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A Generalization of the Principle of Detailed Balancing in μ -Space

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Abstract. The H -theorem in μ -space for a mixture of free molecules or particles A, B, \dots undergoing all sorts of multiple collisions or reactions (creation and annihilation) is generalized to the case, where detailed balancing (DB) does not hold, and for the 3 statistics (BOLTZMANN, BOSE-EINSTEIN, and FERMI-DIRAC). The equilibrium condition is given in terms of the chemical potentials μ_A, μ_B, \dots The transition probabilities between macrocells have to satisfy a weaker condition than DB.

Introduction

This publication, whose main interest will be of a didactic nature, is the demonstration of BOLTZMANN: H ($= \frac{5}{\eta} \tau \alpha$)-theorem in a perfect gas, where different kinds of molecules (or particles) A, B, \dots may collide in arbitrary way and undergo chemical reactions of any type (including the emissions of photons, Φ). We look, how the condition of detailed balancing (DB), which, as BOLTZMANN himself know already¹⁾, is certainly too strong a condition on transition probabilities, *may be weakened, so as to preserve the H -theorem*. We have shown in two earlier papers²⁾³⁾ (referred to as I, II) how this condition may be weakened in Γ space (on account of the unitarity of the S-matrix), which is the only phase space, to which a physical reality may be attributed⁷⁾. However, in lectures on statistical thermodynamics, it is sometimes usefull to treat the perfect gas in μ -space, following BOLTZMANN's original way. Therefore we start, in § 1, with the *Boltzmann Ansatz* for macrocells, generalized to all sorts of multiple collisions and reactions. We are immediately led (§ 2) to his *logarithmic expression for the entropy*, while in Γ space (see I and II), the H -theorem may be demonstrated to hold for any monotonic increasing function, as a *measure of information*. We difference the 3 statistics (BOLTZMANN (Bo), BOSE-EINSTEIN (BE), and FERMI-DIRAC (FD)) through the notion of *induced* (BE) and *anti-induced* (FD) *transition probabilities*, as already PAULI⁴⁾ did (basing himself on the ideas of JORDAN, KRAMERS, OMSTEIN, and BOTHE⁵⁾). However, we assume this 'induction factor' ($\alpha = +1 (-1)$ for BE(FD), $\alpha = 0$ for Bo in PAULI's article) λ_A for molecules of type A in this publication) as an *arbitrary number*. Our *generalization of the DB-condition* (the *consideration of chemical reactions, anti-particles \bar{A}, \bar{B}, \dots , and CPT covariance*) necessitates $\lambda_A = \pm 1$ (or = 0) (§ 3) and states the *law of conservation of statistics* if $\lambda_A \neq 0$ (equation (3.2)). Furthermore, considering the *equilibrium case*, for a non degenerate gas, we find the well-known result for the *chemical potentials* μ_A : (1) Particles Φ which are identical to their anti-particles $\bar{\Phi}$ have zero chemical potential $\mu_\Phi = 0$.

(2) Particles A and anti-particles \bar{A} have numerical equal chemical potentials but of opposite signs: $\mu_{\bar{A}} = -\mu_A$.

Finally we calculate the *chemical constant* i_A for a monoatomic, spinless gas, whose experimental value shows that the constant h , used to define micro-cells, is the PLANCK's *constant*, and establish the law of *mass action*.

1. The BOLTZMANN Collision 'Ansatz'

We consider a perfect *gas* composed of C different sorts of molecules $A B \dots = 12 \dots C$, between which collisions and chemical reactions may occur according to

$$(\nu) \equiv \sum_{A''} \nu''_{A''} A'' \leftarrow \sum_{A'} \nu'_{A'} A' \equiv \nu''_A A + \nu''_B B + \dots \leftarrow \nu'_A A + \nu'_B B + \dots \quad (1.1)$$

The $\nu''_{A''}$'s (final state) and the $\nu'_{A'}$'s (initial state) are *positive integers*. (ν) is a complex of indices

$$(\nu) \equiv \{\dots \nu''_{A''} \dots; \dots \nu'_{A'} \dots\} = \{\nu''_A \nu''_B \dots; \nu'_A \nu'_B \dots\}, \quad (1.1a)$$

describing the collision or reaction. $(-\nu)$ describes the inverse collision or reaction:

$$(-\nu) \equiv \{\dots \nu'_{A'} \dots; \dots \nu''_{A''} \dots\} = \{\nu'_A \nu'_B \dots; \nu''_A \nu''_B \dots\}.$$

For example the reaction $(\nu) \equiv C \leftarrow A + B$, involving 2 initial components A and B combining into C is different from $(2\nu) \equiv 2C \leftarrow 2A + 2B$. For each A , we introduce a *separate μ -space*: $\{p_i, q_i\}$, $i \in 12 \dots f_A$, f_A being the *number of degrees of freedom* of A . Each μ -space is, at first, divided into *micro-cells* of phase volume h^{f_A} (h being PLANCK's *constant*). We further *introduce macrocells* (of different magnitudes) de-numbering them by $a, a' \dots$ or

$$a'_1 a'_2 \dots a''_1 a''_2 \dots \quad \text{for } A, \quad \text{by} \quad b, b' \dots \quad \text{or} \quad b'_1 b'_2 \dots b''_1 b''_2 \dots \quad \text{for } B \quad \text{etc.}$$

Their volume is: for A , $C_a h^{f_A}$; for B , $C_b h^{f_B}$ etc. with

$$C_a \gg 1; \quad C_b \gg 1; \quad \dots \quad (1.2)$$

The occupation numbers of a (for A), b (for B), etc. are

$$N_a \gg 1; \quad N_b \gg 1; \quad \dots \quad (1.3)$$

and the total number of molecules A, B, \dots is a variable number:

$$N_A = \sum_a N_a; \quad N_B = \sum_b N_b; \quad \dots \quad (1.4)$$

For a 'collision' $A \leftarrow A$, the gain (per unit time) of the cell a'' due to a transition $a'' \leftarrow a'$ is, according to BOLTZMANN, $C_{a''} A_{a''; a'} N_{a'}$ and the loss due to the 'inverse collision' is $C_{a'} A_{a'; a''} N_{a''}$, where $A_{a''; a'} \geq 0$ is the *transition probability*. The net gain is:

$$\dot{N}_{a'' (A \leftarrow A)} = \sum_{a'} (C_{a''} A_{a''; a'} N_{a'} - C_{a'} A_{a'; a''} N_{a''}). \quad (1.5, A \leftarrow A)^*)$$

*) $\dot{N}_{a''}(t) = (N_{a''}(t'') - N_{a''}(t')) (t'' - t')^{-1} = \delta N_{a''}/\delta t$ for a period $\delta t = t'' - t' \leq 0$ large compared to the duration of a collision. Thus the 'Boltzmann Ansatz' does not provide a $\delta t > 0$, as often thought.

For a real collision $2A \leftarrow 2A$ we have for the number (per unit time) of simultaneous transitions

$$a''_1 \leftarrow a'_1; \quad a''_2 \leftarrow a'_2: \quad C_{a''_1} C_{a''_2} A_{a''_1 a''_2; a'_1 a'_2} N_{a'_1} N_{a'_2}.$$

The corresponding number of inverse collisions is obtained, changing ' \rightleftharpoons '. The total gain of a given $N_{a''}$ due to this process is:

$$\dot{N}_{a''(2A \leftarrow 2A)} = 2 \sum_{a'_1, a'_2, a''_2} (C_{a''} C_{a''_2} A_{a'' a''_2; a'_1 a'_2} N_{a'_1} N_{a'_2} - C_{a'_1} C_{a'_2} A_{a'_1 a'_2; a'' a''_2} N_{a''} N_{a''_2}). \quad \left. \right\} (1.5, 2A \leftarrow 2A)$$

The factor 2 is due to the fact that

$$A_{a''_1 a''_2; a'_1 a'_2} = A_{a''_2 a''_1; a'_1 a'_2} = A_{a''_1 a''_2; a'_2 a'_1} \geq 0$$

is *symmetric* with respect to the 2 final macrocells and the 2 initial macrocells: Thus, both $A_{a''_1 a''_2; a'_1 a'_2}$ and $A_{a''_2 a''_1; a'_1 a'_2}$ (and their inverse) contribute to (1.5; $2A \rightarrow 2A$).

Let us now consider the simple chemical reaction $(\pm \nu) \equiv C \rightleftharpoons A + B$. We have the transition probabilities

$$A_{a'' b''; c'}^{(\nu)} (\geq 0) \quad \text{and} \quad A_{c'; a'' b''}^{(-\nu)} (\geq 0).$$

They contribute to $\dot{N}_{a''}$ in the form

$$\dot{N}_{a''(A+B \leftarrow C)} = \sum_{c' b''} C_{a''} C_{b''} A_{a'' b''; c'}^{(\nu)} N_{c'} - C_{c'} A_{c'; a'' b''}^{(-\nu)} N_{a''} N_{b''}. \quad (1.5; A+B \leftarrow C)$$

For the most general collision or reaction (ν) (1.1), we have therefore the '*Boltzmann Ansatz*':

$$\begin{aligned} \dot{N}_{a''(\nu)} &= \nu_A'' \sum_{a''_2 \dots b''_{\nu_A''} a'_1 \dots b'_{\nu_B''}} (C_{a''} C_{a''_2} \dots C_{a''_{\nu_A''}} C_{b''_1} \dots C_{b''_{\nu_B''}} \dots \\ &\quad \dots A_{a'' a''_2 \dots a''_{\nu_A''} b''_1 \dots b''_{\nu_B''}; a'_1 \dots a'_{\nu_A'} b'_1 \dots b'_{\nu_B'}} N_{a'_1} \dots N_{a'_{\nu_A'}} N_{b'_1} \dots N_{b'_{\nu_B'}} \dots \\ &\quad - C_{a'_1} \dots C_{a'_{\nu_A'}} C_{b'_1} \dots C_{b'_{\nu_B'}} \dots A_{a'_1 \dots a'_{\nu_A'} b'_1 \dots b'_{\nu_B'}}^{(-\nu)}; a'' a''_2 \dots a''_{\nu_A''} b''_1 \dots b''_{\nu_B''} \dots \\ &\quad N_{a''} N_{a''_2} \dots N_{a''_{\nu_A''}} N_{b''_1} \dots N_{b''_{\nu_B''}} \dots). \end{aligned} \quad \left. \right\} (1.5; \nu)$$

The factor ν_A'' arises from the fact, that the $A_{a''_1 a''_2 \dots a''_{\nu_A''} b''_1 \dots b''_{\nu_B''}; a'_1 \dots}$ and $A_{a'_1 \dots a'_2 \dots a'_{\nu_A'} b''_1 \dots}^{(-\nu)}$ are *symmetric* in the ν_A'' indices a''_i , like the factor 2 in (1.5, $2A \leftarrow 2A$). Now a word why we have introduced *macrocells*. If n' of the *initial* a'_i are equal, the number of collisions is not proportional to $N_{a'_i}^{n'}$ but to

$$N_{a'_i} (N_{a'_i} - 1) \dots \frac{N_{a'_i} - n'}{n'!} (n' \leq \nu_A').$$

If $N_{a'_i} \gg \nu'_A$, we may write $(N_{a'_i})^{n'}$ and absorb the factor $(n'!)^{-1}$ in $A_{\dots; \dots; a'_i a'_i \dots a'_i \dots}^{(\nu)}$. On the other hand, if n'' of the final a''_i are equal, the contribution should be proportional to

$$n'' (C_{a''_i})^{n''} A_{\dots; a''_i a''_i \dots a''_i \dots; a'_1 \dots}^{(\nu)}.$$

But this term arises also $n''!$ times, thus we have also to divide by $n''!$, which may again be absorbed in $A_{\dots; a''_i a''_i \dots a''_i \dots; a'_1 \dots}^{(\nu)}$. Thus (1.5; ν) is correct, if the $A_{\dots; \dots}^{(\nu)}$'s and $A_{\dots; \dots}^{(-\nu)}$'s are properly redefined.

The total net gain in a'' is therefore

$$\dot{N}_{a''} = \frac{1}{2} \sum_{(\nu)} \dot{N}_{a''} (\nu) \quad (1.6)$$

the factor 1/2 being due to the fact that both (ν) and $(-\nu)$ are summed over all collisions and reactions (1.1).

2. The H -Theorem

The H ($= \tilde{\eta} \tau \alpha$)-theorem of Boltzmann states, that a *functional of the occupation numbers*: $-\tilde{\eta} \tau \alpha = S = S [\dots N_a, \dots, N_b, \dots, \dots]$ exists, which for an *adiabatically closed system* $\Sigma = \Sigma_0$ satisfies

$$\dot{S} = \sum_a \frac{\partial S}{\partial N_a} \dot{N}_a + \sum_b \frac{\partial S}{\partial N_b} \dot{N}_b + \dots \equiv - \sum_{a''} g_{a''} \dot{N}_{a''} - \sum_{b''} g_{b''} \dot{N}_{b''} - \dots \geq 0, \quad (2.1)$$

if the ‘Boltzmann Ansatz’ (1.5; ν) (1.6) is accepted. S is to be interpreted as the *entropy* of Σ . The

$$g_a = g_a [\dots N_{a_1}, \dots, N_{b_1}, \dots, \dots] = - \frac{\partial S [\dots]}{\partial N_a}$$

are, at a first view, also functionals of all N_a 's, N_b 's, Substituting (1.5; ν), (1.6) into (2.1) we may, on account of the symmetries, replace $g_{a''_1} \nu''_A$ by $g_{a''_1} + g_{a''_2} + \dots + g_{a''_A}$, obtaining

$$\left. \begin{aligned} \dot{S} = & - \frac{1}{2} \sum_{(\nu)} \sum_{a'_1, \dots, a''_1 \dots b''_B} (g_{a''_1} + \dots + g_{a''_A} + g_{b''_1} + \dots) \\ & \times (C_{a''_1} \dots C_{a''_A} C_{b''_1} \dots A_{a''_1 \dots a''_A \dots b''_1 \dots; a'_1 \dots b'_B}^{(\nu)} N_{a'_1} \dots N_{b'_B} \dots) \\ & - C_{a'_1} \dots C_{b'_B} \dots A_{a'_1 \dots b'_B; a''_1 \dots a''_A \dots b''_1}^{(-\nu)} N_{a''_1} \dots N_{a''_A} N_{b''_1} \dots \end{aligned} \right\} (2.2)$$

the sum being taken over all collisions and reactions (ν) and over all final $(")$ and initial $(')$ macrocells. We may simplify the notation, by introducing the two complexes of indices in the final and initial states of (ν) :

$$\alpha'' = \{a''_1 \dots a''_A b''_1 \dots b''_B \dots\}; \alpha' = \{a'_1 \dots b'_B \dots\};$$

introducing the *sums*:

$$g_{\alpha''} = g_{a''_1} + \cdots + g_{a''_{\nu''_A}} + g_{b''_1} + \cdots; \quad g_{\alpha'} = g_{a'_1} + \cdots \quad (2.3g)$$

and the *products*:

$$C_{\alpha''} = C_{a''_1} C_{a''_2} \cdots C_{a''_{\nu''_A}} C_{b''_1} \cdots \gg 1; \quad C_{\alpha'} = C_{a'_1} \cdots \gg 1, \quad (2.3C)$$

$$N_{\alpha''} = N_{a''_1} N_{a''_2} \cdots N_{a''_{\nu''_A}} N_{b''_1} \cdots \gg 1; \quad N_{\alpha'} = N_{a'_1} \cdots \gg 1, \quad (2.3N)$$

$$\left. \begin{aligned} A_{\alpha''; \alpha'}^{(\nu)} &= A_{a'_1 \cdots a''_{\nu''_A} b''_1 \cdots; a'_1 \cdots b'_{\nu'_B} \cdots}^{(\nu)} \gg 0, \\ A_{\alpha'; \alpha''}^{(-\nu)} &= A_{a'_1 \cdots b'_{\nu'_B} \cdots; a''_1 \cdots a''_{\nu''_A} b''_1 \cdots}^{(-\nu)} \gg 0, \end{aligned} \right\} (2.3A_{\cdot, \cdot}^{(\nu)})$$

(2.2) reduces now to the simple form:

$$\left. \begin{aligned} \dot{S} &= -\frac{1}{2} \sum_{(\nu)} \sum_{\alpha' \alpha''} g_{\alpha''} (C_{\alpha''} A_{\alpha''; \alpha'}^{(\nu)} N_{\alpha'} - C_{\alpha'} A_{\alpha'; \alpha''}^{(-\nu)} N_{\alpha''}) \\ &\equiv -\frac{1}{4} \sum_{(\nu)} \sum_{\alpha' \alpha''} (g_{\alpha''} - g_{\alpha'}) C_{\alpha''} C_{\alpha'} (A_{\alpha''; \alpha'}^{(\nu)} n_{\alpha'} - A_{\alpha'; \alpha''}^{(-\nu)} n_{\alpha''}), \end{aligned} \right\} (2.4)$$

with the products:

$$n_{\alpha''} = \frac{N_{\alpha''}}{C_{\alpha''}} = n_{a''_1} \cdots n_{b''_1} \cdots > 0; \quad n_{\alpha'} = \frac{N_{\alpha'}}{C_{\alpha'}} = n_{a'_1} \cdots n_{b'_1} \cdots > 0, \quad (2.5)$$

where

$$n_a = \frac{N_a}{C_a} \geq 0; \quad n_b = \frac{N_b}{C_b} \geq 0 \quad (2.6)$$

are (in the Boltzmann case) the *mean occupation number of a microcell* inside the macrocell a for A , b for B, \dots . The 2nd, symmetrised equation (2.4), arises from the fact, that we may also write the 1st equation, interchanging $\alpha'' \rightleftarrows \alpha'$ and $(\nu) \rightleftarrows (-\nu)$, and is the half sum of both these expressions.

Now let us first consider *detailed balancing (DB)* expressed by $A_{\alpha''; \alpha'}^{(\nu)} = A_{\alpha'; \alpha''}^{(-\nu)}$ leading to

$$\dot{S} = \frac{1}{4} \sum_{(\nu)} \sum_{\alpha' \alpha''} C_{\alpha''} C_{\alpha'} A_{\alpha''; \alpha'}^{(\nu)} (g_{\alpha''} - g_{\alpha'}) (n_{\alpha''} - n_{\alpha'}) \geq 0. \quad (2.7; DB)$$

The common factor $C_{\alpha''} C_{\alpha'} A_{\alpha''; \alpha'}^{(\nu)}$, being non-negative, (2.7; DB) requires that $g_{\alpha} = g_{\alpha}[n_{\alpha}]$ be a *monotonous increasing function* of $n_{\alpha} > 0$. The $n_{\alpha''}$'s being a *product* (2.5) and the $g_{\alpha''}$'s being a *sum* (2.3 g) over ν''_A macrocells a'' , ν''_B macrocells b'' etc., the only choice is

$$g_{\alpha} = k \log n_{\alpha} \rightarrow g_a = k \log n_a; \quad g_b = k \log n_b; \quad \dots \quad (2.8)$$

where k is a *positive constant* (the *Boltzmann constant*, as we shall see in (4.7)).

However, the principle of detailed balancing (*DB*) is, for an arbitrary choice of macrocells, not valid⁶⁾. Therefore, we introduce the *non-negative* (asymmetric) *function* $L(x, y)$ (for $x, y \geq 0$)

$$L(x, y) = x \int_1^{y/x} dt \log t = y (\log y - \log x) - y + x \geq 0, \quad (2.9)^*$$

which permits to write (2.4) as a sum of 2 terms:

$$\left. \begin{aligned} \dot{S} &= \frac{k}{4} \sum_{(\nu)} \sum_{\alpha'' \alpha'} C_{\alpha''} C_{\alpha'} (A_{\alpha'; \alpha''}^{(-\nu)} L(n_{\alpha'}, n_{\alpha''}) + A_{\alpha''; \alpha'}^{(\nu)} L(n_{\alpha''}, n_{\alpha'})) \\ &+ \frac{k}{4} \sum_{(\nu)} \sum_{\alpha'' \alpha'} (C_{\alpha'} A_{\alpha'; \alpha''}^{(-\nu)} N_{\alpha''} - N_{\alpha'} A_{\alpha'; \alpha''}^{(-\nu)} C_{\alpha''} \\ &+ C_{\alpha''} A_{\alpha''; \alpha'}^{(\nu)} N_{\alpha'} - N_{\alpha''} A_{\alpha''; \alpha'}^{(\nu)} C_{\alpha'}) \geq 0. \end{aligned} \right\} (2.10)$$

The 1st term is non-negative. The N_{α} 's being arbitrary, there is no way to make the 2nd term non-negative. Therefore it has to be equal to zero. As the $N_{\alpha''}$ and $N_{\alpha'}$ are arbitrary, the condition on the transition probabilities is now (*Bo-statistics!*):

$$\sum_{\alpha''} C_{\alpha''} A_{\alpha'; \alpha''}^{(\nu)} = \sum_{\alpha''} A_{\alpha'; \alpha''}^{(-\nu)} C_{\alpha''}. \quad (2.11)$$

This is a much weaker condition than *DB*. It corresponds to the generalization of *DB* put forward by us, in I and II for the Boltzmann case (Bo). $\dot{S} = 0$, i.e. equilibrium is only reached, if, for all (ν) 's we have $n_{\alpha''} = n_{\alpha'}$ or $\log n_{\alpha''} = \log n_{\alpha'}$. We introduce now macrocells a, b, \dots with a *mean energy* E_a for A , E_b for B etc. The transition probabilities differ from zero, only if we have (approximative) *conservation of energy* for each collision or reaction (ν) (1.1)

$$E_{a''_1} + E_{a''_2} + \dots + E_{a''_A} + E_{b''_1} + \dots = E_{a'_1} + E_{a'_2} + \dots + E_{a'_A} + E_{b'_1} + \dots. \quad (2.12)$$

Thus, equilibrium is reached, only if

$$\log n_a = \frac{\mu_A - E_a}{k T}; \quad \log n_b = \frac{\mu_B - E_b}{k T}; \quad \dots \quad (2.13)$$

where the constants μ_A, μ_B, \dots satisfy (cf. 1.1)

$$\nu_A'' \mu_A + \nu_B'' \mu_B + \dots = \nu_A' \mu_A + \nu_B' \mu_B + \dots. \quad (2.14)$$

We shall now demonstrate, that T is the *absolute temperature* and μ_A the *chemical potential* of A . To do this, we consider a variation of external, macroscopic (geometric) parameters $r^* = \{r^{\varrho}\}$, $\varrho \sigma \dots = 12 \dots \omega$, and suppose the energies: $E_a = E_a[r^*]$. Then the *variation* δ of *internal energy* of the gas $U = U_A + U_B + \dots$ is:

$$\left. \begin{aligned} \delta U &= \delta (\sum_a N_a E_a[r^*] + \sum_b N_b E_b[r^*] + \dots) \\ &= (\sum_a \delta N_a \cdot E_a + \sum_b \delta N_b \cdot E_b + \dots) + \delta A^{(in)}, \end{aligned} \right\} (2.15)$$

⁶⁾ This inequality is due to the late W. PAULI. We made use of it in I and II.

where

$$\delta A^{(in)} \equiv K_{\varrho}^{(in)} \varrho r^{\varrho} \equiv (\sum_a N_a \partial_{\varrho} E_a [r] + \sum_b N_b \partial_{\varrho} E_b [r] + \dots) \delta r^{\varrho} \quad (2.16)*$$

is the work due to the ω external (incident) forces $K_{\varrho}^{(in)}$. Substituting in (2.1) (in the form $\delta S = -\sum_a g_a \delta N_a - \sum_b g_b \delta N_b - \dots$) (2.8) and the equilibrium value (2.13), we find

$$\delta S = T^{-1} (\sum_a \delta N_a \cdot E_a + \sum_b \delta N_b \cdot E_b + \dots - \mu_A \delta N_A - \mu_B \delta N_B - \dots) . \quad (2.17)$$

From (2.15), (2.16), and (2.17) follows

$$\delta U = T \delta S + \delta A^{(in)} + \sum_A \mu_A \delta N_A \equiv \delta U [S, r, N_A, N_B, \dots] , \quad (2.18)$$

which is the definition both of T and the μ_A 's**).

3. BE and FD Statistics

BOSE-EINSTEIN (BE) or FERMI-DIRAC (FD) statistics deviate from the *Boltzmann case* (Bo) by *induced* ($\lambda_A > 0$) or *anti-induced* ($\lambda_A < 0$) *transitions* to the macrocell a . We shall now consider C_a^0 as the number of microcells in a , and define, in the formulae of §§ 1 and 2

$$C_a = C_a^0 + \lambda_A N_a , \quad (3.1)$$

λ_A being the 'induction constant', depending but on the substance A . (One might think to introduce a macrocell depending constant λ_a . But, because the choice of macrocells is, up to (2.12) (energy-shells), arbitrary, one must have $\lambda_a = \lambda_A$). $C_{\alpha''}$ and $C_{\alpha'}$ depend now on the occupation numbers $N_{a''_1} \dots, N_{a'_1} \dots$. Thus (2.11) can not be satisfied if $\lambda_A \neq 0$. To make the 2nd term of S in (2.10) zero, we have to consider all products occurring on account of (3.1) $N_{a''_1} N_{a''_2} \dots N_{b''_1} \dots N_{a'_1} \dots$ separately in this 2nd term of (2.10). The *highest power* in the N_a 's requires

$$\lambda_A^{v''} \lambda_B^{v''} \dots = \lambda_A^{v'} \lambda_B^{v'} \dots . \quad (3.2)$$

Then the 2 terms containing $A_{\cdot\cdot}^{(v)}$ (and the 2 terms containing $A_{\cdot\cdot}^{(-v)}$) cancel out separately. In order to show that $\lambda_A = \pm 1$, we have to consider the *anti-molecules* or *antiparticles* \bar{A} , (charge-)conjugated (C) to A . Then the *creation* (v) of v'' pairs $A + \bar{A}$ (or *annihilation* ($-v$)) according to

$$v: \quad v'' (A + \bar{A}) + 2 A \leftarrow 2 A \quad (3.3; v)$$

may occur, if the energy is sufficient. Or, in this case we have (3.2)

$$(\lambda_A \lambda_{\bar{A}})^{v''} \lambda_A^2 = \lambda_A^2 , \quad (3.4; A + \bar{A})$$

*) $\partial_{\varrho} E_a [r] = \partial E_a [r] / \partial r^{\varrho}$.

**) μ_A is the *chemical potential per molecule of particle A* (and not per mole).

which requires $\lambda_A \lambda_{\bar{A}} = +1$, if $\lambda_A \neq 0$. On the other hand we have particles Φ (photons, π^0 mesons) which are *self-(charge-)conjugated* $\Phi = \bar{\Phi}$. In this case the *annihilation* (ν) (or *creation* ($-\nu$)) reaction

$$\nu: \quad \nu'' \Phi \leftarrow A + \bar{A} \quad (3.5; \nu)$$

may occur, where ν'' is *any positive integer*. (3.2) requires in this case $\lambda_\Phi = \lambda_A \lambda_{\bar{A}} = +1$. The Φ -particles are *bosons*. If ν'' is always even, we have $\lambda_\Phi^2 = 1$; $\lambda_\Phi = \pm 1$: The Φ -particles may be *bosons or fermions*. In order to infer, from $\lambda_A \lambda_{\bar{A}} = +1$, $\lambda_A = \lambda_{\bar{A}} = +1$ (bosons) or $\lambda_A = \lambda_{\bar{A}} = -1$ (fermions) for $A \neq \bar{A}$, we have to use the **CPT-theorem**, which states: In an anti-universe $A \rightarrow \bar{A}$ (C), where $t \rightarrow -t$ (T) and where right becomes left (P), the laws of physics should be identical. Only this requirement implies $\lambda_A = \lambda_{\bar{A}} = \pm 1$. Now (3.2) is the *law of conservation of statistics*. For example $C \rightleftarrows A + B$ is satisfied by $\lambda_C = 1$, $\lambda_A = \lambda_B = -1$: Two fermions A and B can only combine into a boson C etc.

The *next higher power* involves one factor λ_A . Then, in order that the $A_{\cdot\cdot\cdot}^{(\nu)}$ terms cancel out again the $A_{\cdot\cdot\cdot}^{(\nu)}$ terms in the 2nd sum in (2.10), we have, the N_a 's being arbitrary, the conditions:

$$\sum_{a''_1} C_{a''_1}^0 A_{a''_1 a''_2 \dots a''_{\nu''_A} b''_1 \dots b'_1 \dots a'_1 \dots b'_{\nu'_B}}^{(\nu)} = \sum_{a''_1} A_{a'_1 \dots b'_1 \dots b'_{\nu'_B}; a''_1 a''_2 \dots a''_{\nu''_A} b''_1 \dots b''_{\nu''_B}}^{(-\nu)} C_{a''_1}^0 \quad (3.4)$$

for *all sums over an index* a''_1, b''_1 (or $a'_1, b'_1 \dots$). This condition is *weaker* than *DB*, but *stronger* than in the Boltzmann case (2.11). (We shall show, in a subsequent publication, how, in the case of *quantized fields* this condition arises from the *unitarity of the S-matrix*). The lower powers in the N_a 's cancel out, if (3.4) is satisfied.

The considerations of § 2, concerning the equilibrium case, are still valid: However n_a is not any longer the mean occupation number per microcell in a , but we have the relation:

$$n_a = \frac{N_a}{C_a} = \frac{N_a}{C_a + \lambda_A N_a} \quad (3.5)$$

which, using (2.13), leads to

$$N_a = C_a^0 (e^{(E_a - \mu_A)/kT} - \lambda_A)^{-1}; \quad \lambda_A = \begin{cases} +1 & BE \\ 0 & Bo \\ -1 & FD \end{cases} \quad (3.6)$$

The equilibrium condition for the chemical potentials (2.14) shows, on account of (3.5), that for self- (C) -conjugated particles (photons π^0 mesons etc.) $\Phi = \bar{\Phi}$ we have

$$\mu_\Phi = 0; \quad \Phi = \bar{\Phi}. \quad (3.7)$$

The chemical potential of self- (C) -conjugated particles Φ is zero. If $A \neq \bar{A}$, we have, on account of (2.14) and (3.5)

$$\mu_A = -\mu_{\bar{A}}; \quad A \neq \bar{A}. \quad (3.8)$$

The chemical potential $\mu_{\bar{A}}$ of anti-molecules A is numerically equal to μ_A but of opposite sign.

The partial differential equations

$$\frac{\partial S [\dots N_a \dots N_b \dots]}{\partial N_a} = -g_a = -k \log n_a$$

may be integrated for arbitrary values of λ_A , valid even in the non equilibrium case. The integration yields

$$S = \sum_A S_A = -k \sum_A \sum_a C_a^0 ((n_a^{-1} - \lambda_A)^{-1} \log n_a + \lambda_A^{-1} \log (1 - n_a \lambda_A)). \quad (3.9)$$

n_a is given by (3.5). The *Boltzmann case* is obtained as the limit $\lambda_A \rightarrow 0$.

$$\lim_{\lambda_A \rightarrow 0} S_A = -k \sum_a N_a (\log n_a - 1); \quad n_a \rightarrow \frac{N_a}{C_a^0}. \quad (3.10)$$

The integration constant in (3.9) or (3.10) must be chosen to be zero, because empty (radiationless) space $N_a = 0$ (or $n_a = 0$) has zero entropy.

4. The BOLTZMANN Approximation

The *Boltzmann approximation*, at equilibrium, is realized if $N_a \ll C_a^0$. In this case, according to (2.13) and (3.5), we have

$$n_a = e^{(\mu_A - E_a)/kT} \cong \left(\frac{N_a}{C_a^0} \right) \left(1 + \lambda_A \frac{N_a}{C_a^0} \right)^{-1} \rightarrow \frac{N_a}{C_a^0} \ll 1, \quad (4.1)$$

and n_a is the *mean occupation number per microcell of volume* $\omega_A = h^3 A$. The 3 statistics BE, FD and Bo give the same result. Multiplying (4.1) with C_a^0 and summing over all a 's, we obtain in terms of the *sum over states* Z_A in μ -space of A

$$Z_A [T, r] = \sum_a C_a^0 e^{-E_a[r]/kT} \rightarrow h^{-3A} \int d\omega_A e^{-H_A [p_A, q_A, r]/kT}, \quad (4.2)^*$$

(with $d\omega_A = dp_1 \dots dp_{f_A} dq_1 \dots dq_{f_A}$ and $H_A [\dots, r] =$ Hamiltonian of a single molecule A), and

$$\sum_a N_a = N_A = e^{\mu_A [T, r, N_A]/kT} Z_A [T, r], \quad (4.3)$$

the *chemical potential* μ_A as a function of T , of the *external parameters* $r = \{r^0\}$ and of N_A . For a *perfect non relativistic gas* in a volume V , we have

$$H_A [\dots] = E_{A0} + (|\vec{p}|^2/2A) + \Phi_A [\vec{q}, r] + H_A^{(int)} [\vec{p}^{3+1} \dots \vec{p}^{3+f_A} q_{3+1} \dots q_{3+f_A}], \quad (4.4)$$

where

$$|\vec{p}|^2 = g^{ik} p_i p_k (i, k = 1, 2, 3), \quad \{\vec{p}, \vec{q}\} = \{p^i, q_i\}$$

are the *translational coordinates* of the centre of mass, and

$$\{\vec{p}^{3+1} \dots \vec{p}^{3+f_A(int)} q_{3+1} \dots q_{3+f_A(int)}\}.$$

are the interior coordinates of the molecule A .

*) The last equation is valid in the *classical approximation*:

$$d\omega_A/h^3 A \equiv C_a^0 \gg 1, \text{ i.e. } h \rightarrow 0.$$

E_{A0} is the rest energy of a molecule A of mass A .

$$g^{ik} = g_{ik} = g^i_k = g^k_i = \pm \delta^k_i$$

is the *Euclidian metric of physical space**). $\phi_A[\vec{q}, \vec{r}]$ is the potential energy, depending on the \vec{r}^q 's. For a gas enclosed in a volume V , we have

$$\phi_A[\vec{q}, \vec{r}] = 0 \quad \text{for} \quad \vec{q} \in V, \quad \phi_A[\vec{q}, \vec{r}] = +\infty \quad \text{for} \quad \vec{q} \notin V.$$

$$Z_A = Z_{A(trans)}[T, V] \cdot Z_{A(int)}[T] \quad (4.5)$$

is a product over a *trans*-(-*lational*) and an *int*-(-*erior*) part. We have

$$Z_{A(trans)}[T, V] \rightarrow e^{-E_{A0}/kT} V (2\pi A k T)^{3/2} h^{-3}. \quad (4.6)$$

For the partial p_A pressure of A , we have, according to

$$\delta A^{(in)} = (- \sum_A p_A) \delta V,$$

in (2.16), and an account of (4.3)

$$\left. \begin{aligned} -p_A &= \sum_a N_a \frac{\partial E_a[V]}{\partial V} = k T e^{\mu_A/kT} \frac{\partial Z_A[T, V]}{\partial V} \\ &= N_A k T \frac{\partial \log Z_A[T, V]}{\partial V} = N_A k T V^{-1}. \end{aligned} \right\} \quad (4.7)$$

Thus k is the *Boltzmann constant*. Computing μ_A in terms of T and p_A we find for *monoatomic gas without spin* ($Z_{(int)}[T] = 1$) (e.g. He^4)

$$\mu_A[T, p_A] = E_{A0} + k T \left(-\frac{5}{2} \log T + \log p_A - \log ((2\pi A)^{3/2} k^{5/2} h^{-3}) \right). \quad (4.8)$$

For a gas with interior degrees of freedom, a term $-k T \log Z_{(int)}[T]$ must be added. If only N_A molecules of A are present, we have $p_A = p$ and $\mu_A = g_A[T, p]$ (*Gibbs potential per molecule*). The *interior energy* is

$$U_A[T] = N_A \frac{\partial(\log Z_A[T, V])}{\partial(-k T)^{-1}} \equiv N_A \left(E_{A0} + \frac{3}{2} k T \right) \equiv N_A (E_{A0} + c_{V_A} T). \quad (4.9)$$

The 2nd and 3rd eq. are only valid for a monoatomic gas A . From the Gibbs identity

$$\text{follows} \quad G_A[T, p_A, N_A] = N_A \mu_A[T, p_A] = U_A - T S_A + p_A V, \quad (4.10)$$

$$\left. \begin{aligned} S_A[T, p_A, N_A] &\equiv N_A s_A[T, p_A] \\ &= N_A \left(\frac{5}{2} k \log T - k \log p_A + k \log ((2\pi A)^{3/2} (k e)^{5/2} h^{-3}) \right) \\ &\equiv N_A (c_{p_A} \log T - k \log p_A + s_A[1,1]), \end{aligned} \right\} \quad (4.11)$$

*) Euclidian metric is necessary to give a lower ($+\delta_k^i$; $T > 0$) or upper ($-\delta_k^i$; $T < 0$) limit for the kinetic energy.

where $s_A [1, 1]$ is the *entropy constant* (per molecule) and $c_{p_A} = 5 k/2$ the *heat capacity at constant pressure* p_A (per molecule). Or, posing $s_A^{(c)} [T \rightarrow 0] = 0$ for the condensed^(c) state of A , the *chemical constant** of A is

$$i_A = \frac{s_A [1, 1] - c_{p_A}}{k} = \log ((2 \pi A)^{3/2} k^{5/2} h^{-3}) \quad (4.12)$$

for a *monoatomic, spinless gas*. (4.11) may be obtained directly from (3.10), if (2.13) and (4.3) are used. (We remark, that in this evaluation of S_A the $N_A \log N_A$ term does not occur. This is due to the fact that we have used only *occupation numbers* N_a in the definition of S (2.1)).

For a mixture of gases, we introduce the concentrations

$$0 \leq c_A = \frac{N_A}{\sum_B N_B} \leq 1; \quad p_A = c_A p; \quad \sum_A c_A = 1 \quad (4.13)$$

and use the definition of the Gibbs potential g_A (per molecule A) related to μ_A by $G = \sum_A N_A \mu_A [T, p, c_A]$

$$\mu_A [T, p, c_A] = \mu_A [T, p_A] \equiv g_A [T, p] + k T \log c_A \quad (4.14)$$

from which the law of mass action follows, using (2.14):

$$\frac{\prod_{A''} c_{A''}^{\nu_{A''}''}}{\prod_{A'} c_{A'}^{\nu_{A'}'}} = \exp (- (k T)^{-1} (\sum_{A''} \nu_{A''}'' g_{A''} - \sum_{A'} \nu_{A'}' g_{A'}) [T, p]) \equiv K^{(v)} [T, p] \quad (4.5)$$

where the $g_A [T, p]$ may be evaluated in terms of the $\mu_A [T, p_A]$ (4.14), using (4.3) and taking account of the interior degrees of freedom.

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*) The chemical constant i_A is defined by the vapor pressure equation

$$\lim_{T \rightarrow 0} \log p [T] = i_A - \frac{w_{A0}^{(g) \leftarrow (c)}}{k T} + \frac{c_{p_A}}{k} \log T \quad (4.12^*)$$

where $w_{A0}^{(g) \leftarrow (c)}$ is the *enthalpy difference* (per molecule) between the gaseous^(g) and the condensed^(c) phase, extrapolated to $T \rightarrow 0$. The heat capacity satisfies $c^{(c)} [T] \rightarrow 0 (\propto T^3)$.