ON THE QUANTUM STATISTICAL BASIS OF NON-EQUILIBRIUM THERMODYNAMICS

J. VLIEGER

STELLINGEN

I

In analogie met gewone Wigner-distributiefuncties, die gebruikt kunnen worden om quantummechanische ensemblegemiddelden als klassieke fasegemiddelden te schrijven, kunnen ook "simultane Wigner-distributiefuncties" worden ingevoerd om quantummechanische tijd-correlatiefuncties als klassieke fasegemiddelden te berekenen.

Hoofdstuk II van dit proefschrift.

II

De Wigner-distributiefuncties van het micro-kanonieke ensemble in de gevallen van Bose-Einstein- en Fermi-Dirac-statistiek kunnen door middel van integraalvergelijkingen worden uitgedrukt in de micro-kanonieke Wigner-distributiefunctie voor Maxwell-Boltzmann-statistiek. Dit is ook mogelijk voor Wigner-distributiefuncties van andere ensembles.

Hoofdstuk III van dit proefschrift.

III

De bewering van Barut, dat Wigner-distributiefuncties alleen gebruikt kunnen worden om verwachtingswaarden van een zeer beperkte klasse van quantummechanische operatoren te berekenen, berust op de door hem gemaakte onjuiste beperkende veronderstelling, dat de pseudo-klassieke functies, die volgens de regel van Weyl met deze operatoren corresponderen, niet van de constante van Planck zouden mogen afhangen.

A. O. Barut, Phys. Rev. **108** (1957) 565.

IV

De door Oppenheim behandelde methode, om de Bloch-vergelijking voor de Wigner-distributiefunctie van het kanonieke ensemble op te lossen door middel van een reeksontwikkeling van deze distributiefunctie naar machten van de constante van Planck, kan alleen worden toegepast in het geval van Maxwell-Boltzmann-statistiek. Zijn bewering, dat deze methode ook gebruikt kan worden in de gevallen van Bose-Einstein- en Fermi-Dirac-statistiek, is onjuist, daar in deze gevallen de kanonieke Wigner-distributiefuncties niet in machtreeksen in de constante van Planck ontwikkeld kunnen worden.

I. Oppenheim, Dissertation, Yale University (1957), part I.

V

Het reële deel van de door Kirkwood ingevoerde complexe quantummechanische distributiefunctie in de faseruimte kan, evenals de Wigner-distributiefunctie, gebruikt worden om ensemblegemiddelden van quantummechanische operatoren als fasegemiddelden van klassieke functies te schrijven, indien men in plaats van de regel van Weyl een iets andere regel voor de correspondentie tussen operatoren en klassieke functies definieert.

J. G. Kirkwood, Phys. Rev. **44** (1933) 31.

VI

De door Butler en Friedman afgeleide exacte uitdrukking voor de quantummechanische toestandssom van een systeem, bestaande uit bosonen, is in feite niets anders dan de als padenintegraal geschreven uitdrukking voor deze toestandssom, die reeds door Feynman was gebruikt als uitgangspunt van zijn theorie over vloeibaar helium.

R. P. Feynman, Phys. Rev. **91** (1953) 1291.
S. T. Butler en M. H. Friedman, Phys. Rev. **98** (1955) 287.

VII

Eenzelfde verband, als er bestaat tussen padenintegralen van Feynman in de quantumtheorie en het variatieprincipe van Hamilton in de klassieke mechanica, bestaat ook tussen padenintegralen in de faseruimte, zoals die door Groenewold zijn ingevoerd, en het zogenaamde gewijzigde variatieprincipe van Hamilton.

R. P. Feynman, Rev. mod. Phys. **20** (1948) 367.
H. J. Groenewold, Kgl. Dan. Vid. Selsk. Mat.-Fys. Medd. **30** (1956) nr. 19.
J. Vlieger, P. Mazur en S. R. de Groot, Physica **25** (1959) 55.

VIII

De door Kramers besproken moeilijkheid om de zogenaamde Darwin-term in de Hamilton-operator van een quantummechanisch systeem van electrisch geladen deeltjes op eenduidige wijze te hermiteïseren, kan worden opgelost. Men kan namelijk bewijzen, dat deze term van een dusdanige vorm is dat een ondubbelzinnige hermiteïsering mogelijk is.

H. A. Kramers, Die Grundlagen der Quantentheorie, Leipzig (1938), pg. 108, 109.

IX

De statistisch mechanische theorie over de druk en de ponderomotorische kracht in een diëlectricum van Mazur en de Groot kan worden uitgebreid tot het geval van een gepolariseerd en gemagnetiseerd medium, met behulp van de Darwin-hamiltoniaan.

P. Mazur en S. R. de Groot, Physica **22** (1956) 657.

X

Voor matig verdichte gassen mag men, bij het berekenen van de gemiddelde correctie op de polariseerbaarheid ten gevolge van de intermoleculaire krachten, niet zonder meer veronderstellen, dat de moleculen steeds op voldoend grote afstanden van elkaar zijn, zodat het uitsluitingsprincipe niet in rekening gebracht behoeft te worden en de dipool-dipool-wisselwerkingsbenadering geldig is.

L. Jansen en P. Mazur, Physica **21** (1955) 193; P. Mazur en L. Jansen, Physica **21** (1955) 208.
P. Mazur en M. Mandel, Physica **22** (1956) 289, 299.

XI

De bewering van Dingle, dat ook in de door Gorter gegeven afleiding van de formule voor het fontein-effect in vloeibaar helium II stilzwijgend verondersteld is dat de entropieën van het normale en het superfluïdum additief zijn, is onjuist.

C. J. Gorter, Physica **15** (1949) 523.
R. B. Dingle, Phil. Mag. **42** (1951) 1080.

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS DR G. SEVENSTER, HOOGLERAAR IN DE FACULTEIT DER GODGELEERDHEID, TEGEN DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP WOENSDAG 22 NOVEMBER 1961 TE 15 UUR

DOOR

JAN VLIEGER

GEBOREN TE LEIDEN IN 1929

Promotor: PROF. DR S. R. DE GROOT

Aan de nagedachtenis van mijn vader

Aan mijn moeder

Op verzoek van de Faculteit der Wis- en Natuurkunde volgen hier enige gegevens over mijn studie.

In 1947 legde ik het eindexamen gymnasium β af aan het Stedelijk Gymnasium te Leiden. In hetzelfde jaar begon ik mijn studie aan de Universiteit te Leiden, alwaar ik in januari 1951 het candidaatsexamen wis- en natuurkunde *A* aflegde. In januari 1954 volgde het doctoraalexamen met hoofdvak natuurkunde en bijvakken wiskunde en mechanica.

Vanaf september 1952 was ik werkzaam op het Instituut-Lorentz voor theoretische natuurkunde te Leiden, aanvankelijk onder leiding van Prof. Dr J. Korringa. Vanaf september 1953 verrichtte ik onder leiding van Prof. Dr S. R. de Groot en Prof. Dr P. Mazur onderzoek, o.m. over de statistische grondslagen van de thermodynamica van niet-evenwichtsprocessen en de statistische mechanica van materie in een electromagnetisch veld.

Van april 1954 tot januari 1956 moest ik mijn werkzaamheden op het Instituut-Lorentz onderbreken voor de vervulling van de militaire dienstplicht.

PUBLICATIES

Thermodynamical theory of galvanomagnetic and thermomagnetic phenomena (met R. Fieschi, S. R. de Groot en P. Mazur), Physica **20** (1954) 245.

On the theory of reciprocal relations between irreversible processes (met S. R. de Groot), Physica **20** (1954) 372.

Relations between path integrals and the variational principles of Hamilton (met P. Mazur en S. R. de Groot), Physica **25** (1959) 55.

On the quantum statistical basis of non-equilibrium thermodynamics (met P. Mazur en S. R. de Groot), Physica **27** (1961) 353, 957, 974.

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On the quantum statistical basis of non-equilibrium thermodynamics (met P. Mazur en S. R. de Groot), Physica 27 (1961) 353, 957, 974.

CONTENTS

INTRODUCTION

In this thesis we shall be concerned with the quantum statistical foundations of the Onsager reciprocal relations in non-equilibrium thermodynamics. We shall make use of Wigner's phase space representation of quantum statistical mechanics. The theory of the foundations of the Onsager relations can thus be developed in a way analogous to the classical treatment, given by de Groot and Mazur [1]).

In chapter I we shall discuss the theory of ordinary Wigner distribution functions. Furthermore we shall introduce the equilibrium distribution function of a set of extensive state variables, which provide a macroscopic description of the system, assuming that these variables are represented by commuting operators in quantum theory. This probability distribution function will be expressed in terms of the Wigner distribution function of the micro-canonical ensemble. The properties of equilibrium distribution functions of extensive variables will be studied.

In chapter II we shall introduce "joint Wigner distribution functions", which may be used for the calculation of quantum mechanical correlation functions. Furthermore we shall define the joint equilibrium distribution function of a set of extensive state variables. This distribution function will be expressed in terms of the joint Wigner distribution function of the micro-canonical ensemble. We shall derive several properties of joint equilibrium distribution functions of extensive variables, in particular the so-called property of detailed balance.

Joint distribution functions of extensive state variables are in general not probability distribution functions. It will be shown, however, that the joint equilibrium distribution function does represent a joint probability, if the set of quantum mechanical operators, corresponding to the state variables, is of a certain class.

The theory of distribution functions of extensive state variables will be used for the well-known derivation of the Onsager reciprocal relations.

The theory in chapters I and II will be developed for Maxwell-Boltzmann statistics only. The extension to the cases of Bose-Einstein and Fermi-Dirac statistics will be given in chapter III.

REFERENCE

1) Groot, S. R. de and Mazur, P., Non-equilibrium thermodynamics, (to be published).

Chapter I

THE THEORY OF ORDINARY WIGNER DISTRIBUTION FUNCTIONS

Synopsis

The quantum statistical theory of Wigner distribution functions is developed to serve as a basis for the derivation of the Onsager reciprocal relations in non-equilibrium thermodynamics. The theory is closely analogous to the classical treatment, given by de Groot and Mazur.

The present chapter deals with the following topics:

1) Time dependence of Wigner distribution functions, which is described by means of a propagator. The properties of this propagator are studied.

2) Equilibrium distribution function of a set of extensive state variables, which provide a macroscopic description of the system, assuming that these variables are represented by commuting operators in quantum theory. This probability distribution function is expressed in terms of the Wigner distribution function of the micro-canonical ensemble, representing thermodynamic equilibrium. The properties of distribution functions of extensive variables, in particular those with regard to the even or odd character of these variables, are studied.

3) Definition of a set of intensive thermodynamic variables, conjugate to the extensive state variables, by means of Boltzmann's entropy postulate.

The theory is developed in the present chapter for Maxwell-Boltzmann statistics.

§ 1. *Introduction.* In the present (I) and in the following chapters (II, III) we shall be concerned with the quantum statistical foundations of the Onsager reciprocal relations [1]) in non-equilibrium thermodynamics. We shall make use of Wigner's phase space representation [2]) of quantum statistical mechanics. Whereas chapter I deals with the theory of ordinary Wigner distribution functions, we shall introduce in chapter II "joint Wigner distribution functions", which is needed for a derivation of the Onsager relations. The theory in I and II is developed for Maxwell-Boltzmann statistics. The extension to the cases of Fermi-Dirac and Bose-Einstein statistics is given in III.

The Wigner distribution function is a phase space distribution function, which may be considered as a quantum statistical analogue of the classical distribution function. Its importance follows from a theorem, due to

Wigner [2], Groenewold [3]) and Irving and Zwanzig [4]). This theorem states that quantum mechanical ensemble averages of operators can be written as phase space averages of classical functions over the Wigner distribution function, if we use Weyl's rule of correspondence [5]) between the quantum mechanical operators and the classical functions. In this way quantum statistical mechanics can be formulated in a manner, closely analogous to the formalism of classical statistical mechanics. The theory of the foundations of non-equilibrium thermodynamics in the present (I) and following chapters (II, III) can thus be developed in a way analogous to the classical treatment, given by de Groot and Mazur [6]).

In § 2 of this chapter we shall study the time dependence of Wigner distribution functions. The time evolution of Wigner distribution functions will be described by means of a propagator [7])[8]). Several properties of this propagator will be derived for later use.

For the macroscopic description of a system we shall introduce a set of extensive state variables, (*e.g.* masses, energies of small sub-systems, containing large numbers of particles). The number of these state variables is much smaller than the number of particles in the system. We shall assume that these variables are represented by commuting operators in quantum theory. In § 3 we shall introduce the probability distribution function of the extensive variables in thermodynamic equilibrium. This distribution function will be written as the phase space average of the classical function, corresponding to a certain projection operator of the state variables, over the Wigner distribution function of the micro-canonical ensemble, representing thermodynamic equilibrium. With the help of this phase space average we shall derive the properties of distribution functions of extensive variables with regard to the character of these variables under reversal of the particle velocities.

Micro-canonical ensemble averages of functions of the extensive state variables can be written as averages over distribution functions of these variables. Since these distribution functions are of a discontinuous type in quantum statistical mechanics, the latter averages have the form of Stieltjes integrals. If we make, however, the assumption that a central limit theorem holds for the state variables under consideration, these distribution functions are approximately continuous, differentiable normal distribution functions. In this approximation it is possible to define probability density functions of the state variables, which are Gaussian. The above mentioned Stieltjes integrals then become ordinary integrals.

In addition to the extensive state variables we shall introduce in § 4 a set of intensive thermodynamic variables. These new variables will be defined by making use of Boltzmann's entropy postulate.

§ 2. *Wigner distribution functions; propagators.* Consider a quantum mechanical ensemble of conservative systems, each containing N point particles with Cartesian coordinates $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$. This set of coordinates will be denoted briefly by the symbol $\boldsymbol{r}^N$. This ensemble is characterized by a density matrix (in coordinate representation)

$$\rho(\boldsymbol{r}'^N, \boldsymbol{r}^N; t) = \textstyle\sum_\mu w_\mu\, \psi_\mu^*(\boldsymbol{r}'^N; t)\, \psi_\mu(\boldsymbol{r}^N; t), \qquad (2\text{-}1)$$

where $w_\mu(\sum_\mu w_\mu = 1;\, w_\mu > 0)$ is the relative number of systems in the state with normalized wave function $\psi_\mu(\boldsymbol{r}^N; t)$, ($\psi_\mu^*$ is the complex conjugate of ψ_μ).

The Wigner distribution function [2] of this quantum mechanical ensemble is defined by

$$f(\boldsymbol{r}^N, \boldsymbol{p}^N; t) \equiv (\pi\hbar)^{-3N} \int \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}\, \rho(\boldsymbol{r}^N + \boldsymbol{y}^N, \boldsymbol{r}^N - \boldsymbol{y}^N; t)\, \mathrm{d}\boldsymbol{y}^N =$$
$$= (\pi\hbar)^{-3N} \textstyle\sum_\mu w_\mu \int \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}\, \psi_\mu^*(\boldsymbol{r}^N + \boldsymbol{y}^N; t)\, \psi_\mu(\boldsymbol{r}^N - \boldsymbol{y}^N; t)\, \mathrm{d}\boldsymbol{y}^N, \qquad (2\text{-}2)$$

where

$$\boldsymbol{p}^N \cdot \boldsymbol{y}^N = \textstyle\sum_{i=1}^N (\boldsymbol{p}_i \cdot \boldsymbol{y}_i) \text{ and } \mathrm{d}\boldsymbol{y}^N = \mathrm{d}\boldsymbol{y}_1\, \mathrm{d}\boldsymbol{y}_2 \ldots \mathrm{d}\boldsymbol{y}_N.$$

Furthermore $\hbar = h/2\pi$, where h is Planck's constant.

Just as a distribution function in classical statistical mechanics a Wigner distribution function is a real function, depending on the coordinates $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ and the variables $\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_N$, which will be called the momenta. The orthogonal $6N$-dimensional space, in which the Wigner distribution function is defined, will be called the phase space. A Wigner distribution function may assume negative values and does not represent a probability density in phase space, in contrast to a classical distribution function, which is a probability density function and consequently always positive.

Using Weyl's rule of correspondence [5] between operators A_{op} and classical functions $A(\boldsymbol{r}^N, \boldsymbol{p}^N)$:

$$A_{op} = \int \zeta(\boldsymbol{\sigma}^N, \boldsymbol{\tau}^N) \exp\{i(\boldsymbol{\sigma}^N \cdot \boldsymbol{r}_{op}^N + \boldsymbol{\tau}^N \cdot \boldsymbol{p}_{op}^N)\}\, \mathrm{d}\boldsymbol{\sigma}^N\, \mathrm{d}\boldsymbol{\tau}^N \rightleftarrows$$
$$\rightleftarrows A(\boldsymbol{r}^N, \boldsymbol{p}^N) = \int \zeta(\boldsymbol{\sigma}^N, \boldsymbol{\tau}^N) \exp\{i(\boldsymbol{\sigma}^N \cdot \boldsymbol{r}^N + \boldsymbol{\tau}^N \cdot \boldsymbol{p}^N)\}\, \mathrm{d}\boldsymbol{\sigma}^N\, \mathrm{d}\boldsymbol{\tau}^N, \qquad (2\text{-}3)$$

it can be shown [2][3][4] that the quantum mechanical ensemble average

$$\bar{A}(t) = \textstyle\sum_\mu w_\mu \int \psi_\mu^*(\boldsymbol{r}^N; t)\, A_{op} \psi_\mu(\boldsymbol{r}^N; t)\, \mathrm{d}\boldsymbol{r}^N \qquad (2\text{-}4)$$

may be written as the following phase space average:

$$\bar{A}(t) = \int A(\boldsymbol{r}^N, \boldsymbol{p}^N)\, f(\boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N. \qquad (2\text{-}5)$$

In eq. (2-3) $\boldsymbol{r}_{op}^N = \boldsymbol{r}^N$, $\boldsymbol{p}_{op}^N = (\hbar/i)(\partial/\partial \boldsymbol{r}^N)$ and

$$\exp\{i(\boldsymbol{\sigma}^N \cdot \boldsymbol{r}_{op}^N + \boldsymbol{\tau}^N \cdot \boldsymbol{p}_{op}^N)\} \equiv \textstyle\sum_{n=0}^\infty (i^n/n!)(\boldsymbol{\sigma}^N \cdot \boldsymbol{r}_{op}^N + \boldsymbol{\tau}^N \cdot \boldsymbol{p}_{op}^N)^n. \qquad (2\text{-}6)$$

Equation (2-5) demonstrates again the formal analogy between Wigner distribution functions and classical distribution functions. From the Weyl correspondence $A_{op} = 1 \rightleftarrows A(\boldsymbol{r}^N, \boldsymbol{p}^N) = 1$ it follows, together with eqs. (2-4) and (2-5), that

$$\int f(\boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N = \sum_\mu w_\mu \int |\psi_\mu(\boldsymbol{r}^N; t)|^2\, \mathrm{d}\boldsymbol{r}^N = \sum_\mu w_\mu = 1. \quad (2\text{-}7)$$

The Wigner distribution function (2-2) is therefore normalized in phase space.

The time dependence of the Wigner distribution function $f(\boldsymbol{r}^N, \boldsymbol{p}^N; t)$, eq. (2-2), is determined by the time dependence of the wave functions $\psi_\mu(\boldsymbol{r}^N; t)$, which are solutions of the Schroedinger wave equation

$$i\hbar\, \partial\psi_\mu(\boldsymbol{r}^N; t)/\partial t = H_{op}\psi_\mu(\boldsymbol{r}^N; t), \quad (2\text{-}8)$$

where H_{op} is the Hamilton operator. The solution of eq. (2-8) is given by

$$\psi_\mu(\boldsymbol{r}^N; t) = \exp\{(-i/\hbar)\, H_{op}t\}\, \psi_\mu(\boldsymbol{r}^N; 0), \quad (2\text{-}9)$$

which can be written in the form

$$\psi_\mu(\boldsymbol{r}^N; t) = \int \psi_\mu(\boldsymbol{r}'^N; 0)\, K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t)\, \mathrm{d}\boldsymbol{r}'^N, \quad (2\text{-}10)$$

with the propagator $K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t)$. From eqs. (2-8) and (2-10) it follows that this propagator satisfies the Schroedinger wave equation

$$i\hbar\, \partial K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t)/\partial t = H_{op}K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t), \quad (2\text{-}11)$$

with the initial condition

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N; 0) = \delta(\boldsymbol{r}'^N - \boldsymbol{r}^N), \quad (2\text{-}12)$$

where H_{op} operates on the variables $\boldsymbol{r}^N$ and where $\delta(\boldsymbol{r}'^N - \boldsymbol{r}^N)$ is a $3N$-dimensional δ-function. It follows from eqs. (2-11) and (2-12) that

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t) = \exp\{(-i/\hbar)\, H_{op}t\}\, \delta(\boldsymbol{r}'^N - \boldsymbol{r}^N), \quad (2\text{-}13)$$

or

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t) = \sum_k \exp\{(-i/\hbar)\, E_k t\}\, \varphi_k^*(\boldsymbol{r}'^N)\, \varphi_k(\boldsymbol{r}^N), \quad (2\text{-}14)$$

where $\varphi_k(\boldsymbol{r}^N)$ are the eigenfunctions and E_k the corresponding eigenvalues of H_{op}:

$$H_{op}\varphi_k(\boldsymbol{r}^N) = E_k\varphi_k(\boldsymbol{r}^N). \quad (2\text{-}15)$$

From eq. (2-14) and the fact that the energy eigenfunctions $\varphi_k(\boldsymbol{r}^N)$ form a complete orthonormal set of functions we find that the propagator $K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t)$ is a unitary matrix of the continuous indices $\boldsymbol{r}'^N$ and $\boldsymbol{r}^N$, *i.e.*:

$$\int K^*(\boldsymbol{r}'^N|\boldsymbol{r}^N; t)\, K(\boldsymbol{r}''^N|\boldsymbol{r}^N; t)\, \mathrm{d}\boldsymbol{r}^N = \delta(\boldsymbol{r}'^N - \boldsymbol{r}''^N), \quad (2\text{-}16)$$

$$\int K^*(\boldsymbol{r}^N|\boldsymbol{r}'^N; t)\, K(\boldsymbol{r}^N|\boldsymbol{r}''^N; t)\, \mathrm{d}\boldsymbol{r}^N = \delta(\boldsymbol{r}'^N - \boldsymbol{r}''^N). \quad (2\text{-}17)$$

Furthermore it follows from eq. (2-14) that

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t) = K^*(\boldsymbol{r}^N|\boldsymbol{r}'^N; -t). \quad (2\text{-}18)$$

Another property of the propagator $K(\boldsymbol{r}'^N|\boldsymbol{r}^N;t)$ follows from the fact that the Hamiltonian is an even function of the particle momenta:

$$H(\boldsymbol{r}^N, \boldsymbol{p}^N) = H(\boldsymbol{r}^N, -\boldsymbol{p}^N). \tag{2-19}$$

Putting

$$H(\boldsymbol{r}^N, \boldsymbol{p}^N) = \int \eta(\boldsymbol{\sigma}^N, \boldsymbol{\tau}^N) \exp\{i(\boldsymbol{\sigma}^N\cdot\boldsymbol{r}^N + \boldsymbol{\tau}^N\cdot\boldsymbol{p}^N)\}\, \mathrm{d}\boldsymbol{\sigma}^N\, \mathrm{d}\boldsymbol{\tau}^N, \tag{2-20}$$

we find from eq. (2-19) and the fact that $H(\boldsymbol{r}^N, \boldsymbol{p}^N)$ is real, that

$$\eta(\boldsymbol{\sigma}^N, \boldsymbol{\tau}^N) = \eta^*(-\boldsymbol{\sigma}^N, \boldsymbol{\tau}^N). \tag{2-21}$$

According to eq. (2-3) the Hamilton operator, corresponding to the Hamiltonian (2-20) is given by

$$H_{op} = \int \eta(\boldsymbol{\sigma}^N, \boldsymbol{\tau}^N) \exp\{i(\boldsymbol{\sigma}^N\cdot\boldsymbol{r}^N_{op} + \boldsymbol{\tau}^N\cdot\boldsymbol{p}^N_{op})\}\, \mathrm{d}\boldsymbol{\sigma}^N\, \mathrm{d}\boldsymbol{\tau}^N \tag{2-22}$$

and we obtain from the last two equations the following property:

$$H_{op} = H^*_{op}. \tag{2-23}$$

From eqs. (2-13) and (2-23) it is found that

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N;t) = K^*(\boldsymbol{r}'^N|\boldsymbol{r}^N;-t), \tag{2-24}$$

which can be transformed into

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N;t) = K(\boldsymbol{r}^N|\boldsymbol{r}'^N;t), \tag{2-25}$$

by using the relation (2-18).

In the presence of an external magnetic field $\boldsymbol{B}$, which may depend on the space coordinates, but which is independent of time, eq. (2-19) becomes

$$H(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B}) = H(\boldsymbol{r}^N, -\boldsymbol{p}^N; -\boldsymbol{B}), \tag{2-26}$$

where $H(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B})$ is the Hamiltonian of the system for a given external magnetic field $\boldsymbol{B}$ and $H(\boldsymbol{r}^N, \boldsymbol{p}^N; -\boldsymbol{B})$ the Hamiltonian of the same system, but with the external field reversed. Eq. (2-23) becomes

$$H_{op}(\boldsymbol{B}) = H^*_{op}(-\boldsymbol{B}), \tag{2-27}$$

whereas eqs. (2-24) and (2-25) become

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{B};t) = K^*(\boldsymbol{r}'^N|\boldsymbol{r}^N;-\boldsymbol{B};-t), \tag{2-28}$$

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{B};t) = K(\boldsymbol{r}^N|\boldsymbol{r}'^N;-\boldsymbol{B};t). \tag{2-29}$$

From (2-2) and (2-10) we find that

$$f(\boldsymbol{r}^N, \boldsymbol{p}^N;t) = (\pi\hbar)^{-3N} \textstyle\sum_\mu w_\mu \int \psi^*_\mu(\boldsymbol{r}''^N;0)\, \psi_\mu(\boldsymbol{r}'''^N;0)\, K^*(\boldsymbol{r}''^N|\boldsymbol{r}^N+\boldsymbol{y}^N;t)$$
$$K(\boldsymbol{r}'''^N|\boldsymbol{r}^N-\boldsymbol{y}^N;t) \exp\{(2i/\hbar)(\boldsymbol{p}^N\cdot\boldsymbol{y}^N)\}\, \mathrm{d}\boldsymbol{r}''^N\, \mathrm{d}\boldsymbol{r}'''^N\, \mathrm{d}\boldsymbol{y}^N. \tag{2-30}$$

Introducing new variables $\boldsymbol{r}'^N$ and $\boldsymbol{y}'^N$ by means of $\boldsymbol{r}''^N = \boldsymbol{r}'^N + \boldsymbol{y}'^N$

and $\boldsymbol{r}'''^N = \boldsymbol{r}'^N - \boldsymbol{y}'^N$, eq. (2-30) becomes

$$f(\boldsymbol{r}^N, \boldsymbol{p}^N; t) =$$
$$= (2/\pi\hbar)^{3N} \sum_\mu w_\mu \int \psi_\mu^*(\boldsymbol{r}'^N + \boldsymbol{y}'^N; 0)\, \psi_\mu(\boldsymbol{r}'^N - \boldsymbol{y}'^N; 0)\, K^*(\boldsymbol{r}'^N + \boldsymbol{y}'^N | \boldsymbol{r}^N + \boldsymbol{y}^N; t)$$
$$K(\boldsymbol{r}'^N - \boldsymbol{y}'^N | \boldsymbol{r}^N - \boldsymbol{y}^N; t) \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{y}'^N \mathrm{d}\boldsymbol{y}^N. \tag{2-31}$$

Using the identity

$$\delta(\boldsymbol{y}''^N - \boldsymbol{y}'^N) = (\pi\hbar)^{-3N} \int \exp\{(2i/\hbar)\, \boldsymbol{p}'^N \cdot (\boldsymbol{y}''^N - \boldsymbol{y}'^N)\}\, \mathrm{d}\boldsymbol{p}'^N, \tag{2-32}$$

eq. (2-31) can be transformed into

$$f(\boldsymbol{r}^N, \boldsymbol{p}^N; t) =$$
$$= (\pi\hbar)^{-3N} (2/\pi\hbar)^{3N} \sum_\mu w_\mu \int \exp\{(2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}''^N)\}\, \psi_\mu^*(\boldsymbol{r}'^N + \boldsymbol{y}''^N; 0)$$
$$\psi_\mu(\boldsymbol{r}'^N - \boldsymbol{y}''^N; 0) \exp\{(-2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}'^N)\}\, K^*(\boldsymbol{r}'^N + \boldsymbol{y}'^N | \boldsymbol{r}^N + \boldsymbol{y}^N; t)$$
$$K(\boldsymbol{r}'^N - \boldsymbol{y}'^N | \boldsymbol{r}^N - \boldsymbol{y}^N; t) \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}\, \mathrm{d}\boldsymbol{y}''^N \mathrm{d}\boldsymbol{y}'^N \mathrm{d}\boldsymbol{y}^N \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N. \tag{2-33}$$

This equation can be written in the form

$$f(\boldsymbol{r}^N, \boldsymbol{p}^N; t) = \int f(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0)\, P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N, \tag{2-34}$$

where we have introduced the propagator[7][8]) of the Wigner distribution function

$$P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t) \equiv$$
$$\equiv (2/\pi\hbar)^{3N} \int \exp\{(-2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}'^N)\}\, K^*(\boldsymbol{r}'^N + \boldsymbol{y}'^N | \boldsymbol{r}^N + \boldsymbol{y}^N; t)$$
$$K(\boldsymbol{r}'^N - \boldsymbol{y}'^N | \boldsymbol{r}^N - \boldsymbol{y}^N; t) \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}\, \mathrm{d}\boldsymbol{y}'^N \mathrm{d}\boldsymbol{y}^N \tag{2-35}$$

and used (2-2). The quantity $P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t)$ is real, but not necessarily positive.

We shall now prove the following theorem. If we have the Weyl correspondences

$$P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; 0) \rightleftarrows P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0) \tag{2-36}$$

and

$$P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t) \rightleftarrows P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t), \tag{2-37}$$

then one has

$$P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t) = \exp\{(-i/\hbar)\, H_{op} t\}\, P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0) \exp\{(i/\hbar)\, H_{op} t\}. \tag{2-38}$$

In order to prove this, we shall use the following theorem, due to Groenewold[3])[9]). If

$$A_{op}\psi(\boldsymbol{r}^N) = \int \psi(\boldsymbol{r}'^N)\, A(\boldsymbol{r}'^N | \boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}'^N, \tag{2-39}$$

then the classical function, corresponding to A_{op}, is given by

$$A(\boldsymbol{r}^N, \boldsymbol{p}^N) = 2^{3N} \int \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}\, A(\boldsymbol{r}^N + \boldsymbol{y}^N | \boldsymbol{r}^N - \boldsymbol{y}^N)\, \mathrm{d}\boldsymbol{y}^N. \tag{2-40}$$

Comparing (2-35) with (2-40) and using (2-37) and (2-39), we obtain

$$P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t)\, \psi(\boldsymbol{r}^N) = (\pi\hbar)^{-3N} \int \psi(\boldsymbol{r}''^N) \exp\{(-2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}'^N)\}$$
$$K^*(\boldsymbol{r}'^N + \boldsymbol{y}'^N | \boldsymbol{r}''^N; t)\, K(\boldsymbol{r}'^N - \boldsymbol{y}'^N | \boldsymbol{r}^N; t)\, \mathrm{d}\boldsymbol{r}''^N \mathrm{d}\boldsymbol{y}'^N, \tag{2-41}$$

which can be transformed into

$$P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t)\, \psi(\boldsymbol{r}^N) = (\pi\hbar)^{-3N} \int \psi(\boldsymbol{r}''^N)\, K(\boldsymbol{r}''^N | \boldsymbol{r}'^N + \boldsymbol{y}'^N; -t)$$
$$\exp\{(-2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}'^N)\}\, K(\boldsymbol{r}'^N - \boldsymbol{y}'^N | \boldsymbol{r}^N; t)\, \mathrm{d}\boldsymbol{r}''^N\, \mathrm{d}\boldsymbol{y}'^N, \tag{2-42}$$

by using eq. (2-18). Eq. (2-42) can be written as

$$P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t)\, \psi(\boldsymbol{r}^N) =$$
$$= (\pi\hbar)^{-3N} \int \psi(\boldsymbol{r}''''^N) K(\boldsymbol{r}''''^N | \boldsymbol{r}'''^N; -t)\, \delta(\boldsymbol{r}'''^N - \boldsymbol{r}'^N - \boldsymbol{y}'^N) \exp\{(-2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}'^N)\}$$
$$\delta(\boldsymbol{r}'^N - \boldsymbol{y}'^N - \boldsymbol{r}''^N) K(\boldsymbol{r}''^N | \boldsymbol{r}^N; t)\, \mathrm{d}\boldsymbol{r}''''^N \mathrm{d}\boldsymbol{r}'''^N \mathrm{d}\boldsymbol{r}''^N \mathrm{d}\boldsymbol{y}'^N. \tag{2-43}$$

Furthermore we find from eqs. (2-42) and (2-12) that

$$P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0)\, \psi(\boldsymbol{r}^N) =$$
$$= (\pi\hbar)^{-3N} \int \psi(\boldsymbol{r}''^N)\, \delta(\boldsymbol{r}''^N - \boldsymbol{r}'^N - \boldsymbol{y}'^N) \exp\{(-2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}'^N)\}$$
$$\delta(\boldsymbol{r}'^N - \boldsymbol{y}'^N - \boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}''^N\, \mathrm{d}\boldsymbol{y}'^N. \tag{2-44}$$

From the last two equations, together with (2-9) and (2-10), we then obtain the result (2-38).

From the theorem (2-36)–(2-38) we shall derive here a partial differential equation for the propagator $P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t)$. It follows from (2-38) that

$$\partial P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t)/\partial t = (-i/\hbar)\{H_{op} P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t) -$$
$$- P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t)\, H_{op}\}. \tag{2-45}$$

Now we have the following Weyl correspondence (Groenewold [3]):

$$(-i/\hbar)\{H_{op} P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t) - P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t)\, H_{op}\} \rightleftarrows$$
$$\rightleftarrows (2/\hbar) H(\boldsymbol{r}^N, \boldsymbol{p}^N) \sin\left\{\frac{\hbar}{2}\left(\frac{6}{6\boldsymbol{r}^N} \cdot \frac{\partial}{\partial \boldsymbol{p}^N} - \frac{6}{6\boldsymbol{p}^N} \cdot \frac{\partial}{\partial \boldsymbol{r}^N}\right)\right\} P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t), \tag{2-46}$$

where the 6-symbol denotes differentiation "to the left". From eq. (2-45) and the Weyl correspondences (2-37) and (2-46) we find that the propagator $P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t)$ satisfies the differential equations

$$\partial P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t)/\partial t = L_{op} P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; t), \tag{2-47}$$

with

$$L_{op} \equiv (2/\hbar)\, H(\boldsymbol{r}^N, \boldsymbol{p}^N) \sin\left\{\frac{\hbar}{2}\left(\frac{6}{6\boldsymbol{r}^N} \cdot \frac{\partial}{\partial \boldsymbol{p}^N} - \frac{6}{6\boldsymbol{p}^N} \cdot \frac{\partial}{\partial \boldsymbol{r}^N}\right)\right\}. \tag{2-48}$$

The initial condition follows from eqs. (2-35) and (2-12):

$$P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; 0) = \delta(\boldsymbol{r}'^N - \boldsymbol{r}^N)\, \delta(\boldsymbol{p}'^N - \boldsymbol{p}^N). \tag{2-49}$$

From eqs. (2-34) and (2-47) we find the following differential equation for the Wigner distribution function $f(\boldsymbol{r}^N, \boldsymbol{p}^N; t)$:

$$\partial f(\boldsymbol{r}^N, \boldsymbol{p}^N; t)/\partial t = L_{op} f(\boldsymbol{r}^N, \boldsymbol{p}^N; t), \tag{2-50}$$

which is the quantum mechanical analogue [7][9] of the Liouville equation in classical statistical mechanics.

Let $P^{(cl)}(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t)$ be the propagator of a classical distribution function. Then $P^{(cl)}(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N$ is the probability to find the system in the range $(\boldsymbol{r}^N, \boldsymbol{p}^N; \mathrm{d}\boldsymbol{r}^N, \mathrm{d}\boldsymbol{p}^N)$ at some time, if initially, a time interval t earlier ($t > 0$), this system was at the point $(\boldsymbol{r}'^N, \boldsymbol{p}'^N)$. The propagator of a classical distribution function is therefore the conditional probability density in phase space, in contrast to the propagator of a Wigner distribution function, which is not a conditional probability density. Furthermore it should be noted, that the propagator $P(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t)$, eq. (2-35), is not a Wigner distribution function, although it is a solution of the quantum mechanical Liouville equation, since a Wigner distribution function with the initial form (2-49) does not exist.

Integration of the expression (2-35) over $(\boldsymbol{r}^N, \boldsymbol{p}^N)$ or $(\boldsymbol{r}'^N, \boldsymbol{p}'^N)$ gives, together with (2-16) and (2-17),

$$\int P(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N = 1, \tag{2-51}$$

$$\int P(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}'^N\, \mathrm{d}\boldsymbol{p}'^N = 1. \tag{2-52}$$

Furthermore it follows from (2-35) and (2-18) that

$$P(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t) = P(\boldsymbol{r}^N, \boldsymbol{p}^N|\boldsymbol{r}'^N, \boldsymbol{p}'^N; -t). \tag{2-53}$$

The influence of the property (2-19) of the Hamiltonian on the propagator $P(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t)$ is found from (2-35) and (2-25):

$$P(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; t) = P(\boldsymbol{r}^N, -\boldsymbol{p}^N|\boldsymbol{r}'^N, -\boldsymbol{p}'^N; t). \tag{2-54}$$

This relation is the quantum mechanical analogue of what is called "invariance under reversal of the motion of the particles" in classical statistical mechanics [6].

In the presence of an external magnetic field $\boldsymbol{B}$ we find, instead of eq. (2-54), from (2-35) and (2-29)

$$P(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B}; t) = P(\boldsymbol{r}^N, -\boldsymbol{p}^N|\boldsymbol{r}'^N, -\boldsymbol{p}'^N; -\boldsymbol{B}; t). \tag{2-55}$$

The magnetic field $\boldsymbol{B}$ must also be reversed, if the "motion of the particles" is reversed.

§ 3. *Equilibrium distribution functions of extensive state variables.* Let us consider an adiabatically insulated system in thermodynamic equilibrium. In quantum statistical mechanics the behaviour of this system is described with the micro-canonical ensemble, given by the density matrix

$$\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = G_{E;\Delta E}^{-1} \textstyle\sum_{E_k \in (E;\Delta E)} \varphi_k^*(\boldsymbol{r}'^N)\, \varphi_k(\boldsymbol{r}^N), \tag{3-1}$$

where $\varphi_k(\boldsymbol{r}^N)$ and E_k are given by eq. (2-15). The summation in (3-1) extends over those quantum numbers k, for which E_k lies in the range

$(E; \Delta E)$, *i.e.* $E - \frac{1}{2}\Delta E < E_k \leqslant E + \frac{1}{2}\Delta E$. The number of eigenvalues E_k in this range is $G_{E;\Delta E}$. Introducing the projection operator $p_{E;\Delta E,op}$ by means of

$$p_{E;\Delta E,op}\, \varphi_k(\boldsymbol{r}^N) = p_{E;\Delta E}(E_k)\, \varphi_k(\boldsymbol{r}^N), \tag{3-2}$$

with

$$p_{E;\Delta E}\,(E_k) = \begin{cases} 1, & \text{if } E_k \in (E;\Delta E) \\ 0, & \text{if } E_k \notin (E;\Delta E) \end{cases}, \tag{3-3}$$

the expression (3-1) can be transformed into

$$\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = G^{-1}_{E;\Delta E} \textstyle\sum_k \varphi^*_k(\boldsymbol{r}'^N)\, p_{E;\Delta E,op}\, \varphi_k(\boldsymbol{r}^N), \tag{3-4}$$

where now the summation extends over all possible quantum numbers k. This equation may alternatively be written as

$$\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = G^{-1}_{E;\Delta E}\, p_{E;\Delta E,op}\, \delta(\boldsymbol{r}'^N - \boldsymbol{r}^N), \tag{3-5}$$

using the fact that the functions $\varphi_k(\boldsymbol{r}^N)$ form a complete orthonormal set. Writing $p_{E;\Delta E}(E_k)$ as the Fourier integral

$$p_{E;\Delta E}(E_k) = \lim_{\substack{\varepsilon\to\infty \\ (\varepsilon>0)}} \int_{-\infty}^{+\infty} \frac{\sin\left(\frac{1}{2}\Delta E\, t/\hbar\right)}{\pi t} \exp\{(-i/\hbar)\, t\, (E_k - E - \varepsilon)\}\, \mathrm{d}t \equiv$$

$$\equiv \int_{-\infty}^{+\infty} \frac{\sin\left(\frac{1}{2}\Delta E\, t/\hbar\right)}{\pi t} \exp\{(-i/\hbar)\, t\, (E_k - E - 0)\}\, \mathrm{d}t, \tag{3-6}$$

we find with (3-2) and (2-15) that

$$p_{E;\Delta E,op} = \int_{-\infty}^{+\infty} \frac{\sin\left(\frac{1}{2}\Delta E\, t/\hbar\right)}{\pi t} \exp\{(-i/\hbar)\, t (H_{op} - E - 0)\}\, \mathrm{d}t. \tag{3-7}$$

Substituting (3-7) into (3-5) and using (2-13), we obtain

$$\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = G^{-1}_{E;\Delta E} \int_{-\infty}^{+\infty} \frac{\sin\left(\frac{1}{2}\Delta E\, t/\hbar\right)}{\pi t} \exp\{(i/\hbar)(E+0)t\}$$

$$K(\boldsymbol{r}'^N|\boldsymbol{r}^N; t)\, \mathrm{d}t. \tag{3-8}$$

Applying the property (2-25) to this equation, we find that

$$\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = \rho_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{r}'^N). \tag{3-9}$$

In the presence of an external magnetic field $\boldsymbol{B}$ we have

$$\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N; \boldsymbol{B}) = \rho_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{r}'^N; -\boldsymbol{B}), \tag{3-10}$$

which follows from (3-8), using the property (2-29) and also

$$G_{E;\Delta E}(\boldsymbol{B}) = G_{E;\Delta E}(-\boldsymbol{B}). \tag{3-11}$$

Eq. (3-11) can be proved by integrating $\rho_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{r}^N; \boldsymbol{B})$ over $\boldsymbol{r}^N$, which gives, independently of $\boldsymbol{B}$, the value 1. Since $K(\boldsymbol{r}^N|\boldsymbol{r}^N; \boldsymbol{B}; t)$ is an even function of $\boldsymbol{B}$, according to (2-29), it follows indeed that $G_{E;\Delta E}(\boldsymbol{B})$ is an even function of $\boldsymbol{B}$.

The Wigner distribution function of the micro-canonical ensemble is

$$f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) =$$
$$= (\pi\hbar)^{-3N} \int \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\} \rho_{E;\Delta E}(\boldsymbol{r}^N + \boldsymbol{y}^N, \boldsymbol{r}^N - \boldsymbol{y}^N)\, \mathrm{d}\boldsymbol{y}^N. \quad (3\text{-}12)$$

It follows from (2-39) and (2-40) that $f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ is the classical function corresponding to the operator $h^{-3N}\rho_{E;\Delta E, op}$, which is defined by means of the relation

$$\rho_{E;\Delta E, op}\psi(\boldsymbol{r}^N) \equiv \int \psi(\boldsymbol{r}'^N)\, \rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}'^N. \quad (3\text{-}13)$$

Substituting (3-5) into this relation, we find that

$$\rho_{E;\Delta E, op} = G^{-1}_{E;\Delta E}\, p_{E;\Delta E, op}. \quad (3\text{-}14)$$

If $p_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ is the classical function corresponding to $p_{E;\Delta E, op}$:

$$p_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) \rightleftarrows p_{E;\Delta E, op}, \quad (3\text{-}15)$$

we then obtain for the Wigner distribution function of the micro-canonical ensemble the following expression:

$$f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = h^{-3N}\, G^{-1}_{E;\Delta E}\, p_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N). \quad (3\text{-}16)$$

Putting

$$\Omega_{E;\Delta E} \equiv h^{3N} G_{E;\Delta E}, \quad (3\text{-}17)$$

eq. (3-16) becomes

$$f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = \Omega^{-1}_{E;\Delta E}\, p_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N). \quad (3\text{-}18)$$

Since $f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ is normalized (*cf.* eq. (2-7)), we have

$$\Omega_{E;\Delta E} = \int p_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N. \quad (3\text{-}19)$$

Applying the property (3-9) to (3-12) we find that

$$f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = f_{E;\Delta E}(\boldsymbol{r}^N, -\boldsymbol{p}^N). \quad (3\text{-}20)$$

In the presence of an external magnetic field $\boldsymbol{B}$ we have

$$f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B}) = f_{E;\Delta E}(\boldsymbol{r}^N, -\boldsymbol{p}^N; -\boldsymbol{B}), \quad (3\text{-}21)$$

which follows from (3-12), together with (3-10).

With regard to eqs. (3-18) and (3-19) we want to make the following remark. The function $p_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ is the quantum mechanical analogue of the function

$$p^{(cl)}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = p_{E;\Delta E}(H(\boldsymbol{r}^N, \boldsymbol{p}^N)) = \left\{\begin{matrix} 1, \text{within the energy shell } (E;\Delta E) \\ 0, \text{elsewhere in phase space} \end{matrix}\right\} \quad (3\text{-}22)$$

in classical statistical mechanics, whereas $\Omega_{E;\Delta E}$ corresponds to the volume in phase space of the energy shell $(E;\Delta E)$:

$$\Omega^{(cl)}_{E;\Delta E} = \int p^{(cl)}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N = \int_{(E;\Delta E)} \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N. \tag{3-23}$$

The function $f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ is the quantum mechanical analogue of the classical distribution function of the micro-canonical ensemble:

$$f^{(cl)}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) =$$

$$= \Omega^{(cl)-1}_{E;\Delta E}\, p^{(cl)}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = \begin{Bmatrix} \Omega^{(cl)-1}_{E;\Delta E}, \text{ within the energy shell } (E;\Delta E) \\ 0, \text{ elsewhere in phase space} \end{Bmatrix}. \tag{3-24}$$

For the macroscopic description of the system we shall use, in addition to the energy E, a set of n extensive state variables $\alpha_1, \alpha_2, \ldots, \alpha_n$. One may think, for instance, of the masses, energies, electric charges of macroscopically infinitesimal sub-regions within the system. These regions must still contain a large number of the constituent particles of the system, so that the principles of statistical mechanics may be applied to them. The number of state variables is much smaller than the number of particles in the system. For convenience a matrix notation will be introduced. We consider the quantities $\alpha_i (i = 1, 2, \ldots, n)$ as the components of a vector $\boldsymbol{\alpha}$. The state of the system can then be represented by a point in the so-called $\boldsymbol{\alpha}$-space, of which the n Cartesian coordinates are the quantities α_i. In classical mechanics the state vector $\boldsymbol{\alpha}$ is a function of $\boldsymbol{r}^N$ and $\boldsymbol{p}^N$. Let $\boldsymbol{\alpha}_{op}$ be the quantum mechanical operator, corresponding to $\boldsymbol{\alpha}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ according to Weyl's rule:

$$\boldsymbol{\alpha}_{op} \rightleftarrows \boldsymbol{\alpha}(\boldsymbol{r}^N, \boldsymbol{p}^N). \tag{3-25}$$

We shall now make the assumption *) that the components $\alpha_{i,op}$ of $\boldsymbol{\alpha}_{op}$ are commuting quantities. The operators $\alpha_{i,op}$ then possess a simultaneous set of eigenfunctions $\chi_\lambda(\boldsymbol{r}^N)$ with corresponding eigenvalues $\alpha_{i,\lambda}$, so that

$$\boldsymbol{\alpha}_{op}\chi_\lambda(\boldsymbol{r}^N) = \boldsymbol{\alpha}_\lambda \chi_\lambda(\boldsymbol{r}^N). \tag{3-26}$$

The state variables are supposed to be normalized in such a way that the average of $\boldsymbol{\alpha}_{op}$ in the micro-canonical ensemble vanishes:

$$\overline{\boldsymbol{\alpha}}^{m.c.} \equiv G^{-1}_{E;\Delta E} \textstyle\sum_{E_k \in (E;\Delta E)} \int \varphi^*_k(\boldsymbol{r}^N)\, \boldsymbol{\alpha}_{op}\varphi_k(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N =$$

$$= \int \boldsymbol{\alpha}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N = 0, \tag{3-27}$$

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*) If the extensive variables are the masses of sub-regions of a system, the corresponding operators commute, since these quantities depend only on the coordinates of the particles. In the case of a crystal lattice, which we divide into a number of sub-regions, the operators, corresponding to the energies of these regions, commute since they refer to different groups of particles. In general, however, the operators, corresponding to extensive state variables, do not commute. We shall, however, make the assumption [10]) that there exists a complete orthonormal set of functions $\chi_\lambda(\boldsymbol{r}^N)$, such that for every function of this set the root mean square deviations $\delta\alpha_{i,\lambda}$ of these operators around their average values $\alpha_{i,\lambda}$ are much smaller than the experimental inaccuracies $\Delta\alpha_{i,\lambda}$, with which the state variables are measured. It is then possible to replace the non-commuting operators by commuting operators $\alpha_{i,op}$, with eigenfunctions $\chi_\lambda(\boldsymbol{r}^N)$ and eigenvalues $\alpha_{i,\lambda}$, (*cf.* eq. (3–26)).

where we have applied the theorem (2-4), (2-5) and used the Weyl correspondence (3-25).

We now define the projection operator

$$p_{op}(\boldsymbol{\alpha}) = \prod_{i=1}^{n} p_{op}(\alpha_i), \tag{3-28}$$

by means of

$$p_{op}(\boldsymbol{\alpha})\,\chi_\lambda(\boldsymbol{r}^N) = p(\boldsymbol{\alpha}_\lambda - \boldsymbol{\alpha})\,\chi_\lambda(\boldsymbol{r}^N), \tag{3-29}$$

where

$$p(\boldsymbol{\alpha}_\lambda - \boldsymbol{\alpha}) = \prod_{i=1}^{n} p(\alpha_{i,\lambda} - \alpha_i), \tag{3-30}$$

with

$$p(\alpha_{i,\lambda} - \alpha_i) = \begin{Bmatrix} 1, & \text{if} & \alpha_{i,\lambda} \leqslant \alpha_i \\ 0, & \text{if} & \alpha_{i,\lambda} > \alpha_i \end{Bmatrix}. \tag{3-31}$$

Writing $p(\alpha_{i,\lambda} - \alpha_i)$ as a Fourier integral, we obtain from the last three equations

$$p_{op}(\boldsymbol{\alpha}) = \int \delta_+(\boldsymbol{k}) \exp\{(-i/\hbar)\,\boldsymbol{k}\cdot(\boldsymbol{\alpha}_{op} - \boldsymbol{\alpha} - 0)\}\,\mathrm{d}\boldsymbol{k}, \tag{3-32}$$

where $\boldsymbol{k}$ is a vector with components $k_1, k_2, \ldots, k_n$ and where

$$\delta_+(\boldsymbol{k}) = \prod_{i=1}^{n} \delta_+(k_i) \tag{3-33}$$

is the product of singular functions

$$\delta_+(k_i) = (2\pi)^{-1} \int_0^\infty \exp(-\,ik_i x_i)\,\mathrm{d}x_i. \tag{3-34}$$

Let $p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})$ be the classical function corresponding to $p_{op}(\boldsymbol{\alpha})$:

$$p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}) \rightleftarrows p_{op}(\boldsymbol{\alpha}). \tag{3-35}$$

Introducing the propagator $Q(\boldsymbol{r}'^N|\boldsymbol{r}^N; \boldsymbol{k})$ by means of

$$\exp\{(-i/\hbar)\,\boldsymbol{k}\cdot\boldsymbol{\alpha}_{op}\}\psi(\boldsymbol{r}^N) \equiv \int \psi(\boldsymbol{r}'^N)\, Q(\boldsymbol{r}'^N|\boldsymbol{r}^N; \boldsymbol{k})\,\mathrm{d}\boldsymbol{r}'^N \tag{3-36}$$

and applying the theorem (2-39), (2-40), we find with (3-32) and (3-35) that

$$p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}) = 2^{3N} \int \exp\{(2i/\hbar)(\boldsymbol{p}^N\cdot\boldsymbol{y}^N)\}\, p(\boldsymbol{r}^N + \boldsymbol{y}^N|\boldsymbol{r}^N - \boldsymbol{y}^N; \boldsymbol{\alpha})\,\mathrm{d}\boldsymbol{y}^N, \tag{3-37}$$

where

$$p(\boldsymbol{r}'^N|\boldsymbol{r}^N; \boldsymbol{\alpha}) = \int \delta_+(\boldsymbol{k}) \exp\{(i/\hbar)\,\boldsymbol{k}\cdot(\boldsymbol{\alpha} + 0)\}Q(\boldsymbol{r}'^N|\boldsymbol{r}^N; \boldsymbol{k})\,\mathrm{d}\boldsymbol{k}. \tag{3-38}$$

It follows from the definition (3-36) of $Q(\boldsymbol{r}'^N|\boldsymbol{r}^N; \boldsymbol{k})$ that this propagator is the solution of

$$i\hbar\,\partial Q(\boldsymbol{r}'^N|\boldsymbol{r}^N; \boldsymbol{k})/\partial\boldsymbol{k} = \boldsymbol{\alpha}_{op}\, Q(\boldsymbol{r}'^N|\boldsymbol{r}^N; \boldsymbol{k}), \tag{3-39}$$

with

$$Q(\boldsymbol{r}'^N|\boldsymbol{r}^N; 0) = \delta(\boldsymbol{r}'^N - \boldsymbol{r}^N), \tag{3-40}$$

(*cf.* eqs. (2-11) and (2-12)). Now we make the assumption that the state variables are even functions of the particle velocities. In the absence of an external magnetic field, we then have

$$\boldsymbol{\alpha}(\boldsymbol{r}^N, \boldsymbol{p}^N) = \boldsymbol{\alpha}(\boldsymbol{r}^N, -\boldsymbol{p}^N), \tag{3-41}$$

(*cf.* eq. (2-19)). It follows from the last three equations that the propagator $Q(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{k})$ possesses similar properties as the propagator $K(\boldsymbol{r}'^N|\boldsymbol{r}^N;t)$ of the Schroedinger wave function. In particular we have

$$Q(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{k}) = Q(\boldsymbol{r}^N|\boldsymbol{r}'^N;\boldsymbol{k}), \tag{3-42}$$

(*cf.* eq. (2-25)). Applying this property to eq. (3-38), we find that

$$p(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{\alpha}) = p(\boldsymbol{r}^N|\boldsymbol{r}'^N;\boldsymbol{\alpha}). \tag{3-43}$$

From (3-37) and (3-43) we then obtain

$$p(\boldsymbol{r}^N,\boldsymbol{p}^N;\boldsymbol{\alpha}) = p(\boldsymbol{r}^N,-\boldsymbol{p}^N;\boldsymbol{\alpha}). \tag{3-44}$$

For the description of the system, one may require also variables, which are odd functions of the particle velocities, (*e.g.* barycentric velocities, magnetizations of small sub-regions of the system). Such state variables will be denoted by $\boldsymbol{\beta} = \beta_1, \beta_2, \ldots, \beta_m$. For both even and odd variables eq. (3-32) becomes

$$p_{op}(\boldsymbol{\alpha},\boldsymbol{\beta}) = \int \delta_+(\boldsymbol{k})\,\delta_+(\boldsymbol{l})\exp\{(-i/\hbar)\,\boldsymbol{k}\cdot(\boldsymbol{\alpha}_{op}-\boldsymbol{\alpha}-0)\}$$
$$\exp\{(-i/\hbar)\,\boldsymbol{l}\cdot(\boldsymbol{\beta}_{op}-\boldsymbol{\beta}-0)\}\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{l}, \tag{3-45}$$

where $\boldsymbol{l}$ is a vector with components $l_1, l_2, \ldots, l_m$. Introducing the propagator $Q(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{k},\boldsymbol{l})$ by means of

$$\exp\{(-i/\hbar)(\boldsymbol{k}\cdot\boldsymbol{\alpha}_{op}+\boldsymbol{l}\cdot\boldsymbol{\beta}_{op})\}\,\psi(\boldsymbol{r}^N) \equiv \int \psi(\boldsymbol{r}'^N)\,Q(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{k},\boldsymbol{l})\,\mathrm{d}\boldsymbol{r}'^N, \tag{3-46}$$

eqs. (3-37) and (3-38) become

$$p(\boldsymbol{r}^N,\boldsymbol{p}^N;\boldsymbol{\alpha},\boldsymbol{\beta}) = 2^{3N}\int \exp\{(2i/\hbar)(\boldsymbol{p}^N\cdot\boldsymbol{y}^N)\}\,p(\boldsymbol{r}^N+\boldsymbol{y}^N|\boldsymbol{r}^N-\boldsymbol{y}^N;\boldsymbol{\alpha},\boldsymbol{\beta})\,\mathrm{d}\boldsymbol{y}^N, \tag{3-47}$$

with

$$p(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{\alpha},\boldsymbol{\beta}) = \int \delta_+(\boldsymbol{k})\,\delta_+(\boldsymbol{l})\exp\{(i/\hbar)\,\boldsymbol{k}\cdot(\boldsymbol{\alpha}+0)\}$$
$$\exp\{(i/\hbar)\,\boldsymbol{l}\cdot(\boldsymbol{\beta}+0)\}\,Q(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{k},\boldsymbol{l})\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{l}. \tag{3-48}$$

For odd variables, in the absence of an external magnetic field, we have

$$\boldsymbol{\beta}(\boldsymbol{r}^N,\boldsymbol{p}^N) = -\boldsymbol{\beta}(\boldsymbol{r}^N,-\boldsymbol{p}^N). \tag{3-49}$$

Using (3-41) and (3-49), we find, instead of eq. (3-42), that

$$Q(\boldsymbol{r}'^N|\boldsymbol{r}^N;\boldsymbol{k},\boldsymbol{l}) = Q(\boldsymbol{r}^N|\boldsymbol{r}'^N;\boldsymbol{k},-\boldsymbol{l}). \tag{3-50}$$

Applying this property to eqs. (3-47), (3-48) and using the relation

$$\delta_+(-l_j) = \delta(l_j) - \delta_+(l_j), \tag{3-51}$$

it follows with (3-46) and the theorem (2-39), (2-40) that

$$p(\boldsymbol{r}^N,\boldsymbol{p}^N;\boldsymbol{\alpha},\boldsymbol{\beta}) = p'(\boldsymbol{r}^N,-\boldsymbol{p}^N;\boldsymbol{\alpha},-\boldsymbol{\beta}-0), \tag{3-52}$$

where $p'(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}, \boldsymbol{\beta})$ is the classical function corresponding to the operator

$$p'_{op}(\boldsymbol{\alpha}, \boldsymbol{\beta}) = \int \delta_+(\boldsymbol{k}) \prod_{j=1}^m \{\delta(l_j) - \delta_+(l_j)\} \exp\{(-i/\hbar)\, \boldsymbol{k}\cdot(\boldsymbol{\alpha}_{op} - \boldsymbol{\alpha} - 0)\}$$
$$\exp\{(-i/\hbar)\, \boldsymbol{l}\cdot(\boldsymbol{\beta}_{op} - \boldsymbol{\beta} - 0)\}\, \mathrm{d}\boldsymbol{k}\, \mathrm{d}\boldsymbol{l}. \tag{3-53}$$

From the last equation we find that

$$p'_{op}(\boldsymbol{\alpha}, \boldsymbol{\beta}) = \prod_{i=1}^n p_{op}(\alpha_i) \prod_{j=1}^m \{1 - p_{op}(\beta_j)\} =$$
$$= \sum_{k=0}^m (-1)^k \sum_{1\leqslant i_1 < i_2 < \ldots < i_k \leqslant m} p_{op}(\alpha_1, \alpha_2, \ldots, \alpha_n, \beta_{i_1}, \beta_{i_2}, \ldots, \beta_{i_k}), \tag{3-54}$$

where $p_{op}(\alpha_1, \alpha_2, \ldots, \alpha_n, \beta_{i_1}, \beta_{i_2}, \ldots, \beta_{i_k})$ is the projection operator for the set of state variables $\alpha_1, \alpha_2, \ldots, \alpha_n, \beta_{i_1}, \beta_{i_2}, \ldots, \beta_{i_k}$, so that

$$p'(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}, \boldsymbol{\beta}) =$$
$$= \sum_{k=0}^m (-1)^k \sum_{1\leqslant i_1 < i_2 < \ldots < i_k \leqslant m} p(\boldsymbol{r}^N, \boldsymbol{p}^N; \alpha_1, \alpha_2, \ldots, \alpha_n, \beta_{i_1}, \beta_{i_2}, \ldots, \beta_{i_k}). \tag{3-55}$$

In the presence of an external magnetic field $\boldsymbol{B}$ eq. (3-50) becomes

$$Q(\boldsymbol{r}'^N | \boldsymbol{r}^N; \boldsymbol{B}; \boldsymbol{k}, \boldsymbol{l}) = Q(\boldsymbol{r}^N | \boldsymbol{r}'^N; -\boldsymbol{B}; \boldsymbol{k}, -\boldsymbol{l}), \tag{3-56}$$

(*cf.* eq. (2-29)) and eq. (3-52) becomes

$$p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}, \boldsymbol{\beta}; \boldsymbol{B}) = p'(\boldsymbol{r}^N, -\boldsymbol{p}^N; \boldsymbol{\alpha}, -\boldsymbol{\beta} - 0; -\boldsymbol{B}). \tag{3-57}$$

The probability

$$P(\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}) \equiv P(\alpha_{1,\lambda} \leqslant \alpha_1, \alpha_{2,\lambda} \leqslant \alpha_2, \ldots, \alpha_{n,\lambda} \leqslant \alpha_n), \tag{3-58}$$

that a system in thermodynamic equilibrium is in a state with

$$\alpha_{1,\lambda} \leqslant \alpha_1, \alpha_{2,\lambda} \leqslant \alpha_2, \ldots, \alpha_{n,\lambda} \leqslant \alpha_n,$$

is equal to the average of the projection operator $p_{op}(\boldsymbol{\alpha})$ in the microcanonical ensemble:

$$P(\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}) = G_{E;\Delta E}^{-1} \sum_{E_k \in (E;\Delta E)} \int \varphi_k^*(\boldsymbol{r}^N)\, p_{op}(\boldsymbol{\alpha})\, \varphi_k(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N. \tag{3-59}$$

Applying the theorem (2-4), (2-5) to this equation and using (3-35), we get

$$P(\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}) = \int p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})\, f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N. \tag{3-60}$$

We now introduce the function

$$F(\boldsymbol{\alpha}) \equiv P(\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}), \tag{3-61}$$

which is the probability distribution function of the extensive state variables in thermodynamic equilibrium. This distribution function is discontinuous, since $\boldsymbol{\alpha}_{op}$ has discrete eigenvalues. The function $F(\boldsymbol{\alpha})$ is introduced here in order to formulate later on the so-called "central limit theorem". It follows from (3-61) and (3-60) that

$$F(\boldsymbol{\alpha}) = \int p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})\, f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N. \tag{3-62}$$

With (3-18) we obtain from the last equation

$$F(\alpha) = \Omega(\alpha)/\Omega_{E;\,\Delta E}, \tag{3-63}$$

where

$$\Omega(\alpha) = \int p(\boldsymbol{r}^N, \boldsymbol{p}^N; \alpha)\, p_{E;\,\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N. \tag{3-64}$$

In the case of both even and odd state variables, eq. (3-62) becomes

$$F(\alpha, \beta) = \int p(\boldsymbol{r}^N, \boldsymbol{p}^N; \alpha, \beta)\, f_{E;\,\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N. \tag{3-65}$$

Applying the relations (3-20) and (3-52), (3-55) to this equation, we get

$$F(\alpha, \beta) = F'(\alpha, -\beta - 0), \tag{3-66}$$

with

$$F'(\alpha, \beta) = \sum_{k=0}^{m} (-1)^k \sum_{1 \leqslant i_1 < i_2 < \ldots < i_k \leqslant m} F(\alpha_1, \alpha_2, \ldots, \alpha_n, \beta_{i_1}, \beta_{i_2}, \ldots, \beta_{i_k}), \tag{3-67}$$

where $F(\alpha_1, \alpha_2, \ldots, \alpha_n, \beta_{i_1}, \beta_{i_2}, \ldots, \beta_{i_k})$ is the reduced distribution function of the state variables $\alpha_1, \alpha_2, \ldots, \alpha_n, \beta_{i_1}, \beta_{i_2}, \ldots, \beta_{i_k}$.

In the presence of an external magnetic field $\boldsymbol{B}$ we have *)

$$F(\alpha, \beta; \boldsymbol{B}) = \int p(\boldsymbol{r}^N, \boldsymbol{p}^N; \alpha, \beta; \boldsymbol{B})\, f_{E;\,\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B})\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N, \tag{3-68}$$

and it follows with (3-21) and (3-57) that

$$F(\alpha, \beta; \boldsymbol{B}) = F'(\alpha, -\beta - 0; -\boldsymbol{B}). \tag{3-69}$$

It follows from (3-28)–(3-31) that the projection operator $p_{op}(\alpha)$ has the following properties:

$$p_{op}(-\infty) = 0, \; p_{op}(+\infty) = 1. \tag{3-70}$$

For the corresponding classical function $p(\boldsymbol{r}^N, \boldsymbol{p}^N; \alpha)$ we therefore have

$$p(\boldsymbol{r}^N, \boldsymbol{p}^N; -\infty) = 0, \; p(\boldsymbol{r}^N, \boldsymbol{p}^N; +\infty) = 1 \tag{3-71}$$

and with eq. (3-62) we find for the distribution function $F(\alpha)$ that

$$F(-\infty) = 0, \; F(+\infty) = 1. \tag{3-72}$$

Introducing the operator $R(\alpha_{op})$ by means of

$$R(\alpha_{op})\, \chi_\lambda(\boldsymbol{r}^N) = R(\alpha_\lambda)\, \chi_\lambda(\boldsymbol{r}^N), \tag{3-73}$$

and writing $R(\alpha_\lambda)$ as the Stieltjes integral

$$R(\alpha_\lambda) = \int R(\alpha)\, \mathrm{d}p(\alpha_\lambda - \alpha), \tag{3-74}$$

we obtain with (3-29)

$$R(\alpha_{op}) = \int R(\alpha)\, \mathrm{d}p_{op}(\alpha). \tag{3-75}$$

*) For point particles it can be shown that, since the energy and the state variables are functions of the coordinates and velocities of these particles only, the expression (3-68) is independent of $\boldsymbol{B}$ in the classical limit.

For the classical function $R(\boldsymbol{r}^N, \boldsymbol{p}^N)$, corresponding to $R(\boldsymbol{\alpha}_{op})$:

$$R(\boldsymbol{r}^N, \boldsymbol{p}^N) \rightleftarrows R(\boldsymbol{\alpha}_{op}), \tag{3-76}$$

we find, using (3-75) and (3-35), that

$$R(\boldsymbol{r}^N, \boldsymbol{p}^N) = \int R(\boldsymbol{\alpha})\, \mathrm{d}p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}). \tag{3-77}$$

It then follows with eqs. (3-77) and (3-62) that the average of $R(\boldsymbol{\alpha}_{op})$ in the micro-canonical ensemble:

$$\begin{aligned}\overline{R(\boldsymbol{\alpha})}^{m.c.} &\equiv G_{E;\Delta E}^{-1} \textstyle\sum_{E_k \in (E;\Delta E)} \int \varphi_k^*(\boldsymbol{r}^N)\, R(\boldsymbol{\alpha}_{op})\, \varphi_k(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N = \\ &= \int R(\boldsymbol{r}^N, \boldsymbol{p}^N)\, f_{E;\,\Delta E}\, (\boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N,\end{aligned} \tag{3-78}$$

can be written as the following Stieltjes integral:

$$\overline{R(\boldsymbol{\alpha})}^{m.c.} = \int R(\boldsymbol{\alpha})\, \mathrm{d}F(\boldsymbol{\alpha}) \equiv \langle R(\boldsymbol{\alpha})\rangle. \tag{3-79}$$

We shall now assume that a central limit theorem *) holds for the extensive state variables under consideration. It then follows that the distribution function $F(\boldsymbol{\alpha})$ is approximately equal to the normal distribution function:

$$\begin{aligned}F(\boldsymbol{\alpha}) \simeq (2\pi k)^{-\frac{n}{2}}\, |\mathsf{g}|^{\frac{1}{2}} \int_{-\infty}^{\alpha_1} \int_{-\infty}^{\alpha_2} \ldots \int_{-\infty}^{\alpha_n} \exp\{-\tfrac{1}{2}k^{-1}(\textstyle\sum_{i,j=1}^{n} g_{ij}\, \alpha_i'\, \alpha_j')\} \\ \mathrm{d}\alpha_1'\, \mathrm{d}\alpha_2' \ldots \mathrm{d}\alpha_n',\end{aligned} \tag{3-80}$$

where $|\mathsf{g}|$ is the determinant of a symmetrical positive definite matrix g with elements g_{ij} and where k is Boltzmann's constant. In this approximation the distribution function (3-61) becomes continuous and differentiable and we can define a function

$$f(\boldsymbol{\alpha}) \equiv \frac{\partial^n F(\boldsymbol{\alpha})}{\partial\alpha_1\, \partial\alpha_2 \ldots \partial\alpha_n}, \tag{3-81}$$

which is the probability density in $\boldsymbol{\alpha}$-space for a system in thermodynamic equilibrium. It follows from the last two equations that this probability density function is Gaussian

$$\begin{aligned}f(\boldsymbol{\alpha}) = (2\pi k)^{-\frac{n}{2}}\, |\mathsf{g}|^{\frac{1}{2}} \exp\{-\tfrac{1}{2}k^{-1}\, (\textstyle\sum_{i,j=1}^{n} g_{ij}\alpha_i\alpha_j)\} = \\ = (2\pi k)^{-\frac{n}{2}}\, |\mathsf{g}|^{\frac{1}{2}} \exp\{-\tfrac{1}{2}k^{-1}(\mathsf{g} : \boldsymbol{\alpha}\boldsymbol{\alpha})\},\end{aligned} \tag{3-82}$$

where $\boldsymbol{\alpha}\boldsymbol{\alpha}$ is the dyadic matrix with elements $\alpha_i\alpha_j$. The function $f(\boldsymbol{\alpha})$ is normalized in $\boldsymbol{\alpha}$-space:

$$\int f(\boldsymbol{\alpha})\, \mathrm{d}\boldsymbol{\alpha} = 1. \tag{3-83}$$

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*) For certain types of extensive state variables, *e.g.* the energies of sub-regions of a crystal, the validity of a central limit theorem can be proved [11] [12]).

In the approximation (3-80) the Stieltjes integral (3-79) becomes the following ordinary integral:

$$\overline{R(\boldsymbol{\alpha})}^{m.c.} = \int R(\boldsymbol{\alpha})\, f(\boldsymbol{\alpha})\, \mathrm{d}\boldsymbol{\alpha} \equiv \langle R(\boldsymbol{\alpha})\rangle. \tag{3-84}$$

The Gaussian probability density (3-82) has mean values

$$\langle \boldsymbol{\alpha}\rangle = 0 \tag{3-85}$$

and variances

$$\langle \boldsymbol{\alpha\alpha}\rangle = k\mathsf{g}^{-1}, \tag{3-86}$$

where g^{-1} is the reciprocal matrix of g.

In the case of both even and odd state variables we have, instead of (3-81):

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}) \equiv \frac{\partial^{n+m} F(\boldsymbol{\alpha},\boldsymbol{\beta})}{\partial\alpha_1 \partial\alpha_2 \ldots \partial\alpha_n\, \partial\beta_1\, \partial\beta_2 \ldots \partial\beta_m}, \tag{3-87}$$

with the normal distribution function $F(\boldsymbol{\alpha}, \boldsymbol{\beta})$. It follows from (3-87), (3-66) and (3-67) that

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}) = f(\boldsymbol{\alpha}, -\boldsymbol{\beta}), \tag{3-88}$$

where we have used the fact that normal distribution functions are continuous. In the Gaussian probability density

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}) = (2\pi k)^{-\frac{n+m}{2}}\, |\mathsf{g}_{\alpha\alpha}|^{\frac{1}{2}}\, |\mathsf{g}_{\beta\beta}|^{\frac{1}{2}} \exp\{-\tfrac{1}{2}k^{-1}\,(\mathsf{g}_{\alpha\alpha} : \boldsymbol{\alpha\alpha} + \mathsf{g}_{\beta\beta} : \boldsymbol{\beta\beta})\} \tag{3-89}$$

no cross-terms between $\boldsymbol{\alpha}$- and $\boldsymbol{\beta}$-variables will occur as a consequence of the relation (3-88). The variances of (3-89) are

$$\langle \boldsymbol{\alpha\alpha}\rangle = k\mathsf{g}_{\alpha\alpha}^{-1},\ \langle \boldsymbol{\beta\beta}\rangle = k\mathsf{g}_{\beta\beta}^{-1},\ \langle \boldsymbol{\alpha\beta}\rangle = 0. \tag{3-90}$$

In the presence of an external magnetic field $\boldsymbol{B}$ we find with (3-69) that

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}; \boldsymbol{B}) = f(\boldsymbol{\alpha}, -\boldsymbol{\beta}; -\boldsymbol{B}). \tag{3-91}$$

In the Gaussian probability density *)

$$f(\boldsymbol{\alpha}, \boldsymbol{\beta}; \boldsymbol{B}) = (2\pi k)^{-\frac{n+m}{2}}\, |\mathsf{g}(\boldsymbol{B})|^{\frac{1}{2}} \exp[-\tfrac{1}{2}k^{-1}\{\mathsf{g}_{\alpha\alpha}(\boldsymbol{B}) : \boldsymbol{\alpha\alpha} + \mathsf{g}_{\alpha\beta}(\boldsymbol{B}) : \boldsymbol{\beta\alpha} + \mathsf{g}_{\beta\alpha}(\boldsymbol{B}) : \boldsymbol{\alpha\beta} + \mathsf{g}_{\beta\beta}(\boldsymbol{B}) : \boldsymbol{\beta\beta}\}] \tag{3-92}$$

now cross-terms between $\boldsymbol{\alpha}$- and $\boldsymbol{\beta}$-variables occur, in contrast to the case that $\boldsymbol{B} = 0$. In the last equation $|\mathsf{g}(\boldsymbol{B})|$ is the determinant of the matrix

*) In the classical limit the expression (3-92) reduces to the form (3-89) for $\boldsymbol{B} = 0$, since in this limit $F(\boldsymbol{\alpha}, \boldsymbol{\beta}; \boldsymbol{B})$ and consequently $f(\boldsymbol{\alpha}, \boldsymbol{\beta}; \boldsymbol{B})$ are independent of $\boldsymbol{B}$.

$$\mathsf{g}(\boldsymbol{B}) = \begin{array}{cc} \begin{array}{cc} \longleftarrow n \longrightarrow & \longleftarrow m \longrightarrow \end{array} & \\ \left[\begin{array}{c:c} \mathsf{g}_{\alpha\alpha}(\boldsymbol{B}) & \mathsf{g}_{\alpha\beta}(\boldsymbol{B}) \\ \hdashline \mathsf{g}_{\beta\alpha}(\boldsymbol{B}) & \mathsf{g}_{\beta\beta}(\boldsymbol{B}) \end{array}\right] & \begin{array}{c} \uparrow n \downarrow \\ \uparrow m \downarrow \end{array} \end{array}. \qquad (3\text{-}93)$$

Since $\mathsf{g}(\boldsymbol{B})$ is symmetrical, the matrices $\mathsf{g}_{\alpha\alpha}(\boldsymbol{B})$ and $\mathsf{g}_{\beta\beta}(\boldsymbol{B})$ are symmetrical and $\mathsf{g}_{\alpha\beta}(\boldsymbol{B})$ is the transposed matrix of $\mathsf{g}_{\beta\alpha}(\boldsymbol{B})$:

$$\mathsf{g}_{\alpha\beta}(\boldsymbol{B}) = \tilde{\mathsf{g}}_{\beta\alpha}(\boldsymbol{B}); \; (g_{\alpha\beta;ij}(\boldsymbol{B}) = g_{\beta\alpha;ji}(\boldsymbol{B})). \qquad (3\text{-}94)$$

It follows from (3-91) and (3-92) that the elements of the matrices $\mathsf{g}_{\alpha\alpha}(\boldsymbol{B})$ and $\mathsf{g}_{\beta\beta}(\boldsymbol{B})$ are even functions of $\boldsymbol{B}$, those of $\mathsf{g}_{\alpha\beta}(\boldsymbol{B})$ and $\mathsf{g}_{\beta\alpha}(\boldsymbol{B})$ odd functions of $\boldsymbol{B}$, whereas $|\mathsf{g}(\boldsymbol{B})|$ is an even function of $\boldsymbol{B}$. The variances of (3-92) are

$$\left.\begin{array}{l} \langle \boldsymbol{\alpha\alpha} \rangle = k\boldsymbol{\gamma}_{\alpha\alpha}(\boldsymbol{B}), \; \langle \boldsymbol{\beta\beta} \rangle = k\boldsymbol{\gamma}_{\beta\beta}(\boldsymbol{B}) \\ \langle \boldsymbol{\alpha\beta} \rangle = k\boldsymbol{\gamma}_{\alpha\beta}(\boldsymbol{B}), \; \langle \boldsymbol{\beta\alpha} \rangle = k\boldsymbol{\gamma}_{\beta\alpha}(\boldsymbol{B}) \end{array}\right\}, \qquad (3\text{-}95)$$

with

$$\mathsf{g}^{-1}(\boldsymbol{B}) = \begin{array}{cc} \begin{array}{cc} \longleftarrow n \longrightarrow & \longleftarrow m \longrightarrow \end{array} & \\ \left[\begin{array}{c:c} \boldsymbol{\gamma}_{\alpha\alpha}(\boldsymbol{B}) & \boldsymbol{\gamma}_{\alpha\beta}(\boldsymbol{B}) \\ \hdashline \boldsymbol{\gamma}_{\beta\alpha}(\boldsymbol{B}) & \boldsymbol{\gamma}_{\beta\beta}(\boldsymbol{B}) \end{array}\right] & \begin{array}{c} \uparrow n \downarrow \\ \uparrow m \downarrow \end{array} \end{array}. \qquad (3\text{-}96)$$

From the properties of the matrices $\mathsf{g}_{\alpha\alpha}(\boldsymbol{B})$, $\mathsf{g}_{\beta\beta}(\boldsymbol{B})$, $\mathsf{g}_{\alpha\beta}(\boldsymbol{B})$ and $\mathsf{g}_{\beta\alpha}(\boldsymbol{B})$ we find the following properties of the matrices $\boldsymbol{\gamma}_{\alpha\alpha}(\boldsymbol{B})$, $\boldsymbol{\gamma}_{\beta\beta}(\boldsymbol{B})$,$\boldsymbol{\gamma}_{\alpha\beta}(\boldsymbol{B})$ and $\boldsymbol{\gamma}_{\beta\alpha}(\boldsymbol{B})$: the matrices $\boldsymbol{\gamma}_{\alpha\alpha}(\boldsymbol{B})$ and $\boldsymbol{\gamma}_{\beta\beta}(\boldsymbol{B})$ are symmetrical and

$$\boldsymbol{\gamma}_{\alpha\beta}(\boldsymbol{B}) = \tilde{\boldsymbol{\gamma}}_{\beta\alpha}(\boldsymbol{B}). \qquad (3\text{-}97)$$

The elements of the matrices $\boldsymbol{\gamma}_{\alpha\alpha}(\boldsymbol{B})$ and $\boldsymbol{\gamma}_{\beta\beta}(\boldsymbol{B})$ are even functions of $\boldsymbol{B}$ and those of $\boldsymbol{\gamma}_{\alpha\beta}(\boldsymbol{B})$ and $\boldsymbol{\gamma}_{\beta\alpha}(\boldsymbol{B})$ odd functions of $\boldsymbol{B}$.

§ 4. *Intensive variables.* In addition to the extensive state variables $\boldsymbol{\alpha}$ we shall now introduce a set of intensive thermodynamic variables $\boldsymbol{X}$. In order to define these variables, we shall make use of Boltzmann's entropy postulate, according to which the entropy $S(\boldsymbol{\alpha})$ of a state $\boldsymbol{\alpha}$, defined with the precision $\Delta\boldsymbol{\alpha}$,is given by

$$S(\boldsymbol{\alpha}) \equiv k \ln \{\Delta\Omega(\boldsymbol{\alpha})/h^{3N}\}, \qquad (4\text{-}1)$$

where $\Delta\Omega(\boldsymbol{\alpha})$ is the n^{th} order difference *) of $\Omega(\boldsymbol{\alpha})$ over the range $(\boldsymbol{\alpha}; \Delta\boldsymbol{\alpha})$. The quantity $\Delta\Omega(\boldsymbol{\alpha})$ reduces in the classical limit to the volume of the region in phase space, where the state variables have values in the range $(\boldsymbol{\alpha}; \Delta\boldsymbol{\alpha})$ and where the energy lies in the range $(E; \Delta E)$. It follows with (3-63) and (3-17) that

$$S(\boldsymbol{\alpha}) = k \ln \{\Delta F(\boldsymbol{\alpha})\} + S_G, \tag{4-2}$$

where

$$S_G \equiv k \ln G_{E;\Delta E} \tag{4-3}$$

is Gibbs' entropy of the micro-canonical ensemble. It follows with (3-61) that $\Delta F(\boldsymbol{\alpha})$ is the probability that the system in thermodynamic equilibrium is in a state with $\boldsymbol{\alpha}_\lambda \in (\boldsymbol{\alpha}; \Delta\boldsymbol{\alpha})$, *i.e.* $\alpha_i - \frac{1}{2}\Delta\alpha_i < \alpha_{i,\lambda} \leqslant \alpha_i + \frac{1}{2}\Delta\alpha_i$. Eq. (4-2) is therefore a relation between the entropy and the probability of a state $\boldsymbol{\alpha}$, defined with the precision $\Delta\boldsymbol{\alpha}$.

In the approximation (3-80), eq. (4-2) becomes

$$S(\boldsymbol{\alpha}) \simeq k \ln \{(2\pi k)^{-\frac{n}{2}} |\mathsf{g}|^{\frac{1}{2}} \Delta\boldsymbol{\alpha}\} - \tfrac{1}{2}(\mathsf{g} : \boldsymbol{\alpha}\boldsymbol{\alpha}) + S_G, \tag{4-4}$$

with $\Delta\boldsymbol{\alpha} = \prod_{i=1}^{n} \Delta\alpha_i$, assuming that the quantities $\Delta\alpha_i$ are much smaller than the half-widths of the Gaussian (3-82). It can be shown that, even for a very precise determination $\Delta\boldsymbol{\alpha}$ of the state $\boldsymbol{\alpha}$, the first term on the right-hand side of eq. (4-4) may be neglected with respect to the third term, so that

$$S(\boldsymbol{\alpha}) \simeq -\tfrac{1}{2}(\mathsf{g} : \boldsymbol{\alpha}\boldsymbol{\alpha}) + S_G. \tag{4-5}$$

Introducing the quantity

$$\Delta S \equiv S(\boldsymbol{\alpha}) - S(0), \tag{4-6}$$

we find that

$$\Delta S = -\tfrac{1}{2}(\mathsf{g} : \boldsymbol{\alpha}\boldsymbol{\alpha}), \tag{4-7}$$

which may be regarded as a Taylor series expansion up to terms of order $\boldsymbol{\alpha}^2$ of $S(\boldsymbol{\alpha})$ around its maximum value.

We now define intensive variables $\boldsymbol{X}$, conjugate to the extensive variables $\boldsymbol{\alpha}$, by means of

$$\boldsymbol{X} \equiv \partial \Delta S / \partial \boldsymbol{\alpha}. \tag{4-8}$$

It then follows with (4-7) that

$$\boldsymbol{X} = -\,\mathsf{g} \cdot \boldsymbol{\alpha}. \tag{4-9}$$

In the case of both $\boldsymbol{\alpha}$- and $\boldsymbol{\beta}$-variables, eq. (4-7) becomes

$$\Delta S = -\tfrac{1}{2}(\mathsf{g}_{\alpha\alpha} : \boldsymbol{\alpha}\boldsymbol{\alpha} + \mathsf{g}_{\beta\beta} : \boldsymbol{\beta}\boldsymbol{\beta}), \tag{4-10}$$

*) The quantity $\Delta\Omega(\boldsymbol{\alpha})$ is defined as follows:
$\Delta\Omega(\boldsymbol{\alpha}) \equiv \sum_{k=0}^{n} (-1)^k \sum_{1 \leqslant i_1 < i_2 < \ldots < i_k \leqslant n} \Omega(a_1 + \frac{1}{2}\Delta a_1, \ldots, a_{i_1-1} + \frac{1}{2}\Delta a_{i_1-1},$
$a_{i_1} - \frac{1}{2}\Delta a_{i_1}, a_{i_1+1} + \frac{1}{2}\Delta a_{i_1+1}, \ldots, a_{i_2-1} + \frac{1}{2}\Delta a_{i_2-1}, a_{i_2} - \frac{1}{2}\Delta a_{i_2}, a_{i_2+1} + \frac{1}{2}\Delta a_{i_2+1}, \ldots,$
$a_{i_k-1} + \frac{1}{2}\Delta a_{i_k-1}, a_{i_k} - \frac{1}{2}\Delta a_{i_k}, a_{i_k+1} + \frac{1}{2}\Delta a_{i_k+1}, \ldots, a_n + \frac{1}{2}\Delta a_n).$

(*cf.* eq. (3-89)) and in the presence of an external magnetic field $\boldsymbol{B}$ we have

$$\Delta S = -\tfrac{1}{2}\{\mathsf{g}_{\alpha\alpha}(\boldsymbol{B}) : \boldsymbol{\alpha\alpha} + \mathsf{g}_{\alpha\beta}(\boldsymbol{B}) : \boldsymbol{\beta\alpha} + \mathsf{g}_{\beta\alpha}(\boldsymbol{B}) : \boldsymbol{\alpha\beta} + \mathsf{g}_{\beta\beta}(\boldsymbol{B}) : \boldsymbol{\beta\beta}\}, \tag{4-11}$$

(*cf.* eq. (3-92)). Defining now the intensive variables

$$\left.\begin{aligned} \boldsymbol{X} &\equiv \partial\Delta S/\partial\boldsymbol{\alpha} \\ \boldsymbol{Y} &\equiv \partial\Delta S/\partial\boldsymbol{\beta} \end{aligned}\right\}, \tag{4-12}$$

we get in the absence of a magnetic field

$$\left.\begin{aligned} \boldsymbol{X} &= -\mathsf{g}_{\alpha\alpha}\cdot\boldsymbol{\alpha} \\ \boldsymbol{Y} &= -\mathsf{g}_{\beta\beta}\cdot\boldsymbol{\beta} \end{aligned}\right\}, \tag{4-13}$$

and in the presence of a magnetic field

$$\left.\begin{aligned} \boldsymbol{X} &= -\mathsf{g}_{\alpha\alpha}(\boldsymbol{B})\cdot\boldsymbol{\alpha} - \mathsf{g}_{\alpha\beta}(\boldsymbol{B})\cdot\boldsymbol{\beta} \\ \boldsymbol{Y} &= -\mathsf{g}_{\beta\alpha}(\boldsymbol{B})\cdot\boldsymbol{\alpha} - \mathsf{g}_{\beta\beta}(\boldsymbol{B})\cdot\boldsymbol{\beta} \end{aligned}\right\}, \tag{4-14}$$

where eqs. (4-10) and (4-11) have been used.

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Chapter II

THE THEORY OF JOINT WIGNER DISTRIBUTION FUNCTIONS AND THE DERIVATION OF THE ONSAGER RECIPROCAL RELATIONS

Synopsis

The quantum statistical theory of Wigner distribution functions, presented in the previous chapter, is used in order to develop the theory of "joint Wigner distribution functions", which may be employed for the calculation of quantum mechanical correlation functions.

The joint equilibrium distribution function of a set of extensive state variables is defined. This distribution function is expressed in terms of the joint Wigner distribution function of the micro-canonical ensemble. The properties of joint equilibrium distribution functions of extensive variables, in particular the so-called property of detailed balance, are studied.

It is shown that joint equilibrium distribution functions, which do in general not represent a probability, are joint probabilities, if the set of quantum mechanical operators, corresponding to the extensive state variables, is of a certain class.

The theory of distribution functions of extensive state variables thus obtained, which is formally the same as developed by de Groot and Mazur on the basis of classical statistical mechanics, is used for the derivation of the Onsager reciprocal relations in non-equilibrium thermodynamics.

The theory is developed in the present chapter for Maxwell-Boltzmann statistics.

§ 1. *Introduction.* In the previous chapter (I) we have developed the theory of ordinary Wigner distribution functions [1]). Using the results obtained in that chapter, we shall develop in the present chapter (II) the theory of "joint Wigner distribution functions". Just as in I, the theory is developed here for Maxwell-Boltzmann statistics only. The extension to the cases of Bose-Einstein and Fermi-Dirac statistics will be given in the following chapter (III).

In § 2 it will be shown that time correlation functions of quantum mechanical operators may be written as phase space averages of the classical functions, corresponding to these operators according to Weyl's rule [2]), over joint phase space distribution functions. These quantum mechanical distribution functions will be called "joint Wigner distribution functions".

We shall express the joint Wigner distribution functions in terms of ordinary Wigner distribution functions and their propagators. From the properties, obtained in I for the last two quantities, we shall then derive several properties of joint Wigner distribution functions.

In § 3 we shall introduce the joint equilibrium distribution function of a set of extensive state variables, which will be defined as the time correlation function of certain projection operators of these state variables in the micro-canonical ensemble. This distribution function will be written as the phase space average of the classical functions, corresponding to these projection operators, over the joint Wigner distribution function of the micro-canonical ensemble. We then derive the property of detailed balance for joint equilibrium distribution functions of extensive variables. The joint equilibrium distribution functions may be used to calculate time correlation functions of arbitrary functions of the state variables in a micro-canonical ensemble.

Joint distribution functions of extensive state variables are in general not probability distribution functions. It will be shown, however, at the end of § 3 that the joint equilibrium distribution function does represent a joint probability, if the set of quantum mechanical operators, corresponding to the state variables, satisfies certain conditions. In the approximation that these distribution functions are continuous and differentiable, it is then possible to define joint probability density functions of the state variables in thermodynamic equilibrium.

The theory of probability density functions of extensive state variables, thus obtained on the basis of quantum statistical mechanics, is formally the same as developed by de Groot and Mazur[3]) on the basis of classical statistical mechanics. The derivation of the Onsager reciprocal relations[4]) can then proceed along the usual lines.

§ 2. *Joint Wigner distribution functions*. In chapter I, eqs. (2-4) and (2-5), we have seen that Wigner distribution functions $f(\boldsymbol{r}^N, \boldsymbol{p}^N; t)$ could be used in order to calculate ensemble averages of quantum mechanical operators as phase space averages of the classical functions, corresponding to these operators according to Weyl's rule I (2-3). We shall introduce in the present section distribution functions $f(\boldsymbol{r}^N, \boldsymbol{p}^N; t; \boldsymbol{r}'^N, \boldsymbol{p}'^N; t + \tau)$, which will enable us to calculate time correlation functions of quantum mechanical operators as phase space averages.

The time correlation of the operators A_{op} and B_{op} in a quantum mechanical ensemble with density matrix I (2-1) is described by means of the correlation function

$$C\{A(t), B(t+\tau)\} =$$
$$= \tfrac{1}{2} \textstyle\sum_\mu w_\mu \int \psi_\mu^*(\boldsymbol{r}^N; t) \{A_{op}B_{op}(\tau) + B_{op}(\tau)\, A_{op}\}\, \psi_\mu(\boldsymbol{r}^N; t)\, \mathrm{d}\boldsymbol{r}^N, \qquad \text{(2-1)}$$

with

$$B_{op}(\tau) \equiv \exp\{(i/\hbar)\, H_{op}\tau\}\, B_{op} \exp\{(-i/\hbar)\, H_{op}\tau\}. \tag{2-2}$$

Let $A(\boldsymbol{r}^N, \boldsymbol{p}^N)$ be the classical function, corresponding to A_{op} according to Weyl's rule:

$$A(\boldsymbol{r}^N, \boldsymbol{p}^N) \rightleftarrows A_{op}, \tag{2-3}$$

then it follows with I (2-36) and I (2-49) that

$$A_{op} = \int A(\boldsymbol{r}'^N, \boldsymbol{p}'^N)\, P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0)\, \mathrm{d}\boldsymbol{r}'^N\, \mathrm{d}\boldsymbol{p}'^N. \tag{2-4}$$

Similarly we have

$$B_{op} = \int B(\boldsymbol{r}'^N, \boldsymbol{p}'^N)\, P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0)\, \mathrm{d}\boldsymbol{r}'^N\, \mathrm{d}\boldsymbol{p}'^N, \tag{2-5}$$

with

$$B(\boldsymbol{r}^N, \boldsymbol{p}^N) \rightleftarrows B_{op}. \tag{2-6}$$

Substituting (2-5) into the right-hand side of (2-2) and using I (2-38), we find that

$$B_{op}(\tau) = \int B(\boldsymbol{r}'^N, \boldsymbol{p}'^N)\, P_{op}\, (\boldsymbol{r}'^N, \boldsymbol{p}'^N; \tau)\, \mathrm{d}\boldsymbol{r}'^N\, \mathrm{d}\boldsymbol{p}'^N. \tag{2-7}$$

Applying (2-4) and (2-7) to (2-1), we get

$$C\{A(t), B(t+\tau)\} =$$

$$= \iint A(\boldsymbol{r}'^N,\boldsymbol{p}'^N) B(\boldsymbol{r}''^N,\boldsymbol{p}''^N) f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)\mathrm{d}\boldsymbol{r}'^N\mathrm{d}\boldsymbol{p}'^N\mathrm{d}\boldsymbol{r}''^N\mathrm{d}\boldsymbol{p}''^N, \tag{2-8}$$

where we have introduced the distribution function

$$f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau) \equiv C\{P(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t), P(\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)\} =$$

$$= \tfrac{1}{2}\textstyle\sum_\mu w_\mu \int \psi_\mu^*(\boldsymbol{r}^N;t)\{P_{op}(\boldsymbol{r}'^N,\boldsymbol{p}'^N;0)\, P_{op}(\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau) +$$

$$+ P_{op}(\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau)\, P_{op}(\boldsymbol{r}'^N,\boldsymbol{p}'^N;0)\}\, \psi_\mu(\boldsymbol{r}^N;t)\, \mathrm{d}\boldsymbol{r}^N. \tag{2-9}$$

We thus obtain the result that the time correlation function of the quantum mechanical operators A_{op} and B_{op} can be written as the phase space average of the classical functions $A(\boldsymbol{r}'^N, \boldsymbol{p}'^N)$ and $B(\boldsymbol{r}''^N, \boldsymbol{p}''^N)$ over the distribution function (2-9).

From the Weyl correspondences I (2-36) and I (2-37) it can be shown [5]) that

$$\tfrac{1}{2}\{P_{op}(\boldsymbol{r}'^N,\boldsymbol{p}'^N;0)\, P_{op}(\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau) + P_{op}(\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau)\, P_{op}(\boldsymbol{r}'^N,\boldsymbol{p}'^N;0)\} \rightleftarrows$$

$$\rightleftarrows P(\boldsymbol{r}'^N,\boldsymbol{p}'^N|\boldsymbol{r}^N,\boldsymbol{p}^N;0)\cos\left\{\frac{\hbar}{2}\left(\frac{6}{6\boldsymbol{r}^N}\cdot\frac{\partial}{\partial\boldsymbol{p}^N} - \frac{6}{6\boldsymbol{p}^N}\cdot\frac{\partial}{\partial\boldsymbol{r}^N}\right)\right\} P(\boldsymbol{r}''^N,\boldsymbol{p}''^N|\boldsymbol{r}^N,\boldsymbol{p}^N;-\tau), \tag{2-10}$$

where the 6-symbol denotes differentiation "to the left". It follows from the last Weyl correspondence and the theorem I (2-4), I (2-5) that the distribution function (2-9) can be written as the following phase space integral over the Wigner distribution function I (2-2):

$$f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)=\int f(\boldsymbol{r}^N,\boldsymbol{p}^N;t)\Big[P(\boldsymbol{r}'^N,\boldsymbol{p}'^N|\boldsymbol{r}^N,\boldsymbol{p}^N;0)$$

$$\cos\left\{\frac{\hbar}{2}\left(\frac{\partial}{\partial\boldsymbol{r}^N}\cdot\frac{\partial}{\partial\boldsymbol{p}^N}-\frac{\partial}{\partial\boldsymbol{p}^N}\cdot\frac{\partial}{\partial\boldsymbol{r}^N}\right)\right\}P(\boldsymbol{r}''^N,\boldsymbol{p}''^N|\boldsymbol{r}^N,\boldsymbol{p}^N;-\tau)\Big]\,\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N. \quad (2\text{-}11)$$

Applying the relations I (2-49) and I (2-53) to this equation and integrating by parts, we find that

$$f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)=\int\delta(\boldsymbol{r}'^N-\boldsymbol{r}^N)\,\delta(\boldsymbol{p}'^N-\boldsymbol{p}^N)\Big[f(\boldsymbol{r}^N,\boldsymbol{p}^N;t)$$

$$\cos\left\{\frac{\hbar}{2}\left(\frac{\partial}{\partial\boldsymbol{r}^N}\cdot\frac{\partial}{\partial\boldsymbol{p}^N}-\frac{\partial}{\partial\boldsymbol{p}^N}\cdot\frac{\partial}{\partial\boldsymbol{r}^N}\right)\right\}P(\boldsymbol{r}^N,\boldsymbol{p}^N|\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau)\Big]\,\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N, \quad (2\text{-}12)$$

so that

$$f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)=f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t)$$

$$\cos\left\{\frac{\hbar}{2}\left(\frac{\partial}{\partial\boldsymbol{r}'^N}\cdot\frac{\partial}{\partial\boldsymbol{p}'^N}-\frac{\partial}{\partial\boldsymbol{p}'^N}\cdot\frac{\partial}{\partial\boldsymbol{r}'^N}\right)\right\}P(\boldsymbol{r}'^N,\boldsymbol{p}'^N|\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau). \quad (2\text{-}13)$$

The distribution function (2-13) is the quantum mechanical analogue of the classical distribution function

$$f^{(cl)}(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)=f^{(cl)}(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t)\,P^{(cl)}(\boldsymbol{r}'^N,\boldsymbol{p}'^N|\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau), \quad (2\text{-}14)$$

which may be used in order to calculate time correlation functions in classical statistical mechanics. The quantity

$$f^{(cl)}(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)\,\mathrm{d}\boldsymbol{r}'^N\mathrm{d}\boldsymbol{p}'^N\mathrm{d}\boldsymbol{r}''^N\mathrm{d}\boldsymbol{p}''^N$$

is the joint probability to find a system of a classical ensemble in the range $(\boldsymbol{r}'^N,\boldsymbol{p}'^N;\mathrm{d}\boldsymbol{r}'^N,\mathrm{d}\boldsymbol{p}'^N)$ at the time t and in $(\boldsymbol{r}''^N,\boldsymbol{p}''^N;\mathrm{d}\boldsymbol{r}''^N,\mathrm{d}\boldsymbol{p}''^N)$ at $t+\tau$. The classical distribution function (2-14) is therefore a joint probability density in phase space and consequently always positive. The quantum analogue (2-13) of this classical joint distribution function will be called a "joint Wigner distribution function". In contrast with a classical joint distribution function, a joint Wigner distribution function may assume negative values and does not represent a joint probability density in phase space.

It follows from (2-13) that

$$\int f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t;\boldsymbol{r}''^N,\boldsymbol{p}''^N;t+\tau)\,\mathrm{d}\boldsymbol{r}'^N\mathrm{d}\boldsymbol{p}'^N=\int f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t)$$

$$\cos\left\{\frac{\hbar}{2}\left(\frac{\partial}{\partial\boldsymbol{r}'^N}\cdot\frac{\partial}{\partial\boldsymbol{p}'^N}-\frac{\partial}{\partial\boldsymbol{p}'^N}\cdot\frac{\partial}{\partial\boldsymbol{r}'^N}\right)\right\}P(\boldsymbol{r}'^N,\boldsymbol{p}'^N|\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau)\,\mathrm{d}\boldsymbol{r}'^N\mathrm{d}\boldsymbol{p}'^N=$$

$$=\int f(\boldsymbol{r}'^N,\boldsymbol{p}'^N;t)\,P(\boldsymbol{r}'^N,\boldsymbol{p}'^N|\boldsymbol{r}''^N,\boldsymbol{p}''^N;\tau)\,\mathrm{d}\boldsymbol{r}'^N\mathrm{d}\boldsymbol{p}'^N, \quad (2\text{-}15)$$

applying partial integration. Since the last member of this equation is equal to the Wigner distribution function at the time $t + \tau$ (*cf.* I (2-34)), we find that

$$\int f(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t; \boldsymbol{r}''^N, \boldsymbol{p}''^N; t+\tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N = f(\boldsymbol{r}''^N, \boldsymbol{p}''^N; t+\tau). \tag{2-16}$$

On the other hand it follows from (2-13) and I (2-51) that

$$\int f(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t; \boldsymbol{r}''^N, \boldsymbol{p}''^N; t+\tau)\, \mathrm{d}\boldsymbol{r}''^N \mathrm{d}\boldsymbol{p}''^N = f(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t). \tag{2-17}$$

Equations (2-16) and (2-17) give the normalization of the joint Wigner distribution function (2-13).

For an adiabatically insulated system in thermodynamic equilibrium, described by a micro-canonical ensemble with density matrix I (3-1), the joint Wigner distribution function (2-9) becomes

$$\begin{aligned} f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau) = \\ = \tfrac{1}{2} G_{E;\Delta E}^{-1} \textstyle\sum_{E_k \in (E;\Delta E)} \int \varphi_k^*(\boldsymbol{r}^N) \{P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0)\, P_{op}(\boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau) + \\ + P_{op}(\boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau)\, P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0)\} \varphi_k(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N, \end{aligned} \tag{2-18}$$

which depends only on the time interval τ and not on the initial time t (stationary distribution function), since the micro-canonical density matrix is independent of t. We may therefore shift the times, appearing in the time dependent operators on the right-hand side of (2-18), with the same amount, so that we obtain

$$\begin{aligned} f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; t) = \\ = \tfrac{1}{2} G_{E;\Delta E}^{-1} \textstyle\sum_{E_k \in (E;\Delta E)} \int \varphi_k^*(\boldsymbol{r}^N) \{P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t)\, P_{op}(\boldsymbol{r}''^N, \boldsymbol{p}''^N; t+\tau) + \\ + P_{op}(\boldsymbol{r}''^N, \boldsymbol{p}''^N; t+\tau)\, P_{op}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t)\} \varphi_k(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N. \end{aligned} \tag{2-19}$$

If we now put $t = -\tau$ in this equation, we find with (2-18) that the following relation holds for the stationary distribution function $f_{E;\Delta E}\ (\boldsymbol{r}'^N,\ \boldsymbol{p}'^N;\ \boldsymbol{r}''^N,\ \boldsymbol{p}''^N;\ \tau)$:

$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau) = f_{E;\Delta E}(\boldsymbol{r}''^N, \boldsymbol{p}''^N; \boldsymbol{r}'^N, \boldsymbol{p}'^N; -\tau). \tag{2-20}$$

For a micro-canonical ensemble eq. (2-13) becomes

$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau) = f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N) \cos\left\{\frac{\hbar}{2}\left(\frac{6}{6\boldsymbol{r}'^N} \cdot \frac{\partial}{\partial \boldsymbol{p}'^N} - \frac{6}{6\boldsymbol{p}'^N} \cdot \frac{\partial}{\partial \boldsymbol{r}'^N}\right)\right\} P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau), \tag{2-21}$$

where $f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N)$ is given by I (3-12). If we now apply the property I (2-54) ("invariance under reversal of the motion of the particles") to the right-hand side of (2-21), we find with I (2-53) and the fact that

$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N)$ is an even function of the particle momenta (eq. I (3-20)), that

$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau) = f_{E;\Delta E}(\boldsymbol{r}'^N, -\boldsymbol{p}'^N; \boldsymbol{r}''^N, -\boldsymbol{p}''^N; -\tau), \quad (2\text{-}22)$$

or with (2-20)

$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau) = f_{E;\Delta E}(\boldsymbol{r}''^N, -\boldsymbol{p}''^N; \boldsymbol{r}'^N, -\boldsymbol{p}'^N; \tau). \quad (2\text{-}23)$$

In the presence of an external magnetic field $\boldsymbol{B}$ the last relation becomes

$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \boldsymbol{B}; \tau) = f_{E;\Delta E}(\boldsymbol{r}''^N, -\boldsymbol{p}''^N; \boldsymbol{r}'^N, -\boldsymbol{p}'^N; -\boldsymbol{B}; \tau), \quad (2\text{-}24)$$

which may be proved in an analogous way as (2-23), using I (2-55) and I (3-21).

The normalization of the stationary joint Wigner distribution function (2-21) is given by

$$\int f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N = f_{E;\Delta E}(\boldsymbol{r}''^N, \boldsymbol{p}''^N), \quad (2\text{-}25)$$

$$\int f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}''^N, \boldsymbol{p}''^N; \tau)\, \mathrm{d}\boldsymbol{r}''^N \mathrm{d}\boldsymbol{p}''^N = f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N), \quad (2\text{-}26)$$

as follows with (2-16) and (2-17).

§ 3. *Joint equilibrium distribution functions of extensive state variables; detailed balance.* In chapter I we have introduced the probability distribution function $F(\boldsymbol{\alpha})$ of a set of extensive state variables in thermodynamic equilibrium, assuming that these variables are represented by commuting operators in quantum theory. According to I (3-61) and I (3-59), this distribution function is given by the micro-canonical ensemble average of the projection operator $p_{op}(\boldsymbol{\alpha})$, defined by I (3-28)–I (3-31).

We shall now introduce the joint equilibrium distribution function $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$, which will be defined as the time correlation function of the projection operators $p_{op}(\boldsymbol{\alpha}')$ and $p_{op}(\boldsymbol{\alpha})$ in a micro-canonical ensemble:

$$\begin{aligned} F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) &\equiv C^{m.c.}\{p(\boldsymbol{\alpha}'), p(\boldsymbol{\alpha}; \tau)\} \equiv \\ &\equiv \tfrac{1}{2} G^{-1}_{E;\Delta E} \textstyle\sum_{E_k \in (E;\Delta E)} \int \varphi^*_k(\boldsymbol{r}^N) \{p_{op}(\boldsymbol{\alpha}')\, p_{op}(\boldsymbol{\alpha}; \tau) + \\ &\quad + p_{op}(\boldsymbol{\alpha}; \tau)\, p_{op}(\boldsymbol{\alpha}')\}\, \varphi_k(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N, \end{aligned} \quad (3\text{-}1)$$

where

$$p_{op}(\boldsymbol{\alpha}; \tau) \equiv \exp\{(i/\hbar)\, H_{op}\tau\}\, p_{op}(\boldsymbol{\alpha})\, \exp\{(-i/\hbar)\, H_{op}\tau\}. \quad (3\text{-}2)$$

The distribution function $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ is stationary, *i.e.* it depends only on the time interval τ and not on the initial time t.

Applying the general formula (2-8) to (3-1) and using the Weyl correspondence I (3-35), we find that

$$\begin{aligned} &F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) = \\ &= \iint p(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{\alpha}')\, p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})\, f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}^N, \boldsymbol{p}^N; \tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N, \end{aligned} \quad (3\text{-}3)$$

where the joint Wigner distribution function $f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}^N, \boldsymbol{p}^N; \tau)$ is given by (2-21).

According to (3-1), $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ is an ensemble average of the anticommutator of two non-commuting projection operators. Although both projection operators have non-negative eigenvalues, their anticommutator may possess negative eigenvalues, so that an ensemble average of this anticommutator may be negative. Therefore $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ does in general not represent a probability in $\boldsymbol{\alpha}$-space, in contrast with the distribution function $F(\boldsymbol{\alpha})$.

In chapter I, eq. (3-79), we have seen that equilibrium distribution functions $F(\boldsymbol{\alpha})$ could be used to calculate micro-canonical ensemble averages of quantum mechanical operators $R(\boldsymbol{\alpha}_{op})$. We shall now prove that joint equilibrium distribution functions $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ may be employed for the calculation of time correlation functions of operators $R_1(\boldsymbol{\alpha}_{op})$ and $R_2(\boldsymbol{\alpha}_{op})$ in micro-canonical ensembles. These correlation functions are given by

$$
\begin{aligned}
&C^{m.c.}\{R_1(\boldsymbol{\alpha}), R_2(\boldsymbol{\alpha}(\tau))\} = \\
&= \tfrac{1}{2}\, G_{E;\Delta E}^{-1} \textstyle\sum_{E_k \in (E;\Delta E)} \int \varphi_k^*(\boldsymbol{r}^N) \{R_1(\boldsymbol{\alpha}_{op})\, R_2(\boldsymbol{\alpha}_{op}(\tau)) + \\
&\qquad\qquad + R_2(\boldsymbol{\alpha}_{op}(\tau))\, R_1(\boldsymbol{\alpha}_{op})\}\, \varphi_k(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N = \\
&= \iint R_1(\boldsymbol{r}'^N, \boldsymbol{p}'^N)\, R_2(\boldsymbol{r}^N, \boldsymbol{p}^N)\, f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}^N, \boldsymbol{p}^N; \tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N,
\end{aligned}
\tag{3-4}
$$

where

$$R_2(\boldsymbol{\alpha}_{op}(\tau)) \equiv \exp\{(i/\hbar)\, H_{op}\tau\}\, R_2(\boldsymbol{\alpha}_{op}) \exp\{(-i/\hbar)\, H_{op}\tau\}, \tag{3-5}$$

and where $R_1(\boldsymbol{r}^N, \boldsymbol{p}^N)$ and $R_2(\boldsymbol{r}^N, \boldsymbol{p}^N)$ are the classical functions, corresponding to $R_1(\boldsymbol{\alpha}_{op})$ and $R_2(\boldsymbol{\alpha}_{op})$ according to Weyl's rule:

$$\left.\begin{aligned} R_1(\boldsymbol{r}^N, \boldsymbol{p}^N) &\rightleftarrows R_1(\boldsymbol{\alpha}_{op}) \\ R_2(\boldsymbol{r}^N, \boldsymbol{p}^N) &\rightleftarrows R_2(\boldsymbol{\alpha}_{op}) \end{aligned}\right\}. \tag{3-6}$$

From I (3-77) we have

$$\left.\begin{aligned} R_1(\boldsymbol{r}^N, \boldsymbol{p}^N) &= \int R_1(\boldsymbol{\alpha})\, \mathrm{d}p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}) \\ R_2(\boldsymbol{r}^N, \boldsymbol{p}^N) &= \int R_2(\boldsymbol{\alpha})\, \mathrm{d}p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha}) \end{aligned}\right\}. \tag{3-7}$$

Substituting these relations into the last member of (3-4) and using (3-3), we find that

$$C^{m.c.}\{R_1(\boldsymbol{\alpha}), R_2(\boldsymbol{\alpha}(\tau))\} = \iint R_1(\boldsymbol{\alpha}')\, R_2(\boldsymbol{\alpha})\, \mathrm{d}F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau). \tag{3-8}$$

From (3-3) and I (3-71), together with (2-25), (2-26) and I (3-62), we find that $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ is normalized in the following way:

$$F(-\infty; \boldsymbol{\alpha}; \tau) = 0,\ F(+\infty; \boldsymbol{\alpha}; \tau) = F(\boldsymbol{\alpha}), \tag{3-9}$$

$$F(\boldsymbol{\alpha}'; -\infty; \tau) = 0,\ F(\boldsymbol{\alpha}'; +\infty; \tau) = F(\boldsymbol{\alpha}'). \tag{3-10}$$

We shall now examine the influence of the properties (2-23) and (2-24) of micro-canonical joint Wigner distribution functions on joint equilibrium distribution functions of extensive state variables. Application of (2-23) to (3-3) gives

$$F(\alpha';\alpha;\tau) =$$
$$= \iint p(\boldsymbol{r}'^N, -\boldsymbol{p}'^N;\alpha')\, p(\boldsymbol{r}^N, -\boldsymbol{p}^N;\alpha)$$
$$f_{E;\Delta E}(\boldsymbol{r}^N, -\boldsymbol{p}^N;\boldsymbol{r}'^N, -\boldsymbol{p}'^N;\tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N, \quad (3\text{-}11)$$

where we have also used the fact that $p(\boldsymbol{r}^N, \boldsymbol{p}^N;\alpha)$ is an even function of the momenta of the particles (eq. I (3-44)). After the transformation of variables $(\boldsymbol{r}'^N, -\boldsymbol{p}'^N) \to (\boldsymbol{r}^N, \boldsymbol{p}^N)$ and $(\boldsymbol{r}^N, -\boldsymbol{p}^N) \to (\boldsymbol{r}'^N, \boldsymbol{p}'^N)$, we then obtain the result

$$F(\alpha';\alpha;\tau) = F(\alpha;\alpha';\tau). \quad (3\text{-}12)$$

If the functions $F(\alpha';\alpha;\tau)$ were true probabilities, relation (3-12) would express the so-called principle of detailed balance or microscopic reversibility. By extension we shall quite generally refer to this relation as the "principle of detailed balance".

In the case of both even and odd state variables eq. (3-3) becomes

$$F(\alpha',\beta';\alpha,\beta;\tau) =$$
$$= \iint p(\boldsymbol{r}'^N, \boldsymbol{p}'^N;\alpha',\beta')\, p(\boldsymbol{r}^N, \boldsymbol{p}^N;\alpha,\beta)$$
$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N;\boldsymbol{r}^N, \boldsymbol{p}^N;\tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N. \quad (3\text{-}13)$$

If we now apply the relations (2-23) and I (3-52), I (3-55) to this equation, we obtain, after the above mentioned transformation of variables, the following expression for detailed balance:

$$F(\alpha',\beta';\alpha,\beta;\tau) = F'(\alpha, -\beta-0;\alpha', -\beta'-0;\tau), \quad (3\text{-}14)$$

where

$$F'(\alpha',\beta';\alpha,\beta;\tau) \equiv \sum_{k=0}^{m}\sum_{l=0}^{m}(-1)^{k+l}\sum_{1\leqslant i_1<i_2<\ldots<i_k\leqslant m}\sum_{1\leqslant j_1<j_2<\ldots<j_l\leqslant m}$$
$$F(\alpha_1',\alpha_2',\ldots,\alpha_n',\beta_{i_1}',\beta_{i_2}',\ldots,\beta_{i_k}';\alpha_1,\alpha_2,\ldots,\alpha_n,\beta_{j_1},\beta_{j_2},\ldots,\beta_{j_l};\tau), \quad (3\text{-}15)$$

with the reduced joint distribution functions

$$F(\alpha_1',\alpha_2',\ldots,\alpha_n',\beta_{i_1}',\beta_{i_2}',\ldots,\beta_{i_k}';\alpha_1,\alpha_2,\ldots,\alpha_n,\beta_{j_1},\beta_{j_2},\ldots,\beta_{j_l};\tau) =$$
$$= \iint p(\boldsymbol{r}'^N, \boldsymbol{p}'^N;\alpha_1',\alpha_2',\ldots,\alpha_n',\beta_{i_1}',\beta_{i_2}',\ldots,\beta_{i_k}')$$
$$p(\boldsymbol{r}^N, \boldsymbol{p}^N;\alpha_1,\alpha_2,\ldots,\alpha_n,\beta_{j_1},\beta_{j_2},\ldots,\beta_{j_l})$$
$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N;\boldsymbol{r}^N, \boldsymbol{p}^N;\tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N. \quad (3\text{-}16)$$

In the presence of an external magnetic field $\boldsymbol{B}$ we have

$$F(\alpha',\beta';\alpha,\beta;\boldsymbol{B};\tau) =$$
$$= \iint p(\boldsymbol{r}'^N, \boldsymbol{p}'^N;\alpha',\beta';\boldsymbol{B})\, p(\boldsymbol{r}^N, \boldsymbol{p}^N;\alpha,\beta;\boldsymbol{B})$$
$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N;\boldsymbol{r}^N, \boldsymbol{p}^N;\boldsymbol{B};\tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N, \quad (3\text{-}17)$$

and the principle of detailed balance becomes

$$F(\boldsymbol{\alpha}', \boldsymbol{\beta}'; \boldsymbol{\alpha}, \boldsymbol{\beta}; \boldsymbol{B}; \tau) = F'(\boldsymbol{\alpha}, -\boldsymbol{\beta} - 0; \boldsymbol{\alpha}', -\boldsymbol{\beta}' - 0; -\boldsymbol{B}; \tau), \quad (3\text{-}18)$$

which follows from (3-17), together with (2-24) and I (3-57).

Just as the distribution function $F(\boldsymbol{\alpha})$, the joint distribution function $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ is of a discontinuous type. In chapter I we have assumed that $F(\boldsymbol{\alpha})$ is approximately equal to the continuous and differentiable normal distribution function, (central limit theorem). We shall now make the assumption that for systems with a large number of degrees of freedom the function $F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ can also be approximated by a continuous and differentiable function. It is then possible to define the function

$$f(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) \equiv \frac{\partial^{2n} F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)}{\partial\alpha_1' \, \partial\alpha_2' \dots \partial\alpha_n' \, \partial\alpha_1 \, \partial\alpha_2 \dots \partial\alpha_n}, \quad (3\text{-}19)$$

which is in general not a probability density in $\boldsymbol{\alpha}$-space, in contrast with $f(\boldsymbol{\alpha})$, eq. I (3-81).

The normalization of $f(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau)$ now follows with (3-9), (3-10) and I (3-81):

$$\int f(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) \, \mathrm{d}\boldsymbol{\alpha}' = f(\boldsymbol{\alpha}), \quad (3\text{-}20)$$

$$\int f(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) \, \mathrm{d}\boldsymbol{\alpha} = f(\boldsymbol{\alpha}'). \quad (3\text{-}21)$$

Furthermore the expression (3-8) for the micro-canonical time correlation function of the operators $R_1(\boldsymbol{\alpha}_{op})$ and $R_2(\boldsymbol{\alpha}_{op})$ can be written as

$$C^{m.c.}\{R_1(\boldsymbol{\alpha}), R_2(\boldsymbol{\alpha}(\tau))\} = \int\int R_1(\boldsymbol{\alpha}') \, R_2(\boldsymbol{\alpha}) \, f(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) \, \mathrm{d}\boldsymbol{\alpha}' \, \mathrm{d}\boldsymbol{\alpha}. \quad (3\text{-}22)$$

The principle of detailed balance (3-12) becomes

$$f(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) = f(\boldsymbol{\alpha}; \boldsymbol{\alpha}'; \tau). \quad (3\text{-}23)$$

In the case of both even and odd state variables we have, instead of (3-19),

$$f(\boldsymbol{\alpha}', \boldsymbol{\beta}'; \boldsymbol{\alpha}, \boldsymbol{\beta}; \tau) \equiv$$
$$\equiv \frac{\partial^{2(n+m)} F(\boldsymbol{\alpha}', \boldsymbol{\beta}'; \boldsymbol{\alpha}, \boldsymbol{\beta}; \tau)}{\partial\alpha_1' \, \partial\alpha_2' \dots \partial\alpha_n' \, \partial\beta_1' \, \partial\beta_2' \dots \partial\beta_m' \, \partial\alpha_1 \, \partial\alpha_2 \dots \partial\alpha_n \, \partial\beta_1 \, \partial\beta_2 \dots \partial\beta_m}, \quad (3\text{-}24)$$

and we find with (3-14) and (3-15) that

$$f(\boldsymbol{\alpha}', \boldsymbol{\beta}'; \boldsymbol{\alpha}, \boldsymbol{\beta}; \tau) = f(\boldsymbol{\alpha}, -\boldsymbol{\beta}; \boldsymbol{\alpha}', -\boldsymbol{\beta}'; \tau). \quad (3\text{-}25)$$

In the presence of an external magnetic field $\boldsymbol{B}$ it follows with (3-18) that

$$f(\boldsymbol{\alpha}', \boldsymbol{\beta}'; \boldsymbol{\alpha}, \boldsymbol{\beta}; \boldsymbol{B}; \tau) = f(\boldsymbol{\alpha}, -\boldsymbol{\beta}; \boldsymbol{\alpha}', -\boldsymbol{\beta}'; -\boldsymbol{B}; \tau). \quad (3\text{-}26)$$

The expressions (3-23), (3-25) and (3-26) for detailed balance are the basis for a derivation of the Onsager reciprocal relations, which will be given in § 5 of this chapter.

As stated above, the joint equilibrium distribution function $F(\alpha'; \alpha; \tau)$ is in general, *i.e.* for an arbitrary set of commuting operators $\alpha_{i,op}$ $(i = 1,2,\dots,n)$, not a probability. We shall, however, prove that $F(\alpha'; \alpha; \tau)$ does represent a probability, if this set of operators is of a special class, satisfying certain conditions.

We divide the energy scale into intervals $(E_\mu; \Delta E_\mu)$, where ΔE_μ are the experimental inaccuracies in measurements of the energy of the system. Each interval is supposed to contain a large number of eigenvalues E_k of the Hamilton operator H_{op}. We now suppose that the eigenfunctions $\chi_\lambda(\mathbf{r}^N)$ of the set of commuting operators $\alpha_{i,op}$ may be obtained from the eigenfunctions $\varphi_k(\mathbf{r}^N)$ of H_{op} by means of such unitary transformation, that each $\chi_\lambda(\mathbf{r}^N)$ is only a linear combination of energy eigenfunctions $\varphi_k(\mathbf{r}^N)$, which belong to the same range $(E_\mu; \Delta E_\mu)$. In this case the eigenfunctions $\chi_\lambda(\mathbf{r}^N)$ may conveniently be denoted by $\chi_{\mu,\nu}(\mathbf{r}^N)$, where the index μ refers to the energy range $(E_\mu; \Delta E_\mu)$. We then find with I (3-2) and I (3-3) that

$$p_{E_\mu;\Delta E_\mu,op}\, \chi_{\mu',\nu}(\mathbf{r}^N) = \delta_{\mu\mu'}\, \chi_{\mu',\nu}(\mathbf{r}^N), \tag{3-27}$$

where $\delta_{\mu\mu'}$ is the Kronecker symbol.

We now define the operator

$$E_{op} \equiv \textstyle\sum_\mu E_\mu p_{E_\mu;\Delta E_\mu,op}. \tag{3-28}$$

It follows with I (3-2) and I (3-3) that this operator possesses the same eigenfunctions $\varphi_k(\mathbf{r}^N)$ as the Hamilton operator H_{op}, whereas the differences between the corresponding eigenvalues of these operators are always smaller than ΔE_μ. Therefore in a macroscopic description, in which we do not distinguish between values of the energy of order ΔE_μ, we may use E_{op}, instead of H_{op}, as the operator, representing the energy of the system *). The operator E_{op} will be called the macroscopic energy operator **).

On the other hand it follows from (3-27) and (3-28) that

$$E_{op}\chi_{\mu,\nu}(\mathbf{r}^N) = E_\mu \chi_{\mu,\nu}(\mathbf{r}^N). \tag{3-29}$$

Denoting the eigenvalues of $\boldsymbol{\alpha}_{op}$ by $\boldsymbol{\alpha}_{\mu,\nu}$, eq. I (3-26) becomes

$$\boldsymbol{\alpha}_{op}\, \chi_{\mu,\nu}(\mathbf{r}^N) = \boldsymbol{\alpha}_{\mu,\nu}\, \chi_{\mu,\nu}(\mathbf{r}^N). \tag{3-30}$$

The macroscopic energy operator therefore commutes with the operators $\alpha_{i,op}$. The index μ is the quantum number of the macroscopic energy, whereas ν is an additional quantum number, which describes the various eigenstates of $\boldsymbol{\alpha}_{op}$ for a given value of this energy.

Since the functions $\chi_{\mu,\nu}(\mathbf{r}^N)$ for fixed μ may be obtained by means of a unitary transformation from the functions $\varphi_k(\mathbf{r}^N)$, belonging to the energy

*) It should be noted, however, that E_{op} does not describe the motion of the particles of the system, in contrast with the Hamilton operator H_{op}.

**) The definition (3-28) of macroscopic or gross energy operator is due to van Kampen [6]).

range $(E_\mu;\Delta E_\mu)$, we find that the density matrix of the micro-canonical ensemble (*cf.* I (3-1)) can be written as

$$\rho_{E_\mu;\Delta E_\mu}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = G^{-1}_{E_\mu;\Delta E_\mu} \textstyle\sum_{E_k \in (E_\mu;\Delta E_\mu)} \varphi_k^*(\boldsymbol{r}'^N)\, \varphi_k(\boldsymbol{r}^N) =$$
$$= G^{-1}_{E_\mu;\Delta E_\mu} \textstyle\sum_\nu \chi^*_{\mu,\nu}(\boldsymbol{r}'^N)\, \chi_{\mu,\nu}(\boldsymbol{r}^N). \tag{3-31}$$

If we now choose in (3-1) for $(E;\Delta E)$ one of the ranges $(E_\mu;\Delta E_\mu)$, we find with (3-31) that

$$F(\boldsymbol{\alpha}';\boldsymbol{\alpha};\tau) = \tfrac{1}{2}G^{-1}_{E_\mu;\Delta E_\mu}$$
$$\textstyle\sum_\nu \int \chi^*_{\mu,\nu}(\boldsymbol{r}^N)\{p_{op}(\boldsymbol{\alpha}')\,p_{op}(\boldsymbol{\alpha};\tau) + p_{op}(\boldsymbol{\alpha};\tau)\,p_{op}(\boldsymbol{\alpha}')\}\,\chi_{\mu,\nu}(\boldsymbol{r}^N)\,\mathrm{d}\boldsymbol{r}^N. \tag{3-32}$$

With I (3-29)–I (3-31) we obtain

$$F(\boldsymbol{\alpha}';\boldsymbol{\alpha};\tau) = G^{-1}_{E_\mu;\Delta E_\mu} \sum_{\substack{\nu \\ (\boldsymbol{\alpha}_{\mu,\nu}\leqslant\boldsymbol{\alpha}')}} \int \chi^*_{\mu,\nu}(\boldsymbol{r}^N)\, p_{op}(\boldsymbol{\alpha};\tau)\,\chi_{\mu,\nu}(\boldsymbol{r}^N)\,\mathrm{d}\boldsymbol{r}^N, \tag{3-33}$$

where the summation extends over those quantum numbers ν, for which $\boldsymbol{\alpha}_{\mu,\nu} \leqslant \boldsymbol{\alpha}'$ with a fixed value of the quantum number μ. It follows from (3-33) and (3-31), that $F(\boldsymbol{\alpha}';\boldsymbol{\alpha};\tau)$ may be interpreted as the joint probability that a system in thermodynamic equilibrium is in a state with $\boldsymbol{\alpha}_{\mu,\nu} \leqslant \boldsymbol{\alpha}'$ at some initial time and in a state with $\boldsymbol{\alpha}_{\mu,\nu} \leqslant \boldsymbol{\alpha}$ after a time interval τ. From (3-19) we then find that $f(\boldsymbol{\alpha}';\boldsymbol{\alpha};\tau)$ is the joint probability density of the state variables in thermodynamic equilibrium.

In the following sections we shall assume that relevant sets of operators $\alpha_{i,op}$ for extensive variables are of the special class described above.

§ 4. *Conditional probability density functions of extensive state variables.* The conditional probability density $P(\boldsymbol{\alpha}_0|\boldsymbol{\alpha};t)$ for the micro-canonical ensemble is defined as the quotient of the joint probability density $f(\boldsymbol{\alpha}_0;\boldsymbol{\alpha};t)$ and the probability density $f(\boldsymbol{\alpha}_0)$:

$$P(\boldsymbol{\alpha}_0|\boldsymbol{\alpha};t) \equiv \frac{f(\boldsymbol{\alpha}_0;\boldsymbol{\alpha};t)}{f(\boldsymbol{\alpha}_0)}. \tag{4-1}$$

We shall now prove that $P(\boldsymbol{\alpha}_0|\boldsymbol{\alpha};t)$ is equal to a special non-equilibrium probability density function in $\boldsymbol{\alpha}$-space.

Let us suppose that a measurement has indicated that a system with an energy in the range $(E_\mu;\Delta E_\mu)$ is at a given time, say $t = 0$, in a specified state in the range $(\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0)$. According to the postulate of equal *a priori* probability this system is then represented by an ensemble with density matrix

$$\rho^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}(\boldsymbol{r}'^N, \boldsymbol{r}^N;0) = G^{(\mu)-1}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0} \sum_{\substack{\nu \\ (\boldsymbol{\alpha}_{\mu,\nu}\in(\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0))}} \chi^*_{\mu,\nu}(\boldsymbol{r}'^N)\,\chi_{\mu,\nu}(\boldsymbol{r}^N), \tag{4-2}$$

where the summation extends over those quantum numbers ν, for which $\boldsymbol{\alpha}_{\mu,\nu}$ (with a fixed value of μ) lies in the range $(\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0)$, and where $G^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}$ is the number of eigenvalues $\boldsymbol{\alpha}_{\mu,\nu}$ in this range. The probability

$P_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}; t)$, that this system is in a state with $\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}$ at the time t ($t \geqslant 0$), is then given by

$$P_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}; t) = \\ = G^{(\mu)-1}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0} \sum_{\nu \atop (\boldsymbol{\alpha}_{\mu,\nu} \in (\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0))} \int \chi^*_{\mu,\nu}(\boldsymbol{r}^N)\, p_{op}(\boldsymbol{\alpha}; t)\, \chi_{\mu,\nu}(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N, \tag{4-3}$$

with the projection operator (3-2).

We now introduce the non-equilibrium distribution function

$$F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) \equiv P_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}_\lambda \leqslant \boldsymbol{\alpha}; t). \tag{4-4}$$

It can then be shown that

$$F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) = \frac{\Delta_{\boldsymbol{\alpha}_0} F(\boldsymbol{\alpha}_0; \boldsymbol{\alpha}; t)}{\Delta F(\boldsymbol{\alpha}_0)}, \tag{4-5}$$

where $\Delta_{\boldsymbol{\alpha}_0} F(\boldsymbol{\alpha}_0; \boldsymbol{\alpha}; t)$ is the n^{th} order difference *) of $F(\boldsymbol{\alpha}_0; \boldsymbol{\alpha}; t)$ over the range $(\boldsymbol{\alpha}_0; \Delta\boldsymbol{\alpha}_0)$ with constant $\boldsymbol{\alpha}$ and where $\Delta F(\boldsymbol{\alpha}_0)$ is the n^{th} order difference of $F(\boldsymbol{\alpha}_0)$ over this range. In order to prove this relation we note that it follows from (3-33) that

$$\Delta_{\boldsymbol{\alpha}_0} F(\boldsymbol{\alpha}_0; \boldsymbol{\alpha}; t) = G^{-1}_{E_\mu;\Delta E_\mu} \sum_{\nu \atop (\boldsymbol{\alpha}_{\mu,\nu} \in (\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0))} \int \chi^*_{\mu,\nu}(\boldsymbol{r}^N)\, p_{op}(\boldsymbol{\alpha}; t)\, \chi_{\mu,\nu}(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N, \tag{4-6}$$

and from I (3-61), I (3-59) and (3-31), together with I (3-28) –I (3-31), that

$$\Delta F(\boldsymbol{\alpha}_0) = G^{-1}_{E_\mu;\Delta E_\mu} \sum_\nu \int \chi^*_{\mu,\nu}(\boldsymbol{r}^N)\, \Delta p_{op}(\boldsymbol{\alpha}_0)\, \chi_{\mu,\nu}(\boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}^N = G^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0} / G_{E_\mu;\Delta E_\mu}. \tag{4-7}$$

From (4-3), (4-4), (4-6) and (4-7) we then obtain the relation (4-5).

Since we have assumed that the distribution functions $F(\boldsymbol{\alpha}_0)$ and $F(\boldsymbol{\alpha}_0; \boldsymbol{\alpha}; t)$ may be approximated by continuous and differentiable functions, we find from (4-5) that

$$F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) = \frac{\partial^n F(\boldsymbol{\alpha}_0; \boldsymbol{\alpha}; t) / \partial\alpha_{0,1}\, \partial\alpha_{0,2} \ldots \partial\alpha_{0,n}}{f(\boldsymbol{\alpha}_0)}, \tag{4-8}$$

where we have used the definition I (3-81) of $f(\boldsymbol{\alpha}_0)$.

We now define the non-equilibrium probability density function

$$f_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) \equiv \frac{\partial^n F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t)}{\partial\alpha_1\, \partial\alpha_2 \ldots \partial\alpha_n}. \tag{4-9}$$

From (4-9), (4-8), (3-19) and (4-1) we then find that

$$f_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) = P(\boldsymbol{\alpha}_0 \mid \boldsymbol{\alpha}; t). \tag{4-10}$$

Let $f^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}(\boldsymbol{r}^N, \boldsymbol{p}^N; t)$ be the Wigner distribution function of the ensemble with density matrix $\rho^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}(\boldsymbol{r}'^N, \boldsymbol{r}^N; t)$, which for $t = 0$ has the form (4-2).

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*) For the definition of this quantity see footnote on page 20.

Then it follows from (4-4), (4-3), (3-2) and the theorem I (2-4), I (2-5) that

$$F_{\alpha_0}(\alpha; t) = \int p(\mathbf{r}^N, \mathbf{p}^N; \alpha)\, f^{(\mu)}_{\alpha_0;\Delta\alpha_0}(\mathbf{r}^N, \mathbf{p}^N; t)\, \mathrm{d}\mathbf{r}^N\, \mathrm{d}\mathbf{p}^N, \tag{4-11}$$

where we have used the Weyl correspondence I (3-35).

In an analogous way as the distribution function $F(\alpha)$ in chapter I has been used to calculate the micro-canonical ensemble average of an operator $R(\alpha_{op})$ (*cf.* I (3-79)), the distribution function $F_{\alpha_0}(\alpha; t)$ may now be employed for the calculation of the average of this operator in the ensemble with initial density matrix (4-2). This ensemble average is given by

$$\overline{R(\alpha)}^{\alpha_0}(t) \equiv G^{(\mu)-1}_{\alpha_0;\Delta\alpha_0} \sum_{\nu\,(\alpha_{\mu,\nu}\in(\alpha_0;\Delta\alpha_0))} \int \chi^*_{\mu,\nu}(\mathbf{r}^N)\, R(\alpha_{op}(t))\, \chi_{\mu,\nu}(\mathbf{r}^N)\, \mathrm{d}\mathbf{r}^N =$$

$$= \int R(\mathbf{r}^N, \mathbf{p}^N)\, f^{(\mu)}_{\alpha_0;\Delta\alpha_0}(\mathbf{r}^N, \mathbf{p}^N; t)\, \mathrm{d}\mathbf{r}^N\, \mathrm{d}\mathbf{p}^N, \tag{4-12}$$

where

$$R(\alpha_{op}(t)) \equiv \exp\{(i/\hbar)\, H_{op}t\}\, R(\alpha_{op})\, \exp\{(-i/\hbar)\, H_{op}t\}, \tag{4-13}$$

and where $R(\mathbf{r}^N, \mathbf{p}^N)$ is the classical function corresponding to $R(\alpha_{op})$ according to Weyl's rule. If we now substitute I (3-77) into the last member of (4-12), we find with (4-11) that

$$\overline{R(\alpha)}^{\alpha_0}(t) = \int R(\alpha)\, \mathrm{d}F_{\alpha_0}(\alpha; t), \tag{4-14}$$

or with (4-9)

$$\overline{R(\alpha)}^{\alpha_0}(t) = \int R(\alpha)\, f_{\alpha_0}(\alpha; t)\, \mathrm{d}\alpha. \tag{4-15}$$

Applying the relation (4-10) to the last equation we obtain

$$\overline{R(\alpha)}^{\alpha_0}(t) = \int R(\alpha)\, P(\alpha_0|\alpha; t)\, \mathrm{d}\alpha, \tag{4-16}$$

which has the form of a conditional average, *i.e.* an average over the conditional probability density $P(\alpha_0|\alpha; t)$.

§ 5. *Derivation of the Onsager reciprocal relations.* The proof of the Onsager reciprocal relations [4]) now proceeds along the usual lines (*cf.* reference [3])). One assumes that the conditional averages of the extensive state variables obey linear differential equations of first order:

$$\frac{\partial \overline{\alpha}^{\alpha_0}(t)}{\partial t} = -\mathsf{M}\cdot\overline{\alpha}^{\alpha_0}(t), \tag{5-1}$$

where M is the matrix of real phenomenological coefficients and where $t \geqslant 0$.

The formal solution of (5-1) is given by

$$\overline{\alpha}^{\alpha_0}(t) = \exp(-\mathsf{M}t)\cdot\alpha_0, \tag{5-2}$$

where the matrix $\exp(-\mathsf{M}t)$ is given by its series development. From this equation we find, together with I (3-84) and I (3-86), that

$$\int \overline{\alpha}^{\alpha_0}(t)\, \alpha_0 f(\alpha_0)\, d\alpha_0 = \exp(-\mathsf{M}t)\cdot \int \alpha_0\alpha_0 f(\alpha_0)\, d\alpha_0 = k \exp(-\mathsf{M}t)\cdot \mathsf{g}^{-1}. \tag{5-3}$$

On the other hand it follows with (4-16) and (4-1) that

$$\int \overline{\alpha}^{\alpha_0}(t)\, \alpha_0 f(\alpha_0)\, d\alpha_0 = \int\int \alpha\alpha_0 f(\alpha_0; \alpha; t)\, d\alpha_0\, d\alpha, \tag{5-4}$$

so that we have

$$k \exp(-\mathsf{M}t)\cdot \mathsf{g}^{-1} = \int\int \alpha\alpha_0 f(\alpha_0; \alpha; t)\, d\alpha_0\, d\alpha. \tag{5-5}$$

If we now apply the principle of detailed balance (3-23) to the right-hand side of this equation, we find, interchanging the dummy variables α_0 and α:

$$\begin{aligned} k \exp(-\mathsf{M}t)\cdot \mathsf{g}^{-1} &= \int\int \alpha\alpha_0 f(\alpha; \alpha_0; t)\, d\alpha_0\, d\alpha = \\ &= \int\int \alpha_0\alpha f(\alpha_0; \alpha; t)\, d\alpha_0\, d\alpha = k\mathsf{g}^{-1}\cdot \exp(-\widetilde{\mathsf{M}}t), \end{aligned} \tag{5-6}$$

where we have used the fact that the matrix g is symmetrical and where $\widetilde{\mathsf{M}}$ is the transposed matrix of M. It follows from this equation that the matrix M satisfies the relation

$$\mathsf{M}\cdot \mathsf{g}^{-1} = \mathsf{g}^{-1}\cdot \widetilde{\mathsf{M}}. \tag{5-7}$$

If we now define

$$\mathsf{L} \equiv \mathsf{M}\cdot \mathsf{g}^{-1}, \tag{5-8}$$

which is the matrix of phenomenological coefficients, if (5-1) is written, with the help of the expression I (4-9) for the intensive variables $\boldsymbol{X}$, as

$$\frac{\partial \overline{\alpha}^{\alpha_0}(t)}{\partial t} = \mathsf{L}\cdot \overline{\boldsymbol{X}}^{\alpha_0}(t), \tag{5-9}$$

we obtain with (5-7) the Onsager reciprocal relations

$$\mathsf{L} = \widetilde{\mathsf{L}}. \tag{5-10}$$

In the case of both even and odd state variables eq. (5-1) becomes

$$\left.\begin{aligned} \frac{\partial \overline{\alpha}^{\alpha_0,\beta_0}(t)}{\partial t} &= -\mathsf{M}_{\alpha\alpha}\cdot \overline{\alpha}^{\alpha_0,\beta_0}(t) - \mathsf{M}_{\alpha\beta}\cdot \overline{\beta}^{\alpha_0,\beta_0}(t) \\ \frac{\partial \overline{\beta}^{\alpha_0,\beta_0}(t)}{\partial t} &= -\mathsf{M}_{\beta\alpha}\cdot \overline{\alpha}^{\alpha_0,\beta_0}(t) - \mathsf{M}_{\beta\beta}\cdot \overline{\beta}^{\alpha_0,\beta_0}(t) \end{aligned}\right\}. \tag{5-11}$$

First we consider the case that no external magnetic field is present. With the expressions I (4-13) for $\boldsymbol{X}$ and $\boldsymbol{Y}$, eq. (5-11) may be written as

$$\left.\begin{aligned} \frac{\partial \overline{\alpha}^{\alpha_0,\beta_0}(t)}{\partial t} &= \mathsf{L}_{\alpha\alpha}\cdot \overline{\boldsymbol{X}}^{\alpha_0,\beta_0}(t) + \mathsf{L}_{\alpha\beta}\cdot \overline{\boldsymbol{Y}}^{\alpha_0,\beta_0}(t) \\ \frac{\partial \overline{\beta}^{\alpha_0,\beta_0}(t)}{\partial t} &= \mathsf{L}_{\beta\alpha}\cdot \overline{\boldsymbol{X}}^{\alpha_0,\beta_0}(t) + \mathsf{L}_{\beta\beta}\cdot \overline{\boldsymbol{Y}}^{\alpha_0,\beta_0}(t) \end{aligned}\right\}, \tag{5-12}$$

where

$$\left.\begin{aligned} \mathsf{L}_{\alpha\alpha} &\equiv \mathsf{M}_{\alpha\alpha}\cdot\mathsf{g}_{\alpha\alpha}^{-1} \\ \mathsf{L}_{\alpha\beta} &\equiv \mathsf{M}_{\alpha\beta}\cdot\mathsf{g}_{\beta\beta}^{-1} \\ \mathsf{L}_{\beta\alpha} &\equiv \mathsf{M}_{\beta\alpha}\cdot\mathsf{g}_{\alpha\alpha}^{-1} \\ \mathsf{L}_{\beta\beta} &\equiv \mathsf{M}_{\beta\beta}\cdot\mathsf{g}_{\beta\beta}^{-1} \end{aligned}\right\}. \tag{5-13}$$

One can then derive along the same lines as above, using detailed balance in the form (3-25), the following Onsager relations:

$$\left.\begin{aligned} \mathsf{L}_{\alpha\alpha} &= \tilde{\mathsf{L}}_{\alpha\alpha} \\ \mathsf{L}_{\alpha\beta} &= -\tilde{\mathsf{L}}_{\beta\alpha} \\ \mathsf{L}_{\beta\beta} &= \tilde{\mathsf{L}}_{\beta\beta} \end{aligned}\right\}. \tag{5-14}$$

Secondly we consider the case that an external magnetic field $\boldsymbol{B}$ is present. With I (4-14) we find again eq. (5-12), if we put

$$\left.\begin{aligned} \mathsf{L}_{\alpha\alpha}(\boldsymbol{B}) &\equiv \mathsf{M}_{\alpha\alpha}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\alpha\alpha}(\boldsymbol{B}) + \mathsf{M}_{\alpha\beta}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\beta\alpha}(\boldsymbol{B}) \\ \mathsf{L}_{\alpha\beta}(\boldsymbol{B}) &\equiv \mathsf{M}_{\alpha\alpha}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\alpha\beta}(\boldsymbol{B}) + \mathsf{M}_{\alpha\beta}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\beta\beta}(\boldsymbol{B}) \\ \mathsf{L}_{\beta\alpha}(\boldsymbol{B}) &\equiv \mathsf{M}_{\beta\alpha}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\alpha\alpha}(\boldsymbol{B}) + \mathsf{M}_{\beta\beta}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\beta\alpha}(\boldsymbol{B}) \\ \mathsf{L}_{\beta\beta}(\boldsymbol{B}) &\equiv \mathsf{M}_{\beta\alpha}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\alpha\beta}(\boldsymbol{B}) + \mathsf{M}_{\beta\beta}(\boldsymbol{B})\cdot\mathsf{\gamma}_{\beta\beta}(\boldsymbol{B}) \end{aligned}\right\}. \tag{5-15}$$

The Onsager reciprocal relations now become

$$\left.\begin{aligned} \mathsf{L}_{\alpha\alpha}(\boldsymbol{B}) &= \tilde{\mathsf{L}}_{\alpha\alpha}(-\boldsymbol{B}) \\ \mathsf{L}_{\alpha\beta}(\boldsymbol{B}) &= -\tilde{\mathsf{L}}_{\beta\alpha}(-\boldsymbol{B}) \\ \mathsf{L}_{\beta\beta}(\boldsymbol{B}) &= \tilde{\mathsf{L}}_{\beta\beta}(-\boldsymbol{B}) \end{aligned}\right\}, \tag{5-16}$$

as follows with the expression (3-26) for detailed balance.

In connection with the derivation of the Onsager reciprocal relations, given above, we want to make the following remark: it follows from (5-5) and (3-22) that

$$k\exp(-\mathsf{M}t)\cdot\mathsf{g}^{-1} = \tilde{\mathsf{C}}^{m.c.}\{\boldsymbol{\alpha}, \boldsymbol{\alpha}(t)\}, \tag{5-17}$$

where $\mathsf{C}^{m.c.}\{\boldsymbol{\alpha}, \boldsymbol{\alpha}(t)\}$ is the micro-canonical correlation matrix of the extensive state variables, with elements $C^{m.c.}\{\alpha_i, \alpha_j(t)\}$ $(i, j = 1, 2, \ldots, n)$. From (5-8) and (5-17) we find that

$$\mathsf{L} = -\lim_{t\downarrow 0}\frac{\tilde{\mathsf{C}}^{m.c.}\{\boldsymbol{\alpha}, \boldsymbol{\alpha}(t)\} - \tilde{\mathsf{C}}^{m.c.}\{\boldsymbol{\alpha}, \boldsymbol{\alpha}(0)\}}{kt}, \tag{5-18}$$

where t approaches zero from the positive side.

At first sight this expression seems to be different from the expression for the matrix of phenomenological coefficients, given by Kubo, Yokota and Nakajima [7]), (*cf.* formula (3.14) of this reference). It should be noted, however, that the result (5-18) is only valid, if the set of quantum mechanical operators $\alpha_{i,op}$, corresponding to the extensive state variables, is of the special class, described at the end of § 3, whereas formula (3.14) of reference [7]) holds for an arbitrary set of operators $\alpha_{i,op}$. The latter formula must therefore also be calculated for a set of operators of this class. One then obtains an expression for the matrix of phenomenological coefficients of the same form as (5-18).

§ 6. *Markoff processes.* In the preceding section only those aspects of the processes $\boldsymbol{\alpha}(t)$ have been considered, which were needed for a derivation of the Onsager reciprocal relations. We shall discuss in the present section a further assumption, which is usually made concerning the nature of the processes $\boldsymbol{\alpha}(t)$, to wit that these processes are Markoffian. This assumption implies that the conditional probability density $P(\boldsymbol{\alpha}_0 | \boldsymbol{\alpha}; t)$ satisfies the so-called Smoluchowski equation

$$P(\boldsymbol{\alpha}_0 | \boldsymbol{\alpha}; t + \tau) = \int P(\boldsymbol{\alpha}_0 | \boldsymbol{\alpha}'; t)\, P(\boldsymbol{\alpha}' | \boldsymbol{\alpha}; \tau)\, \mathrm{d}\boldsymbol{\alpha}'. \tag{6-1}$$

This equation holds if one assumes that the Wigner distribution function $f^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}(\boldsymbol{r}^N, \boldsymbol{p}^N; t)$, introduced in § 4, is approximately given by

$$f^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}(\boldsymbol{r}^N, \boldsymbol{p}^N; t) \simeq \textstyle\sum_\sigma w_\sigma(t)\, f^{(\mu)}_{\boldsymbol{\alpha}_\sigma;\Delta\boldsymbol{\alpha}_\sigma}(\boldsymbol{r}^N, \boldsymbol{p}^N; 0), \tag{6-2}$$

where the Wigner distribution functions $f^{(\mu)}_{\boldsymbol{\alpha}_\sigma;\Delta\boldsymbol{\alpha}_\sigma}(\boldsymbol{r}^N, \boldsymbol{p}^N; 0)$ correspond to the density matrices

$$\rho^{(\mu)}_{\boldsymbol{\alpha}_\sigma;\Delta\boldsymbol{\alpha}_\sigma}(\boldsymbol{r}'^N, \boldsymbol{r}^N; 0) = G^{(\mu)-1}_{\boldsymbol{\alpha}_\sigma;\Delta\boldsymbol{\alpha}_\sigma} \sum_{\substack{\nu \\ (\boldsymbol{\alpha}_{\mu,\nu} \in (\boldsymbol{\alpha}_\sigma;\Delta\boldsymbol{\alpha}_\sigma))}} \chi^*_{\mu,\nu}(\boldsymbol{r}'^N)\, \chi_{\mu,\nu}(\boldsymbol{r}^N), \tag{6-3}$$

(*cf.* (4-2)) and where σ numbers the different ranges $(\boldsymbol{\alpha}_\sigma; \Delta\boldsymbol{\alpha}_\sigma)$, into which we have divided $\boldsymbol{\alpha}$-space. This is the so-called assumption of "repeated randomness". It is the quantum statistical analogue of the assumption in classical statistical mechanics that non-stationary distribution functions, which are initially uniform over regions in phase space, where the state variables have values in ranges $(\boldsymbol{\alpha}_\sigma; \Delta\boldsymbol{\alpha}_\sigma)$ and where the energy lies in the range $(E; \Delta E)$, remain "sufficiently" uniform in the course of time over these regions.

Now it follows from (4-11) that

$$\Delta F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) = \int \Delta p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})\, f^{(\mu)}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}(\boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N, \tag{6-4}$$

where $\Delta F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t)$ and $\Delta p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})$ are the n^{th} order differences of $F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t)$ and $p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})$ respectively over the range $(\boldsymbol{\alpha}; \Delta\boldsymbol{\alpha})$. Substituting (6-2) into the right-hand side of this equation, we find that

$$\Delta F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) = \textstyle\sum_\sigma w_\sigma(t)\, \Delta F_{\boldsymbol{\alpha}_\sigma}(\boldsymbol{\alpha}; 0). \tag{6-5}$$

From (4-4) and (4-3), together with I (3-28)–I (3-31), we have

$$\Delta F_{\boldsymbol{\alpha}_\sigma}(\boldsymbol{\alpha}_{\sigma'}; 0) = \delta_{\sigma\sigma'}, \tag{6-6}$$

where $\delta_{\sigma\sigma'}$ is the Kronecker symbol. From the last two equations we then obtain

$$w_\sigma(t) = \Delta F_{\alpha_0}(\alpha_\sigma; t), \tag{6-7}$$

so that (6-2) becomes

$$f^{(\mu)}_{\alpha_0;\Delta\alpha_0}(\boldsymbol{r}^N, \boldsymbol{p}^N; t) \simeq \Sigma_\sigma\, \Delta F_{\alpha_0}(\alpha_\sigma; t)\, f^{(\mu)}_{\alpha_\sigma;\Delta\alpha_\sigma}(\boldsymbol{r}^N, \boldsymbol{p}^N; 0). \tag{6-8}$$

It follows from (6-4), (6-8) and I (2-34) that

$$\begin{aligned}
&\Delta F_{\alpha_0}(\alpha; t + \tau) = \\
&= \int\!\!\int f^{(\mu)}_{\alpha_0;\Delta\alpha_0}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t) P(\boldsymbol{r}'^N, \boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, \boldsymbol{p}^N; \tau)\, \Delta p(\boldsymbol{r}^N, \boldsymbol{p}^N; \alpha)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N = \\
&\quad = \Sigma_\sigma\, \Delta F_{\alpha_0}(\alpha_\sigma; t) \int\!\!\int f^{(\mu)}_{\alpha_\sigma;\Delta\alpha_\sigma}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; 0)\, P(\boldsymbol{r}'^N, \boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, \boldsymbol{p}^N; \tau) \\
&\quad\quad \Delta p(\boldsymbol{r}^N, \boldsymbol{p}^N; \alpha)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N = \Sigma_\sigma\, \Delta F_{\alpha_0}(\alpha_\sigma; t)\, \Delta F_{\alpha_\sigma}(\alpha; \tau),
\end{aligned} \tag{6-9}$$

or with (4-9)

$$f_{\alpha_0}(\alpha; t + \tau) = \int f_{\alpha_0}(\alpha'; t)\, f_{\alpha'}(\alpha; \tau)\, \mathrm{d}\alpha'. \tag{6-10}$$

If we now apply (4-10) to this result, we finally obtain the Smoluchowski equation (6-1).

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Chapter III

BOSE-EINSTEIN AND FERMI-DIRAC STATISTICS

Synopsis

The quantum statistical theory of Wigner distribution functions, which has been developed in the two previous chapters for Maxwell-Boltzmann statistics, is extended in the present chapter to the cases of Bose-Einstein and Fermi-Dirac statistics.

§ 1. *Introduction.* The theory of the quantum statistical foundations of the Onsager reciprocal relations in non-equilibrium thermodynamics in the two previous chapters (I, II) has been developed for Maxwell-Boltzmann statistics only. No special requirements were made concerning the symmetry character of the wave functions with respect to the coordinates of the particles. In the present chapter (III) we shall discuss the changes in the theory of I and II, arising from the influence of special symmetry properties of the wave functions in the particle coordinates. We shall treat the cases of Bose-Einstein statistics (symmetrical wave functions) and Fermi-Dirac statistics (antisymmetrical wave functions).

We shall establish an integral relation between the Wigner distribution function of the micro-canonical ensemble for Bose-Einstein (Fermi-Dirac) statistics and the micro-canonical Wigner distribution function for Maxwell-Boltzmann statistics. This relation will then be used to derive several formulae for Bose-Einstein (Fermi-Dirac) statistics from the corresponding formulae for Maxwell-Boltzmann statistics.

§ 2. *Bose-Einstein and Fermi-Dirac statistics.* We consider a quantum mechanical ensemble of conservative systems, each containing N identical point particles. In the case of Bose-Einstein statistics the wave functions $\psi_\mu^+(\boldsymbol{r}^N; t)$ of the systems in this ensemble are symmetrical in the particle coordinates, in the case of Fermi-Dirac statistics the wave functions $\psi_\mu^-(\boldsymbol{r}^N; t)$ are antisymmetrical, *i.e.*

$$\psi_\mu^\pm(P\boldsymbol{r}^N; t) = \delta_P^\pm \psi_\mu^\pm(\boldsymbol{r}^N; t), \tag{2-1}$$

where Pr^N is a permutation of the particle coordinates and where $\delta_P^+ = 1$ for any permutation, whereas $\delta_P^- = 1$ for even and $\delta_P^- = -1$ for odd permutations.

It follows from (2-1) that for both kinds of statistics the Wigner distribution functions

$$f^{\pm}(\boldsymbol{r}^N, \boldsymbol{p}^N; t) \equiv$$
$$\equiv (\pi h)^{-3N} \sum_\mu w_\mu^\pm \int \exp\{(2i/h)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\} \psi_\mu^{\pm *}(\boldsymbol{r}^N + \boldsymbol{y}^N; t)\, \psi_\mu^\pm(\boldsymbol{r}^N - \boldsymbol{y}^N; t)\, \mathrm{d}\boldsymbol{y}^N \quad (2\text{-}2)$$

are symmetrical in the particle phases:

$$f^\pm(P\boldsymbol{r}^N, P\boldsymbol{p}^N; t) = f^\pm(\boldsymbol{r}^N, \boldsymbol{p}^N; t), \quad (2\text{-}3)$$

where $(P\boldsymbol{r}^N, P\boldsymbol{p}^N)$ is a permutation of the particle phases.

The propagators of the wave functions $\psi_\mu^\pm(\boldsymbol{r}^N; t)$ and the Wigner distribution functions $f^\pm(\boldsymbol{r}^N, \boldsymbol{p}^N; t)$ are again solutions of the differential equations (2-11) and (2-47) in chapter I, and the initial conditions I (2-12) and I (2-49) may be employed in unaltered form.

We shall now express the Wigner distribution functions $f^\pm_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ of the micro-canonical ensemble for Bose-Einstein and Fermi-Dirac statistics in terms of the micro-canonical Wigner distribution function $f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ for Maxwell-Boltzmann statistics. To this end we shall first establish a relation between the micro-canonical density matrices

$$\rho^\pm_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = G^{\pm\,-1}_{E;\Delta E} \sum_{E_k^\pm \in (E;\Delta E)} \varphi_k^{\pm *}(\boldsymbol{r}'^N)\, \varphi_k^\pm(\boldsymbol{r}^N) \quad (2\text{-}4)$$

for Bose-Einstein (Fermi-Dirac) statistics and the density matrix $\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N)$, eq. I (3-1). With the projection operator $p_{E;\Delta E,op}$, eq. (2-4) may be transformed into

$$\rho^\pm_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = G^{\pm\,-1}_{E;\Delta E} \sum_k \varphi_k^{\pm *}(\boldsymbol{r}'^N)\, p_{E;\Delta E,op}\, \varphi_k(\boldsymbol{r}^N). \quad (2\text{-}5)$$

Now in the cases of Bose-Einstein and Fermi-Dirac statistics we have the completeness relations

$$\sum_k \varphi_k^{\pm *}(\boldsymbol{r}'^N)\, \varphi_k^\pm(\boldsymbol{r}^N) = (N!)^{-2} \sum_{P,Q} \delta_P^\pm \delta_Q^\pm \delta(P\boldsymbol{r}'^N - Q\boldsymbol{r}^N), \quad (2\text{-}6)$$

where the summation in the right-hand side extends over all possible permutations $P\boldsymbol{r}'^N$ and $Q\boldsymbol{r}^N$ of the particle coordinates. Eq. (2-5) may therefore be written as

$$\rho^\pm_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = (N!)^{-2}\, G^{\pm\,-1}_{E;\Delta E} \sum_{P,Q} \delta_P^\pm \delta_Q^\pm\, p_{E;\Delta E,op}\, \delta(P\boldsymbol{r}'^N - Q\boldsymbol{r}^N), \quad (2\text{-}7)$$

where $p_{E;\Delta E,op}$ operates on the variables $\boldsymbol{r}^N$.

The density matrices $\rho^\pm_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N)$, eq. (2-7), may now be expressed in terms of the density matrix $\rho_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N)$, eq. I (3-5), by means of the following integral equations:

$$\rho^\pm_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{r}^N) = \int \rho_{E;\Delta E}(\boldsymbol{r}'''^N, \boldsymbol{r}''^N)\, K^\pm_{E;\Delta E}(\boldsymbol{r}'''^N, \boldsymbol{r}''^N \,|\, \boldsymbol{r}'^N, \boldsymbol{r}^N)\, \mathrm{d}\boldsymbol{r}'''^N\, \mathrm{d}\boldsymbol{r}''^N, \quad (2\text{-}8)$$

with the kernels

$$K^{\pm}_{E;\Delta E}(\boldsymbol{r}'''^N, \boldsymbol{r}''^N \,|\, \boldsymbol{r}'^N, \boldsymbol{r}^N) \equiv$$

$$\equiv (N!)^{-2} \frac{G_{E;\Delta E}}{G^{\pm}_{E;\Delta E}} \Sigma_{P,Q}\, \delta^{\pm}_P \delta^{\pm}_Q \delta(\boldsymbol{r}'''^N - P\boldsymbol{r}'^N)\, \delta(\boldsymbol{r}''^N - Q\boldsymbol{r}^N), \tag{2-9}$$

using the fact that $p_{E;\Delta E, op}$ is symmetrical with respect to the coordinates of the identical particles.

With the help of the last two equations, it is now possible to express the Wigner distribution functions

$$f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = (\pi\hbar)^{-3N} \int \exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}$$

$$\rho^{\pm}_{E;\Delta E}(\boldsymbol{r}^N + \boldsymbol{y}^N, \boldsymbol{r}^N - \boldsymbol{y}^N)\, \mathrm{d}\boldsymbol{y}^N \tag{2-10}$$

in terms of the Wigner distribution function $f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$, eq. I (3-12), by means of the integral equations *)

$$f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = \int f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N)\, P^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, \boldsymbol{p}^N)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N, \tag{2-11}$$

with the kernels

$$P^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, \boldsymbol{p}^N) \equiv$$

$$\equiv (2/\pi\hbar)^{3N} (N!)^{-2} \frac{G_{E;\Delta E}}{G^{\pm}_{E;\Delta E}} \Sigma_{P,Q}\, \delta^{\pm}_P\, \delta^{\pm}_Q \int \exp\{(-2i/\hbar)(\boldsymbol{p}'^N \cdot \boldsymbol{y}'^N)\}$$

$$\delta(\boldsymbol{r}'^N + \boldsymbol{y}'^N - P\boldsymbol{r}^N - P\boldsymbol{y}^N)\, \delta(\boldsymbol{r}'^N - \boldsymbol{y}'^N - Q\boldsymbol{r}^N + Q\boldsymbol{y}^N)$$

$$\exp\{(2i/\hbar)(\boldsymbol{p}^N \cdot \boldsymbol{y}^N)\}\, \mathrm{d}\boldsymbol{y}'^N \mathrm{d}\boldsymbol{y}^N, \tag{2-12}$$

(*cf.* also reference [1]), eq. (25) **)).

It follows from (2-12) that

$$P^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, \boldsymbol{p}^N) = P^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, -\boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, -\boldsymbol{p}^N). \tag{2-13}$$

Applying this property to (2-11) and using the fact that $f_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ is an even function of the particle momenta (eq. I (3-20)), we find that the Wigner distribution functions $f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ are also even in the particle momenta:

$$f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N) = f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, -\boldsymbol{p}^N). \tag{2-14}$$

In the presence of an external magnetic field $\boldsymbol{B}$ we get from (2-12)

$$P^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B}) = P^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, -\boldsymbol{p}'^N \,|\, \boldsymbol{r}^N, -\boldsymbol{p}^N; -\boldsymbol{B}), \tag{2-15}$$

using the fact that $G_{E;\Delta E}(\boldsymbol{B})$ and $G^{\pm}_{E;\Delta E}(\boldsymbol{B})$ are even functions of $\boldsymbol{B}$, (*cf.*

*) The derivation of (2-11), (2-12) proceeds along the same lines as the derivation in chapter I of (2-34), (2-35) from (2-2) and (2-10).

**) It should be noted, however, that the right-hand side of this equation must be multiplied with a proper normalization factor since the Wigner distribution functions $w(\boldsymbol{r}, \boldsymbol{p})$ and $f^{\pm}(\boldsymbol{r}, \boldsymbol{p})$ are supposed to be normalized in phase space.

I (3-11)). From (2-11), (2-15) and I (3-21) we then obtain the relations

$$f^{\pm}_{E;\Delta E}\,(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B}) = f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, -\boldsymbol{p}^N; -\boldsymbol{B}), \tag{2-16}$$

which have the same form as I (3-21).

Substituting the expression I (3-16) into the right-hand side of (2-11), we find with (2-12) that

$$f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N,\boldsymbol{p}^N) = \Omega^{\pm\,-1}_{E;\Delta E} \int p_{E;\,\Delta E}(\boldsymbol{r}'^N,\boldsymbol{p}'^N)\; P^{\pm}(\boldsymbol{r}'^N,\boldsymbol{p}'^N\,|\,\boldsymbol{r}^N,\boldsymbol{p}^N)\;\mathrm{d}\boldsymbol{r}'^N\,\mathrm{d}\boldsymbol{p}'^N, \tag{2-17}$$

with

$$\Omega^{\pm}_{E;\Delta E} \equiv h^{3N}\, G^{\pm}_{E;\Delta E} \tag{2-18}$$

and the kernels *)

$$\begin{aligned} P^{\pm}(\boldsymbol{r}'^N, \boldsymbol{p}'^N\,|\,\boldsymbol{r}^N, \boldsymbol{p}^N) \equiv \\ \equiv (2/\pi\hbar)^{3N}\,(N!)^{-2}\, \textstyle\sum_{P,\,Q}\, \delta^{\pm}_{P}\delta^{\pm}_{Q} \int \exp\{(-2i/\hbar)(\boldsymbol{p}'^N\cdot \boldsymbol{y}'^N)\} \\ \delta(\boldsymbol{r}'^N + \boldsymbol{y}'^N - P\boldsymbol{r}^N - P\boldsymbol{y}^N)\;\delta(\boldsymbol{r}'^N - \boldsymbol{y}'^N - Q\boldsymbol{r}^N + Q\boldsymbol{y}^N) \\ \exp\{(2i/\hbar)\,(\boldsymbol{p}^N\cdot \boldsymbol{y}^N)\}\;\mathrm{d}\boldsymbol{y}'^N\,\mathrm{d}\boldsymbol{y}^N. \end{aligned} \tag{2-19}$$

Since the Wigner distribution functions $f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)$ are normalized, we obtain from (2-17)

$$\Omega^{\pm}_{E;\Delta E} = \int\!\!\int p_{E;\,\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N)\; P^{\pm}(\boldsymbol{r}'^N, \boldsymbol{p}'^N\,|\,\boldsymbol{r}^N, \boldsymbol{p}^N)\;\mathrm{d}\boldsymbol{r}'^N\,\mathrm{d}\boldsymbol{p}'^N\,\mathrm{d}\boldsymbol{r}^N\,\mathrm{d}\boldsymbol{p}^N. \tag{2-20}$$

The expressions (2-17) and (2-20) now take the place of the expressions (3-18) and (3-19) in chapter I.

For the equilibrium distribution function of extensive state variables we have

$$F(\boldsymbol{\alpha}) = \int p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})\; f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, \boldsymbol{p}^N)\;\mathrm{d}\boldsymbol{r}^N\,\mathrm{d}\boldsymbol{p}^N, \tag{2-21}$$

(*cf.* I (3-62)). Substituting (2-17) into the right-hand side of this equation we find that

$$F(\boldsymbol{\alpha}) = \Omega^{\pm}(\boldsymbol{\alpha})/\Omega^{\pm}_{E;\Delta E}, \tag{2-22}$$

where

$$\begin{aligned} \Omega^{\pm}(\boldsymbol{\alpha}) \equiv \\ \equiv \int\!\!\int p_{E;\,\Delta E}(\boldsymbol{r}'^N,\boldsymbol{p}'^N) P^{\pm}(\boldsymbol{r}'^N,\boldsymbol{p}'^N\,|\,\boldsymbol{r}^N,\boldsymbol{p}^N)\, p(\boldsymbol{r}^N,\boldsymbol{p}^N;\boldsymbol{\alpha})\,\mathrm{d}\boldsymbol{r}'^N\mathrm{d}\boldsymbol{p}'^N\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N, \end{aligned} \tag{2-23}$$

(*cf.* I (3-63) and I (3-64)).

Boltzmann's entropy postulate I (4-1) becomes in the cases of Bose-Einstein and Fermi-Dirac statistics

$$S(\boldsymbol{\alpha}) \equiv k \ln\{\Delta\Omega^{\pm}(\boldsymbol{\alpha})/h^{3N}\}, \tag{2-24}$$

where $\Delta\Omega^{\pm}(\boldsymbol{\alpha})$ are the n^{th} order differences of $\Omega^{\pm}(\boldsymbol{\alpha})$ over the range $(\boldsymbol{\alpha};\,\Delta\boldsymbol{\alpha})$. Gibbs' entropy of the micro-canonical ensemble is given by

$$S_G \equiv k \ln G^{\pm}_{E;\Delta E}, \tag{2-25}$$

*) The classical analogue of (2-19) is the kernel

$$P^{(cl)}(\boldsymbol{r}'^N, \boldsymbol{p}'^N|\boldsymbol{r}^N, \boldsymbol{p}^N) \equiv (N!)^{-2}\,\textstyle\sum_P\, \delta(\boldsymbol{r}'^N - P\boldsymbol{r}^N)\;\delta(\boldsymbol{p}'^N - P\boldsymbol{p}^N),$$

which may be obtained by considering only the terms with $P = Q$ in (2-19).

(*cf.* I (4-3)). The intensive thermodynamic variables $\boldsymbol{X}$ are again defined by means of I (4-8).

The joint Wigner distribution functions (2-13) and (2-21) in chapter II must be replaced by

$$f^{\pm}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t; \boldsymbol{r}^N, \boldsymbol{p}^N; t+\tau) = f^{\pm}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; t)$$

$$\cos\left\{\frac{\hbar}{2}\left(\frac{6}{6\boldsymbol{r}'^N}\cdot\frac{\partial}{\partial \boldsymbol{p}'^N} - \frac{6}{6\boldsymbol{p}'^N}\cdot\frac{\partial}{\partial \boldsymbol{r}'^N}\right)\right\} P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; \tau) \qquad \text{(2-26)}$$

and

$$f^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}^N, \boldsymbol{p}^N; \tau) = f^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N)$$

$$\cos\left\{\frac{\hbar}{2}\left(\frac{6}{6\boldsymbol{r}'^N}\cdot\frac{\partial}{\partial \boldsymbol{p}'^N} - \frac{6}{6\boldsymbol{p}'^N}\cdot\frac{\partial}{\partial \boldsymbol{r}'^N}\right)\right\} P(\boldsymbol{r}'^N, \boldsymbol{p}'^N | \boldsymbol{r}^N, \boldsymbol{p}^N; \tau) \qquad \text{(2-27)}$$

in the cases of Bose-Einstein and Fermi-Dirac statistics.

It is immediately seen, that the relations II (2-23) and II (2-24) are also valid in the cases of Bose-Einstein and Fermi-Dirac statistics, since the properties of Wigner distribution functions and propagators, which were needed in II for the derivation of these relations, also hold in these cases. We therefore have in the absence of an external magnetic field:

$$f^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}^N, \boldsymbol{p}^N; \tau) = f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, -\boldsymbol{p}^N; \boldsymbol{r}'^N, -\boldsymbol{p}'^N; \tau), \qquad \text{(2-28)}$$

and in the presence of a magnetic field:

$$f^{\pm}_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{B}; \tau) = f^{\pm}_{E;\Delta E}(\boldsymbol{r}^N, -\boldsymbol{p}^N; \boldsymbol{r}'^N, -\boldsymbol{p}'^N; -\boldsymbol{B}; \tau). \qquad \text{(2-29)}$$

For the joint equilibrium distribution functions of extensive state variables, we get

$$F(\boldsymbol{\alpha}'; \boldsymbol{\alpha}; \tau) = \int\int p(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{\alpha}')\, p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})$$
$$f_{E;\Delta E}(\boldsymbol{r}'^N, \boldsymbol{p}'^N; \boldsymbol{r}^N, \boldsymbol{p}^N; \tau)\, \mathrm{d}\boldsymbol{r}'^N \mathrm{d}\boldsymbol{p}'^N \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N, \qquad \text{(2-30)}$$

(*cf.* II (3-3)), and for the non-equilibrium distribution function $F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t)$, introduced in § 4 of chapter II, we now obtain

$$F_{\boldsymbol{\alpha}_0}(\boldsymbol{\alpha}; t) = \int p(\boldsymbol{r}^N, \boldsymbol{p}^N; \boldsymbol{\alpha})\, f^{(\mu)\pm}_{\boldsymbol{\alpha}_0;\Delta\boldsymbol{\alpha}_0}(\boldsymbol{r}^N, \boldsymbol{p}^N; t)\, \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N, \qquad \text{(2-31)}$$

(*cf.* II (4-11)).

The further development of the theory of the foundations of the Onsager reciprocal relations for Bose-Einstein and Fermi-Dirac statistics proceeds along the same lines as in the case of Maxwell-Boltzmann statistics.

REFERENCE

1) Schram, K. and Nijboer, B. R. A., Physica **25** (1959) 733.

SAMENVATTING

In dit proefschrift worden de quantumstatistische grondslagen van de reciprociteitsrelaties van Onsager in de thermodynamica van niet-evenwichtsprocessen behandeld. Daarbij wordt gebruik gemaakt van de beschrijving van de quantumstatistica met behulp van Wigner-distributiefuncties. Deze quantummechanische distributiefuncties, die in de faseruimte gedefinieerd zijn, vertonen overeenkomst met de distributiefuncties in de klassieke statistische mechanica. De theorie van de grondslagen van de Onsager-relaties wordt derhalve behandeld op een wijze, die analoog is aan de klassieke behandelingswijze van de Groot en Mazur.

In hoofdstuk I wordt de theorie van gewone Wigner-distributiefuncties behandeld. Verder wordt de evenwichtsdistributiefunctie van de extensieve toestandsvariabelen, welke het systeem macroscopisch beschrijven, ingevoerd, waarbij de veronderstelling wordt gemaakt, dat de quantummechanische operatoren, die met deze variabelen corresponderen, onderling verwisselbaar zijn. Deze waarschijnlijkheidsdistributiefunctie kan worden uitgedrukt in de Wigner-distributiefunctie van het micro-kanonieke ensemble. Verschillende eigenschappen van evenwichtsdistributiefuncties van extensieve variabelen worden afgeleid.

In hoofdstuk II worden "simultane Wigner-distributiefuncties" ingevoerd, die gebruikt kunnen worden om quantummechanische correlatiefuncties te berekenen. Verder wordt de simultane evenwichtsdistributiefunctie van de extensieve toestandsvariabelen van het systeem gedefinieerd. Deze distributiefunctie kan worden uitgedrukt in de simultane Wigner-distributiefunctie van het micro-kanonieke ensemble. De eigenschappen van simultane evenwichtsdistributiefuncties, in het bijzonder de zogenaamde eigenschap van microscopische reversibiliteit, worden afgeleid.

In het algemeen zijn simultane distributiefuncties van extensieve variabelen geen waarschijnlijkheidsdistributiefuncties. Men kan echter bewijzen, dat de simultane evenwichtsdistributiefunctie een simultane waarschijnlijkheid voorstelt, indien de quantummechanische operatoren, die met de toestandsvariabelen van het systeem corresponderen, van een speciale klasse zijn.

De theorie van distributiefuncties van extensieve variabelen wordt tenslotte gebruikt voor de bekende afleiding van de reciprociteitsrelaties van Onsager.

De theorie, behandeld in de hoofdstukken I en II, is alleen geldig voor Maxwell-Boltzmann-statistiek. In hoofdstuk III wordt de theorie uitgebreid tot de gevallen van Bose-Einstein- en Fermi-Dirac-statistiek.

De theorie van distributiefuncties met gemengde variabelen wordt tenslotte gebruikt voor de beknopte afleiding van de [illegible] van Uehling.

De theorie, behandeld in de hoofdstukken I en II, is alleen geldig voor Maxwell-Boltzmann-statistiek. In hoofdstuk III wordt de theorie uitgebreid tot de gevallen van Bose-Einstein- en Fermi-Dirac-statistiek.

SAMENVATTING

In dit proefschrift worden de quantummechanische grondslagen van de [illegible] behandeld. Hierbij wordt gebruik gemaakt van de beschrijving van de quantummechanica met behulp van Wigner-distributiefuncties. [illegible] distributiefuncties, die in de [illegible] overeenkomen met de distributiefuncties van de klassieke statistische mechanica. De theorie van de [illegible] wordt [illegible] behandeld op een wijze, die analoog is aan de klassieke behandeling van de Groot en Mazur.

In hoofdstuk I wordt de theorie van gewone Wigner-distributiefuncties behandeld. Verder wordt [illegible] variabelen [illegible] operatoren [illegible] Wigner-distributiefunctie [illegible] variabelen worden [illegible].

In hoofdstuk II worden [illegible] Wigner-distributiefuncties [illegible] quantummechanische [illegible] variabelen van het systeem [illegible] Wigner-distributiefunctie [illegible].

In het algemeen zijn [illegible] quantummechanische [illegible] van het systeem [illegible].