or the results which characterize the equilibrium state. The comparison of the experimental and theoretical results is thus an indication of both the validity of the chosen kinetic theory and the validity of the theoretical methods used to extract the hydrodynamic kinetic theory. There is still the additional requirement that any kinetic theory ought to be derivable from a purely mechanistic approach, i.e., Liouville's equation, but we shall not stress this point here.

After these somewhat lengthy remarks we would like to enter into the main subject of this paper, namely, that of envisaging the somewhat more complicated problem of chemical dynamics from the mesoscopic point of view. This is of course not the first time the problem is approached this way and some comments are pertinent to justify such an attempt. From the phenomenological point of view chemically reactive systems still pose a large number of unresolved questions. Among the most relevant is the fact that the macroscopic rate equations are highly nonlinear and only until very recently the features of these nonlinearities are being unveiled.[5] Also, the validity of the Arrhenius equation still by far the most trusted form of systematizing chemical data, is not clearly understood.[6] In the linear nonequilibrium regime, chemical relaxation has always been studied under the assumption that viscous effects, if present, are negligible and only until very recently[7] it has been appreciated that this may not always be true. Furthermore experimental data can be used to obtain values for the viscoreaction coefficient and the bulk viscosity, a fact that has not been duly explored. Our microscopic understanding of these questions together with those arising from considerations similar to the ones mentioned earlier in connection with the Boltzmann equations is rather poor. Boltzmann's equation itself has been proposed by several authors[8] to account for reactive collisions but so far the information extracted from it directly comparable with well established results is still quite meager. For instance, the fact that for local chemical equilibrium the chemical affinity must vanish just as it does in global equilibrium was established only a couple of years ago.[9] Also, calculation of chemical contributions to transport properties have been barred by the enormous difficulties encountered in measuring or calculating chemical cross sections. In the nondilute system very recently Dahler *et al.*[10] made the attempt of using an Enskog-type equation for studying chemical reactions but many basic questions within the realm of kinetic theory were not tackled, for instance, the unavoidable question of proving an H theorem, thus establishing the unidirectional time approach to equilibrium. Some other questions pertaining to the characteristics of the local equilibrium state are not touched, and neither is the general structure of the equations governing the equilibrium state, which we expect to be different from that of the ideal system.

This paper has been written in the spirit of giving some answers both to the formal problems related to the inherent structure of a kinetic theory and in particular to those present in a chemically reactive system where only bimolecular reactions take place and whose density is moderate enough to call for a better approximation than the one involved in the Boltzmann-like equations. There are essentially three important features in this work that ought to be stressed. Firstly, one is related to the general structure of the theory which has been also quoted earlier[11] in different contexts. A kinetic equation is proposed such that it is compatible with the body of phenomenological results known from linear irreversible and equilibrium thermodynamics. No first principle derivation of it is even attempted. Secondly, an H theorem is proved to hold true assuming the usual microscopic reversibility properties of the differential cross section. This result is valid even for velocity and orientation dependent cross sections. Thirdly, the equations governing the thermodynamic equilibrium state of the system are uniquely determined by the boundary conditions, which reflect themselves in the compatibility conditions, which the otherwise arbitrary functions entering in the kinetic equation have to satisfy. No explicit calculation for any relevant quantities are given here. This requires a great deal of space and will be presented elsewhere.

For the sake of clarity the material is divided in four sections. Section II is fully devoted to an explanation of the physical content of the proposed Enskog-like equation. In Sec. III four theorems expressing the compatibility (in the sense explained in more detail in Refs. 11 and 12) of the proposed kinetic theory with thermodynamics are proved. The proofs require one compatibility condition that restricts the choice of the phenomenological quantities entering the Enskog-like equation. The compatibility condition is then discussed in a special case in more detail in Sec. IV.

II. THE ENSKOG-LIKE EQUATION

The state of an N-component fluid will be described by a function $f:\Omega\times\mathbf{R}^3\times I\times\mathfrak{z}_N\times\mathbf{R}\to\mathbf{R}_+$, $(\vec{r},\vec{v},\xi,i,t)\to f(\vec{r},\vec{v},\xi,i,t)$. $\Omega\subset\mathbf{R}^3$ is a bounded domain in which the system considered is confined, ξ is an internal quantum number characterizing the internal degrees of freedom of the particles composing the system considered, I denotes the set of all internal quantum numbers, $\mathfrak{z}_N\equiv\{1,2,\ldots,N\}$, $i\in\mathfrak{z}_N$ labels the ith component, $\mathbf{R}_+$ denotes the positive real line, and t denotes the time. The quantity $f(\vec{r},\vec{v},\xi,i,t)$ is the number of particles of the ith component at $d\vec{v}$ around $\vec{v}$ with the internal quantum number (considered here for simplicity as a continuous parameter) at $d\xi$ around ξ at time t. We shall assume periodic boundary conditions on the boundary $\partial\Omega$ of Ω. The set of all admissible states is denoted by H. We introduce also

$$n(\vec{r},i,t)=\int d\vec{v}\int d\xi\, f(\vec{r},\vec{v},\xi,i,t)\,.$$

The equation governing the time evolution of f can be suggested by following the Enskog modification of the Boltzmann intuitive arguments.[2,10] In order to guarantee the compatibility with thermodynamics and hydrodynamics in the sense of Refs. 11 and 12, we have to make, however, some modifications that do not follow from the Enskog intuitive arguments. The time-evolution equations considered in this paper are rather complicated mathematical objects, it is therefore important to use an appropriate compact notation that simplifies the calculations. The following Enskog-like equation governing the time evolution of f will be studied in this paper:

$$\begin{aligned}\frac{\partial f}{\partial t}=-v_\alpha\partial_\alpha f+\sum_K dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\theta((w_\alpha-v_\alpha)\kappa_\alpha)\\ \times\{\epsilon_K^2(\vec{v}',\vec{w}',\vec{\kappa}',i',j')\chi_K(n;\vec{r}',\vec{R}',i',j')M_K(i',j')D_K(\vec{r}',\vec{R}',\vec{\kappa}',i',j')\exp[f^*(X')+f^*(Y')]\\ -\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)\chi_K(n;\vec{r},\vec{R},i,j)M_K(i,j)D_K(\vec{r},\vec{R},\vec{\kappa},i,j)\exp[f^*(X)+f^*(Y)]\}\,.\end{aligned}\qquad(2.1)$$

In the rest of this section we explain the notation. The properties restricting the choice of the so far unspecified quantities entering (2.1) that are introduced in the rest of this section are the most general properties allowing to prove the compatibility of the dynamic theory based on (2.1) with thermodynamics (in the sense introduced in Ref. 12) and allowing to consider the usual Enskog equation discussed in Ref. 12 as well as the equations discussed in Ref. 10 as particular cases of (2.1). It will be clear that a particular case of (2.1) is the usual Enskog equation; the equations discussed in Ref. 10 are also particular examples of (2.1).

Whenever it is possible, we use $X\equiv(\vec{r},\vec{v},\xi,i)$, $Y\equiv(\vec{R},\vec{w},\eta,j)$, $\int dY\equiv\sum_{j=1}^{N}\int_{\Omega}d\vec{R}\int d\vec{w}\int d\eta$; $\partial_\alpha=\partial/\partial r_\alpha$, $a_\alpha b_\alpha\equiv\sum_{\alpha=1}^{3}a_\alpha b_\alpha$; κ is a unit vector, $K=1,2,3,\ldots$ labels the type of interaction during the collisions. We adopt the convention that if $K=1$ the collisions are elastic, if $K=2$ the collisions are inelastic, and if $K=3,4,\ldots$ chemical bimolecular reactions occur during the collisions. The function θ is the step function, $\theta(x)=1$ if $x\geqslant 0$, $\theta(x)=0$ if $x<0$.

By T_K we denote the transformation $(X,Y,\kappa)\rightleftarrows(X',Y',\vec{\kappa}')$, where $X'\equiv(\vec{r}',\vec{v}',\xi',i')$, $Y'\equiv(\vec{R}',\vec{w}',\eta',j')$. If two particles, one with coordinates X, the other with coordinates Y collide, their coordinates after the collision are X', Y'. We shall assume that T_K satisfies the following properties:

(a) T_K is one to one, $T_K^2=\hat{1}$ ($\hat{1}$ denotes the identity transformation) and thus the absolute value of the Jacobian of T_K equals one.

(b) In the case of elastic and inelastic collisions $i'=i, j'=j$; in the case of, for example, the chemical reaction $1+2\rightleftarrows 3+4$, $1'=3$, $2'=4$, $3'=1$, $4'=2$.

(c) $\vec{r}'=\vec{r}+\tau_K(\vec{r},\vec{R},i,j)$, $\vec{R}'=\vec{R}+\tau_K(\vec{r},\vec{R},i,j)$; τ_K satisfies the following property:

$$\tau_K(\vec{r}',\vec{R}',i',j')=-\tau_K(\vec{r},\vec{R},i,j)\,,$$

if $i'=i, j'=j$, then $\tau\equiv 0$. Thus in the case of the elastic and inelastic collisions $\vec{r}'=\vec{r}$, $\vec{R}'=\vec{R}$, in the case of a chemical reaction, the particle of the type i at $\vec{r}$ and the particle of the type j at $\vec{R}$ react and emerge as new particles, the particles of the type i', at $\vec{r}'$, the particle of the type j' at $\vec{R}'$.

(d) In the case of elastic collision $\xi'=\xi$, $\eta'=\eta$, $v'_\alpha=v_\alpha+(2\mu_{ij}/m_i)(w_\gamma-v_\gamma)\kappa_\gamma\kappa_\alpha$, $w'_\alpha=w_\alpha-(2\mu_{ij}/m_i)\times(w_\gamma-v_\gamma)\kappa_\gamma\kappa_\alpha$, $\kappa'_\alpha=-\kappa_\alpha$; $(\mu_{ij})^{-1}=(m_i)^{-1}+(m_j)^{-1}$; m_i is the mass of the particle of the ith component. In the case of inelastic collisions and reactive collisions the relations are more general. The following properties are, however, always satisfied: (i) $(w_\alpha-v_\alpha)\kappa_\alpha=(w'_\alpha-v'_\alpha)\kappa'_\alpha$; (ii) let $\tilde{J}(X,Y,\vec{\kappa})=(\vec{r},-\vec{v},\xi,i,\vec{R},-\vec{w},\eta,j,-\vec{\kappa})$, the transformations T_K and $\tilde{J}$ commute; (iii) a constant, $m_i\vec{v}+m_j\vec{w}$ and $\frac{1}{2}m_iv^2+\frac{1}{2}m_jw^2+e(\xi,i)+e(\eta,j)$ are the complete set of invariants of T_K; $e(\xi,i)$ is the inner energy of the particle of the ith component associated with the value ξ of the internal quantum number.

The quantity $\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)$ denotes the cross section of the binary collision. We shall assume that $\epsilon_K^2>0$,

$$\epsilon_K^2(\vec{v}',\vec{w}',\vec{\kappa}',i',j')=\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)$$

and

$$\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)=\epsilon_K^2(\vec{w},\vec{v},-\vec{\kappa},j,i)\,.$$

The quantities $\chi_K(n;\vec{r},\vec{R},i,j)$ are introduced in the Enskog-like equation (2.1) to account for the short-range correlation between two particles. They are assumed to be functionals of $n(\vec{r},i)$, $n(\vec{R},j)$, they are always positive and in addition

$$\begin{aligned}\chi_K(n;\vec{r},\vec{R},i,j)&=\chi_K(n;\vec{r}'\vec{R}',i',j')\\&=\chi_K(n;\vec{R},\vec{r},j,i)\,.\end{aligned}$$

If $K=1$ and $K=2$ then $M_K(i,j)=1$ for all $i,j=1,\ldots,N$. In the case of a chemical reaction, say $1+2\rightleftarrows 3+4$,

$$M_K(i,j)=\begin{bmatrix}0&1&0&0&0\ldots0\\1&0&0&0&0\ldots0\\0&0&0&1&0\ldots0\\0&0&1&0&0\ldots0\\\cdot&&&&\\\vdots&&&&\\0&0&0&0&0\ldots0\end{bmatrix}\,. \tag{2.2}$$

For any K, it is always true that $M_K(i,j)=M_K(j,i)$ and $M_K(i,j)=M_K(i',j')$.

The quantity D_K takes care of the relation between the positions of the ith particle at $\vec{r}$ and the jth particle at $\vec{R}$ during the collision. In the case of the elastic collision $D_1(\vec{r},\vec{R},\vec{\kappa},i,j)=\delta((\vec{R}-\vec{r}+\frac{1}{2}(\epsilon_i+\epsilon_j)\vec{\kappa})$, δ denotes the Dirac delta function and ϵ_i is the diameter of the particle of the ith component. We shall always assume that (i) $D_K(\vec{r}',\vec{R},\vec{\kappa}',i',j')=D_K(\vec{r},\vec{R},-\vec{\kappa},i,j)$, (ii) $D_K(\vec{R},\vec{r},\vec{\kappa},j,i)=D_K(\vec{r},\vec{R},-\vec{\kappa},i,j)$ holds for all K; moreover, $D_K(\vec{r},\vec{R},\vec{\kappa},i,j)\geqslant 0$ for all $K,\vec{r},\vec{R},\vec{\kappa},i,j$.

The function $f^*(X)$ is related to $f(X)$ by $f^*(X)=\delta S(f)/\delta f(X)$, where S is an arbitrary sufficiently regular function of f except that $f\rightarrow f^*$ is one to one and $S(Jf)=S(f)$, where $Jf(\vec{r},\vec{v},\xi,i)=f(\vec{r},-\vec{v},\eta,i)$. If, for example,

$$S=\int dX f(X)[\ln f(X)-1]+Q(n)\,, \tag{2.3}$$

where Q depends only on $n(\vec{r},i)=\int d\vec{v}\int d\xi\, f(X)$ and the second derivative of Q with respect to n is always positive, then S satisfies the above requirements and, moreover, $\exp[f^*(X)+f^*(Y)]=B(n)\times f(X)f(Y)$;

$$B(n)=\exp\left(\frac{\delta Q}{\delta n(\vec{r},i)}+\frac{\delta Q}{\delta n(\vec{R},j)}\right).$$

If for some reasons we can consider Q as small (as we shall see in the next section the quantity S that we shall consider will be indeed as in (2.3), where $Q\sim\epsilon^3$; ϵ is a small parameter of the order of the diameter of the particles), then by neglecting the small terms ($\sim\epsilon^k$, $k>3$) we recover the usual Enskog equation. The importance and necessity of the ansatz according to which $f(X)f(Y)$ in the collision term is replaced by $\exp[f^*(X)+f^*(Y)]$ becomes evident during the discussion of the Enskog-like equation in Sec. III. There are also arguments developed by van Kampen[13] that can be used to justify the ansatz.

All the quantities introduced in (2.1) (i.e., ϵ_K^2, χ_K, M_K, D_K, S) must satisfy the properties introduced above but otherwise are arbitrary. We shall show in Sec. III that if in addition they satisfy the compatibility condition (3.6) then the dynamical theory defined by (2.11) is compatible with thermodynamics in the sense of Refs. 11 and 12. This will be our main result and we shall not go further. The more detailed specification of $(\epsilon_K^2, \chi_K, M_K, D_K, S)$ can be found either by comparing some consequences of (2.1) with experimental results or by comparing some consequences of (2.1) with other theories [e.g., the thermodynamic equation state implied by (2.1), see (3.13), can be compared with the thermodynamic equation of state obtained by following Gibb's recipe-equilibrium statistical mechanics—and in this way we can relate the quantities entering (2.1) to the quantities entering the Gibbs theory].

III. COMPATIBILITY OF THE ENSKOG-LIKE EQUATION WITH THERMODYNAMICS

We shall follow the structure of the discussion of the compatibility of a dynamical theory with thermodynamics established in paper I.[12] Mainly the new features appearing due to occurrence of chemical reactions will be pointed out. For the same reasons as in Ref. 12, we introduce the involution $J:\mathcal{H}\to\mathcal{H}$ by $f(\vec{r},\vec{v},\xi,i)\xrightarrow{J}f(\vec{r},-\vec{v},\xi,i)$; $J\circ J$ is the identity operator. The involution J splits the right-hand side of (2.1), denoted formally as $\mathcal{R}(f)$ into two parts $\mathcal{R}^{\pm}(f)=\frac{1}{2}[\mathcal{R}(f)\pm J\mathcal{R}(Jf)]$ and $\mathcal{R}(f)=\mathcal{R}^{+}(f)+\mathcal{R}^{-}(f)$. We observe that

$$\mathcal{R}^{+}(f)=\sum_K\int dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\theta((w_\alpha-v_\alpha)\kappa_\alpha)\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)\chi_K(n;\vec{r},\vec{R},i,j)M_K(i,j)$$
$$\times D_K^{+}(\vec{r},\vec{R},\vec{\kappa},i,j)\{\exp[f^*(X')+f^*(Y')]-\exp[f^*(X)+f^*(Y)]\}\,. \tag{3.1}$$

$$\mathcal{R}^{-}(f)=-v_\alpha\partial_\alpha f+\tfrac{1}{2}\sum_K\int dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)\chi_K(n;\vec{r},\vec{R},i,j)M_K(i,j)$$
$$\times D_K^{-}(\vec{r},\vec{R},\vec{\kappa},i,j)\{\exp[f^*(X')+f^*(Y')]+\exp[f^*(X)+f^*(Y)]\}\,, \tag{3.2}$$

where

$$D_K^{\pm}(\vec{r},\vec{R},\vec{\kappa},i,j)=\tfrac{1}{2}[D_K(\vec{r},\vec{R},-\vec{\kappa},i,j)\pm D_K(\vec{r},\vec{R},\vec{\kappa},i,j)]\,.$$

Let S be the functional of f satisfying the two properties introduced in the previous section [S is not necessarily defined by (2.3)]. Let $dS/dt\,|_+$ denote the change of S in time if only $\mathcal{R}^{+}(f)$ generates the time evolution.

Theorem III.1.

$$\left.\frac{dS}{dt}\right|_+=\int dX\, f^*(X)\mathcal{R}^{+}(f)\leqslant 0\,. \tag{3.3}$$

The equality in (3.3) holds if and only if

$$f\in\tilde{\mathcal{E}}_+=\{f\in\mathcal{H}\,|\,\mathcal{R}^{+}(f)=0\}=\{f\in\mathcal{H}\,|\,f^*(X)|=a(\vec{r},i)-b[\tfrac{1}{2}m_i v^2+e(\xi,i)]+c_\alpha m_i v_\alpha\}\,,$$

the functions $a(\vec{r},i)$ are arbitrary except that they have to satisfy $M_K(i,j)[a(\vec{r}',i')+a(\vec{R}',j')-a(\vec{r},i)-a(\vec{R},j)]=0$ for all i,j,K; b and c_α, $(a=1,2,3)$ are constants.

Proof. Two transformations $X\rightleftharpoons Y$, $\vec{\kappa}\to-\vec{\kappa}$ and $(X,Y,\vec{\kappa})\rightleftharpoons(X',Y',\vec{\kappa}')$ applied subsequently lead to

$$\left.\frac{dS}{dt}\right|_{+}=\frac{1}{4}\sum_K\int dX\int dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\theta((w_\alpha-v_\alpha)\kappa_\alpha)\epsilon_K^2(\vec{v},\vec{w},\kappa,i,j)\chi_K(n;\vec{r},\vec{R},i,j)$$
$$\times M_K(i,j)D_K^{+}(\vec{r},\vec{R},\vec{\kappa},i,j)\{(f^*(X)+f^*(Y)]-[f^*(X')+f^*(Y')]\}\tag{3.4}$$
$$\times\{\exp[f^*(X')+f^*(Y')]-\exp[f^*(X)+f^*(Y)]\}\,.$$

We put $x=[f^*(X')+f^*(Y')]$, $y=[f^*(X)+f^*(Y)]$ and use the inequality $(y-x)(e^x-e^y)\leq 0$; the equality holds if and only if $x=y$. In order to solve the equation $x=y$, we use the complete set of invariants of the transformations T_K, Q.E.D.

We shall assume now that S is defined by (2.3). Thus $f^*(X)=\ln f(X)+q(n;\vec{r},i)$ where $q(n;\vec{r},i)=\delta Q/\delta n(\vec{r},i)$. Consequently

$$\tilde{\mathcal{E}}_+=\{f\in\mathcal{H}\,|\,f(X)=n(\vec{r},i)\exp(\mathfrak{N}-b[\tfrac{1}{2}m_iv^2+e(\xi,i)]+c_\alpha m_iv_\alpha)\}\,,\tag{3.5}$$

where $\mathfrak{N}$ is determined by the requirement $\int d\vec{v}\int d\xi f(X)=n(\vec{r},i)$, and $n(\vec{r},i)$ satisfy the relations $M_K(i,j)[a(\vec{r}',i')+a(\vec{R}',j')-a(\vec{r},i)-a(\vec{R},j)]=0$ for all i,j,K; $a(\vec{r},i)=\mathfrak{N}+q(n;\vec{r},i)+\ln n(\vec{r},i)$. Note that if one considers only elastic collisions then $i'=i$, $j'=j$, $\vec{r}'=\vec{r}$, $\vec{R}'=\vec{R}$, always and therefore the additional constraint on $a(\vec{r},i)$ is a trivial identity.

Theorem III.2. Let $Q(n)$ introduced in (2.3) be related to the quantities $(\epsilon_K^2,\chi_K,M_K,D_K)$ by

$$-v_\alpha\partial_\alpha q(n;\vec{r},i)=\sum_K\int dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)\chi_K(n;\vec{r},\vec{R},i,j)M_K(i,j)$$
$$\times D_K^{-}(\vec{r},\vec{R},\vec{\kappa},i,j)f(Y)\exp[q(n;\vec{r},i)+q(n;\vec{R},j)]\,,\tag{3.6}$$

where

$$q(n;\vec{r},i)=\frac{\delta Q}{\delta n(\vec{r},i)}\,.$$

Then the solution to the problem

$$f\in\mathcal{E}_+,\quad\text{where}\quad\mathcal{E}_+=\{f\in\tilde{\mathcal{E}}_+\,|\,f=Jf\}\,,$$
$$\mathcal{R}^-(f)\,|_{\mathcal{E}_+}=0\,,\tag{3.7}$$

subject to the boundary conditions

$$f^*\,|_{\partial\Omega}=-\tfrac{1}{2}\sigma_1(m_iv^2+e(\xi,i))-\sigma_2(i)\,,$$

where $\sigma_1,\sigma_2(i),i=1,\ldots,N$, are constants satisfying

$$M_K(i,j)[\sigma_2(i)+\sigma_2(j)-\sigma_2(i')-\sigma_2(j')]=0$$

for all K,i,j, (i.e., the thermodynamic equilibrium states $\mathcal{E}$ according to the definition in Refs. 12 and 11) are equivalent to the solutions of

$$\frac{\delta W}{\delta f(\vec{r},\vec{v},\xi,i)}=0\,,\tag{3.8}$$

where

$$W=S+\sigma_1\mathfrak{e}_1+\sum_{i=1}^{N}\sigma_2(i)\mathfrak{e}_2(i)\,,$$

$$\mathfrak{e}_1=\int dX[\tfrac{1}{2}m_iv^2+e(\xi,i)]f(X)\,,\tag{3.9}$$

$$\mathfrak{e}_2(i)=\int d\vec{v}\int_\Omega d\vec{r}\int d\xi f(X)\,.$$

Proof. We note first that $\tilde{\mathcal{E}}_+$ with $\vec{c}\equiv 0$ is exactly $\mathcal{E}_+$. By inserting $f(X)=n(\vec{r},i)\exp[\mathfrak{N}-\sigma_1(\tfrac{1}{2}m_iv^2+e(\xi,i))]$ into $\mathcal{R}^-(f)=0$ and by using (3.5) and (3.6), we obtain

$$-v_\alpha\partial_\alpha\left(\ln n(\vec{r},i)+\frac{\delta Q}{\delta n(\vec{r},i)}\right)=0\,.\tag{3.10}$$

Assuming the boundary conditions (3.7), the solutions to (3.10) are equivalent to the solutions of

$$\frac{\delta\mathcal{V}}{\delta n(\vec{r},i)}=0\,,$$

where

$$\mathcal{V}=\sum_{i=1}^{N}\int_\Omega d\vec{r}\,n(\vec{r},i)[\ln n(\vec{r},i)-1]+Q(n)\,.\tag{3.11}$$

The additional constraint on $n(\vec{r},i)$ appearing in the definition of $\tilde{\mathcal{E}}_+$ [see (3.5)] is clearly satisfied if the N constants $\sigma_2(i)$ are not independent but satisfy

$$M_K(i,j)[\sigma_2(i)+\sigma_2(j)-\sigma_2(i')-\sigma_2(j')]=0 \tag{3.12}$$

for all K,i,j.

We extend now the function $\mathcal{V}$ defined only on $\mathcal{E}_+$ into the function W defined on $\mathcal{H}$ such that $W|_{\mathcal{E}_+}=\mathcal{V}$ and the solutions to $\delta W/\delta f=0$ are equivalent to (3.7). The function W introduced in (3.9) is clearly such a function. Q.E.D.

According to the discussion in Paper I, solutions to (3.7) are the equilibrium states studied by thermodynamics. Let us denote all the equilibrium states by $\mathcal{E}$. If we define

$$\sigma_{N+2}=-k_B\frac{1}{\omega}\,W|_{\mathcal{E}}\,, \tag{3.13}$$

where k_B is the Boltzmann constant and ω denotes the volume of Ω, then since

$$\frac{\partial\sigma_{N+2}}{\partial\sigma_1}=-\frac{1}{\omega}c_1|_{\mathcal{E}}\,,\quad \frac{\partial\sigma_{N+2}}{\partial\sigma_2(i)}=\frac{1}{\omega}c_2(i)|_{\mathcal{E}}\,,$$

we obtain $\sigma_1=1/T$ (T is the temperature), $\sigma_2(i)=-\mu_i/T$ (μ_i is the chemical potential of the ith component), and $\sigma_{N+2}=p/T$ (p is the pressure). The constraint (3.12) is the familiar constraint expressing that affinity associated with the chemical reaction of the type K equals zero. It is interesting to note that the appearance of chemical reactons changes W [see (3.6)] and therefore [see (3.13)] also the thermodynamical equation of state. Thus, not only the constraint (3.12) changes the thermodynamical relations of chemically reacting components, but also the dependence of p/T on $1/T$ and μ_i/T itself is changed if the components react chemically. In order to find more explicitly how the thermodynamic equation of state is influenced by the chemical reactions the relation (3.6) must be considered in detail. A special case is discussed in Sec. IV.

We note that if we would use in (2.1) $f(X)f(Y)$ instead of $\exp[f^*(X)+f^*(Y)]$, then it would be impossible to relate the constraint due to the chemical reaction that would appear in specification of $\bar{\mathcal{E}}_+$, to the constraint (3.12) (except, of course, in the Boltzmann theory whereas we have already pointed out there is no difference between the collision operator with $f(X)f(Y)$ and with $\exp[f^*(X)+f^*(Y)]$ since $Q\equiv 0$ in (2.3)).

Theorem III.3. Let (3.6) be satisfied. Moreover, let

$$f_0(\vec{r},\vec{v},\xi,i)=n_0(i)\exp[\mathfrak{N}-\sigma_1(\tfrac{1}{2}m_iv^2+e(\xi,i))]$$

be an equilibrium state [i.e., solution to (3.7) or equivalently to (3.8)] such that $n_0(i)$ is independent of $\vec{r}$ and $A=D^2W|_{f_0}$ (i.e., the second derivative of W with respect to f evaluated at f_0). Thus $W=W_0+(\varphi,A\varphi)+\theta(\varphi^3)$, where $W_0=W|_{f_0}$, $f(X)=f_0(X)[1+\varphi(X)]$, (,) denotes the L_2 inner product. We shall denote by P the linear part of $\mathfrak{R}$ (the linearization around f_0), and $P^\pm$ is the linear part of $\mathfrak{R}^\pm$.

Then P^+ is formally self-adjoint and dissipative with respect to the inner product $(.,A.)$ [i.e., $(\varphi,AP^+\varphi)\leq 0$ for all φ in the domain of P^+], and P^- is formally skew-adjoint with respect to the same inner product $(.,A.)$.

Proof. We observe that $A\varphi(X)=A_1\varphi(X)-A_2\varphi(X)$, where $A_1\varphi(X)=f_0(X)\varphi(X)$ and $A_2\varphi(X)=\int dYA(X,Y)\varphi(Y)$,

$$A(X,Y)=f_0(X)f_0(Y)\,\frac{\delta^2Q}{\delta n(\vec{r},i)\delta n(\vec{R},j)}\bigg|_{f_0}\,.$$

By following the proof of Theorem III.1 one finds easily that AP^+ is formally self-adjoint and dissipative with respect to the inner product (., .). The operator A_2 does not enter the discussion. We shall proceed to prove that AP^- is formally skew-adjoint:

$$P^-\varphi(X)=P_1\varphi(X)+P_2\varphi(X)\,,$$

$$P_1\varphi(X)=-v_\alpha\partial_\alpha\varphi(X)$$

$$P_2\varphi(X)=P_{21}\varphi(X)+P_{22}\varphi(X)+P_{23}\varphi(X)+P_{24}\varphi(X)+P_{25}\varphi(X)\,,$$

$$P_{21}\varphi(X)=\tfrac{1}{2}\sum_K\int dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\,\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)M_K(i,j)D_K^-(\vec{r},\vec{R},\vec{\kappa},i,j)$$

$$+f_0(Y)\chi_{K0}(n;\vec{r},\vec{R},i,j)\,e^{[q_0(n;\vec{r},i)+q_0(n;\vec{R},j)]}\varphi(X')\,,$$

where

$$
\begin{aligned}
&q_0(n;\vec{r},i)=\left.\frac{\delta Q}{\delta n(\vec{r},i)}\right|_{f_0}, \quad \chi_{K0}=\chi_K|_{f_0},\\
&P_{22}\varphi(X)=\tfrac{1}{2}\sum_K\int dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\chi_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)M_K(i,j)D_K^-(\vec{r},\vec{R},\vec{\kappa},i,j)\\
&\qquad\qquad +f_0(Y)\chi_{K0}(n;\vec{r},\vec{R},i,j)\exp[q_0(n;\vec{r},i)+q_0(n;\vec{R},j)]\varphi(Y'),\\
&P_{23}\varphi(X)=\tfrac{1}{2}\sum_K\int dY\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)M_K(i,j)D_K^-(\vec{r},\vec{R},\vec{\kappa},i,j)\\
&\qquad\qquad +f_0(Y)\chi_{K0}(n;\vec{r},\vec{R},i,j)\exp[q_0(n;\vec{r},i)+q_0(n;\vec{R},j)]\varphi(Y),\\
&P_{24}\varphi(X)=\sum_K\int dY\int dZ\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)M_K(i,j)D_K^-(\vec{r},\vec{R},\vec{\kappa},i,j)\\
&\qquad\qquad +f_0(Y)f_0(Z)\exp[q_0(n;\vec{r},i)+q_0(n;\vec{R},j)]\chi_{K0}'(n;\vec{r},\vec{R},\vec{\rho},i,j,k)\varphi(Z),\\
&Z=(\vec{\rho},\vec{\nu},\xi,k),\quad \chi_{K0}'(n;\vec{r},\vec{R},\vec{\rho},i,j,k)=\left.\frac{\delta\chi_K(n;\vec{r},\vec{R},i,j)}{\delta n(\vec{\rho},k)}\right|_{f_0},\\
&P_{25}\varphi(X)=\sum_K\int dY\int dZ\int d\vec{\kappa}(w_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{w},\vec{k},i,j)M_K(i,j)D_K^-(\vec{r},\vec{R},\vec{\varkappa},i,j)\\
&\qquad\qquad +f_0(Y)f_0(Z)\exp[q_0(n;\vec{r},i)+q_0(n;R,j)]\chi_{K0}(n;\vec{r},\vec{R},i,j)\\
&\qquad\qquad \times[q_0'(n;\vec{r},\vec{\rho},i,k)+q_0'(n;\vec{R},\vec{\rho},j,k)]\varphi(Z),\\
&q_0'(n;\vec{r},\vec{\rho},i,k)=\frac{\delta q(n;\vec{r},i)}{\delta n(\vec{\rho},k)}\,.
\end{aligned}
\tag{3.14}
$$

By using $\int dX\mathfrak{R}_E(f)=0$, where $\mathfrak{R}(f)=-v_\alpha\partial_\alpha f+\mathfrak{R}_E(f)$, we obtain $AP^-=A_1P_1+A_1P_2-A_2P_1$. Straightforward verification shows that $A_1P_1, A_1P_{21}, A_1P_{22}$ are separately formally skew-adjoint operators. It remains to prove that $A_1P_{23}+A_1P_{24}+A_1P_{25}-A_2P_1$ is a formally skew-adjoint operator. We shall differentiate (3.6) with respect to $n(\vec{R},j)$. We obtain

$$
-v_\alpha\frac{\partial}{\partial r_\alpha}\left.\frac{\delta^2 Q}{\delta n(\vec{r},i)\delta n(\vec{R},j)}\right|_{f_0}=B_1+B_2+B_3,
\tag{3.15}
$$

$$
\begin{aligned}
B_1=&\sum_K\int d\vec{w}\int d\eta\int d\vec{\kappa}\,(w_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,j)\chi_{K0}(n;\vec{r},\vec{R},i,j)D_K^-(\vec{r},\vec{R},\vec{\kappa},i,j)\\
&\qquad\times M_K(i,j)\exp[q_0(n;\vec{r},i)+q_0(n,\vec{R},j)]\exp[\mathfrak{N}-b(\tfrac{1}{2}m_jw^2+e(\eta,j)],\\
B_2=&\sum_K\int dZ\int d\vec{\kappa}(\nu_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{w},\vec{\kappa},i,k)D_K^-(\vec{r},\vec{\rho},\vec{\kappa},i,k)M_K(i,k)f_0(Z)\\
&\qquad\times\exp[q_0(n;\vec{r},i)+q_0(n;\vec{\rho},k)]\chi_{K0}'(n;\vec{r},\vec{\rho},\vec{R},i,k,j),\\
B_3=&\sum_K\int dZ\int d\vec{\kappa}\,(\nu_\alpha-v_\alpha)\kappa_\alpha\epsilon_K^2(\vec{v},\vec{\nu},\vec{\kappa},i,k)\chi_{K0}(n;\vec{r},\vec{\rho},i,k)D_K^-(\vec{r},\vec{\rho},\vec{\kappa},i,k)\\
&\qquad\times M_K(i,k)f_0(Z)\exp[q_0(n;\vec{r},i)+q_0(\vec{\rho},k)][q_0'(n;\vec{r},\vec{R},i,j)+q_0'(n;\vec{\rho},\vec{R},k,j)]\,.
\end{aligned}
$$

The expression $(\psi,A_2P_1\varphi)$ is equal to

$$
\begin{aligned}
-(\psi,A_2P_1\varphi)&=\int dX\int dY f_0(X)f_0(Y)\frac{\delta^2 Q}{\delta n(\vec{r},i)\delta n(\vec{R},j)}w_\alpha\psi(X)\frac{\partial}{\partial R_\alpha}\varphi(Y)\\
&=-\int dX\int dY\,f_0(X)f_0(Y)\frac{\partial}{\partial R_\alpha}\left.\frac{\delta Q}{\partial n(\vec{r},i)\delta n(\vec{R},j)}\right|_{f_0}w_\alpha\psi(X)\varphi(Y)\,.
\end{aligned}
\tag{3.16}
$$

The second equality in (3.16) was obtained by integrating by parts. It follows from (3.16), (3.15), and (3.14) that indeed $A_1P_{23}+A_1P_{24}+A_1P_{25}-A_2P_1$ is a formally skew-adjoint operator. Q.E.D.

The three previous theorems imply that $dW/dt\leqslant 0$, provided the time evolution is governed only by the linearized Enskog-like kinetic equation $\partial\varphi/\partial t = P\varphi$ and the terms proportional to φ^k, $k \geq 3$ are neglected. We can prove, however, independently, following the idea of Resibois,[14] that $dW/dt \leq 0$ provided only (3.16) is satisfied.

Theorem III.4. Let (3.6) be satisfied. Then

$$dW/dt \leq 0\,. \tag{3.17}$$

The equality in (3.17) holds if and only if $f \in \tilde{\mathcal{S}}_+$. The quantity W is defined in (3.9) and $\tilde{\mathcal{S}}_+$ is introduced in Theorem III.1.

Proof. It is clear that $d\mathcal{C}_1/dt = 0$ and $d/dt\sum_i \sigma_2(i)\mathcal{C}_2(i) = 0$. It remains to prove that

$$\frac{dS}{dt} = \int dX f^*(X)[-v_\alpha \partial_\alpha f(X)] + \int dX f^*(X)\mathcal{R}_E(f) \leq 0\,. \tag{3.18}$$

The second term in (3.18) is equal to

$$\begin{aligned}\sum_K \int dX \int dY \int d\vec{\kappa}\,(w_\alpha - v_\alpha)\kappa_\alpha \theta((w_\alpha - v_\alpha)\kappa_\alpha)\epsilon_K^2(\vec{\mathrm{v}},\vec{\mathrm{w}},\vec{\kappa},i,j)\chi_K(n;\vec{\mathrm{r}},\vec{\mathrm{R}},i,j)M_K(i,j)\\ \times D_K(\vec{\mathrm{r}}',\vec{\mathrm{R}}',\vec{\kappa}',i',j')f^*(X)\exp[f^*(X)+f^*(Y')]\\ -\sum_K \int dX \int dY \int d\vec{\kappa}\,(w_\alpha - v_\alpha)\kappa_\alpha \theta((w_\alpha - v_\alpha)\kappa_\alpha)\epsilon_K^2(\vec{\mathrm{r}},\vec{\mathrm{R}},\vec{\kappa},i,j)f^*(X)\exp[f^*(X)+f^*(Y)]\,.\end{aligned} \tag{3.19}$$

We rewrite the first term in (3.19) by using the transformations $(X,Y,\vec{\kappa}) \rightleftharpoons (X',Y',\vec{\kappa}')$ and $X \rightleftharpoons Y, \vec{\kappa} \to -\vec{\kappa}$, both terms are then rewritten by using the transformation $X \rightleftharpoons Y, \vec{\kappa} \to -\vec{\kappa}$. We show that the second term in (3.18) is equal to

$$\begin{aligned}\tfrac{1}{2}\sum_K \int dX \int dY \int d\vec{\kappa}\,(w_\alpha - v_\alpha)\kappa_\alpha \theta((w_\alpha - v_\alpha)\kappa_\alpha)\epsilon_K^2(\vec{\mathrm{v}},\vec{\mathrm{w}},\vec{\kappa},i,j)\chi_K(n;\vec{\mathrm{r}},\vec{\mathrm{R}},i,j)M_K(i,j)\\ \times \chi_K(n;\vec{\mathrm{r}},\vec{\mathrm{R}},\vec{\kappa},i,j)[f^*(X')+f^*(Y')-f^*(X)-f^*(Y)]\exp[f^*(X)+f^*(Y)]\,.\end{aligned} \tag{3.20}$$

By using the inequality $e^x(y-x) \leq e^y - e^x$ (setting $x = [f^*(X)+f^*(Y)]$), $y = [f^*(X')+f^*(Y')]$ we have

$$\begin{aligned}\int dX f^*(X)\mathcal{R}_E(f) \leq \tfrac{1}{4}\sum_K \int dX \int dY \int d\vec{\kappa}\,(w_\alpha - v_\alpha)\kappa_\alpha \epsilon_K^2(\vec{\mathrm{v}},\vec{\mathrm{w}},\vec{\kappa},i,j)\chi_K(n;\vec{\mathrm{r}},\vec{\mathrm{R}},i,j)\\ \times M_K(i,j)D_K(\vec{\mathrm{r}},\vec{\mathrm{R}},\vec{\kappa},i,j)\{\exp[f^*(X')+f^*(Y')] - \exp[f^*(X)+f^*(Y)]\}\,.\end{aligned} \tag{3.21}$$

By using (3.6), we show that $\int dX f^*(X) v_\alpha \partial_\alpha f(X)$ is equal to the right-hand side of (3.21) and thus $dS/dt \leq 0$ and also $dW/dt \leq 0$. Q.E.D.

IV. A PARTICULAR FORM OF THE COMPATIBILITY CONDITION (3.6)

Theorems III.2–III.4 require the validity of the compatibility condition (3.6) that restricts the freedom in the choice of the quantities $(\epsilon_K^2, \chi_K, M_K, D_K)$ entering phenomenologically into the Enskog-like equation (2.1), and relates these quantities to $Q(n)$ which forms part of the nonequilibrium entropy S. We shall now discuss the compatibility condition (3.6) in more detail for a special case. Assuming that ϵ_K^2 is independent of $\vec{\mathrm{v}},\vec{\mathrm{w}},\vec{\kappa}$ we denote $\epsilon_K^2 = \epsilon_{K,ij}^2$ and furthermore set $\epsilon_{K,ij}^2 \sim \epsilon$, where ϵ is a small number. Only the terms proportional to 1, ϵ, ϵ^2, ϵ^3 will be considered. The quantity $\tilde{D}_K$ is assumed to depend only on $\vec{\mathrm{l}} = \vec{\mathrm{r}} - \vec{\mathrm{R}}$. Then the compatibility condition (3.6) implies

$$\begin{aligned}\frac{\partial}{\partial r_\alpha}\,\frac{\delta Q}{\partial n(\vec{\mathrm{r}},i)} = \sum_K \sum_j \epsilon_{K,ij}^2 \int d\vec{\mathrm{l}} \int d\vec{\kappa}\,\kappa_\alpha \tilde{D}_K(\vec{\mathrm{l}},\vec{\kappa},i,j)M_K(i,j)\\ \times \tilde{\chi}_K(n;\vec{\mathrm{r}},\vec{\mathrm{l}},i,j)n(\vec{\mathrm{r}}-\vec{\mathrm{l}},j)\,,\end{aligned} \tag{4.1}$$

where $\tilde{\chi}_K$ denotes χ_K in the new variables $\vec{\mathrm{r}}$ and $\vec{\mathrm{l}}$. Assuming, moreover that, $\tilde{\chi}_K$ is sufficiently many times differentiable as a function of n, we write

$$\tilde{\chi}_K(n;\vec{\mathrm{r}},\vec{\mathrm{l}},i,j)n(\vec{\mathrm{r}}-\vec{\mathrm{l}},j) = \tilde{\chi}_K(n;\vec{\mathrm{r}},0,i,j)n(\vec{\mathrm{r}},j) + \left(\frac{\partial}{\partial l_\gamma}[\tilde{\chi}_K(n;\vec{\mathrm{r}},\vec{\mathrm{l}},i,j)n(\vec{\mathrm{r}}-\vec{\mathrm{l}},j)]\right)\bigg|_{l=0} l_\gamma + \cdots \tag{4.2}$$

Inserting (4.2) into (4.3), we have that,

$$\frac{\partial}{\partial r_\alpha}\,\frac{\delta Q}{\delta n(\vec{r},i)} = \sum_K \sum_j \epsilon^2_{K,ij} C_{K\alpha\gamma}(i,j) M_K(i,j) \left(\frac{\partial}{\partial l_\gamma}\,\tilde{\chi}_K n\right)\bigg|_0 , \tag{4.3}$$

where

$$C_{K\alpha\gamma} = \int_\Omega d\vec{l} \int d\vec{\kappa}\, \kappa_\alpha l_\gamma \tilde{D}^-_K(\vec{l},\vec{\kappa},i,j) .$$

We assume that $\tilde{D}^-_K$ is such that $C_{K\alpha\gamma}(i,j) = C_K(i,j)\delta_{\alpha\gamma} \sim \epsilon$, thus

$$\frac{\partial}{\partial r_\alpha}\,\frac{\delta Q}{\delta n(\vec{r},i)} = \sum_K \sum_j C_K(i,j)\epsilon^2_{K,ij} M_K(i,j) \left(\frac{\partial}{\partial l_\alpha}\,\tilde{\chi}_K n\right)\bigg|_{\vec{l}=0} . \tag{4.4}$$

The last assumption is that $\tilde{\chi}_K$ depends only on $n(\frac{1}{2}(\vec{r}+\vec{R}),k)$. Thus

$$\left(\frac{\partial}{\partial l_\alpha}\,\tilde{\chi}_K n\right)\bigg|_{\vec{l}=0} = \tfrac{1}{2}\sum_k \tilde{\chi}'_K(n;\vec{r},i,j,k) n(\vec{r},j)\partial_\alpha n(\vec{r},k) - \tilde{\chi}_K(n;\vec{r},i,j)\partial_\alpha n(\vec{r},j) , \tag{4.5}$$

where

$$\tilde{\chi}'_K(n;\vec{r},i,j,k) = \frac{\delta\tilde{\chi}_K(n;\vec{r}-\frac{1}{2}l,i,j)}{\delta n(r-\frac{1}{2}l,k)}\bigg|_{\vec{l}=0} .$$

Let us consider now the functional

$$Q(n) = \sum_K \sum_j \int_\Omega d\vec{R}\, n(\vec{R},j)\,\frac{\delta\Xi_K(n)}{\delta n(\vec{R},j)} , \tag{4.6}$$

where Ξ is an arbitrary sufficiently regular and local function of n [i.e., $\Xi_K(n) = \sum_k \int d\vec{r}\, F(\vec{r},k)$, where $F(\vec{r},k)$ depends only on $n(\vec{r},j)$, $j=1,\ldots,N$, not on $n(\vec{R},j)$, $\vec{R}\neq\vec{r}$]. Straightforward verification shows that if

$$\frac{1}{2}\,\frac{\delta^2\Xi_K(n)}{\delta n(\vec{r},i)\delta n(\vec{r},j)} = \epsilon^2_{K,ij} C_K(i,j) M_K(i,j) \chi_K(n;\vec{r},i,j) , \tag{4.7}$$

then (3.6) is satisfied, provided of course all the assumptions defining the special case discussed in this section are satisfied. The relation (4.7) also implies that,

$$\frac{\delta\chi_K(n;\vec{r},i,j)}{\delta n(\vec{r},k)} = \frac{\delta\chi_K(n;\vec{r},i,k)}{\delta n(\vec{r},j)} = \frac{\delta\chi_K(n;\vec{r},k,j)}{\delta n(\vec{r},i)} . \tag{4.8}$$

V. DISCUSSION

The condition (3.6) guarantees that the time-evolution equation (2.1) postulated in this paper as the starting point enjoys all the properties that indicate the compatibility of the dynamical theory based on (2.1) with thermodynamics. The physical meaning of the condition (3.6) thus lies in the clear physical meaning of its consequences. The four theorems that we proved imply that Eq. (2.1) together with the compatibility condition (3.6) has the same physical appeal as the Boltzmann equation. Eq. (2.1) is of course expected to be applicable in more general situations than the Boltzmann equation. The Boltzmann equation can be obtained as a particular case of (2.1) if the phenomenological quantities entering (4.1) are appropriately chosen. We note that in such a case the compatibility condition (3.6) is trivially satisfied. For the Enskog-like kinetic equation (2.1), we have found the entropy functional S. The condition (3.6) tells us how the functions χ entering phenomenologically into (2.1) will appear in the entropy functional. Moreover, we have identified also the entropy production σ. The entropy production σ is equal to the right-hand side of (3.4). We shall now attempt a comparison between our approach and results and some other approaches and results. This will give us additional insight into the physical meaning of (3.6).

First of all we note that the condition (3.6) implies that the general condition of compatibility of Raveche and Green[15] is satisfied. The physical arguments on the basis of which the Raveche-Green condition has been obtained, can therefore serve also in our particular case to provide a physical interpretation of (3.6). Following the spirit of the approach developed by Raveche and Green, we shall restrict (2.1) to $\mathcal{S}_+$ and divide the resulting equation by $n(\vec{r},i)$. The right-hand side of the equation which is obtained coincides exactly with the right-hand side of (3.6). We shall interpret it physically as the mean force on the molecule at $\vec{r}$. The Raveche-Green condition is the statement that this force is conservative (i.e., curl of the force is equal to zero). It is evident that the curl of the left-hand side of (3.6) is equal to zero, thus if (3.6) is satisfied, then the Raveche-Green condition also is satisfied.

Another possible attempt to obtain an additional physical insight into (3.6) can be directed as follows. We shall not accept (2.1) as our starting point. Instead, we shall accept as our starting point the Liouville equation together with a sequence of steps that finally leads to (2.1). Since there must be some physical considerations associated with the chosen steps, one could interpret (3.6) by putting it into the context of these physical arguments. An example of the discussion of the Enskog equation where the starting point is chosen to be the Liouville equation and a particular sequence of necessary steps is developed in Ref. 4 for the case of a one-component fluid with no chemical reactions. In Paper I,[12] we have shown how our condition (3.6) is interpreted in this context. To the best of our knowledge, there is, however, no further example of a discussion of (2.1) from a microscopic point of view (i.e., from the Liouville equation together with contractions of information leading to the time-evolution equations for lower-order distribution functions) we cannot, therefore, go any further. The decomposition of $\mathcal{R}(f)$ in the Enskog-like kinetic equation $\partial f/\partial t=\mathcal{R}(f)$ into the sum $\mathcal{R}^+(f)$ and $\mathcal{R}^-(f)$ plays the fundamental role in our discussion. The decomposition used in this paper has been obtained with the help of the involution $J:\mathcal{H}\to\mathcal{H}$, defined by $Jf(\vec{r},\vec{v},\xi,i)=f(\vec{r},-\vec{v},\xi,i)$, that in turn served to define the thermodynamic equilibrium states among all possible states. The Theorems III.1–III.3 provide another interpretation of $\mathcal{R}^+(f)$ and $\mathcal{R}^-(f)$. The part $\mathcal{R}^+(f)$ can be called the dissipative part of $\mathcal{R}(f)$ since at least in a small neighborhood of a regular equilibrium state the quantity S changes in time (decreases) only due to $\mathcal{R}^+(f)$. The dissipative part $\mathcal{R}^+(f)$ controls the approach to the thermodynamic equilibrium states while the part $\mathcal{R}^-(f)$ determined the thermodynamic equilibrium states themselves and the thermodynamic equation of state. Xystris and Dahler[10] have used another decomposition of $\mathcal{R}(f)$ into, in their terminology, source and flux parts. In the case of the Boltzmann equation the source part coincides with the collision operator and thus also with $\mathcal{R}^+$, the flux part coincides with the free flow term and thus also with $\mathcal{R}^-$. In the case of the Enskog equation the source part and $\mathcal{R}^+$ as well as the flux part and $\mathcal{R}^-$ are different. It can be proved that $\int d\vec{r}\int d\vec{v}\,\varphi(\vec{r},\vec{v})\mathcal{R}_s(f)=0$ if $\varphi=a(\vec{r})$, or $\varphi=b(\vec{r})v^2$, or $\varphi=c(\vec{r})v$, where $a,b,\vec{c}$ are arbitrary functions of $\vec{r}$, and $\mathcal{R}_s(f)$ denotes the source part. We have seen that the decomposition on $\mathcal{R}^+$ and $\mathcal{R}^-$ that we are suggesting is closely related to the properties of the entropy and thermodynamics. The decomposition on the source and flux parts appear to be formally convenient for the discussion of hydrodynamics. A less formal discussion of hydrodynamics can be obtained by considering the spectrum of the linearized operator P (see Refs. 16 and 17).

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