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THERMODYNAMICS OF SIMPLE MIXTURES OF FLUIDS WITH APPLICATION TO SECOND SOUND AND LIQUID HELIUM

by

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1. Thermodynamic processes

a. Objective of thermodynamics of mixtures of fluids. The objective of thermodynamics of mixtures of ν fluids is the determimations of the fields of

$$\begin{aligned} &\varrho_\alpha(x_n, t) \;-\; \text{densities},\\ (1.1)\qquad &v_i^\alpha(x_n, t) \;-\; \text{velocities},\\ &T(x_n, t) \;-\; \text{temperature} \end{aligned}$$

at all points of the body and at all times.

In order to achieve this objective, we need field equations and in thermodynamics it is customary to derive these from the equations of balance of mechanics and thermodynamics.

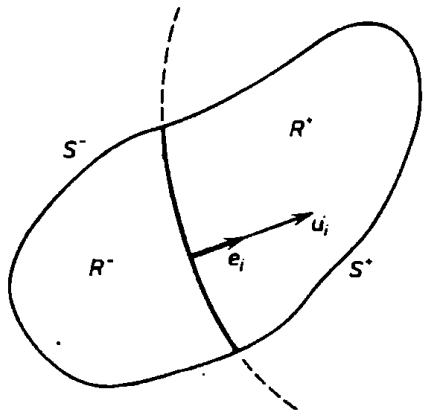
b. Equations of balance.

α. *General.* If Ψ is any additive property of the body we may write the balance of Ψ in a material volume V consisting of regular parts R^+ and R^- and of a singular surface s in the form

$$(1.2)\qquad \int\limits_{R^+ + R^-} \frac{\partial \overset{\nu}{\psi}}{\partial t}\, dv + \iint\limits_{S^+ + S^-} (\overset{\nu}{\psi} v_i + \overset{\nu}{\Phi}_i)\, da_i - \iint\limits_{s} [\overset{\nu}{\psi}]\, u_i\, da_i - \int\limits_{R^+ + R^-} (\overset{\nu}{\sigma} + \overset{\nu}{S})\, dv$$

$$= \frac{d}{dt} \iint\limits_{s} \overset{s}{\psi}\, da - \int\limits_{\partial s} \overset{s}{\Phi}_i \tau_i\, ds + \int\limits_{s} (\overset{s}{\sigma} + \overset{s}{S})\, da.$$

$\overset{v}{\psi}$ and $\overset{s}{\psi}$ are the volume density and surface density of Ψ, respectively, and similarly $\overset{v}{\Xi}$, $\overset{v}{S}$ and $\overset{s}{\Xi}$, $\overset{s}{S}$ are the densities of production and supply in the volume and on the surface. $\overset{v}{\Phi}_i$ and $\overset{s}{\Phi}_i$ are the densities of the non-convective flux of Ψ through S^+, S^- and ∂s, respectively. u_i is the normal velocity of the singular surface and τ_i is a unit tangent vector on s which is normal to the line ∂s. The square bracket $[\psi]$ stands for $\psi^+ - \psi^-$ as usual.



Singular surfaces play an important role in thermodynamics of mixtures since they represent walls separating different bodies. As far as possible we shall neglect the surface densities and in particular we shall always consider $\overset{s}{\psi}$ and $\overset{s}{S}$ as zero.

In regular points of the body equation (1.2) implies the differential equation

$$\frac{\partial \overset{v}{\psi}}{\partial t} + \frac{\partial}{\partial x_i}(\overset{v}{\psi} v_i + \overset{v}{\Phi}_i) = \overset{v}{\sigma} + \overset{v}{S}, \tag{1.3}$$

whereas on the singular surface it implies the jump condition

$$[\overset{v}{\psi}(v_i - u_i) + \overset{v}{\Phi}_i] e_i = \lim_{A \to 0} \frac{1}{A}\left(- \int_{\partial A} \overset{s}{\Phi}_i \tau_i \, ds + \iint_A \overset{s}{\sigma} da \right), \tag{1.4}$$

where A is an infinitesimal area on s.

β. *Equations of balance for mass, momentum and energy.* The conservation laws of mass, momentum and energy are special cases of the general equation of balance with properties and definitions that are summarized in the table

(1.5)

Ψ	$\overset{v}{\psi}$	$\overset{v}{\Phi}_j$	$\overset{v}{\sigma}$	$\overset{v}{S}$	$\overset{s}{\Phi}_j$	$\overset{s}{\sigma}$
Mass	ϱ	0	0	0	0	0
Momentum	ϱv_i	$-t_{ij}$	0	ϱf_i	$-\overset{s}{t}_{ij}$	0
Energy	$\varrho(\varepsilon + \frac{1}{2}v^2)$	$-t_{ij}v_i + q_j$	0	$\varrho(f_i v_i + r)$	$-\overset{s}{t}_{ij}v_i + \overset{s}{q}_j$	0

All productions are zero since mass, momentum and energy are conserved in "closed bodies". Moreover the non-convective mass fluxes $\overset{v}{\Phi}_j$, $\overset{s}{\Phi}_j$ as well as the mass-supply $\overset{v}{S}$ are zero, because there is no flux of mass through a material surface nor is there any supply of mass.

It follows that the equation of mass in regular points and on singular surfaces reads

$$\frac{\partial \varrho}{\partial t}+\frac{\partial \varrho v_j}{\partial x_j}=0, \qquad [\varrho(v_i-u_i)]\,e_i=0. \tag{1.6}$$

Similarly, simply by insertion, we obtain the equation of balance of momentum in regular points and on singular surfaces

$$\begin{gathered}\frac{\partial \varrho v_i}{\partial t}+\frac{\partial}{\partial x_j}(\varrho v_i v_j-t_{ij})=\varrho f_i,\\ [\varrho v_i(v_j-u_j)-t_{ij}]\,e_j=\lim_{A\to 0}\frac{1}{A}\left(\int_{\partial A}\overset{s}{t}_{ij}\tau_j\,ds\right).\end{gathered} \tag{1.7}$$

t_{ij} is the stress tensor in the body and $\overset{s}{t}_{ij}\tau_j$ is the force per line element on the singular surface. f_i is the specific body force, usually gravitational. In a non-internal frame f_i contains the specific inertial forces

$$i_i=2\Omega_{ik}(v_k-\dot{b}_k)-\Omega_{ik}^2(x_k-b_k)+\dot{\Omega}_{ik}(x_k-b_k)-\ddot{b}_i \tag{1.8}$$

consisting of Coriolis force, centrifugal torce, Euler force and force of relative translation. Ω_{ik} is the matrix of angular velocity of the non-inertial frame with respect to an inertial one and b_i is the radius vector between the origines of the two frames.

Finally, we write the balance of energy in regular and singular points

$$\begin{gathered}\frac{\partial \varrho(\varepsilon+\frac{1}{2}v^2)}{\partial t}+\frac{\partial}{\partial x_j}\left(\varrho(\varepsilon+\tfrac{1}{2}v^2)v_j-t_{ij}v_i+q_j\right)=\varrho(f_i v_i+r),\\ [\varrho(\varepsilon+\tfrac{1}{2}v^2)(v_j-u_j)-t_{ij}v_i q_j]\,e_j=\lim_{A\to 0}\frac{1}{A}\int_{\partial A}(\overset{s}{t}_{ij}v_i\tau_j-\overset{s}{q}_j\tau_j)\,ds.\end{gathered} \tag{1.9}$$

ε and q_j are the specific value and the flux of internal energy respectively and ϱr is the density of its supply due to radiation. $\overset{s}{q}_j$ is the flux of internal energy along the singular surface which we shall always neglect.

The reason for splitting the energy into two parts, viz. integral energy $\varrho\varepsilon$ and kinetic energy $\frac{1}{2}\varrho v^2$ is that these contributions have different transformation properties as we shall see. The same is true for the decomposition of the fluxes and the supply of energy.

γ. *Equations of blance of moment of momentum, kinetic energy and*

internal energy. Multiplication of the blance of momentum by $\varepsilon_{kei} x_i$ leads to the equation

$$\frac{\partial \varrho (\mathbf{x} \times \mathbf{v})_k}{\partial t} + \frac{\partial}{\partial x_j}\left(\varrho (\mathbf{x} \times \mathbf{v})_k v_j - \varepsilon_{kei} x_e t_{ij}\right) = \varepsilon_{kij} t_{ij} + (\mathbf{x} \times \varrho \mathbf{f})_k \tag{1.10}$$

which has the form of an equation of balance for moment of momentum whose density is $\varrho(\mathbf{x} \times \mathbf{v})_k$. Therefore, $\varepsilon_{kij} t_{ij}$ must be interpreted as the density of production of moment of momentum and if we assume that moment of momentum is conserved, which is a valid assumption in non-polar fluids, we conclude that the stress must be symmetric:

$$t_{ij} = t_{ji}. \tag{1.11}$$

Multiplication of the belance of momentum by v_i leads to the equation

$$\frac{\partial \frac{1}{2}\varrho v^2}{\partial t} + \frac{\partial}{\partial x_j}\left(\tfrac{1}{2}\varrho v^2 v_j - t_{ij} v_i\right) = -t_{ij}\frac{\partial v_i}{\partial x_j} + \varrho f_i v_i, \tag{1.12}$$

which is the balance of kinetic energy, whose density is $\frac{1}{2}\varrho v^2$. The term $-t_{ij}\dfrac{\partial v_i}{\partial x_j}$ is the density of production of kinetic energy.

Subtraction of the balance of kinetic energy from the balance of energy (1.9) leads to the balance of internal energy, also called the *first law of thermodynamics*.

$$\frac{\partial \varrho \varepsilon}{\partial t} + \frac{\partial}{\partial x_j}(\varrho \varepsilon v_j + q_j) = t_{ij}\frac{\partial v_i}{\partial x_j} + \varrho r, \tag{1.13}$$

whose production density is $t_{ij}\,\partial v_i/\partial x_j$.

The balance of internal energy on a singular surface results from combining the jump conditions $(1.9)_2$ and $(1.7)_2$. It is necessary for this to assume that the velocity on the singular surface element A is the same everywhere and is equal to u_i, the normal velocity of the surface. In that case, $(1.9)_2$ can be written as [1]

$$[\varrho(\varepsilon + \tfrac{1}{2}v^2)(v_j - u_j) - t_{ij} v_i + q_j]\, e_j = \lim_{A \to 0} \frac{1}{A}\left(u_i \int_{\partial A} t^s_{ij} \tau_j \, ds\right) \tag{1.14}$$

and now the limit of the integral may be eliminated between (1.14) and (1.7) with the result

$$[q_j - t_{ij}(v_i - u_i)]\, e_j + [\varepsilon + \tfrac{1}{2}(v_k - u_k)(v_k - u_k)]\, \varrho (v_j - u_j)\, e_j = 0, \tag{1.15}$$

where the mass balance on the surface has also been used. This is the balance of internal energy on the singular surface.

---

[1] Recall that $\overset{s}{q}_j$ is neglected here.

In particular, for an impermeable surface and if the tangential velocities vanish on both sides, (1.15) reduces to the simple statement that the normal component of the flux of internal energy has no jump on the singular surface.

δ. *Equations of balance for the constituents.* The equations of balance of mass, momentum and energy of the constituents of a mixture have the same forms as those for a single body, except that the productions are not zero, because the partial quantities need not be conserved. We have

$$\frac{\partial \varrho_\alpha}{\partial f} + \frac{\partial}{\partial x_j}(\varrho_\alpha v_j^\alpha) = \tau_\alpha, \tag{1.16$_1$}$$

$$\frac{\partial \varrho_\alpha v_i^\alpha}{\partial f} + \frac{\partial}{\partial x_j}(\varrho_\alpha v_i^\alpha v_j^\alpha - t_{ij}^\alpha) = m_i^\alpha + \varrho_\alpha f_i^\alpha, \tag{1.16$_2$}$$

$$\frac{\partial \varrho_\alpha(\varepsilon_x + \frac{1}{2}v_\alpha^2)}{\partial f} + \frac{\partial}{\partial x_j}\left(\varrho_\alpha(\varepsilon_\alpha + \tfrac{1}{2}v_\alpha^2)v_j^\alpha - t_{ij}^\alpha v_i^\alpha + q_i^\alpha\right) = e_\alpha + \varrho_\alpha(f_i^\alpha v_i^\alpha + r_\alpha). \tag{1.16$_3$}$$

Here τ^α, m_i^α and e_α are the production densities of the constituents due to chemical reaction and to the exchange of momentum and energy between the constituents.

The production densities must obey the conditions

$$\sum_{\alpha=1}^{\nu} \tau_\alpha = 0, \quad \sum_{\alpha=1}^{\nu} m_i^\alpha = 0, \quad \sum_{\alpha=1}^{\nu} e_\alpha = 0, \tag{1.17}$$

which express the conservation of mass, momentum and energy of the mixture as a whole.

The production densities τ_α of mass are further restricted by stoichiometric requirements, by which only so many are independent as there are independent chemical reactions. Let the index a ($a = 1, 2, \ldots, n$) denote a chemical reaction, of which there are n independent ones and let γ_α^a be the stoichiometric coefficient of constituent α with molecular weight M_α in reaction a. Then the observation of mass in each reaction requires

$$\sum_{\alpha=1}^{\nu} \gamma_\alpha^a M_\alpha \mu = 0 \tag{1.18}$$

where μ is a reference mass which we take to be the mass of a hydrogen atom. The number density of chemical reactions of type a occurring per unit time is called the *reaction rate density* and is denoted by Λ^a. The mass production of constituent α is then easily seen to be given by

$$\tau_\alpha = \sum_{\alpha=1}^{n} (\gamma_\alpha^a M_\alpha \mu)\Lambda^a. \tag{1.19}$$

Thus, indeed, the number of independent mass productions is equal to n, the number of reaction rate densities.

The partial equations of balance of mass, momentum and energy on a singular surface are somewhat problematic because of the production terms. Indeed, in general there will be production of mass, momentum and energy on those surfaces and in that case the jump conditions provide no useful information, unless we know how big the production is. Therefore, we shall avoid using the partial equations of balance on the surface with one exception, the balance of mass.

For most singular surfaces of thermodynamics we can safely say that there is no mass production on them, and in that case the conservation of mass requires

$$[\varrho_\alpha(v_i^\alpha - u_i)]\, e_i = 0, \tag{1.20}$$

which states that the mass of constituent α that flows into the surface on one side, comes out on the other side.

ε. *Equations of balance for the mixture.* Summation of all equations of balance of mass leads to

$$\frac{\partial \sum_{\alpha=1}^{\nu} \varrho_\alpha}{\partial t} + \frac{\partial}{\partial x_j}\Big(\sum_{\alpha=1}^{\nu} \varrho_\alpha v_j^\alpha\Big) = 0.$$

With the definitions

$$\varrho = \sum_{\alpha=1}^{\nu} \varrho_\alpha \quad \text{and} \quad v_i \equiv \sum_{\alpha=1}^{\nu} \frac{\varrho_\alpha}{\varrho} v_i^\alpha \tag{1.21}$$

for the density and the velocity of the mixture we obtain the equation of balance of the mixture

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_j}{\partial x_i} = 0, \tag{1.22}$$

which has the same form as the equation of balance of mass for a single body.

We shall now proceed to do the same to the equations of balance of momentum and energy of the mixture, namely make them formally identical to the corresponding equations in a single body. And we shall choose the definitions of stress, internal energy and flux of internal energy accordingly.

First of all we define a diffusion velocity $u_i^\alpha = v_i^\alpha - v_i$ which, by (1.21), satisfies the identity

$$\sum_{\alpha=1}^{\nu} \varrho_\alpha u_i^\alpha = 0. \tag{1.23}$$

If we define the stress of the mixture by

$$t_{ij} = \sum_{\alpha=1}^{\nu} (t_{ij}^\alpha - \varrho_\alpha u_i^\alpha u_j^\alpha), \tag{1.24}$$

we obtain from $(1.16)_2$ by summation over all α the babarice of momentum of the mixture, viz.

$$\frac{\partial \varrho v_i}{\partial f}+\frac{\partial}{\partial x_j}(\varrho v_i v_j - t_{ij}) = \sum_{\alpha=1}^{\nu} \varrho_\alpha f_i^\alpha. \tag{1.25}$$

Similarly the definition of the specific internal energy ε and of the flux of internal energy q_i by

$$\varepsilon \equiv \sum_{\alpha=1}^{\nu} \frac{\varrho_\alpha}{\varrho}(\varepsilon_\alpha+\tfrac{1}{2}u_\alpha^2) \quad \text{and} \quad q_i = \sum_{\alpha=1}^{\nu} (q_i^\alpha+\varrho_\alpha(\varepsilon_\alpha+\tfrac{1}{2}u_\alpha^2)u_i^\alpha - t_{ji}^\alpha u_j^\alpha) \tag{1.26}$$

and summation over all equations $(1.16)_3$ leads to the balance of energy for the mixture, viz.

$$\frac{\partial \varrho(\varepsilon+\frac{1}{2}v^2)}{\partial t}+\frac{\partial}{\partial x_j}(\varrho(\varepsilon+\tfrac{1}{2}v^2)v_j - t_{ij}v_i+q_j) = \sum_{\alpha=1}^{\nu} \varrho_\alpha(f_i^\alpha v_i^\alpha + r_\alpha) \tag{1.27}$$

which again has the same form as the energy balance for a singel body. The equations of balance of internal energy can be obtained from (1.25) and (1.27) in the same manner as is a single body and the result is also the same:

$$\frac{\partial \varrho\varepsilon}{\partial t}+\frac{\partial}{\partial x_j}(\varrho\varepsilon v_j+q_j) = t_{ij}\frac{\partial v_i}{\partial x_j}+\sum_{\alpha=1}^{\nu} \varrho_\alpha(f_i^\alpha u_i^\alpha + r_\alpha) \tag{1.28}$$

except that there is a supply of internal energy due to body forces, viz. the power of the body forces on the diffusive motion.

On a singular surface the equations of balance for the mixture have the same form as those for a single body and, in particular, the balance of mass and the balance of internal energy reads

$$\begin{aligned} &[\varrho(v_i-u_i)]\,e_i = 0,\\ &[q_j - t_{ij}(v_i-u_i)]\,e_j + [\varepsilon+\tfrac{1}{2}(v_k-u_k)(v_k-u_k)]\,\varrho(v_j-u_j)\,e_j = 0. \end{aligned} \tag{1.29}$$

c. Constitutive relations

α. *Thermodynamic processes.* We recall that we wish to determinate $4\nu+1$ fields ϱ_α, v_i^α and T and for that we need $4\nu+1$ field equations. These are usually based upon the equations of balance of mass and momentum of the constituents and upon the equation of balance of internal energy of the mixture.

$$\begin{aligned} &\frac{\partial \varrho_\alpha}{\partial f}+\frac{\partial}{\partial x_j}(\varrho_\alpha v_j^\alpha) = \sum_{a=1}^{n} (\gamma_\alpha^a M_\alpha \mu)\Lambda^a,\\ &\frac{\partial \varrho_\alpha v_i^\alpha}{\partial f}+\frac{\partial}{\partial x_j}(\varrho_\alpha v_i^\alpha v_j^\alpha - f_{ij}^\alpha) = m_i^\alpha + \varrho_\alpha f_i^\alpha, \qquad (\alpha = 1, 2, \ldots, \nu),\\ &\frac{\partial \varrho\varepsilon}{\partial f}+\frac{\partial}{\partial x_j}(\varrho\varepsilon v_j+q_j) = t_{ij}\frac{\partial v_i}{\partial x_j}+\sum_{\alpha=1}^{\nu} \varrho_\alpha(f_i^\alpha u_i^\alpha + r_\alpha). \end{aligned} \tag{1.30}$$

But clearly these equations are not field equations for ϱ_α, v_i^α, T in the present form. For one, they contain the body forces f_i^α and the radiative supplies r_α; these quantities we suppose to be given functions of x, t ignoring the difficulties which the determination of r_α may make. More importantly, even with f_i^α and r_α, equations (1.30) contain the new quantities

$$\Lambda^a,\ t_{ij}^\alpha,\ m_i^\alpha,\ \varepsilon,\ q_i. \tag{1.31}$$

These are called *constitutive quantities* and experience tells us that they are related to the thermodynamic fields $\varrho_\alpha(x_n, t)$, $v_i(x_n, t)$ and $T(x_n, t)$ in a materially dependent manner by what we call *constitutive relations*.

In particular, if the constitutive relations have the general forms

$$\begin{aligned}
&\Lambda^a = \Lambda^a(\varrho_\beta, v_i\beta, T, T_{,i}) \qquad (a = 1, 2, \ldots, n),\\
&t_{ij}^\alpha = t_{ij}^\alpha(\ldots) \quad \text{with} \quad \sum_{\alpha=1}^{\nu} t_{ij}^\alpha = \sum_{\gamma=1}^{\nu} t_{ji}^\gamma,\\
&m_i^\alpha = m_i^\alpha(\ldots) \quad \text{with} \quad \sum_{\alpha=1}^{\nu} m_i^\alpha = 0,\\
&\varepsilon = \varepsilon(\ldots)\\
&q_i = q_i(\ldots)
\end{aligned} \tag{1.32}$$

we say that they characterize a *simple mixture of inviscid fluids.* ([2])

If the constitutive functions were known explicitly, we could eliminate Λ^a, t_{ij}^α, m_i^α, ε and q_i between the balance equations (1.30) and the constitutive relations (1.32) and thus obtain a set of explicit field equations. Every solution $\varrho_\alpha(x_n, t)$, $v_i^\alpha(x_n, t)$, $T(x_n, t)$ is called a *thermodynamic process.*

If indeed the constitutive functions were known, the determination of a thermodynamic process $\varrho_\alpha(x_n, t)$, $v_i^\alpha(x_n, t)$, $T(x_n, t)$ would be a purely mathematical problem. However, there is no material, for which the constitutive equations are indeed known and therefore the main task of thermodynamics is to find restrictions on the generality of the constitutive functions, and, if possible, to reduce them to a number of coefficients which, maybe, the experimenter can measure.

In this effort thermodynamics makes use of universal physical principles of which the most important two are the *principle of material objectivity* and the *entropy principle.*

β. *Objective scalars, vectors and tensors under Galilei transformations.* Under a Galilei transformation

$$\bar{x}_i = O_{ij}x_j + R_i t \tag{1.33}$$

([2]) In mixtures of viscous fluids we should have to add velocity gradients to the list of variables. Also in non-simple mixtures the constitutive equations may depend on gradients of the densities. Both additions offer but slight complications to the theory, however here, where I am mostly interested in a systematic presentation of ideas, I prefer to forego these complications.

a quantity is called a *scalar*, *vector* or *tensor*, respectively, if it transforms according to the laws

$$\bar{S} = S, \quad \bar{V}_i = O_{ij} V_j, \quad \bar{T}_{ij} = O_{ik} O_{jl} T_{kl}. \tag{1.34}$$

Among the variables the densities ϱ_α and the temperature T are scalars, therefore the gradient of temperature is a vector, but the velocities are not, since we have by (1.33)

$$\bar{v}_i = O_{ij} v_j + R_i \tag{1.35}$$

but the relative velocities are vectors, e.g. $u_i^\alpha = v_i^\alpha - v_i$.

Among the constitutive quantities the reaction rate densities and the internal energy ε are scalars, the flux of internal energy q_i is a vector ([3]) and the stresses are tensors. Also the body forces f_i^α are vectors while the radiative energy supplies are scalars.

That leaves the density of momentum production which presents something of a problem. Indeed, the momentum balance $(1.30)_2$ may be written as

$$\varrho_\alpha \left(\frac{\partial v_i^\alpha}{\partial t} + v_j^\alpha \frac{\partial v_i^\alpha}{\partial x_j} \right) - \frac{\partial t_{ij}^\alpha}{\partial x_j} - \varrho_\alpha f_i^\alpha = m_i^\alpha - \tau_\alpha v_i^\alpha. \tag{1.36}$$

All terms on the left hand side are vectors under Galilei transformations and since the momentum balance is valid in all Galilei frames, its right-hand side, viz. $m_i^\alpha - \tau_\alpha v_i^\alpha$ must also be a vector. Thus m_i^α is not a vector. Roughly speaking, we may say that the production of momentum m_i^α contains two parts: the momentum production that goes along with chemical production and which is not objective, and an interaction force between the constituents which is objective. We prefer objective quantities as constitutive quantities and therefore we shall formulate a constitutive equation for $m_i^\alpha - \tau_\alpha v_i^\alpha$ rather than for m_i^α.

Also we prefer to write constitutive equations for

$$\begin{aligned} \varepsilon_I &\equiv \varepsilon - \sum_{\alpha=1}^{\nu} \frac{1}{2} \frac{\varrho_\alpha}{\varrho} u_\alpha^2, \\ q_i^I &\equiv q_i - \sum_{\alpha=1}^{\nu} \frac{1}{2} \varrho_\alpha u_\alpha^2 u_i^\alpha \end{aligned} \tag{1.37}$$

rather than for ε and q_i. The reason for this preference is that we shall formulate constitutive equations that are linear in relative velocities and temperature gradients and we wish to be able to say that there are fluids for which these equations are exact. Therefore the explicit non-linear terms included in ε and q_i by their definitions (1.26) must be subtracted before a linearity assumption on ε and q_i makes sense.

([3]) Indeed this is the sole reason why the energy and the energy flux are split into internal and kinetic parts. The first ones are scalars and vectors while the second ones are not.

With all this the constitutive relations for a simple inviscid mixture have the general forms

$$
(1.38)\qquad
\begin{aligned}
&\Lambda^a = \Lambda^a(\varrho_\beta, v_i^\beta, T, T_i) && (a = 1, 2, \ldots, n),\\
&t_{ij}^\alpha = t_{ij}^\alpha(\ldots) && \text{with} \quad \sum_{\alpha=1}^{\nu} t_{ij}^\alpha = \sum_{\alpha=1}^{\nu} t_{ji}^\alpha,\\
&m_i^\alpha - \tau_\alpha v_i^\alpha = M_i^\alpha(\ldots) && \text{with} \quad \sum_{\alpha=1}^{\nu} M_i^\alpha = -\sum_{\alpha=1}^{\nu-1} \tau_\alpha (v_i^\alpha - v_i),\\
&\varepsilon_1 = \varepsilon_1(\ldots),\\
&q_i^1 = q_i^1(\ldots).
\end{aligned}
$$

γ. *Principle of material objectivity*. The principle of material objectivity with respect to Galilei transformations states that the constitutive functions have the same form in all Galilei frames. Thus if

$$
(1.39)\qquad C = \mathscr{C}(\varrho_\beta, v_i^\beta, T, T_i)
$$

stands for any one of the constitutive relations (1.38) we must have

$$
(1.40)\qquad \bar{C} = \mathscr{C}(\bar{\varrho}_\beta, \bar{v}_i^\beta, \bar{T}, \bar{T}_i)
$$

in the new frame. Note that the constitutive *function* $\mathscr{C}$ is the same one while its value has changed, unless C means a scalar.

The above relation for scalar, vectorial and tensorial constitutive quantities reads

$$
(1.41)\qquad
\begin{aligned}
&S(\varrho_\beta, v_i^\beta, T, T_{1i}) = S(\varrho_\beta, O_{ij} v_j^\beta + R_i, T, O_{ij} T_{2j}),\\
&O_{ij} V_j(\ldots) = V_i(\ldots), \qquad O_{ij} O_{kl} T_{jl}(\ldots) = T_{ik}(\ldots).
\end{aligned}
$$

These relations must hold for all O_{ij} and R_i and in particular they must hold for $O_{ij} = \delta_{ij}$ and $R_i = -v_i^\nu$. In this case the relations may be summarized in the form

$$
C(\varrho_\beta, v_i^\beta, T, T_{1i}) = \mathscr{C}(\varrho_\beta, v_i^\beta, T, T_{1i}),
$$

whence we conclude that the constitutive quantities cannot depend on all ν velocities independently, but only on the $\nu - 1$ relative velocities

$$
(1.42)\qquad V_i^\alpha = v_i^\alpha - v_i^\nu
$$

which are objective vectors.

The requirement (1.41) of material objectivity may therefore be written in a reduced form as

$$
(1.43)\qquad
\begin{aligned}
&S(\varrho_\beta, V_i^\beta, T, T_{1i}) = S(\varrho_\beta, O_{ij} V_j^\beta, T, O_{ij} T_{ij}),\\
&O_{ij} V_j(\ldots) = V_i(\ldots), \qquad O_{ik} O_{jl} T_{kl}(\ldots) = T_{ij}(\ldots),
\end{aligned}
$$

and we express this by saying that the constitutive functions must be scalar, vectorial and tensorial *isotropic* functions, respectively.

There are general representation theorems for isotropic functions, i.e. solutions of the above functional equations. We do not need these here, since we shall only be interested in those parts of the constitutive functions that are linear in V_i^β and T_{1i}. In other words we shall disregard all products of V_i^α and T_{1i} among each other. In this case the most general form of the constitutive equations compatible with the isotropy requirement (1.43) is

$$
\begin{aligned}
&\Lambda^a = \Lambda^a(\varrho_\beta, T), \qquad t_{ij}^\alpha = -p^\alpha(\varrho_\beta, T)\,\delta_{ij},\\
&m_i^\alpha - \tau_\alpha v_i^\alpha = \sum_{\beta=1}^{\nu-1} M_v^{\alpha\beta} V_i^\beta + M_T^\alpha T_{,i},\\
&q_i^I = \sum_{\beta=1}^{\nu-1} q_v^\beta V_i^\beta - kT_{,i}, \qquad \varepsilon^I = \varepsilon^I(\varrho_\beta, T).
\end{aligned}
\tag{1.44}
$$

p^α is called the *partial pressure* and k is the *heat conductivity*. The coefficients $M_v^{\alpha\beta}$, M_T^α, q_v^α and k may all depend on ϱ_β and T. The values $M_v^{\alpha\beta}$ and M_T^α are not all independent, because of the restrictions (1.17) on m_i^α and τ_α. These imply

$$
\sum_{\alpha=1}^{\nu} M_v^{\alpha\beta} = 0 \quad \text{and} \quad \sum_{\alpha=1}^{\nu} M_T^\alpha = 0. \tag{1.45}
$$

Equations (1.44) are the most general linear constitutive relations that are compatible with the principle of material objectivity. We conclude that this requirement has reduced the $12\nu+n+2$ unknown functions of $4\nu+4$ variables each of equations (1.38) to $\nu(\nu+1)+n+1$ functions of only $\nu+1$ variables each. For small values of ν is a considerable and enormously useful reduction.

2. Entropy principle

a. Purpose of the entropy principle. Drastic as the restrictions of the principle of material objectivity on the constitutive functions may be, they still leave us with the large number of coefficient-functions of equations (1.44). The Entropy Principle is used to acquire some knowledge of these coefficient functions.

For this purpose it is unnecessary to include the external supplies f_i^α and r^α in the analysis, because the restrictions on the constitutive equations are unaffected by the presence or absence of those supplies.

b. The entropy postulate. I state the entropy postulate in 4 parts:

i. (*Entropy balance*) There exists an additive quantity, the entropy, whose equation of balance in regular points of the body we write as

$$\frac{\partial \varrho\eta}{\partial t}+\frac{\partial}{\partial x_j}(\varrho\eta v_j+\Phi_j)=\sigma. \tag{2.1}$$

ii. (*Constitutive property*) The specific entropy η and the entropy flux Φ are an objective scalar and vector, respectively, for Galilei transformations and both are given by constitutive relations that obey the Principle of Material Objectivity. In particular, in a simple mixture of inviscid fluids we have

$$\eta=\eta(\varrho_\beta, T), \qquad \Phi_i=\sum_{\beta=1}^{\nu-1}\varphi_v^\beta V_i^\beta+\varphi_T T_{,i}, \tag{2.2}$$

where φ_v^β and φ_T may be functions of ϱ_β, T.

iii. (*Entropy inequality*) The entropy production σ is non-negative for all thermodynamic processes, so that the inequality

$$\frac{\partial \varrho\eta}{\partial t}+\frac{\partial}{\partial x_j}(\varrho\eta v_j+\Phi_j)\geqslant 0 \tag{2.3}$$

holds.

iv. (*Ideal diathermal walls*) An ideal wall has no entropy production so that we have

$$[\Phi_i e_i]+[\eta]\varrho(v_j-u_j)e_j=0, \tag{2.4}$$

if the ideal wall is modelled by a singular surface. If the wall is also diathermal, temperature is continuous across it

$$[T]=0. \tag{2.5}$$

The key to the evaluation of the entropy principle is the statement that the entropy inequality must be satisfied for all thermodynamic processes; that is to say that the entropy inequality need not hold for all fields of ϱ_α, v_i^α and T, but only for those that are solutions of the field equations. We may say that the field equations provide constraints upon the fields that must satisfy the entropy inequality.

I-Shih Liu has shown that we may get rid of these constraints by the use of Lagrange multipliers: Liu showed that the new inequality

$$\begin{aligned}\frac{\partial \varrho_\eta}{\partial t}+\frac{\partial}{\partial x_j}(\varrho_\eta v_j+\Phi_j)-\sum_{\alpha=1}^{\nu}\Lambda^{\varrho_\alpha}\left(\frac{\partial \varrho_\alpha}{\partial t}+\frac{\partial \varrho_\alpha v_j^\alpha}{\partial x_j}-\tau_\alpha\right)-\\ -\sum_{\alpha=1}^{\nu}\Lambda^{v_i^\alpha}\left(\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t}+\frac{\partial}{\partial x_j}(\varrho_\alpha v_i^\alpha v_j^\alpha-t_{ij}^\alpha)-m_i^\alpha\right)-\\ -\Lambda^\varepsilon\left(\frac{\partial \varrho_\varepsilon}{\partial t}+\frac{\partial}{\partial x_j}(\varrho_\varepsilon v_j+q_j)-t_{ij}\frac{\partial v_i}{\partial x_j}\right)\geqslant 0\end{aligned} \tag{2.6}$$

must hold for all fields $\varrho_\alpha(x_n, t)$, $v_i^\alpha(x_n, t)$, $T(x_n, t)$ rather than only for thermodynamic processes. The coefficients Λ^{ϱ_α}, $\Lambda^{v_i^\alpha}$ and Λ^ε may be functions of the variables that occur in the constitutive equations (1.32).

We recall our objective, viz. to find restrictions on the coefficient functions on (1.44). The entropy inequality is supposed to help us in this; but at present it seems that we are moving away from this goal, because we have introduced the new quantities η and Φ_i and the Lagrange multipliers Λ^{ϱ_α}, $\Lambda^{v_i^\alpha}$ and Λ^ε. These are merely auxiliary quantities and we must remove them from the final results.

c. Evaluation of the entropy principle.

α. *Results from the entropy inequality.* Insertion of the constitutive equations η, Φ_i, t_{ij}^α, Λ^α, $m_i^\alpha - \tau_\alpha v_i^\alpha$, ε and q_i into inequality (2.6) leads to an inequality whose left-hand side is explicitly linear on the derivatives.

$$\frac{\partial T}{\partial t},\ T_{,ik},\ \frac{\partial \varrho_\beta}{\partial t},\ \varrho_{\beta,i},\ \frac{\partial v_i^\beta}{\partial t},\ v_{i,j}^\beta. \tag{2.7}$$

Since the inequality must hold for all fields ϱ_α, v_i^α and T, it must hold in particular for arbitrary values of the derivatives (2.7). Therefore we could violate the inequality if the term with these derivatives were present on its left-hand side. It follows that the coefficients of the derivatives must vanish and this argument leads to the following conditions

$$\frac{\partial \eta}{\partial T} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial T} = 0, \tag{2.8$_1$}$$

$$\frac{\partial \Phi_i}{\partial T_{,j}} - \Lambda^\varepsilon \frac{\partial q_i}{\partial T_{,j}} = 0, \tag{2.8$_2$}$$

$$\frac{\partial \eta}{\partial \varrho_\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varrho_\beta} + \frac{1}{\varrho}(\eta - \Lambda^\varepsilon \varepsilon) - \frac{1}{\varrho}\Lambda^{\varrho_\beta} - \frac{1}{\varrho} v_k^\beta \Lambda^{v_k^\beta} = 0, \tag{2.8$_3$}$$

$$\frac{\partial \Phi_j}{\partial \varrho_\beta} - \Lambda^\varepsilon \frac{\partial \eta_j}{\partial \varrho_\beta} - \varrho\left(\frac{\partial \eta}{\partial \varrho_\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varrho_\beta}\right) u_j^\beta - \sum_{\alpha=1}^{\nu} \Lambda^{v_j^\alpha} \frac{\partial p^\alpha}{\partial \varrho_\beta} + \Lambda^\varepsilon t_{ij} \frac{1}{\varrho} u_i^\beta = 0, \tag{2.8$_4$}$$

$$\frac{\partial \eta}{\partial v_i^\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial v_i^\beta} - \frac{\varrho_\beta}{\varrho} \Lambda^{v_i^\beta} = 0 \quad (\beta = 1, 2, \ldots, \nu - 1), \tag{2.8$_5$}$$

$$\sum_{\beta=1}^{\nu-1} \left(\frac{\partial \eta}{\partial v_i^\beta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial v_i^\beta}\right) - \frac{\varrho_\nu}{\varrho} \Lambda^{v_i^\beta} = 0, \tag{2.8$_6$}$$

$$\left(\frac{\partial \eta}{\partial \varrho_\alpha} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varrho_\alpha}\right)\delta_{ij} - \frac{1}{\varrho_\alpha \varrho}\left(\frac{\partial \Phi_j}{\partial v_i^\alpha} - \Lambda^\varepsilon \frac{\partial q_j}{\partial v_i^\alpha}\right) - \frac{1}{\varrho} \Lambda^{v_i^\alpha} u_j^\alpha - \tag{2.8$_7$}$$

$$- \frac{1}{\varrho^2} \Lambda^\varepsilon t_{ij} = 0 \quad (\alpha = 1, 2, \ldots, \nu - 1),$$

$$(2.8)_8 \qquad \left(\frac{\partial \eta}{\partial \varrho_\nu} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varrho_\nu}\right)\delta_{ij} + \frac{1}{\varrho\varrho_\nu}\sum_{\beta=1}^{\nu}\left(\frac{\partial \Phi_j}{\partial v_i^\beta} - \Lambda^\varepsilon \frac{\partial q_j}{\partial v_i^\beta}\right) - \frac{1}{\varrho}\Lambda^{v_i^\nu} u_j^\nu - \frac{1}{\varrho^2}\Lambda^\varepsilon t_{ij} = 0.$$

There remains the residual inequality

$$(2.9) \qquad \left(\frac{\partial \Phi_j}{\partial T} - \Lambda^\varepsilon \frac{\partial q_j}{\partial T} - \sum_{\alpha=1}^{\nu} \Lambda^{v_j^\alpha}\frac{\partial p_\alpha}{\partial T}\right) T_{,i} + \sum_{\alpha=1}^{\nu} \Lambda^{\varrho_\alpha}\tau_\alpha + \sum_{\alpha=1}^{\nu} \Lambda^{v_i^\alpha} m_i^\alpha \geqslant 0.$$

We proceed to evaluate these conditions and start with $(2.8)_{5,6}$. We note that η is independent of V_i^β and in ε it is only the explicit term $\sum_{\alpha=1}^{\nu} \frac{1}{2}\frac{\varrho_\alpha}{\varrho} u_\alpha^2$ that depends on V_i^β. By use of the identities

$$(2.10) \qquad u_i^\alpha = \sum_{\gamma=1}^{\nu-1}\left(\delta_{\alpha\gamma} - \frac{\varrho_\gamma}{\varrho}\right) V_i^\gamma \quad \text{and} \quad V_i^\gamma = \sum_{\beta=1}^{\nu-1}\left(\delta_{\gamma\beta} + \frac{\varrho_\beta}{\varrho_\nu}\right) u_i^\beta$$

we find $\dfrac{\partial \varepsilon}{\partial V_i \beta} = \dfrac{\varrho_\beta}{\varrho} u_i^\beta$ and thus the equations $(2.8)_{5,6}$ can be written as

$$(2.11) \qquad \Lambda^{v_i^\beta} = -\Lambda^\varepsilon u_i^\beta,$$

so that the Lagrange multipliers $\Lambda^{v_i^\beta}$ are now reduced to Λ^ε.

Equations $(2.8)_{1,3}$ may be written as

$$\frac{\partial \varrho\eta}{\partial T} = \Lambda \frac{\partial \varrho\varepsilon_I}{\partial T}, \qquad \frac{\partial \varrho\eta}{\partial \varrho_\beta} = \Lambda^\varepsilon \frac{\partial \varrho\varepsilon_I}{\partial \varrho_\beta} + \Lambda^{\varrho\beta} + \Lambda^\varepsilon \frac{1}{2} u_\beta^2 - \Lambda^\varepsilon v_k^\beta u_k^\beta,$$

and thus it is obvious that Λ^ε can only spend on ϱ_β and T. Also $\Lambda^{\alpha\beta}$ can be decomposed into a velocity dependent part and a part $\Lambda_I^{\varrho\beta}$ that depends on ϱ_β and T only:

$$\Lambda^{\varrho\beta} = \Lambda_T^{\varrho\beta}(\varrho_\delta, T) + \Lambda^\varepsilon\left(v_i^\beta u_i^\beta - \frac{1}{2}u_\beta^2\right).$$

We may then summarize the two equations for $\partial\varrho\eta/\partial T$ and $\partial\varrho\eta/\partial\varrho_\beta$ in the form

$$(2.12) \qquad d(\varrho\eta) = \Lambda^\varepsilon \frac{\partial \varrho\varepsilon_I}{\partial T} dT + \sum_{\alpha=1}^{\nu}\left(\Lambda^\varepsilon \frac{\partial \varrho\varepsilon_I}{\partial \varrho_\alpha} + \Lambda_I^{\varrho_\alpha}\right) d\varrho_\alpha.$$

If we multiply $(2.8)_7$ by ϱ_α and $(2.8)_8$ by ϱ_ν and sum over all of these equations, we obtain

$$(2.13) \qquad \begin{aligned} \Lambda^\varepsilon \sum_{\alpha=1}^{\nu} p_\alpha &= -\sum_{\alpha=1}^{\nu} \varrho\varrho_\alpha\left(\frac{\partial \eta}{\partial \varrho_\alpha} - \Lambda^\varepsilon \frac{\partial \varepsilon_I}{\partial \varrho_\alpha}\right) \quad \text{or by (2.12)} \\ \Lambda^\varepsilon \sum_{\alpha=1}^{\nu} p_\alpha &= -\sum_{\alpha=1}^{\nu} \varrho_\alpha \Lambda_I^{\varrho_\alpha} + \varrho(\eta - \Lambda^\varepsilon \varepsilon_I). \end{aligned}$$

On the other hand, when we subtract $(28)_8$ from $(28)_7$ we get

$$\frac{\partial \Phi_j}{\partial V_i^\beta} - \Lambda^\varepsilon \frac{\partial q_j^I}{\partial V_i^\beta} = \sum_{\alpha=1}^{\nu} \left(\varrho_\alpha \delta_{\beta\alpha} - \frac{\varrho_\beta \varrho_\alpha}{\varrho}\right)\left(\frac{\partial \varrho\eta}{\partial \varrho_\alpha} - \Lambda^\varepsilon \frac{\partial \varrho\varepsilon_I}{\partial \varrho_\alpha}\right) \quad (\beta = 1, 2, \ldots, \nu-1).$$

If we combine that with $(2.8)_2$ we obtain by integration

$$\begin{aligned}
\Phi_j &= \Lambda^\varepsilon q_j^I + \sum_{\beta=1}^{\nu-1} \sum_{\alpha=1}^{\nu} \left(\varrho_\beta \delta_{\beta\alpha} - \frac{\varrho_\beta \varrho_\alpha}{\varrho}\right)\left(\frac{\partial \varrho\eta}{\partial \varrho_\alpha} - \Lambda^\varepsilon \frac{\partial \varrho\varepsilon_I}{\partial \varrho_\alpha}\right) V_i^\beta, \\
\Phi_j &= \Lambda^\varepsilon q_j^I + \sum_{\alpha=1}^{\nu} \varrho_\alpha u_i^\alpha \left(\frac{\partial \varrho\eta}{\partial \varrho_\alpha} - \Lambda^\varepsilon \frac{\partial \varrho\varepsilon_I}{\partial \varrho_\alpha}\right), \\
\Phi_j &= \Lambda^\varepsilon q_j + \sum_{\alpha=1}^{\nu} \varrho_\alpha u_i^\alpha \left(\frac{\partial \varrho\eta}{\partial \varrho_\alpha} - \Lambda^\varepsilon \frac{\partial \varrho\varepsilon}{\partial \varrho_\alpha}\right), \\
\Phi_j &= \Lambda^\varepsilon q_j^I + \sum_{\alpha=1}^{\nu} \varrho_\alpha u_i^\alpha \Lambda_I^{\varrho_\alpha}.
\end{aligned} \tag{2.14}$$

There remain the equations $(2.8)_4$ which, by (2.14) and previous results may be rewritten in the form

$$\frac{\partial \Lambda^\varepsilon}{\partial \varrho_\gamma} q_j^I + \sum_{\alpha=1}^{\nu} \left(\varrho_\alpha \frac{\partial \Lambda_I^{\varrho_\alpha}}{\partial \varrho_\gamma} + \Lambda^\varepsilon \frac{\partial p^\alpha}{\partial \varrho_\gamma}\right) u_j^\alpha = 0,$$

whence follows

$$\frac{\partial \Lambda^\varepsilon}{\partial \varrho_\beta} = 0 \quad \text{and} \quad \varrho_\alpha \frac{\partial \Lambda_I^{\varrho_\alpha}}{\partial \varrho_\gamma} + \Lambda^\varepsilon \frac{\partial p^\alpha}{\partial \varrho_\gamma} = 0, \tag{2.15}$$

since this relation must hold for all $T_{,i}$ and u_i^α.(4) Thus Λ^ε depends only on T. With the knowledge so far gleaned from the entropy inequality the residual inequality assumes the form

$$\begin{aligned}
&\left(\frac{d\Lambda^\varepsilon}{dT} q_j^I + \sum_{\alpha=1}^{\nu} \left(\varrho_\alpha \frac{\partial \Lambda_I^{\varrho_\alpha}}{\partial T} + \Lambda^\varepsilon \frac{\partial p^\alpha}{\partial T}\right) u_j^\alpha\right) T_{,j} - \\
&\quad - \Lambda^\varepsilon \sum_{\alpha=1}^{\nu} (m_i^\alpha - \tau_\alpha v_i^\alpha) u_i^\alpha + \sum_{a=1}^{n} \Big(\sum_{\alpha=1}^{\nu} (\Lambda_I^{\varrho_\alpha} - \frac{1}{2}\Lambda^\varepsilon u_\alpha^2)\Big) \gamma_k^a M_a \mu \Lambda^a \geqslant 0.
\end{aligned} \tag{2.16}$$

β. *Results from the entropy inequality for a single fluid.* The results (2.11)

(4) Proper account must be taken of the identity $\sum_{\alpha=1}^{\nu} \varrho_\alpha u_i^\alpha = 0$ but still $(2.15)_2$ comes out as written when we make use of (2.13).

through (2.16) exhaust the restrictions that can be obtained from the entropy inequality. In particular, for a single fluid these results reduce to

$$
(2.17)\qquad
\begin{aligned}
&\Lambda^{v_i^\beta} = 0,\\
&d(\varrho\eta) = \Lambda^\varepsilon \frac{\partial \varrho\varepsilon_I}{\partial T} dT + \left(\Lambda^2 \frac{\partial \varrho\varepsilon_I}{\partial \varrho} + \Lambda^\varrho\right) d\varrho,\\
&\Lambda^\varepsilon p = -\varrho\Lambda^\varrho + \varrho(\eta - \Lambda^\varepsilon \varepsilon),\\
&\Phi_j = \Lambda^\varepsilon \varrho_j, \quad \frac{\partial \Lambda^\varepsilon}{\partial \varrho} = 0, \quad \frac{dd^\varepsilon}{dT} q_i T_{,j} \geqslant 0.
\end{aligned}
$$

Equations $(2.17)_{2,3}$ may be combined to give

$$
(2.18)\qquad d\eta = \Lambda^\varepsilon \left(d\varepsilon - \frac{p}{\varrho z} d\varrho\right)
$$

which shows that Λ^ε is an integrating factor of the Pfaffien form $d\varepsilon - (p/\varrho z)\, d\varrho$. This fact provides the easiest possibility to identify Λ^ε in a single fluid. Since thermostatics defines the absolute temperature as *the* integrating denominator that depends on temperature only. Thus, since Λ^ε is only a function of temperature, we obtain

$$
(2.19)\qquad \Lambda^\varepsilon = \frac{1}{T}.
$$

γ. *An integrability condition and an inequality on a transport coefficient for a single fluid as prototypes of thermodynamic restrictions.* Equations (2.17) and (2.18) when combined with (2.19) include

$$
(2.20)\qquad
\begin{aligned}
&d\eta = \frac{1}{T}\left(d\varepsilon - \frac{p}{\varrho^2} d\varrho\right),\\
&\Phi_j = \frac{q_j}{T},\\
&-q_i T_{1i} \geqslant 0.
\end{aligned}
$$

The first one is called the *Gibbs equation*, the second one relates the entropy flux to the heat flux and the third one is the dissipation inequality for heat-conduction. The Gibbs equation $(2.20)_1$ implies an integrability condition for η, viz.

$$
(2.21)\qquad \varrho^2 \frac{\partial \varepsilon}{\partial \varrho} = p - T\frac{\partial p}{\partial T},
$$

and the inequality $(2.20)_3$ together with the constitutive equation $(1.44)_4$ for g_i simplified for a single fluid implies $\varkappa T_{,i} T_{,i} \geqslant 0$ so that we conclude

$$
(2.22)\qquad \varkappa \geqslant 0.
$$

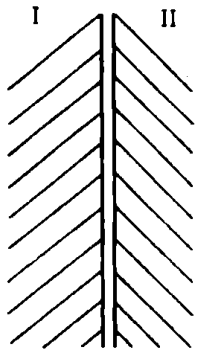
The two conditions (2.21), (2.22) are typical for the kind of restrictions which we may obtain from thermodynamics:

(2.21) provides a restriction on the two constitutive functions $\varepsilon(\varrho, T)$ and $p(\varrho, T)$ by equating two derivatives. That relation permits us to calculate $\varepsilon(\varrho, T)$ if only $p(\varrho, T)$ has been measured for all ϱ and T, and if the specific heat $\partial\varepsilon/\partial T$ has been measured for *one* ϱ and all T. Once $\varepsilon(\varrho, T)$ has been calculated, we may calculate $\eta(\varrho, T)$ by integration of the Gibbs equation $(2.20)_1$. Thus the determination of $\varepsilon(\varrho, T)$ and $\eta(\varrho, T)$ requires only measurements of pressure and specific heat and we may assume that we have thus determined the functions $\varepsilon(\varrho, T)$ and $\eta(\varrho, T)$ for all fluids of interest to us.

Inequality (2.22) implies that the flux of internal energy is always opposite to the temperature gradient in a single fluid.

δ. *Λ^ε and $\Lambda_r^{\varrho\alpha}$ in mixture, chemical potentials.* Before conditions (2.11) through (2.16) become useful restrictions on the constitutive functions of a mixture we must determine Λ^ε and $\Lambda_I^{\varrho\alpha}$ for a mixture. This is done by making use of the jump condition (2.4) at an ideal diathermal wall.

First we apply this jump condition to an impermeable ideal diathermal wall which separates a mixture I from a single fluid II. By (2.5) and (2.4) we



have $[T] = 0$, $[\Phi_i e_i] = 0$ and $\Phi_i = \Lambda^\varepsilon q_i$ on both sides, since the wall is impermeable. Hence $[\Lambda^\varepsilon(T) q_i] e_i = 0$, but since $[q_i e_i] = 0$ as a consequence of the balance of internal energy (see (1.15)), we obtain

$$[\Lambda^\varepsilon(T)] = 0 \quad \text{or} \quad \Lambda_{\mathrm{I}}^\varepsilon(T) = \Lambda_{\mathrm{II}}^\varepsilon(T). \tag{2.23}$$

Thus $\Lambda^\varepsilon(T)$ is a universal function and since we already know that $\Lambda^\varepsilon = 1/T$ in a single fluid, we conclude that

$$\Lambda^\varepsilon = 1/T \tag{2.24}$$

also holds in a mixture. Next we apply the jump condition (2.4) to a semi-permeable ideal diathermal wall. Let this wall be permeable for constituents γ so that we have

$$v_i^\alpha = u_i \quad (\alpha \neq \gamma) \quad \text{and} \quad v_i = u_i + \frac{\varrho_\gamma}{\varrho}(v_i^\gamma + u). \tag{2.25}$$

The jump condition reads

$$[\Phi_i]\, e_i + [\eta]\, \varrho (v_i - u_i)\, e_i = 0$$

and with Φ_i as determined in $(2.14)_4$, since T is continuous, we get

$$[q_i^I e_i] + T\left[\eta + \sum_{\beta=1}^{\nu}\left(\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho}\right)\Lambda_I^{\varrho\beta}\right]\varrho(v_l - u_l)\, e_l = 0. \tag{2.26}$$

On the other hand, the balance of internal energy on the wall has the form (1.15), viz.

$$[q_i e_i] - \left[\frac{t_{ij} e_j e_j}{\varrho} - \varepsilon + \tfrac{1}{2}(v_k - u_k)(v_k - u_k)\right]\varrho(v_l - u_l)\, e_l = 0,$$

or, if we introduce q_i^I and ε^I and make use of $t_{ij} = \sum_{\alpha=1}^{\nu} p_\alpha \delta_{ij} - \sum_{\alpha=1}^{\nu} \varrho_\alpha u_i^\alpha u_j^\alpha$

$$[q_i^I e_i] + \left[\frac{\sum_{\beta=1}^{\nu} p\beta}{\varrho} + \varepsilon_\tau + \tfrac{1}{2}(v_k^\gamma - u_k)(v_k^\gamma - u_k)\right]\varrho(v_l - u_l)\, e_l = 0. \tag{2.27}$$

Thus, in (2.26) and (2.27) we have two relations for $[q_i^x e_i]$. We eliminate this quantity between the two equations and obtain

$$\left[\varepsilon_1 - T\eta + \tfrac{1}{2}(v_k - u_k)(v_k - u_k) + \frac{\sum_{\alpha=1}^{\nu} p_\alpha}{\varrho} - T\sum_{\beta=1}^{\nu}\left(\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho}\right)\Lambda_1^{\varrho\beta}\right] = 0.$$

To simplify this expression we can make use of (2.13) and obtain

$$[-T\Lambda_1^{\varrho\gamma} + \tfrac{1}{2}(v_k^\gamma - u_k)(v_k^\gamma - u_k)] = 0. \tag{2.28}$$

We conclude that the quantity in square brackets is continuous across a semi-permeable ideal wall. This quantity is therefore quite important and it is given a name of its own, namely *chemical potential* of constituent γ, usually denoted by μ^γ.

$$\mu^\gamma = -T\Lambda_I^{\varrho\gamma} + \tfrac{1}{2}(v_k^\gamma - u_k)(v_k^\gamma - u_k). \tag{2.29}$$

The part of μ^γ which is independent of velocity is denoted by μ_γ^I:

$$\mu_1^\gamma = -T\Lambda_1^{\varrho\gamma}. \tag{2.30}$$

ε. *Summary of results from the entropy principle.* No that we have identified the Lagrange multipliers Λ^ε and $\Lambda^{\varrho\varepsilon}$ as the inverse of the absolute

temperature and the chemical potentials, respectively, we may rewrite our results (2.12) through (2.16) in terms of these quantities. We get

$$
\begin{aligned}
&d(\varrho\eta) = \frac{1}{T}\Big(d(\varrho\varepsilon_1) - \sum_{\alpha=1}^{\nu} \mu_\alpha^1\, d\varrho_\alpha\Big),\\
&\sum_{\gamma=1}^{\nu} \frac{\varrho_\gamma}{\varrho}\mu_\gamma^1 = \varepsilon_1 - T\eta + \frac{\sum_{\beta=1}^{\nu} \varrho_\beta}{\varrho},\\
&\Phi_i = \frac{q_i - \sum_{\alpha=1}^{\nu} \varrho_\alpha u_i^\alpha (\mu_1^\alpha + \frac{1}{2}u_\alpha^2)}{T},\\
&\frac{\partial \mu_1^\alpha}{\partial \varrho_\gamma} = \frac{1}{\varrho_\alpha}\frac{\partial p^\alpha}{\partial \varrho_\gamma},
\end{aligned}
\tag{2.31}
$$

$$
\begin{bmatrix}
\dfrac{k}{T^2} & \dfrac{1}{2}\Big\{-\dfrac{q_v^\alpha}{T} - \Big[-\Big(\dfrac{M_T^\alpha}{\varrho_\alpha} - \dfrac{M_T^\nu}{\varrho_\nu}\Big) - \Big(\dfrac{1}{\varrho_\alpha}\dfrac{\partial p_\alpha}{\partial T} - \dfrac{1}{\varrho_\nu}\dfrac{\partial p_\nu}{\partial T}\Big) + \\
& \qquad + T\dfrac{\partial \frac{\mu_1^\alpha - \mu_1^\nu}{T}}{\partial T}\Big]\sum_{\gamma=1}^{\nu-1}\Big(\varrho_\alpha \delta_{\alpha\gamma} - \dfrac{\varrho_\alpha \varrho_\gamma}{\varrho}\Big)\Big\} \\
\dfrac{1}{2}[m] & -\dfrac{1}{T}\Big(\dfrac{M_v^{\alpha\beta}}{\varrho_\alpha} - \dfrac{M_v^{\nu\beta}}{\varrho_\nu}\Big)\sum_{\gamma=1}^{\nu-1}\Big(\varrho_\alpha \delta_{\alpha\gamma} - \dfrac{\varrho_\alpha \varrho_\gamma}{\varrho}\Big)
\end{bmatrix} \times
$$

$$
\times \begin{bmatrix} T_{ij} \\ V_j^\alpha \end{bmatrix}\begin{bmatrix} T_{ij} \\ V_j^\alpha \end{bmatrix} - \frac{1}{T}\sum_{\alpha=1}^{n}\Big(\sum_{\alpha=1}^{\nu-1} \mu_1^\alpha - \mu_1^\nu + \tfrac{1}{2}V_\alpha^2\Big) p_\alpha^a M_\alpha \mu \Lambda^a \geqslant 0.
$$

To express the results in terms of chemical potentials is recommended, because the chemical potentials can be measured by virtue of their continuity at a semi-permeable wall since they are known in a single fluid. Indeed, from $(2.31)_2$ we conclude that in a single fluid the chemical potential is equal to $\varepsilon - T\eta + p/\varrho$ and thus can be determined from measurements of pressure and specific heat as explained before.

$(2.31)_1$ is called the *Gibbs equation for mixtures* and $(2.31)_3$ is the *Gibbs–Duhem equation*. $(2.31)_3$ gives the relation between the flux of entropy, the flux of internal energy and the diffusion fluxes $\varrho_\alpha u_i^\alpha$. $(2.31)_4$ is a relation that is specific to simple mixtures, i.e., it does not hold for nonsimple mixtures where gradients of density are among the variables.

But the implications of $(2.31)_4$ are drastic indeed. If we differentiate that

equation with respect to ϱ_β, the right-hand side must be symmetric in β and γ since obviously the left-hand side is. This leads to the condition

$$\delta_{\alpha\beta}\frac{\partial p^\alpha}{\partial \varrho_\gamma} = \delta_{\alpha\gamma}\frac{\partial p^\alpha}{\partial \varrho_\beta}.$$

We choose $\alpha = \beta \neq \gamma$ and obtain $\partial p^\alpha/\partial \varrho_\gamma$ for $\alpha \neq \gamma$. Thus p^α depends only on ϱ_α and not of any other density. By $(2.31)_4$ the same is true for μ_1^α and therefore $(2.31)_1$ requires

$$\frac{\partial^2 \varrho(\varepsilon - T\eta)}{\partial \varrho_\alpha \, \partial \varrho_\gamma} = 0 \quad \text{for} \quad \alpha \neq \gamma,$$

whence follows by integration

$$\varrho(\varepsilon - T\eta) = \sum_{\alpha=1}^{\nu} \varrho_\alpha \psi_\alpha(\varrho_\alpha, T), \tag{2.32}$$

so that the free energy density $\varrho(\varepsilon - T\eta)$ is a sum of parts of which each one is a function of only *one* density and temperature. Since $\varrho\eta = -(\partial\varrho(\varepsilon - T\eta))/\partial T$ holds, the same decomposition is valid for $\varrho\eta$ and $\varrho\varepsilon_1$:

$$\varrho\eta = \sum_{\alpha=1}^{\nu} \varrho_\alpha \eta_\alpha(\varrho_\alpha, T) \quad \text{and} \quad \varrho\varepsilon_1 = \sum_{\alpha=1}^{\nu} \varrho_\alpha \varepsilon_\alpha(\varrho_\alpha, T). \tag{2.33}$$

I repeat that this is a special property of simple mixtures.

The left-hand side of the residual inequality $(2.31)_5$ may be considered the production density of entropy; it consists of several parts:

i) a term due to chemical reactions,

ii) a term due to heat conduction, this is the one which is quadratic in $T_{,i}$,

iii) a term due to diffusion which is the term that is quadratic in $V_i\gamma$,

iv) a mixed term with gradients of temperature and relative velocities.

$(2.31)_5$ implies a number of inequalities which follow from the requirement that the matrix in $(2.31)_5$ be non-negative definite. The conclusions from this requirement are cumbersome to write and therefore we consider only the case of a binary mixture, i.e., two constituents. In this case the matrix

$$\begin{bmatrix} +\dfrac{\varkappa}{T^2} & -\dfrac{1}{2}\left\{\dfrac{q_\nu^1}{T} + \dfrac{\varrho_1\varrho_2}{\varrho}\left[\left(\dfrac{M_T^1}{\varrho_1} - \dfrac{M_T^2}{\varrho_2}\right) - \dfrac{\partial\left(\dfrac{p_1}{\varrho_1} - \dfrac{p_2}{\varrho_2}\right)}{\partial T} - T\dfrac{\partial\dfrac{\mu_1^1 - \mu_2^2}{T}}{\partial T}\right]\right\} \\ -\dfrac{1}{2}\{m\} & -\dfrac{1}{T}M_\nu^{11} \end{bmatrix}$$

must be positive definite and we must have

$$(2.34)\qquad k \geqslant 0, \quad M_\nu^{11} \leqslant 0, \quad -\frac{kM_\nu^{11}}{T} - \frac{1}{4}\left\{\frac{q_\nu^1}{T} + \frac{\varrho_1\varrho_2}{\varrho}\left[\left(\frac{M_T^1}{\varrho_1} - \frac{M_T^2}{\varrho_2}\right) - \frac{\partial\left(\frac{p_1}{\varrho_1} - \frac{p_2}{\varrho_2}\right)}{\partial T} + T\frac{\partial\frac{\mu_1^1 - \mu_1^2}{T}}{\partial T}\right]\right\}^2 \geqslant 0.$$

This means that a temperature gradient creates a heat flux in the opposite direction and that a diffusion velocity creates a force opposite to its own direction. The least inequality is difficult to interpret, but we shall yet find some use for it.

The law of mass-action. The entropy production on the left-hand side of the residual inequality $(2.31)_5$ may be considered to be a function of $\Lambda_1, \Lambda_2, \ldots, \Lambda_n, \varrho_{n+1}, \ldots, \varrho_\nu, T, T_{,j}, v_i^\gamma$. That function has a minimum, namely zero value, in equilibrium, which is the state where the temperature is uniform, no diffusion occurs and the reaction rates are zero. Thus we may write

$$\sum(\Lambda_1 \ldots \Lambda_n, \varrho_{n+1} \ldots \varrho_\nu, T, T_{,j}, V_i^a)|_E = \sum(0, 0, \varrho_{n+1}, \varrho_n, T, 0, 0) = 0.$$

Necessary conditions for this minimum are the vanishing of the derivatives of Σ with respect to $T_{,i}$, V_i^a and Λ^a in equilibrium. The first two conditions are identically satisfied and the vanishing of the derivative of Σ with respect to Λ^a leads to the condition

$$(2.35)\qquad \sum_{a=1}^{\nu} \mu_1^a|_E\, \gamma_a^a M_a = 0 \qquad (a = 1, 2, \ldots, n).$$

This condition is called the *law of mass action.* It provides as many restrictions upon the ν densities ϱ_a and temperature T as there are independent reactions.

Because of the conservation of mass in the reaction which by (1.18) can be expressed as $\sum_{a=1}^{\nu} \gamma_a^a M_a = 0$ the law of mass action reads

$$(2.36)\qquad \sum_{a=1}^{\nu} (\mu_1^a - \mu_1^\nu)|_E\, \gamma_a^a M_a = 0 \qquad (a = 1, 2, \ldots, n).$$

Thus, in particular, in a binary mixture we conclude that in equilibrium the chemical potentials of the two constituents must be equal.

d. Transport equations for diffusion and heat condition.

α. *Constitutive equations for q_i^1 and $m_i^a - \tau_a v_i^a$.* Despite of all the thermodynamic development of the previous sections the gain of knowledge of the

constitutive coefficients in q_i^1 and $m_i^\alpha - \tau_\alpha v_i^\alpha$ is minimal. We recall the constitutive equations for these quantities

$$
(2.37)\qquad
\begin{aligned}
m_i^\alpha - \tau_\alpha v_i^\alpha &= \sum_{\beta=1}^{\nu-1} M_V^{\alpha\beta} V_i^\beta + M_T^\alpha T_{,i},\\
q_i^1 &= \sum_{\beta=1}^{\nu-1} q_\nu^\beta V_i^\beta - kT_{,i}.
\end{aligned}
$$

Inequalities (2.34) restrict the generality of the coefficients, but that is all we know about them.

β. *The phenomenological equations of linear irreversible thermodynamics.* Linear irreversible thermodynamics is an alternative theory of mixtures which formulates constitutive equations, so-called *phenomenological equations*, for the flux of internal energy and the diffusion-fluxes. Theses fluxes come out as linear combinations of the gradient of $1/T$ and the gradients of $(\mu^\beta - \mu^\nu)/T$ viz.

$$
(2.38)\qquad
\begin{aligned}
\varrho_\alpha u_i^\alpha &= \sum_{\beta=1}^{\nu-1} l_{\alpha\beta}\left(-\frac{\partial((\mu^\beta-\mu^\nu)/T)}{\partial x_i}\right) + \tilde{l}_\alpha \frac{\partial(1/T)}{\partial x_i},\\
q_i &= \sum_{\beta=1}^{\nu-1} l_\beta\left(-\frac{\partial((\mu^\beta-\mu^\nu)/T)}{\partial x_i}\right) + \lambda \frac{\partial(1/T)}{\partial x_i}.
\end{aligned}
$$

Equations $(2.38)_1$ for the diffusion fluxes are sometimes called *Fick's law of diffusion.*

The coefficients in these equations are called as follows

$L_{\alpha\beta}$ – diffusion coefficients,

$\tilde{L}_\alpha$ – coefficients of thermal diffusion,

L_β – diffusion-thermocoefficients,

and linear irreversible thermodynamics postulates symmetry relations for these coefficients, namely

$$
(2.39)\qquad l_{\alpha\beta} = l_{\beta\alpha} \quad \text{and} \quad \tilde{l}_\alpha = l_\alpha.
$$

These symmetry relations are also called *Onsager relations.*

Linear irreversible thermodynamics is not quite equivalent to the theory of mixtures presented here, in fact the present theory is superior in one important aspect which concerns the speed of propagation of disturbances in the density of the constituents and we come back to this point in the next section. However, there is a large class of processes where the two theories lead to the same results and I shall proceed to show under what conditions my equations (2.37) can be rewritten in the form (2.38) of linear irreversible thermodynamics. After that I shall show that the present theory can *derive* the symmetry relations (2.39), which are *postulated* by linear irreversible thermodynamics for a subclass of simple-inviscid mixtures of fluids.

γ. *Fick's law of diffusion as a mutilated form of the equations of balance of partial momenta.* We recall the equation of balance of momentum of constituent α from $(1.16)_2$

$$\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\varrho_\alpha v_i^\alpha v_j^\alpha - t_{ij}^\alpha) = m_i^\alpha.$$

By use of the equation of balance of mass of constituent α we rewrite this in the form

$$\varrho_\alpha\left(\frac{\partial v_i^\alpha}{\partial t} + v_j^\alpha \frac{\partial v_i^\alpha}{\partial x_j}\right) - \frac{\partial t_{ij}^\alpha}{\partial x_j} = m_i^\alpha - \tau_\alpha v_i^\alpha$$

or with $\dot{v}_i \alpha \equiv \partial v_i^\alpha/\partial t + v_j\, \partial v_i^\alpha/\partial x_j$ as the acceleration of the constituent α in the frame where the mixture is at rest.

$$\varrho_\alpha \dot{v}_i^\alpha + u_j^\alpha \frac{\partial v_i^\alpha}{\partial x_j} - \frac{\partial t_{ij}^\alpha}{\partial x_j} = m_i^\alpha - \tau_\alpha v_i^\alpha \qquad (\alpha = 1, 2, \ldots, \nu). \tag{2.40}$$

We insert the constitutive equations (1.44) for t_{ij}^α and $m_i^\alpha - \tau_\alpha v_i^\alpha$ and delete the term $u_j^\alpha\, \partial v_i^\alpha/\partial x_j$ which is considered small in near-equilibrium process since both the relative velocities and the velocity gradients are small. Thus we obtain after division by

$$\dot{v}_i^\alpha + \frac{1}{\varrho_\alpha}\frac{\partial p^\alpha}{\partial x_i} = \sum_{\beta=1}^{\nu-1} \frac{M_\nu^{\alpha\beta}}{\varrho_\alpha} V_i^\beta + \frac{M_T^\alpha}{\varrho_\alpha} T_{,i}.$$

Furthermore we ignore the acceleration ([4]) and we subtract the νth equation from all others; we use $(2.31)_4$ and obtain

$$\frac{\partial \mu^\alpha - \mu^\nu}{\partial x_i} + \left(\frac{\partial\left(\frac{\mu_\alpha}{\varrho_\alpha} - \frac{\mu_\nu}{\varrho_\nu}\right)}{\partial T} - \frac{\partial \mu^\alpha - \mu^\nu}{\partial T}\right) T_{,i} = \sum_{\beta=1}^{\nu-1}\left(\frac{M_\nu^{\alpha\beta}}{\varrho_\alpha} - \frac{M_\nu^{\nu\beta}}{\varrho_\nu}\right) V_i^\beta + \left(\frac{M_T^\alpha}{\varrho_\alpha} - \frac{M_T^\nu}{\varrho_\nu}\right) T_{,i}$$

or after a slight reshuffling of terms

$$\sum_{\beta=1}^{\nu-1}\left(\frac{M_\nu^{\alpha\beta}}{\varrho_\alpha} - \frac{M_\nu^{\nu\beta}}{\varrho_\nu}\right) V_i^\beta$$
$$= T\frac{\partial \frac{\mu^\alpha - \mu^\nu}{T}}{\partial x_i} + T^2\left[\left(\frac{M_T^\alpha}{\varrho_\alpha} - \frac{M_T^\nu}{\varrho_\nu}\right) + T\frac{\partial \frac{\mu^\alpha - \mu^\nu}{T}}{\partial T} - \frac{\partial\left(\frac{p^\alpha}{\varrho_\alpha} - \frac{p^\nu}{\varrho_\nu}\right)}{\partial T}\right]\frac{\partial \frac{1}{T}}{\partial x_i}.$$

([4]) Note that this cannot be justified by assumptions of linearity but is an additional assumption, which is needed, if we wish to compare equations (2.37) and (2.38). In my opinion the necessity of this assumption is the gravest shortcoming of linear irreversible thermodynamics.

We recall that $M_\nu^{\nu\beta} = -\sum_{\alpha=1}^{\nu-1} M_\nu^{\alpha\beta}$ holds ([5]) and rewrite the last equation in the form

$$\sum_{\beta\gamma=1}^{\nu-1} F_{\alpha\gamma} M_V^{\gamma\beta} V_i^\beta = T\frac{\partial\dfrac{\mu^\alpha-\mu^\nu}{T}}{\partial x_i} + T^2 D_\alpha \frac{\partial\dfrac{1}{T}}{\partial x_i}, \tag{2.41}$$

where we have defined for abbrevation

(2.42)

$$F_{\alpha\gamma} = \left(\frac{1}{\varrho_\alpha}\delta_{\alpha\gamma}+\frac{1}{\varrho_\nu}\right) \quad \text{and} \quad D_\alpha = \left(\frac{M_T^\alpha}{\varrho_\alpha}-\frac{M_T^\nu}{\varrho_\nu}\right)+T\frac{\partial\dfrac{\mu^\alpha-\mu^\nu}{T}}{\partial T}-\frac{\partial\left(\dfrac{\mu^\alpha}{\varrho_\alpha}-\dfrac{\mu^\nu}{\varrho_\nu}\right)}{\partial T}.$$

With $(2.42)_1$ we have $V_i^\beta = -\sum_{\delta=1}^{\nu-1} F_{\beta\delta}\varrho_\delta u_i^\delta$ from $(2.10)_2$ and thus the left-hand side of (2.41) reads

$$\sum_{\beta,\gamma,\delta=1}^{\nu-1} F_{\alpha\gamma} M_V^{\gamma\beta} F_{\beta\delta}\varrho_\delta u_i^\delta.$$

We solve that equation for $\varrho_\delta u_i^\delta$ and obtain

$$\varrho_\delta u_i^\delta = \sum_{\alpha=1}^{\nu-1}\underbrace{\left(-T\sum_{\gamma,\beta=1}^{\nu-1}\bar{F}_{\delta\gamma}^{-1}\bar{M}_V^{\gamma\beta}\bar{F}_{\beta\alpha}^{-1}\right)}_{l_{\delta\alpha}}\left(-\frac{\partial\dfrac{\mu^\alpha-\mu^\nu}{T}}{\partial x_i}\right)+ \underbrace{+\left(T^2\sum_{\alpha,\beta,\gamma=1}^{\nu-1}\bar{F}_{\delta\gamma}^{-1}\bar{M}_V^{\gamma\beta}F_{\beta\alpha}D_\alpha\right)}_{\bar{l}_\delta}\frac{\partial\dfrac{1}{T}}{\partial x_i}. \tag{2.43}$$

Comparison of (2.43) with the phenomenological equations $(2.38)_1$ shows that the coefficients $l_{\gamma\alpha}$ and $\bar{l}_\alpha$ must be identified as indicated by the brackets in (2.43).

It remains to rewrite the equation $(2.37)_2$ in the form $(2.38)_2$. This is easily done by inverting (2.41) to get V_i^β and insert that into $(2.37)_2$. We obtain

$$q_i = \sum_{\alpha=1}^{\nu-1}\underbrace{\left(-T\sum_{\beta,\gamma=1}^{\nu-1} q_V^\beta\bar{M}_V^{\beta\gamma}\bar{F}_{\gamma\alpha}^{-1}\right)}_{L_\alpha}\frac{\partial\dfrac{\mu^\alpha-\mu^\nu}{T}}{\partial x_i}+ \underbrace{+\left(T^2\sum_{\alpha,\beta,\gamma=1}^{\nu-1}\bar{M}_V^{\beta\gamma}\bar{F}_{\gamma\alpha}^{-1}D_\alpha+T^2k\right)}_{\lambda}\frac{\partial\dfrac{1}{T}}{\partial x_i}. \tag{2.44}$$

([5]) This is true unless there are chemical reactions which we shall exclude for the present argument.

We compare this with the phenomenological equation $(2.38)_2$ and conclude that the coefficients l_β and λ must be identified as indicated by the brackets.

δ. *Symmetry relations.* In equations (2.43) and (2.44) we recognize the two phenomenological equations of linear irreversible thermodynamics, the first one being Fick's law of diffusion. We have derived these equations here under restrictive assumptions, the most important one being that the acceleration is neglected. As a consequence of this systematic development we know a little more about the coefficients $L_{\alpha\beta}$ and $\tilde{L}_\alpha$, L_α than linear irreversible thermodynamics does and we shall use this knowledge to derive the symmetry relations (2.39) which are ordinarily postulated as Onsager relations.

This ist not possible in general but we shall now make some reasonable assumptions on the coefficients $M_V^{\alpha\beta}$ and q_v^β which will allow us to derive (2.39).

Truesdell has shown that under certain conditions $L_{\delta\alpha} = L_{\alpha\delta}$ can be proved. We noticed from (2.43) that this symmetry will hold, if $M_v^{\alpha\beta}$ is symmetric and that can be proved from the conservation of momentum. The argument runs as follows: ([6])

We introduce $M_V^{\alpha\nu} \equiv -\sum_{\beta=1}^{\nu-1} M_V^{\alpha\beta}$ and rewrite the constitutive equation (1.44) in the form

$$
\begin{aligned}
(2.45) \qquad m_i^\alpha &= \sum_{\beta=1}^{\nu-1} M_V^{\alpha\beta}(v_i^\beta - v_i^\gamma) \\
&= \sum_{\beta=1}^{\nu-1} M_V^{\alpha\beta}(v_i^\beta - v_i^\alpha) - \sum_{\beta=1}^{\nu-1} M_V^{\alpha\beta}(v_i^\gamma - v_i^\alpha) \\
&= \sum_{\beta=1}^{\nu} M_V^{\alpha\beta}(v_i^\alpha - v_i^\beta).
\end{aligned}
$$

The advantage of this form of the constitutive equations for m_i^α is that the coefficients $M_V^{\alpha\beta}$ (including $M_V^{\alpha\beta}$) now have a very suggestive meaning, because they determine how the relative motion of constituents α and β affects constituent α. In particular, it is then reasonable to assume, that for a large subclass of simple mixtures the following special properties hold

(i) $M_v^{\alpha\beta}$ independent of ϱ_γ $(\gamma \neq \alpha, \beta)$,

(ii) $M_v^{\alpha\beta} \to 0$ for $\varrho_\gamma \to 0$.

Truesdell says that the mixture exhibits binary drags only, if (i) is true. And (ii) states that there is no drag on constituent α from constituent β, if the latter is absent.

([6]) Without loss of generality we may disregard temperature gradients for this argument.

Because of momentum conservation we must have

$$\sum_{\alpha,\beta=1}^{\nu} M_v^{\alpha\beta}(v_i^\alpha - v_i^\beta) = 0, \qquad \text{or} \qquad \sum_{\alpha=1}^{\nu} M_v^{[\alpha\beta]} v_i^\alpha = 0,$$

or, since this must hold for all α,

$$\sum_{\beta=1}^{\nu} M_v^{[\alpha\beta]} = 0.$$

This means that the sum of all elements in a row (and in a column) of the matrix $M_v^{[\alpha\beta]}$ must be zero. In particular, in a binary mixture we have $M_V^{[\alpha,\beta]} = \begin{bmatrix} 0 & \alpha \\ -\alpha & 0 \end{bmatrix}$ and since all rows must add up to zero, we get $\alpha = 0$. In a mixture of theree constituents we have

$$M_v^{[\alpha\beta]} = \begin{bmatrix} 0 & \alpha & -\alpha \\ -\alpha & 0 & \alpha \\ \alpha & -\alpha & 0 \end{bmatrix}.$$

Now if the above conditions (i) and (ii) hold for $M_v^{\alpha\beta}$ they must also hold for the symmetric and antisymmetric parts of $M_v^{\alpha\beta}$. Thus $M_v^{[1,2]}$ is independent of ϱ_3, $M_v^{[1,3]}$ is independent of ϱ_2 and $M_v^{[2,3]}$ is independent of ϱ_1. But they are all the same. Hence α is a constant and by condition (ii) that constant is zero.

Mixtures of more than three constituents can be reduced to the case of three by condition (ii). Thus we have shown the symmetry of the diffusion coefficients $L_{\delta\alpha}$.

Next we investigate the symmetry relation $(2.39)_2$. A comparison of (2.43) and (2.44) shows that we have to prove

$$-T \sum_{\beta,\gamma=1}^{\nu-1} q_V^\beta \overset{-1}{M}{}_V^{\beta\gamma} \overset{-1}{F}_{\gamma\alpha} = T^2 \sum_{\beta,\gamma,\delta=1}^{\nu-1} \overset{-1}{F}_{\alpha\gamma} \overset{-1}{M}{}_V^{\gamma\beta} \overset{-1}{F}_{\beta\delta} D_\delta.$$

$F_{\alpha\gamma}$, as well as $\overset{-1}{F}_{\alpha\gamma} = (\varrho_\alpha \delta_{\alpha\gamma} - \varrho_\alpha \varrho_\gamma/\varrho)$, is a symmetric matrix and we have just proved, under the conditions (i) and (ii), that $M_V^{\alpha\beta}$ is symmetric. Therefore we may write the above condition in the form

$$(2.46) \qquad \sum_{\gamma,\beta=1}^{\nu-1} \overset{-1}{F}_{\alpha\gamma} \overset{-1}{M}{}^{\gamma\beta} \Bigg[q_V^\beta + T \sum_{\delta=1}^{\nu-1} \overset{-1}{F}_{\beta\delta} \Bigg(\left(\frac{M_T^\delta}{\varrho_\delta} - \frac{M_T^\nu}{\varrho_\gamma} \right) + T \frac{\partial \dfrac{\mu^\delta - \mu^\nu}{T}}{\partial T} - \frac{\partial \dfrac{\mu^\delta}{\varrho_\delta} - \dfrac{\mu^\nu}{\varrho_\nu}}{\partial T} \Bigg) \Bigg] = 0.$$

Obviously, this cannot be proved without further special assumptions. I believe though that it is reasonable to suppose that there is a large subclass of simple mixtures for which

(iii) $M_T^\alpha = 0$ holds, so that the temperature gradient does not affect the interaction force $m_i^\alpha - \tau_\alpha v_i^\alpha$, and

(iv) q_V^β is given as

$$\begin{aligned} q_V^\beta &= \sum_{\alpha=1}^{\nu} \varrho_\alpha(\varepsilon_\alpha + p_\alpha/\varrho_\alpha) \sum_{\alpha=1}^{\nu-1} (\delta_{\alpha\beta} - \varrho_\beta/\varrho) \\ &= \sum_{\alpha=1}^{\nu} (\varepsilon_\alpha + p_\alpha/\varrho_\alpha)\ \bar{F}^{1}_{\alpha\beta} \quad \text{with} \quad \sum_{\alpha=1}^{\nu} \bar{F}^{1}_{\alpha\beta} = 0, \\ &= \sum_{\delta=1}^{\nu-1} \bar{F}^{1}_{\beta\delta}(\varepsilon_\delta - \varepsilon_\nu + p^\delta/\varrho_\delta - p^\nu/\varrho_\nu). \end{aligned}$$

This assumption is motivated by definition (1.26) of q_i and it is tantamount to assuming that the partial flux of internal energy q_i^α does not depend on the relative velocities.

Together the two conditions (iii) and (iv) severely restrict the thermomechanical interaction. If they are valid, (2.46) reads

$$\sum_{\gamma,\beta,\delta=1}^{\nu-1} \bar{F}^{1}_{\alpha\gamma}\ \bar{M}^{1\,\gamma\beta}\ \bar{F}^{1}_{\beta\delta}\left[\varepsilon_\delta + \frac{p^\delta}{\varrho_\delta} + T^2\frac{\partial(\mu^\delta/T)}{\partial T} - T\frac{\partial(\mu^\delta/\varrho_\delta)}{\partial T} - \left(\varepsilon_\nu + \frac{\mu^\nu}{\varrho_\nu} + T^2\frac{\partial(\mu^\nu/T)}{\partial T} - T\frac{\partial(\mu^\nu/\varrho_\nu)}{\partial T}\right)\right]. \tag{2.47}$$

We have seen that in a simple mixture p^α and μ^α depend only on ϱ_α and T and that $\varrho\eta$ and $\varrho\varepsilon$ are sums of terms $\varrho_\alpha\eta_\alpha$ and $\varrho_\alpha\varepsilon_\alpha$, respectively, that depend only on ϱ_α and T. Thus the constituents behave like single fluids and there must be a Gibbs equation of the form $(2.20)_1$ for each of them

$$d\eta_\alpha = \frac{1}{T}d\varepsilon_\alpha - \frac{\mu_\alpha}{\varrho_\alpha^2}d\varrho_\alpha.$$

This implies an integrability condition $\varrho_\alpha^2\,\partial\varepsilon_\alpha/\partial\varrho_\alpha = p_\alpha - T\partial\mu_\alpha/\partial T$ and if that is introduced into in (2.47), we get

$$\sum_{\gamma,\beta,\delta=1}^{\nu-1} \bar{F}^{1}_{\alpha\gamma}\ \bar{M}^{1\,\gamma\beta}\ \bar{F}^{1}_{\beta\delta}\left[\frac{\partial\varrho_\delta\varepsilon_\delta}{\partial\varrho_\delta} + T^2\frac{\partial(\mu^\delta/T)}{\partial T} - \left(\frac{\partial\varrho_\nu\varepsilon_\nu}{\partial\varrho_\nu} + T^2\frac{\partial(\mu^\nu/T)}{\partial T}\right)\right] = 0. \tag{2.48}$$

Once again, since we have seen that a simple mixture is but the sum of single fluids the Gibbs equation $(2.31)_1$ falls apart in ν independent equations of the form

$$d(\varrho_\alpha\eta_\alpha) = \frac{1}{T}d\varrho_\alpha\varepsilon_\alpha - \frac{\mu_\alpha}{T}d\varrho_\alpha$$

which can be rewritten in the form

$$d(\varrho_\alpha \eta_\alpha - \frac{1}{T}\varrho_\alpha \varepsilon_\alpha) = \frac{1}{T^2}\varrho_\alpha \varepsilon_\alpha dT - \frac{\mu_\alpha}{T} d\varrho_\alpha .$$

This equation implies the integrability condition $\frac{\partial \varrho_\alpha \varepsilon_\alpha}{\partial \varrho_\alpha} = -T^2 \frac{\partial \mu_\alpha / T}{\partial T}$ and thus we see that (2.48) is satisfied, i.e. we have proved the symmetry relations (2.39) of linear irreversible thermodynamics under the conditions (i) through (iv) of p. 568 and p. 570. It is to be stressed that in the proof no recourse was taken to statistical arguments which usually considered the basis for Onsager relations of the type (2.39).

3. Diffusion and wave propagation in simple mixtures

a. Alternative form of field equations in mixtures. We have seen that the field equations for

$$\varrho_\alpha(x_n, t),\ v_i^\alpha(x_n, t),\ T(x_n, t)$$

for mixtures are based upon the equations of balance of masses and momenta of the constituents and upon the balance of internal energy of the mixture, viz. for a non-reacting mixture

$$\begin{gathered} \frac{\partial \varrho_\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\varrho_\alpha v_j^\alpha) = 0, \qquad \frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\varrho_\alpha v_i^\alpha v_j^\alpha - t_{ij}^\alpha) = m_i^\alpha, \\ \frac{\partial \varrho \varepsilon}{\partial t} + \frac{\partial}{\partial x_j}(\varrho \varepsilon v_j + q_j) = t_{ij}\frac{\partial v_i}{\partial x_j}. \end{gathered} \tag{3.1}$$

These equations must be supplemented by constitutive relations which we have reduced by linearity, material objectivity and the entropy inequality in the previous chapter, so that we have ([6])

$$t_{ij}^\alpha = -p_\alpha(\varrho_\alpha, T)\delta_{ij},$$

$$m_i^\alpha = \sum_{\beta=1}^{\nu-1} M_V^{\alpha\beta} V_i^\beta \quad \text{with}$$

$$\begin{bmatrix} \frac{k}{T^2} & \left\{ -\frac{q_\nu^\alpha}{T} + \left[\frac{\partial\left(\frac{p^\alpha}{\varrho_\alpha} - \frac{p^\nu}{\varrho_\nu}\right)}{\partial T} - T\frac{\partial \frac{\mu_1^\alpha - \mu_1^\nu}{T}}{\partial T} \right] \sum_{\gamma=1}^{\nu-1}\left(\varrho_\alpha \delta_{\alpha\mu} - \frac{\varrho_\alpha \varrho_\gamma}{\varrho}\right) \right\} \\ \frac{1}{2}[m] & -\frac{1}{T}\left(\frac{M_\nu^{\alpha\beta}}{\varrho_\alpha} - \frac{M_\nu^{\gamma\beta}}{\varrho_\nu}\right)\sum_{\gamma=1}^{\nu-1}\left(\varrho_\alpha \delta_{\alpha\gamma} - \frac{\varrho_\alpha \varrho_\gamma}{\varrho}\right) \end{bmatrix},$$

([6]) We investigate the subclass of simple mixtures here, for which in the last section we have proved the symmetry relation (2.38), i.e. in particular $M_T^\alpha = 0$.

$$q_i^{\mathrm{I}} = \sum_{\beta=1}^{\nu-1} q_V^\beta V_i^\beta - kT_{1i} \quad \text{with} \quad q_V^\beta = \sum_{\delta=1}^{\nu-1}\left(\varrho_\beta \delta_{\beta\delta} - \frac{\varrho_\beta \varrho_\delta}{\varrho}\right)\left(\varepsilon_\delta - \frac{\mu^\delta}{\varrho_\delta} - \left(\varepsilon_\nu - \frac{\mu^\nu}{\varrho_\nu}\right)\right),$$

$$\varepsilon_{\mathrm{I}} = \sum_{\alpha=1}^{\nu} \frac{\varrho_\alpha}{\varrho}\varepsilon_\alpha(\varrho_\alpha, T) \quad \text{with} \quad \varrho_\alpha^2 \frac{\partial \varepsilon}{\partial \varrho_\alpha} = p_\alpha - T\frac{\partial p_\alpha}{\partial T}.$$

It is often useful in the theory of mixtures to replace the set of variables $\varrho_\alpha, v_i^\alpha, T (\alpha = 1, 2, \ldots, \nu)$ by the set $\varrho, c_\alpha, v_i, J_i^\alpha, T \ (\alpha = 1, 2, \ldots, \nu-1)$, where $c_\alpha \equiv \varrho_\alpha/\varrho$ is the concentration of constituent α and $J_i^\alpha \equiv \varrho_\alpha u_i^\alpha$ is its diffusion flux. This change of variables is useful, if ϱ and v_i are constant as they very nearly are in a diffusion process. Thus with the new choice two variables drop out, while with the old choice we have merely an awkward constraint on the variables.

With this new choice of variables it is appropriate to rewrite the equations of balance so that the new variables occur explicitly. We obtain

$$\begin{aligned}
&\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_j}{\partial x_j} = 0,\\
&\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho v_i v_j - t_{ij}) = 0,\\
&\frac{\partial \varrho \varepsilon}{\partial t} + \frac{\partial}{\partial x_j}(\varrho \varepsilon v_j + q_j) = t_{ij}\frac{\partial v_i}{\partial x_j},\\
&\varrho_\alpha\left(\frac{\partial c_\alpha}{\partial t} + v_j \frac{\partial c_\alpha}{\partial x_j}\right) + \frac{\partial J_i^\alpha}{\partial x_i} = 0 \quad (\alpha = 1, 2, \ldots, \nu-1),\\
&\frac{\partial J_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}\left(J_i^\alpha v_j^\alpha - (t_{ij}^\alpha - c_\alpha t_{ij})\right) = t_{ij}\frac{\partial c_\alpha}{\partial x_j} - J_j^\alpha \frac{\partial v_i}{\partial x_j} + m_i^\alpha.
\end{aligned} \tag{3.3}$$

It is also useful to rewrite the constitutive equations in the new variables and we obtain

$$\begin{aligned}
t_{ij}^\alpha &= -p_\alpha(\varrho \cdot c_\alpha, T)\delta_{ij},\\
m_i^\alpha &= \sum_{\beta,\gamma=1}^{\nu-1} M_V^{\alpha\beta}\left(\frac{1}{\varrho_\gamma}\delta_{\beta\gamma} + \frac{1}{\varrho_\nu}\right)J_i^\gamma,\\
q_i^{\mathrm{I}} &= \sum_{\beta,\gamma=1}^{\nu-r} q_\nu^\beta\left(\frac{1}{\varrho_\gamma}\delta_{\beta\gamma} + \frac{1}{\varrho_\nu}\right)J_i^\gamma - kT_{1i},\\
\varepsilon_{\mathrm{I}} &= \sum_{\alpha=1}^{\nu} c_\alpha \varepsilon_\alpha(\varrho \cdot c_\alpha, T),
\end{aligned} \tag{3.4}$$

where ε, $p = \sum_{\alpha=1}^{\nu} p_\alpha$ and μ^α are related to each other by the fact that the Gibbs equation $(2.31)_1$ holds which now ought to be written in the form

$$d\eta = \frac{1}{T}\left(d\varepsilon_1 - \frac{p}{\varrho_2} d\varrho - \sum_{\alpha=1}^{\nu-1} (\mu_1^\alpha - \mu_1^\nu)\, dc_\alpha\right). \tag{3.5}$$

This implies the following integrability conditions

$$\begin{gathered} \varrho^2 \frac{\partial \varepsilon_1}{\partial \varrho} = p - T\frac{\partial p}{\partial T}; \quad \frac{\partial \varepsilon_1}{\partial c_\alpha} = \mu_1^\alpha - \mu_1^\nu - T\frac{\partial \mu_1^\alpha - \mu_1^\nu}{\partial T}; \\ \frac{\partial p}{\partial c_\alpha} = \varrho^2 \frac{\partial \mu_1^\alpha - \mu_1^\nu}{\partial \varrho}. \end{gathered} \tag{3.6}$$

Also q_V^β and $M_V^{\alpha\beta}$ must obey the inequalities that were implied by the positive definiteness of the matrix in (3.2).

b. Linear wave equations for a binary mixture. Even though the field equations that result from a combination of (3.3) and (3.4) are fairly much simplified it is not easy, of course to solve initial and boundary value problems with them.

However, one type of solution can always easily be had, namely small amplitude waves, the so-called *sound waves.* We shall investigate these now and it is then appropriate to make the following further simplifications.

(i) We linearize the equation of balance around a state in which all velocities vanish and densities and temperature are uniform. Thus we shall ignore non-linear terms in the gradients of densities, velocities and temperature as well as products of relative velocities among themselves and with those gradients.

(ii) For simplicity we consider only a binary mixture.

(iii) We shall consider only adiabatic sound propagation.

As is well known from sound propagation in single fluids, the assumption of adiabaticity is a very good one. Its mathematical expression is vanishing heat conductivity, i.e., $k = 0$ and therefore the inequality $(2.34)_3$ implies

$$q_V^1 = T\frac{\varrho_1 \varrho_2}{\varrho}\frac{\partial(p_1/\varrho_1 - p_2/\varrho_2)}{\partial T} - T^2 \frac{\partial((\mu_1^1 - \mu_1^2)/T)}{\partial T}. \tag{3.7}$$

We denote quantities that refer to the uniform reference state by a superposed zero and derivatives such as $\partial\varepsilon/\partial\varrho$ and $\partial p_\alpha/\partial T$ by ε_ϱ and μ_T^α, respectively. Moreover, we abbreviate $\mu^1 - \mu^2$ by μ.

Insertion of the constitutive relations (3.4) into the equations of balance (3.3) and use of the restrictive conditions (3.6) leads to

$$
\begin{aligned}
&\frac{\partial \varrho}{\partial t}+\mathring{\varrho}\frac{\partial v_i}{\partial x_i}=0, \qquad \mathring{\varrho}\frac{\partial c}{\partial t}+\frac{\partial J_i}{\partial x_i}=0,\\
&\varrho_0\frac{\partial v_i}{\partial t}+\mathring{p}_\varrho\frac{\partial \varrho}{\partial x_i}+\mathring{p}_c\frac{\partial c}{\partial x_i}+\mathring{p}_T\frac{\partial T}{\partial x_i}=0,\\
&\frac{\partial J_i}{\partial t}=\mathring{M}_V^{11}\frac{\mathring{\varrho}}{\mathring{\varrho}_1\mathring{\varrho}_2}J_i-\frac{\mathring{\varrho}_1\mathring{\varrho}_2}{\mathring{\varrho}}\left(\mathring{\mu}_\varrho\frac{\partial \varrho}{\partial x_i}+\mathring{\mu}_c\frac{\partial c}{\partial x_i}+\left(\frac{\mathring{p}_T^1}{\mathring{\varrho}_1}-\frac{\mathring{p}_T^2}{\mathring{\varrho}_2}\right)\frac{\partial T}{\partial x_i}\right)=0,\\
&\frac{\partial T}{\partial t}+\frac{\mathring{\varepsilon}_c}{\mathring{\varepsilon}_T}\frac{\partial c}{\partial t}-\frac{\mathring{T}}{\mathring{\varrho}^2}\frac{\mathring{p}_T}{\mathring{\varepsilon}_T}\frac{\partial \varrho}{\partial t}+\frac{\mathring{T}}{\mathring{\varrho}\mathring{\varepsilon}_T}\left(\frac{\mathring{p}_T^1}{\mathring{\varrho}_1}-\frac{\mathring{p}_T^2}{\mathring{\varrho}_2}+\frac{\mathring{M}}{\mathring{T}}-\mathring{\mu}_T\right)\frac{\partial J_i}{\partial x_i}=0,
\end{aligned}
\tag{3.8}
$$

From $(3.8)_3$ we conclude that curl $\mathbf{v}$ is constant in time and $(3.8)_4$ implies that the time derivative of curl $\mathbf{J}$ is proportional to curl $\mathbf{J}$ itself. Thus, if we assume that curl $\mathbf{v}$ and curl $\mathbf{J}$ are zero initially, they will continue to be zero.

It is an easy matter within in linear theory to eliminate J_i, v_i and T from the field equations (3.8) and thus we obtain after some calculation

$$
\begin{aligned}
&\frac{\partial^2 \varrho}{\partial t^2}-\left[\mu_\varrho+\frac{Tp_T^2}{\varrho^2\varepsilon_T}\right]\Delta\varrho-\left[p_c+\frac{T}{\varepsilon_T}p_1-\left(\frac{p_T^1}{\varrho_1}-\frac{p_T^2}{\varrho_2}\right)\right]\Delta c=0,\\
&\frac{\partial^2 c}{\partial t^2}-M_V^{11}\frac{\varrho}{\varrho_1\varrho_2}\frac{\partial c}{\partial t}-\frac{\varrho_1\varrho_2}{\varrho^2}\left[\mu_c+\frac{T}{\varepsilon_T}\left(\frac{p_T^1}{\varrho_1}-\frac{p_T^2}{\varrho_2}\right)^2\right]\Delta c-\\
&\qquad -\frac{\varrho_1\varrho_2}{\varrho^4}\left[p_c+\frac{T}{\varepsilon_T}\mu_1\left(\frac{p_T^1}{\varrho_1}-\frac{p_T^2}{\varrho_2}\right)\right]\Delta\varrho=0.
\end{aligned}
\tag{3.9}
$$

where for convenience in notation I have dropped the superposed zeros on the coefficients.

Before we reduce those equations further, we shall discuss a special case which is quite instructive. Namely, consider the case in which the coefficient

$$
W\equiv p_c+\frac{T}{\varepsilon_T}p_T\left(\frac{p_T^1}{\varrho_1}-\frac{p_T^2}{\varrho_2}\right)
\tag{3.10}
$$

vanishes. In this case the two equations (3.9) are uncoupled. The first one is the well-known wave equation for adiabatic sound propagation with the velocity

$$
V_\varrho=\sqrt{p_\varrho+\frac{Tp_T^2}{\varrho^2\varepsilon_T}}.
\tag{3.11}
$$

Note that the radicand can be written as $(\partial p/\partial\varrho)_\eta$. The second equation is a

hyperbolic equation, the so-called *telegraph equation*, which describes the propagation of damped waves with the velocity

$$V_c = \sqrt{\frac{\varrho_1 \varrho_2}{\varrho^z}\left(\mu_c + \frac{T}{\varepsilon_T}\left(\frac{p_T^1}{\varrho_1} - \frac{p_T^2}{\varrho_2}\right)\right)}. \tag{3.12}$$

We may call this the velocity of "second sound", whereby (3.11) is the velocity of "first sound".

In equation (3.9), without the interaction term, the second derivative is usually neglected. This corresponds to the dropping of the acceleration in the momentum balance (2.40). Thus one obtains

$$M_V^{11}\frac{\partial c}{\partial t} + \left[\mu_c + \frac{T}{\varepsilon_T}\left(\frac{p_1^1}{\varrho_1} - \frac{p_1^2}{\varrho_2}\right)^2\right]\Delta c = 0, \tag{3.13}$$

and this is the ordinary diffusion equation, which is parabolic.

We note that, while it is conceivable that the coefficient in (3.10) may vanish for a given mixture, it does not in general vanish for a mixture of ideal gases. Indeed with $p_\alpha = \varrho \frac{R}{M_\alpha} T$ and $\varepsilon_\alpha = z_\alpha \frac{R}{M_\alpha} T + \beta_\alpha$ we obtain

$$W = \varrho R T\left(\frac{1}{M_1} - \frac{1}{M_2}\right)\left(1 + \frac{\varrho_1/M_1 + \varrho_2/M_2}{z_1 \varrho_1/M_1 + z_2 \varrho_2/M_2}\right) \tag{3.14}$$

and this is zero if and only if $M_1 = M_2$ holds.

We note also that V_ϱ, the ordinary adiabatic speed of sound comes out in an ideal gas as

$$V_\varrho = \sqrt{\frac{\varrho_1(z_1+1)(1/M_1) + \varrho_2(z_2+1)(1/M_2)}{\varrho_1 z_1(1/M_1) + \varrho_2 z_2(1/M_2)}\left(\frac{\varrho_1}{\varrho}\cdot\frac{1}{M_1} + \frac{\varrho_2}{\varrho}\frac{1}{M_2}\right)}\sqrt{RT}, \tag{3.15}$$

wheares the spead of the second sound is

$$V_c = \sqrt{\frac{\varrho_1 \varrho_2}{\varrho^2}\left(\frac{\varrho}{\varrho_1}\frac{1}{M_1} + \frac{\varrho}{\varrho_2}\frac{1}{M_2} + \frac{1/M_1 - 1/M_2}{\frac{\varrho_1}{\varrho}\frac{z_1}{M_1} + \frac{\varrho_2}{\varrho}\frac{z_2}{M_2}}\left(\frac{1}{M_1} - \frac{1}{M_2}\right)\right)}\sqrt{RT}. \tag{3.16}$$

If W does not vanish we must reduce equations (3.9) further. We eliminate ϱ between them and obtain

$$\frac{\partial^4 c}{\partial t^4} - M_V''\frac{\varrho}{\varrho_1 \varrho_2}\frac{\partial^3 c}{\partial t^3} - (V_\varrho^2 + V_c^2)\frac{\partial \Delta c}{\partial t^2} + \tag{3.17}$$
$$+ M_V''\frac{\varrho}{\varrho_1 \varrho_2} V_\varrho^2 \frac{\partial \Delta c}{\partial t} + \left(V_\varrho^2 - V_c^2 - \frac{\varrho_1 \varrho_2}{\varrho_4} W^2\right)\Delta\Delta c = 0.$$

This is again a wave equation describing the propagation of two waves with the velocities

$$V_{\pm} = \sqrt{2}\sqrt{V_\varrho^2 V_c^2 - \frac{(\varrho_1 \varrho_2/\varrho_4) W^2}{V_\varrho^2 + V_c^2}} \times \frac{1}{\sqrt{1 \pm \sqrt{1 - 4\frac{V_\varrho^2 V_c^2 - (\varrho_1 \varrho_2/\varrho_4) W^2}{(V_\varrho^2 - V_c^2)}}}}. \tag{3.18}$$

As W tends to zero, V_+ tends to V_c and V_- tends to V_ϱ. Thus we may say that V_+ is "primarily" the speed of propagation of disturbances in concentration, i.e., the speed of second sound, while V_- is primarily the speed of propagation of disturbances in density, i.e., the speed of first sound.

c. Amplitudes of first and second sound. We consider longitudinal one-dimensional sinusoidal sound waves propagating on the direction $x_1 = x$ so that

$$\begin{aligned} \varrho &= \varrho_0 + \bar{\varrho} e^{i(wt - hx)}, \\ c &= c_0 + \bar{c} e^{i(wt - hx)}, \\ v &= \bar{v} e^{i(wt - hx)}, \\ J &= \bar{J} e^{i(wt - hx)}, \\ T &\doteq T_0 + \bar{T} e^{i(wt - hx)}. \end{aligned} \tag{3.19}$$

Insertion into (3.8) leads to the system of algebraic equations

$$\begin{aligned}
&u\bar{\varrho} && -\mathring{\varrho}\bar{v} && && = 0, \\
& && \varrho u\bar{c} && -J && = 0, \\
&-p_\varrho \bar{\varrho} && -p_c \bar{c} && +\mathring{\varrho} u\bar{v} && -\mathring{p}_T \bar{T} = 0, \\
&\frac{\varrho_1 \varrho_2}{\varrho}\mu_\varrho \bar{\varrho} && -\frac{\varrho_1 \varrho_2}{\varrho}\mu_c \bar{c} && +u\left(1 + iM_V'' \frac{\varrho}{\varrho_1 \varrho_2}\frac{1}{w}\right)J && -\frac{\varrho_1 \varrho_2}{\varrho}\left(\frac{p_T^1}{\varrho_1} - \frac{p_T^2}{\varrho_2}\right)\bar{T} = 0, \\
&-\frac{T}{\varrho^2}\frac{p_T}{\varepsilon_T} u\bar{\varrho} && && -\frac{T}{\varrho \varepsilon_T}\left(\frac{p_T^1}{\varrho_1} - \frac{p_T^2}{\varrho_2}\right)J + && u\bar{T} = 0,
\end{aligned}$$

where $u \equiv \omega/k$ is the phase velocity of the wave. We eliminate $\bar{\varrho}$, $\bar{v}$ and $\bar{T}$ from these equations and obtain a homogenious systems of algebraic equations for $\bar{v}$ and J, viz.

$$-\varrho\left(p_c + \frac{Tp_T^2}{\varrho^2 \varepsilon_T} - n^2\right)\bar{v} - \frac{1}{\varrho}\left(p_c + T\frac{p_T}{\varepsilon_T}\left(\frac{p_T^1}{\varrho_1} - \frac{p_T^2}{\varrho_2}\right)\right)J = 0,$$

$$-\frac{\varrho_1 \varrho_2}{\varrho_2}\left(\varrho^2 \mu_\varrho - \frac{\varrho^2}{p_T}\left(\frac{p_T^1}{\varrho_1} - \frac{p_T^2}{\varrho_1}\right)(p_\varrho - u^2)\right)\bar{v} - \left(\frac{\varrho_1 \varrho_2}{\varrho_2}\left(\mu_c - \frac{p_c}{p_T}\left(\frac{p_T^1}{\varrho_1} - \frac{p_T^2}{\varrho_2}\right)\right) - \right.$$

$$\left. - u^2\left(1 + iM_V'' \frac{\varrho}{\varrho_1 \varrho_2}\frac{1}{W}\right)\right)\bar{J} = 0.$$

For simplicity in this agreement we assume that first and second sounds are uncoupled which means that the coefficient of interaction defined in (3.10) is equal to zero. In that case we may rewrite the last two equations in the forms

$$
\begin{aligned}
&\left(p_\varrho+\frac{Tp_T^2}{\varrho^2\varepsilon_T}-u^2\right)\bar{v} &&= 0,\\
(3.21)\quad &\frac{\varrho_1\varrho_2}{p_T}\left(\frac{p_T^1}{\varrho_1}-\frac{p_T^2}{\varrho_2}\right)\left(p_\varrho+\frac{Tp_T^2}{\varrho^2\varepsilon_T}-u^2\right)\bar{v}- \\
&-\left(\frac{\varrho_1\varrho_2}{\varrho^2}\left(M_c+\frac{T}{\varepsilon_T}\left(\frac{p_T^1}{\varrho_1}-\frac{p_T^2}{\varrho_2}\right)^2\right)-u^2\left(1+iM_V''\frac{\varrho}{\varrho_1\varrho_2}\frac{1}{W}\right)\right)\bar{J} &&= 0.
\end{aligned}
$$

For this homogeneous set of two algebraic equations to have a non-trivial solution the determinant must vanish which means either (with definitions (3.11), (3.12))

$$
(3.22)\qquad u^2 = U_1^2 = V_\varrho^1 \quad \text{or} \quad u^2 = U_2^2 = V_c^2\frac{1}{1+iM_V''\dfrac{\varrho}{\varrho_1\varrho_2}\dfrac{1}{W}}.
$$

U_1 is the phase speed of the first sound. From (3.21) we conclude that a wave propagating with that speed has $\bar{J}-0$. U_2 is a complex phase speed, i.e., a wave propagation with that speed is damped. From (3.21) it follows that this wave has $\bar{v}=0$.

We conclude that in a first sound wave the mixture as a whole moves, i.e., there is no relative motion of the constituents and therefore, by $(3.20)_2$, we have $c=0$: also there is no damping. On the other hand, in a second soud wave the mixture as a whole is at rest and one constituent moves against the other such that the center of mass is at rest. Correspondingly $\bar{\varrho}=0$, which is to say that the wave leaves the density unaffected.

From $(3.20)_{1,2,3}$ we obtain

$$
(3.23)\qquad \bar{T}=\frac{1}{p_T}\left((u^2-p_\varrho)\,\bar{\varrho}-p_c\,\bar{c}\right),
$$

whence it follows that a temperature wave accompanies both the first and the second sound.

4. Liquid helium 4 as a special binary mixture

a. Assumptions leading to Landau's theory of liquid helium. Tisza and Landau have formulated theories of liquid helium which may be fitted into the thermodynamic theory of binary mixtures provided that the following three assumptions are valid.

i. (*Mixture character*)

The first assumption states that the single liquid to which the noble gas He 4 condenses behaves like a mixture. This strange assumption is motivated by quantum mechanics and it may be more proper to speak of two phases rather than two constituents of a mixture. Indeed, quantum mechanics and quantum statistics provide for the possibility of having a phase composed of atoms in their ground state and another phase of atoms in energetically elevated states. These are the supercomponent and the normal component of Landau's mixture theory respectively. We shall denote these by the indices 1 or s for the supercomponent and 2 or n for the normal component. As is fitting for a mixture of two phases we must assume that one phase can be converted into the other as the thermodynamic state might require. In other words we must allow for "chemical" reactions in the theory.

ii. (*No dissipation*)

The supercomponent is endowed with very remarkable properties. In particular it is assumed to be non-viscous and also its dynamical interaction with the normal component is assumed to be zero.

While the normal component has viscosity and heat conductivity, it is possible to ignore these features in the study of wave propagation just like this is done in the study of the leading terms of sound propagation in an ordinary mixture.

In fact, in the study of wave propagation in Helium we assume that there is no dissipation at all, not even dissipation due to the conversion of one constituent into the other. In other words the residual entropy inequality $(2.31)_5$ is satisfied with the equality sign. Inspection of that inequality shows, that this assumption of vanishing dissipation in a binary mixture can be satisfied by

$$k = 0, \quad M_v^{11} = 0 \quad \text{and} \quad \mu = 0. \text{ (}^7\text{)} \tag{4.1}$$

$(4.1)_3$ requires a comment. It would be possible to suppress chemical dissipation by disallowing chemical reactions and in fact we have done that in the previous section. But this assumption would contradict the observations which rather clearly imply that there is a free and easy transition from supercomponent to the normal component and vice versa. Thus we ensure the freedom from dissipation by making the other factor, viz. μ in the chemical entropy production equal to zero.

---

(7) μ is the difference of the chemical potentials of the constituents. Nonlinear terms like $\frac{1}{2}u_\alpha^2$ in the entropy production are ignored here.

This has rather severe implications, because μ ist a function of ϱ_1, ϱ_z and T and $\mu = 0$ is therefore an algebraic dependence between those fields. This constraint ensables us to ignore one of the field equations and we shall choose to ignore the mass balance for the superfluid. Another way of putting this is to say that – when all the fields have been determined from the remaining equations and $\mu = 0$ – this mass balance may be used to calculate the "chemical" production τ_s of the supercomponent.

iii. (*Vanishing entropy*)
We assume

$$\eta_1 = 0, \tag{4.2}$$

so that the supercomponent has no entropy. This assumption is motivated by quantum statistics which suggests that the superfluid may be the phase of helium that prevails at absolute zero and there the entropy vanishes according to Nernst's and Planck's formulation of the third law of thermodynamics.

b. Landau's linearized equations. The basic equations of Landau's theory of liquid helium are the equations of balance of the masses and momenta of the constituents and the balance of internal energy of the mixture, just like in the theories presented heretofore. The only exception is that we ignore the balance of mass of the supercomponent, because we have the constraint $(4.1)_3$ which replaces one equation.

Also for convenience we rearrange the equations and choose

$$\begin{aligned}
&\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_j}{\partial x_j} = 0, && \text{balance of mass of the mixture,}\\
&\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho v_i v_j - t_{ij}) = 0, && \text{balance of momentum of the mixture,}\\
&\partial \varrho_s v_i^s + \frac{\partial}{\partial x_j}(\varrho_s v_i^s v_j^s - t_{ij}^s) = m_i^s, && \text{balance of momentum of supercomponent,}\\
&\frac{\partial \varrho \varepsilon}{\partial t} + \frac{\partial}{\partial x_j}(\varrho \varepsilon v_j + q_j) = t_{ij}\frac{\partial v_i}{\partial x_j}, && \text{balance of internal energy.}
\end{aligned} \tag{4.3}$$

as the basic equations for the treatment of liquid helium. With one field equation replaced by the condition $\mu = 0$ this is certainly a permissible choice, i.e., we have the correct number of equations for the fields ϱ_s, ϱ_n, v_i^s, v_i^n and T.

But, of course, we also need constitutive relations and for those we pick the equations characterizing simple mixtures

$$
\begin{aligned}
&\eta = \sum_{\alpha=1}^{2} \frac{\varrho_\alpha}{\varrho} \eta_\alpha(\varrho_\alpha, T),\\
&\varepsilon = \sum_{\alpha=1}^{2} \frac{\varrho_\alpha}{\varrho} \varepsilon_\alpha(\varrho_\alpha, T) \quad \text{with} \quad d\eta_\alpha = \frac{1}{T}\left(d\varepsilon_\alpha - \frac{p_\alpha}{\varrho_\alpha^2} d\right) \frac{\partial \varepsilon_\alpha}{\partial \varrho_\alpha} = p_\alpha - T\frac{\partial p_x}{\partial T},\\
(4.4)\quad &t_{ij}^\alpha = -p^\alpha(\varrho_\alpha, T)\delta_{ij},\\
&m_i^s - T_s v_i^s = M_V^{11} V_i^1 + M_T^1 T_{1i} \quad \text{with} \quad M_V^{11} = 0\\
&q_i = q_V^1 V_i^1 + k T_{1i} \quad \text{with} \quad k = 0, q.
\end{aligned}
$$

In $(4.4)_5$ the condition $k = 0$ is imposed, we have ignore heat conduction. In fact, we shall assume a little changed set $q_i^\alpha = 0$ in definition $(1.26)_2$ of the flux of internal energy. In that case q_V^1 is given by the expression listed in Sect. 3, as we have seen earlier, viz. on p. 568 and p. 570. In fact the set $M_v^{11} = 0$, because we ignore the interaction force between the constituents and M_T^1 vanishes by the following argument: Since M, and M_v^{11} are zero and q_v^1 is given by $(4.4)_5$ we conclude from (2.34) that (note that $M_T^2 = -M_T^1$)

$$
\begin{aligned}
M_T^1 = \frac{\varrho_1 \varrho_2}{\varrho}\frac{1}{T}\Bigg[& T\frac{\partial(p_1/\varrho_1 - p_2/\varrho_2)}{\partial T} + \varrho\left(\frac{\partial \varepsilon}{\partial \varrho_1} - \frac{\partial \varepsilon}{\partial \varrho_2}\right) -\\
& -(\varepsilon_1 - \varepsilon_2) - \left(\frac{p_1}{\varrho_1} - \frac{p_2}{\varrho_2}\right)\Bigg]
\end{aligned}
$$

$$
\begin{aligned}
\text{with } \frac{\partial \varepsilon}{\partial \varrho_1} - \frac{\partial \varepsilon}{\partial \varrho_2} &= \frac{1}{\varrho}\varepsilon_1 + \frac{\varrho_1}{\varrho}\frac{\partial \varepsilon_1}{\partial \varrho_1} - \frac{1}{\varrho}\varepsilon_2 - \frac{\varrho_2}{\varrho}\frac{\partial \varepsilon}{\partial \varrho_2}\\
&= \frac{1}{\varrho}(\varepsilon_1 - \varepsilon_2) + \frac{1}{\varrho}\left(\varrho_1 \frac{\partial \varepsilon}{\partial \varrho_1} - \varrho_2 \frac{\partial \varepsilon}{\partial \varrho_2}\right),
\end{aligned}
$$

$$
M_T = \frac{\varrho_1 \varrho_2}{\varrho}\frac{1}{T}\left[\frac{1}{\varrho_1}\left(\varrho_1^2 \frac{\partial \varepsilon_1}{\partial \varrho_1} - p_1 + T\frac{\partial p_1}{\partial T}\right) - \frac{1}{\varrho_2}\left(\varrho_2^2 \frac{\partial \varepsilon_2}{\partial \varrho_2} - p_2 + T\frac{\partial p_2}{\partial T}\right)\right],
$$

$$
M_T = 0, \quad \text{because of } (4.4)_2.
$$

Insertion of these constituive equations into the equations of balance (4.3) and linearization of these in the usual manner leads to

$$
(4.5)\quad
\begin{aligned}
&\frac{\partial \varrho}{\partial t} + \mathring{\varrho}\frac{\partial v_i}{\partial x_i} = 0,\\
&\mathring{\varrho}\frac{\partial v_i}{\partial t} + \frac{\partial p}{\partial x_i} = 0,\\
&\mathring{\varrho}\frac{\partial v_i^1}{\partial t} + \frac{\partial p_1}{\partial x_i} = 0,\\
&\mathring{\varrho}\frac{\partial \varepsilon}{\partial t} + \mathring{q}_V^1 \frac{\partial v_j}{\partial x_j} = -p\frac{\partial v_i}{\partial x_i}.
\end{aligned}
$$

The equations $(4.5)_{1,2}$ are already in Landau's form, but $(4.5)_{3,4}$ can still be simplified considerably by use of our knowledge on simple mixtures.

On $(4.5)_3$: We write

$$\begin{aligned}\frac{\partial p^1}{\partial x_i} &= \sum_{\beta=1}^{2} \frac{\partial p^1}{\partial \varrho_\beta}\frac{\partial \varrho_\beta}{\partial x_i} + \frac{\partial p^2}{\partial T}\frac{\partial T}{\partial x_i} \quad \text{or with } (2.31)_4 \\ &= \sum_{\beta=1}^{2} \varrho_1 \frac{\partial p^1}{\partial \varrho_\beta}\frac{\partial \varrho_\beta}{\partial x_i} + \frac{\partial p^1}{\partial T}\frac{\partial T}{\partial x_i} \\ &= \varrho_1 \frac{\partial \mu_1}{\partial x_i} - \left(\varrho_1 \frac{\partial \mu_1}{\partial T} - \frac{\partial p_1}{\partial T}\right)\frac{\partial T}{\partial x_i} \\ &= \varrho_1 \frac{\partial \mu_1}{\partial x_i} - \frac{\partial(\varrho_1 \mu_1 - p_1)}{\partial T}\frac{\partial T}{\partial x_i}.\end{aligned}$$

The Gibbs–Duhem equation $(2.31)_2$ is satisfied for each component in a simple mixture, so that in particular we have $\varrho_1 \mu_1 = \varrho_1 \varepsilon_1 - T\varrho_1 \eta_1 + p_1$. Therefore we get

$$\frac{\partial p^1}{\partial x_i} = \varrho_1 \frac{\partial \mu_1}{\partial x_i} - \left(\varrho_1 \left(\frac{\partial \varepsilon_1}{\partial T} - \frac{1}{T}\frac{\partial \eta_1}{\partial T}\right)\varrho_1 \eta_1\right)\frac{\partial T}{\partial x_i}.$$

The last two terms vanish, because of the Gibbs equation $(4.4)_2$ and because $\eta_1 = 0$ holds in liquid helium. Also since $\mu = 0$ holds, the Gibbs–Duhem equation implies $\mu_1 = \varepsilon - T\eta + p/\varrho$ and therefore we have

$$\frac{\partial p^1}{\partial x_i} = \varrho_1 \frac{\partial \mu_1}{\partial x_i}.$$

The Gibbs relation $(2.31)_1$ can be rewritten by use of the Gibbs–Duhem equation in the form

$$T d\eta = d\varepsilon - \frac{p}{\varrho_2} d\varrho - \sum_{\alpha=1}^{\nu-1} (\mu_\alpha - \mu_\nu)\, dc_\alpha$$

or in our case with $\mu_1 = \mu_2$

$$d\left(\varepsilon - T\eta + \frac{\mu}{\varrho}\right) = d\mu_1 = -\eta dT + \frac{1}{\varrho} dp.$$

Thus we get

$$\begin{aligned}\frac{\partial p^1}{\partial x_i} &= -\varrho_1 \eta \frac{\partial T}{\partial x_i} + \frac{\varrho_1}{\varrho}\frac{\partial p}{\partial x_i} \quad \text{or with } (4.5)_2, \\ \frac{\partial p^1}{\partial x_i} &= -\varrho_1 \eta \frac{\partial T}{\partial x_i} - \varrho_1 \frac{\partial v_i}{\partial t}.\end{aligned} \tag{4.6}$$

On $(4.5)_4$: From $(4.4)_5$ we read off $\varrho_V^1 = (\varrho_1 \varrho_2/\varrho)(\varepsilon_1 + p_1/\varrho_1 - (\varepsilon_2 + p_2/\varrho_2))$

and since the Gibbs–Duhem equations is satisfied for each constituent separately in a simple mixture, we have

$$\mu^1 = -T\eta^1 + p^1/\varrho^1,$$
$$\mu^2 = -T\eta^2 + p^2/\varrho_2 \text{ with } \eta^1 = 0,\ \mu^1 = \mu^2,\ \eta^2 = (\varrho/\varrho^2)\eta,$$
$$\varepsilon^1 + p_1/\varrho_1 - \varepsilon^2 + p^2/\varrho_2 = -T\left(\frac{\varrho}{\varrho_2}\right)\eta,$$

so that

$$q_V^1 = -T\varrho_1\eta. \tag{4.7}$$

Also we have

$$\varrho\frac{\partial\varepsilon}{\partial t} + p\frac{\partial p_i}{\partial x_i} = \varrho\frac{\partial\varepsilon}{\partial T}\frac{\partial T}{\partial t} + \varrho\left(\frac{\partial\varepsilon}{\partial\varrho} - \frac{p}{\varrho^2}\right)\frac{\partial\varrho}{\partial t} + \varrho\frac{\partial\varepsilon}{\partial c}\frac{\partial c}{\partial t}$$

and

$$\frac{\partial\varepsilon}{\partial\varrho} - \frac{p}{\varrho^2} = -\frac{1}{\varrho^2}\frac{\partial p}{\partial T}$$

which is an integratability condition for η following from the Gibbs equation $Td\eta = d\varepsilon - \frac{n}{\varrho^2}\varrho - \mu dc$. Thus

$$\varrho\frac{\partial\varepsilon}{\partial t} + p\frac{\partial}{\partial x_i} = \varrho T\frac{\partial\eta}{\partial T}\frac{\partial T}{\partial t} - \frac{1}{\varrho^2}T\frac{\partial p}{\partial T}\frac{\partial\varrho}{\partial t} + \varrho\frac{\partial\varepsilon}{\partial c}\frac{\partial c}{\partial t}$$
$$= \varrho T\frac{\partial\eta}{\partial t} - \varrho T\frac{\partial\eta}{\partial\varrho}\frac{\partial\varrho}{\partial t} - \frac{1}{\varrho^2}T\frac{\partial\eta}{\partial T}\frac{\partial\varrho}{\partial t} - \varrho\left(T\frac{\partial\eta}{\partial c} - \frac{\partial\varepsilon}{\partial c}\right)\frac{\partial c}{\partial t}.$$

Again from the Gibbs equation in the form $d(\varepsilon - T\eta) = -\eta dT - \frac{p}{\varrho^2}d\varrho + \mu dc$ we obtain

$$\frac{\partial\eta}{\partial\varrho} = \frac{1}{\varrho^2}\frac{\partial p}{\partial T} \quad \text{and} \quad T\frac{\partial\eta}{\partial c} - \frac{\partial\varepsilon}{\partial c} = -\mu = 0,$$

so that we get

$$\varrho\frac{\partial\varepsilon}{\partial t} + p\frac{\partial v_i}{\partial x_i} = \varrho T\frac{\partial\eta}{\partial t}. \tag{4.8}$$

We combine (4.6) through (4.8) with $(4.5)_{3,4}$ and obtain

$$\frac{\mathring{\varrho}_2}{\mathring{\varrho}}\frac{\partial V_i}{\partial t} - \mathring{\eta}\frac{\partial T}{\partial x_i} = 0, \quad \frac{\partial\eta}{\partial t} - \frac{\mathring{\varrho}_1}{\mathring{\eta}}\mathring{\eta}\frac{\partial V_i}{\partial x_i} = 0. \tag{4.9}$$

Equations $(4.5)_{1,2}$ and equations $(4.9)_{1,2}$ are Landau's equations for liquid helium. We can see now how they fit into a general theory of simple mixtures.

c. Landau's wave equations. It is an easy matter to eliminate v_i between the two equations $(4.5)_{1,2}$ and V_i between $(4.9)_{1,2}$. We get from this

$$\frac{\partial^2 \varrho}{\partial t^2} - \Delta p = 0 \quad \text{and} \quad \frac{\partial^2 \eta}{\partial t^2} - \eta^2 \frac{\varrho_1}{\varrho_2} \Delta T = 0. \tag{4.10}$$

Normally, of course, we should consider p and η as functions of ϱ, c and T, but since $\mu(\varrho, c, T) = 0$ holds, we can drop c (say) from this list of variables and only retain ϱ, T. Alternatively we may consider ϱ and η as functions of p and T which traditionally is the preferred choice of variables.

Thus we write

$$\frac{\partial^2 \varrho}{\partial t^2} = \frac{\partial \varrho}{\partial T}\frac{\partial^2 T}{\partial t^2} + \frac{\partial \varrho}{\partial p}\frac{\partial^2 p}{\partial t^2},$$

$$\frac{\partial^2 \eta}{\partial t^2} = \frac{\partial \eta}{\partial T}\frac{\partial^2 T}{\partial t^2} + \frac{\partial \eta}{\partial p}\frac{\partial^2 p}{\partial t^2}$$

and obtain from (4.10)

$$\begin{gathered} \left(\frac{\partial^2 p}{\partial t^2} - \frac{\partial p}{\partial \varrho}\right)_T \Delta p + \left(\frac{\partial p}{\partial \varrho}\right)_T \left(\frac{\partial \varrho}{\partial T}\right)_p \frac{\partial^2 T}{\partial t^2} = 0, \\ \left(\frac{\partial \eta}{\partial p}\right)_T \frac{\partial^2 p}{\partial t^2} + \frac{c_p}{T}\frac{\partial^2 T}{\partial t^2} - \eta^2 \frac{\varrho_1}{\varrho_2} \Delta T = 0, \end{gathered} \tag{4.11}$$

where $c_p \equiv T(\partial \eta / \partial T)$ is the specific heat.

Note that $\left(\frac{\partial \eta}{\partial p}\right)_T = -\frac{1}{\varrho}\left(\frac{\partial \varrho}{\partial T}\right)_p$ holds which is an integrability condition for $\varepsilon - T\eta - p/\varrho$ since the Gibbs equation may be written in the form $d\left(\varepsilon - T\eta + \frac{p}{\varrho}\right) = -\eta dT + \frac{1}{\varrho} dp + \mu dc$. Therefore the two equations (4.11) decouple if the thermal expansion $(\partial \varrho / \partial T)_p$ vanishes. In that case we obtain

$$\frac{\partial^2 p}{\partial t^2} - \left(\frac{\partial p}{\partial \varrho}\right) \Delta p = 0 \quad \text{and} \quad \frac{\partial^2 T}{\partial t^2} - \left(\frac{\varrho_1}{\varrho_2}\frac{T\eta^2}{c_p}\right) \Delta T = 0. \tag{4.12}$$

These are both hyperbolic equations which describe the propagation of waves with the speeds

$$V_1 = \sqrt{\left(\frac{\partial p}{\partial T}\right)_1} \quad \text{and} \quad V_2 = \sqrt{\frac{\varrho_1}{\varrho_2}\frac{T\eta^2}{c_p}}. \tag{4.13}$$

We call these the velocities of first and second sound, respectively.

If we cannot ignore the thermal expansion, we obtain one wave equ-

ation of fourth order instead of two equations of second order each. Indeed, by elimination of T (say) from the two equations (4.11) we get

$$\left(\frac{c_p}{T}-\left(\frac{\partial p}{\partial \varrho}\right)_T\left(\frac{\partial \varrho}{\partial p}\right)_T\left(\frac{\partial \eta}{\partial p}\right)_T\right)\frac{\partial^4 p}{\partial t^4}-$$
$$-\left(\left(\frac{\partial p}{\partial \varrho}\right)_T\frac{c_p}{T}+\eta^2\frac{\varrho_1}{\varrho_2}\right)\frac{\partial \Delta_p}{\partial t^2}+\eta^2\frac{\varrho_1}{\varrho_2}\left(\frac{\partial p}{\partial \varrho}\right)_T\Delta\Delta p=0,$$

or with $\left(\frac{\partial p}{\partial \varrho}\right)_T\left(\frac{\partial \varrho}{\partial T}\right)_p=-\left(\frac{\partial p}{\partial T}\right)_\varrho$ and $\left(\frac{\partial \eta}{\partial p}\right)_T=\frac{1}{\varrho_2}\left(\frac{\partial \varrho}{\partial T}\right)_p$ so that

$$\frac{c_p}{T}+\frac{1}{\varrho_2}\left(\frac{\partial p}{\partial T}\right)_\varrho\left(\frac{\partial \varrho}{\partial T}\right)_p=\frac{c_v}{T}$$

holds

$$\frac{\partial^4 p}{\partial t^4}=\left(\frac{c_p}{c_v}\left(\frac{\partial p}{\partial \varrho}\right)_T+\frac{T\eta^2}{c_v}\frac{\varrho_1}{\varrho_2}\right)\frac{\partial^2 \Delta p}{\partial t^2}+\frac{T\eta^2}{c_v}\frac{\varrho_1}{\varrho_2}\left(\frac{\partial p}{\partial \varrho}\right)_T\Delta\Delta p=0. \tag{4.14}$$

The equation predicts the propagation of waves with the two speeds

$$V_\pm=\sqrt{\frac{1}{2}\left[\left(\frac{\partial \varrho}{\partial p}\right)_\eta+\frac{T\eta^2}{\varrho_v}\frac{\varrho_1}{\varrho_2}\right]\pm\sqrt{\frac{1}{4}\left[\left(\frac{\partial p}{\partial \varrho}\right)_\eta+\frac{T\eta^2}{c_v}\frac{\varrho_1}{\varrho_2}\right]^2-\frac{T\eta^2}{c_v}\frac{\varrho_1}{\varrho_2}\left(\frac{\partial p}{\partial \varrho}\right)_T}} \tag{4.15}$$

where $(\partial p/\partial \varrho)_\eta \equiv (c_p/c_v)(\partial p/\partial \varrho)_T$ is the adiabatic compressibility. In the case where $(d\varrho/\partial T)_p = 0$ holds, we have $c_p = c_v$ and therefore the adiabatic compressibility is equal to the isothermal compressibility and $V_\pm$ reduce to the two velocities $V_{1,2}$ of equations (4.14).

d. Amplitudes of first and second sound. Just like we have considered the amplitudes of longitudinal one-dimensional sinusoidal sound waves in the case of the non-reacting binary mixture, we shall do so here. Therefore we insert

$$\begin{aligned} p &= p_0+\bar{p}e^{i(\omega t-kx)},\\ v_1^1 &= \bar{v}^1 e^{i(\omega t-kx)},\\ v_1^2 &= \bar{v}^2 e^{i(\omega t-kx)},\\ T &= T_0+\bar{T}e^{i(\omega t-kx)}, \end{aligned} \tag{4.16}$$

into the Landau linear equations $(4.5)_{1,2}$ and (4.9) and obtain

$$\begin{aligned} &\left(\frac{\partial \varrho}{\partial T}\right)_p u\bar{T}+\left(\frac{\partial \varrho}{\partial p}\right)_T u\bar{p}-\varrho_1\bar{v}^1-\varrho_2\bar{v}^2=0,\\ &-\bar{p}+u\varrho_1\bar{v}^1+u\varrho_2\bar{v}^2=0,\\ &-\eta\bar{T}-u\frac{\varrho_2}{\varrho}\bar{v}^1+u\frac{\varrho_2}{\varrho}\bar{v}^2=0,\\ &\frac{c_p}{T}u\bar{T}+\frac{1}{\varrho^2}\left(\frac{\partial \varrho}{\partial T}\right)_p\bar{p}+\eta\frac{\varrho_1}{\varrho}\bar{v}^1+\eta\frac{\varrho_1}{\varrho}\bar{v}^2=0. \end{aligned} \tag{4.17}$$

where $u = \omega/k$.

We eliminate $\bar{T}$ and $\bar{p}$ and obtain

$$\left[\left(\frac{T}{c_p}\frac{\varrho_1}{\varrho_2}\left(\frac{\partial\varrho}{\partial T}\right)_p-\frac{\varrho_2}{\varrho}\right)u^2+\frac{\eta^2}{c_p}\frac{T\varrho_1}{\varrho}\right]\bar{v}_1+$$
$$+\left[\left(\frac{\eta T}{c_p}\frac{\varrho_2}{\varrho^2}\left(\frac{\partial\varrho}{\partial T}\right)+\frac{\varrho_2}{\varrho}\right)u^2-\frac{\eta^2}{c_p}\frac{T\varrho_1}{\varrho}\right]\bar{v}_2=0,$$
$$\left[\left(\left(\varrho_1\frac{\partial\varrho}{\partial p}\right)_T-\frac{1}{\eta}\frac{\varrho_2}{\varrho}\left(\frac{\partial\varrho}{\partial T}\right)_p\right)u^2-\varrho_1\right]\bar{v}_1+$$
$$+\left[\left(\varrho_2\left(\frac{\partial\varrho}{\partial p}\right)_T+\frac{1}{\eta}\frac{\varrho_2}{\varrho}\left(\frac{\partial\varrho}{\partial T}\right)_p\right)u^2-\varrho_2\right]\bar{v}_2=0.$$

Again we restrict the attention to the case where the first and second sound are uncoupled, i.e. the case $(\partial\varrho/\partial T)_p=0$ and obtain

$$\left(\eta^2\frac{T}{c_p}\varrho_1-\varrho_2u^2\right)(\bar{v}_1-\bar{v}_2)=0,\quad\text{and}$$
$$\left(\left(\frac{\partial\varrho}{\partial p}\right)_T u^2-1\right)(\varrho_1\bar{v}_1+\varrho_2\bar{v}_2)=0. \tag{4.18}$$

These equations have non-trivial solutions only if

$$u^2=V_1^2\quad\text{or}\quad u^2=V_2^2,$$

where $V_{1,2}$ are the velocities (4.13) of the first and second sound. From (4.18) we conclude that a wave propagating with V_1^2 has $V_1=V_2$ while a wave propagating with V_2^2 has $\varrho_1\bar{v}_1+\varrho_2\bar{v}_2=0$.

We thus see that in a first sound wave the two constituents move with the same speed, i.e., the mixture moves as a whole and there is no relative motion. On the other hand, in a second sound wave the mixture is at rest and the constituents are in relative motion. Also from (4.17) it is clear that $\bar{p}=0$ in a second sound wave and that $\bar{T}$ is zero in a first sound wave.

These considerations have given rise to the expresion that the first sound is a pressure wave while the second sound is a temperature wave. Of course, if there is some thermal expansion, both sounds are connected both with pressure and temperature waves, even though, for small values of $(\partial\varrho/\partial T)_p$, one will have a much smaller amplitude than the other.

e. Liquid helium in rotation.

α. *Vortex lines.* Of all the peculiar properties of liquid helium the most extraordinary one is the manner in which the superfluid achieves a rigid rotation. Indeed, Landau when he derived the equation governing liquid helium suggested that curl $\mathbf{v}_s=0$ holds always, so that the superfluid could not possibly be put into a rigid rotation.

As far as I can determine the reason for the assumption curl $\mathbf{v}_s=0$ was

that Landau believed both in the momentum balance $(4.3)_3$ with the constitutive equations (4.4) and in his equation $(4.5)_3$ which he writes as

$$\frac{\partial v_i^s}{\partial t} + \frac{\partial\left(\mu_1 + \frac{1}{2}v_s^2\right)}{\partial x_i} = 0.\text{(}^8\text{)} \tag{4.19}$$

In fact the two equations can be brought into agreement only, if curl $\mathbf{v}_s = 0$.

However, it is now known that the superfluid can rotate. This was found out when a vessel with liquid helium was set into rotation, because the shape of the free surface was clear evidence that both the normal fluid and the superfluid were rotating rigidly.

Still, even after this was known, the idea of the superfluid always having curl $\mathbf{v}_s = 0$ was not given up. It was saved by an originally unlikely hypothetical construction which, however, has later been confirmed.

The idea is that the superfluid forms a great number of localized vortex lines with a quantized vortex strength and that outside these vortex lines the fluid is in irrotational motion. This is indeed possible, but it requires that the velocity $\mathbf{v}^s$ falls off hyperbolically with the distance from the vortex line, because curl $\mathbf{v}_s = 0$ rads

$$\left(\frac{\partial v_z}{\partial \varrho} - \frac{\partial v_\varphi}{\partial z}; \frac{\partial v_r}{\partial z} - \frac{\partial v_z}{\partial r}; \frac{\partial v_\varphi}{\partial r} - \frac{\partial v_r}{\partial \varphi}\right) = 0$$

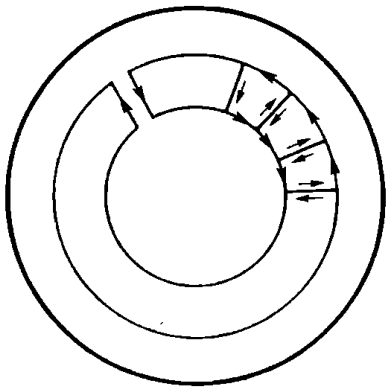
in cylinder coordinates where $(v_r, v_\varphi, v_z) = (\dot{r}, r^2\dot{\varphi}, \dot{z})$. We assume that around the vortex line in z-direction we have $\dot{r} = 0$, $\dot{\varphi} = \dot{\varphi}(r)$, $\dot{z} = 0$ and obtain $\dot{\varphi} = C/r^2$ so that the physical component of the velocity is $v\langle\varphi\rangle = C/r$. The vortex strength $\oint v\langle\varphi\rangle r d\varphi$ is an integer multiple of h/m where h is Planck's constant and m is the mass of a helium atom. For certain reasons which do not interest us here $\oint v\langle\varphi\rangle r d\varphi$ is simple equal to h/m, so that we have $C = \hbar/m$ with $\hbar = h/2\pi$.

The whole rotating vessel is supposed to be filled densely with such vortex lines and thus the viewer from above would see a picture like in the figure. With all these complicated vortex flows in the superfluid of the vessel one should think that no order can appear in the long range, and yet that is the case, because all the superposed vortex flows imitate a rigid rotation. This is seen as follows:

We calculate the circulation $\oint \mathbf{v}d\mathbf{l}$ along the indicated path surrounding a circular ring and this is obviously equal to $2\pi r dr n h/m_1$, where n is the density of vortex lines of the dimension $\left[\frac{1}{\text{cm}^2}\right]$:

$$\oint \mathbf{v}d\mathbf{l} = 2\pi r dr n \frac{h}{m}.$$

(8) Note that in $(4.5)_3$ $\partial p/\partial x_i$ can be replaced by $\varrho_1(\partial\mu^1/\partial x)$ as was shown on p. 581 Landau has the term $\partial(v_s^2/2)/\partial x_s^2$ which I have neglected in (4.5), because that equation was linearized. Of course, I have also neglected the term $\mathbf{v}_s \times \text{curl}\, \mathbf{v}_s$.



Hence follows, since v is only a function of r

$$v(r+dr)\,2\pi(r+dr)-v(r)\,2\pi r = 2\pi r dr h\frac{h}{m},$$

$$\left(\frac{dv}{dr}r+v\right)2\pi = 2\pi n\frac{h}{m}r, \tag{4.20}$$

$$v(r) = n\frac{h}{2m}r,$$

provided that n is constant over r. This is indeed the velocity field of a rigid rotation with the angular velocity $\Omega = nh/2m$.

We calculate the energy E associated with the rotational motion of one vortex of length Lwhose empty core has the radius a while its exterior radius is b.

$$E = \int_a^b\int_0^l \frac{\varrho_s}{2}(\langle\varrho\rangle)^2\,2\pi r dr dh, \qquad E = \pi l\frac{\hbar^2}{m^2}\varrho_s \ln\frac{f}{u}.$$

If there are n vortices per unit area, then we have $n\pi b^2 = 1$ and thus

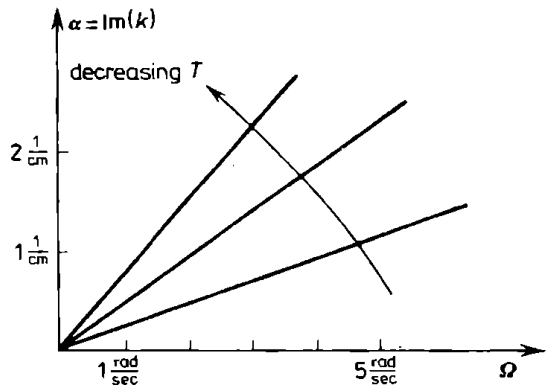
$$E = \pi L\frac{h^2}{m^2}\varrho_s \ln\frac{1}{\sqrt{\pi u^2}\sqrt{n}}.$$

The energy density due to the vortex l is therefore

$$\varrho\varepsilon_n = -\frac{\pi}{2}\frac{h^2}{m^2}\varrho_s \ln. \tag{4.21}$$

β. *Attenuation of second sound in rotation.* As we have seen in the previous sections for the first and the second were undamped under the assumptions here, i.e., essentially if we ignore viscosity and the inductivity. Experiments show that these assumptions are good for quite a big range of frequency.

However, now we are dealing with helium in rotation and here experiments show that the second sound is damped. The damping is independent of the frequency of the wave, but it grows linearly with the angular velocity Ω of rotation. The figure gives the typical behaviour.



In view of the existence of vortex lines in rotations it is nearly imperative to assume that the damping in rotation is due to the vortex lines, and indeed, Hall and Vinen have suggested that the damping is due to frictional forces between the normal component of liquid helium and the vortex lines.

The idea of Hall & Vinen makes sense on two counts: Firstly, it provides an immediate quantative understanding of the damping on the rotational velocity, because we have seen in (4.20) that Ω determines the number of vortex lines and obviously, the more there are the bigger is the dynamic interaction with the normal component. Secondly, in the case that the axis of rotation is perpendicular to the relative velocity of the constituents, Hall & Vinen's interaction force is in the direction of that relative velocity. Thus it is a frictional force much like $M_v^{11} V_i$ that we have considered in the previous chapters and that force gave rise to a damping of sinusoidal waves that was independent of frequency.

γ. *A field theory for rotating liquid helium.* ([9]) Despite the success of the theory of Hall & Vinen it leaves something to be desired. Indeed, in that theory the vortex lines are either there or not; they are "applied from the outside", so to speak much like a magnetic field would be applied from the outside. But there is no governing equation for the vortex field which would indicate how the vortices change density and direction.

I proceed to propose such an equation. It seems that the easiest propositions one can think is in this context is a conservation law for the vortex flux across a material surface. Let w_i be an axial vector in the

([9]) This and the following section give an account of research going on by W. Dreyer and I. Müller and the results are tentative.

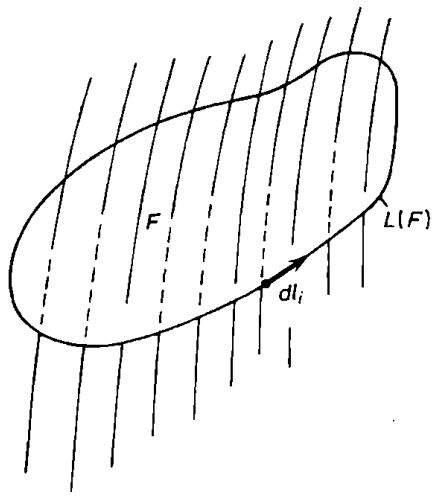
direction of the vortex lines and let $|w| = u$ be the number of vortex lines intersecting a unit area at right angles. The integral

$$\iint_{\pm} w_i \, da_i$$

is then called the *vortex flux accross F*, and we say that the vortex flux is *conserved* if on a material surface F it satisfies the conservation law

$$\frac{d}{dt}\iint_F w_i \, du_i + \oint_{L(F)} F_i \, dl_i = 0. \tag{4.22}$$

$L(F)$ is the line around F and F_i may be called the *flow of* $\mathbf{w}$. By this law the vortex flux through F changes according to the flow F_i across the boundary



$L(F)$ of F. There is no production of vortex flux inside F and that is why (4.22) is called a *conservation law*.

The transport theorem for material surfaces allows us to rewrite (4.22) in the form

$$\iint_F \left(\frac{\partial w_i}{\partial t} + \mathrm{curl}_i (\mathbf{w} \cdot \mathbf{v} + \mathbf{F}) \right) da_i = 0,$$

provided there are no singular surfaces intersecting F. Since this conservation law must hold for all F, we obtain its local form viz.

$$\frac{\partial w_i}{\partial t} + \mathrm{curl}_i (\mathbf{w} \cdot \mathbf{v} + \mathbf{F}) = 0. \tag{4.23}$$

Now we consider it the objective of a theory of liquid helium in rotation to determine the fields

$$\varrho, \varrho_s, v_i, v_i^s, T \text{ and } w_i, \tag{4.24}$$

and we propose to derive the necessary field equations from the equations of balance

$$
\begin{aligned}
&\frac{\partial \varrho}{\partial t}+\frac{\partial}{\partial x_j}(\varrho v_j)=0,\\
&\frac{\partial \varrho_s}{\partial t}+\frac{\partial}{\partial x_j}(\varrho_s v_j^s)=\tau_s,\\
&\frac{\partial \varrho v_i}{\partial t}+\frac{\partial}{\partial x_j}(\varrho v_i v_j-t_{ij})=2R_{ik}(v_k-\dot{b}_k)-R_{ik}^2(x_k-b_k)+\dot{R}_{ik}(x_k-b_k)+\ddot{b}_i,\\
&\frac{\partial \varrho_s v_i^s}{\partial t}+\frac{\partial}{\partial x_j}(\varrho_s v_i^s v_j-t_{ij}^s)\\
&\qquad\qquad =m_i^s-2\dot{R}_{ik}(v_k^s-\dot{b}_k)-R_{ik}^2(x_k-b_k)+\dot{R}_{ik}(x_k-b_k)\ddot{b}_i,\\
&\frac{\partial \varrho\varepsilon}{\partial t}+\frac{\partial}{\partial x_j}(\varrho\varepsilon v_j+q_j)-t_{ij}\frac{w_i}{\partial x_j},\\
&\frac{\partial w_i}{\partial t}+\mathrm{rot}_i(\mathbf{w}\times\mathbf{v}+\mathbf{F})=0.
\end{aligned}
\tag{4.25}
$$

These are the equations of balance of partial masses and momenta and of internal energy as well as the conservation law for the vortex flux. The equations of balance $(4.25)_{1,5}$ are the same ones as before except that now we are dealing with a rotating body and it is appropriate therefore to choose a non-inertial frame of reference so that the inertial forces appear in the equations of balance of momenta.

Of course, we need constitutive equations now in order to convert equations (4.25) into field equations and we shall take it for granted here in this short first presentation, that the constitutive equations do not differ in their form from (4.4) for non-rotating helium. There is only one exception from this which will be explained below and, of course, F_i needs a constitutive equation. In particular, we shall again assume that $\mu = 0$, so that we may disregard $(4.25)_2$ as a field equation.

Moreover, to simplify things we shall assume that Ω_{ik} does not depend on time and that $b_i \equiv 0$, Ω_{ik} will be so small that the effect of the centrifugal force may be neglected.

The only constitutive equation that must definitely be altered for the rotation is the one for ε, because we have seen in (4.21) that the vortices contribute to the energy. Thus

$$
\varrho\varepsilon=\sum_{\alpha=1}^{2}\varrho_\alpha\varepsilon_\alpha(\varrho_{\alpha 1}\,T)-\frac{\pi\hbar^2}{2m^2}\varrho_s\sqrt{W^2}\,\ln(\pi a^2\sqrt{\omega^2}).
\tag{4.26}
$$

Also we must formulate a constitutive equation for F_i and we take the simplest possible one, viz.

$$
F_i=\alpha V_i,
\tag{4.27}
$$

which ensure, despite its simplicity, that the number of vortex lines in a rotating vessel changes, if the field of relative velocity of the two constituents is that of a shearing motion; this is expected to be the case when we increase the rate of the vessel, because supposedly the normal component will rapidly adjust its velocity accordingly, while the supercomponent will follow later.

δ. *A proposition for the description of the damping of second sound in rotating liquid helium.* Under the conditions described in the last section and if we linearize we come back to Landau's equations with just one addition if we restrict the attention to processes with $v \equiv 0$ and $p \equiv \text{const}$, that are appropriate for the description of the second sound. That addition is due to the dependence of ε on w. Remembering that $\varrho_s = \varrho_s(p, T)$ and p is constant, we get

$$\varrho \frac{\partial \varepsilon}{\partial t} = \varrho c \frac{\partial T}{\partial t} - \underbrace{\frac{a\hbar^2}{2m^2} \varrho_s (1 + \ln au^2 + \ln \sqrt{w^2})}_{\equiv b \equiv \varrho \frac{\partial \varepsilon}{\partial \sqrt{w^2}}} \frac{w_i}{\sqrt{w_2}} \frac{\partial w_i}{\partial t}$$

The first two of Landau's equations $(4.5)_{1,2}$ and (4.9) are identically satisfied in the case of the second sound, and the last two read

$$\begin{aligned} &\frac{\partial V_i}{\partial t} - \frac{\varrho}{\varrho_n} \eta \frac{\partial T}{\partial x_i} = 2\Omega_{ij} V_j, \\ &c \frac{\partial T}{\partial t} + b \frac{w_k}{\sqrt{w^2}} \frac{\partial w_k}{\partial t} - \frac{\varrho_s}{\varrho} T\eta \frac{\partial V_i}{\partial x_i} = 0, \end{aligned} \tag{4.28}$$

and in addition we have $(4.25)_6$ with $v_i \equiv 0$ and with the constitutive equation $F_i = \alpha V_i$ from (4.26)

$$\frac{\partial w_i}{\partial t} + \alpha \operatorname{rot} V_i = 0. \tag{4.29}$$

We investigate small sinusoidal waves that propagate into 1-direction

$$\begin{aligned} w_i &= \frac{2m}{h} \Omega \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} + \bar{w}_i e^{i(wt - hx)}, \\ V_i &= \qquad\qquad \bar{V}_i e^{i(wt - hx)}, \\ T &= T_0 \qquad\quad + \bar{T} e^{i(wt - hx)}. \end{aligned} \tag{4.30}$$

Insertion into the equations (4.28), (4.29) with $\Omega_{ij} = \begin{bmatrix} 0 & \Omega & 0 \\ -\Omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ leads to

the results $V_3 = 0$ and $w_1 = w_2 = 0$ and for the remining amplitudes it provides a homogeneous algebraic systems of 4 equations, viz.

$$
\begin{aligned}
&\tilde{u}V_1 + \frac{i}{h}2\Omega V_2 + \frac{\varrho}{\varrho_n}\eta T &&= 0,\\
-\frac{i}{k}2\Omega V_1 \quad &+ u\bar{V}_2 &&= 0,\\
\frac{\varrho_s}{\varrho}T\eta\bar{V}_1 \quad &+ cu\bar{T} + buw_3 &&= 0,\\
-\alpha\bar{V}_2 \quad &+ uW_3 &&= 0,
\end{aligned}
\tag{4.31}
$$

where $u = w/k$. It is immediately obvious that the wave is no longer longitudinal, but contains a transverse component, because of the influence of the Coriolis force.

Setting the determinant of system (4.31) equal to zero gives us the dispersion relation

$$\frac{1}{u^2}\left(\frac{\varrho_s}{\varrho_n}\eta^2 T + i2\alpha b\eta\frac{\Omega}{w}\right) = c,$$

where a term (Ω^2/w) was neglected. Thus we obtain

$$\frac{k}{w} = \frac{1}{\sqrt{(\varrho_s/\varrho_p)(T\eta^2/c)}}\left(1 + i\frac{\alpha b}{(\varrho_s/\varrho_n)\,T\eta}\frac{\Omega}{w}\right). \tag{4.32}$$

For $\Omega = 0$ this is real, i.e. there is no damping and the phase speed w/k is equal to the speed $\sqrt{(\varrho_s/\varrho_n)(T\eta^2/c)}$ of second sound. But for $\Omega \neq 0$ there is an attenuation

$$\alpha = \operatorname{Im} k = \frac{1}{\sqrt{(\varrho_s/\varrho_n)(T\eta^2/c)}}\frac{\alpha b}{(\varrho_s/\varrho_n)\,T\eta}\Omega \tag{4.33}$$

which is proportional to Ω and independent of w just as it is observed.

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