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Non-relativistic Thermodynamics IV (Sign Questions and Onsager Symmetry Relations in Phenomenological Theory)

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(13. VIII. 63)

Abstract. The signs of thermodynamical state functions are defined in terms of the sign of absolute temperature T. 1) The 2nd Law's principle of evolution determines the signs of the (symmetrised) phenomenological coefficients $L_{(\alpha\beta)}$. 2) The 2nd Law's principle of (cinetic) equilibrium determines the signs of the remaining state functions (mass densities of the chemical components A in a C(>1)-component fluid, its elastic modulus, and other state functions appearing in the coupled linearised equations of motion). These sign conditions show that the solutions of these equations are damped waves existing only in the future. It is remarkable, that the phenomenological coefficients satisfy Onsager's symmetry relation $L_{AB} = L_{BA}$ for the diffusion of substances $AB \dots = 12 \dots C$, if both principles are applied.

§ 1. Introduction and Conclusion

The aim of this article, in which the author wishes to express his admiration to Prof. W. Heitler's work, is twofold: It is a complement to a previous paper on the questions of sign of certain local thermodynamical state functions $f[s ...] = f(\vec{x} t)$ in r. (= relativistic) phenomenological theory of a one component fluid III⁴). We investigate the analogous questions for the n.r. (= non-relativistic) case, postulating Galilei-covariance, for a fluid composed of C chemical components, numbered by AB... = 12...C. The symbols AB... are also used to denote the unites of mass AB mass of the mole of AB. We deduce a the symmetry condition on the Onsager phenomenological coefficients AB defined as linear relations between the densities of conduction-(diffusion-) currents AB defined as linear relations between the densities of conduction-(diffusion-) currents AB defined as linear relations denote the unites of conduction-(diffusion-) currents AB defined as linear relations between the densities of conduction-(diffusion-) currents AB defined as linear relations denote the unites of conduction-(diffusion-) currents AB defined as linear relations between the densities of conduction-(diffusion-) currents AB defined as linear relations denote the unites of conduction-(diffusion-) currents AB defined as linear relations denote the unites of conduction-(diffusion-) currents AB defined as linear relations denoted the unites of conduction-(diffusion-) currents AB defined as linear relations denoted the unites of conduction-(diffusion-) currents AB defined as linear relations denoted the unites of conduction-(diffusion-) currents AB defined as linear relations denoted the unites of conduction-(diffusion-) currents AB defined as linear relations denoted the unites of conduction-(diffusion-) currents AB defined as linear relations denoted the unites of conduction denoted the unites of conduction density densi

$$\overrightarrow{j}_S = -L_{SS} \overrightarrow{\text{grad}} T - \Sigma_B L_{SB} \overrightarrow{\text{grad}} \mu_B,$$
(1.1_S)

$$\overrightarrow{j}_A = -L_{AS} \overrightarrow{\operatorname{grad}} T - \Sigma_B L_{AB} \overrightarrow{\operatorname{grad}} \mu_B.$$
 (1.1_A)

Among the local state variables $s(\vec{x} t)$ and $n_A(\vec{x} t)$ (densities of entropy S and of quantity N_A of component A) figures, in the non static case the d(=3) velocity components of the fluid $v^i(\vec{x} t)$ ($\vec{v} = \{v^i\}$; $\vec{x} = \{x^i\}$; $i k \ldots = 12 \ldots d$; d = 3). In order

^{*)} T and μ_A are the local absolute temperature and the local chemical potential of component A.

to avoid additional local state variables, $\vec{v}(\vec{x})$ has to be defined as the (local) velocity of the centre of mass in a volume element $dV(\vec{x}) = \mathfrak{g} \ dx^1 \ dx^2 \dots dx^{d*}$).

This implies a *first restriction* (see (2.27)) on the L_{AB} 's.

$$\Sigma_A A \overrightarrow{j}_A (\overrightarrow{x} t) = 0 , \qquad (1.2)$$

$$\Sigma_A A L_{AB}(\vec{x} t) = 0.$$
 (1.3)

From the 2nd law (principle of evolution: $\dot{S}(t) \geq 0$ for a closed system) follows that the coefficients in (1.1)

$$\begin{cases}
T^{-1} L_{SS}, & T^{-1} L_{(SB)} \\
T^{-1} L_{(AS)}, & T^{-1} L_{(AB)}
\end{cases} (\vec{x} t) \ge 0$$
(1.4)***

forms a non-negative quadratic form.

The 2nd law's principle of equilibrium (S = maximum, for a closed system in cinetic equilibrium) leads to a relation symmetric to (1.3)

$$\Sigma_B L_{AB}(\vec{x} t) B = 0.$$
 (1.5)

In phenomenological theory, the masses $A \ B \dots C$ are arbitrary constante. Therefore, the Onsager relations

$$L_{AB}(\vec{x}\ t) = L_{BA}(...) = L_{(AB)}(\vec{x}\ t)$$
 (1.6)**)

follow from phenomenological theory.

(The Onsager relations are $L_{\alpha\beta} = L_{\beta\alpha} = L_{(\alpha\beta)}$ ***) (if no magnetic field is present) for all phenomenological coefficients, relating «thermodynamical currents» J_{α} to «thermodynamical forces» X_{α} ($J_{\alpha} = \Sigma_{\beta} L_{\alpha\beta} X_{\beta}$). They follow only from statistical thermodynamics (see 1) 2) 3)). However, the Onsager relations for diffusion of substance are already consequences of phenomenological theory.

Further consequences of the principle of evolution apply to the transversal and longitudinal viscosities η and ξ

$$(T^{-1} \eta) (\vec{x} t) \ge 0; \quad (T^{-1} \xi) (\vec{x} t) \ge 0$$
 (1.7)

and to the bilinear form formed from longitudinal viscosity $\xi = d^{-2} L_{00}$ and the Onsager coefficients of local reaction rates L_{0a} , L_{a0} and L_{ab} referring to the r possible chemical reactions $ab \dots = 12 \dots r$ given by the stochiometric coefficients v_{aA} (= pos. and neg. integers):

$$\boxed{\Sigma_A \, \nu_{aA} \, A = 0 \,,} \tag{1.8}$$

^{*)} \mathfrak{g} is a constant scalar density (= | det $(g_{..})$ |, if a metric g_{ik} is assumed (see § 2)).

^{**)} From (1.3) and (1.5) follows, for arbitrary mass values $AB \dots C$: $L_{AB} = \lambda L_{BA}$. This can be seen by the following argument: Given the L_{AB} 's, (1.3) determines the *unknown* A's up to a common factor λ_1 ($A \rightarrow \lambda_1 A$, $B \rightarrow \lambda_1 B$, ...). The A's (or B's) must also satisfy (1.5). Therefore we must have $L_{AB} = \lambda_2 L_{BA}$. Applied to L_{AA} , λ_2 must be = 1. Thus (1.6) follows.

^{***)} Indices in round brackets (A B), (i k), ... imply symmetry. Square brackets [A B], [ik], ... signify antisymmetry.

$$\begin{cases}
T^{-1} L_{00}, & T^{-1} L_{(0b)} \\
T^{-1} L_{(a0)}, & T^{-1} L_{(ab)}
\end{cases} (\vec{x} t) \ge 0.$$
(1.9)***

(The index o applies to the longitudinal viscosity).

The principle of equilibrium (fluid with constant translational and angular velocity) requires conditions on mass density m and metric g_{ik}

$$\{(T^{-1} m) (\vec{x} t) g_{ik}\} = \{(T^{-1} \Sigma_A A n_A (\vec{x} t) g_{ik}\} \ge 0, \qquad (1.10)$$

on the elastic modulus

$$a[s...n_A...] = (s^2 u_{ss} + 2 s \Sigma_A n_A u_{sn_A} + \Sigma_A \Sigma_B n_A n_B u_{n_A n_B}),$$
 (1.11)*)

$$(T^{-1} a) (\dot{x} t) \ge 0, (1.12)$$

on the heat capucity per unit volume c

$$c^{-1}(\vec{x}\,t) = (T^{-1}\,T_s)[s\,\ldots\,n_A\,\ldots] \ge 0 \tag{1.13}*)$$

and on other bilinear forms (see (3.12)) of local state variables.

There is no loss of generality, if the *metric is assumed positive* **) (1.10), and the A's are assumed positive masses. Thus mass, elastic modulus, viscosities and all other state functions (the $L_{\alpha\beta}$'s) have a well defined sign in terms of T. This leads to coupled equations of motion for

$$\partial_t s(\vec{x}\,t)$$
, $\partial_t n_A(\vec{x}\,t)$ and $\partial_t v^i(\vec{x}\,t)$ (see III⁴)⁵)),

which lead, in the linear approximation, to damped waves, which exist only for $t \ge 0$ (if the initial state is given for t = 0).

We apologize for deducing several well known results (see 2)). However, making extensive use of *Galilei-covariance*, we prepare the way for an article on the r. C (>1)-component fluid, based on *Lorentz-covariance*, where several difficulties occur, which we failed to see, when writing I^4).

§ 2. The Equations of Motion (Continuity Eqs. Following from the 1st and 2nd Law)

We denote by V the volume, the interior part of space \vec{x} inside the *time dependent* closed surface $C(\vec{y}t) = 0$ and by $d\sigma_i(\vec{y}t)$ the covariant surface element $(= \pm \mathfrak{g} dy^1 \dots dy^{i-1} dy^{i+1} \dots dy^d)$.

A capital letter F(t) is an extensive quantity (with the exception of $T(\vec{x} t)$) and $f(\vec{x} t) = f[s(\vec{x} t), ...]$ the corresponding density (= local state function). The time variation of $F(t) = \int_{V} (dV f)(\vec{x} t)$ is:

$$\dot{F}(t) = \int\limits_{V} (dV \ \partial_{t} f) \ (\vec{x} \ t) + \oint\limits_{V} (d\sigma_{i} \ v^{i} \ f) \ (\vec{y} \ t) , \qquad (2.1)$$

***) See eq (2.46).

^{*)} $u_s[s \dots n_A \dots] = \partial u[s \dots n_A \dots]/\partial s; u_{ss} = \dots; u_{sn_A}[\dots] = \partial^2 u[\dots]/\partial s \partial n_A; u_{n_A n_B} = \dots$

^{**)} As g_{ik} is constant, we may use euclidian metric $g_{ik} = \delta_k^i$.

 $v^i(\vec{y}\,t)$ is the velocity of the surface $C(\vec{y}\,t)=0$. The cause of this variation is due 1) to a source density $\varrho_F(\vec{x}\,t)$ and 2) to an $influx-j_F^i(\vec{y}\,t)$ through $C(\ldots)=0$:

$$\dot{F}(t) = \int\limits_{V} (dV \,\varrho_F) \,(\vec{x} \,t) - \oint\limits_{V} (d\sigma_i \,j_F^i) \,(\vec{y} \,t) \,. \tag{2.2}$$

Assuming these two relations for all possible C(...) = 0's Gauss's theorem leads to the inhomogenous continuity eq.:

$$(\partial_t f + \partial_k (v^k f + j_F^k)) (\vec{x} t) = \varrho_F (\vec{x} t).$$
 (2.3)

The current density of F is separated in a convective $v^k f$ and a conductive (= diffusion) part j_F^k .

The 1st law expresses the conservation of energy H, momentum Π_i and of the C quantities of substance N_A . In the continuity equation for H, we separate the conductive flow in heat flow q^i , flow of work a^i and flow of chemical energy c^i

$$(\partial_t h + \partial_k (v^k h + q^k + a^k + c^k)) (\vec{x} t) = \varrho_H (\vec{x} t) = (v^i k_i) (\vec{x} t), \qquad (2.9H)$$

where $k_i(\vec{x} t)$ is the density of (external) volume force. For Π_i , we write $j_{H_i}^k = -\tau^k_i$ (= -stress tensor)

$$\left| \left(\partial_t \pi_i + \partial_k (v^k \pi_i - \tau^k_i) \right) (\vec{x} t) = k_i (\vec{x} t) \right|$$
 (2.9 Π_i)

and for N_A

$$(\partial_t n_A + \partial_k (v^k n_A + j_A^k)) (\ddot{x} t) = \varrho_A (\ddot{x} t) = \Sigma_a \nu_{aA} \omega_a (\ddot{x} t), \qquad (2.9N_A)$$

where ω_a (\vec{x} t) is the local reaction rate of the a^{th} reaction (1.7). (2.9 Π_i) is connected with the homogeneity of space $\{x^i\}$. If space is isotropic (metric $x_i = g_{ik} \, x^k$, $g_{ik} = \text{const.}$), the 1st law contains the conservation of angular momentum $M_{ik} = M_{[ik]} = \int dV \, (x_i \, \pi_k - x_k \, \pi_i)$:

$$(\partial_{t}(x_{i}\pi_{k} - x_{k}\pi_{i}) + \partial_{l}(v^{l}(x_{i}\pi_{k} - x_{k}\pi_{i}) - (x_{i}\tau^{l}_{k} - x_{k}\tau^{l}_{i})))(\vec{x}t) = (x_{i}k_{k} - x_{k}k_{i})(\vec{x}t).$$
(2.9 M_{ik})

 $(2.9\Pi_i)$ and $(2.9M_{ik})$ imply the symmetry $(\partial_i x^k = \delta_i^k)$

$$(v_i \pi_k - \tau_{ik}) (\hat{x} t) = (v_k \pi_i - \tau_{ki}) (\hat{x} t).$$
 (2.10)

The integral forms of the 1st law (2.2) are

$$\dot{H}(t) = P_{Q}(t) + P_{A}(t) + P_{C}(t)
= \left(-\oint_{V} (d\sigma_{i} q^{i}) (\vec{y} t) \right) + \left(\int_{V} (dV k_{i} v^{i}) (\vec{x} t) + \oint_{V} (d\sigma_{k} \tau^{k}_{i} v^{i}) (\vec{y} t) \right)
+ \left(-\oint_{V} (d\sigma_{i} c^{i}) (\vec{y} t) \right),$$
(2.11H)

$$\dot{\Pi}_{i}(t) = K_{i}(t) = \int\limits_{V} (dV \ k_{i}) \ (\vec{x} \ t) + \oint\limits_{V} (d\sigma_{k} \ \tau^{k}_{i}) \ (\vec{y} \ t) , \qquad (2.11\Pi_{i})$$

$$\dot{N}_{A}(t) = \int\limits_{V} (dV \,\varrho_{A}) \,(\vec{x} \,t) - \oint\limits_{V} (d\sigma_{i} \,j_{A}^{i}) \,(\vec{y} \,t) , \qquad (2.11N_{A})$$

$$\begin{split} \dot{M}_{ik}(t) &= D_{ik}(t) \;, \\ &= \int\limits_{V} \left(dV \; (x_i \; k_k - x_k \; k_i) \right) (\vec{x} \; t) + \oint\limits_{V} \left(d\sigma_l \; (y_i \; \tau^l_{\;k} - y_k \; \tau^l_{\;i}) \right) (\vec{y} \; t) \;, \end{split}$$

where P_Q etc. are the powers of heat Q, work A and chemical energy C. K_i and $D_{ik} = D_{[ik]}$ are the total force and its total momentum.

The 2nd law states the principle of evolution for the entropy S. In its equation of continuity $(\partial_t s + \partial_k (v^k s + j_S^k)) (\vec{x} t) = i (\vec{x} t) \ge 0, \qquad (2.12)$

the source density $i(\vec{x} t)$ (= density of irreversibility) is non negative. The integral form is

$$\dot{S}(t) = \dot{S}^{(interior)}(t) + \dot{S}^{(exterior)}(t) = \int\limits_{V} (dV \ i) \ (\vec{x} \ t) - \oint\limits_{V} (d\sigma_k \ j_S^k) \ (\vec{y} \ t) , \quad (2.13) *$$

with $\dot{S}^{(interior)} > 0$.

We add now Newton's axiom, defining mass density $m(\vec{x} t)$, in the form

$$\pi_i(\vec{x}\,t) = m(\vec{x}\,t)\,v_i(\vec{x}\,t)\,, \tag{2.14}$$

which implies the metric g_{ik} . The continuity equation $(2.9\Pi_i)$ takes the form

$$\left(\left(v_{i}\left(\partial_{t}m+\partial_{k}(v^{k}\,m)\right)+m\,\dot{v_{i}}-\partial_{k}\,\tau^{k}_{i}\right)\left(\vec{x}\,t\right)=k_{i}\left(\vec{x}\,t\right),\tag{2.15}$$

where \dot{v}_i is the substantial acceleration, defined as the substantial time derivative of any local function f(x t): $| \dot{f}(\vec{x} t) \equiv (\partial_t f + v^k \partial_k f)(\vec{x} t). |$ (2.16)

We remark that any continuity eq. (2.3) may be written as

$$(2.17)$$

$$(\dot{f} + f \partial_k v^k + \partial_k \dot{j}_F^k) (\dot{x} t) = \varrho_F (\dot{x} t).$$

We now turn to Galilei-covariance. The Galilei transformation

$$x^{i} = x^{i} - v_{0}^{i} t, \quad t = t + t_{0},$$
 (2.18)

(with constants v_0^i and t_0) defines Galilei-covariant tensors

$$f^{ik} \cdots_{lm \dots} (\dot{x}'t) = f^{ik} \cdots_{lm \dots} (x t).$$
 (2.19)

$$\dot{S}(t) \geqslant -\oint\limits_{\dot{V}} (d\sigma_i \ T^{-1} \ q^i) \ (\vec{y} \ t) \ . \tag{2.13*}$$

^{*)} On account of (2.39) we have

The velocity field $v^i(\vec{x}'t) = v^i(\vec{x}t) - v^i_0$ is not covariant. However v^i , $\partial_i v^k$ and $\partial_k v^k = \operatorname{div} \vec{v}$ are covariant. The same is true for $f^{ik} \cdots_{lm}$, defined by (2.16), if $f^{ik} \cdots_{lm}$ is Galilei-covariant. Thus, if τ^k_i and k_i in (2.15) are Galilei-covariant, the strong continuity eq. for mass $M = \int_{V}^{\infty} (dV m) (\vec{x} t)$ holds:

$$j_M^i = 0$$
, $\varrho_M = 0$, $\left(\partial_t m + \partial_k (v^k m)\right) (\vec{x} t) = 0$, (2.20)

$$\dot{M}(t) = 0, \qquad (2.21)$$

expressing the strong conservation of mass M. The equations of motion (2.20) and Newton's law

$$(m \ \vec{v_i}) \ (\vec{x} \ t) = (m \ (\partial_t v_i + v^k \ \partial_k v_i)) \ (\vec{x} \ t)$$

$$= (\partial_k \tau^k_i + k_i) \ (\vec{x} \ t)$$

$$(2.22)$$

replace $(2.9\Pi_i)$.

If we chose as independent local state variables, the d+1+C variables $\{v_i, s, n_A\}$ $(\vec{x}\ t)$, we have to satisfy the d+1+C+2 eqs. of motion: (2.22) for $\partial_t v_i$, (2.12) for $\partial_t s$, (2.9 N_A) for $\partial_t n_A$, (2.9H) for $\partial_t h$, and (2.20) for $\partial_t m$. This implies that m=m [... v_i ... s ... n_A ...] and h=h [... v_i ... s ... n_A ...] are given state functions: Their 2 eqs. of motion must be consequences of the d+1+C eqs. of motion for the independent variables $\partial_t v_i$, $\partial_t s$ and $\partial_t n_A$. Galilei-covariance for m reduces m to m [s ... n_A ...]. The 2 eqs. for $\partial_t m$ and $\partial_t h$ lead to 2 different expressions for the Galilei-covariant entropy source i (\vec{x} t). As the form i (\vec{x} t) resulting from $\partial_t m$ (2.20) can not be made non negative, a simple consideration leads to the result that the derivatives $\partial/\partial n_A$ of m:

$$m_{v^2}[...] = 0; \quad m_{n_A}[...n_A...] = A; \quad m_s[...] = 0,$$
 (2.23)

must be C constants: $A B \dots C$, the molar masses. Thus we have

$$m\left[\ldots n_{A}\ldots\right] = \Sigma_{A} A n_{A} \left(\vec{x} t\right). \tag{2.24}$$

No constant of integration can appear, on account of (2.20). However, $(2.9N_A)$ implies

$$\varrho_M = \Sigma_A A \varrho_A (\vec{x} t) = 0 , \qquad (2.25)$$

which combined with the 2nd eq. (2.9 N_A) leads to Lavoisier's law (1.8) stating the conservation of mass in every chemical reaction $ab \dots r^*$). The condition $\vec{j}_M = 0$ (2.20) implies

$$(\vec{v} \ m) \ (\vec{x} \ t) = \Sigma_A \ A \ (n_A \ \vec{v} + \vec{j_A}) \ (\vec{x} \ t) \equiv \Sigma_A \ A \ (n_A \ \vec{v_A}) \ (\vec{x} \ t) \ ,$$
 (2.27)

$$n_A \leftrightarrow j_A^{\alpha}(x)$$
; $x = \{x^{\alpha}\}$; $\alpha \beta \dots = 12 \dots n$; $n = d + 1$)

must be postulated. This is a further proof that Galilei-transformations are not the limit of Lorentz-transformations.

^{*)} Lavoisier's law is thus a consequence of Galilei-covariance in n.r. theory. It is interesting to note that no corresponding conservation law holds in r. theory (see III⁴)). In order to obtain correspondance, continuity eqs. for

where $\vec{v}_A(\vec{x}\,t)$ is the velocity of component A. (2.24) and (2.27) define $\vec{v}(\vec{x}\,t)$ as the velocity of the local centre of mass. (1.2) and (1.3) are its consequences.

We now consider $\partial_t h$ (2.9H), using the d+1+C eqs. of motion (2.22), (2.12) and (2.9 N_A):

$$\begin{split} \partial_{t}h &= h^{i} \; \partial_{t}v_{i} + h_{s} \; \partial_{t} \; s + h_{n_{A}} \; \partial_{t}n_{A} \; , \\ &= - \; \partial_{k}(v^{k} \; h + \not p \; v^{k} + h_{s} \; j_{S}^{k} + \Sigma_{A} \; h_{n_{A}} \; j_{A}^{k}) + h^{i} \; m^{-1} \; k_{i} \\ &+ v^{i} \; (s \; \partial_{i}h_{s} + \Sigma_{A} \; n_{A} \; \partial_{i}h_{n_{A}} - h^{k} \; \partial_{i}v_{k}) + h^{i} \; m^{-1} \; \partial_{k}\tau^{k}_{i} \\ &+ (h_{s} \; i + j_{S}^{i} \; \partial_{i}h_{s} + \Sigma_{A} \; j_{A}^{i} \; \partial_{i}h_{n_{A}} + \Sigma_{A} \; h_{n_{A}} \; \varrho_{A}) \; , \end{split}$$
 (2.28)

with the abreviations $h^i = (\partial h [\dots v_i \dots s \dots n_A \dots]/\partial v_i) (\vec{x} t)$ and

$$p[\dots v_i \dots s \dots n_A \dots] = (s h_s + \sum_A n_A h_{n_A} - h) (\vec{x} t).$$
 (2.29)

The 2nd member of (2.28) must be transformed in such a way as giving rise to the divergence $\partial_k(v^k h + \ldots)$ in (2.9H) plus the source term $\varrho_H = v^i k_i$. But, this 2nd term of (2.9H) appears only, if we identify in the 2nd term of (2.28) with ϱ_H :

$$(h^i \ m^{-1} = v^i) \ (\vec{x} \ t) \ , \tag{2.30}$$

from which results, by integration

$$h[\dots v_i \dots s \dots n_A \dots] = \frac{1}{2} m[\dots n_A \dots] v^2 + u[s \dots n_A \dots].$$
 (2.31)*)

The integration «constant» u [...] being the density of interior energy

$$U = \int\limits_{V} (dV \ u) \ (\vec{x} \ t) \ .$$

Furthermore (2.29) becomes the Galilei-invariant scalar pression

$$p[s...n_A...] = (s u_s + \Sigma_A n_A u_{n_A} - u) (\vec{x} t).$$
 (2.32)

The factor of v^i in the 3rd term is its gradiant

$$\partial_{i} p \left(\vec{x} t \right) = \left(s \ \partial_{i} h_{s} + \Sigma_{A} \ n_{A} \ \partial_{i} h_{n_{A}} - h^{k} \ \partial_{i} v_{k} \right) \left[\dots v_{i} \dots s \dots n_{A} \dots \right],
= \left(s \ \partial_{i} u_{s} + \Sigma_{A} \ n_{A} \ \partial_{i} u_{A} \right) \left[s \dots n_{A} \dots \right]$$
(2.33)

the second equality deriving from (2.31) and (2.23). It is function of the scalar state variables $[s \ldots n_A \ldots]$ and their 1st space derivatives $[\partial_i s, \ldots \partial_i n_A \ldots]$. Decomposing the stress tensor τ^{ik} in an elastic (e) and a frictional (f) part

$$\tau^{ik} = \tau^{ik(e)} + \tau^{ik(f)} = -g^{ik} p + \tau^{ik(f)}, \qquad (2.34)$$

$$\varSigma_A \, \tfrac{1}{2} \, A \, \, n_A \, \, v_A^2 \, = \, \tfrac{1}{2} \, m \, \, v^2 + \varSigma_A \, \, A \, \, n_A \, \, (\vec{v}_A - \vec{v}, \, \vec{v}) \, + \, \tfrac{1}{2} \, \varSigma_A \, \, A \, \, n_A \, \, |\, \vec{v}_A - \vec{v} \, |^2$$

(the 2nd term disappears on account of (2.27)), the Galilei-covariant last term (= $1/2 \sum A n_A^{-1} |\vec{j}_A|^2$) is missing. This is due to the fact, that we do not consider the \vec{j}_A 's (or \vec{v}_A 's) as being among the d+1+C state variables. Physically, it means neglecting the cinetic energy of diffusion (see 2)).

^{*)} It is remarkable that in the cinetic energy density term, which one would expect to have the form

the 2nd and 3rd term in (2.28) can, due to (2.30), be written as

$$v^{i} \left(\partial_{i} p + \partial_{k} \tau^{k}_{i} \right) = -\partial_{k} \left(-\tau^{k(f)}_{i} v^{i} \right) - v_{ik} \tau^{i k(f)}, \tag{2.35}$$

where

$$2 v_{ik} (\vec{x} t) = (\partial_i v_k + \partial_k v_i) (\vec{x} t) = 2 v_{(ik)}$$
 (2.36)

is the symmetric, Galilei-covariant, velocity gradient. Its appearence is due to the symmetry

$$au^{i\;k}= au^{(i\;k)}$$

resulting from conservation of angular momentum (2.10) and Newton's axiom (2.14). The first term of (2.35) may be combined with $p v^k$ in the divergence in (2.28) giving rise to the flow of work

$$a^k = -\tau^k{}_i v^i . \tag{2.38}$$

The other terms (aside from $h v^k$) in this divergence are the heat flow

$$q^{k} = h_{s} j_{S}^{k} = u_{s} j_{S}^{k} \equiv T j_{S}^{k}$$
 (2.39)

and the flow of chemical energy

$$c^{k} = \Sigma_{A} h_{n_{A}} j_{A}^{k} = \Sigma_{A} u_{n_{A}} j_{A}^{k} \equiv \Sigma_{A} \mu_{A} j_{A}^{k}, \qquad (2.40) *)$$

where the absolute temperature T and the C chemical potentials μ_A are the local state functions

$$T(\vec{x} t) = u_s[s \dots n_A \dots]; \quad \mu_A(\vec{x} t) = u_{n_A}[s \dots n_A \dots].$$
 (2.41)

The 2nd term in (2.35) adds to the last term of (2.28) defining the density of irreversibility as

$$i(\vec{x} t) = T^{-1}(\vec{x} t) \left[\left(\Sigma_a \omega_a \mu_a + \frac{1}{d} \tau_l^{l(f)} v_k^k \right) + \left(j_S^i \left(-\partial_i T \right) + \Sigma_A j_A^i \left(-\partial_i \mu_A \right) \right) + \left(\tau^{i k(f)(0)} v_{ik}^{(0)} \right) \right] \ge 0,$$
(2.42)

where

$$\mu_a = -\Sigma_A \, \nu_{aA} \, \mu_A; \quad a \, b \, \dots = 1, \, 2 \, \dots \, r \,$$
 (2.43)

is the «thermodynamical force» of reaction a. $\tau^{ik(0)}$ and $v_{ik}^{(0)}$ are the trace-less irreducible parts of symmetric tensors:

$$v_{ik}^{(0)} = v_{ik} - \frac{1}{d} g_{ik} v_l^l. (2.44)$$

^{*)} \vec{q} and \vec{c} are Galilei-covariant vectors, the dependence on v^2 in $h_{n_A} = (1/2) A v^2 + u_{n_A}$ drops out in the sum on account of (1.2).

Thus $(T\ i)\ (\vec{x}\ t)$ is a sum of products of (r+1)+(1+C)+1 unknown «thermodynamical currents» $J_{\alpha}\ (\alpha\ \beta\ ... = 12\ ...\ (r+C+3))$ with the corresponding «thermodynamical forces» X_{α} , separating into scalars $(\omega_a, \tau_l^{l(l)})$, vectors (j_S^i, j_A^i) and an irreducible tensor $\tau^{i\,k(f)\,(0)}$. Furthermore, $(T\ i)\ (\vec{x}\ t)$ must be a Galilei-covariant scalar. The «forces» $X_{\alpha}\ (=(\mu_a, d^{-1}\ v_k^k),\ (-\partial_i T, -\partial_i \mu_A)$ and $v_{ik}^{(0)})$ being Galilei-covariant, the Onsager coefficients $L_{\alpha\beta}\ (\vec{x}\ t)$ in $J_{\alpha}=\Sigma_{\beta}\ L_{\alpha\beta}\ X_{\beta}$ must be Galilei-covariant state functions, satisfying

$${T^{-1} L_{(\alpha \beta)}} [s \dots n_A \dots] \ge 0,$$
 (2.45)

which may however depend on space-derivatives $\partial_{i_1 \dots i_n}^n s \ (\vec{x} \ t) \dots$ If we neglect these space derivatives, i.e. if we assume them to be *local state variables*, the $L_{\alpha\beta}$'s must be scalars. This leads to

$$\tau_l^{l(l)} = L_{00} \frac{1}{d} v_l^l + \Sigma_b L_{0b} \mu_b, \quad \omega_a = L_{a0} \frac{1}{d} v_l^l + \Sigma_b L_{ab} \mu_b$$
 (2.46)

for the scalar «currents», to (1.1) for the vector «currents» and to

$$\tau^{i\,k(f)\,(0)} = 2\,\,\eta\,\,v^{i\,k(0)} \tag{2.47}$$

for the tensor «current». The signes are defined in terms of $T(\vec{x} t)$ by (1.9), (1.4) and (1.7).

§ 3. The State of Cinetical Equilibrium

The most general equilibrium is given by the maximum of the entropy-functional $S[s()] = \int (dV s)(\vec{x})$, with the constraints on the functionals of the 1st law:

$$H\left[\ldots\right]=H'$$
; $\Pi_{i}\left[\ldots\right]=\Pi'_{i}$; $M_{ik}\left[\ldots\right]=M'_{ik}$.

If chemical reactions are possible, no constraints are imposed on the CN_A [...]'s, but on the quantities of the I chemical elements N_P [...] = N_P (P, Q ... = 12 ... I = H, D, He, ..., U, Pu, ...) (where P, Q ... symbolise also the masses of the atom-gram). We have the relations

$$\Sigma_P \, \nu_{AP} \, P - A \equiv \Sigma_P \, \nu_{AP} \, P + \nu_{AA} \, A = 0 \tag{3.1A}$$

which apply also to the mass values and are the stochiometric relations (1.8) ($v_{AP} = pos.$ integers, $v_{AA} = -1$) for complete dissociation of A. Further we have evidently

$$N_P\left[\dots n_A\dots\right] = \Sigma_A \nu_{AP} \int (dV n_A) (\vec{x}). \tag{3.2}$$

The necessary and sufficient condition for equilibrium, is, as we have shown in III (annex)4):

$$\Psi\left[\dots v_{i}()\dots s()\dots n_{A}()\dots\right] = \int (dV \,\psi\left[\dots v_{i}\dots s\dots n_{A}\dots\right]) \,(\vec{x})$$

$$= \left(S + \vartheta \,H - \zeta^{i} \,\Pi_{i} - \frac{1}{2} \,\omega^{i\,k} \,M_{i\,k} - \Sigma_{P} \,\beta_{P} \,N_{P}) \,[\dots] = \text{maximum.} \right) (3.3)$$

 ϑ , ζ^i , $\omega^{ik} = \omega^{[ik]}$ and β_P are Lagrange multiplyers. The 1st variation $\delta^{(1)}\Psi[\ldots] = 0$ is the extremum condition. It yelds (see III⁴)):

$$\psi^{i}(\vec{x}) = \vartheta \, m \, v^{i} - m \, (\zeta^{i} + \chi_{k} \, \omega^{k \, i}) \equiv 0 \,, \tag{3.4}$$

$$\psi_s(\vec{x}) = 1 + \vartheta \ u_s = 1 + \vartheta \ T(\vec{x}) \equiv 0 , \qquad (3.4_s)$$

$$\psi_{n_A}(\vec{x}) = \vartheta \left(A \frac{v^2}{2} + u_{n_A} \right) - A \left(\zeta^i + x_k \, \omega^{k\,i} \right) v_i - \Sigma_P \, v_{AP} \, \beta_P \equiv 0 \,.$$
 (3.4_{n_A})

 (3.4^i) implies a translation + rotation with constant linear and angular velocity of the fluid:

$$\vec{v}(\vec{x}) = (\vec{\zeta} + [\vec{\omega} \wedge \vec{x}]) \, \vartheta^{-1} \,. \tag{3.5}$$

 (3.4_s) shows that $T(\vec{x}) = -\vartheta^{-1}$ is independent of space. (3.4_{n_A}) gives the chemical potentials the form

$$\mu_A(\vec{x}) = \mu_A(0) + \frac{1}{2} A v^2(\vec{x}),$$
 (3.6)

$$\mu_A(0) = \Sigma_P \, \nu_{AP} \, \vartheta^{-1} \, \beta_P \, (\equiv \Sigma_P \, \nu_{AP} \, \mu_P(0)) \,.$$
 (3.7)

On account of (3.1), this implies local chemical equilibrium with respect to total dissociation

$$(\Sigma_P \nu_{AP} \mu_P + \nu_{AA} \mu_A) (\vec{x}) = 0.$$
 (3.8*A*)*)

As all other r reactions a can be combined from the C reactions (3.1A) and (3.8A), chemical equilibrium is thus assured at every point \vec{x} , i.e. (2.43) gives

$$\mu_a(\vec{x}) = 0. \tag{3.9}$$

As from (3.5) follows $v_{ik}(x) = 0$, the irreversibility $i(\vec{x})$ (2.42) disappears for the scalar and tensorial terms.

We have now to verify that the equations of motion ((2.22), (2.9 N_A) and (2.12) with $k_i(\vec{x}) = 0$) are satisfied. As $\tau^{ik(f)}$ disappears on account of $v_{ik} = 0$ and $\mu_a = 0$ ((2.46), (2.47)). (2.22) reduces to (on account of T = const. (2.33), (2.41), (2.24) and (3.6)):

$$(m \ \dot{v_i} + \partial_i p) \ (x) = (m \ v^k \ \partial_k v_i + \Sigma_A \ n_A \ \partial_i \mu_A) = 2 \ \Sigma_A \ A \ (n_A \ v^k \ v_{ki}) \ (\vec{x}) = 0 \ . \ (3.10)$$

The Equations (2.12) for \dot{s} and (2.9 N_A) for \dot{n}_A , written in the Galilei-covariant form (2.7), are satisfied, if $\operatorname{div} \vec{j}_S = \operatorname{div} \vec{j}_A = 0$: ϱ_A disappears on account of (2.46), because $v_l^l = \mu_a = 0$. Furthermore $i(\vec{x})$ vanishes now for all 3 terms. Thus, as T is constant, the condition $\operatorname{div} \vec{j}_S = \operatorname{div} \vec{j}_A = 0$ implies

$$\Sigma_B L_{SB} B = 0 \tag{3.11}$$

and necessitates (1.5). (div $\overrightarrow{\text{grad}} \mu_B = B \text{ div } \overrightarrow{\text{grad}} v^2/2 \neq 0$).

Thus (2.12) and (2.9 N_A) lead to

$$\dot{s}(\vec{x}) = 0; \quad \dot{n}_A(\vec{x}) = 0.$$
(3.12)

^{*)} On account of (2.25), which implies (1.8), where A are now the molar masses.

Or, substantial time derivatives f of scalar state functions disappear for (3.5). It is remarkable, that the eqs. of motion for a one-component fluid (in r. and n.r. (see III⁴)) theory) are identically satisfied. For a C(>1)-component fluid, we have however the restrictions (1.5) and (3.11) on the Onsager coefficients in n.r. theory*).

The 2nd variation $\delta^{(2)}\Psi[\ldots] \leq 0$ is a necessary condition (see III4), annex). It implies

$$\begin{pmatrix} \psi^{i\,k}, \, \psi^{i}_{s}, & \psi^{i}_{n_{B}} \\ \psi^{k}_{s}, & \psi_{s\,s}, & \psi_{s_{n_{B}}} \\ \psi^{k}_{n_{A}}, \, \psi_{n_{A}\,s}, \, \psi_{n_{A}\,n_{B}} \end{pmatrix} (\vec{x}) \leq 0 ,$$
 (3.12)

which implies (see (3.4))

$$\left\{-\psi^{i\,k} = -\vartheta\,m\,g^{i\,k} = \left(\frac{m}{T}\right)(\vec{x})\,g^{i\,k}\right\} \ge 0\,\,\,(3.13^{i\,k})$$

$$-\psi_{ss} = -\vartheta \ u_{ss} = \left(\frac{T_s}{T}\right) [s \dots n_A \dots] = c^{-1} (\vec{x}) \ge 0 , \qquad (3.13_{ss})$$

$$-\psi_{sn_A} = -\vartheta u_{sn_A} = \left(\frac{u_{sn_A}}{T}\right)(\vec{x}), \qquad (3.13_{sn_A})$$

$$\left\{-\psi_{n_A n_B} = -\vartheta \ u_{n_A n_B} = \left(\frac{u_{n_A n_B}}{T}\right) (\vec{x})\right\} \ge 0. \tag{3.13}_{n_A n_B}$$

(3.13) has for consequence that a) the metric must be euclidien $\{g^{ik}\} \geq 0**$ and that the mass density and therefore $A n_A(\vec{x} t)$ have the sign of T. (3.13_{ss}, _{sn_A} and _{n_An_B}) give to the elastic modulus (1.11) the sign of T.

The sign condition on the Onsager coefficients (2.45) resulting from the 2nd law's principle of evolution and on the ψ , s (3.13) from the 2nd law's principle of equilibrium have as a consequence that the solution of the linearised coupled equations for \dot{v}^i , \dot{s} and \dot{n}_A ((2.22), (2.9 N_A) and (2.12)) are damped waves existing only in the future $t \geq 0$, if the initial local states are given for all \dot{x} at $t = III^4$)⁵).

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^{*)} We shall discuss the analogous conditions for a C(>1)-component fluid in r, theory in a subsequent paper (V).

^{**)} $\{g_{ik}\} \leqslant 0$ is of course also possible, if (m/T) $(\vec{x}) \leqslant 0$.