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Compatibility of the Enskog kinetic theory with thermodynamics. I

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It is proved that the solutions to the Enskog equation for an N-component gas enjoy the nice properties that are known in the context of the Boltzmann equation, to indicate its compatibility with thermodynamics, provided some restrictions are imposed on the functions χ. The functions χ are introduced in the Enskog equation in order to account for correlations among particles.

I. INTRODUCTION

The state of an N-component gas is described in kinetic theory by the one-particle distribution function $f(\vec{r},\vec{v},i,t)$; $f(\vec{r},\vec{v},i,t)d\vec{r}d\vec{v}$ denotes the number of particles of the ith component at $d\vec{r}$ about $\vec{r}$ with velocities in $d\vec{v}$ about $\vec{v}$ at time t. We shall assume periodic-boundary conditions on the boundary $\partial\Omega$ of the domain Ω confining the systems concerned. It follows from the interpretation of $f(\vec{r},\vec{v},i,t)$ that $f(\vec{r},\vec{v},i,t)\geq 0$ for all $\vec{r}\in\Omega$, $\vec{v}\in R^3$, $i=1,\ldots,N$ and all times. We introduce moreover $n(\vec{r},i,t)=\int d\vec{v}f(\vec{r},\vec{v},i,t)$.

Boltzmann[1] has proposed the following equation governing the time evolution of $f(\vec{r},\vec{v},i,t)$: [we omit, hereafter, t in $f(\vec{r},\vec{v},i,t)$]

$$\frac{\partial f(\vec{r},\vec{v},i)}{\partial t}=-v_\alpha\frac{\partial}{\partial r_\alpha}f(\vec{r},\vec{v},i)+\sum_{j=1}^{N}\int d\vec{\nu}\int d\vec{\kappa}\,y\,\theta(y)\epsilon_{ij}^2[f(\vec{r},\vec{v}',i)f(\vec{r},\vec{\nu}',j)-f(\vec{r},\vec{v},i)f(\vec{r},\vec{\nu},j)], \tag{1.1}$$

$y=(\nu_\alpha-v_\alpha)\kappa_\alpha$, $\vec{\kappa}$ is a unit vector, θ is the step function [$\theta(x)=1$ for $x>0$, $\theta(x)=0$ for $x\leq 0$] in the term corresponding to (i,j) the velocities $(\vec{v},\vec{\nu})$ are related to $(\vec{v}',\vec{\nu}')$ by the two-parameter (the parameters are $\vec{\kappa}$) family of transformations $v'_\alpha=v_\alpha+(2\mu_{ij}/m_i)(\nu_\gamma-v_\gamma)\kappa_\gamma\kappa_\alpha$; $\nu'=\nu_\alpha-(2\mu_{ij}/m_i)(\nu_\gamma-v_\gamma)\kappa_\gamma\kappa_\alpha$, $1/\mu_{ij}=1/m_i+1/m_j$, m_i is the mass of the particle of ith component. The transformation $(\vec{v},\vec{\nu})\to(\vec{v}',\vec{\nu}')$ is the transformation of the velocities of two colliding particles, $(\vec{v},\vec{\nu})$ are the velocities before the collision, and $(\vec{v}',\vec{\nu}')$ are the velocities after the collision. It is assumed in (1.1) that the particles are hard spheres interacting only due to the hard-core potential, $\epsilon_{ij}=\frac{1}{2}(\epsilon_i+\epsilon_j)$, where ϵ_i is the diameter of the particle of the ith component.

Once a kinetic equation [for example (1.1)] is suggested, three important types of questions arise.

(i) Does there exist an approach, as the time goes to ∞, of solutions of the kinetic equation to a time-independent state that could be identified with the state considered in thermodynamics? What is the thermodynamic equation of state implied by the kinetic equation?

(ii) Is it possible to replace the kinetic equation by the hydrodynamic equations if our interest is focused only on the long-time behavior of solutions to the kinetic equation? What is the error that we make by the replacement? What are the kinetic coefficients in the hydrodynamic equations?

(iii) Is it possible to derive the kinetic equation from a more microscopic view of the system considered, for example, from the Hamiltonian dynamics of the particle composing the system? What error we make by replacing the Hamilton dynamics by the kinetic equation?

We shall refer to (i) as the problem of the compatibility of the kinetic theory with thermodynamics, to (ii) as the problem of the compatibility of the kinetic theory with hydrodynamics, and to (iii) as the problem of the compatibility of the Hamiltonian dynamics with the kinetic theory.

All three problems were extensively studied for the Boltzmann equation (1.1), none of them is, however, solved completely. The results relevant to problem (i) are summed up in four theorems in Sec. II. These results strongly indicate the existence of the approach to equilibrium but do not constitute its formal proof [for example, even the problem of the existence of solutions to (1.1) remains open[2]]. The thermodynamic equation of state implied by (1.1) is the thermodynamic equation of state of an ideal gas. The problem (ii) is usually approached by the Enskog-Chapman method. Again, a complete answer to the questions (ii) is lacking. Comparison of the theoretical results obtained in the study of (i) and (ii) with the experimental observations indicate that the dilute gases constitute the range of validity of the Boltzmann equation (1.1); i.e., for dilute gases the experimental results well agree with theoretic results. There are many partial results to problem (iii).[3,4] A complete formal derivation is, however, again missing. In order to increase the range of validity of the Boltzmann equation, Enskog[5] has suggested a modification of (1.1), namely,

$$\frac{\partial f}{\partial t}=\mathfrak{R}(f)\,,$$

where

$$\mathfrak{R}(f)=-v_\alpha\frac{\partial}{\partial r_\alpha}f+\sum_{j=1}^{N}\int_\Omega d\vec{\rho}\int d\vec{\nu}\int d\vec{\kappa}\,y\,\theta(y)\epsilon_{ij}^{2}[\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})\chi(n;i,j,\vec{r},\vec{\rho})f(\vec{r},\vec{v}',i)f(\vec{\rho},\vec{\nu}',j)$$
$$-\delta(\vec{\rho}-\vec{r}+\epsilon_{ij}\vec{\kappa})\chi(n;i,j,\vec{r},\vec{\rho})f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)]\,. \tag{1.2}$$

Comparing (1.2) and (1.1) we see that if $\chi\equiv 1$ and the terms proportional to ϵ_{ij}^{k}, $k\geq 3$ are neglected then (1.2) reduces to (1.1). The Enskog modification takes into account the topological constraints during binary collisions due to the finiteness of the diameter of particles, and through the function χ the existence of correlations among particles.

In the original Enskog theory,[5] the function χ is chosen to be the equilibrium pair distribution function for a uniform system evaluated at the density $(\vec{r}+\vec{\rho})/2$. By studying problem (ii) Barajas *et al.*[6] observed that with this choice of χ the Enskog equation (1.2) is not, in general, compatible with hydrodynamics. van Beijeren and Ernst[7] proposed a "modified" Enskog equation in which χ is the equilibrium pair distribution function for a system of spatially nonuniform composition. Résibois[8,9] then considered also problem (i) for the modified Enskog equation and proved the H theorem for this equation [Theorem III.4 in our list of results that are relevant to problem (ii); see Sec. II]. Problem (iii) is considered in Refs. 7–11.

Our objective in this paper is to consider problem (i) in the context of the Eq. (1.2) in which the functions χ are considered to be arbitrary. More precisely, we want to prove the four results that are introduced in Sec. II and that are known to indicate the compatibility of the Boltzmann kinetic theory with thermodynamics for (1.2) with arbittrary χ. Our results imply that these four theorems can be proved provided the functions χ are not completely arbitrary. The choice of χ is restricted by requiring that the functions χ satisfy a compatibility condition. This condition also shows how χ enters into the thermodynamic equation of state implied by (1.2). The modified Enskog equation[7,8,9] represents one example for which the compatibility condition is satisfied. In the context of this equation, our Theorem III.4 extends the Résibois H theorem[8,9] to the N-component gas. The other three theorems that allow, for example, to identify the entropy production, constitute addition results relevant to the problem of the compatibility of the modified Enskog equation with thermodynamics. Our results in this paper extend therefore the results obtained in Refs. 8 and 9 and also the results in Refs. 10, 12 and 13, where some of the theorems were proved for Eq. (1.2), in which the terms proportional to ϵ_{ij}^{k}, $k\geq 4$ are neglected. We conclude that arguments favoring one particular Enskog equation or further restricting the class of Enskog equations have to come from the study of problems (ii) and (iii) and from the comparison of theoretical and experimental results. An attempt to find the class of the admissible functions χ on the basis of the study of problem (ii) has been made, in the context of Eq. (1.2) in which the terms proportional to ϵ_{ij}^{k}, $k\geq 4$ are neglected in Ref. 14. In the context of the general equation (1.2) the same attempt was made by Piña.[15] The results obtained in Refs. 14 and 15 indicate that the requirement of the compatibility of the Enskog equation (1.2) with hydrodynamics implies no new compatibility condition. Only the same compatibility condition as that obtained in this paper arises again.

II. BOLTZMANN EQUATION

The purpose of this section is to explain why the Boltzmann equation is compatible with thermodynamics. The concept of compatibility introduced here will retain its meaning also outside the context of the Boltzmann equation. The pattern of the study of the compatibility in this section will be followed in the next section within the context of the Enskog equation. All results about the solutions of the Boltzmann equation appearing in this section are well known and will be presented without proofs. In fact, since (1.1) can be considered as a special case of (1.2), the proofs in Sec. III also represent proofs of the theorems in this section.

A. Definition of the thermodynamic equilibrium states

Boltzmann has shown that the Maxwell distribution function describing, according to Maxwell, a thermodynamic equilibrium state in terms of the one-particle distribution function, is the only time-independent solution of the Boltzmann equation that is, moreover, invariant with respect to the change of the sign of the velocity. We shall adopt this observation as our definition of the thermodynamic equilibrium states in kinetic theory. Thus, if $\partial f/\partial t = \mathcal{R}(f)$ is our kinetic equation then the set $\mathcal{E}$ of the thermodynamic equilibrium states is defined by

$$\mathcal{E} = \{f \in \mathcal{H} \,|\, \mathcal{R}(f) = 0, \quad Jf = f\}\,,$$

where $\mathcal{H}$ denotes the set of all admissible states considered, $Jf(\vec{r}, \vec{v}, t) = f(\vec{r}, -\vec{v}, t)$. It follows easily from this definition that $\mathcal{E}$ can be equivalently obtained as

$$\mathcal{E} = \{f \in \mathcal{H} \,|\, \mathcal{R}^+(f) = 0, \quad \mathcal{R}^-(f) = 0, \quad Jf = f\}\,,$$

where

$$\mathcal{R}(f) = \mathcal{R}^+(f) + \mathcal{R}^-(f)\,,$$

$$\mathcal{R}^\pm(f) = \tfrac{1}{2}[\mathcal{R}(f) \pm J\mathcal{R}(Jf)]\,.$$

We observe that in the case of the Boltzmann equation $\mathcal{R}^-(f) = -v_\alpha(\partial/\partial r_\alpha)f$ and $\mathcal{R}^+(f)$ is the Boltzmann collision operator. We shall also introduce $\tilde{\mathcal{E}}_+ = \{f \in \mathcal{H} \,|\, \mathcal{R}^+(f) = 0\}$ and $\mathcal{E}_+ = \{f \in \mathcal{H} \,|\, \mathcal{R}^+(f) = 0,\ Jf = f\}$.

The same definition of the thermodynamic equilibrium states is used in the context of nonequilibrium thermodynamics (see Chap. IV, paragraph 3 of Ref. 16). In this context $f \equiv (\alpha_1, \ldots, \alpha_n, \beta_1, \ldots, \beta_m)$, $J(\alpha_1, \ldots, \alpha_n, \beta_1, \ldots, \beta_m) = (\alpha_1, \ldots, \alpha_n, -\beta_1, \ldots, -\beta_m)$, $(\alpha_1, \ldots, \alpha_n)$ are the α variables, and $(\beta_1, \ldots, \beta_m)$ are the β variables.

B. Properties of the solutions to the Boltzmann equation

We proceed to find $\mathcal{E}$ by solving $\mathcal{R}^+(f) = 0$ (Theorem II.1) and $\mathcal{R}^-(f)|_{\mathcal{E}_+} = 0$ (Theorem II.2). The last two theorems then sum up the properties of the solutions to the Boltzmann equation indicating that the thermodynamic equilibrium states are approached as the time goes to infinity.

Theorem II.1. Let S be defined as follows:

$$S = \sum_{i=1}^{N} \int_\Omega d\vec{r} \int d\vec{v} f(\vec{r}, \vec{v}, i)[\ln f(\vec{r}, \vec{v}, i) - 1] + Q(n)\,, \tag{2.1}$$

where $Q(n)$ is an arbitrary function of $n(\vec{r}, i)$. Then

$$\left.\frac{dS}{dt}\right|_+ \leq 0\,, \tag{2.2}$$

and the equality in (2.2) holds if and only if

$$f \in \tilde{\mathcal{E}}_+\,,$$

$$\tilde{\mathcal{E}}_+ = \{f \in \mathcal{H} \,|\, \mathcal{R}^+(f) = 0\} \equiv \{f \in \mathcal{H} \,|\, \ln f(\vec{r}, \vec{v}, i) = \ln n(\vec{r}, i) + \mathfrak{N} - \tfrac{1}{2} m_i b v^2 + c_\alpha m_i v_\alpha\}\,;$$

b and $\vec{c}$ are arbitrary functions of $\vec{r}$ and independent of $\vec{v}$ and i, $\mathfrak{N}$ is determined by requiring $n(\vec{r}, i) = \int d\vec{v} f(\vec{r}, \vec{v}, i)$. By $dS/dt|_+$ we denote the change in time of S if only $\mathcal{R}^+$ governs the time evolution.

The problem $\mathcal{R}^-(f)|_{\mathcal{E}_+} = 0$ can be written as $b = \sigma_1 = \text{const}$ and $\delta\mathcal{V}/\delta n(\vec{r}, i) = 0$, where

$$\mathcal{V} = \sum_{i=1}^{N} \int_\Omega d\vec{r}\, n(\vec{r}, i)[\ln n(\vec{r}, i) - 1] + \sum_{i=1}^{N} [\sigma_2(i) + \mathfrak{N}]\, c_2(i)\,. \tag{2.3}$$

$c_2(i) = \int_\Omega d\vec{r} \int d\vec{v} f(\vec{r}, \vec{v}, i)$ and $\sigma_2(i)$ are constants entering the boundary conditions

$$\ln f(\vec{r}, \vec{v}, i)|_{\partial\Omega} = \sigma_2(i) + \mathfrak{N} - \tfrac{1}{2}\sigma_1 m_i v^2\,. \tag{2.4}$$

The function $\mathcal{V}$ extends to a function

$$W = S + \sigma_1 c_1 + \sum_{i=1}^{N} \sigma_2(i) c_2(i)\,, \tag{2.5}$$

where S is defined in (2.1) with $Q(n) \equiv 0$ and

$$c_1 = \tfrac{1}{2} \sum_{i=1}^{N} \int_\Omega d\vec{r} \int d\vec{v}\, m_i v^2 f(\vec{r}, \vec{v}, i)\,.$$

We observe that $W|_{\mathcal{E}_+} = \mathcal{V}$ and the solutions to the problem of finding the thermodynamic equilibrium states $\mathcal{E}$ [i.e., the solutions to $\mathcal{R}^+(f) = 0$, $\mathcal{R}^-(f)|_{\mathcal{E}_+} = 0$, and $Jf = f$ subject to the boundary conditions (2.4)] are equivalent to the solutions of

$$\delta W/\delta f = 0\,. \tag{2.6}$$

We shall sum up the results in the following theorem.

Theorem II.2. Let $Q(n) \equiv 0$. Then the solutions to the problem $\mathcal{R}^+(f) = 0$, $\mathcal{R}^-(f)|_{\mathcal{E}_+} = 0$, $f = Jf$ subject to the boundary conditions (2.4) are equivalent to the solutions of (2.6).

The next problem is to prove that the thermodynamic equilibrium states are indeed approached as the time goes to infinity. In the context of this problem we mention two theorems.

Theorem II.3. Let $Q(n)\equiv 0$. Moreover, let $f_0(\vec{r},\vec{v},i)=n_0(i)\exp(\mathfrak{N}-\frac{1}{2}\sigma_1 m_i v^2)$ be a thermodynamic equilibrium state such that $n_0(i)$ is independent of $\vec{r}$. Let $A=D^2W|_{f_0}$ (i.e., A is equal to the second derivative of W with respect to f evaluated at f_0). Thus, $W=W|_{f_0}+(\varphi,A\varphi)+O(\varphi^3)$, $f(\vec{r},\vec{v},i)=f_0(v,i)[1+\varphi(\vec{r},\vec{v},i)]$, and $(.\,,.)$ denotes the L_2 inner product, i.e., $(\varphi,\psi)=\int_\Omega d\vec{r}\int d\vec{v}\,\varphi(\vec{r},\vec{v})\psi(\vec{r},\vec{v})$. Note that A is a positive definite operator. Let P denote the linear part of $\mathcal{R}$ (the linearization around f_0), and let $P^{\pm}$ denote the linear parts of $\mathcal{R}^{\pm}$. Then P^{+} is formally self-adjoint and dissipative with respect to the inner product $(.,A.)$ (i.e., $(\varphi,AP^{+}\varphi)\leqslant 0$ for all φ in the domain of P^{+}), and P^{-} is formally skew-adjoint with respect to the same inner product $(.,A.)$.

Theorem II.4. Let $Q(n)\equiv 0$. Then

$$dW/dt\leqslant 0\,. \tag{2.7}$$

The equality in (2.7) holds if and only if $f\in\tilde{\mathcal{S}}_{+}$.

Theorem II.3 implies the approach to the thermodynamic equilibrium state f_0, provided the time evolution is governed by the linearized operator P and provided suitable boundary conditions allow upgrading of the formal self-adjointness and the formal skew-adjointness to self-adjointness and skew-adjointness.[17] Theorem II.4 is the familiar Boltzmann H theorem for the Boltzmann equation that was proved already by Boltzmann.[1] Notice that the functional W is introduced in (2.5) as a linear combination of $(N+1)$, constants of motion $[dc_1/dt=0,\ dc_2(i)/dt=0,\ i=1,\ldots,N]$, and the Boltzmann H function.

C. The thermodynamic equation of state implied by the Boltzmann equation

The functional W has appeared in the previous paragraph in the study of the thermodynamic equilibrium states and in the study of the approach to the thermodynamic equilibrium states as the time goes to infinity. If the kinetic equation is given then W is determined (up to a multiplicative and additive constant) by requiring (1) $dW/dt\leqslant 0$, (2) $\mathcal{S}=\{f\in\mathcal{H}\,|\,\mathcal{R}(f)=0, Jf=f\}=\{f\in\mathcal{H}\,|\,\delta W/\delta f=0, Jf=f\}$, and (3) $W(f)=W(Jf)$. The thermodynamic equation of state implied by (1.1) is obtained as follows. We introduce

$$\sigma_{N+2}=-(k_B/\omega)W|_{\mathcal{S}}\,, \tag{2.8}$$

where k_B is the Boltzmann constant and ω is the volume of Ω. We observe that σ_{N+2} becomes a function of σ_1 and $\sigma_2(i)$, $i=1,\ldots,N$. Moreover, a direct calculation implies

$$\frac{\partial\sigma_{N+2}}{\partial\sigma_1}=-\frac{k_B}{\omega}c_1\Big|_{\mathcal{S}},\quad \frac{\partial\sigma_{N+2}}{\partial\sigma_2(i)}=-\frac{k_B}{\omega}c_2(i)\Big|_{\mathcal{S}}. \tag{2.9}$$

The physical meaning of f implies the meaning of $(k_B/\omega)c_1|_{\mathcal{S}}$ (energy density), and $(k_B/\omega)c_2(i)|_{\mathcal{S}}$ (mass density of ith component). The relation (2.9) between σ_{N+2} and $\sigma_1,\sigma_2(i), i=1,\ldots,N$ is the thermodynamic equation of state implied by (1.1) (ideal-gas thermodynamic equation of state) provided $\sigma_1=1/T$; T is the temperature $\sigma_2(i)=-\mu_i/T$, μ_i is the chemical potential of the ith component $\sigma_{N+2}=p/T$, and p is the pressure.

In the rest of this paper, we replace (1.1) by (1.2) and we keep the definition of the thermodynamic equilibrium states introduced in Sec. II A unchanged. We keep the construction of the thermodynamic equation of state introduced in Sec. II C [see (2.8)] unchanged, and we prove the four theorems introduced in Sec. II B. This consideration of the compatibility of a kinetic equation with the thermodynamics has been already introduced in Ref. 13.

III. ENSKOG EQUATION

We shall now replace the Boltzmann equation (1.1) by the Enskog equation (1.2) and prove the four theorems introduced in the previous section. We observe that

$$\begin{aligned}\mathcal{R}^{+}(f)=&\tfrac{1}{2}\sum_{j=1}^{N}\int_\Omega d\vec{\rho}\int d\vec{\nu}\int d\vec{\kappa}\,y[\theta(y)-\theta(-y)]\epsilon_{ij}^{2}[\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\kappa)\chi(n;i,j,\vec{r},\vec{\rho})f(\vec{r},\vec{v}',i)f(\vec{\rho},\vec{\nu}',j)\\&-\delta(\vec{\rho}-\vec{r}+\epsilon_{ij}\vec{\kappa})\chi(n,i,j,\vec{n},\rho)f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)]\\=&\tfrac{1}{2}\sum_{j=1}^{N}\int_\Omega d\vec{\rho}\int d\vec{\nu}\int d\vec{\kappa}\,y\theta(y)\epsilon_{ij}^{2}\chi(n;i,j,\vec{r},\vec{\rho})[\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})+\delta(\vec{\rho}-\vec{r}+\epsilon_{ij}\vec{\kappa})]\\&\times[f(\vec{r},\vec{v}',i)f(\vec{\rho},\vec{\nu}',j)-f(\vec{r};\vec{v},i)f(\vec{\rho},\vec{\nu},j)]\,,\end{aligned} \tag{3.1}$$

$$\begin{aligned}\mathcal{R}^{-}(f)=&-v_\alpha\partial_\alpha f+\tfrac{1}{2}\sum_{j=1}^{N}\int_\Omega d\vec{\rho}\int d\vec{\nu}\int d\vec{\kappa}\,y\epsilon_{ij}^{2}\chi(n;i,j,\vec{r},\vec{\rho})\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})\\&\times[f(\vec{r},\vec{v}',i)f(\vec{\rho},\vec{\nu}',j)+f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)]\,.\end{aligned} \tag{3.2}$$

It follows from the properties of the transformations $(\vec{v},\vec{\nu})\rightarrow(\vec{v}\,',\vec{\nu}\,')$ that the solutions of $\mathcal{R}^{+}(f)=0$ consist of functions $\ln f(\vec{r},\vec{v},i)=\ln n(r,i)+\mathfrak{N}-\frac{1}{2}\sigma_1 m_i v^2+c_\alpha m_i v_\alpha$, where σ_1 and $\vec{c}$ are constants and $\mathfrak{N}$ is determined by $\int d\vec{v} f=n(\vec{r},i)$. In the previous section σ_1 and $\vec{c}$ could depend on $\vec{r}$. In order to show that there are no other solutions to $\mathcal{R}^{+}(f)=0$ we prove the following theorem.

Theorem III.1. Let S be defined as in Eq. (2.1) and $\chi(n,i,j,\vec{r},\vec{\rho})$ are positive for all $i,j,\vec{r},\vec{\rho}$, and symmetric with respect to the interchange of i,j and $\vec{r},\vec{\rho}$.

Then

$$dS/dt\,\big|_{+}\leqslant 0 \tag{3.3}$$

and the equality in (3.3) holds if and only if $f\in\tilde{\mathcal{E}}_{+}$, where $\tilde{\mathcal{E}}_{+}=\{f\in\mathcal{H}\,|\,\mathcal{R}^{+}(f)=0\}$. The set $\tilde{\mathcal{E}}_{+}$ is identical to $f\in\mathcal{H}$ which are solutions to $f(\vec{r},\vec{v}\,',i)f(\vec{\rho},\vec{\nu}\,',j)=f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)$ for all $i,j,\vec{r},\vec{\rho}=\vec{r}\pm\epsilon_{ij}\vec{\kappa}$, $|\vec{\kappa}|=1$, and $\vec{v},\vec{\nu}$ such that $(\nu_\alpha-v_\alpha)\kappa_\alpha>0$. Thus $\tilde{\mathcal{E}}_{+}$ is composed of $f\in\mathcal{H}$ such that $\ln f(\vec{r},\vec{v},i)=\ln n(\vec{r},i)+\mathfrak{N}-\frac{1}{2}\sigma_1 m_i v^2+c_\alpha m_i v_\alpha$; $\sigma_1,\vec{c}$ are constants and $\mathfrak{N}$ is determined by requiring $n(\vec{r},i)=\int d\vec{v} f(\vec{r},\vec{v},i)$.

Proof. We note first that $\sum_{i=1}^{N}\int_\Omega d\vec{r}\int d\vec{v}\,\varphi(\vec{r},i)\mathcal{R}^{+}(f)=0$ (it is also true that $\sum_{i=1}^{N}\int_\Omega d\vec{r}\int d\vec{v}\,\varphi(\vec{r},i)\mathcal{R}_E(f)=0$), where φ is an arbitrary function independent of $\vec{v}$ and $\mathcal{R}_E(f)$ is the second term on the right-hand side of (2.2). Thus

$$\frac{dS}{dt}\bigg|_{+}=\sum_{i=1}^{N}\int_\Omega d\vec{r}\int d\vec{v}\ln f(\vec{r},\vec{v},i)\mathcal{R}^{+}(f)\,. \tag{3.4}$$

Two subsequent transformations $\vec{\rho}\rightleftarrows\vec{r}$, $\vec{v}\rightleftarrows\vec{\nu}$, $i\rightleftarrows j$, $\vec{\kappa}\rightleftarrows-\vec{\kappa}$, and $(\vec{v},\vec{\nu})\rightleftarrows(\vec{v}\,',\vec{\nu}\,')$, $\vec{\kappa}\rightleftarrows-\vec{\kappa}$ on the right-hand side of (3.4) lead to

$$\begin{aligned}\frac{dS}{dt}\bigg|_{+}=\frac{1}{8}\sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\int d\vec{\nu}\int d\vec{\kappa}\,y\,\theta(y)\epsilon_{ij}^{2}\,\chi(n;i,j,\vec{r},\vec{\rho})&\\ \times[\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})+\delta(\rho-\vec{r}+\epsilon_{ij}\vec{\kappa})]\ln\frac{f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)}{f(\vec{r},\vec{v}\,',i)f(\vec{\rho},\vec{\nu}\,',j)}&\\ \times[f(\vec{r},\vec{v}\,',i)f(\vec{\rho},\vec{\nu}\,',j)-f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)]\,.&\end{aligned} \tag{3.5}$$

It should be stressed that $\tilde{\mathcal{E}}_{+}$ associated with the Boltzmann equation (the set of the local equilibrium states) and $\tilde{\mathcal{E}}_{+}$ associated with the Enskog equations are different. The latter is much smaller (since σ_1 and $\vec{c}$ are constants, not arbitrary functions of $\vec{r}$ as in the case of the Boltzmann equation). It can be seen immediately from (3.5) that $dS/dt\,|_{+}(f)$ as well as $\mathcal{R}^{+}(f)$ for

$$f(\vec{r},\vec{v},i)=n(\vec{r},i)\exp(-\tfrac{1}{2}\sigma_1 m_i v^2+m_i v_\alpha c_\alpha)\,,$$

where σ_1 and $\vec{c}$ depend on $\vec{r}$, are not in general equal to zero. The appearance of the smaller $\tilde{\mathcal{E}}_{+}$ in the context of the Enskog equation is a consequence of the nonlocality of collisions introduced in the Enskog theory.

Theorem III.2. Let $Q(n)$ introduced in (2.1) be related to $\chi(n;i,j,\vec{r},\vec{\rho})$ by

$$\begin{aligned}\frac{\partial}{\partial r_\alpha}\frac{\delta Q}{\delta n(\vec{r},i)}=\sum_{j=1}^{N}\int_\Omega d\vec{\rho}\,\delta(|\vec{r}-\vec{\rho}|-\epsilon_{ij})&\\ \times\epsilon_{ij}(\rho_\alpha-r_\alpha)\chi(n;i,j,\vec{r},\vec{\rho})n(\vec{\rho},j)&\end{aligned} \tag{3.6}$$

and $\chi(i,j,\vec{r},\vec{\rho})$ satisfy the conditions introduced in Theorem III.1.

Then the solutions to the problem

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

subject to the boundary conditions

$$[\ln f(\vec{r},\vec{v},i)-\delta Q/\delta n(\vec{r},i)]\,|_{\partial\Omega}=\sigma_2(i)+\mathfrak{N}-\tfrac{1}{2}\sigma_1 m_i v^2\,.$$

σ_1, $\sigma_2(i)$ and $i=1,\ldots,N$ are constants, thus the thermodynamic equilibrium states according to the definition in Sec. II, are equivalent to the solutions of

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

where

$$\begin{aligned}&W=S+\sigma_1 c_1+\sum_{i=1}^{N}\sigma_2(i)c_2(i)\,,\\ &c_1=\frac{1}{2}\sum_{i=1}^{N}\int_\Omega d\vec{r}\int d\vec{v}\,v^2 m_i f(\vec{r},\vec{v},i)\,,\\ &c_2(i)=\int_\Omega d\vec{r}\int d\vec{v} f(\vec{r},\vec{v},i)\,.\end{aligned} \tag{3.9}$$

Proof.

$$\mathcal{R}^{-}(f)\,|_{\mathcal{E}_{+}}=e^{-\sigma_1 m_i v^2/2}\bigg(-v_\alpha\partial_\alpha n(\vec{r},i)-v_\alpha\sum_{j=1}^{N}\int_\Omega d\vec{\rho}\int d\vec{\kappa}\,\kappa_\alpha\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})\epsilon_{ij}^{2}\,\chi(n;i,j,\vec{r},\vec{\rho})n(\vec{r},i)n(\vec{\rho},j)\bigg)\,. \tag{3.10}$$

Thus

$$\mathcal{R}^-(f)\big|_{\mathcal{S}_+} = -v_\alpha\Big(\partial_\alpha \ln(\vec{r},i) + \sum_{j=1}^{N} \int_\Omega d\vec{\rho} \int d\vec{\kappa}\, \kappa_\alpha \delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})\epsilon_{ij}^2 \chi(n;i,j,\vec{r},\vec{\rho}) n(\vec{\rho},j)\Big)$$
$$= -v_\alpha\Big(\partial_\alpha \ln(\vec{r},i) + \sum_{j=1}^{N} \int_\Omega d\vec{\rho}\, \delta(|\vec{\rho}-\vec{r}|-\epsilon_{ij})(\rho_\alpha - r_\alpha)\epsilon_{ij} \chi(n;i,j,\vec{r},\vec{\rho}) n(\vec{\rho},j)\Big) = 0\,. \tag{3.11}$$

If (3.6) is satisfied then

$$\delta\mathcal{V}/\delta n(\vec{r},i) = 0 \equiv \mathcal{R}^-(f)\big|_{\mathcal{S}_+} = 0\,,$$

where

$$\mathcal{V} = \sum_{i=1}^{N} \int_\Omega dr\, n(\vec{r},i)[\ln n(\vec{r},i) - 1] + Q(n) + \sum_{i=1}^{N} [\sigma_2(i) + \mathfrak{N}]\, c_2(i)\,. \tag{3.12}$$

We extend now the function $\mathcal{V}$ defined only on $\mathcal{S}_+$ into the function W defined on $\mathcal{H}$ such that $W|_{\mathcal{S}_+} = \mathcal{V}$ 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.

Theorem III.3. Let (3.6) be satisfied and $\chi(n;i,j,\vec{r},\vec{\rho})$ are positive and symmetric with respect to the interchange of i,j and $\vec{r},\vec{\rho}$. Moreover, let $f_0(\vec{r},\vec{v},i) = n_0(i)\exp(-\frac{1}{2}\sigma_1 m_i v^2)$ be an equilibrium state [i.e., the solution to (3.7) or equivalently to (3.8)], such that $n_0(i)$ is independent of $\vec{r}$ and $A = D^2 W|_{f_0}$ (i.e., the second derivative of W with respect to f evaluated at f_0) is a positive definite operator. Thus $W = W_0 + (\varphi, A\varphi) + O(\varphi^3)$, where $W_0 = W|_{f_0}$, $f(\vec{r},\vec{v},i) = f_0(\vec{r},\vec{v},i)[1+\varphi(\vec{r},\vec{v},i)]$, and $(.,.)$ denotes the L_2 inner product (see Theorem II.3). In view of the thermodynamic interpretation of $W|_{\mathcal{S}}$, the requirement that A is positive definite implies that f_0 is thermodynamically stable. We shall denote by P the linear part of $\mathcal{R}$ (the linearization around f_0), and $P^\pm$ is the linear part of $\mathcal{R}^\pm$.

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

$$A\varphi(\vec{r},\vec{v},i) = A_1\varphi(\vec{r},\vec{v},i) + A_2\varphi(\vec{r},\vec{v},i), \tag{3.13}$$

where

$$A_1\varphi(\vec{r},\vec{v},i) = f_0(\vec{r},\vec{v},i)\varphi(\vec{r},\vec{v},i)\,,$$

$$A_2\varphi(\vec{r},\vec{v},i) = \sum_{j=1}^{N} \int_\Omega d\vec{\rho} \int d\vec{\nu}\, \mathcal{A}(i,j,\vec{r},\vec{\rho},\vec{v},\vec{\nu})\varphi(\vec{\rho},\vec{\nu},j)\,,$$

$$\mathcal{A}(i,j,\vec{r},\vec{v},\vec{\nu}) = f_0(\vec{v},i) f_0(\vec{\nu},j)\delta^2 Q/\delta n(\vec{r},i)\delta n(\vec{\rho},j)\big|_{f_0}\,.$$

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 invalidate the discussion. We shall proceed to prove that AP^- is formally skew-adjoint:

$$P^-\varphi(\vec{r},\vec{v},i) = P_1^-\varphi(\vec{r},\vec{v},i) + P_2^-\varphi(\vec{r},\vec{v},i)\,,$$
$$P_1\varphi(\vec{r},\vec{v},i) = -v_\alpha \partial_\alpha \varphi(\vec{r},\vec{v},i)\,,$$
$$P_2^-\varphi(\vec{r},\vec{v},i) = (P_{21}+P_{22}+P_{23}+P_{24})\varphi(\vec{r},\vec{v},i)\,,$$
$$P_{21}\varphi(\vec{r},\vec{v},i) = \tfrac{1}{2}\sum_{j=1}^{N} \int_\Omega d\vec{\rho} \int d\vec{\nu} \int d\vec{\kappa}\, y\,\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa}) f_0(\vec{\nu},j)\epsilon_{ij}^2 \chi_0(n;i,j,\vec{r},\vec{\rho})\varphi(\vec{r},\vec{v}',i)\,, \tag{3.14}$$
$$P_{22}\varphi(\vec{r},\vec{v},i) = \tfrac{1}{2}\sum_{j=1}^{N} \int_\Omega d\vec{\rho} \int d\vec{\nu} \int d\vec{\kappa}\, y\,\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa}) f_0(\vec{\nu},j)\epsilon_{ij}^2 \chi_0(n;i,j,\vec{r},\vec{\rho})\varphi(\vec{\rho},\vec{\nu}',j)\,,$$
$$P_{23}\varphi(\vec{r},\vec{v},i) = \tfrac{1}{2}\sum_{j=1}^{N} \int_\Omega d\vec{\rho} \int d\vec{\nu} \int d\vec{\kappa}\, y\,\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa}) f_0(\vec{\nu},j)\epsilon_{ij}^2 \chi_0(n;i,j,\vec{r},\vec{\rho})\varphi(\vec{r},\vec{\nu},j)\,,$$
$$P_{24}\varphi(\vec{r},\vec{v},i) = \tfrac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N} \int_\Omega d\vec{\rho} \int d\vec{R} \int d\vec{\nu} \int d^3w \int d\vec{\kappa}\, f_0(\vec{\nu},j) f_0(\vec{w},k)$$
$$\times\, \delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})\epsilon_{ij}^2\, \delta\chi(n;i,j,\vec{r},\vec{\rho})/\delta n(\vec{R},k)\big|_{f_0}\varphi(\vec{R},\vec{w},k)\,.$$

By $\chi_0(n;i,j,\vec{r},\vec{\rho})$ we have denoted $\chi(n;i,j,\vec{r},\vec{\rho})|_{f_0}$. Now

$$AP^- = (A_1 + A_2)(P_1^- + P_2^-) = A_1P_1^- + A_1P_2^- + A_2P_1^- \tag{3.15}$$

(note that $A_2P_2^-\varphi \equiv 0$). By a straightforward verification we show that $A_1P_1^-, A_1P_{21}, A_1P_{22}$ are separately formally skew-adjoint operators. It remains to prove that $A_1P_{23} + A_1P_{24} + A_2P_1^-$ is a formally skew-adjoint operator. To do so we shall differentiate (3.6) with respect to $n(\vec{\rho},j)$. This yields

$$\frac{\partial}{\partial r_\alpha}\frac{\delta^2 Q}{\delta n(\vec{r},i)\delta n(\vec{\rho},j)} = B_{1\alpha} + B_{2\alpha}, \tag{3.16}$$

where

$$B_{1\alpha} = \delta(|\vec{r}-\vec{\rho}| - \epsilon_{ij})\epsilon_{ij}^2(r_\alpha - \rho_\alpha)\chi_0(n;i,j,\vec{r},\vec{\rho}),$$

$$B_{2\alpha} = \sum_{k=1}^{N}\int_\Omega d\vec{R}\,\delta(|\vec{r}-\vec{R}| - \epsilon_{ik})\epsilon_{ik}(r_\alpha - R_\alpha)\left(\frac{\delta\chi(n;i,k,\vec{r},\vec{R})}{\delta n(\vec{\rho},j)}n(\vec{R},k)\right)\Bigg|_{f_0}.$$

Writing explicitly $(\psi, A_2P_2^-\varphi)$, we have

$$\begin{aligned}(\psi, A_2P_1^-\varphi) &= \sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\int d\vec{\nu}\,\psi(\vec{r},\vec{v},i)f_0(\vec{v},i)f_0(\vec{\rho},j)\frac{\delta^2 Q}{\delta n(\vec{r},i)\delta n(\vec{\rho},j)}\Bigg|_{f_0}\left(-\nu_\alpha\frac{\partial}{\partial\rho_\alpha}\varphi(\vec{\rho},\vec{\nu},j)\right)\\ &= \sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\int d\vec{\nu}\,f_0(\vec{v},i)f_0(\vec{\nu},j)\nu_\alpha\psi(\vec{r},\vec{v},i)\varphi(\vec{\rho},\vec{\nu},j)\frac{\partial}{\partial\rho_\alpha}\left(\frac{\delta^2 Q}{\delta n(\vec{r},i)\delta n(\vec{\rho},j)}\right)\Bigg|_{f_0}.\end{aligned} \tag{3.17}$$

The second equality in (3.17) is obtained by integrating by parts. By using (3.16) we can write (3.17) as

$$(\psi, A_2P_1^-\varphi) = (\psi, C_1\varphi) + (\psi, C_2\varphi), \tag{3.18}$$

where

$$\begin{aligned}(\psi, C_1\varphi) &= \sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\int d\vec{\nu}\,f_0(\vec{v},i)f_0(\vec{\nu},j)\\ &\qquad\times v_\alpha\psi(\vec{r},\vec{v},i)\varphi(\vec{\rho},\vec{\nu},j)\delta(|\vec{r}-\vec{\rho}| - \epsilon_{ij})\epsilon_{ij}(r_\alpha - \rho_\alpha)\chi_0(i,j,\vec{r},\vec{\rho})\\ (\psi, C_2\varphi) &= \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int_\Omega d\vec{R}\int d\vec{v}\int d\vec{\nu}\,f_0(\vec{v},i)f_0(\vec{\nu},j)\\ &\qquad\times\delta(|\vec{\rho}-\vec{R}| - \epsilon_{jk})\epsilon_{jk}(\rho_\alpha - R_\alpha)\left(\frac{\delta\chi(j,k,\vec{\rho},\vec{R})}{\delta n(\vec{r},i)}n(\vec{R},k)\right)\Bigg|_{f_0}.\end{aligned} \tag{3.19}$$

Straightforward verification shows that $(A_1P_{23} + C_1)$ and $(A_1P_{24} + C_2)$ are separately formally skew-adjoint operators. We have thus proved that AP^- is a formally skew-adjoint operator with respect to the inner product $(.,.)$, thus identically that P^- is a formally skew-adjoint operator with respect to the inner product $(.,A.)$.

The three previous theorems imply that $dW/dt \leqslant 0$ provided the time evolution is governed only by the linearized Enskog kinetic equation $\partial\rho/\partial t = P\varphi$ and the terms proportional to φ^k, $k \geqslant 3$ are neglected. It can be proved, however that, $dW/dt \leqslant 0$ provided only (3.6) is satisfied and $\chi(i,j,\vec{r},\vec{\rho})$ are positive and symmetric under the interchange of i,j and $\vec{r},\vec{\rho}$. The following theorem and its proof is a straightforward generalization of the theorem of Résibois.[9]

Theorem III.4. Let (3.6) be satisfied, and $\chi(n;i,j,\vec{r},\vec{\rho})$ are positive and symmetric under the interchange of i,j and $\vec{r},\vec{\rho}$.

Then

$$dW/dt \leqslant 0.$$

The equality in (3.19) holds if and only if $f \in \mathcal{S}_+$. The function W is defined in (3.9) and $\mathcal{S}_+$ is introduced in Theorem III.1.

Proof. It is clear that $dc_1/dt = 0$, $dc_2(i)/dt = 0$, and $i = 1, \ldots, N$. It remains to show that $dS/dt \leqslant 0$. We write $S = S_0 + Q$, where $S_0 = \sum_{i=1}^{N}\int_\Omega d\vec{r}\int d\vec{v} f(\vec{r},\vec{v},i)[\ln f(\vec{r},\vec{v},i) - 1]$:

$$\frac{dS}{dt} = \left(\frac{\delta S_0}{\delta f}, \mathcal{R}(f)\right) + \left(\frac{\delta Q}{\delta n}, -v_\alpha\partial_\alpha f\right), \tag{3.20}$$

$$\begin{aligned}\left(\frac{\delta S_0}{\delta f},\mathcal{R}(f)\right)\\ =\sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\int d\vec{\nu}\int d\vec{\kappa}\, y\theta(y)\ln f(\vec{r},\vec{v},i)[\,\delta(\vec{\rho}-\vec{r}-\epsilon_{ij}\vec{\kappa})\epsilon_{ij}^{2}\chi(n;i,j,\vec{r},\vec{\rho})f(\vec{r},\vec{v}',i)f(\vec{\rho},\vec{\nu}',j)\\ -\delta(\vec{\rho}-\vec{r}+\epsilon_{ij}\vec{\kappa})\epsilon_{ij}^{2}\chi(n;i,j,\vec{r},\vec{\rho})f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)]\,.\end{aligned}\tag{3.21}$$

The first term is rewritten by using the transformations $(\vec{v},\vec{\nu})\rightleftarrows(\vec{v}',\vec{\nu}')$ and $\vec{\kappa}\rightleftarrows-\vec{\kappa}$. Both terms are then rewritten by using the transformations $\vec{v}\rightleftarrows\vec{\nu}$, $\vec{\rho}\rightleftarrows\vec{r}$; $i\rightleftarrows j$, and $\vec{\kappa}\rightleftarrows-\vec{\kappa}$. We obtain

$$\begin{aligned}\left(\frac{\delta S_0}{\delta f},\mathcal{R}(f)\right)=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\int d\vec{\nu}\int d\vec{\kappa}\, y\theta(y)\delta(\vec{\rho}-\vec{r}+\epsilon_{ij}\vec{\kappa})\epsilon_{ij}^{2}\chi(n;i,j,\vec{r},\vec{\rho})f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)\\ \times\ln\frac{f(\vec{r},\vec{v}',i)f(\vec{\rho},\vec{\nu}',j)}{f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)}\,.\end{aligned}\tag{3.22}$$

Following Résibois,[9] we shall use the inequality $x\ln(y/x)\leqslant y-x$ for positive x and y; the equality holds if and only if $x=y$. We thus obtain

$$\begin{aligned}\left(\frac{\delta S_0}{\delta f},\mathcal{R}(f)\right)\leqslant\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\int d\vec{\nu}\int d\vec{\kappa}\, y\theta(y)\epsilon_{ij}^{2}\chi(n;i,j,\vec{r},\vec{\rho})\delta(\vec{\rho}-\vec{r}+\epsilon_{ij}\vec{\kappa})\\ \times[f(\vec{r},\vec{v}',i)f(\vec{\rho},\vec{\nu}',j)-f(\vec{r},\vec{v},i)f(\vec{\rho},\vec{\nu},j)]\\ =\sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\,\delta(|\vec{\rho}-\vec{r}|-\epsilon_{ij})\epsilon_{ij}(\rho_\alpha-r_\alpha)\chi(n;i,j,\vec{r},\vec{\rho})n(\vec{r},i)\left(\int d\vec{\nu}\nu_\alpha f(\vec{\rho},\vec{\nu},j)\right).\end{aligned}\tag{3.23}$$

The second term on the right-hand side of (3.20) becomes

$$\begin{aligned}\left(\frac{\delta Q}{\delta n},-v_\alpha\partial_\alpha f\right)=\sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\int d\vec{v}\,\frac{\delta Q}{\delta n(\rho,j)}\left(-v_\alpha\frac{\partial}{\partial\rho_\alpha}f(\vec{\rho},\vec{v},j)\right)\\ =\sum_{i=1}^{N}\sum_{j=1}^{N}\int_\Omega d\vec{r}\int_\Omega d\vec{\rho}\,\frac{\partial}{\partial\rho_\alpha}\left(\frac{\delta Q}{\delta n(\vec{\rho},j)}\right)\left(\int d\vec{v}v_\alpha f(\vec{\rho},\vec{v},j)\right).\end{aligned}\tag{3.24}$$

It follows from (3.6) that $dS/dt\leqslant 0$ and the equality holds if and only if $f\in\bar{\mathcal{S}}_{+}$. It should be stressed that Theorem III.4 does not imply Theorem III.1. In the case of the Boltzmann equation the Theorems II.1 and and II.4 are just trivial reformulations of each other.

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

The starting point of this paper is Eq. (1.2), where $\chi(n;i,j,\vec{r},\vec{\rho})$ is considered as the phenomenological input. We have found that in order for (1.2) to possess the important properties that indicates the compatibility of the dynamical theory based on (1.2) with thermodynamics, the choice of χ must be restricted by the requirements that $\chi>0$; χ is symmetric with respect to the interchange of i,j and $\vec{r},\vec{\rho}$, and by the compatibility condition to be satisfied Eq. (3.6). In this section, we shall restrict the choice of χ by some additional *ad hoc* assumptions and observe what the compatibility condition (3.6) tells us in this particular case.

We shall assume that $\chi(n;i,j,\vec{r},\vec{\rho})$ depends only on $n(\vec{R}_{ij},i)$, $i=1,\ldots,N$ [and not, for example, on $\partial/\partial r_\alpha n(\vec{r},i)$], $\vec{R}_{ij}=\vec{r}+a_{ij}\vec{l}$, and $\vec{l}=\vec{\rho}-\vec{r}$. The constants a_{ij}, $(i=1,\ldots,N)$ remain unspecified.

Similarly, we assume that $Q(n)=\int_\Omega d\vec{r}\tilde{Q}(n;\vec{r})$, where $\tilde{Q}(n;\vec{r})$ depends only on $n(\vec{r},i)$ $(i=1,\ldots,N)$. Moreover, we shall assume $\epsilon_{ij}\sim\epsilon$, where ϵ is a small parameter. Only the terms up to and including ϵ^3 will be considered. Under these assumptions the compatibility condition (3.6) takes the form

$$\begin{aligned}\frac{4\pi}{3}\sum_{j=1}^{N}\epsilon_{ij}^{3}\left(\chi_0\frac{\partial}{\partial r_\alpha}n(\vec{r},j)+n(\vec{r},j)\sum_{k=1}^{N}\chi'_{0k}\frac{\partial}{\partial r_\alpha}n(\vec{r},k)a_{ij}\right)\\ =\sum_{j=1}^{N}Q''_{0ij}\frac{\partial}{\partial r_\alpha}n(\vec{r},j)\,,\end{aligned}\tag{4.1}$$

where χ_0 depends only on $n(\vec{r},i)$, $i=1,\ldots,N$, $\chi'_{0k}=\delta\chi/\delta n(\vec{r},k)|_o$ [the symbol $|_o$ means evaluated at $n(\vec{r},i)$, $i=1,\ldots,N$], and $Q''_{0ij}=\delta^2Q/\delta n(\vec{r},i)\delta n(\vec{r},j)|_o$. It is convenient now to represent the functional Q in the form

$$Q(n)=\sum_{k=1}^{N}\int d\vec{r}\,n(\vec{r},k)\,\Xi'_k\,,\tag{4.2}$$

where $\Xi_k' = \delta\Xi/\delta n(\vec{r},k)$; Ξ is an arbitrary functional of $n(\vec{r},i)$, $i=1,\ldots,N$. Eq. (4.1) then implies that

$$\tfrac{4}{3}\pi\epsilon_{ij}^3\,\chi(n;i,j) = 2\Xi_{ij}'' \tag{4.3}$$

provided $a_{ij}=\frac{1}{2}$ for all $i,j=1,\ldots,N$, $\Xi_{ij}''=\delta^2\Xi/\delta n(\vec{r},i)\delta n(\vec{r},j)$. Eq. (4.2) then implies, for example that,

$$\epsilon_{ij}^3\,\frac{\delta\chi(n;i,j)}{\delta n(\vec{r},k)} = \epsilon_{kj}^3\,\frac{\delta\chi(n;k,j)}{\delta n(\vec{r},i)}\,. \tag{4.4}$$

We can now imagine that we repeat the discussion of Secs. II and III for $\mathcal{R}(f)$ defined by neglecting in the Enskog equations the terms proportional to ϵ^k, $k\geq 4$. It follows from the results of Sec. III that all four theorems must be true. The corresponding theorems can also be proved independently. In fact, Theorems III.1–III.3 have been proved in Ref. 13 and the fourth theorem has been discussed in Refs. 10 and 13. The condition (4.3) appeared in Ref. 13 in a way analogous as (3.6) appeared in this paper.

Finally, we point out once again that if $Q(n)$ is known then the thermodynamic equation of state is known [see (2.1), (3.9), (2.8), and (2.9)]

$$\frac{p}{k_BT} = -\frac{1}{\omega}\,W\!\left(n_{eq};\frac{\mu_1}{k_BT},\ldots,\frac{\mu_N}{k_BT},\frac{1}{k_BT}\right),$$

where k_B is the Boltzmann constant, p is the pressure, μ_i is the chemical potential of the ith component, T is the temperature, ω is the volume

$$W\!\left(n;\frac{\mu_1}{k_BT},\ldots,\frac{\mu_N}{k_BT},\frac{1}{k_BT}\right) = \sum_{i=1}^{N}\int_\Omega d\vec{r}\,n(\vec{r},i)[\ln n(\vec{r},i)-1] + Q(n) + \sum_{i=1}^{N}\left(-\frac{\mu_i}{k_BT}+\mathfrak{N}\right)\int_\Omega d\vec{r}\,n(\vec{r},i)\,,$$

N is determined by

$$\int d\vec{v}\,\exp\!\left(\mathfrak{N}-\frac{1}{2k_BT}v^2\right)=1\,,$$

and n_{eq} is the solution of

$$\delta W\!\left(n;\frac{\mu_1}{k_BT},\ldots,\frac{\mu_N}{k_BT},\frac{1}{k_BT}\right)\Big/\;\delta n(\vec{r},i)=0\;(i=1,\ldots,N)\,.$$

We note that, for example, in the case of the one-component system, the van der Waals correction, due to the hard-core potential, to the ideal-gas equation of state is reproduced if we choose $\chi(n)=(1-Bn)^{-1}$, $B=\frac{2}{3}\pi\epsilon^3$. Then $\Xi'(n)=-\ln(1-Bn)$ according to (4.3) and $p/k_BT=n+Bn^2/(1-Bn)$.

V. DISCUSSION

In the first part of this section, we shall discuss the physical meaning of the compatibility condition (3.6). The second part will be then devoted to the discussion of the balance of entropy and to our answers to some questions asked by Résibois in Sec. 4 of Ref. 9.

(i) We have shown that if (1.2) is accepted as an empirical equation governing the time evolution of fluid with the quantities χ representing the phenomenological quantities (to be determined by comparing theoretical predictions with observations), then (1.2) is compatible with thermodynamics provided (3.6) is satisfied, $\chi>0$, and χ is symmetric with respect to the interchange of i,j and $\vec{r},\vec{p}$. The physical meaning of (3.6) is therefore determined by the clear physical meaning of its consequences (the results contained in the four theorems). The relations (3.6) show how the functions χ entering (1.2) phenomenologically appear in the entropy functional associated with (1.2) and consequently also in the thermodynamic equation of state implied by (1.2).

(ii) Raveche and Green in Ref. 18 have found a general condition restricting the choice of possible truncations in the Yvon, Born, and Green hierarchy. Their condition applied to our case says that the curl of the right-hand side of (3.6) equals zero. Because clearly the curl of the left-hand side of (3.6) equal zero, the Raveche-Green condition is satisfied provided (3.6) is satisfied. The physical arguments associated with the Raveche-Green condition can be thus associated also with (3.6).

(iii) Our results are independent of a particular choice of a scheme of modifications of the Liouville equation that can be shown to lead to (1.2). Many such schemes have been proposed. We mention the elegant schema due to Grad (see, e.g., Ref. 10) or the schema proposed by Résibois.[8,9] An insight into the physical meaning of (3.6) can be obtained by putting (3.6) into the context of the chosen schema. If we choose the Resibois schema then (3.6) will correspond to his equation (25b) that, as he says, "imitates for our particular nonequilibrium ensemble, the well-known equilibrium hierarchy for hard spheres."

At the end of Ref. 9 Résibois raises the question as to whether the balance of the entropy associated with the Enskog equation can be written in the form $S=\int_\Omega d\vec{r}\, s(\vec{r},t)$:

$$\frac{\partial s(\vec{r},t)}{\partial t}=-\frac{\partial}{\partial r_\alpha}J_{s\alpha}(\vec{r},t)+\sigma(\vec{r},t)\,, \tag{5.1}$$

where $\sigma(\vec{r},t)\leqslant 0$ is the local entropy production and J_S is the entropy flux. On the basis of the result proved by Résibois (Theorem III.4 in our paper is the generalization of Résibois's result in the case of N-component fluid), it follows only that $dS/dt\leqslant 0$ [provided his equation (25b), or in our case (3.6), is satisfied]. We have obtained

$$\frac{dS}{dt}=\left.\frac{dS}{dt}\right|_- +\left.\frac{dS}{dt}\right|_+ ,$$

where

$$\left.\frac{dS}{dt}\right|_- =\int_\Omega d\vec{r}\int d\vec{v}\,\frac{\delta S}{\delta f(\vec{r},\vec{v})}\,\mathcal{R}^-(f)$$

and

$$\left.\frac{dS}{dt}\right|_+ =\int_\Omega d\vec{r}\int d\vec{v}\,\frac{\delta S}{\delta f(\vec{r},\vec{v},)}\,\mathcal{R}^+(f)\,.$$

The Theorem III.1 implies

$$\left.\frac{dS}{dt}\right|_+ \leqslant 0\,,$$

where the equality holds if and only if $f\in\bar{\bar{\mathcal{E}}}_+$. The Theorem III.3 implies $dS/dt|_-=0$ [provided (3.6) is satisfied] if the time evolution is governed by the linearized Enskog equation and the terms proportional to φ^k $(k\geqslant 3)$ are neglected. We can therefore suggest in this case the following identification:

$$\left.\frac{dS}{dt}\right|_+ =\int_\Omega d\vec{r}\,\sigma(\vec{r},t)$$

and

$$\left.\frac{dS}{dt}\right|_- =-\int d\vec{r}\,\frac{\partial}{\partial r_\alpha}J_{s\alpha}(\vec{r},t)=0\,.$$

Thus, $\mathcal{R}^+(f)$ enters only into the entropy production and $\mathcal{R}^-(f)$ only into the entropy flux. In general, however, $dS/dt|_-\leqslant 0$ [provided (3.6) is satisfied] and the equality holds if and only if $f\in\bar{\bar{\mathcal{E}}}_+$. This statement is proved by following exactly the proof of Theorem III.4 where $\mathcal{R}(f)$ is replaced by $\mathcal{R}^-(f)$. It is therefore impossible to identify $dS/dt|_-$ with $-\int_\Omega d\vec{r}(\partial/\partial r_\alpha)J_{s_\alpha}(\vec{r},t)$ [since $\int_\Omega d\vec{r}(\partial/\partial r_\alpha)J_{s_\alpha}(\vec{r},t)=0$ provided appropriate boundary conditions are assumed] in the case of the nonlinear Enskog equation and thus the decomposition of dS/dt suggested in (5.1) remains unclear.

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