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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  $A B \dots = 12 \dots C$ , 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*  $f[s \dots] = f(\vec{x} t)$  in  $r$ . (= relativistic) phenomenological theory of a one component fluid III<sup>4</sup>). 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  $A B \dots = 12 \dots C$ . The symbols  $A B \dots$  are also used to denote the *unites of mass* ( $A$  = mass of the mole of  $A$ ). We deduce a the *symmetry condition on the Onsager phenomenological coefficients*  $L_{AB}$  defined as linear relations between the *densities of conduction-(diffusion-) currents*  $\vec{j}_A(\vec{x} t)$  of  $A$  (including the *conductive entropy* ( $S$ ) -flow  $\vec{j}_S(\vec{x} t)$ ) and the «*thermodynamical forces*» -  $\overrightarrow{\text{grad}} T(\vec{x} t)$  and -  $\overrightarrow{\text{grad}} \mu_A(\vec{x} t)$ \*:

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

$$\vec{j}_A = -L_{AS} \overrightarrow{\text{grad}} T - \sum_B L_{AB} \overrightarrow{\text{grad}} \mu_B. \quad (1.1_A)$$

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*  $v^i(\vec{x} t)$  ( $\vec{v} = \{v^i\}$ ;  $\vec{x} = \{x^i\}$ ;  $i k \dots = 12 \dots d$ ;  $d = 3$ ). In order

\*)  $T$  and  $\mu_A$  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*  $dV(\vec{x}) = g dx^1 dx^2 \dots dx^d$ \*).

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

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

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

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

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

forms a *non-negative quadratic form*.

The *2nd law's principle of equilibrium* ( $S = \text{maximum}$ , for a closed system in kinetic equilibrium) leads to a relation symmetric to (1.3)

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

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

$$\boxed{L_{AB}(\vec{x} t) = L_{BA}(\dots) = L_{(AB)}(\vec{x} t)} \quad (1.6) **)$$

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*»  $J_\alpha$  to «*thermodynamical forces*»  $X_\alpha$  ( $J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta$ ). They follow only from *statistical thermodynamics* (see <sup>1</sup><sup>2</sup><sup>3</sup>)). 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*  $\eta$  and  $\xi$

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

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  $a b \dots = 12 \dots r$  given by the stoichiometric coefficients  $v_{aA}$  (= pos. and neg. integers):

$$\boxed{\Sigma_A v_{aA} A = 0,} \quad (1.8)$$

\*)  $g$  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  $A B \dots C$ :  $L_{AB} = \lambda L_{BA}$ . 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  $\lambda_1$  ( $A \rightarrow \lambda_1 A$ ,  $B \rightarrow \lambda_1 B$ , ...). The  $A$ 's (or  $B$ 's) must also satisfy (1.5). Therefore we must have  $L_{AB} = \lambda_2 L_{BA}$ . Applied to  $L_{AA}$ ,  $\lambda_2$  must be = 1. Thus (1.6) follows.

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

$$\left\{ \begin{array}{l} T^{-1} L_{00}, \quad T^{-1} L_{(0b)} \\ T^{-1} L_{(a0)}, \quad T^{-1} L_{(ab)} \end{array} \right\} (\vec{x} t) \geq 0. \quad (1.9) ^{***}$$

(The index  $0$  applies to the longitudinal viscosity).

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

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

on the *elastic modulus*

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

$$(T^{-1} a) (\vec{x} t) \geq 0, \quad (1.12)$$

on the *heat capacity per unit volume*  $c$

$$c^{-1} (\vec{x} t) = (T^{-1} T_s) [s \dots n_A \dots] \geq 0 \quad (1.13) ^*$$

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

$$\partial_t s (\vec{x} t), \quad \partial_t n_A (\vec{x} t) \quad \text{and} \quad \partial_t v^i (\vec{x} t) \quad (\text{see III}^4)^5),$$

which lead, *in the linear approximation, to damped waves, which exist only for  $t \geq 0$*  (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 ( $= \pm g dy^1 \dots dy^{i-1} dy^{i+1} \dots dy^d$ ).

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

$$\dot{F}(t) = \int_V (dV \partial_t f) (\vec{x} t) + \oint_V (d\sigma_i v^i f) (\vec{y} t), \quad (2.1)$$

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

$^{**})$  As  $g_{ik}$  is constant, we may use *euclidian metric*  $g_{ik} = \delta_{ik}^2$ .

$^{***})$  See eq (2.46).

$v^i(\vec{y} t)$  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  $C(\dots) = 0$ :

$$\boxed{\dot{F}(t) = \int_V (dV \varrho_F) (\vec{x} t) - \oint_V (d\sigma_i j_F^i) (\vec{y} t).} \quad (2.2)$$

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

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

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*  $\Pi_i$  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*  $c^i$

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

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

$$\boxed{(\partial_t \pi_i + \partial_k (v^k \pi_i - \tau^k_i)) (\vec{x} t) = k_i (\vec{x} t)} \quad (2.9\Pi_i)$$

and for  $N_A$

$$\boxed{(\partial_t n_A + \partial_k (v^k n_A + j_A^k)) (\vec{x} t) = \varrho_A (\vec{x} t) = \sum_a v_{aA} \omega_a (\vec{x} t),} \quad (2.9N_A)$$

where  $\omega_a(\vec{x} t)$  is the *local reaction rate* of the  $a^{\text{th}}$  reaction (1.7). (2.9\Pi\_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*  $M_{ik} = M_{[ik]} = \int dV (x_i \pi_k - x_k \pi_i)$ :

$$\boxed{(\partial_t (x_i \pi_k - x_k \pi_i) + \partial_l (v^l (x_i \pi_k - x_k \pi_i) - (x_i \tau^l_k - x_k \tau^l_i))) (\vec{x} t) = (x_i k_k - x_k k_i) (\vec{x} t).} \quad (2.9M_{ik})$$

(2.9\Pi\_i) and (2.9M<sub>ik</sub>) imply the symmetry ( $\partial_i x^k = \delta_i^k$ )

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

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

$$\begin{aligned} \dot{H}(t) &= P_Q(t) + P_A(t) + P_C(t) \\ &= \left( - \oint_V (d\sigma_i q^i) (\vec{y} t) \right) + \left( \int_V (dV k_i v^i) (\vec{x} t) + \oint_V (d\sigma_k \tau^k_i v^i) (\vec{y} t) \right) \\ &\quad + \left( - \oint_V (d\sigma_i c^i) (\vec{y} t) \right), \end{aligned} \quad \left. \right\} (2.11H)$$

$$\dot{H}_i(t) = K_i(t) = \int_V (dV k_i) (\vec{x} t) + \oint_V (d\sigma_k \tau^k i) (\vec{y} t), \quad (2.11H_i)$$

$$\dot{N}_A(t) = \int_V (dV \varrho_A) (\vec{x} t) - \oint_V (d\sigma_i j_A^i) (\vec{y} t), \quad (2.11N_A)$$

$$\left. \begin{aligned} \dot{M}_{ik}(t) &= D_{ik}(t), \\ &= \int_V (dV (x_i k_k - x_k k_i)) (\vec{x} t) + \oint_V (d\sigma_l (y_i \tau^l k - y_k \tau^l i)) (\vec{y} t), \end{aligned} \right\} (2.11M_{ik})$$

where  $P_Q$  etc. are the *powers of heat*  $Q$ , *work*  $\mathbf{A}$  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

$$\boxed{(\partial_t s + \partial_k (v^k s + j_S^k)) (\vec{x} t) = i (\vec{x} t) \geq 0}, \quad (2.12)$$

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

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

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

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

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

which implies the metric  $g_{ik}$ . The continuity equation (2.9H<sub>i</sub>) takes the form

$$\boxed{((v_i (\partial_t m + \partial_k (v^k m)) + m \dot{v}_i - \partial_k \tau^k i) (\vec{x} t) = k_i (\vec{x} t)}, \quad (2.15)$$

where  $\dot{v}_i$  is the *substantial acceleration*, defined as the *substantial time derivative of any local function*  $f (x t)$ :

$$\boxed{\dot{f} (\vec{x} t) \equiv (\partial_t f + v^k \partial_k f) (\vec{x} t)}. \quad (2.16)$$

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

$$\boxed{(\dot{f} + f \partial_k v^k + \partial_k j_F^k) (\vec{x} t) = \varrho_F (\vec{x} t)}. \quad (2.17)$$

We now turn to *Galilei-covariance*. The Galilei transformation

$$\vec{x}^i = x^i - v_0^i t, \quad 't = t + t_0, \quad (2.18)$$

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

$$\boxed{'f^{ik} \dots {}_{lm} \dots ('\vec{x} 't) = f^{ik} \dots {}_{lm} \dots (x t)}. \quad (2.19)$$

\*) On account of (2.39) we have

$$\dot{S}(t) \geq - \oint_V (d\sigma_i T^{-1} q^i) (\vec{y} t). \quad (2.13*)$$

The velocity field  $'v^i ('\vec{x}' t) = v^i (\vec{x} t) - v_0^i$  is *not covariant*. However  $\dot{v}^i$ ,  $\partial_t v^k$  and  $\partial_k v^k = \text{div } \vec{v}$  are covariant. The same is true for  $\dot{f}^{ik\dots}_{\dots m\dots}$ , defined by (2.16), if  $f^{ik\dots}_{\dots m\dots}$  is Galilei-covariant. Thus, if  $\tau^k_i$  and  $k_i$  in (2.15) are Galilei-covariant, the *strong continuity eq. for mass*  $M = \int_V (dV m) (\vec{x} t)$  holds:

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

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

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

$$\boxed{(m \dot{v}_i) (\vec{x} t) = (m (\partial_t v_i + v^k \partial_k v_i)) (\vec{x} t) \\ = (\partial_k \tau^k_i + k_i) (\vec{x} t)} \quad (2.22)$$

replace (2.9II<sub>i</sub>).

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  $\partial_t s$ , (2.9N<sub>A</sub>) for  $\partial_t n_A$ , (2.9H) for  $\partial_t h$ , and (2.20) for  $\partial_t m$ . This implies that  $m = m [\dots v_i \dots s \dots n_A \dots]$  and  $h = h [\dots v_i \dots s \dots n_A \dots]$  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  $m [s \dots n_A \dots]$ . 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  $m$ :

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

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

$$m [\dots n_A \dots] = \Sigma_A A n_A (\vec{x} t). \quad (2.24)$$

No constant of integration can appear, on account of (2.20). However, (2.9N<sub>A</sub>) implies

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

which combined with the 2nd eq. (2.9N<sub>A</sub>) leads to *Lavoisier's law* (1.8) stating the *conservation of mass in every chemical reaction a b ... r\**). The condition  $\vec{j}_M = 0$  (2.20) implies

$$(\vec{v} m) (\vec{x} t) = \Sigma_A A (n_A \vec{v} + \vec{j}_A) (\vec{x} t) \equiv \Sigma_A A (n_A \vec{v}_A) (\vec{x} t), \quad (2.27)$$

\*) 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 III<sup>4</sup>)). In order to obtain correspondance, continuity eqs. for

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

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

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 (2.9N<sub>A</sub>):

$$\left. \begin{aligned} \partial_t h &= h^i \partial_t v_i + h_s \partial_t s + h_{n_A} \partial_t n_A, \\ &= -\partial_k(v^k h + \rho v^k + h_s j_S^k + \sum_A h_{n_A} j_A^k) + h^i m^{-1} k_i \\ &\quad + v^i (s \partial_i h_s + \sum_A n_A \partial_i h_{n_A} - h^k \partial_i v_k) + h^i m^{-1} \partial_k \tau^k_i \\ &\quad + (h_s i + j_S^i \partial_i h_s + \sum_A j_A^i \partial_i h_{n_A} + \sum_A h_{n_A} \varrho_A), \end{aligned} \right\} \quad (2.28)$$

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

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

The 2nd member of (2.28) must be transformed in such a way as giving rise to the divergence  $\partial_k(v^k h + \dots)$  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  $\varrho_H$ :

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

from which results, by integration

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

The integration «constant»  $u [\dots]$  being the *density of interior energy*

$$U = \int_V (dV u)(\vec{x} t).$$

Furthermore (2.29) becomes the *Galilei-invariant scalar pressure*

$$\rho [s \dots n_A \dots] = (s u_s + \sum_A n_A u_{n_A} - u)(\vec{x} t). \quad (2.32)$$

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

$$\left. \begin{aligned} \partial_i \rho(\vec{x} t) &= (s \partial_i h_s + \sum_A n_A \partial_i h_{n_A} - h^k \partial_i v_k) [\dots v_i \dots s \dots n_A \dots], \\ &= (s \partial_i u_s + \sum_A n_A \partial_i u_A) [s \dots n_A \dots] \end{aligned} \right\} \quad (2.33)$$

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

$$\tau^{i k} = \tau^{i k(e)} + \tau^{i k(f)} = -g^{i k} \rho + \tau^{i k(f)}, \quad (2.34)$$

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

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

(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<sup>2</sup>).

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

$$v^i (\partial_i \dot{p} + \partial_k \tau^k_i) = -\partial_k (-\tau^{k(f)}_i v^i) - v_{i k} \tau^{i k(f)}, \quad (2.35)$$

where

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

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

$$\boxed{\tau^{i k} = \tau^{(i k)}}$$

resulting from *conservation of angular momentum* (2.10) and Newton's axiom (2.14).

The first term of (2.35) may be combined with  $\dot{p} v^k$  in the divergence in (2.28) giving rise to the *flow of work*

$$\boxed{a^k = -\tau^k_i v^i.} \quad (2.38)$$

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

$$\boxed{q^k = h_s j_S^k = u_s j_S^k \equiv T j_S^k} \quad (2.39)$$

and the *flow of chemical energy*

$$\boxed{c^k = \sum_A h_{n_A} j_A^k = \sum_A u_{n_A} j_A^k \equiv \sum_A \mu_A j_A^k,} \quad (2.40)^*$$

where the *absolute temperature*  $T$  and the *C chemical potentials*  $\mu_A$  are the local state functions

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

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

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

where

$$\boxed{\mu_a = -\sum_A v_{a A} \mu_A; \quad a b \dots = 1, 2 \dots r} \quad (2.43)$$

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

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

\* $\vec{q}$  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»  $J_\alpha$  ( $\alpha \beta \dots = 12 \dots (r + C + 3)$ ) with the corresponding «thermodynamical forces»  $X_\alpha$ , separating into scalars ( $\omega_a, \tau_l^{(f)}$ ), 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  $v_{i k}^{(0)}$ ) being Galilei-covariant, the Onsager coefficients  $L_{\alpha \beta} (\vec{x} t)$  in  $J_\alpha = \sum_\beta L_{\alpha \beta} X_\beta$  must be Galilei-covariant state functions, satisfying

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

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

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

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

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

for the tensor «current». The signs 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*:

$$H [\dots] = H'; \quad \Pi_i [\dots] = \Pi'_i; \quad M_{ik} [\dots] = M'_{ik}.$$

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

$$\sum_P \nu_{AP} P - A \equiv \sum_P \nu_{AP} P + \nu_{AA} A = 0 \quad (3.1A)$$

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

$$N_P [\dots n_A \dots] = \sum_A \nu_{AP} \int (dV n_A) (\vec{x}). \quad (3.2)$$

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

$$\left. \begin{aligned} \Psi [\dots v_i (\ ) \dots s (\ ) \dots n_A (\ ) \dots] &= \int (dV \psi [\dots v_i \dots s \dots n_A \dots]) (\vec{x}) \\ &= (S + \vartheta H - \zeta^i \Pi_i - \frac{1}{2} \omega^{ik} M_{ik} - \sum_P \beta_P N_P) [\dots] = \text{maximum.} \end{aligned} \right\} \quad (3.3)$$

$\vartheta$ ,  $\zeta^i$ ,  $\omega^{ik} = \omega^{[ik]}$  and  $\beta_P$  are Lagrange multipliers. The 1st variation  $\delta^{(1)}\Psi[\dots] = 0$  is the extremum condition. It yields (see III<sup>4</sup>)):

$$\psi^i(\vec{x}) = \vartheta m v^i - m (\zeta^i + x_k \omega^{ki}) \equiv 0, \quad (3.4^i)$$

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

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

(3.4<sup>i</sup>) implies a *translation + rotation with constant linear and angular velocity* of the fluid:

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

(3.4<sub>s</sub>) shows that  $T(\vec{x}) = -\vartheta^{-1}$  is *independent of space*. (3.4<sub>n\_A</sub>) gives the chemical potentials the form

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

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

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

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

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

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

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), (2.9N<sub>A</sub>) 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  $T = \text{const.}$  (2.33), (2.41), (2.24) and (3.6)):

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

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

$$\sum_B L_{SB} B = 0 \quad (3.11)$$

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

Thus (2.12) and (2.9N<sub>A</sub>) lead to

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

\*) On account of (2.25), which implies (1.8), where  $A$  are now the molar masses.

Or, substantial time derivatives  $\dot{f}$  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 III<sup>4</sup>)) 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  $\delta^{(2)}\Psi[\dots] \leq 0$  is a necessary condition (see III<sup>4</sup>), annex). It implies

$$\left\{ \begin{array}{l} \psi^{i k}, \psi_s^i, \psi_{n_B}^i \\ \psi_s^k, \psi_{s s}, \psi_{s n_B} \\ \psi_{n_A}^k, \psi_{n_A s}, \psi_{n_A n_B} \end{array} \right\} (\vec{x}) \leq 0, \quad (3.12)$$

which implies (see (3.4))

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

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

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

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

(3.13) has for consequence that a) *the metric must be euclidian*  $\{g^{i k}\} \geq 0$ \*\*) and that the *mass density and therefore A n\_A(x t)* have the sign of  $T$ . (3.13<sub>s s</sub>, <sub>s n\_A</sub> and <sub>n\_A n\_B</sub>) 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  $\psi^i$ ,  $s$  (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  $\vec{x}$  at  $t = \text{III}^4$ )<sup>5</sup>).

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## References

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

\*\*)  $\{g_{i k}\} \leq 0$  is of course also possible, if  $(m/T) (\vec{x}) \leq 0$ .