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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 $A, B, \ldots$ 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 $\mu_A, \mu_B, \ldots$ 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 $(= \tilde{\eta}^{\tilde{\zeta}} \tau \alpha)$-*theorem* in a perfect gas, where different kinds of molecules (or particles) $A, B, \ldots$ 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* ($D\,B$), which, as BOLTZMANN himself know already[1]), 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 papers[2])[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 attributed[7]). 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 PAULI[4]) did (basing himself on the ideas of JORDAN, KRAMERS, OMSTEIN, and BOTHE[5])). 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* $\bar{A}$, $\bar{B}, \ldots$, 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 $A\,B\ldots = 12\ldots C$, between which collisions and chemical reactions may occur according to

$$(\nu) \equiv \Sigma_{A''}\, \nu''_{A''}\, A'' \leftarrow \Sigma_{A'}\, \nu'_{A'}\, A' \equiv \nu''_A\, A + \nu''_B\, B + \cdots \leftarrow \nu'_A\, A + \nu'_B\, B + \cdots . \quad (1.1)$$

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

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

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

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

For example the reaction $(\nu) \equiv C \leftarrow A + B$, involving 2 initial components A and B combining into C is different from $(2\,\nu) \equiv 2\,C \leftarrow 2\,A + 2\,B$. For each A, we introduce a *separate μ-space*: $\{p_i, q_i\}$, $i\,k \ldots = 12\ldots f_A$, 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 $a, a' \ldots$ or

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

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

$$C_a \gg 1; \quad C_b \gg 1; \quad \ldots . \quad (1.2)$$

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

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

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

$$N_A = \Sigma_a\, N_a; \quad N_B = \Sigma_b\, N_b; \quad \ldots . \quad (1.4)$$

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 $A_{a'';\,a'} \geqslant 0$ is the *transition probability*. The net gain is:

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

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*) $\dot{N}_{a''}(t) = (N_{a''}(t'') - N_{a''}(t'))\,(t'' - t')^{-1} = \delta N_{a''}/\delta t$ for a period $\delta t = t'' - t' \lessgtr 0$ 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 $2\,A \leftarrow 2\,A$ 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:

$$\left.\begin{aligned} \dot{N}_{a''(2A \leftarrow 2A)} = 2 \sum_{a_1', a_2', a_2''} (&C_{a''}\, C_{a_2''}\, A_{a'' a_2'';\, a_1' a_2'}\, N_{a_1'}\, N_{a_2'} \\ &- C_{a_1'}\, C_{a_2'}\, A_{a_1' a_2';\, a'' a_2''}\, N_{a''}\, N_{a_2''})\,. \end{aligned}\right\} \quad (1.5,\, 2\,A \leftarrow 2\,A)$$

The factor 2 is due to the fact that

$$A_{a_1'' a_2'';\, a_1' a_2'} = A_{a_2'' a_1'';\, a_1' a_2'} = A_{a_1'' a_2'';\, a_2' a_1'} \geqslant 0$$

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; $2\,A \rightarrow 2\,A$).

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

$$A^{(\nu)}_{a'' b'';\, c'}\ (\geqslant 0) \quad \text{and} \quad A^{(-\nu)}_{c';\, a'' b''}\ (\geqslant 0)\,.$$

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

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

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

$$\left.\begin{aligned} \dot{N}_{a''(\nu)} = \nu_A'' \sum_{a_2'' \ldots b_{\nu_B''}'' a_1' \ldots b_{\nu_B'}'} (&C_{a''}\, C_{a_2''} \ldots C_{a_{\nu_A''}''}\, C_{b_1''} \ldots C_{b_{\nu_B''}''} \ldots \\ &\ldots A^{(\nu)}_{a'' a_2'' \ldots a_{\nu_A''}'' b_1'' \ldots b_{\nu_B''}'';\, a_1' \ldots a_{\nu_A'}'\, b_1' \ldots b_{\nu_B''}' \ldots}\, N_{a_1'} \ldots N_{a_{\nu_A'}'}\, N_{b_1'} \ldots N_{b_{\nu_B'}'} \\ &- C_{a_1'} \ldots C_{a_{\nu_A'}'}\, C_{b_1'} \ldots C_{b_{\nu_B'}'} \ldots A^{(-\nu)}_{a_1' \ldots a_{\nu_A'}'\, b_1' \ldots b_{\nu_B'}' \ldots;\, a'' a_2'' \ldots a_{\nu_A''}''\, b_1'' \ldots b_{\nu_B''}'' \ldots} \\ &N_{a''}\, N_{a_2''} \ldots N_{a_{\nu_A''}''}\, N_{b_1''} \ldots N_{b_{\nu_B''}''} \ldots). \end{aligned}\right\} \quad (1.5;\, \nu)$$

The factor ν_A'' arises from the fact, that the $A^{(\nu)}_{a_1'' a_2'' \ldots a_{\nu_A''}'' b_1'' \ldots;\, a_1' \ldots}$ and $A^{(-\nu)}_{a_1' \ldots;\, a_1'' a_2'' \ldots a_{\nu_A''}'' b_1'' \ldots}$ are *symmetric* in the ν_A'' indices a_i'', like the factor 2 in (1.5, $2\,A \leftarrow 2\,A$). 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 $N^{n'}_{a_i'}$ but to

$$N_{a_i'}\,(N_{a_i'} - 1) \cdots \frac{N_{a_i'} - n'}{n'!}\ (n' \leqslant \nu_A')\,.$$

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

$$n'' \, (C_{a''_i})^{n''} \, A^{(\nu)}_{\ldots a''_i a''_i \ldots a''_i \ldots; a'_1 \ldots} \, .$$

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

The total net gain in a'' is therefore

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

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

$$\dot{S} = \Sigma_a \frac{\partial S}{\partial N_a} \dot{N}_a + \Sigma_b \frac{\partial S}{\partial N_b} \dot{N}_b + \cdots \equiv - \Sigma_{a''} \, g_{a''} \, \dot{N}_{a''} - \Sigma_{b''} \, g_{b''} \, \dot{N}_{b''} - \cdots \geqslant 0 \, , \tag{2.1}$$

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

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

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 $g_{a''_1} + g_{a''_2} + \cdots + g_{a''_{\nu''_A}}$, obtaining

$$\left.\begin{aligned} \dot{S} = - \frac{1}{2} \, \Sigma_{(\nu)} \, \Sigma_{a'_1 \ldots, a''_1 \ldots b''_{\nu''_B} \ldots} \, (g_{a''_1} + \cdots + g_{a''_{\nu''_A}} + g_{b''_1} + \cdots) \\ \times \, (C_{a''_1} \ldots C_{\nu''_A} \, C_{b''_1} \ldots A^{(\nu)}_{a''_1 \ldots a''_{\nu''_A} b''_1 \ldots; a'_1 \ldots b'_{\nu'_B} \ldots} \, N_{a'_1} \ldots N_{b'_{\nu'_B}} \ldots \\ - \, C_{a'_1} \ldots C_{b'_{\nu'_B}} \ldots A^{(-\nu)}_{a'_1 \ldots b'_{\nu'_B} \ldots; a''_1 \ldots a''_{\nu''_A} b''_1 \ldots} \, N_{a''_1} \ldots N_{a''_{\nu''_A}} \, N_{b''_1} \ldots) \, , \end{aligned}\right\} \tag{2.2}$$

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):

$$\alpha'' = \{a''_1 \ldots a''_{\nu''_A} \, b''_1 \ldots b''_{\nu''_B} \ldots\}; \; \alpha' = \{a'_1 \ldots b'_{\nu'_B} \ldots\};$$

introducing the *sums*:

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

and the *products*:

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

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

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

(2.2) reduces now to the simple form:

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

with the products:

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

where

$$n_a = \frac{N_a}{C_a} \geqslant 0 ; \quad n_b = \frac{N_b}{C_b} \geqslant 0 \tag{2.6}$$

are (in the Boltzmann case) the *mean occupation number of a microcell* inside the macrocell a for A, b for $B, \ldots$. 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 $A^{(\nu)}_{\alpha'';\alpha'} = A^{(-\nu)}_{\alpha';\alpha''}$ leading to

$$\dot{S} = \frac{1}{4} \Sigma_{(\nu)} \Sigma_{\alpha'\alpha''} C_{\alpha''} C_{\alpha'} A^{(\nu)}_{\alpha'';\alpha'} (g_{\alpha''} - g_{\alpha'}) (n_{\alpha''} - n_{\alpha'}) \geqslant 0 . \tag{2.7; DB}$$

The common factor $C_{\alpha''} C_{\alpha'} A^{(\nu)}_{\alpha'';\alpha'}$, 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

$$g_\alpha = k \log n_\alpha \to g_a = k \log n_a ; \quad g_b = k \log n_b ; \quad \ldots \tag{2.8}$$

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 valid[6]). Therefore, we introduce the *non-negative* (asymmetric) *function* $L(x, y)$ (for $x, y \geqslant 0$)

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

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

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

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*!):

$$\Sigma_{\alpha''} C_{\alpha''} A^{(\nu)}_{\alpha';\alpha'} = \Sigma_{\alpha''} A^{(-\nu)}_{\alpha';\alpha''} C_{\alpha''} . \tag{2.11}$$

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 $a, b, \ldots$ 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)

$$E_{a''_1} + E_{a''_2} + \cdots + E_{a''_{\nu''_A}} + E_{b''_1} + \cdots = E_{a'_1} + E_{a'_2} + \cdots + E_{a'_{\nu'_A}} + E_{b'_1} + \cdots . \tag{2.12}$$

Thus, equilibrium is reached, only if

$$\log n_a = \frac{\mu_A - E_a}{k\,T} ; \quad \log n_b = \frac{\mu_B - E_b}{k\,T} ; \quad \ldots \tag{2.13}$$

where the constants $\mu_A\, \mu_B, \ldots$ satisfy (cf. 1.1)

$$\nu''_A \mu_A + \nu''_B \mu_B + \cdots = \nu'_A \mu_A + \nu'_B \mu_B + \cdots . \tag{2.14}$$

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 $r^\cdot = \{r^\varrho\}$, $\varrho\, \sigma \ldots = 12 \ldots \omega$, and suppose the energies: $E_a = E_a [r^\cdot]$. Then the *variation* $\boldsymbol{\delta}$ *of internal energy* of the gas $U = U_A + U_B + \cdots$ is:

$$\left.\begin{aligned} \boldsymbol{\delta} U &= \boldsymbol{\delta} \left(\Sigma_a N_a E_a [r^\cdot] + \Sigma_b N_b E_b [r^\cdot] + \cdots \right) \\ &= \left(\Sigma_a \delta N_a \cdot E_a + \Sigma_b \delta N_b \cdot E_b + \cdots \right) + \delta A^{(in)} , \end{aligned}\right\} \tag{2.15}$$

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

where

$$\delta A^{(in)} \equiv K_\varrho^{(in)} \varrho\, r^\varrho \equiv (\Sigma_a N_a \delta_\varrho E_a [r^\cdot] + \Sigma_b N_b \partial_\varrho E_b [r^\cdot] + \cdots) \delta r^\varrho \quad (2.16)^*)$$

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

$$\boldsymbol{\delta} S = T^{-1} (\Sigma_a \delta N_a \cdot E_a + \Sigma_b \delta N_b \cdot E_b + \cdots - \mu_A \delta N_A - \mu_B \delta N_B - \cdots) . \quad (2.17)$$

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

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

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 $N_{a_1''} \ldots, N_{a_1'} \ldots$. Thus (2.11) can not be satisfied if $\lambda_A \neq 0$. To make the 2nd term of $\dot{S}$ in (2.10) zero, we have to consider all products occurring on account of (3.1) $N_{a_1''} N_{a_2''} \ldots N_{b_1''} \ldots N_{a_1'} \ldots$ separately in this 2nd term of (2.10). The *highest power* in the N_a's requires

$$\lambda_A^{\nu_A''} \lambda_B^{\nu_B''} \cdots = \lambda_A^{\nu_A'} \lambda_B^{\nu_B'} \cdots . \quad (3.2)$$

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

$$\nu: \quad \nu'' (A + \overline{A}) + 2 A \leftarrow 2 A \quad (3.3; \nu)$$

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

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

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

**) 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

$$\nu: \quad \nu'' \Phi \leftarrow A + \bar{A} \tag{3.5; ν}$$

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 $A \to \bar{A}$ (***C***), where $t \to -t$ (***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 $A^{(-\nu)}_{\cdot;\cdot}$ terms cancel out again the $A^{(\nu)}_{\cdot;\cdot}$ terms in the 2nd sum in (2.10), we have, the N_a's being arbitrary, the conditions:

$$\Sigma_{a_1''} C^0_{a_1''} A^{(\nu)}_{a_1'' a_2'' \ldots a_{\nu''_A}'' b_1'' \ldots ; b_1' \ldots a_1' \ldots b_{\nu'_B}'} = \Sigma_{a_1''} A^{(-\nu)}_{a_1' \ldots b_1' \ldots b_{\nu'_B}' ; a_1'' a_2'' \ldots a_{\nu''_A}'' b_1'' \ldots} C^0_{a_1''} \tag{3.4}$$

for *all sums over an index* a_1'', b_1'' (or a_1', b_1' ...). 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:

$$n_a = \frac{N_a}{C_a} = \frac{N_a}{C_a^0 + \lambda_A N_a} \tag{3.5}$$

which, using (2.13), leads to

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

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

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

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

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

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

The partial differential equations

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

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

$$S = \Sigma_A\, S_A = -\,k\, \Sigma_A\, \Sigma_a\, C_a^0\, ((n_a^{-1} - \lambda_A)^{-1} \log n_a + \lambda_A^{-1} \log\, (1 - n_a \lambda_A))\,. \tag{3.9}$$

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

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

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

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

and n_a is the *mean occupation number per microcell of volume* $\omega_A = h^{f_A}$. 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

$$Z_A\,[T, r^{\cdot}] = \Sigma_a\, C_a^0\, e^{-E_a[r^{\cdot}]/kT} \to h^{-f_A} \int d\omega_A\, e^{-H_A[p_{\cdot A}\, q_A\, r^{\cdot}]/kT}\,, \tag{4.2*}$$

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

$$\Sigma_a\, N_a = N_A = e^{\mu_A[T, r^{\cdot}, N_A]/kT}\, Z_A\,[T, r^{\cdot}]\,, \tag{4.3}$$

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

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

where

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

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

$$\{p^{3+1} \ldots p^{3+f_{A(int)}}\, q_{3+1} \ldots q_{3+f_{A(int)}}\}\,.$$

are the interior coordinates of the molecule A.

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

$$d\omega_A/h^{f_A} \equiv C_a^0 \gg 1, \text{ i.e. } h \to 0.$$

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

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

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

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

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

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

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

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

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

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)

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

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*

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

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

$$G_A\,[T, p_A, N_A] = N_A\, \mu_A\,[T, p_A] = U_A - T\, S_A + p_A\, V\,, \tag{4.10}$$

follows

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

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*) Euclidian metric is necessary to give a lower ($+\,\delta^i_k$; $T > 0$) or upper ($-\,\delta^i_k$; $T < 0$) limit for the cinetic 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 $s_A^{(c)}\,[T \to 0] = 0$ for the condensed$^{(c)}$ state of A, the *chemical constant**) of A is

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

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

$$0 \leqslant c_A = \frac{N_A}{\Sigma_B\,N_B} \leqslant 1\,; \quad p_A = c_A\,p\,; \quad \Sigma_A\,c_A = 1 \tag{4.13}$$

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

$$\mu_A\,[T, p, c_A] = \mu_A\,[T, p_A] \equiv g_A\,[T, p] + k\,T \log c_A \tag{4.14}$$

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

$$\frac{\Pi_{A''}\,c_{A''}^{\nu''_{A''}}}{\Pi_{A'}\,c_{A'}^{\nu'_{A'}}} = \exp\left(-\,(k\,T)^{-1}\,(\Sigma_{A''}\,\nu''_{A''}\,g_{A''} - \Sigma_{A'}\,\nu'_{A'}\,g_{A'})\,[T, p]\right) \equiv K^{(\nu)}\,[T, p] \tag{4.5}$$

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

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

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