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On thermodynamics of a gas
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by

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ABSTRACT. — The form of the entropy inequality is determined for a gas whose vibrational energy is not—in non-equilibrium—determined by the temperature. Phenomenological and statistical arguments are employed to derive an inequality that differs from the Clausius Duhen inequality in two terms.

1. INTRODUCTION

This paper presents an effort to formulate a thermodynamic theory of a gas with one scalar internal variable that represents the specific vibrational energy of the molecules of a gas. The equations of balance of mass, momentum and internal energy customary in thermodynamics are here supplemented by a general equation of balance for the vibrational energy. These equations of balance and simple constitutive equations give rise to field equations which a thermodynamic process must satisfy. The constitutive equations are subject to restrictions imposed by the requirement that the entropy principle is valid for all thermodynamic processes. The form of the entropy inequality adopted here goes back to ideas set forth by Müller and Liu in [1] and [2] respectively and the evaluation of this inequality uses the method of Lagrange multipliers developed by Liu in [3]. The entropy flux is shown to depend on the flux of internal energy and on the flux of the vibrational energy. Similarly, the supply of entropy contains one term dependent on the supply of internal energy and another term dependent on the supply of vibrational energy.

A statistical calculation allows the determination of the constitutive functions for the internal energy and the entropy and thus offers the possibility to identify the Lagrange multipliers of the phenomenological theory in non-equilibrium.

2. PHENOMENOLOGICAL THEORY
OF A GAS WITH VIBRATING MOLECULES

a) Equations of balance, constitutive equations, thermodynamic processes

In a gas whose molecules can vibrate with one frequency the following fields are of macroscopic interest

$$
\begin{aligned}
&\rho(\chi_n, t) \quad - \text{density (*)},\\
&v_i(\chi_n, t) \quad - \text{velocity},\\
&T(\chi_n, t) \quad - \text{(absolute) temperature},\\
&\varepsilon^V(\chi_n, t) \quad - \text{specific vibrational energy}.
\end{aligned}
\tag{2.1}
$$

The inclusion of the field $\varepsilon^V(\chi_n, t)$ among this list is motivated by the observation that, when the gas undergoes rapid changes, the energy stored in the vibrational motion of the molecules is not determined by the temperature.

The field equations for the determination of the fields (2.1) are based upon the equations of balance of mass, momentum, internal energy, viz.

$$
\begin{aligned}
&\dot{\rho} + \rho_{,i} v_{i,i} = 0\\
&\rho \dot{v}_i - t_{ij,j} = \rho f_i \;(*),\\
&\rho \dot{\varepsilon} + q_{i,i} = t_{ij} v_{i,j} + \rho r
\end{aligned}
\tag{2.2}
$$

and upon an equation of balance for the vibrational energy

$$
\rho \dot{\varepsilon}_V + q^V_{i,i} = \sigma + \rho r^V
\tag{2.3}
$$

In the equations (2.2) and (2.3) t_{ij} is the stress, q_i the flux of internal energy, ε the specific internal energy which includes the vibrational energy, while f_i represents the external body force and r and r^V are the supplies of internal energy and of vibrational energy respectively, both due to the absorption of radiation by the gas molecules. q^V_i is the flux of vibrational energy and

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(*) Cartesian tensor notation is used throughout this paper, whereby indices such as n or ij in χ_n or t_{ij} denote cartesian components of the position vector and the stress tensor respectively. Further, a comma denotes differentiation with respect to a spatial variable and Einstein's summation convention is employed. Thus for instance $q_{i,i}$ means the divergence of the heat flux.

σ is the density of its production due to the interaction of the gas molecules among each other. A comma denotes spatial differentiation and a superposed dot denotes the material time derivative.

For given external supplies $f_i(\chi_n, t)$, $r(\chi_n, t)$ and $r^V(\chi_n, t)$ the equations (2.2) and (2.3) furnish field equations for the fields (2.1) if supplemented by constitutive equations which relate t_{ij}, q_i, q_i^V, ε and σ to the fields ρ, v_i, T and ε^V in a materially dependent manner. I choose the following simple constitutive relations

$$\varepsilon = \varepsilon(\rho, \text{T}, \varepsilon^V),$$
$$\sigma = \sigma(\rho, \text{T}, \varepsilon^V),$$
$$q_i = q_i(\rho, \text{T}, \varepsilon^V, \text{T}_{,i}, \varepsilon_{,i}^V) = \alpha \text{T}_{,i} + \beta \varepsilon_{,i}^V,$$
$$q_i^V = q_i^V(\rho, \text{T}, \varepsilon^V, \text{T}_{,i}, \varepsilon_{,i}^V) = \alpha^V \text{T}_{,i} + \beta^V \varepsilon_{,i}^V, \qquad (2.4)$$
$$t_{ij} = t_{ij}(\rho, \text{T}, \varepsilon^V, v_{(i,j)}) = -p\delta_{ij} + \nu v_{l,l}\delta_{ij} + 2\mu\left(v_{(i,j)} - \frac{1}{3}v_{l,l}\delta_{ij}\right)(*),$$

where the coefficients α, β, α^V, β^V, p, ν and μ may depend on ρ, T, ε^V just as ε and σ do; $-\alpha$ is called heat conductivity, p is called pressure and μ and ν are called viscosity and volume viscosity respectively. Elimination of ε, σ, q_i, q_i^V and t_{ij} between (2.2), (2.3) and (2.4) provides a set of field equations for arbitrarily prescribed functions of $f_i(\chi_n, t)$, $r(\chi_n, t)$ and $r^V(\chi_n, t)$. Every solution $\rho(\chi_n, t)$, $v_i(\chi_n, t)$, $T(\chi_n, t)$ and $\varepsilon^V(\chi_n, t)$ of these field equations is called a *thermodynamic process* in the gases considered here.

b) Entropy principle and its general consequences

Let η denote the specific entropy, Φ_i the entropy flux and s the external supply of entropy and assume that η and Φ_i are given—in the gases under consideration—by the constitutive equations

$$\eta = \eta(\rho, \text{T}, \varepsilon^V)$$
$$\Phi_i = \Phi_i(\rho, \text{T}, \varepsilon^V, \text{T}_{,i}, \varepsilon_{,i}^V) = \varphi(\rho, \text{T}, \varepsilon^V)\text{T}_{,i} + \psi(\rho, \text{T}, \varepsilon^V)\varepsilon_{,i}^V, \qquad (2.5)$$

while s is a linear function of f_i, r and r^V of the type

$$s = \lambda_i f_i + \lambda r + \lambda^V r^V, \qquad (2.6)$$

where λ_i, λ and λ^V may depend on ρ, T, ε^V, $\text{T}_{,i}$, $\varepsilon_{,i}^V$, in a manner dependent on material. The right hand side of (2.5) makes it clear that Φ_i is a linear function of $\text{T}_{,i}$ and $\varepsilon_{,i}^V$. This explicit form of the constitutive equation is used later in the derivation of equation (2.14), although the coefficients φ and ψ do not appear again.

(*) Round indices indicate symmetrization.

The entropy principle adopted here requires that the inequality

$$\rho\dot{\eta} + \Phi_{i,i} - \rho s \geq 0 \text{ (*)} \qquad (2.7)$$

hold for all thermodynamic processes.

According to this principle the entropy inequality (2.7) need not be satisfied for all fields $\rho(\chi_n, t)$, $v_i(\chi_n, t)$, $T(\chi_n, t)$, $\varepsilon^V(\chi_n, t)$ and $f_i(\chi_n, t)$, $r(\chi_n, t)$, $r^V(\chi_n, t)$ but only for thermodynamic processes. In other words, the fields $\rho(\chi_n, t)$ through $r^V(\chi_n, t)$ for which the entropy inequality must hold are constrained to be solutions of the field equations (2.2), (2.3) and (2.4). Liu has shown in [3] that we may rid ourselves of these constraints by the use of Lagrange multipliers Λ^ρ, Λ^{Vi}, Λ and Λ^V which can in general be functions of ρ, v_i, T, ε^V, $T_{,i}$, $\varepsilon^V_{,i}$, and f_i, r, r^V. He proved that the statement that (2.7) be satisfied for all thermodynamic processes implies the statement that the new inequality

$$\rho\dot{\eta} + \Phi_{i,i} - \rho s - \Lambda^\rho(\dot{\rho} + \rho v_{i,i}) - \Lambda^{Vi}(\rho\dot{v}_i - t_{ij,j} - \rho f_i)$$
$$- \Lambda(\rho\dot{\varepsilon} + q_{i,i} - t_{ij}v_{i,j} - \rho r) - \Lambda^V(\rho\dot{\varepsilon}^V + q^V_{i,i} - \sigma - \rho r^V) \geq 0 \qquad (2.8)$$

be satisfied for arbitrary analytic fields ρ, v_i, T, ε^V, f_i, r and r^V.

When the constitutive equations (2.4) and (2.5) are introduced into (2.8) as well as the assumption (2.6), what results on the left hand side of this inequality is an expression linear in

$$\dot{\rho}, \dot{v}_i, \dot{T}, \dot{\varepsilon}^V, \rho_{,i}, T_{,ij}, \varepsilon^V_{,ij}, \qquad (2.9)$$

Therefore and because each one of these quantities can be chosen arbitrarily, the inequality (2.8) could easily be violated, if any term containing a quantity (2.9) would contribute to its left hand side. To avoid this we must have the following conditions which are easily verified:

$$\rho\left(\frac{\partial\eta}{\partial\rho} - \Lambda\frac{\partial\varepsilon}{\partial\rho}\right) - \Lambda^\rho = 0, \qquad (2.10)_1$$

$$\Lambda^{Vi} = 0, \qquad (2.10)_2$$

$$\frac{\partial\eta}{\partial T} - \Lambda\frac{\partial\varepsilon}{\partial T} = 0, \qquad (2.10)_3$$

$$\frac{\partial\eta}{\partial\varepsilon^V} - \Lambda\frac{\partial\varepsilon}{\partial\varepsilon^V} - \Lambda^V = 0, \qquad (2.10)_4$$

$$\frac{\partial\Phi_i}{\partial\rho} - \Lambda\frac{\partial q_i}{\partial\rho} - \Lambda^V\frac{\partial q^V_i}{\partial\rho} = 0, \qquad (2.10)_5$$

$$\frac{\partial\Phi_i}{\partial T_{,j}} - \Lambda\frac{\partial q_i}{\partial T_{,j}} - \Lambda^V\frac{\partial q^V_i}{\partial T_{,j}} = 0, \qquad (2.10)_6$$

(*) The assumption that Φ_i be given by a constitutive equation of its own is due to Müller (see [1]) and replaces the more customary assumption that the entropy flux be equal to the heat flux divided by the absolute temperature. The assumption (2.6) concerning the form of the entropy supply is an obvious adaptation of an idea of Liu presented in [2].

$$\frac{\partial \Phi_i}{\partial \varepsilon_{,j}^{\mathrm{V}}} - \Lambda \frac{\partial q_i}{\partial \varepsilon_{,j}^{\mathrm{V}}} - \Lambda^{\mathrm{V}} \frac{\partial q_i^{\mathrm{V}}}{\partial \varepsilon_{,j}^{\mathrm{V}}} = 0. \qquad (2.10)_7$$

Since $\Lambda^{\mathrm{V}i} = 0$, the remaining inequality reads

$$\left(\frac{\partial \Phi_i}{\partial T} - \Lambda \frac{\partial q_i}{\partial T} - \Lambda^{\mathrm{V}} \frac{\partial q_i^{\mathrm{V}}}{\partial T}\right) T_{,i} + \left(\frac{\partial \Phi_i}{\partial \varepsilon^{\mathrm{V}}} - \Lambda \frac{\partial q_i}{\partial \varepsilon^{\mathrm{V}}} - \Lambda^{\mathrm{V}} \frac{\partial q_i^{\mathrm{V}}}{\partial \varepsilon^{\mathrm{V}}}\right) \varepsilon_{,i}^{\mathrm{V}}$$

$$+ (\Lambda t_{ij} - \rho \Lambda^\rho \delta_{ij}) v_{i,j} + \Lambda^{\mathrm{V}} \sigma + \rho \lambda_i f_i + \rho(\lambda - \Lambda) r + \rho(\lambda^{\mathrm{V}} - \Lambda^{\mathrm{V}}) r^{\mathrm{V}} \geq 0, \quad (2.11)$$

and since by $(2.10)_{3,1}$ Λ and Λ^{V} are independent of f_i, r and r^{V} we recognize that the left hand side of (2.11) is linear in the arbitrary quantities f_i, r and r^v. Thus we conclude by the same argument, which led to (2.10), that

$$\lambda_i = 0 \quad , \quad \lambda = \Lambda \quad , \quad \lambda^{\mathrm{V}} = \Lambda^{\mathrm{V}} \qquad (2.12)$$

holds, whence it follows that the entropy supply is related to the supplies of internal and vibrational energy as follows

$$s = \Lambda r + \Lambda^{\mathrm{V}} r^{\mathrm{V}}. \qquad (2.13)$$

The equations $(2.4)_{3,4}$ and $(2.5)_2$ show that q_i, q_i^{V} and Φ_i depend linearly on $T_{,i}$ and $\varepsilon_{,i}^{\mathrm{V}}$ and therefore a trivial calculation shows that $(2.10)_{6,7}$ imply the equation

$$\Phi_i = \Lambda q_i + \Lambda^{\mathrm{V}} q_i^{\mathrm{V}} \qquad (2.14)$$

for the entropy flux. Equation $(2.10)_5$ requires further that

$$\frac{\partial \Lambda}{\partial \rho} = 0 \qquad \text{and} \qquad \frac{\partial \Lambda^{\mathrm{V}}}{\partial \rho} = 0 \text{ (*)}. \qquad (2.15)$$

I rewrite $(2.10)_{3,4}$ and eliminate Λ^ρ, Φ_i, λ_i, λ and λ^{V} from (2.11) by use of $(2.10)_1$, (2.12) and (2.13) thus getting

$$\frac{\partial \eta}{\partial T} = \Lambda \frac{\partial \varepsilon}{\partial T}, \qquad (2.16)$$

$$\frac{\partial \eta}{\partial \varepsilon^{\mathrm{V}}} = \Lambda \frac{\partial \varepsilon}{\partial \varepsilon^{\mathrm{V}}} + \Lambda^{\mathrm{V}}, \qquad (2.17)$$

$$\left(\Lambda t_{ij} - \rho^2 \left(\frac{\partial \eta}{\partial \rho} - \Lambda \frac{\partial \varepsilon}{\partial \rho}\right) \delta_{ij}\right) v_{(i,j)} + \Lambda^{\mathrm{V}} \sigma +$$

$$+ \begin{pmatrix} \alpha \dfrac{\partial \Lambda}{\partial T} + \alpha^{\mathrm{v}} \dfrac{\partial \Lambda^{\mathrm{V}}}{\partial T} & \dfrac{1}{\alpha}\left[\alpha \dfrac{\partial \Lambda}{\partial \varepsilon^{\mathrm{V}}} + \alpha^{\mathrm{v}} \dfrac{\partial \Lambda^{\mathrm{V}}}{\partial \varepsilon^{\mathrm{V}}} + \beta \dfrac{\partial \Lambda}{\partial T} + \beta^{\mathrm{v}} \dfrac{\partial \Lambda^{\mathrm{V}}}{\partial T}\right] \\ \dfrac{1}{2}\left[\alpha \dfrac{\partial \Lambda}{\partial \varepsilon^{\mathrm{V}}} + \alpha^{\mathrm{v}} \dfrac{\partial \Lambda^{\mathrm{V}}}{\partial \varepsilon^{\mathrm{V}}} + \beta \dfrac{\partial \Lambda}{\partial T} + \beta^{\mathrm{v}} \dfrac{\partial \Lambda^{\mathrm{V}}}{\partial T}\right] & \beta \dfrac{\partial \Lambda}{\partial \varepsilon^{\mathrm{V}}} + \beta^{\mathrm{v}} \dfrac{\partial \Lambda^{\mathrm{V}}}{\partial \varepsilon^{\mathrm{V}}} \end{pmatrix}$$

$$\begin{pmatrix} T_{,i} \\ \varepsilon_{,i}^{\mathrm{V}} \end{pmatrix}\begin{pmatrix} T_{,i} \\ \varepsilon_{,i}^{\mathrm{V}} \end{pmatrix} \geq 0 \quad (2.18)$$

(*) There is an alternative to (2.15) as a consequence of $(2.10)_5$, but that requires that q_i and q_i^{v} be parallel which I think is unlikely to be true in general.

The left hand side of the residual entropy inequality (2.18) is called the density of *entropy production* and denoted by Σ. From (2.16) and (2.17) follows

$$\frac{\partial \Lambda}{\partial \varepsilon^V} \frac{\partial \varepsilon}{\partial T} - \frac{\partial \Lambda}{\partial T} \frac{\partial \varepsilon}{\partial \varepsilon^V} - \frac{\partial \Lambda^V}{\partial T} = 0 \qquad (2.19)$$

as an integrability condition for η.

The relations (2.13) through (2.19) exhaust the general consequences of the entropy principle. All of them contain the Lagrange multipliers Λ, Λ^V whose equilibrium values I now proceed to calculate.

c) Consequences of the entropy principle in equilibrium

If the external supplies are absent, *equilibrium* is characterized by uniform and time-independent fields of density, velocity, temperature and vibrational energy. Inspection of (2.3) and (2.18) shows that the densities of both the production of vibrational energy and the production of entropy vanish in equilibrium:

$$\sigma\mid_E = 0 \qquad \text{and} \qquad \Sigma\mid_E = 0 \text{ (*)}. \qquad (2.20)$$

When we assume that $\sigma(\rho,\ T,\ \varepsilon^V)$ is invertible with respect to ε^V, equation (2.20)$_1$ states that in equilibrium ε^V is a function of ρ and T so that

$$\varepsilon^V\mid_E = \varepsilon^V(\rho,\ T) \qquad (2.21)$$

holds. The interdependence of the variables expressed by this relation leads to the following identities for every function $F(\rho,\ T,\ \varepsilon^V)$

$$\begin{aligned}
\frac{\partial F}{\partial \rho}\bigg|_E &= \frac{\partial F\mid_E}{\partial \rho} - \frac{\partial F}{\partial \varepsilon^V}\bigg|_E \frac{\partial \varepsilon^V\mid_E}{\partial \rho}, \\
\frac{\partial F}{\partial T}\bigg|_E &= \frac{\partial F\mid_E}{\partial T} - \frac{\partial F}{\partial \varepsilon^V}\bigg|_E \frac{\partial \varepsilon^V\mid_E}{\partial T}.
\end{aligned} \qquad (2.22)$$

The entropy production density Σ is obviously a function of the variables ρ, T, ε^V, $T_{,i}$, $\varepsilon^V_{,i}$ $v_{(i,j)}$. With the already assumed invertibility of $\sigma(\rho,\ T,\ \varepsilon^V)$ we may also consider Σ as a function of the form

$$\Sigma = \Sigma(\rho,\ T,\ \sigma,\ T_{,i},\ \varepsilon^V_{,i},\ v_{(i,j)})$$

and from (2.20) we infer that the entropy production assumes its minimum, namely zero, in equilibrium. Thus of necessity we must have

$$\frac{\partial \Sigma}{\partial X_A}\bigg|_E = 0 \qquad \text{and} \qquad \frac{\partial^2 \Sigma}{\partial X_A \partial X_B}\bigg|_E - \text{positive semi-definite, } \quad (2.23)$$

where X_A stands for any one of the variables σ, $T_{,i}$, $\varepsilon^V_{,i}$, $v_{(i,j)}$.

(*) The index E denotes equilibrium.

From $(2.23)_1$ one concludes immediately

$$\Lambda^V |_E = 0,$$

$$\frac{\partial \eta}{\partial \rho}\bigg|_E = \Lambda |_E \left(\frac{\partial \varepsilon}{\partial \rho}\bigg|_E - \frac{p |_E}{\rho^2}\right), \qquad (2.24)$$

and these two equations together with (2.16), (2.17) and with the identities (2.22) applied to η and ε imply the equation

$$d\eta |_E = \Lambda |_E \left(\frac{\partial \varepsilon |_E}{\partial T} \alpha T + \left(\frac{\partial \varepsilon |_E}{\partial \rho} - \frac{p |_E}{\rho^2}\right) d\rho\right). \qquad (2.25)$$

Thus we come to identify the equilibrium value of the Lagrange multiplier Λ with the reciprocal of the absolute temperature

$$\Lambda |_E = \frac{1}{T} \qquad (2.26)$$

because classical thermostatics of fluids and gases defines the absolute temperature as *the* integrating denominator of the expression

$$d\varepsilon |_E - \frac{p |_E}{\rho^2} \alpha d$$

that leads to entropy as the integral function.

The equations (2.25) and (2.26) imply the equation

$$\frac{1}{T} = \frac{\dfrac{\partial p |_E}{\partial T}}{p |_E - \rho^2 \dfrac{\partial \varepsilon |_E}{\partial \rho}} \qquad (2.27)$$

which is the central result of thermostatics of fluids and gases, well-known since Clausius.

From $(2.24)_1$ and (2.26) we conclude that $\dfrac{\partial \Lambda^V |_E}{\partial \rho} = 0$ and $\dfrac{\partial \Lambda |_E}{\partial \rho} = 0$ hold and since by (2.15) Λ and Λ^V are independent of ρ, the identities (2.22) applied to Λ and Λ^V lead to the conditions :

$$\frac{\partial \Lambda}{\partial \varepsilon^V}\bigg|_E \frac{\partial \varepsilon^V |_E}{\partial \rho} = 0 \qquad \text{and} \qquad \frac{\partial \Lambda^V}{\partial \varepsilon^V}\bigg|_E \frac{\partial \varepsilon^V |_E}{\partial \rho} = 0 \qquad (2.28)$$

which can be satisfied in various ways, the most natural one being that $\dfrac{\partial \varepsilon^V |_E}{\partial \rho} = 0$ holds.

It is a routine matter to evaluate the condition $(2.23)_2$. This condition

imposes the following restrictions upon the coefficients in (2.4) and upon the Lagrange multipliers

$$\alpha|_E + T^2 \left(\alpha|_E \frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E + \alpha^V|_E \frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E \right) \frac{\partial\varepsilon^V|_E}{\partial T} \leq 0,$$

$$\left(\beta|_E \frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E + \beta^V|_E \frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E \right) \geq 0,$$

$$\left[\frac{\alpha|_E}{T^2} + \left(\alpha|_E \frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E + \alpha^V|_E \frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E \right) \frac{\partial\varepsilon^V|_E}{\partial T} \right] \left[\beta|_E \frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E + \beta^V|_E \frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E \right]$$

$$+ \frac{1}{4} \left[\frac{\beta|_E}{T^2} - \left(\alpha|_E - \beta|_E \frac{\partial\varepsilon|_E}{\partial T} \right) \frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E + \left(\beta^V|_E \frac{\partial\varepsilon^V|_E}{\partial T} - \alpha^V|_E \right) \frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E \right]^2 \geq 0,$$

$$\text{(2.29)}$$

$$\mu|_E \geq 0,$$

$$\nu|_E \geq 0,$$

$$\frac{\partial\Lambda^V}{\partial\sigma}\Big|_E \geq 0,$$

$$\frac{1}{T}\nu|_E \frac{\partial\Lambda^V}{\partial\sigma}\Big|_E - \frac{1}{4} \left\{ \left(\frac{1}{T}\frac{\partial p}{\partial\varepsilon^V}\Big|_E + T\frac{\partial p|_E}{\partial T}\frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E \right) \frac{\partial\varepsilon_V}{\partial\sigma}\Big|_E \right\}^2 \geq 0.$$

For the derivation of (2.29) use has been made of most of the previous results (2.15) through (2.28).

d) Discussion of the results of the phenomenological theory

In the last section it has been possible to calculate the equilibrium values of the Lagrange multipliers Λ and Λ^V as $\frac{1}{T}$ and zero respectively. Thus the thermostatic result (2.27) could be regained and $\mu|_E$ and $\nu|_E$ could be shown to be non-negative. Apart from these results, however, even the equilibrium results still depend on unknown properties of Λ and Λ^V, namely on $\frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E$ and $\frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E$; of course, $\frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E$ and $\frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E$ are not independent, because from (2.19) and from the identities (2.22) applied to Λ and Λ^V one concludes that

$$\frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E \left(\frac{\partial\varepsilon}{\partial T}\Big|_E + \frac{\partial\varepsilon^V|_E}{\partial T}\frac{\partial\varepsilon}{\partial\varepsilon^V}\Big|_E \right) = - \frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E \frac{\partial\varepsilon^V|_E}{\partial T} - \frac{1}{T^2}\frac{\partial\varepsilon}{\partial\varepsilon^V}\Big|_E \quad \text{(2.30)}$$

must hold. Clearly it would be desirable to learn more about the Lagrange multipliers Λ and Λ^V, or at least about $\frac{\partial\Lambda}{\partial\varepsilon^V}\Big|_E$ or $\frac{\partial\Lambda^V}{\partial\varepsilon^V}\Big|_E$, but that would

require additional assumptions about the entropy flux or the entropy supply which I am not prepared to make (*).

Instead, I shall now proceed to consider a simple statistical model which will permit the determination of the functions

$$\varepsilon = \varepsilon(\rho, T, \varepsilon^V) \quad \text{and} \quad \eta = \eta(\rho, T, \varepsilon^V)$$

and thereby—in virtue of equations (2.16), (2.17)—the determination of $\Lambda(T, \varepsilon^V)$ and $\Lambda^V(T, \varepsilon^V)$.

I remark that the results of this chapter are applicable to materials with an arbitrary scalar internal variable, as long as the constitutive equations are of the form (2.4) and (2.5). Indeed, nothing but wording and notation has so far suggested that the internal variable in the present case is a vibrational energy. This case was chosen for easy visualization and because it lends itself to the statistical consideration of the next chapter.

3. STATISTICAL THEORY
OF A GAS WITH VIBRATING MOLECULES

The objective of this section is the statistical calculation of the specific internal energy and the specific entropy of a gas of N non-interacting molecules with translational energy E^T, vibrational energy E^V in a volume V (**). Let p_c, p_n and p_{x_i} be the probabilities that one molecule has kinetic energy $\frac{m}{2}c^2$, vibrational energy $hv\left(n + \frac{1}{2}\right)$ and position $\chi_i \in V$, where m and v are mass and eigenfrequency of the molecule, h is Planck's constant and n may range over all integers 0, 1, 2, ... These probabilities are obviously constrained by the equations

$$\sum_{0 \leqslant c < \infty} p_c = 1, \qquad \sum_{n=0}^{\infty} p_n = 1, \qquad \sum_{\chi_i \in V} p_{\chi_i} = 1, \qquad (3.1)$$

and by the requirement that the expectation values of the kinetic and vibra-

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(*) Obviously, if we were to assume that $\Phi_i = \frac{1}{T} q_i$ holds, or $s = \frac{1}{T} r$, which assumptions are both frequently made, the problem explained above would no exist and, in particular $\left.\frac{\partial \Lambda^V}{\partial \varepsilon^V}\right|_E$ and $\left.\frac{\partial \Lambda^V}{\partial \varepsilon^V}\right|_E$ would both vanish. However, in view of the results of the statistical considerations of the next section, these assumptions cannot be trusted.

(**) The possibility that the molecules may also have rotational energy could be taken into account, but is ignored here for the simplicity of the argument.

tional energies of the molecules be equal to the mean values of these energies, viz.

$$\frac{E^T}{N} = \sum_{0 \leqslant c < \infty} \frac{m}{2} c^2 p_c \quad , \quad \frac{E^V}{N} = \sum_{n=0}^{\infty} h\nu \left(n + \frac{1}{2}\right) p_n. \tag{3.2}$$

The mean value of entropy is given by

$$\frac{H}{N} = -k \sum_{0 \leqslant c < \infty} \sum_{n=0}^{\infty} \sum_{\chi_i \in V} p_c p_n p_{\chi_i} \ln (p_c p_n p_{\chi_i}). \tag{3.3}$$

We find the probability distribution that makes $\dfrac{H}{N}$ a maximum, while it satisfies the constraints (3.1) and (3.2) in the usual manner by forming the expression

$$\frac{H}{kN} - \alpha \left(\sum_{0 \leqslant c < \infty} p_c - 1 \right) - \beta \left(\sum_{n=0}^{\infty} p_n - 1 \right) - \gamma \left(\sum_{\chi_i \in V} p_{\chi_i} - 1 \right)$$

$$- \delta \left(\sum_{0 \leqslant c < \infty} \frac{m}{2} c^2 p_c - \frac{E^T}{N} \right) - \varphi \left(\sum_{n=0}^{\infty} h\nu \left(n + \frac{1}{2}\right) p_n - \frac{E^V}{N} \right)$$

where α, β, γ, δ, φ are Lagrange multipliers, and setting its derivatives with respect to p_c, p_n and p_{χ_i} equal to zero. The result is

(with $\quad C_1 \equiv e^{-\alpha-1} \quad , \quad C_2 \equiv e^{-\beta-1} \quad , \quad C_3 \equiv e^{-\gamma-1}$)

$$p_c = C_1 e^{-\delta \frac{m}{2} c^2} \quad , \quad p_n = C_2 e^{-\varphi h\nu \left(n + \frac{1}{2}\right)} \quad , \quad p_{\chi_i} = C_3,$$

and C_1, C_2, C_3, δ and φ must be determined from the constraints: let the number of speeds between c and $c + dc$ be $X 4\pi c^2 dc$ and let the number of positions in dV be $Y dV$ where X and Y are constant factors of proportionality. Thus the sum over the values of c and χ_i are converted into integrals while the sum over n can easily be calculated; one obtains

$$p_c = \frac{1}{X} \sqrt{\frac{3m}{4\pi \frac{E^T}{N}}}^{\,3} e^{-\frac{3}{4} \frac{mc^2}{E^T/N}} \quad , \quad p_n = \frac{\left(\dfrac{E^V}{Nh\nu} - \dfrac{1}{2}\right)^n}{\left(\dfrac{E^V}{Nh\nu} + \dfrac{1}{2}\right)^{n+1}} \quad , \quad p_{\chi_i} = \frac{1}{YV}.$$

The entropy calculated with these probability distributions follows from (3.3) and one obtains

$$H = \frac{3}{2} kN - kN \ln \left(\frac{1}{XY} \frac{1}{V} \sqrt{\frac{3m}{4\pi E^T/N}} \right)^3 - kN$$

$$\left\{ \left(\frac{E^V}{Nh\nu} - \frac{1}{2} \right) \ln \left(\frac{E^V}{Nh\nu} - \frac{1}{2} \right) - \left(\frac{E^V}{Nh\nu} + \frac{1}{2} \right) \ln \left(\frac{E^V}{Nh\nu} + \frac{1}{2} \right) \right\}. \tag{3.4}$$

In the statistical theory we take the translational energy E^T as a measure of temperature or, more explicitly, we set

$$\frac{E^T}{N} = \frac{3}{2}k\text{T}. \tag{3.5}$$

With (3.5) the equation $E = E^T + E^V$ and (3.4) determine energy and entropy as functions of volume, temperature *and* of the vibrational energy E^V. Division of $E = E^T + E^V$ and (3.4) by the total mass Nm gives the specific values of internal energy and entropy in terms of the variables $\rho = \dfrac{Nm}{V}$, T and $\varepsilon^V = \dfrac{E^V}{Nm}$

$$\varepsilon = \frac{3}{2}\frac{k}{m}\text{T} + \varepsilon^V,$$

$$\eta = -\frac{k}{m}\ln \rho + \frac{3}{2}\frac{k}{m}\ln \text{T} - \frac{k}{m} \tag{3.6}$$

$$\left[\left(\frac{m\varepsilon^V}{h\nu} - \frac{1}{2}\right)\ln\left(\frac{m\varepsilon^V}{h\nu} - \frac{1}{2}\right) - \left(\frac{m\varepsilon^V}{h\nu} + \frac{1}{2}\right)\ln\left(\frac{m\varepsilon^V}{h\nu} + \frac{1}{2}\right)\right] + \text{const.}$$

If $m\varepsilon^V \gg h\nu$ is assumed, the last equation assumes the form

$$\eta = -\frac{k}{m}\ln \rho + \frac{3}{2}\frac{k}{m}\ln \text{T} + \frac{k}{m}\ln \varepsilon^V + \text{const.} \tag{3.7}$$

4. SYNOPSIS AND DISCUSSION

a) Synopsis of the phenomenological and the statistical calculation

The explicit form (3.6) of the constitutive functions for ε and η permits the calculation of the Lagrange multipliers Λ and Λ^V for a gas with vibrating molecules from the equations (2.16), (2.17). The results are obviously

$$\Lambda = \frac{1}{\text{T}},$$

$$\Lambda^V = -\frac{k}{h\nu}\ln \frac{1 - \dfrac{h\nu}{2m\varepsilon^V}}{1 + \dfrac{h\nu}{2m\varepsilon^V}} - \frac{1}{\text{T}} \tag{4.1}$$

and in the case that $h\nu \ll m\varepsilon^V$ holds, $(4.1)_2$ reads

$$\Lambda^V = \frac{k}{m}\frac{1}{\varepsilon^V} - \frac{1}{\text{T}}. \tag{4.2}$$

The following results will all be based on (4.2) rather than (4.1)$_2$, because thus they will assume a simpler form. The reader can easily obtain the corresponding results based on (4.1)$_2$ himself.

The two equations (2.13) and (2.14) now assume the forms

$$s = \frac{1}{T} r + \left(\frac{k}{m} \frac{1}{\varepsilon^V} - \frac{1}{T} \right) r^V,$$

$$\Phi_i = \frac{1}{T} q_i + \left(\frac{k}{m} \frac{1}{\varepsilon_V} - \frac{1}{T} \right) q_i^V, \tag{4.3}$$

while the equations (2.15) and (2.19) are identically satisfied.

Equation (2.24)$_1$ implies

$$\varepsilon^V \big|_E = \frac{k}{m} T \tag{4.4}$$

which, of course, is the only acceptable result in view of the equipartition theorem of statistical mechanics (*). From (2.24)$_2$ we conclude that

$$p \big|_E = \rho \frac{k}{m} T$$

which again is natural, since the statistical model is one appropriate for an ideal gas. Equation (2.26) is satisfied here, in fact, by (4.1) this equation even holds in non-equilibrium in the present case. Both equations (2.28) are now satisfied, because $\dfrac{\partial \varepsilon_V|_E}{\partial \rho} = 0$ holds. $\dfrac{\partial \Lambda}{\partial \varepsilon^V} = 0$ and $\dfrac{\partial \Lambda^V}{\partial \varepsilon^V}\bigg|_E = -\dfrac{m}{k} \dfrac{1}{T^2}$ according to (4.1)$_1$ and (4.2) and therefore the equilibrium equations (2.29)$_{1,2,3,7}$ assume the forms

$$\alpha \big|_E - \alpha^V \big|_E \leq 0,$$

$$\beta^V \big|_E \leq 0,$$

$$[\alpha \big|_E - \alpha^V \big|_E] \left[\frac{m}{k} \beta^V \big|_E \right] - \frac{1}{4} \left[\beta \big|_E - \frac{m}{k} \left(\frac{m}{k} \beta^V \big|_E - \alpha^V \big|_E \right) \right]^2 \geq 0, \tag{4.5}$$

$$\frac{1}{T} v \big|_E \frac{\partial \Lambda^V}{\partial \sigma} \bigg|_E - \frac{1}{4} \frac{1}{T^2} \left(\frac{\partial p}{\partial \varepsilon^V} \bigg|_E \right)^2 \left(\frac{\partial \varepsilon^V}{\partial \sigma} \bigg|_E \right)^2 \geq 0.$$

b) Discussion of some results

Since translational and vibrational energy of the molecules are the two contributors to the total internal energy so that $\varepsilon = \varepsilon_T + \varepsilon^V$ holds, it is suggested also to split the flux of internal energy according to

$$q_i = q_i^T + q_i^V, \tag{4.6}$$

(*) Of course, if $h\nu \ll m\varepsilon^V$ is not satisfied the equipartition theorem is not expected to hold and neither is (4.4); in fact, this equation is replaced by Planck's formula for the vibrational energy of a system of oscillators.

where q_i^T is the flux of translational energy of q_i^V, as before, the flux of vibrational energy. If this is done the entropy flux $(4.3)_2$ assumes the suggestive form

$$\Phi_i = \frac{q_i^T}{T} + \frac{q_i^V}{m/k\varepsilon^V} \tag{4.7}$$

and the constitutive relations for q_i^T and q_i^V are

$$\begin{aligned} q_i^T &= (\alpha - \alpha^V)T_{,i} + (\beta - \beta^V)\varepsilon_{,i}^V, \\ q_i^V &= \alpha^V T_{,i} + \beta^V \varepsilon_{,i}^V. \end{aligned} \tag{4.8}$$

Thus we conclude from $(4.5)_{1,2}$ that a temperature gradient gives rise to a flux of translational energy opposite to its direction and that a gradient of ε^V gives rise to a flux of vibrational energy opposite to its direction.

In a manner analogous to the decomposition (4.6) of the flux of internal energy we may split the supply of internal energy into two parts

$$r = r^T + r^V, \tag{4.9}$$

where r^T denotes a supply of translational energy. Thus from $(4.3)_1$ we get

$$s = \frac{r^T}{T} + \frac{r^V}{m/k\varepsilon^V}. \tag{4.10}$$

In general we expect both contributions to s to be present and their relation will be determined by the nature of the incident radiation as well as by the atomic structure of the oscillators. If there is only absorption of radiation by the vibrational motion, so that $r^T = 0$ holds, we have

$$s = \frac{r}{m/k\varepsilon^V} \tag{4.11}$$

and we conclude that, given a certain supply of internal energy r, its contribution to the supply of entropy is determined by the vibrational energy *and not by the temperature*. This result is somewhat reminiscent of an assumption made by Gurtin and Williams [4], according to which s equals $\frac{r}{\varphi}$, where the « volume-relevant temperature » φ is a scalar constitutive quantity; but the analogy is not complete, since in these authors' work Φ_i is assumed to be equal to $\frac{q_i}{T}$ which is not born out by (4.7).

We continue to assume that $\frac{\partial \varepsilon^V}{\partial \sigma} \neq 0$ and conclude from $(4.5)_4$ that, if the volume viscosity is zero, the derivative $\frac{\partial p}{\partial \varepsilon^V}\Big|_E$ must also vanish; therefore, in this case the difference $\varepsilon^V - \varepsilon^V|_E$ cannot lead to a linear departure from the equilibrium pressure. This result recalls an observation by Meix-

ner [5] in linear irreversible thermodynamics where a linear dependence of the pressure on an internal variable is linked to the volume viscosity.

At least in principle it is possible—by an appropriate approximation scheme—to find the coefficients in the equations (4.8) from the kinetic theory of gases based on the Boltzmann equation for vibrating molecules. Some discussion of this topic and references to relevant papers can be found in [6].

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