ON THE FOUNDATIONS OF CLASSICAL STATISTICAL PHYSICS

J. VAN DER LINDEN

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS DR. J. DANKMEIJER, HOOGLERAAR IN DE FACULTEIT DER GENEESKUNDE, TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG 26 JANUARI 1966 TE 16 UUR

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Promotor: Prof. Dr. P. Mazur

The incorporation of thermodynamics within mechanics is a classic and generally familiar instance of a reduction of dissimilar theories.

Ernest Nagel, The Structure of Science

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CONTENTS

INTRODUCTION

The branch of theoretical physics investigating the foundations of statistical physics, consists of two parts. The first part tries to explain why it is permissible to use a statistical phase average of a relevant mechanical quantity, instead of its time average (the ergodic problem). The second part is interested in the existence and other properties of the so-called thermodynamic limit of the functions of statistical thermodynamics (the asymptotic problem). A treatment of these problems can be either classical or quantal, but in this thesis only the first possibility comes up for discussion. As a matter of fact, the theory of statistical physics can only be considered to be founded in a satisfactory way, if the underlying properties of the interaction potential are in agreement with what is known from other fields of molecular physics. Since at first this was found to be too hard a task, simplifying potential models were introduced. Until almost half a century after Gibbs' rather intuitive ensemble theory (1902),the interaction had to be even altogether neglected (separable system, *e.g.* the ideal gas) in order to get any results. This period was closed in a brilliant way by the work of Khinchin.

The asymptotic problem consists of at least three separate existence-of-a-limit questions for each of the three formalisms of statistical thermodynamics (microcanonical, canonical and grand canonical); the most important properties to be established for the limit functions are the equivalence relations (implying that each formalism generates the same thermodynamics). Now for a separable system, the asymptotic problem reduces to the equivalence question, and the method of proof developed by Khinchin is characterized by the application of the central limit theorem of probability theory.

The investigation of real systems was opened by Van Hove's paper on the existence of the thermodynamic limit of the canonical free energy (1949). The treatment of this limit and the corresponding one in the grand canonical formalism (the pressure), has finally been drawn out of the stage of unsatisfactory potential models by Fisher and Ruelle, independently (1963/64). About the same time Griffiths derived a remarkably simple theorem with the consequence that actually five instead of two limits were established definitely.

A crucial requirement of the pair potential, found in this recent work, is the "stability", which means the following. Taking into account only the fact that the pair potential has a finite minimum, the minimum interaction energy $E_N^{(0)}$ of N particles is seen to satisfy the inequality "$E_N^{(0)} \geqslant$ a negative constant times N^p" with $p = 2$. For $1 < p \leqslant 2$, however, the free energy per particle blows up for $N \to \infty$, whereas for $0 \leqslant p \leqslant 1$, it may tend to a finite limit. Therefore the potential is called stable if the inequality is satisfied with $p = 1$. The Lennard-Jones potential, for example, is shown to be stable, and to accomplish actually the existence of the limits mentioned above.

The object of investigation which has led to this thesis, has been the extension of the asymptotic results for real systems to the equivalence question, following up the ideas of Khinchin concerning the use of probability theory. The derivation of the equivalence relations given in chapter I, is based on a potential which is stable and "strongly tempered" (*i.e.* negative at large enough distances). The method of proof is a synthesis of elements due to Khinchin (application of the central limit theorem) and Fisher (use of subadditivity). Moreover the number of functions for which the thermodynamic limit is shown to exist, is increased with two microcanonical ones: the entropy and the temperature.

Since this first chapter is written in the form of a research report (it will appear as such in "Physica"), it is rather compact. Therefore a second chapter is added which elaborates some points only referred to in chapter I. The following scheme of correspondences should be noted:

	Chapter I	Chapter II
§ 2.	thermodynamics	§ 1.
	statistical functions	§ 3.
	ergodic problem	§ 2, § 5.
	stability of the interaction	§ 6.
	Griffiths' theorem	Appendix
§ 4.	Khinchin's asymptotic results	§ 4, § 5.
§ 6.	phase transition problem	§ 6, Appendix

Chapter I

ON THE ASYMPTOTIC PROBLEM OF STATISTICAL THERMODYNAMICS FOR A REAL SYSTEM

§ 1. *Introduction.* Statistical thermodynamics gives a prescription how to determine "thermodynamic analogies" from a statistical function (canonical or grand canonical partition function; in the microcanonical case there is some ambiguity). These analogies are supposed to represent asymptotically the corresponding thermodynamic functions in the "thermodynamic limit". The first question we encounter is therefore: (a) does the existence of such limits indeed follow from the properties of the interaction entering in the definition of the statistical functions? This question may be split into two parts: (a′) for those analogies which are simply proportional to the logarithm of a statistical function (microcanonical entropy, canonical free energy, and grand canonical pressure), (a″) for all others. As is well-known, the limit functions to which (a′) refers, imply the knowledge of all other thermodynamic functions, so that we may ask: (b) whether the latter determination agrees with the limit functions to which (a″) refers. Furthermore, there is the important question concerning: (c) the equivalence of the various formalisms, on the basis of the relations between any two of the statistical functions. All this together constitutes the asymptotic problem of statistical thermodynamics (for a detailed statement, and a survey of its treatment in sections 3–5, see section 2).

At first separable systems (for example the ideal gas) were considered. Then the canonical and grand canonical partition functions factorize, so that in these formalisms the questions (a) and (b) present no difficulty. The treatment of the remaining problem for such systems in general (*i.e.* without reference to the internal structure of the non-interacting components), has been brought into its simplest form by Khinchin[1]). The feature of his approach is that the asymptotic evaluation of a statistical function (structure function or canonical partition function) is conceived as a limit problem of probability theory, to which the so-called central limit theorem is applicable.

Then the way was paved for the consideration of nonseparable systems where (a) and (b), in the canonical and the grand canonical formalisms, are also problematic. The treatment of (a′) in these cases has had an evolution of its own: from the consideration of systems with hard core-finite range interaction, to the latest developments on the basis of very general interaction properties (a review of this has been given by Ruelle[2]). In its earliest stage the approach to these existence problems has served as a basis for Yamamoto and Matsuda[3]) in extending Khinchin's work on the equivalence problem, and in its recent stage it has done so again for us (for a discussion of the various methods involved, including that of our previous paper[4]), see section 6).

In dealing with (a″) and (b), as well as with (c), we have also taken advantage of the conditions on the interchangeability of the thermodynamic limit and differentiation, found recently by Griffiths[5]) (in connection with a treatment of the question (a′) in the quantum canonical formalism for a spin system).

§ 2. *Statement of the asymptotic problem.* In classical statistical thermodynamics one determines from the Hamiltonian function of a system the Gibbsian analogies of its thermodynamic functions. For a system of N identical point particles with mass m and pair interaction, the Hamiltonian function $\mathscr{H}_N$ depends on the configuration $\boldsymbol{r}^N \equiv (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ and the set of momenta $\boldsymbol{p}^N \equiv (\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N)$ as follows,

$$\mathscr{H}_N(\boldsymbol{r}^N, \boldsymbol{p}^N) = \frac{(\boldsymbol{p}^N)^2}{2m} + \sum_{\substack{i,j=1\\ i<j}}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|), \tag{1}$$

where u is the pair potential. All positions $\boldsymbol{r}_i (i = 1, \ldots, N)$ are restricted to the volume V of the system.

Besides N and V, we will consider the following thermodynamic quantities: E, the internal energy, S, the entropy divided by k (Boltzmann's constant), β, the inverse absolute temperature divided by k, F, the free energy multiplied by $-\beta$, μ, the chemical potential multiplied by $-\beta$, and p, the pressure multiplied by β. Instead of the extensive quantities V, E, S and F, we will mostly use their specific values $v = V/N$, $e = E/N$, $s = S/N$ and $f = F/N$. Of the set of seven intensive quantities thus obtained, two are independently variable. For any choice of them we have

$$f = s - \beta e, \tag{2}$$

$$\mu = f - pv. \tag{3}$$

There are three alternative ways in common use to determine thermodynamic analogies from $\mathscr{H}_N$, each of which is based on one of the statistical functions Σ_N, Φ_N and Ξ_V given by

$$\Sigma_N(E, V) = \frac{1}{N!} \iint \mathrm{d}\boldsymbol{r}^N \, \mathrm{d}\boldsymbol{p}^N \sigma\{E - \mathscr{H}_N(\boldsymbol{r}^N, \boldsymbol{p}^N)\},$$

$$(\Sigma_0(E, V) \equiv \sigma(E)), \quad -\infty < E < \infty, \tag{4}$$

where σ denotes the unit-step function,

$$\Phi_N(\beta, V) = \frac{1}{N!} \iint \mathrm{d}\boldsymbol{r}^N \, \mathrm{d}\boldsymbol{p}^N \exp\{-\beta \mathscr{H}_N(\boldsymbol{r}^N, \boldsymbol{p}^N)\},$$

$$(\Phi_0(\beta, V) \equiv 1), \quad 0 < \beta < \infty, \tag{5}$$

and

$$\Xi_V(\beta, \mu) = \sum_{N=0}^{\infty} e^{-\mu N} \Phi_N(\beta, V), \qquad -\infty < \mu < \infty. \tag{6}$$

According to the microcanonical formalism, the logarithm of the function (4) is the analogy $S_N^{(\mathrm{m})}$ of S as a function of N, E and V, or written with specific values,

$$s_N^{(\mathrm{m})}(e, v) = \frac{1}{N} \log \Sigma_N(Ne, Nv)\, *). \tag{7}$$

The analogies of the remaining thermodynamic functions are derived from this basic one by means of "thermodynamic" formulae:

$$\beta_N^{(\mathrm{m})}(e, v) = \frac{\partial s_N^{(\mathrm{m})}(e, v)}{\partial e}, \tag{8}$$

$$p_N^{(\mathrm{m})}(e, v) = \frac{\partial s_N^{(\mathrm{m})}(e, v)}{\partial v}, \tag{9}$$

and (2) and (3) applied to this formalism.

The connection of this theory with thermodynamics is based on two suppositions. The first one is: the sequence of functions defined by (7) for $N = 0, 1, 2, 3, \ldots$ attains a finite limit $s^{(\mathrm{m})}$,

$$\lim_{N\to\infty} s_N^{(\mathrm{m})}(e, v) = s^{(\mathrm{m})}(e, v), \tag{10}$$

which operation may be interchanged with differentiation so that for (8) and (9)

$$\lim_{N\to\infty} \beta_N^{(\mathrm{m})}(e, v) = \beta^{(\mathrm{m})}(e, v) \equiv \frac{\partial s^{(\mathrm{m})}(e, v)}{\partial e}, \tag{11}$$

$$\lim_{N\to\infty} p_N^{(\mathrm{m})}(e, v) = p^{(\mathrm{m})}(e, v) \equiv \frac{\partial s^{(\mathrm{m})}(e, v)}{\partial v}. \tag{12}$$

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*) For our purpose this is the most convenient one of the two alternative microcanonical entropy analogies; see furthermore section 5.

The second supposition is that these limit functions are the true thermodynamic functions. Then $s_N^{(m)}$, $\beta_N^{(m)}$, *etc.* are very good approximations for macroscopic systems ($N \approx 10^{23}$) to s, β, *etc.* as functions of e and v. If we do not use specific quantities, we say that $S_N^{(m)}$, $\beta_N^{(m)}$, *etc.* are asymptotically equal to S, β, *etc.* as functions of N, E and V in the thermodynamic limit.

The aim of the investigation of the foundations of statistical thermodynamics is the reduction of the above suppositions (and others still to be mentioned) to consequences of properties of the interaction between the particles. The second of the above mentioned suppositions gives rise in this way to the ergodic problem of statistical thermodynamics. This problem has not yet been solved in a satisfactory way, and therefore it is of importance already to establish, in addition to the existence of $s^{(m)}$, its proper behaviour with e and v, *i.e.* concavity in both variables. All questions concerning existence and other properties of the different analogies, defined according to the microcanonical as well as the other formalisms, in the thermodynamic limit (including the equivalence question) constitute the asymptotic problem.

The other formalisms are the canonical one, according to which the logarithm of (5) is the analogy $F_N^{(c)}$ of F as a function of N, β and V, and the grand canonical one, relating the logarithm of (6) as analogy to the quantity pV as a function of V, β and μ. Similar to (7), (8) and (9) we have, respectively

$$f_N^{(c)}(\beta, v) = \frac{1}{N} \log \Phi_N(\beta, Nv), \tag{13}$$

$$e_N^{(c)}(\beta, v) = -\frac{\partial f_N^{(c)}(\beta, v)}{\partial \beta}, \tag{14}$$

$$p_N^{(c)}(\beta, v) = \frac{\partial f_N^{(c)}(\beta, v)}{\partial v}, \tag{15}$$

and

$$p_V^{(g)}(\beta, \mu) = \frac{1}{V} \log \Xi_V(\beta, \mu), \tag{16}$$

$$\frac{1}{v_V^{(g)}(\beta, \mu)} = -\frac{\partial p_V^{(g)}(\beta, \mu)}{\partial \mu}, \tag{17}$$

$$\frac{e_V^{(g)}(\beta, \mu)}{v_V^{(g)}(\beta, \mu)} = -\frac{\partial p_V^{(g)}(\beta, \mu)}{\partial \beta}. \tag{18}$$

The supposed (thermodynamic) limit properties of these functions are

$$\lim_{N\to\infty} f_N^{(c)}(\beta, v) = f^{(c)}(\beta, v) \tag{19}$$

with $f^{(c)}$ convex in β and concave in v,

$$\lim_{N\to\infty} e_N^{(c)}(\beta, v) = e^{(c)}(\beta, v) \equiv -\frac{\partial f^{(c)}(\beta, v)}{\partial \beta}, \tag{20}$$

$$\lim_{N\to\infty} p_N^{(c)}(\beta, v) = p^{(c)}(\beta, v) \equiv \frac{\partial f^{(c)}(\beta, v)}{\partial v}, \tag{21}$$

and

$$\lim_{V\to\infty} p_V^{(g)}(\beta, \mu) = p^{(g)}(\beta, \mu) \tag{22}$$

with $p^{(g)}$ convex both in β and μ,

$$\lim_{V\to\infty} v_V^{(g)}(\beta, \mu) = v^{(g)}(\beta, \mu) \equiv -1 \Bigg/ \frac{\partial p^{(g)}(\beta, \mu)}{\partial \mu}, \tag{23}$$

$$\lim_{V\to\infty} e_V^{(g)}(\beta, \mu) = e^{(g)}(\beta, \mu) \equiv -v^{(g)}(\beta, \mu)\, \frac{\partial p^{(g)}(\beta, \mu)}{\partial \beta}. \tag{24}$$

Note that the above mentioned convexity properties follow at once from the existence of (19) and (22), respectively, since according to (5) and (6) we have

$$B_N^{(c)}(\beta, V) \equiv \frac{\partial^2 \log \Phi_N(\beta, V)}{\partial \beta^2} > 0, \tag{25}$$

$$\frac{\partial^2 \log \Xi_V(\beta, \mu)}{\partial \beta^2} > 0, \tag{26}$$

$$B_V^{(g)}(\beta, \mu) \equiv \frac{\partial^2 \log \Xi_V(\beta, \mu)}{\partial \mu^2} > 0. \tag{27}$$

These inequalities state that before the limit of (13) or (16) is taken, the (conserved) convexity properties are already present. If a function is convex (or concave), it has to be continuous, whereas its derivative as a monotonous function has only a countable number of jump discontinuities. In the following we will have to take into account these jump discontinuities for the limit functions (20) and (23). According to thermodynamics, they are interpreted as first-order phase transitions in the $e-\beta$ diagram at constant v, and in the $v-\mu$ diagram at constant β. For the sake of simplicity we assume only one transition point β_t where $e^{(c)}$ jumps from $e_{t,1}$ to $e_{t,2}$ ($> e_{t,1}$) and one transition point μ_t where $v^{(g)}$ jumps from $v_{t,1}$ to $v_{t,2}$ ($> v_{t,1}$).

The concavity properties of (10) and (19) cannot be established for (7) and (13), respectively (before the limit is taken). Moreover, according to the thermodynamic interpretation, the limit functions (11), (12) and (21) have to be monotonous without jump discontinuities, so that it is also a part of the asymptotic problem to prove in addition to the existence of $\beta^{(m)}$ its continuity in e, and in addition to that of $p^{(\mathrm{m})}$ and $p^{(\mathrm{c})}$, their continuity in v.

By equivalence of the various formalisms of statistical thermodynamics in the thermodynamic limit, we mean the identity of the various limit functions obtained for the same quantity if expressed in the same variables by means of Legendre transformation. It follows that the equivalence of the microcanonical and the canonical formalisms is established by the relation (*cf.* (2))

$$s^{(\mathrm{m})}(e, v) = f^{(\mathrm{c})}(\alpha(e, v), v) + \alpha(e, v)\, e, \tag{28}$$

where the function α is defined by

$$e^{(\mathrm{c})}(\alpha(e, v), v) = e. \tag{29}$$

Likewise the canonical and the grand canonical formalisms are equivalent if (*cf.* (3))

$$f^{(\mathrm{c})}(\beta, v) = p^{(\mathrm{g})}(\beta, \lambda(\beta, v))\, v + \lambda(\beta, v) \tag{30}$$

with

$$v^{(\mathrm{g})}(\beta, \lambda(\beta, v)) = v. \tag{31}$$

The assumptions about the interaction, which will be made in this paper, are those of stability and of strong tempering. The interaction is called stable if there exists a finite positive number u_0 such that

$$\mathscr{U}_N(\boldsymbol{r}^N) \equiv \sum_{\substack{i,j=1\\ i<j}}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \geqslant -Nu_0 \tag{32}$$

for all N*). The application of this property is quite simple. Using (1), the integration over momentum space in (4) and (5) may be performed, giving

$$\Sigma_N(E, V) = \frac{(2\pi m)^{3N/2}}{N!} \int \mathrm{d}\boldsymbol{r}^N \, \frac{\{E - \mathscr{U}_N(\boldsymbol{r}^N)\}^{3N/2}}{\Gamma\left(\dfrac{3N}{2} + 1\right)}\, \sigma\{E - \mathscr{U}_N(\boldsymbol{r}^N)\}, \tag{33}$$

$$\Phi_N(\beta, V) = \frac{1}{N!} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \int \mathrm{d}\boldsymbol{r}^N \exp\{-\beta \mathscr{U}_N(\boldsymbol{r}^N)\}. \tag{34}$$

Therefore, due to (32), we have the inequalities

$$\Sigma_N(E, V) \leqslant \frac{V^N}{N!} \frac{\{2\pi m(E + Nu_0)\}^{3N/2}}{\Gamma\left(\dfrac{3N}{2} + 1\right)}, \tag{35}$$

$$\Phi_N(\beta, V) \leqslant \frac{V^N}{N!} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \mathrm{e}^{N\beta u_0}, \tag{36}$$

*) According to Ruelle [6]) a sufficient condition for stability is the existence of a function $\varphi(|\boldsymbol{r}|) \leqslant u(|\boldsymbol{r}|)$ with the properties: $0 < \varphi(0) < \infty$, $\int \mathrm{d}\boldsymbol{r} \exp(-i\boldsymbol{t}\cdot\boldsymbol{r})\cdot\varphi(|\boldsymbol{r}|) \geqslant 0$ for any real vector $\boldsymbol{t}$.

and furthermore for (6)

$$\Xi_V(\beta, \mu) \leqslant \exp\left\{\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} V\, e^{-\mu+\beta u_0}\right\}. \tag{37}$$

The interaction is called strongly tempered if there exists a finite positive number r_0 such that

$$\sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \leqslant 0 \text{ whenever } |\boldsymbol{r}_i - \boldsymbol{r}_j| \geqslant r_0,$$
$$(i = 1, \ldots, N_1;\, j = N_1 + 1, \ldots, N) \tag{38}$$

for any division of N into N_1 and $N - N_1$. A Lennard-Jones type potential, for example, has both the properties (32) [7] and (38).

On this basis we will achieve the following results:

1°. (in section 3) independent proofs of the existence of the limits (10), (19) and (22) and their proper behaviour, elaborating and extending the principle which Fisher [8] indicated for the case of (19). A theorem due to Griffiths [5] states: if a sequence of functions with nondecreasing derivatives converges, then the sequence of these derivatives tends to the derivative of the limit function of the original sequence in points where the latter derivative is continuous. Therefore, according to (25)–(27), we may, in that section, consider also (20), (23) and (24) to be established outside phase transitions. With all this knowledge as preparation, we come to our main point:

2°. (in section 4) proofs of (28) and (30). The derivation of these equivalence relations builds further on the work of Khinchin [1] for ideal systems. Finally we discuss:

3°. (in section 5) remaining questions. In particular we prove (11) by means of a certain generalization of the preceding treatment, but the problems (12) and (21) are not solved.

§3. *Proof of the existence of the functions* $s^{(m)}$, $f^{(c)}$ *and* $p^{(g)}$. Let the system considered be enclosed in a cylinder with a cross section of arbitrary but fixed shape and area A, and situated parallel to the z axis with lower and upper surfaces at $z = H$ and $z = H'$, respectively. The volume V is assumed to change only by varying $H' - H$, *i.e.* at constant A. Hence, keeping V/N constant in the thermodynamic limit means essentially that $(H' - H)/N$ and A are kept constant, and, furthermore, differentiations with respect to V or v are performed at constant A. One has, therefore, a parametrical dependence of the statistical thermodynamic functions on A, which is of course also expected from thermodynamics: for instance p (divided by β), which is the pressure measured on the upper surface when the lower surface is fixed, is not the same function of the specific volume v for a capillary and for a cylinder with macroscopic cross section. Note that what in the latter case is usually called "the" pressure, is strictly speaking the limit for A tending to infinity. The question of the dependence of the thermodynamic limit functions on A (and in particular also whether they possess a finite limit for A tending to infinity) is, however, outside the scope of our subject. As we do not consider systems for different values of A, we shall not write the dependence on A anywhere explicitly.

Corresponding to a volume V we introduce an extended volume V^* defined by x, y in A and $H - \frac{1}{2}r_0 \leqslant z \leqslant H' + \frac{1}{2}r_0$. Then the domain of each space integration in (4) and (5) may be taken to be V^* instead of V, if we add a "wall potential",

$$w(\boldsymbol{r}) = \begin{cases} 0 \text{ for } x, y \text{ in } A, \text{ and } H \leqslant z \leqslant H', \\ \infty \text{ for } x, y \text{ in } A, \text{ and } H - \frac{1}{2}r_0 \leqslant z \leqslant H, H' \leqslant z \leqslant H' + \frac{1}{2}r_0, \end{cases} \tag{39}$$

to the potential energy:

$$\mathscr{U}_N^*(\boldsymbol{r}^N) = \mathscr{U}_N(\boldsymbol{r}^N) + \sum_{i=1}^{N} w(\boldsymbol{r}_i). \tag{40}$$

With the corresponding Hamiltonian function $\mathscr{H}_N^*$ we have

$$\Sigma_N^*(E, V^*) \equiv \frac{1}{N!} \iint \mathrm{d}\boldsymbol{r}^N \, \mathrm{d}\boldsymbol{p}^N \sigma\{E - \mathscr{H}_N^*(\boldsymbol{r}^N, \boldsymbol{p}^N)\} = \Sigma_N(E, V), \tag{41}$$

$$\Phi_N^*(\beta, V^*) \equiv \frac{1}{N!} \iint \mathrm{d}\boldsymbol{r}^N \, \mathrm{d}\boldsymbol{p}^N \exp\{-\beta\mathscr{H}_N^*(\boldsymbol{r}^N, \boldsymbol{p}^N)\} = \Phi_N(\beta, V). \tag{42}$$

Obviously the difference r_0A between V^* and V becomes negligible in the thermodynamic limit, in the sense that:

$$\lim_{V\to\infty} \frac{V^*}{V} = \lim_{V\to\infty} \frac{V + r_0A}{V} = 1, \text{ or } \lim_{N\to\infty} v_{(N)} = v. \tag{43}$$

where $v_{(N)} (N = 1, 2, 3, \ldots)$ is the sequence $v + r_0A, v + \frac{1}{2}r_0A, v + \frac{1}{3}r_0A, \ldots$ The introduction of V^* is, however, a device to derive, on the basis of (38), some very useful inequalities for the statistical functions (see *e.g.* (49) and (50)). This would not have been possible with the variable V.

It is the advantage of our assumption about varying the volume (in only one dimension), that it makes possible a way of dividing a system into subsystems which are determined by their volume alone. For a value H'' of z between H and H' we obtain two subvolumes of V^*: $V_1^*(H - \frac{1}{2}r_0 \leqslant \leqslant z \leqslant H'')$ and $V^* - V_1^*(H'' \leqslant z \leqslant H' + \frac{1}{2}r_0)$. Then, if $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_1}$ lie in V_1^* and $\boldsymbol{r}_{N_1+1}, \ldots, \boldsymbol{r}_N$ in $V^* - V_1^*$, we have for (40)

$$\mathscr{U}_N^*(\boldsymbol{r}^N) \leqslant \mathscr{U}_{N_1}^*(\boldsymbol{r}^{N_1}) + \mathscr{U}_{N-N_1}^*(\boldsymbol{r}^{(N-N_1)}), \tag{44}$$

where $\boldsymbol{r}^{(N-N_1)} \equiv (\boldsymbol{r}_{N_1+1}, \ldots, \boldsymbol{r}_N)$. Indeed as far as u is concerned, the opposite sign could according to (38) hold only for a configuration with at least one particle between $z = H'' - \frac{1}{2}r_0$ and $z = H'' + \frac{1}{2}r_0$, but in that case the right-hand side of the inequality is infinite due to w. Splitting each space integration over V^* in (41) into one over V_1^* and one over $V^* - V_1^*$, and using the fact that $\mathscr{H}_N^*$ is invariant with respect to particle permutation, we get a sum of integrations over $\boldsymbol{r}^{N_1}$ and $\boldsymbol{r}^{(N-N_1)}$, ($\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_1}$ in V_1^*; $\boldsymbol{r}_{N_1+1}, \ldots, \boldsymbol{r}_N$ in $V^* - V_1^*$; $N_1 = 0, 1, 2, \ldots, N$), each with its proper binomial coefficient. Then, applying (44) for the different values of N_1, we find

$$\Sigma_N^*(E, V^*) \geqslant \sum_{N_1=0}^{N} \frac{1}{N_1!(N-N_1)!} \iint \mathrm{d}\boldsymbol{r}^{N_1}\, \mathrm{d}\boldsymbol{p}^{N_1} \iint \mathrm{d}\boldsymbol{r}^{(N-N_1)}\, \mathrm{d}\boldsymbol{p}^{(N-N_1)} \cdot$$

$$\cdot \sigma\{E - \mathscr{H}_{N_1}^*(\boldsymbol{r}^{N_1}, \boldsymbol{p}^{N_1}) - \mathscr{H}_{N-N_1}^*(\boldsymbol{r}^{(N-N_1)}, \boldsymbol{p}^{(N-N_1)})\}, \quad (45)$$

where $\boldsymbol{p}^{(N-N_1)} \equiv (\boldsymbol{p}_{N_1+1}, \ldots, \boldsymbol{p}_N)$.

Using the identity $\sigma(x) = \int \mathrm{d}x_1\, \delta(x_1)\, \sigma(x - x_1)$, where δ is the Dirac function, we obtain, putting $x = E - \mathscr{H}_{N_1}^* - \mathscr{H}_{N-N_1}^*$ and $x_1 = E_1 - \mathscr{H}_{N_1}^*$,

$$\Sigma_N^*(E, V^*) \geqslant \sum_{N_1=0}^{N} \int_{-\infty}^{\infty} \mathrm{d}E_1 \Omega_{N_1}^*(E_1, V_1^*)\, \Sigma_{N-N_1}^*(E - E_1, V^* - V_1^*). \quad (46)$$

Here the function Ω_N^* is defined by

$$\Omega_N^*(E, V^*) = \frac{1}{N!} \iint \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N\, \delta\{E - \mathscr{H}_N^*(\boldsymbol{r}^N, \boldsymbol{p}^N)\}, \; (\Omega_0^*(E, V^*) \equiv \delta(E)), \quad (47)$$

or equivalently

$$\Omega_N^*(E, V^*) = \frac{\partial \Sigma_N^*(E, V^*)}{\partial E}. \quad (48)$$

Result (46) is important for the development in the next section. An inequality containing only the function Σ_N^* may be derived from (45) by application of the following property of the unit-step function: $\sigma(x) \geqslant \sigma(x_1) \cdot \sigma(x - x_1)$, giving

$$\Sigma_N^*(E, V^*) \geqslant \sum_{N_1=0}^{N} \Sigma_{N_1}^*(E_1, V_1^*)\, \Sigma_{N-N_1}^*(E - E_1, V^* - V_1^*). \quad (49)$$

Since $\exp x \equiv \exp x_1 \cdot \exp(x - x_1)$, we have similarly for (42) on the basis of (44),

$$\Phi_N^*(\beta, V^*) \geqslant \sum_{N_1=0}^{N} \Phi_{N_1}^*(\beta, V_1^*)\, \Phi_{N-N_1}^*(\beta, V^* - V_1^*). \quad (50)$$

Now the inequalities (49) and (50) hold equally well, when all terms except one on the right-hand side are dropped, and it is in this form that (50) has been recognized by Fisher[8]) to provide a way of proving (19) by means of the limit theorem for subadditive functions[9]). In fact, for the sequence of functions (*cf.* (13))

$$f_N^*(\beta, v^*) = \frac{1}{N} \log \Phi_N^*(\beta, Nv^*), \tag{51}$$

($N = 0, 1, 2, \dots$; v^* independent of N) it thus follows that

$$Nf_N^*(\beta, v^*) \geqslant N_1 f_{N_1}^*(\beta, v^*) + (N - N_1)\, f_{N-N_1}^*(\beta, v^*). \tag{52}$$

This inequality expresses the fact that, at constant β and v^*, $-N$ times f_N^* is a subadditive function of N, and therefore the application of the limit theorem gives

$$\lim_{N\to\infty} f_N^*(\beta, v^*) = \sup_{N\to\infty} f_N^*(\beta, v^*) \equiv f^*(\beta, v^*). \tag{53}$$

The possibility that the limit function f^* is either $-\infty$ or $+\infty$ may be excluded. Since Φ_N^* vanishes only for $V^* \leqslant r_0 A$, $f_N^* = -\infty$ for $N \leqslant r_0 A/v^*$, and larger otherwise. Furthermore, according to (36) we have

$$f_N^*(\beta, v^*) \leqslant \log \left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}} v^* + 1 + \beta u_0. \tag{54}$$

Hence f^* is finite for $0 < \beta < \infty$ and $0 < v^* < \infty$.

As already has been remarked, f^* is convex in β since f_N^* possesses this property. The concavity of f^* in v^* follows from yet another inequality for (51), (with N even),

$$f_N^*(\beta, \tfrac{1}{2}(v_1^* + v_2^*)) \geqslant \tfrac{1}{2}\{f_{\frac{1}{2}N}^*(\beta, v_1^*) + f_{\frac{1}{2}N}^*(\beta, v_2^*)\}, \tag{55}$$

which may be derived from (50) by retaining again one special term on the right-hand side. When we apply the limit (53) to this inequality, it reduces to the definition of concavity for f^* as a function of v^*,

$$f^*(\beta, \tfrac{1}{2}(v_1^* + v_2^*)) \geqslant \tfrac{1}{2}\{f^*(\beta, v_1^*) + f^*(\beta, v_2^*)\}. \tag{56}$$

Consequently f^* is also continuous in v^*.

It appears that the limit function f^* has all the desired properties, but the limit (53) is not precisely the one we want to take (*i.e.* (19))*). In the appendix we prove that (52) implies not only the existence of the limit (53), but also its uniformity in a variable in which f_N^* and f^* are both continuous, and, moreover, f_N^* is increasing. The dependence of (51) and (53) on v^* meets these conditions, and consequently, using also (13), (42) and (43), we may conclude that

$$f^{(c)}(\beta, v) \equiv \lim_{N\to\infty} f_N^{(c)}(\beta, v) = \lim_{N\to\infty} f_N^*(\beta, v_{(N)}) = f^*(\beta, v). \tag{57}$$

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*) Fisher [8]) considers a system including a wall potential, which in our language is equivalent to calling V^* "the" volume. Then (53) is already the proper limit. This is also the case in his subsequent paper [10]) on the same subject, where the treatment has been altered in order to deal with volume increase in all three dimensions.

This result confirms the idea that the difference between V^* and V has no effect on the thermodynamic limit functions, in the case of $f^{(c)}$: it may be determined either from (19) or from (53).

From (50) as the basic inequality, we have therefore derived the existence and proper behaviour of the limit (19). It will be clear that the case of the limit (10) may be treated in a similar way, starting from (49) instead of from (50), by considering first the sequence of functions (*cf.* (7))

$$s_N^*(e, v^*) = \frac{1}{N} \log \Sigma_N^*(Ne, Nv^*), \tag{58}$$

($N = 0, 1, 2, \dots$; v^* independent of N). It has the same property as expressed by (52) for the sequence of functions (51), so that in analogy to (53) we have

$$\lim_{N\to\infty} s_N^*(e, v^*) = \sup_{N\to\infty} s_N^*(e, v^*) \equiv s^*(e, v^*). \tag{59}$$

The question of the finiteness of the limit function s^* is slightly more complicated than in the foregoing case, since Σ_N^* vanishes not only for $V^* \leqslant r_0 A$, but also for $E \leqslant E_N^{(0)*}$, where

$$E_N^{(0)*}(V^*) \equiv \min_{\boldsymbol{r}^N} \mathscr{U}_N^*(\boldsymbol{r}^N) = \min_{\boldsymbol{r}^N} \mathscr{U}_N(\boldsymbol{r}^N) \equiv E_N^{(0)}(V). \tag{60}$$

Let us examine what (44) means for this function (60). The minimum of the right-hand side of (44) is equal to the sum of $E_{N_1}^{(0)*}$ and $E_{N-N_1}^{(0)*}$, and larger than the left-hand side for the configuration(s) in which this minimum is reached. In its turn this value of the left-hand side is larger than $E_N^{(0)*}$, so that

$$E_N^{(0)*}(V^*) \leqslant E_{N_1}^{(0)*}(V_1^*) + E_{N-N_1}^{(0)*}(V^* - V_1^*). \tag{61}$$

We see that, for $V^* = Nv^*$, $E_N^{(0)*}$ is a subadditive function of N, and conclude therefore that the following limit exists,

$$\lim_{N\to\infty} \frac{1}{N} E_N^{(0)*}(Nv^*) = \inf_{N\to\infty} \frac{1}{N} E_N^{(0)*}(Nv^*) \equiv e^{(0)*}(v^*). \tag{62}$$

By iteration we obtain from (61) for $N \geqslant 1$,

$$E_N^{(0)*}(Nv^*) \leqslant E_1^{(0)*}(v^*) + E_{N-1}^{(0)*}((N-1)\, v^*) \leqslant \dots \leqslant NE_1^{(0)*}(v^*), \tag{63}$$

so that, since $E_1^{(0)*} = 0$ and moreover, according to (32), $E_N^{(0)*} \geqslant -Nu_0$, the limit function $e^{(0)*}$ is found to be finite. The inequality (61) may also be used to show that $e^{(0)*}$ is convex, and consequently continuous. Then, noting furthermore the fact that $E_N^{(0)*}$ is decreasing in V^* (the more room, the less restrictions on the composition of a minimum configuration), we have

$$e^{(0)}(v) \equiv \lim_{N\to\infty} \frac{1}{N} E_N^{(0)}(Nv) = \lim_{N\to\infty} \frac{1}{N} E_N^{(0)*}(Nv_{(N)}) = e^{(0)*}(v), \tag{64}$$

just as in the case of $f^{(c)}$.

Now, according to (62), the condition $e > E_N^{(0)*}/N$ for s_N^* to be larger than $-\infty$, becomes $e > e^{(0)*}$ for s^*. Since furthermore, according to (35),

$$s_N^*(e, v^*) \leqslant \log(\tfrac{4}{3}\pi m(e + u_0))^{\frac{3}{2}} v^* + \tfrac{5}{2}, \tag{65}$$

the function s^* is finite for $e^{(0)*} < e < \infty$ and $0 < v^* < \infty$. From (49) it may also be derived that this limit function is concave in both e and v^*,

$$s^*(\tfrac{1}{2}(e_1 + e_2), \tfrac{1}{2}(v_1^* + v_2^*)) \geqslant \tfrac{1}{2}\{s^*(e_1, v_1^*) + s^*(e_2, v_2^*)\}, \tag{66}$$

implying its continuity, and, together with the fact that s_N^* is increasing, the uniformity of the limit (59), all in both variables. On the grounds of this uniformity in v^*, we again conclude that the starred and the unstarred limit function are indentical,

$$s^{(m)}(e, v) \equiv \lim_{N\to\infty} s_N^{(m)}(e, v) = \lim_{N\to\infty} s_N^*(e, v_{(N)}) = s^*(e, v). \tag{67}$$

Finally we have for

$$\Xi_{V^*}^*(\beta, \mu) \equiv \sum_{N=0}^{\infty} e^{-\mu N} \Phi_N^*(\beta, V^*) = \Xi_V(\beta, \mu), \tag{68}$$

according to (50), the inequality

$$\Xi_{V^*}^*(\beta, \mu) \geqslant \Xi_{V_1^*}^*(\beta, \mu)\, \Xi_{V^*-V_1^*}^*(\beta, \mu). \tag{69}$$

Therefore the case of the limit (22) may also be treated similarly to that of (19). The applications of the limit theorem and of (43) can be connected in a simple way,

$$p^{(g)}(\beta, \mu) = \lim_{V^*\to\infty} \frac{V^*}{V} \cdot \frac{1}{V^*} \log \Xi_{V^*}^*(\beta, \mu) = \sup_{V^*\to\infty} \frac{1}{V^*} \log \Xi_{V^*}^*(\beta, \mu), \tag{70}$$

and the finiteness of the limit function for $0 < \beta < \infty$ and $-\infty < \mu < \infty$, follows easily from the inequalities $\Xi_V \geqslant 1$ and (37).

With the results obtained so far, the possibilities for using (44) are by no means exhausted yet, as will appear in the next section.

§ 4. *Equivalence of the various formalisms.* The inequalities based on a division of V^* into two parts, (*e.g.* (46) and (49)), may be generalized to a division into n parts. Keeping in mind that the right-hand side of (46) is larger than that of (49), one obtains in this way the result

$$\Sigma_N^*(E, V^*) \geqslant \sum_{N_1=0}^{\infty} \dots \sum_{N_{n-1}=0}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}E_1 \dots \int_{-\infty}^{\infty} \mathrm{d}E_{n-1} \prod_{l=1}^{n-1} \Omega_{N_l}^*(E_l, V_l^*) \cdot$$

$$\cdot \Sigma_{N_n}^*(E_n, V_n^*) \geqslant \sum_{N_1=0}^{\infty} \dots \sum_{N_{n-1}=0}^{\infty} \prod_{l=1}^{n} \Sigma_{N_l}^*(E_l, V_l^*),$$

$$(N_n \equiv N - \sum_{l=1}^{n-1} N_l, E_n \equiv E - \sum_{l=1}^{n-1} E_l, V_n^* \equiv V^* - \sum_{l=1}^{n-1} V_l^*), \tag{71}$$

which will be used here to prove the equivalence of the microcanonical and canonical formalisms. To this end we may introduce „specific values" defined per subsystem, as a halfway stage between the extensive quantities of the whole system and their specific values defined per particle. Denoting them by a bar over the symbol ($\bar{N} = N/n$, $\bar{E} = E/n$, $\bar{V} = V/n$, $\bar{S} = S/n$ and $\bar{F} = F/n$) we have *e.g.* (*cf.* (7)),

$$\bar{S}_{n,\bar{N}}^{(m)}(\bar{E}, \bar{V}) = \frac{1}{n} \log \Sigma_{n\bar{N}}(n\bar{E}, n\bar{V}). \tag{72}$$

It may be seen from the way (71) is derived, that these inequalities still hold if, for $\bar{N}$ integer, only the term with $N_1 = \dots = N_{n-1} = \bar{N}$ is retained in the summations. Choosing, furthermore, $V_1^* = \dots = V_{n-1}^* = \bar{V}^*$ and in the last member $E_1 = \dots = E_{n-1} = \bar{E}$, we find on taking logarithms and dividing by n,

$$\bar{S}_{n,\bar{N}}^*(\bar{E}, \bar{V}^*) \geqslant {}^{(n)}\bar{S}_{n,\bar{N}}^*(\bar{E}, \bar{V}^*) \geqslant S_{\bar{N}}^*(\bar{E}, \bar{V}^*)(\equiv \log \Sigma_{\bar{N}}^*(\bar{E}, \bar{V}^*)). \tag{73}$$

Here the function ${}^{(n)}\Sigma_N^*$ to which ${}^{(n)}\bar{S}_{n,\bar{N}}^*$ is related by means of (72), is given by

$${}^{(n)}\Sigma_N^*(E, V^*) = \int_{-\infty}^{\infty} \mathrm{d}E_1 \dots \int_{-\infty}^{\infty} \mathrm{d}E_{n-1} \prod_{l=1}^{n-1} \Omega_{\bar{N}}^*(E_l, \bar{V}^*)\, \Sigma_{\bar{N}}^*(E_n, \bar{V}^*),$$

$$(E_n \equiv E - \sum_{l=1}^{n-1} E_l). \tag{74}$$

The inequalities (73) may be interpreted in the following way: in the first step the interaction between the (identical) subsystems is neglected, but not the existence of an energy distribution among them, whereas in the second step the latter influence of this interaction is also omitted (i.e. the subsystems are isolated). After the first step, the set of subsystems constitutes an ideal system of n components. This kind of system has been studied asymptotically for n tending to infinity by Khinchin[1]) with the help of the central limit theorem of probability theory. Hence we will get to know the asymptotic properties of ${}^{(n)}\Sigma_N^*$ and ${}^{(n)}\bar{S}_{n,\bar{N}}^*$ for n tending to infinity at constant $\bar{N}$, $\bar{E}$ and $\bar{V}^*$, by adopting Khinchin's treatment.

With (47), the function (42) may also be written as

$$\Phi^*_N(\beta, V^*) = \int_{-\infty}^{\infty} \mathrm{d}E \, \mathrm{e}^{-\beta E} \Omega^*_N(E, V^*), \tag{75}$$

which shows that the (positive) function $\exp(-\beta E)\, \Omega^*_N / \Phi^*_N$ may be considered as the frequency function (or probability density) of a continuous random variable E, with parameters N, β and V^*. Differentiating (74) partially with respect to E,

$$^{(n)}\Omega^*_N(E, V^*) \equiv \frac{\partial\, ^{(n)}\Sigma^*_N(E, V)}{\partial E} = \int_{-\infty}^{\infty} \mathrm{d}E_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}E_{n-1} \prod_{l=1}^{n} \Omega^*_{\bar{N}}(E_l, \bar{V}^*),$$

$$\left(E_n \equiv E - \sum_{l=1}^{n-1} E_l\right), \tag{76}$$

we then see that $\exp(-\beta E)\, ^{(n)}\Omega^*_N / (\Phi^*_{\bar{N}})^n$ is the frequency function of the sum E of n identical (*i.e.* with the same $\bar{N}$, β and $\bar{V}^*$) independent random variables $E_1, \ldots E_n$. Now the central limit theorem states that such a frequency function becomes, for large n, Gaussian in the variable

$$\xi = \frac{1}{\sqrt{n}}\,(E - nE^*_{\bar{N}}), \quad \left(E^*_{\bar{N}}(\beta, \bar{V}^*) \equiv -\frac{\partial \log \Phi^*_{\bar{N}}(\beta, \bar{V}^*)}{\partial \beta}\right), \tag{77}$$

with variance $B^*_{\bar{N}}$, so that, as a first result, we obtain

$$\lim_{\substack{n\to\infty \\ N/n=\bar{N},\ V^*/n=\bar{V}^*}} \sqrt{n}\, \exp\{-\beta(\sqrt{n}\xi + nE^*_{\bar{N}})\} \cdot {}^{(n)}\Omega^*_N(\sqrt{n}\xi + nE^*_{\bar{N}}, V^*)/\{\Phi^*_{\bar{N}}(\beta, \bar{V}^*)\}^n =$$

$$= (2\pi B^*_{\bar{N}})^{-\frac{1}{2}} \exp(-\tfrac{1}{2}\xi^2/B^*_{\bar{N}}), \quad \left(B^*_{\bar{N}}(\beta, \bar{V}^*) \equiv \frac{\partial^2 \log \Phi^*_{\bar{N}}(\beta, \bar{V}^*)}{\partial \beta^2} > 0\right). \tag{78}$$

In fact Khinchin has proved a more detailed version of the central limit theorem, giving also the order of the remainder. With this, he derived a second result, relating the asymptotic behaviour of $^{(n)}\Sigma^*_N$ to that of $^{(n)}\Omega^*_N$,

$$\lim_{\substack{n\to\infty \\ N/n=\bar{N},\ V^*/n=\bar{V}^*}} \frac{^{(n)}\Sigma^*_N(nE^*_{\bar{N}}(\beta, \bar{V}^*), V^*)}{^{(n)}\Omega^*_N(nE^*_{\bar{N}}(\beta, \bar{V}^*), V^*)} = \frac{1}{\beta}. \tag{79}$$

The connection between (78) and (79) will become transparent from the following considerations (not intended as a proof). According to (74) and (76) (the latter equation with $n-1$ instead of n), we have

$$^{(n)}\Sigma^*_N(E, V^*) = \int_{-\infty}^{\infty} \mathrm{d}E_1\, ^{(n-1)}\Omega^*_{N-\bar{N}}(E - E_1, V^* - \bar{V}^*)\, \Sigma^*_{\bar{N}}(E_1, \bar{V}^*). \tag{80}$$

Under certain conditions the limit (78) will also exist for a sequence of values ξ_n converging to ξ as n tends to infinity, instead of for constant ξ. Applying this, in the case of $n-1$ instead of n in (78), for the values $\xi_{n-1} = (n-1)^{-\frac{1}{2}} \cdot \cdot (E^*_{\bar{N}} - E_1)$, converging to $\xi = 0$, we find

$$\lim_{\substack{n\to\infty \\ N/n=\bar{N},\ V^*/n=\bar{V}^*}} \frac{{}^{(n-1)}\Omega^*_{N-\bar{N}}(nE^*_{\bar{N}}(\beta, \bar{V}^*) - E_1, V^* - \bar{V}^*)}{{}^{(n)}\Omega^*_N(nE^*_{\bar{N}}(\beta, \bar{V}^*), V^*)} = \frac{\mathrm{e}^{-\beta E_1}}{\Phi^*_{\bar{N}}(\beta, \bar{V}^*)}, \quad (81)$$

where (78) has been used also in a straightforward way for $\xi = 0$. Then, multiplying both sides of this equation by $\Sigma^*_{\bar{N}}$ with $\bar{E} = E_1$, and integrating over E_1, it reduces to (79) if on the left-hand side the limit is interchanged with the integration and (80) is used, whereas on the right-hand side an integration by parts is performed and (48) and (75) are used.

The limit of ${}^{(n)}\bar{S}^*_{n,\bar{N}}$ for n tending to infinity, following now from (72) (for ${}^{(n)}\Sigma^*_N$ instead of Σ_N), (79) and (78), is

$$\lim_{n\to\infty} {}^{(n)}\bar{S}^*_{n,\bar{N}}(E^*_{\bar{N}}(\beta, \bar{V}^*), \bar{V}^*) = \lim_{\substack{n\to\infty \\ N/n=\bar{N},\ V^*/n=\bar{V}^*}} \frac{1}{n} \log {}^{(n)}\Omega^*_N(nE^*_{\bar{N}}(\beta, \bar{V}^*), V^*) =$$
$$= \log \Phi^*_{\bar{N}}(\beta, \bar{V}^*) + \beta E^*_{\bar{N}}(\beta, \bar{V}^*). \quad (82)$$

Substituting $\bar{E} = E^*_{\bar{N}}$ into (73), we find therefore, for n tending to infinity,

$$\bar{N}s^*\left(\frac{1}{\bar{N}} E^*_{\bar{N}}(\beta, \bar{V}^*),\ \frac{1}{\bar{N}} \bar{V}^*\right) \geqslant \log \Phi^*_{\bar{N}}(\beta, \bar{V}^*) +$$
$$+ \beta E^*_{\bar{N}}(\beta, \bar{V}^*) \geqslant S^*_{\bar{N}}(E^*_{\bar{N}}(\beta, \bar{V}^*), \bar{V}^*), \quad (83)$$

where in the left-hand member (58) and (59) have been applied for $N = n\bar{N}$, *etc.*

Introducing again the usual specific values, we may write (83) as

$$s^*(e^*_N(\beta, v^*), v^*) \geqslant f^*_N(\beta, v^*) + \beta e^*_N(\beta, v^*) \geqslant s^*_N(e^*_N(\beta, v^*), v^*), \quad (84)$$

with $\bar{N}$ changed formally into N (the original $N = n\bar{N}$ has disappeared). If we study now this result for N tending to infinity, the limit (82) for an infinite number of subsystems is succeeded by the thermodynamic limit of a subsystem. The limit of the function f^*_N being given by (53), we may conclude for the function e^*_N according to Griffiths[5]) (whose theorem was already quoted at the end of section 2) that, on the grounds of (25) (for Φ^*_N instead of Φ_N),

$$\lim_{N\to\infty} e^*_N(\beta, v^*) = -\lim_{N\to\infty} \frac{\partial f^*_N(\beta, v^*)}{\partial\beta} = -\frac{\partial f^*(\beta, v^*)}{\partial\beta} = e^*(\beta, v^*) \text{ for } \beta \neq \beta_t(v^*). \quad (85)$$

The discontinuity point(s) β_t of e^*, where the existence of this limit cannot be proved, are indeed the transition point(s) mentioned in the second section, because according to (57) we have

$$e^*(\beta, v) = -\frac{\partial f^{(\mathrm{c})}(\beta, v)}{\partial \beta} \equiv e^{(\mathrm{c})}(\beta, v). \tag{86}$$

Using (85), the left-hand member of (84) (with s^* continuous in e) and the right-hand member of this inequality (with the limit (59) uniform in e, due to the theorem of the appendix), appear to converge to the same limit function

$$s^*(e^*(\beta, v^*), v^*) = f^*(\beta, v^*) + \beta e^*(\beta, v^*) \text{ for } \beta \neq \beta_{\mathrm{t}}(v^*). \tag{87}$$

Hence, with (57), (67), (86) and (29), we have established the equivalence relation (28), as yet only for e outside the interval $e_{\mathrm{t},1} < e < e_{\mathrm{t},2}$.

Differentiating (28) partially with respect to e, we find that

$$\beta^{(\mathrm{m})}(e, v) = \alpha(e, v). \tag{88}$$

For all e in the interval $e_{\mathrm{t},1} \leqslant e \leqslant e_{\mathrm{t},2}$, the function α has (as the inverse function of $e^{(\mathrm{c})}$ at constant v), the value β_{t}. Since we have shown that $s^{(\mathrm{m})}$ is concave in e, the function $\beta^{(\mathrm{m})}$ is nonincreasing in that variable. Consequently the identity of $\beta^{(\mathrm{m})}$ and α, which (88) establishes for e not in the interval $e_{\mathrm{t},1} < e < e_{\mathrm{t},2}$, must also hold within. Then we obtain by means of integration the equivalence relation (28),

$$s^{(\mathrm{m})}(e, v) = \beta_{\mathrm{t}}(e - e_{\mathrm{t},1}) + s^{(\mathrm{m})}(e_{\mathrm{t},1}, v) = \\ = \beta_{\mathrm{t}} e + f^{(\mathrm{c})}(\beta_{\mathrm{t}}, v) \text{ for } e_{\mathrm{t},1} \leqslant e \leqslant e_{\mathrm{t},2}. \tag{89}$$

With this result the equivalence of the microcanonical and the canonical formalisms is completely proved.

Turning now to the case of the equivalence of the canonical and the grand canonical formalisms, we generalize (50) to

$$\Phi^*_N(\beta, V^*) \geqslant \sum_{N_1=0}^{\infty} \cdots \sum_{N_{n-1}=0}^{\infty} \prod_{l=1}^{n} \Phi^*_{N_l}(\beta, V^*_l),$$
$$\left(N_n \equiv N - \sum_{l=1}^{n-1} N_l,\ V^*_n \equiv V^* - \sum_{l=1}^{n-1} V^*_l\right). \tag{90}$$

The right-hand side of this inequality is of course again larger than one of its terms, so that, in analogy to (73), we now have

$$\overline{F}^*_{n,\bar{N}}(\beta, \overline{V}^*) \geqslant {}^{(n)}\overline{F}^*_{n,\bar{N}}(\beta, \overline{V}^*) \geqslant F^*_{\bar{N}}(\beta, \overline{V}^*)(\equiv \log \Phi^*_{\bar{N}}(\beta, \overline{V}^*)), \tag{91}$$

where ${}^{(n)}\overline{F}^*_{n,\bar{N}}$ is related to

$${}^{(n)}\Phi^*_N(\beta, V^*) = \sum_{N_1=0}^{\infty} \cdots \sum_{N_{n-1}=0}^{\infty} \prod_{l=1}^{n} \Phi^*_{N_l}(\beta, \overline{V}^*), \left(N_n \equiv N - \sum_{l=1}^{n-1} N_l\right), \tag{92}$$

in the usual way (*cf.* (72)). This function may again be evaluated asymptotically for n tending to infinity, with the help of the central limit theorem of probability theory. In this case, in view of (6), functions of the form $\exp(-\mu N)\,\Phi^*_N/\Xi^*_{V^*}$ are considered as the relative frequency of a discrete random variable N, with parameters β, μ and V^*. The only result we need here is that

$$\lim_{\substack{n\to\infty \\ V^*/n=\bar{V}^*}} \sqrt{n}\,\exp(-\mu n N^*_{\bar{V}^*})\,{}^{(n)}\Phi^*_{nN^*_{\bar{V}^*}}(\beta, V^*)/\{\Xi^*_{\bar{V}^*}(\beta,\mu)\}^n = (2\pi B^*_{\bar{V}^*})^{-\frac{1}{2}},$$

$$\left(N^*_{\bar{V}^*}(\beta,\mu) \equiv -\frac{\partial \log \Xi^*_{\bar{V}^*}(\beta,\mu)}{\partial\mu},\ B^*_{\bar{V}^*}(\beta,\mu) \equiv \frac{\partial^2 \log \Xi^*_{\bar{V}^*}(\beta,\mu)}{\partial\mu^2} > 0\right), \tag{93}$$

(corresponding to (78) for $\xi = 0$), for integer values of $N^*_{\bar{V}^*}$.

Now, to cope with the latter condition, we choose $\bar{V}^*$ equal to that value $V^*_{\bar{N}}$ for which $N^*_{\bar{V}^*} = \bar{N}$, or, if there are more of these values, to the largest of them. Then it follows from (93) that (*cf.* 82))

$$\lim_{n\to\infty} {}^{(n)}\bar{F}^*_{n,\bar{N}}(\beta, V^*_{\bar{N}}(\beta,\mu)) = \log \Xi^*_{V^*_{\bar{N}(\beta,\mu)}}(\beta,\mu) + \mu\bar{N}, \tag{94}$$

and furthermore, with (91), that (*cf.* (84), and note that we write again N instead of $\bar{N}$)

$$f^*(\beta, v^*_N(\beta,\mu)) \geqslant p^*_N(\beta,\mu)\,v^*_N(\beta,\mu) + \mu \geqslant f^*_N(\beta, v^*_N(\beta,\mu)), \tag{95}$$

where $v^*_N = V^*_N/N$ and

$$p^*_N(\beta,\mu) = \frac{1}{V^*_N(\beta,\mu)} \log \Xi^*_{V^*_{N(\beta,\mu)}}(\beta,\mu). \tag{96}$$

Since V^*_N tends with N to infinity, the sequence of functions (96) converges to the limit function (70), already established for V^* tending to infinity continuously. In the same way the application (23) of Griffiths' theorem to this case, implies that

$$\lim_{N\to\infty} v^*_N(\beta,\mu) = -1\bigg/\frac{\partial p^{(g)}(\beta,\mu)}{\partial\mu} \equiv v^{(g)}(\beta,\mu) \text{ for } \mu \neq \mu_t(\beta). \tag{97}$$

Using also the limit (53) and its uniformity in v^*, we now obtain from (95) the result

$$f^{(c)}(\beta, v^{(g)}(\beta,\mu)) = p^{(g)}(\beta,\mu)\,v^{(g)}(\beta,\mu) + \mu \text{ for } \mu \neq \mu_t(\beta), \tag{98}$$

or with (31), the equivalence relation (30) for v not in the interval $v_{t,1} < v < v_{t,2}$.

This proof of the equivalence of the canonical and the grand canonical formalisms may be completed in analogy to (88)–(89). Differentiating (30) partially with respect to v, we find that

$$p^{(c)}(\beta, v) = p^{(g)}(\beta, \lambda(\beta, v)). \tag{99}$$

Since the function $p^{(c)}$ is nondecreasing in v, and the function λ has the value

μ_t for all v in the interval $v_{t,1} \leqslant v \leqslant v_{t,2}$, the relation (99) must hold as well for these values of v. Consequently (30) also follows,

$$f^{(c)}(\beta, v) = p^{(g)}(\beta, \mu_t)(v - v_{t,1}) + f^{(c)}(\beta, v_{t,1}) =$$
$$= p^{(g)}(\beta, \mu_t)\, v + \mu_t \quad \text{for} \quad v_{t,1} \leqslant v \leqslant v_{t,2}. \tag{100}$$

The equivalence relation (30) may also be established by means of a maximum term evaluation [6, 10], but the advantage of our approach is its overall applicability and simplicity.

It will be clear that the two equivalences established above already imply the equivalence of the microcanonical and grand canonical formalisms. The latter could, however, also have been established directly from the inequality (71), with the help of the so-called two-dimensional central limit theorem[3]. Note that then we need, in addition to the limit (23), the application of Griffiths' theorem to (70) on the grounds of (26), resulting together in (24), (all this for v_N^* instead of $v_V^{(g)}$ *etc.*).

In the next section we will again pay attention to convergence problems within each formalism, for the solution of which, the knowledge of the equivalence of the various formalisms studied above, is of advantage.

§ 5. *Remaining questions.* We first consider the problem of proving (11), where $\beta_N^{(m)}$ is given by (8) and $s^{(m)}$ by (10). As we have shown in section 3 that $s^{(m)}$ is concave, or $\beta^{(m)}$ nonincreasing in e, one could think of an application of Griffiths' theorem, this time to the sequence of functions $-s_N^{(m)}$. It cannot be decided, however, that these functions are convex in e. Using (33) we find

$$\frac{\partial^2 \log \Sigma_N(E, V)}{\partial E^2} = \frac{3N}{2}\left(\frac{3N}{2} - 1\right)\left[\frac{1}{\Sigma_N(E, V)} \int \mathrm{d}\boldsymbol{r}^N \left(\frac{1}{E - \mathscr{U}_N(\boldsymbol{r}^N)}\right)^2 \cdot\right.$$
$$\cdot \frac{\{E - \mathscr{U}_N(\boldsymbol{r}^N)\}^{3N/2}}{\Gamma\left(\dfrac{3N}{2} + 1\right)} \sigma\{E - \mathscr{U}_N(\boldsymbol{r}^N)\} +$$
$$\left. - \left(\frac{1}{\Sigma_N(E, V)} \int \mathrm{d}\boldsymbol{r}^N \frac{1}{E - \mathscr{U}_N(\boldsymbol{r}^N)} \frac{\{E - \mathscr{U}_N(\boldsymbol{r}^N)\}^{3N/2}}{\Gamma\left(\dfrac{3N}{2} + 1\right)} \sigma\{E - \mathscr{U}_N(\boldsymbol{r}^N)\}\right)^2\right] +$$
$$- \frac{2}{3N}\left(\frac{\partial \log \Sigma_N(E, V)}{\partial E}\right)^2, \tag{101}$$

and there is no reason why the first term on the right-hand side of this equation (with, between square brackets, a positive quantity of the type (25)–(27)) should be smaller than the absolute value of the last term. But (101) also shows that, in order to apply Griffiths' theorem, there is another possibility. Since this equation implies that

$$\frac{\partial^2 s_N^{(m)}(e, v)}{\partial e^2} > -\tfrac{2}{3}(\beta_N^{(m)}(e, v))^2, \tag{102}$$

the function $s_N^{(m)} + \frac{1}{2}Ce^2$ (C a positive constant) is convex in e, if $\frac{2}{3}(\beta_N^{(m)})^2 < C$. Hence we may state as sufficient conditions for the sequence of functions $\beta_N^{(m)}$ to converge to $\beta^{(m)}$, that this sequence must be bounded from above, and $\beta^{(m)}$ has to be continuous in e.

This continuity can be proved for all $e^{(0)} < e < \infty$, using the equivalence expression (88). According to (13), (19) and (34) we have

$$\lim_{N\to\infty} \frac{1}{N} \log Q_N(\beta, Nv) = f^{(c)}(\beta, v) - \log\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}, \tag{103}$$

where

$$Q_N(\beta, V) = \frac{1}{N!}\int \mathrm{d}\boldsymbol{r}^N \exp\{-\beta\mathscr{U}_N(\boldsymbol{r}^N)\}. \tag{104}$$

It follows from this definition of the so-called configurational integral Q_N that its second partial logarithmic derivative with respect to β is positive, so that $\log Q_N$ is convex in this variable. The limit function (103) therefore also has this property, whence

$$\frac{\partial^2 f^{(c)}(\beta, v)}{\partial\beta^2} \geqslant \frac{3}{2\beta^2} > 0, \tag{105}$$

(infinite for $\beta = \beta_t$). The impossibility that $\partial e^{(c)}/\partial\beta = -\partial^2 f^{(c)}/\partial\beta^2 = 0$ means that the inverse function α of $e^{(c)}$ (at constant v) is continuous in e, and according to (88), this is therefore also the case with $\beta^{(m)}$.

The existence of an upper bound to the sequence of functions $\beta_N^{(m)}$, we have been able to prove only in a rather indirect way. Let us introduce the function

$$\Lambda_N(\kappa, E, V) = \frac{1}{N!}\iint \mathrm{d}\boldsymbol{r}^N\, \mathrm{d}\boldsymbol{p}^N \sigma\{E - \mathscr{H}_N(\boldsymbol{r}^N, \boldsymbol{p}^N)\} \exp\left\{-\kappa\frac{(\boldsymbol{p}^N)^2}{2m}\right\},$$

$$(\Lambda_0(\kappa, E, V) \equiv \sigma(E)), \quad -\infty < \kappa < \infty. \tag{106}$$

For $\kappa = 0$ this function reduces to Σ_N, and for $\kappa \neq 0$ it still has the properties we have already established for Σ_N. To begin with, Λ_N satisfies an equivalent of the inequality (35). Furthermore, introducing Λ_N^* in the usual way, (46) and (49) hold for Λ_N^* and $\partial\Lambda_N^*/\partial E$ instead of Σ_N^* and Ω_N^* respectively, since the exponential in (106) factorizes. Consequently the existence of a finite limit

$$l(\kappa, e, v) \equiv \lim_{N\to\infty} l_N(\kappa, e, v), \text{ with } l_N(\kappa, e, v) = \frac{1}{N}\log\Lambda_N(\kappa, \mathrm{Ne}, \mathrm{Nv}), \tag{107}$$

can be established for $e > e^{(0)}$, by means of another application of the limit theorem for subadditive functions leading to (*cf.* (59) and (67)),

$$\lim_{N\to\infty} l_N^*(\kappa, e, v^*) = \sup_{N\to\infty} l_N^*(\kappa, e, v^*) = l(\kappa, e, v^*). \tag{108}$$

Moreover, we may employ the relation (75) to define a generalization of Φ_N, and with (106) and (104) we find that it is a trivial one,

$$\begin{aligned}\Psi_N(\kappa, \beta, V) &\equiv \int_{-\infty}^{\infty} \mathrm{d}E\, \mathrm{e}^{-\beta E} \frac{\partial \Lambda_N(\kappa, E, V)}{\partial E} = \\ &= \frac{1}{N!} \iint \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \exp\left\{-\beta \mathscr{H}_N(\boldsymbol{r}^N, \boldsymbol{p}^N) - \kappa \frac{(\boldsymbol{p}^N)^2}{2m}\right\} = \\ &= \left(\frac{2\pi m}{\beta+\kappa}\right)^{3N/2} Q_N(\beta, V) = \left(\frac{\beta}{\beta+\kappa}\right)^{3N/2} \Phi_N(\beta, V),\end{aligned} \tag{109}$$

assuming $\kappa > -\beta$. Hence we have at once, using (13) and (19),

$$g(\kappa, \beta, v) \equiv \lim_{N\to\infty} g_N(\kappa, \beta, v) = f^{(c)}(\beta, v) + \log\left(\frac{\beta}{\beta+\kappa}\right)^{\frac{3}{2}},$$

$$\text{where } g_N(\kappa, \beta, v) = \frac{1}{N} \log \Psi_N(\kappa, \beta, Nv). \tag{110}$$

Note that this equation implies that $\partial g/\partial\beta$ is continuous in β except for β_t.

Now the relation (75) is the basis for the derivation of the equivalence of the microcanonical and canonical formalisms given in section 4. In a completely analogous way we obtain here (*cf.* (87) and (86))

$$l\left(\kappa, -\frac{\partial g}{\partial\beta}, v\right) = g(\kappa, \beta, v) - \beta \frac{\partial g}{\partial\beta}, \left(-\frac{\partial g(\kappa, \beta, v)}{\partial\beta} \equiv e^{(c)}(\beta, v) + \right.$$

$$\left. - \frac{3}{2} \frac{\kappa}{\beta(\beta+\kappa)}\right) \text{ for } \beta \neq \beta_t(v), \tag{111}$$

or, with γ the inverse function of $-\partial g/\partial\beta$ at constant κ and v (*cf.* (28) and (89)),

$$l(\kappa, e, v) = g(\kappa, \gamma(\kappa, e, v), v) + \gamma(\kappa, e, v)\, e \tag{112}$$

for all $e > e^{(0)}$. The function γ satisfies (*cf.* (29))

$$e^{(c)}(\gamma(\kappa, e, v), v) - \frac{3}{2} \frac{\kappa}{\gamma(\kappa, e, v)\{\gamma(\kappa, e, v) + \kappa\}} = e, \tag{113}$$

or, according to (29),

$$\gamma(\kappa, e, v) = \alpha\left(e + \frac{3}{2} \frac{\kappa}{\gamma(\kappa, e, v)\{\gamma(\kappa, e, v) + \kappa\}}, v\right). \tag{114}$$

Furthermore one may verify that $\gamma \geqslant \beta$ for $e \leqslant e^{(c)} - \frac{3}{2}$ and $-\beta < \kappa \leqslant \beta^2$.

As far as the dependence of the function (106) on E is concerned, it behaves in a „microcanonical" way. For $\kappa = 0$ the new functions l, g and γ reduce to the old ones $s^{(m)}$, $f^{(c)}$ and α, respectively. Obviously the dependence of (106) on κ has a "canonical" character, *e.g.* expressed by the inequality

$$\frac{\partial^2 \log \Lambda_N(\kappa, E, V)}{\partial \kappa^2} > 0, \tag{115}$$

which makes possible the application of Griffiths' theorem to the case of the limit (107), giving

$$\lim_{N\to\infty} \frac{\partial l_N(\kappa, e, v)}{\partial \kappa} = \frac{\partial l(\kappa, e, v)}{\partial \kappa} \tag{116}$$

if $\partial l/\partial \kappa$ is continuous in κ. Since it follows from (112) with (110) and (113), that

$$\frac{\partial l(\kappa, e, v)}{\partial \kappa} = -\frac{3}{2}\,\frac{1}{\gamma(\kappa, e, v) + \kappa}, \tag{117}$$

this function is continuous if γ is continuous. We see from (114) that $\lim_{\kappa\to 0} \gamma = \alpha$, thanks to the continuity of α in e (following from (105)), so that the condition on (116) is certainly satisfied for $\kappa = 0$.

It is precisely for the derivation of the limit (116) for $\kappa = 0$ (actually with, instead of e, a sequence of values $e_{(N)}$ converging to e, but that is a refinement) that we have introduced the above generalization. We will now first put this result into a more convenient form, and then use it for the final proof that the sequence of functions $\beta_N^{(m)}$ is bounded from above. The function $\partial l_N/\partial \kappa$ for $\kappa = 0$ is most easily evaluated by writing (106) in the form

$$\Lambda_N(\kappa, E, V) =$$

$$= \int_{-\infty}^{E} \mathrm{d}E' \,\frac{1}{N!} \iint \mathrm{d}\boldsymbol{r}^N \,\mathrm{d}\boldsymbol{p}^N \delta\{E' - \mathscr{H}_N(\boldsymbol{r}^N, \boldsymbol{p}^N)\} \exp[-\kappa\{E' - \mathscr{U}_N(\boldsymbol{r}^N)\}] =$$

$$= \int_{-\infty}^{E} \mathrm{d}E' \,\frac{1}{N!} \int \mathrm{d}\boldsymbol{r}^N \exp[-\kappa\{E' - \mathscr{U}_N(\boldsymbol{r}^N)\}] \,\frac{\mathrm{d}}{\mathrm{d}E'} \int \mathrm{d}\boldsymbol{p}^N \sigma\{E' - \mathscr{H}_N(\boldsymbol{r}^N, \boldsymbol{p}^N)\} =$$

$$= \int_{-\infty}^{E} \mathrm{d}E' \,\frac{(2\pi m)^{3N/2}}{N!} \int \mathrm{d}\boldsymbol{r}^N \exp[-\kappa\{E' - \mathscr{U}_N(\boldsymbol{r}^N)\}] \cdot$$

$$\cdot \frac{\{E' - \mathscr{U}_N(\boldsymbol{r}^N)\}^{3N/2-1}}{\Gamma\left(\frac{3N}{2}\right)} \,\sigma\{E' - \mathscr{U}_N(\boldsymbol{r}^N)\}, \tag{118}$$

using the fact that the derivative of σ is the δ-function, and integrating over the momenta just as in (33). Thus we find that $-(1/\frac{3}{2}N)\,\partial\Lambda_N/\partial\kappa$ for $\kappa = 0$ is equal to the function

$$\Theta_N(E, V) \equiv \frac{(2\pi m)^{3N/2}}{N!} \int \mathrm{d}\boldsymbol{r}^N \frac{\{E - \mathscr{U}_N(\boldsymbol{r}^N)\}^{3N/2+1}}{\Gamma\left(\dfrac{3N}{2} + 2\right)} \sigma\{E - \mathscr{U}_N(\boldsymbol{r}^N)\}, \quad (119)$$

and therefore the limit (116) for $\kappa = 0$ becomes

$$\lim_{N\to\infty} \frac{\Theta_N(Ne, Nv)}{\Sigma_N(Ne, Nv)} = \frac{1}{\alpha(e, v)}, \quad (120)$$

(Λ_N reducing to Σ_N and γ to α). Noting that, according to (33) and (119), $\Sigma_N = \partial\Theta_N/\partial E$, and that $\alpha = \beta^{(\mathrm{m})}$, we may write this result also in the form

$$\lim_{N\to\infty} \frac{\partial t_N(e, v)}{\partial e} = \beta^{(\mathrm{m})}(e, v), \text{ with } t_N(e, v) = \frac{1}{N} \log \Theta_N(Ne, Nv). \quad (121)$$

As $\Omega_N = \partial\Sigma_N/\partial E = \partial^2\Theta_N/\partial E^2$, and (for $N \geqslant 1$) Θ_N, Σ_N and $\partial^3\Theta_N/\partial E^3$ are positive functions, we have

$$\Theta_N(E + \delta, V) > \tfrac{1}{2}\delta^2\Omega_N(E, V), \text{ or}$$

$$\beta_N^{(\mathrm{m})}(e, v) = \frac{\Omega_N(Ne, Nv)}{\Sigma_N(Ne, Nv)} < \frac{2}{\delta^2} \frac{\Theta_N(Ne + \delta, Nv)}{\Sigma_N(Ne, Nv)}, \quad (122)$$

where δ is an arbitrary positive constant. Now we may write

$$\Theta_N(\mathrm{Ne} + \delta, Nv) \equiv \exp Nt_N\left(e + \frac{\delta}{N}, v\right) = \exp\Bigl\{Nt_N(e, v) +$$

$$+ \delta\tau_N\left(e + \vartheta_N \frac{\delta}{N}, v\right)\Bigr\} \equiv \Theta_N(Ne, Nv) \exp \delta\tau_N\left(e + \vartheta_N \frac{\delta}{N}, v\right), \quad (123)$$

where $\tau_N \equiv \partial t_N/\partial e$ and $0 < \vartheta_N < 1$. Now the values $e_{(N)} = e + \vartheta_N\delta/N$ ($N = 1, 2, 3, \ldots$) constitute a sequence converging to e, and we therefore have for the function l_N that

$$\lim_{N\to\infty} l_N(\kappa, e_{(N)}, v) = l(\kappa, e, v), \quad (124)$$

because the limit (108) is uniform in e (again using the theorem of the appendix). The argument leading to (120) or (121) may therefore be repeated on the basis of (124) giving

$$\lim_{N\to\infty} \tau_N(e_{(N)}, v) = \beta^{(\mathrm{m})}(e, v), \quad (125)$$

whence, for N large enough,

$$\tau_N(e_{(N)}, v) < 2\beta^{(m)}(e, v). \tag{126}$$

Since, moreover, according to (119), (32) and (33),

$$\frac{\Theta_N(Ne, Nv)}{\Sigma_N(Ne, Nv)} \leqslant \frac{2}{3}(e + u_0), \tag{127}$$

we conclude from (122), (123) and (126) that, for N large enough,

$$\beta_N^{(m)}(e, v) < \frac{4}{3}\,\frac{e + u_0}{\delta^2}\exp\{2\delta\beta^{(m)}(e, v)\}. \tag{128}$$

As $\beta^{(m)}$ is nonincreasing in e, the right-hand side of this inequality can be bounded in any interval for $e^{(0)} < e < \infty$, and we have reached our goal.

The function Ω_N is frequently used instead of Σ_N to determine thermodynamic analogies for the microcanonical formalism, and indeed it is a consequence of (10) and (11) (established just now) that

$$\lim_{N\to\infty} o_N(e, v) = s^{(m)}(e, v) \quad \text{with} \quad o_N(e, v) = \frac{1}{N}\log \Omega_N(Ne, Nv). \tag{129}$$

Then again it must be asked whether $\partial o_N/\partial e$ and $\partial o_N/\partial v$ converge to $\beta^{(m)}$ and $p^{(m)}$, respectively. In the first case an affirmative answer can be given at once for reasons similar to those above. Corresponding to (102), we have

$$\frac{\partial^2 o_N(e, v)}{\partial e^2} > -2\left(\frac{\partial o_N(e, v)}{\partial e}\right)^2, \tag{130}$$

and (for $N \geqslant 2$) to (122),

$$\frac{\partial o_N(e, v)}{\partial e} < \frac{3}{\delta^3}\,\frac{\Theta_N(Ne + \delta, Nv)}{\Omega_N(Ne, Nv)}, \tag{131}$$

so that the result (126) (with the analogue of (127) for Θ_N/Ω_N) is conclusive here too. Note that also Θ_N could play the role of Σ_N: according to (10) and (120), t_N (defined in (121)) converges to $s^{(m)}$, whereas in (121) we have already the property corresponding to (11).

It is quite probable that the problems (12) and (21) are consequences of (10) and (19), respectively, and Griffiths' theorem. More in particular, the latter should then be applied in the same way as in the case of (11), *i.e.* on the basis of the properties: the sequences of functions $\partial^2 s_N^{(m)}/\partial v^2$ (or $\partial^2 o_N/\partial v^2$) and $\partial^2 f_N^{(c)}/\partial v^2$ are bounded from below, and the functions $p^{(m)}$ and $p^{(c)}$ are continuous in v. Our attempts to prove these statements have as yet not yielded any result. It should be noted that the proofs can perhaps only be obtained on the basis of somewhat more specific properties of the interaction than (32) and (38)*).

§ 6. *Discussion.* It will have become clear that the asymptotic problem of statistical thermodynamics may be indicated schematically as follows: we have the statistical relation

$$
\begin{aligned}
\exp \nu\varphi_\nu^{(1)}(x_1) &= \int \mathrm{e}^{-\nu x_1 x_2}\, \mathrm{d} \exp \nu\varphi_\nu^{(2)}(x_2),\\
\text{or} \qquad &= \sum_{x_2} \mathrm{e}^{-\nu x_1 x_2} \exp \nu\varphi_\nu^{(2)}(x_2),
\end{aligned}
\tag{132}
$$

and we want to derive from it, on the basis of certain assumptions about the system, the conjugate relations

$$
\varphi^{(1)}(x_1) = x_1 \frac{\mathrm{d}\varphi^{(1)}}{\mathrm{d}x_1} + \varphi^{(2)}\left(-\frac{\mathrm{d}\varphi^{(1)}}{\mathrm{d}x_1}\right)
$$

$$
\text{and} \quad \varphi^{(2)}(x_2) = \frac{\mathrm{d}\varphi^{(2)}}{\mathrm{d}x_2} x_2 + \varphi^{(1)}\left(\frac{\mathrm{d}\varphi^{(2)}}{\mathrm{d}x_2}\right), \tag{133}
$$

with

$$\varphi^{(1)}(x_1) = \lim_{\nu\to\infty} \varphi_\nu^{(1)}(x_1), \tag{134}$$

$$\varphi^{(2)}(x_2) = \lim_{\nu\to\infty} \varphi_\nu^{(2)}(x_2), \tag{135}$$

$$\frac{\mathrm{d}\varphi^{(1)}}{\mathrm{d}x_1} = \lim_{\nu\to\infty} \frac{\mathrm{d}\varphi_\nu^{(1)}}{\mathrm{d}x_1}, \tag{136}$$

$$\frac{\mathrm{d}\varphi^{(2)}}{\mathrm{d}x_2} = \lim_{\nu\to\infty} \frac{\mathrm{d}\varphi_\nu^{(2)}}{\mathrm{d}x_2}. \tag{137}$$

In the various cases the pair of functions $\varphi_\nu^{(1)}$ and $\varphi_\nu^{(2)}$ represents: (I) $f_N^{(c)}$ and $s_N^{(m)}$ (at constant v), (II) $p_V^{(g)}$ and $f_{V/v}^{(c)}/v$ (at constant β; note that here $x_2 = v^{-1}$), and (III) $p_V^{(g)}$ and $s_{V/v}^{(m)}/v$ (if the problem is conceived as "two-dimensional"). The treatment of the asymptotic problem developed in this

*) For instance we have made attempts with a replacement of (32) by

$$\sum_{j=2}^{N} u(|r_1 - r_j|) \geqslant -u_0,$$

for all N, but again without useful results. It may be remarked that, on the other hand, (38) is too strong for at least some of the proofs of this paper. The existence of the canonical free energy in the thermodynamic limit can be shown [10]) by taking instead

$$u(|r_1 - r_2|) \leqslant D/|r_1 - r_2|^{3+\varepsilon} \ (D \text{ and } \varepsilon > 0) \text{ for } |r_1 - r_2| \geqslant r_0,$$

(weak tempering). We have not tried, however, to base our investigation throughout on this assumption, because a potential, positive at arbitrarily large distances, seems to us to be a matter of only academic interest.

paper will now be discussed in connection with previous work, stressing the methodological aspects.

Khinchin[1]) considered case I and proved for a system without interaction, by means of the central limit theorem, (133) with $\varphi^{(1)} \equiv \varphi_\nu^{(1)}$, and (135) simultaneously. Then a subsequent asymptotic evaluation led to (137). This approach is also applicable to the other cases.

Yamamoto and Matsuda[3]) (hard core-finite range interaction, case III) constructed a "π-system" of n cells to which Khinchin's method may be applied for n tending to infinity. Their aim was to show subsequently that this π-system and the real system have common thermodynamic limit properties, but their treatment of this part cannot be considered to be satisfactory.

Mazur and the present author[4]) (hard core-finite range interaction, case I) started from (134), not bothering about its derivation. Then it was shown that, outside phase transition points of any order,

$$\frac{\mathrm{d}^p\varphi^{(1)}}{\mathrm{d}x_1^p} = \lim_{\nu\to\infty} \frac{\mathrm{d}^p\varphi_\nu^{(1)}}{\mathrm{d}x_1^p} \quad \text{for all } p \geqslant 1. \tag{138}$$

Using this result, (133) and (135) were established simultaneously by applying more general limit theorems of probability theory than the central limit theorem. The drawback of this approach is that an as yet unknown aspect of the phase transition problem is involved: since the method breaks down for an x_1-interval consisting merely of phase transition points of *arbitrary* orders, one should like to have the existence of such intervals excluded. Moreover, the use of the property (105) prevents transposition into the other cases.

The method of the present paper (stable and strongly tempered interaction, case I, II and in principle also III) has again some relation to that of Yamamoto and Matsuda. The difference in the construction of a "π-system" is that ours does not contain the intercellular interaction, even as an "external force". Note that, according to our treatment, (135) is first derived on the same footing as (134), and then used for the proof of (133). As, moreover, we needed (138) only for $p = 1$ (*i.e.* (136)), the phase transition points to be dealt with were those of first order, for which it is known that they form a countable set.

APPENDIX

Consider a sequence of numbers $\varphi_N (N \to \infty)$, which satisfy the inequality

$$N\varphi_N \geqslant N_1\varphi_{N_1} + (N - N_1)\,\varphi_{N-N_1} \quad \text{if} \quad N \geqslant N_1, \tag{A 1}$$

and are finite for $N \geqslant N_0$. For any two integers p and q, (A 1) implies (by iteration) that $\varphi_{pq} \geqslant \varphi_q$. Suppose that $(p + 1)\ q \leqslant N \leqslant (p + 2)\,q$ (or

$q \leqslant N - pq \leqslant 2q - 1$) and $q \geqslant N_0$. Then, applying (A 1) once more with $N_1 = pq$, we find that

$$\varphi_N \geqslant \frac{pq}{N}\varphi_q + \frac{N-pq}{N}\varphi_{N-pq} \geqslant$$

$$\geqslant \varphi_q - \frac{N-pq}{N}(\varphi_q - \varphi_{q_1}), \qquad \text{(A 2)}$$

where q_1 is an integer such that φ_{q_1} is the smallest of the $q - 1$ numbers $\varphi_q, \ldots, \varphi_{2q-1}$. With $N - pq < 2q$, we therefore deduce the inequality

$$\varphi_N \geqslant \varphi_q - \frac{2q}{N}(\varphi_q - \varphi_{q_1}) \quad \text{if} \quad N \geqslant q, \qquad \text{(A 3)}$$

as a corollary of (A 1). The content of the limit theorem for subadditive functions[9]) (in the case of a discrete variable), is that a sequence of numbers φ_N satisfying (A 3), (rather than (A 1)), possesses a finite limit if it is bounded from above. This limit is equal to the least upper bound of the sequence,

$$\lim_{N\to\infty} \varphi_N = \sup_{N\to\infty} \varphi_N \equiv \varphi. \qquad \text{(A 4)}$$

Now let φ_N be a function of $x (x_1 \leqslant x \leqslant x_2)$, for which the above holds at constant x (q_1 and φ becoming also functions of x, the first one integer-valued). Then we shall prove the following theorem: if φ_N is a continuously increasing function of x for each N, and φ is continuous in x, it follows that the convergence of the sequence of functions φ_N to φ is uniform in x.

Proof: With $\varphi_q(x) \leqslant \varphi_q(x_2) (\leqslant \varphi(x_2)$ according to (A 4)) and $\varphi_{q_1(x)}(x) \geqslant \geqslant \varphi_{q_1(x)}(x_1)$, (A 3) becomes

$$\varphi_N(x) \geqslant \varphi_q(x) - \frac{2q}{N}\{\varphi(x_2) - \varphi_{q_1(x)}(x_1)\} \text{ if } N \geqslant q. \qquad \text{(A 5)}$$

According to (A 4) it is possible to find for every $\varepsilon > 0$ and x, a value $N(\varepsilon, x)$ of N such that

$$0 \leqslant \varphi(x) - \varphi_{N(\varepsilon,x)}(x) \leqslant \tfrac{1}{4}\varepsilon \qquad \text{(A 6)}$$

and, moreover,

$$0 \leqslant \varphi(x_1) - \varphi_N(x_1) \leqslant \varepsilon \quad \text{for} \quad N \geqslant N(\varepsilon, x). \qquad \text{(A 7)}$$

Furthermore, due to the continuity of both φ_N and φ, there exists a neighbourhood $|x' - x| \leqslant \delta(\varepsilon, x)$ of x, where

$$|\varphi_{N(\varepsilon,x)}(x') - \varphi_{N(\varepsilon,x)}(x)| \leqslant \tfrac{1}{4}\varepsilon \qquad \text{(A 8)}$$

and

$$|\varphi(x') - \varphi(x)| \leqslant \tfrac{1}{4}\varepsilon. \qquad \text{(A 9)}$$

Using (A 6), (A 8) and (A 9), we see that, for $|x' - x| \leqslant \delta(\varepsilon, x)$,

$$0 \leqslant \varphi(x') - \varphi_{N(\varepsilon, x)}(x') \leqslant \tfrac{3}{4}\varepsilon, \tag{A 10}$$

and furthermore, using also (A 5) with x' instead of x and q equal to $N(\varepsilon, x)$, that

$$0 \leqslant \varphi(x') - \varphi_N(x') \leqslant \tfrac{3}{4}\varepsilon + \frac{2N(\varepsilon, x)}{N} \{\varphi(x_2) - \varphi(x_1) + \varepsilon\}$$
$$\text{if} \quad N \geqslant N(\varepsilon, x). \tag{A 11}$$

Here we have, moreover, applied (A 7), which is possible because $q_1(x') \geqslant q = N(\varepsilon, x)$. From (A 11) it follows that

$$|\varphi(x') - \varphi_N(x')| \leqslant \varepsilon \text{ for } |x' - x| \leqslant \delta(\varepsilon, x) \text{ and } N \geqslant N'(\varepsilon, x), \tag{A 12}$$

where N' is given by $2N(\varepsilon, x)\{\varphi(x_2) - \varphi(x_1) + \varepsilon\}/\frac{1}{4}\varepsilon$. According to the Heine-Borel theorem, it is possible to determine a finite number of points $x_i(x_1 < x_i < x_2,\ 3 \leqslant i \leqslant n)$ such that their neighbourhoods $|x' - x_i| \leqslant \delta(\varepsilon, x_i)$ cover the interval $x_1 \leqslant x \leqslant x_2$. With $N(\varepsilon)$ the largest of the integers $N'(\varepsilon, x_3), \ldots, N'(\varepsilon, x_n)$, we have therefore

$$|\varphi(x) - \varphi_N(x)| \leqslant \varepsilon \quad \text{for} \quad x_1 \leqslant x \leqslant x_2 \quad \text{and} \quad N \geqslant N(\varepsilon), \tag{A 13}$$

i.e. $\varphi_N(x)$ tends to $\varphi(x)$ uniformly in the given interval.

It may be remarked that the numbers of an increasing sequence satisfy (A 3) in a trivial way ($\varphi_{q_1} = \varphi_q$ gives $\varphi_N \geqslant \varphi_q$ if $N \geqslant q$). Consequently the statements of this appendix also apply in this special case: (A 4) is then very well-known, and also the theorem about uniformity may be found in some mathematical textbooks[11]), (the condition that φ_N must be increasing in x being superfluous). In fact the above proof is an extension of that given in the case of an increasing sequence of functions.

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Chapter II

SURVEY OF RELATED TOPICS

§ 1. *The Legendre transformation in thermodynamics*[1]). As a consequence of the two basic laws of thermodynamics, there exists for a single-component equilibrium system with mole number M, characterized by the volume V as the only external parameter, a fundamental relation

$$dE = T\,dS - p\,dV + \mu\,dM. \tag{1}$$

This equation expresses the fact that the change of the internal energy E is entirely built up by the changes $T\,dS$ in the thermal energy, $-p\,dV$ in mechanical energy, and $\mu\,dM$ in the "chemical" energy. Here the absolute temperature T and the pressure p are, like V and M, positive quantities, while the entropy S and the chemical potential μ may attain, like E, all real values. Mathematically (1) says that E may be written as a function of S, V and M (the characteristic function), with the remaining thermodynamic functions as its first order partial derivatives. Due to the fact that E, S, V and M are all extensive quantities, this characteristic function has the property

$$E(S, V, M) = Me(s, v), \tag{2}$$

where we have adopted the usual notation for specific values per mole (*i.e.* extensive quantities divided by M): the same letter in small type. With (2) we obtain from (1) the relations

$$de = T\,ds - p\,dv \tag{3}$$

and

$$\mu = e - Ts + pv, \tag{4}$$

which show that the intensive quantities T, p and μ are functions of s and v.

If the system is in stable equilibrium, it satisfies the two stability criteria

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,M} = \left(\frac{\partial T}{\partial S}\right)_{V,M} > 0 \tag{5}$$

and

$$-\left(\frac{\partial p}{\partial V}\right)_{T,M} > 0. \tag{6}$$

The first one states that, at constant V and M, T is an increasing function of S. Since this function is also continuous ($\partial T/\partial S$ is equal to T/C_V, and it is well-known that the heat capacity C_V never vanishes), there exists a one-to-one correspondence between values of T and S, and therefore the set T, V and M describes the thermodynamic state just as well as the set S, V and M. In fact, in (6) the independent variables are T, V, M. Furthermore, since p is a continuous function of V at constant T and $M(-\partial p/\partial V$ is equal to $1/V\kappa_T$, with κ_T the nonvanishing compressibility), we see from (6) that T, P and M is yet another equivalent set of variables.

Now a change of independent variables must be accompanied by a change of characteristic function, and the appropriate way to do this is by means of a Legendre transformation. The Legendre transform F of E with respect to S,

$$F = E - TS, \tag{7}$$

is the Helmholtz free energy. From (1) and (7) we derive as the new fundamental relation

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}M, \tag{8}$$

so that indeed F may be written as a function of T, V and M, which is the new characteristic function. Note that the function S determined by (8) is the inverse (at constant V and M) of the function T determined by (1), and therefore increasing, even if the system is not in stable equilibrium, but in phase transition (of the first order, according to the classification of Ehrenfest[2]) where

$$\left(\frac{\partial T}{\partial S}\right)_{V,M} = 0, \tag{9}$$

(or C_V infinite). In both cases we have

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,M} = -\left(\frac{\partial S}{\partial T}\right)_{V,M} < 0. \tag{10}$$

A phase transition at a certain value of T, is characterized by a jump discontinuity of the function S (at constant V and M), so that in this case a whole range of S-values corresponds to one value of T.

Corresponding to the change from the set T, V, M to the set T, p, M, the Gibbs free energy is introduced as the Legendre transform of F with respect to V, and is found to be equal, according to (4) and (7), to $M\mu$. The fundamental relation becomes

$$\mathrm{d}(M\mu) = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}M, \tag{11}$$

from which it follows that

$$M\,\mathrm{d}\mu = -S\,\mathrm{d}T + V\,\mathrm{d}p, \quad \text{or} \quad \mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p. \tag{12}$$

The latter (so-called Gibbs-Duhem) relation shows that μ may be written as a function of T and p, so that the dependence of the characteristic function $M\mu$ on M is a mere proportionality. Here a phase transition at a certain value of p, is characterized by a jump discontinuity of the function V (at constant T and M), or a V-interval where

$$\left(\frac{\partial p}{\partial V}\right)_{T,M} = 0, \tag{13}$$

(or κ_T infinite).

In view of what is found in statistical thermodynamics, we also mention the alternative possibility of transforming F with respect to M instead of V, corresponding to a change of the independent variables into the set T, μ and V. Then the characteristic function obtained (which does not have a name), is equal to $-Vp$, with p a function of T and μ. In this connection we must consider in analogy to (6) or (13), the properties of the quantity

$$\left(\frac{\partial \mu}{\partial M}\right)_{T,V} = \left(\frac{\partial \mu}{\partial p}\right)_{T,V} \left(\frac{\partial p}{\partial M}\right)_{T,V} = -\frac{V^2}{M^2}\left(\frac{\partial p}{\partial V}\right)_{T,M}, \tag{14}$$

which is seen to be positive for a system in stable equilibrium and to vanish for one in phase transition. The evaluation of $\partial\mu/\partial p$ in (14) is deduced from (12), and furthermore use has been made of the fact that p as an intensive quantity, can depend on V and M only through V/M. Indeed, from (3) and (7) it follows that

$$\mathrm{d}f = -s\,\mathrm{d}T - p\,\mathrm{d}v, \tag{15}$$

and hence that f, s and p may be written as functions of T and v.

We will conclude this section with a systematic enumeration of the important thermodynamic formulae. For a better connection with statistical thermodynamics, the „entropy representation" is adopted, introducing the quantity

$$\beta = (kT)^{-1}, \tag{16}$$

(k = Boltzmann's constant), as a thermodynamic function instead of T, and redefining S, p, μ and F as follows:

$$\left.\begin{array}{ll} k^{-1}S & \to S \\ \beta p & \to p \\ -\beta\mu & \to \mu \\ -\beta F & \to F \end{array}\right\} \text{ in the "entropy representation".} \tag{17}$$

The Legendre transforms of S, such as (*cf.* (7) and (4))

$$F = S - \beta E \tag{18}$$

and

$$Vp = F - \mu M = S - \beta E - \mu M, \tag{19}$$

are called in general Massieu functions.

1). E, V and M independent variables:
characteristic function (*cf.* (2))

$$S(E, V, M) = Ms(e, v), \tag{20}$$

with partial derivatives of first order

$$\left(\frac{\partial S}{\partial E}\right)_{V,M} = \left(\frac{\partial s}{\partial e}\right)_v = \beta(e, v) > 0, \tag{21}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,M} = \left(\frac{\partial s}{\partial v}\right)_e = p(e, v) > 0, \tag{22}$$

$$\left(\frac{\partial S}{\partial M}\right)_{E,V} = s(e, v) - \beta(e, v)\, e - p(e, v)\, v = \mu(e, v), \tag{23}$$

and of second order (only relevant ones)

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{V,M} = \frac{1}{M}\left(\frac{\partial^2 s}{\partial e^2}\right)_v = \frac{1}{M}\left(\frac{\partial \beta}{\partial e}\right)_v \leqslant 0, \tag{24}$$

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_{E,M} = \frac{1}{M}\left(\frac{\partial^2 s}{\partial v^2}\right)_e = \frac{1}{M}\left(\frac{\partial p}{\partial v}\right)_e \leqslant 0. \tag{25}$$

2). β, V and M independent variables (Legendre transformation (18) of (20)):
characteristic Massieu function

$$F(\beta, V, M) = Mf(\beta, v), \tag{26}$$

with partial derivatives

$$\left(\frac{\partial F}{\partial \beta}\right)_{V,M} = M\left(\frac{\partial f}{\partial \beta}\right)_v = -Me(\beta, v) = -E(\beta, V, M), \tag{27}$$

$$\left(\frac{\partial F}{\partial V}\right)_{\beta,M} = \left(\frac{\partial f}{\partial v}\right)_\beta = p(\beta, v) > 0, \tag{28}$$

$$\left(\frac{\partial F}{\partial M}\right)_{\beta,V} = f(\beta, v) - p(\beta, v)\, v = \mu(\beta, v), \tag{29}$$

$$\left(\frac{\partial^2 F}{\partial \beta^2}\right)_{V,M} = M\left(\frac{\partial^2 f}{\partial \beta^2}\right)_v = -\left(\frac{\partial E}{\partial \beta}\right)_{V,M} > 0, \tag{30}$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{\beta,M} = \frac{1}{M}\left(\frac{\partial^2 f}{\partial v^2}\right)_\beta = \frac{1}{M}\left(\frac{\partial p}{\partial v}\right)_\beta \leqslant 0. \tag{31}$$

3). β, V and μ independent variables (Legendre transformation (19) of (26)):
characteristic Massieu function

$$Vp(\beta,\mu) \equiv \left(\frac{\partial Vp}{\partial V}\right)_{\beta,\mu} > 0. \tag{32}$$

with

$$\left(\frac{\partial Vp}{\partial \mu}\right)_{\beta,V} = V\left(\frac{\partial p}{\partial \mu}\right)_{\beta} = -V/v(\beta,\mu) = -M(\beta,V,\mu), \tag{33}$$

$$\left(\frac{\partial Vp}{\partial \beta}\right)_{V,\mu} = V\left(\frac{\partial p}{\partial \beta}\right)_{\mu} = -Ve(\beta,\mu)/v(\beta,\mu) = -E(\beta,V,\mu), \tag{34}$$

$$\left(\frac{\partial^2 Vp}{\partial \mu^2}\right)_{\beta,V} = -\left(\frac{\partial M}{\partial \mu}\right)_{\beta,V} > 0, \tag{35}$$

$$\left(\frac{\partial^2 Vp}{\partial \beta^2}\right)_{V,\mu} = -\left(\frac{\partial E}{\partial \beta}\right)_{V,\mu} > 0. \tag{36}$$

In section 3 it will be seen that these three choices of independent variable sets correspond to the three important formalisms of statistical mechanics. But first, in the next section, we will focus our attention on the problem of the justification of statistical mechanics from general dynamics.

§ 2. *Statement of the ergodic problem of statistical mechanics* [3]. Given the interaction of a system of N particles, one can determine its "microscopic" behaviour according to the laws of mechanics, and, if N is supposed to be very large (something in the order of 10^{20}), also its "macroscopic" behaviour as predicted by statistical mechanics. The question is: what is the relationship between the two? We shall discuss this question by considering in particular the concept of "pressure".

For a classical system of N identical particles with mass m and pair interaction, confined in a volume V, the evolution in the time t of the configuration $\boldsymbol{r}^N \equiv (\boldsymbol{r}_1, \dots \boldsymbol{r}_N)$ is governed by the set of Newtonian equations of motion

$$m\,\frac{\mathrm{d}^2\boldsymbol{r}_i}{\mathrm{d}t^2} = \sum_{\substack{j=1\\ j\neq i}}^{N} \boldsymbol{F}(\boldsymbol{r}_i,\boldsymbol{r}_j) + \boldsymbol{F}_V(\boldsymbol{r}_i), \qquad (i = 1, \dots, N). \tag{37}$$

Here $\boldsymbol{F}$ is the interparticle force, derivable from the pair potential u,

$$\boldsymbol{F}(\boldsymbol{r},\boldsymbol{r}') = -\frac{\partial}{\partial \boldsymbol{r}}\, u(|\boldsymbol{r}-\boldsymbol{r}'|), \qquad (\boldsymbol{r} \neq \boldsymbol{r}'), \tag{38}$$

whereas $\boldsymbol{F}_V$ is the external force causing the particles to remain inside the volume V. The latter force has a singular character, as may be seen from its derivation from the wall potential u_V,

$$F_V(\mathbf{r}) = -\frac{\partial}{\partial \mathbf{r}} u_V(\mathbf{r}), \tag{39}$$

with

$$u_V(\mathbf{r}) = \begin{cases} 0 & \text{for } \mathbf{r} \text{ inside } V, \\ \infty & \text{otherwise.} \end{cases} \tag{40}$$

Obviously F_V acts only at the wall, and is then infinite; averaged over the time, however, the force between the system and the wall is finite, giving rise to the pressure. Let us consider the simple case of a cylindrical container, situated parallel to the z-axis, with lower and upper surfaces (of area A) at $z = H$ and $z = H'$ respectively. Then the pressure $p_{N,V}$ on these surfaces is the average total reaction force per unit area,

$$p_{N,V} = \pm \frac{1}{A} \overline{\sum_{i=1}^{N} F_{V;z}(\mathbf{r}_i)}, \quad \begin{matrix} (+ \text{ sign at } z = H, \text{ and} \\ - \text{ sign at } z = H'). \end{matrix} \tag{41}$$

In order to define such averages over the evolution in time of the system in a proper way, it is convenient to introduce the momenta

$$\mathbf{p}_i = m \frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t}, \qquad (i = 1, \ldots N), \tag{42}$$

of the particles as independent variables in addition to their positions. The set of momenta $\mathbf{p}^N \equiv (\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and the configuration $\mathbf{r}^N$ constitute the "phase" of the system, which may be conceived as a point in a $6N$-dimensional Euclidian space. From (37) and (42) it follows with (38) and (39) that

$$\frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t} = -\frac{\partial \mathscr{H}_{N,V}}{\partial \mathbf{r}_i}, \quad \frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = \frac{\partial \mathscr{H}_{N,V}}{\partial \mathbf{p}_i}, \qquad (i = 1, \ldots, N), \tag{43}$$

where $\mathscr{H}_{N,V}$ is the Hamiltonian function of the system, given by

$$\mathscr{H}_{N,V}(\mathbf{p}^N, \mathbf{r}^N) = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{\substack{i,j=1 \\ i<j}}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N} u_V(\mathbf{r}_i). \tag{44}$$

The $6N$ Hamiltonian equations of motion (43) are of the first order (whereas the $3N$ Newtonian ones of the second order). Consequently the trajectory of the representative point of the system in phase space $(-\infty < t < \infty)$ is uniquely determined by one phase (say $\mathbf{p}^{(0)N}$, $\mathbf{r}^{(0)N}$ at $t = t_0$):

$$\mathbf{p}_i = \mathbf{p}_{i,N,V}(\mathbf{p}^{(0)N}, \mathbf{r}^{(0)N}, t - t_0), \quad \mathbf{r}_i = \mathbf{r}_{i,N,V}(\mathbf{p}^{(0)N}, \mathbf{r}^{(0)N}, t - t_0), \qquad (i = 1, \ldots, N). \tag{45}$$

Hence we may define the time average, in general for a phase function $\mathscr{A}_N$ (not depending on t explicitly) as follows:

$$\overline{\mathscr{A}}_{N,V}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}, t_0) \equiv \overline{\mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)} =$$

$$= \lim_{\tau\to\infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} \mathrm{d}t \mathscr{A}_N(\boldsymbol{p}^N_{N,V}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}, t-t_0), \boldsymbol{r}^N_{N,V}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}, t-t_0)). \quad (46)$$

It is easy to show that this definition is independent of t_0. Moreover, according to Birkhoff's theorems[4]), if $\mathscr{A}_N$ is integrable over an invariant part Σ of phase space (*i.e.* a set of trajectories) with finite volume, then $\overline{\mathscr{A}}_{N,V}$ exists for $\boldsymbol{p}^{(0)N}$, $\boldsymbol{r}^{(0)N}$ "almost everywhere" in Σ, and we have

$$\iint_\Sigma \mathrm{d}\boldsymbol{p}^{(0)N}\, \mathrm{d}\boldsymbol{r}^{(0)N}\, \overline{\mathscr{A}}_{N,V}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}) =$$

$$= \lim_{\tau\to\infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} \mathrm{d}t \iint_\Sigma \mathrm{d}\boldsymbol{p}^{(0)N}\, \mathrm{d}\boldsymbol{r}^{(0)N} \cdot$$

$$\cdot \mathscr{A}_N(\boldsymbol{p}^N_{N,V}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}, t-t_0), \boldsymbol{r}^N_{N,V}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}, t-t_0)) =$$

$$= \iint_\Sigma \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N). \quad (47)$$

Here the first step is the essential one, whereas the second step is a consequence of Liouville's theorem ,which states that, on the basis of (43), the Jacobian $\partial(\boldsymbol{p}^N, \boldsymbol{r}^N)/\partial(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}) = 1$ for all t.

Now the time average (41) may be expressed in terms of the time average of a regular phase function by means of the so-called virial theorem. It is obvious that

$$\overline{\frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N} p_{i;z} z_i} = \lim_{\tau\to\infty} \frac{1}{\tau} \{p_{i,N,V;z}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}, \tau) \cdot$$

$$\cdot z_{i,N,V}(\boldsymbol{p}^{(0)N}, \boldsymbol{r}^{(0)N}, \tau) - p^{(0)}_{i;z} z^{(0)}_i\} = 0. \quad (48)$$

On the other hand, (43) gives with (44), (39) and (42), that

$$\frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N} p_{i;z} z_i = - \sum_{\substack{i,j=1\\ i<j}}^{N} \frac{\partial u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)}{\partial z_i} z_i + \sum_{i=1}^{N} F_{V;z}(\boldsymbol{r}_i)\, z_i +$$

$$+ \sum_{i=1}^{N} \frac{p^2_{i:z}}{m}. \quad (49)$$

Remembering that $F_{V;z}$ acts only for $z_i = H$ and $z_i = H'$, we see that the time average of the middle term on the right-hand side of (49) is, according to (41), equal to $p_{N,V}\, A(H - H') \equiv -p_{N,V}V$. Hence (48) states that

$$p_{N,V}V = \overline{\mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)}, \tag{50}$$

where

$$\mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N) = \sum_{i=1}^{N} \frac{p_{i;z}^2}{m} - \sum_{\substack{i,j=1\\ i<j}}^{N} \frac{\partial u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)}{\partial z_i} z_i. \tag{51}$$

If we relate to any phase function $\mathscr{A}_N$ another phase function $\overline{\mathscr{A}}_{N,V}$ in such a way that it is equal to the time average (46) of $\mathscr{A}_N$ for all points of the trajectory passing through $\boldsymbol{p}^{(0)N}$, $\boldsymbol{r}^{(0)N}$, then we obtain a so-called constant of the motion. In general a constant of the motion is characterized by a vanishing „substantial" time derivative. Therefore it follows from (43) that also $\mathscr{H}_{N,V}$ is a constant of the motion, or that $\overline{\mathscr{H}}_{N,V} \equiv \mathscr{H}_{N,V}$. If we prescribe the value of this constant, which is the energy E of the system, then we know that the motion takes place in the $(6N-1)$-dimensional hypersurface in phase space determined by $\mathscr{H}_{N,V} = E$. We calculate the "area" $\Omega_{N,V}$ of this hypersurface as the limit, for $\varepsilon \to 0$, of the volume of the part of phase space for which $E \leqslant \mathscr{H}_{N,V} \leqslant E + \varepsilon$, divided by ε,

$$\Omega_{N,V}(E) = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \{\Sigma_{N,V}(E + \delta) - \Sigma_{N,V}(E)\} \equiv \frac{\mathrm{d}\Sigma_{N,V}(E)}{\mathrm{d}E}, \tag{52}$$

where $\Sigma_{N,V}$ is the phase volume determined by $\mathscr{H}_{N,V} \leqslant E$,

$$\Sigma_{N,V}(E) = \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \sigma\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}. \tag{53}$$

Since the derivative of the unit step function σ is the δ-function, (52) is equivalent with

$$\Omega_{N,V}(E) = \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}. \tag{54}$$

Now an obvious hypothesis is that the probability to hit upon a trajectory with a value of $\overline{\mathscr{G}}_{N,V}$ between G and $G + \varepsilon$ is equal to the fraction of the area $\Omega_{N,V}$ for which $G \leqslant \overline{\mathscr{G}}_{N,V} \leqslant G + \varepsilon$. Hence we may speak of a distribution of G-values, with distribution function

$$D_{E,N,V}(G) = \frac{1}{\Omega_{N,V}(E)} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\} \cdot \sigma\{G - \overline{\mathscr{G}}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}, \tag{55}$$

and frequency function

$$\Delta_{E,N,V}(G) \equiv \frac{\mathrm{d}}{\mathrm{d}G} D_{E,N,V}(G) = \frac{1}{\Omega_{N,V}(E)} \cdot \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}\, \delta\{G - \overline{\mathscr{G}}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}. \tag{56}$$

Applying (47) for Σ equal to the phase "shell" $E \leqslant \mathscr{H}_{N,V} \leqslant E+\varepsilon$, and $\mathscr{A}_N = \mathscr{G}_N$, we find, for $\varepsilon \to 0$, that

$$\iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N \overline{\mathscr{G}}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\} = \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N \mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}, \tag{57}$$

or, with (56), that

$$\int_{-\infty}^{\infty} \mathrm{d}G\, G\, \Delta_{E,N,V}(G) = \overset{-(\mathrm{m})}{G}_{N,V}(E). \tag{58}$$

Here we have introduced the so-called microcanonical phase average of a phase function $\mathscr{A}_N$:

$$\overset{-(\mathrm{m})}{A}_{N,V}(E) = \frac{1}{\Omega_{N,V}(E)} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}. \tag{59}$$

The equation (58) states that the mean value of the distribution determined by (55) or (56) is equal to $\overset{-(\mathrm{m})}{G}_{N,V}$. Now the ergodic problem, as conceived by Khinchin[5]), is to prove on the basis of the properties of $\mathscr{H}_{N,V}$ and $\mathscr{G}_N$, that, for macroscopic systems, the frequency function $\Delta_{E,N,V}$ is sharply peaked at this mean value. In that case the occurrence of G-values differing much from $\overset{-(\mathrm{m})}{G}_{N,V}$ is highly improbable, and the use of the microcanonical formalism of statistical mechanics is justified. The smaller the ratio is of a distribution's variance to the square of its mean value, the sharper its frequency function is peaked. For the variance corresponding to (56) we have

$$\int_{-\infty}^{\infty} \mathrm{d}G \{G - \overset{-(\mathrm{m})}{G}_{N,V}(E)\}^2 \Delta_{E,N,V}(G) = \frac{1}{\Omega_{N,V}(E)} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N$$

$$\{\overline{\mathscr{G}}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N) - \overset{-(\mathrm{m})}{G}_{N,V}(E)\}^2\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\} \leqslant \frac{1}{\Omega_{N,V}(E)} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N$$

$$\overline{\{\mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N) - \overset{-(\mathrm{m})}{G}_{N,V}(E)\}^2\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}} = \frac{1}{\Omega_{N,V}(E)} \cdot$$

$$\cdot \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N \{\mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N) - \overset{-(\mathrm{m})}{G}_{N,V}(E)\}^2\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}, \tag{60}$$

where the inequality is due to Schwarz' inequality: $\overset{-2}{\mathscr{A}}_N \leqslant \overline{\mathscr{A}^2_N}$, for $\mathscr{A}_N = \mathscr{G}_N - \overset{-(\mathrm{m})}{G}_{N,V}$, and the second equality is an application of (57) for $(\mathscr{G}_N - \overset{-(\mathrm{m})}{G}_{N,V})^2$ instead of for $\mathscr{G}_N$. As the right-hand sides of (58) and (60) may be conceived as the mean value and the variance respectively of a distribution with frequency function

$$\Delta^{(m)}_{N,V}(E;G) = \frac{1}{\Omega_{N,V}(E)} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \delta\{E - \mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}\cdot$$
$$\cdot\delta\{G - \mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\}, \qquad (61)$$

it follows that (56) is always more sharply peaked than this function $\Delta^{(m)}_{N,V}$. Hence for the ergodic theorem it suffices to study the properties of (61) for macroscopic systems.

It may be remarked that the approach to the ergodic theorem on the basis of metric indecomposability of the hypersurface $\mathscr{H}_{N,V} = E$, is contained as a special case in the above. The hypersurface $\mathscr{H}_{N,V} = E$ is called metrically indecomposable (or transitive), if it cannot be split into two invariant parts of non-vanishing area. This means that any other constant of the motion existing besides $\mathscr{H}_{N,V}$ must be constant almost everywhere on this hypersurface (otherwise it would be possible to find two invariant parts of non-vanishing area for values of this constant of the motion smaller and larger respectively, than a certain number). Since $\overline{\mathscr{G}}_{N,V}$ is such a constant of the motion, it then follows from (57) that it is equal to $\overset{-(m)}{G}_{N,V}$ almost everywhere on the hypersurface $\mathscr{H}_{N,V} = E$(*i.e.* ergodicity, independent of the size of the system). The frequency function (56) is in this case equal to the δ-function of $G - \overset{-(m)}{G}_{N,V}$, and therefore as sharply peaked as possible. This point is, however, not likely to be realized for nonvanishing interaction, and not necessary anyway.

§ 3. *The various formalisms of statistical physics*[6]). In (classical) statistical mechanics the phase average of a phase function $\mathscr{A}_N$ is defined as

$$\overset{-(\text{phase})}{A}_{N,V} \equiv \overline{\mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)}^{(\text{phase})} = \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N \mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\, \rho_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N) \qquad (62)$$

with a normalized phase density $\rho_{N,V}$:

$$\iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \rho_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N) = 1. \qquad (63)$$

Here and in the future we suppose each of the integrations over $\boldsymbol{r}_i (i = 1, \ldots$ $\ldots, N)$ to be restricted to the volume V. In (59) we met already the microcanonical phase average with density

$$\rho^{(m)}_{N,V}(E; \boldsymbol{p}^N, \boldsymbol{r}^N) = \delta\{E - \mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\}/\Omega_{N,V}(E), \qquad (64)$$

(with $\mathscr{H}_N$ we indicate the Hamiltonian function $\mathscr{H}_{N,V}$ without the wall potentials). The other possibility of interest is the canonical phase average with density

$$\rho^{(c)}_{N,V}(\beta; \boldsymbol{p}^N, \boldsymbol{r}^N) = \exp\{-\beta\mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\}/\Phi_{N,V}(\beta), \qquad (65)$$

where β is real and positive, and, according to (63),

$$\Phi_{N,V}(\beta) = \int\int \mathrm{d}\boldsymbol{p}^N \, \mathrm{d}\boldsymbol{r}^N \exp\{-\beta \mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\}. \tag{66}$$

Using (54), we may derive the relationship

$$\Phi_{N,V}(\beta) = \int_{-\infty}^{\infty} \mathrm{d}E \, \mathrm{e}^{-\beta E} \, \Omega_{N,V}(E), \tag{67}$$

and in the same way with (59),

$$\overset{-(\mathrm{c})}{A}_{N,V}(\beta) = \frac{1}{\Phi_{N,V}(\beta)} \int_{-\infty}^{\infty} \mathrm{d}E \, \mathrm{e}^{-\beta E} \, \Omega_{N,V}(E) \, \overset{-(\mathrm{m})}{A}_{N,V}(E). \tag{68}$$

In this section we will derive for these phase averages of the functions $\mathscr{H}_N$ and $\mathscr{G}_N$, some expressions which connect statistical mechanics with statistical thermodynamics. Note that both $\mathscr{H}_N$ and $\mathscr{G}_N$ consist of a part depending only on the momenta, and a part depending only on the configuration. Thus $\mathscr{H}_N = \mathscr{T}_N + \mathscr{U}_N$, where

$$\mathscr{T}_N(\boldsymbol{p}^N) = \sum_{i=1}^{N} \frac{|\boldsymbol{p}_i|^2}{2m} \tag{69}$$

is the kinetic energy, and

$$\mathscr{U}_N(\boldsymbol{r}^N) = \sum_{\substack{i,j=1\\ i<j}}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \tag{70}$$

the potential energy of the system in V. In the same way $\mathscr{G}_N = \mathscr{S}_N + \mathscr{V}_N$, where

$$\mathscr{S}_N(\boldsymbol{p}^N) = \sum_{i=1}^{N} \frac{p_{i;z}^2}{m} \tag{71}$$

and

$$\mathscr{V}_N(\boldsymbol{r}^N) = -\sum_{\substack{i,j=1\\ i<j}}^{N} \frac{\partial u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)}{\partial z_i} z_i. \tag{72}$$

Obviously $\overset{-(\mathrm{m})}{H}_{N,V} = E$, so that (68) gives, with (67),

$$\overset{-(\mathrm{c})}{H}_{N,V}(\beta) = \frac{1}{\Phi_{N,V}(\beta)} \int_{-\infty}^{\infty} \mathrm{d}E \, \mathrm{e}^{-\beta E} \, \Omega_{N,V}(E) \, E = -\frac{\partial \log \Phi_{N,V}(\beta)}{\partial \beta}. \tag{73}$$

Using the fact that $p_{i;z}/m = \partial \mathscr{H}_N / \partial p_{i;z}$ for an integration by parts, we find with (53), that

$$\frac{1}{N} \overset{-(\mathrm{m})}{S}_{N,V}(E) = \Sigma_{N,V}(E)/\Omega_{N,V}(E) = \left\{ \frac{\partial \log \Sigma_{N,V}(E)}{\partial E} \right\}^{-1}. \tag{74}$$

Hence (68) gives, with (52) and (67),

$$\frac{1}{N}\overset{-(c)}{S}_{N,V}(\beta)=\frac{1}{\Phi_{N,V}(\beta)}\int_{-\infty}^{\infty}\mathrm{d}E\,\mathrm{e}^{-\beta E}\,\Sigma_{N,V}(E)=\frac{1}{\beta}. \tag{75}$$

The phase average of $\mathscr{T}_N$ are equal to $\frac{3}{2}$ times those of $\mathscr{S}_N$. In order to deal with $\mathscr{G}_N$, let us differentiate (53) with respect to V (at constant area A of the cylinder). This is best done as follows: first transform each z-coordinate in such a way that the integration volume becomes a cylinder of unit height, then differentiate, and finally transform back. The result is

$$\frac{\partial\Sigma_{N,V}(E)}{\partial V}=\frac{N}{V}\,\Sigma_{N,V}(E)-\frac{1}{V}\iint\mathrm{d}\boldsymbol{p}^N\,\mathrm{d}\boldsymbol{r}^N\,\delta\{E-\mathscr{H}_N(\boldsymbol{p}^N,\boldsymbol{r}^N)\}\cdot\sum_{i=1}^{N}\frac{\partial\mathscr{H}_N(\boldsymbol{p}^N,\boldsymbol{r}^N)}{\partial z_i}\,z_i, \tag{76}$$

or, using also (74),

$$\frac{1}{V}\overset{-(m)}{G}_{N,V}(E)=\frac{\partial\Sigma_{N,V}(E)}{\partial V}\Big/\Omega_{N,V}(E)=\frac{\partial\log\Sigma_{N,V}(E)}{\partial V}\Big/\frac{\partial\log\Sigma_{N,V}(E)}{\partial E}. \tag{77}$$

For the canonical phase average of $\mathscr{G}_N$ we obtain therefore from (68), with (75),

$$\frac{1}{V}\overset{-(c)}{G}_{N,V}(\beta)=\frac{1}{\Phi_{N,V}(\beta)}\int_{-\infty}^{\infty}\mathrm{d}E\,\mathrm{e}^{-\beta E}\,\frac{\partial\Sigma_{N,V}(E)}{\partial V}=\frac{1}{\beta}\,\frac{\partial\log\Phi_{N,V}(\beta)}{\partial V}. \tag{78}$$

Assuming the ergodicity of the phase function $\mathscr{G}_N$, statistical thermodynamics starts with the identification, for macroscopic systems, of (77) with the thermodynamic pressure as a function of E, V and N (N equals the quantity M multiplied by Avogadro's number.) Then, if we suppose the "asymptotic problem" for the microcanonical and canonical formalisms to be solved, also the identification of every other thermodynamic function with its statistical "analogies" may be made. The result is that the logarithms of the statistical functions

$$\Sigma_N(E,V)\equiv\Sigma_{N,V}(E)/N!\quad\text{or}\quad\Omega_N(E,V)\equiv\Omega_{N,V}(E)/N! \tag{79}$$

and

$$\Phi_N(\beta,V)\equiv\Phi_{N,V}(\beta)/N! \tag{80}$$

determine asymptotically, as characteristic functions, the descriptions 1) and 2) respectively, given for a thermodynamic system in section 1. Note that the first possibility in (79) is, in view of (77), more fundamental than the second one. For the choice of Σ_N, moreover, the microcanonical phase average (74) of $\mathscr{S}_N/N$ is identified with the thermodynamic quantity β^{-1}, just like the canonical one (75).

We do not intend to go into the details of the asymptotic problem here, but will only point out a particular aspect of it: the functions $\mathscr{H}_N$, $\mathscr{S}_N$ (or $\mathscr{T}_N$) and $\mathscr{G}_N$ must be shown to belong to the class of phase functions $\mathscr{A}_N$ with the property

$$\lim_{N\to\infty} \frac{1}{N} \overset{-(\mathrm{m})}{A}_{N,Nv}(Ne) = \lim_{N\to\infty} \frac{1}{N} \overset{-(\mathrm{c})}{A}_{N,Nv}(\alpha(e, v)), \tag{81}$$

(including the existence of the limits). The meaning of α in this equivalence relation for phase averages follows for $\mathscr{A}_N = \mathscr{S}_N$, with (74) and (75),

$$\lim_{N\to\infty} \frac{\Sigma_{N,Nv}(Ne)}{\Omega_{N,Nv}(Ne)} = \frac{1}{\alpha(e, v)}. \tag{82}$$

Taking $\mathscr{A}_N = \mathscr{H}_N$, (81) becomes

$$e = \lim_{N\to\infty} \frac{1}{N} \overset{-(\mathrm{c})}{\mathscr{H}}_{N,Nv}(\alpha(e, v)), \tag{83}$$

so that, using (73), we may also say that α is the inverse function of

$$e^{(c)}(\beta, v) = -\lim_{N\to\infty} \frac{1}{N} \frac{\partial \log \Phi_{N,Nv}(\beta)}{\partial \beta} \tag{84}$$

at constant v.

Repeating in an analogous way the transition from the microcanonical to the canonical formalism as given by the relation (68), by defining

$$\overset{-(\mathrm{g})}{A}_V(\beta, \mu) = \frac{1}{\Xi_V(\beta, \mu)} \sum_{N=0}^{\infty} \mathrm{e}^{-\mu N} \Phi_N(\beta, V)\, \overset{-(\mathrm{c})}{A}_{N,V}(\beta), \tag{85}$$

where μ is real, and

$$\Xi_V(\beta, \mu) = \sum_{N=0}^{\infty} \mathrm{e}^{-\mu N} \Phi_N(\beta, V), \tag{86}$$

we arrive at the grand canonical formalism. If we suppose that the canonical-grand canonical asymptotic problem is solved too, the new description appears to be the third one of section 1, asymptotically determined by the logarithm of the statistical function (86) as the characteristic function.

Corresponding to (81), we must have for the same class of phase functions,

$$\lim_{N\to\infty} \frac{1}{Nv} \overset{-(\mathrm{c})}{A}_{N,Nv}(\beta) = \lim_{V\to\infty} \frac{1}{V} \overset{-(\mathrm{g})}{A}_V(\beta, \lambda(\beta, v)). \tag{87}$$

The grand canonical average of $\mathscr{S}_N$ is, according to (75), (85) and (86), given by

$$\overset{-(\mathrm{g})}{S_V}(\beta,\mu) = -\frac{1}{\beta}\,\frac{\partial \log \Xi_V(\beta,\mu)}{\partial\mu}, \tag{88}$$

and hence we see that, similarly to the relationship between α and (84), λ in (87) is the inverse function of

$$v^{(g)}(\beta,\mu) = -\left\{\lim_{V\to\infty}\frac{1}{V}\,\frac{\partial \log \Xi_V(\beta,\mu)}{\partial\mu}\right\}^{-1} \tag{89}$$

at constant β. An expression for λ directly in terms of a limit (*cf.* (82)) may be found by considering the statistical analogies of the thermodynamic quantity μ. Since $N \gg M$, the differentiation with respect to M may be replaced by the computation of the difference for two successive values of N, so that from (29) we obtain as a canonical analogue of μ the logarithm of Φ_N/Φ_{N-1}. Treating Φ_{N-1}/Φ_N as a canonical average, (85) yields, with (86), indeed $e^{-\mu}$ as the appropriate grand canonical average. From these observations the existence of the following equivalence relation may be conjectured (*cf.* (87)),

$$\lim_{N\to\infty}\frac{\Phi_{N-1}(\beta,Nv)}{\Phi_N(\beta,Nv)} = e^{-\lambda(\beta,v)}. \tag{90}$$

Note that, since according to (78), (85) and (86),

$$\frac{1}{V}\overset{-(\mathrm{g})}{G_V}(\beta,\mu) = \frac{1}{\beta}\,\frac{\partial \log \Xi_V(\beta,\mu)}{\partial V}, \tag{91}$$

there are two grand canonical pressure analogies, which must be asymptotically equivalent.

$$\lim_{V\to\infty}\frac{\partial \log \Xi_V(\beta,\mu)}{\partial V} = \lim_{V\to\infty}\frac{1}{V}\log \Xi_V(\beta,\mu). \tag{92}$$

If the limit on the left-hand side is known to exist, then (92) holds according to l'Hôpital's rule; the reverse is, however, not true in general. This question together with (90) and its microcanonical-canonical counterpart

$$\lim_{N\to\infty}\frac{\Sigma_{N-1}(Ne,Nv)}{\Sigma_N(Ne,Nv)} = \lim_{N\to\infty}\frac{\Phi_{N-1}(\alpha(e,v),Nv)}{\Phi_N(\alpha(e,v),Nv)}, \tag{93}$$

may be considered as supplementary to the asymptotic problem.

Note that all functions introduced above for a finite system, are continuous in their continuous variables. Discontinuities such as we expect for some functions in phase transitions, can therefore be mathematically sharp only in the thermodynamic limit.

§ 4. *The limit theorems of probability theory*[7]). Any real function D of a real variable ξ, which is nondecreasing, with values between 0 and 1, and normalized according to

$$\int_{\xi=-\infty}^{\xi=\infty} \mathrm{d}D(\xi) = 1. \tag{94}$$

may be conceived as the distribution function of a random variable. Three other ways are used to characterize a distribution, which in general are equivalent to the knowledge of the distribution function:

1. by means of the characteristic function

$$\psi(\tau) = \int_{\xi=-\infty}^{\xi=\infty} \mathrm{e}^{i\tau\xi}\, \mathrm{d}D(\xi), \tag{95}$$

2. by means of the set of moments

$$\mu_p = \int_{\xi=-\infty}^{\xi=\infty} \xi^p\, \mathrm{d}D(\xi), \quad (p = 0, 1, 2, \ldots), \tag{96}$$

3. if the random variable is continuous, by means of the frequency function

$$\Delta(\xi) = \frac{\mathrm{d}D}{\mathrm{d}\xi} \geqslant 0, \tag{97}$$

and if the random variable is discrete with values $\xi_k (k = 0, 1, 2, \ldots)$, *i.e.* if D is of the form

$$D(\xi) = \sum_{k=0}^{\infty} \omega_k \sigma(\xi - \xi_k), \; (\omega_k > 0, \xi_0 < \xi_1 < \xi_2 \ldots), \tag{98}$$

(with σ the unit-step function), by means of the set of relative frequencies $\omega_k (k = 0, 1, 2, \ldots)$. (Every distribution is a linear combination of these two types, and therefore we will consider only the pure cases, the second one in fact with ξ_k a linear function of k).

The normalization (94) gives

$$\psi(0) = \mu_0 = \int_{-\infty}^{\infty} \mathrm{d}\xi \Delta(\xi) = \sum_{k=0}^{\infty} \omega_k = 1. \tag{99}$$

Since, according to (95) and (96), we have

$$\mu_p = p! \left(\frac{\mathrm{d}^p \psi(\tau)}{\mathrm{d}(i\tau)^p} \right)_{\tau=0}, \tag{100}$$

the numbers $\mu_p/p!$ are the coefficients in the series expansion of ψ in powers of $i\tau$. Equivalently we may use the coefficients in the expansion of $\log \psi$, the so-called cumulants:

$$\kappa_p = \left(\frac{\mathrm{d}^p \log \psi(\tau)}{\mathrm{d}(i\tau)^p} \right)_{\tau=0}, \quad (p = 0, 1, 2, \ldots), \tag{101}$$

($i.e.$ $\kappa_0 \equiv 0$, $\kappa_1 \equiv \mu_1$, the mean value, $\kappa_2 \equiv \frac{1}{2}(\mu_2 - \mu_1^2) > 0$, half the variance, *etc.*). Furthermore we note that (95) may be written with (97) as

$$\psi(\tau) = \int_{-\infty}^{\infty} \mathrm{d}\xi \; \mathrm{e}^{i\tau\xi} \Delta(\xi), \tag{102}$$

and with (98) as

$$\psi(\tau) = \sum_{k=0}^{\infty} \mathrm{e}^{i\tau\xi_k} \omega_k. \tag{103}$$

Now we are interested in the following question: if for a sequence of distributions there exists a limit distribution according to one of the above ways of determination, does this limit distribution also follow from the other ways? In particular we want to get from 2. (or rather the cumulants) to 3. Two general limit theorems of probability theory[7]) enable us to go from 2., *via* the distribution function description, to 1:

A) if a sequence of distribution functions $D_n(n \to \infty)$ tends to a continuous distribution function D, then the corresponding sequence of characteristic functions $\psi_n(n \to \infty)$ tends to ψ uniformly in any finite τ-interval, where ψ is the characteristic function corresponding to D (First limit theorem),

B) if for a sequence of distributions all moments $\mu_{p|n}$ (or cumulants $\kappa_{p|n}$) exist, and tend for $n \to \infty$ to limits $\mu_p(\kappa_p)$ which are the moments (cumulants) corresponding to a distribution function D, then the sequence of distribution functions $D_n(n \to \infty)$ tends to D in all points of continuity, provided that the limit distribution is uniquely determined by its set of moments (cumulants) (converse of the Second limit theorem).

In view of the applications of probability theory in statistical physics, we need not consider the last step, from 1. to 3., in general, but only for Gaussian limit distributions (of sequences with $\mu_{1|n} \equiv \kappa_{1|n} = 0$), most simply (and uniquely) characterized by the set of cumulants

$$\kappa_2 = B, \kappa_p = 0 \quad \text{for} \quad p \geqslant 3. \tag{104}$$

On the basis of the above theorems we may therefore proceed from the following property: given a positive number ε, there is a value n_0 of n such that

$$|\psi_n(\tau) - \exp(-\tfrac{1}{2}B\tau^2)| < \tfrac{1}{2}\varepsilon^2 \quad \text{for} \quad |\tau| \leqslant \frac{1}{\varepsilon} \quad \text{and} \quad n \geqslant n_0(\varepsilon), \tag{105}$$

or

$$\int_{-C/\varepsilon}^{C/\varepsilon} \mathrm{d}\tau \; |\psi_n(\tau) - \exp(-\tfrac{1}{2}B\tau^2)| < C\varepsilon \quad \text{for} \quad n \geqslant n_0(\varepsilon), \tag{106}$$

where C is an arbitrary positive constant.

For a distribution of a continuous random variable, the frequency function

Δ is obtained from (102) by Fourier inversion:

$$\Delta(\xi) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\tau \, \mathrm{e}^{-i\tau\xi} \, \psi(\tau). \tag{107}$$

Now in order to investigate whether

$$\lim_{N\to\infty} \Delta_n(\xi) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\tau \, \mathrm{e}^{-i\tau\xi - \frac{1}{2}B\tau^2} = (2\pi B)^{-\frac{1}{2}} \exp(-\tfrac{1}{2}\xi^2/B), \tag{108}$$

we may write

$$2\pi \, |\Delta_n(\xi) - (2\pi B)^{-\frac{1}{2}} \exp(-\tfrac{1}{2}\xi^2/B)| \leqslant \int_{-C/\varepsilon}^{C/\varepsilon} \mathrm{d}\tau \, |\psi_n(\tau) - \exp(-\tfrac{1}{2}B\tau^2)| +$$

$$+ \int_{C/\varepsilon \leqslant |\tau| \leqslant \infty} \mathrm{d}\tau \, |\psi_n(\tau)| + \int_{C/\varepsilon \leqslant |\tau| \leqslant \infty} \mathrm{d}\tau \exp(-\tfrac{1}{2}B\tau^2). \tag{109}$$

Noting that (with transformation of τ into τ^{-1}),

$$\int_{C/\varepsilon}^{\infty} \mathrm{d}\tau \, \mathrm{e}^{-\frac{1}{2}B\tau^2} = \int_{0}^{\varepsilon/C} \mathrm{d}\tau \, \tau^{-2} \, \mathrm{e}^{-\frac{1}{2}B/\tau^2} < \frac{\mathrm{e}^{-1}}{\frac{1}{2}BC} \, \varepsilon, \tag{110}$$

we conclude from (109) and (106) that a sufficient condition to have (108) is, that a value n_1 of n can be found such that

$$\int_{C/\varepsilon \leqslant |\tau| \leqslant \infty} \mathrm{d}\tau \, |\psi_n(\tau)| < C'\varepsilon \quad \text{for} \quad n \geqslant n_1(\varepsilon), \tag{111}$$

where C' is some positive number. This condition[8]) will appear to be satisfied in our applications. Note that the limit (108) established in this way is uniform in ξ.

An important special case of a sequence of distributions tending for $n \to \infty$ to the Gaussian one, is that of the sum distribution of n independent identical random variables with vanishing mean values, provided that this sum is divided by $\sqrt{n}$ (Central limit theorem, alternatively also for non-identical random variables). The independence is expressed for continuous variables by

$$\Delta_n(\xi) = \sqrt{n} \int_{-\infty}^{\infty} \mathrm{d}\xi_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}\xi_{n-1} \prod_{l=1}^{n} \Delta_1(\xi_l), \quad (\xi_n \equiv \sqrt{n}\xi - \sum_{l=1}^{n-1} \xi_l), \tag{112}$$

and for discrete random variables (linear in k) by

$$\xi_{k|n} = \frac{1}{\sqrt{n}} \sum_{l=1}^{n} \xi_{k_l|1}, \quad \omega_{k|n} = \sum_{k_1=0}^{\infty} \ldots \sum_{k_{n-1}=0}^{\infty} \prod_{l=1}^{n} \omega_{k_l|1}, \quad (k_n \equiv k - \sum_{l=1}^{n-1} k_l). \tag{113}$$

From (102) and (112), as well as from (103) and (113), it follows that

$$\psi_n(\tau) = \left\{\psi_1\left(\frac{\tau}{\sqrt{n}}\right)\right\}^n, \tag{114}$$

and furthermore, according to (101), that

$$\kappa_{p|n} = n^{1-p/2}\kappa_{p|1}. \tag{115}$$

Indeed these cumulants tend to (104) with $B = \kappa_{2|1}$ for $n \to \infty$ ($\kappa_{1|1} = 0$).

The case of a sequence of distributions of a discrete random variable, we will consider only for the above example (113). With

$$\xi_{k|1} = x(k - m_1), \quad \text{where} \quad m_1 = \sum_{k=0}^{\infty} k\omega_{k|1} \tag{116}$$

(so that $\mu_{1|1} = 0$), we have

$$\xi_{k|n} = x(k - nm_1)/\sqrt{n}, \tag{117}$$

and consequently, by inversion of (103),

$$\omega_{k|n} = \frac{x}{2\pi\sqrt{n}} \int_{-\pi\sqrt{n}/x}^{\pi\sqrt{n}/x} \mathrm{d}\tau\psi_n(\tau)\, \mathrm{e}^{-i\xi_{k|n}\tau}. \tag{118}$$

In analogy to (108)–(111) we find that

$$\lim_{n\to\infty} \sqrt{n}\omega_{k|n}/x = (2\pi B)^{-\frac{1}{2}} \exp(-\tfrac{1}{2}\xi^2/B), \quad (k = \xi\sqrt{n}/x + nm_1), \tag{119}$$

if for each positive number ε a value n_1 of n may be found such that

$$\int_{C/\varepsilon\leqslant|\tau|\leqslant\pi\sqrt{n}/x} \mathrm{d}\tau\, |\psi_n(\tau)| < C'\varepsilon \quad \text{for} \quad n \geqslant n_1(\varepsilon), \tag{120}$$

which will appear to be possible merely as a consequence of (114) and (116) Khinchin[9]) has shown that the characteristic function ψ of any distribution of the discrete random variable (116) has the property

$$|\psi_1(\tau)| \leqslant \vartheta,\ (0 < \vartheta < 1), \quad \text{for} \quad 0 < |\tau| \leqslant \pi/x. \tag{121}$$

Hence we obtain, using also (116), the inequality

$$\int_{C/\varepsilon\leqslant|\tau|\leqslant\pi\sqrt{n}/x} \mathrm{d}\tau\, |\psi_n(\tau)| = \sqrt{n} \int_{C/\varepsilon\sqrt{n}\leqslant|\tau|\leqslant\pi/x} \mathrm{d}\tau\, |\psi_1(\tau)|^n < \pi\sqrt{n}\vartheta^n/x, \tag{122}$$

which is certainly sufficient for having (120).

The theory of this section may be generalized to simultaneous distributions of two (or more) random variables. Then we have, for continuous random variables, the relations (*cf.* (107) and (101))

$$\Delta(\xi, \eta) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\tau\, \mathrm{d}v\, \mathrm{e}^{-i(\tau\xi+v\eta)}\, \psi(\tau, v), \tag{123}$$

$$\kappa_{p,q} = \left(\frac{\mathrm{d}^{p+q}\log\psi(\tau, v)}{\mathrm{d}(i\tau)^p\, \mathrm{d}(iv)^q}\right)_{\tau=v=0}, \quad (p, q = 0, 1, 2, \ldots), \tag{124}$$

and we want to investigate, when (with $\kappa_{1,0|n} = \kappa_{0,1|n} = 0$)

$$\lim_{n\to\infty} \kappa_{2,0|n} = B_1, \lim_{n\to\infty} \kappa_{1,1|n} = B_2, \lim_{n\to\infty} \kappa_{0,2|n} = B_3,$$
$$\text{with} \quad B_1B_3 - B_2^2 \equiv B^2 > 0,$$
$$\lim_{n\to\infty} \kappa_{p,q|n} = 0 \quad \text{for} \quad p, q \geqslant 3, \tag{125}$$

whether

$$\lim_{n\to\infty} \Delta_n(\xi, \eta) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\tau\, \mathrm{d}v\, \mathrm{e}^{-i(\tau\xi + v\eta) - \frac{1}{2}(B_1\tau^2 + 2B_2\tau v + B_3v^2)} =$$
$$= (2\pi B)^{-1} \exp\{-\tfrac{1}{2}(B_3\xi^2 - 2B_2\xi\eta + B_1\eta^2)/B^2\}, \tag{126}$$

("two-dimensional" Central limit theorem in the case of simultaneous sum distributions of independent random variables).
Since the limit theorems ***A***) and ***B***) may be applied here too, we generalize (105)–(111). Noting that (*cf.* and use (110))

$$\int_{C/\varepsilon}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\tau\, \mathrm{d}v\, \mathrm{e}^{-\frac{1}{2}(B_1\tau^2 + 2B_2\tau v + B_3v^2)} \leqslant \int_{C/\varepsilon}^{\infty} \mathrm{d}\tau\, \mathrm{e}^{-\frac{1}{2}B_1\tau^2} \int_{-\infty}^{\infty} \mathrm{d}v\, \mathrm{e}^{|B_2|\tau v - \frac{1}{2}B_3v^2} =$$
$$= \sqrt{\frac{2\pi}{B_3}} \int_{C/\varepsilon}^{\infty} \mathrm{d}\tau\, \mathrm{e}^{-\frac{1}{2}B^2\tau^2/B_3} < \sqrt{2\pi B_3}\, \frac{\mathrm{e}^{-1}}{\frac{1}{2}B^2C}\, \varepsilon, \tag{127}$$

we may require a property similar to (111) for the double integrals of $|\psi_n|$ $(C_1/\varepsilon \leqslant |\tau| \leqslant \infty, -\infty \leqslant v \leqslant \infty$ and $-\infty \leqslant \tau \leqslant \infty, C_2/\varepsilon \leqslant |v| \leqslant \infty)$ for n large enough.

§ 5. *The asymptotic properties of a separable system*[5]). A separable system of n identical components is characterized by a Hamiltonian function of the form (with $\bar{N} \equiv N/n$, $\bar{V} \equiv V/n$)

$$^{(n)}\mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N) = \sum_{l=1}^{n} \mathscr{H}^{(l)}_{\bar{N},\bar{V}}, \tag{128}$$

where $\mathscr{H}^{(l)}_{\bar{N},\bar{V}}$ is the Hamiltonian function (44) for the particles numbered from $(l-1)\,\bar{N} + 1$ till $l\bar{N}$. Moreover, instead of the factor $1/N!$ introduced in (79) and (80), we use for a separable system the factor $(1/\bar{N}!)^n$, *e.g.*

$$^{(n)}\Omega_N(E, V) \equiv \frac{1}{(\bar{N}!)^n} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \delta\{E - {}^{(n)}\mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}.\ ^*) \tag{129}$$

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*) Khinchin [5]) in fact considered an ideal system, the characterization of which one gets from (128) and (129) by putting $n = N$, and (in accordance) $\bar{N} = 1$, but $\bar{V} = V$. The asymptotic evaluations then are performed for $N \to \infty$ (V constant).

Any phase function of the same form as (128):

$$^{(n)}\mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N) = \sum_{l=1}^{n} \mathscr{A}_N^{(l)}, \tag{130}$$

is called a sum function of the phase function $\mathscr{A}_N$. For such a function we want to evaluate asymptotically for $n \to \infty$ ($\overline{N}$ and $\overline{V}$ constant), the microcanonical phase average (59), which may be written as

$$^{(n)}\overset{-(\mathrm{m})}{A}_{N,V}(E) = n\,^{(n)}\Omega_N^{\dagger}(E, V)/^{(n)}\Omega_N(E, V), \tag{131}$$

with

$$^{(n)}\Omega_N^{\dagger}(E, V) = \frac{1}{n(\overline{N}!)^n} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, ^{(n)}\mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\, \delta\{E - {}^{(n)}\mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\}, \tag{132}$$

(note that for $\mathscr{A}_N \equiv 1$ we have $^{(n)}\Omega_N^{\dagger} = {}^{(n)}\Omega_N$).

Using the identity for δ-functions

$$\delta(x) = \int_{-\infty}^{\infty} \mathrm{d}x_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}x_{n-1} \prod_{l=1}^{n-1} \delta(x_l)\, \delta(x - \sum_{l=1}^{n-1} x_l), \tag{133}$$

we deduce from (132), with (128) and (130), that

$$^{(n)}\Omega_N^{\dagger}(E, V) = \frac{1}{(\overline{N}!)^n} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N\, \mathscr{A}_{\overline{N}}^{(n)} \delta\{E - \sum_{l=1}^{n} \mathscr{H}_{\overline{N},\overline{V}}^{(l)}\} =$$

$$= \int_{-\infty}^{\infty} \mathrm{d}E_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}E_{n-1} \prod_{l=1}^{n-1} \Omega_{\overline{N}}(E_l, \overline{V})\, \Omega_{\overline{N}}^{\dagger}(E - \sum_{l=1}^{n-1} E_l, \overline{V}), \tag{134}$$

where

$$\Omega_N^{\dagger}(E, V) = \frac{1}{N!} \iint \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N \mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\, \delta\{E - \mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\} =$$

$$= \overset{-(\mathrm{m})}{A}_{N,V}(E)\, \Omega_N(E, V), \tag{135}$$

Now in view of (67) and (73), the function

$$\Delta(\xi) = \exp\left\{-\beta\left(\xi - \frac{\partial \log \Phi_N(\beta, V)}{\partial \beta}\right)\right\} \Omega_N\left(\xi - \frac{\partial \log \Phi_N(\beta, V)}{\partial \beta}, V\right) \Big/ \Phi_N(\beta, V) \tag{136}$$

may be conceived as the frequency function determining the distribution of a continuous random variable ξ with vanishing mean value. Supposing that the function (135) is positive, or that

$$\overset{-(\mathrm{m})}{A}_{N,V}(E) \geqslant 0, \tag{137}$$

we generalize (136) to a frequency function

$$\Delta^{\dagger}(\xi) = \exp\left\{-\beta\left(\xi - \frac{\partial \log \Phi^{\dagger}_N(\beta, V)}{\partial\beta}\right)\right\}\cdot$$

$$\cdot\,\Omega^{\dagger}_N\left(\xi - \frac{\partial \log \Phi^{\dagger}_N(\beta, V)}{\partial\beta}, V\right)\bigg/\Phi^{\dagger}_N(\beta, V), \qquad (138)$$

where

$$\Phi^{\dagger}_N(\beta, V) = \frac{1}{N!}\iint \mathrm{d}\boldsymbol{p}^N\,\mathrm{d}\boldsymbol{r}^N \mathscr{A}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\exp\{-\beta\mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\} =$$

$$= \overset{-(\mathrm{c})}{A}_{N,V}(\beta)\,\Phi_N(\beta, V), \qquad (139)$$

(the normalization being ensured by (68)). Then, on the basis of (134), we conclude that the frequency function

$$\Delta_n(\xi) = \sqrt{n}\,\exp\left\{-\beta\left(\sqrt{n}\xi - \frac{\partial \log {}^{(n)}\Phi^{\dagger}_N(\beta, V)}{\partial\beta}\right)\right\}\cdot$$

$$\cdot\,{}^{(n)}\Omega^{\dagger}_N\left(\sqrt{n}\xi - \frac{\partial \log {}^{(n)}\Phi^{\dagger}_N(\beta, V)}{\partial\beta}, V\right)\bigg/{}^{(n)}\Phi^{\dagger}_N(\beta, V), \qquad (140)$$

where

$${}^{(n)}\Phi^{\dagger}_N(\beta, V) = \{\Phi_{\bar{N}}(\beta, \bar{V})\}^{n-1}\,\Phi^{\dagger}_{\bar{N}}(\beta, \bar{V}), \qquad (141)$$

determines the sum distribution of n independent continuous random variables, of which $n-1$ are identical (or all n if $\mathscr{A}_N \equiv 1$), with vanishing mean values and their sum divided by $\sqrt{n}$ (*cf.* (112)). We now have, instead of (114) and (115),

$$\psi_n(\tau) = \left\{\psi_1\left(\frac{\tau}{\sqrt{n}}\right)\right\}^{n-1}\psi^{\dagger}_1\left(\frac{\tau}{\sqrt{n}}\right) \qquad (142)$$

and

$$\kappa_{p|n} = n^{-p/2}\{(n-1)\,\kappa_{p|1} + \kappa^{\dagger}_{p|1}\} \qquad (143)$$

respectively, which again leads to the limit (108) with $B = \kappa_{2|1}$ for $n \to \infty$, provided that we know the condition (111) to be satisfied.

In order to deal with this condition, let us extend the function Φ_N (given by (66) or (67)) to complex values s of its argument β:

$$\Phi_N(s, V) = \frac{1}{N!}\iint \mathrm{d}\boldsymbol{p}^N\,\mathrm{d}\boldsymbol{r}^N \exp\{-s\mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\} =$$

$$= \int_{-\infty}^{\infty}\mathrm{d}E\;\mathrm{e}^{-sE}\,\Omega_N(E, V), \qquad (144)$$

(in absolute value smaller than when evaluated for the real part of s, and hence finite for Re $s > 0$). Then the characteristic function corresponding to (136) may be written as

$$\psi(\tau) = \frac{1}{\Phi_N(\beta, V)} \int_{-\infty}^{\infty} \mathrm{d}E \exp\left\{i\tau\left(E + \frac{\partial \log \Phi_N(\beta, V)}{\partial\beta}\right) - \beta E\right\} \Omega_N(E, V) =$$

$$= \exp\left\{i\tau \frac{\partial \log \Phi_N(\beta, V)}{\partial\beta}\right\} \Phi_N(\beta - i\tau, V)/\Phi_N(\beta, V). \tag{145}$$

Using the fact that $\mathscr{H}_N = \mathscr{T}_N + \mathscr{U}_N$, we can perform the integration over the momenta in (144), giving

$$\Phi_N(s, V) = \frac{1}{N!}\left(\frac{2\pi m}{s}\right)^{3N/2} \int \mathrm{d}\boldsymbol{r}^N \exp\{-s\mathscr{U}_N(\boldsymbol{r}^N)\}. \tag{146}$$

Consequently we have, according to (145),

$$|\psi(\tau)| \leqslant \left(\frac{\beta}{|\beta - i\tau|}\right)^{3N/2}, \tag{147}$$

and, furthermore, according to (142), noting that also $|\psi_1^\dagger| \leqslant 1$,

$$|\psi_n(\tau)| \leqslant \left\{\left(\frac{\beta}{|\beta - i\tau/\sqrt{n}|}\right)^{\frac{1}{2}(n-1)}\right\}^{3\bar{N}} < \frac{\beta^2}{\tau^2} \text{ for } n \geqslant 3, \tag{148}$$

which inequality is certainly sufficient for having (111).

The above application of the central limit theorem yields for $\mathscr{A}_N \equiv 1$ Khinchin's[5]) first asymptotic result:

$$\lim_{\substack{n\to\infty \\ N/n=\bar{N}, V/n=\bar{V}}} \sqrt{n} \exp\left\{-\beta\left(\sqrt{n}\xi - n\frac{\partial \log \Phi_{\bar{N}}(\beta, \bar{V})}{\partial\beta}\right)\right\} \cdot$$

$$\cdot {}^{(n)}\Omega_N\left(\sqrt{n}\xi - n\frac{\partial \log \Phi_{\bar{N}}(\beta, \bar{V})}{\partial\beta}, V\right) \Big/ \{\Phi_{\bar{N}}(\beta, \bar{V})\}^n =$$

$$= (2\pi\kappa_{2|1})^{-\frac{1}{2}} \exp(-\tfrac{1}{2}\xi^2/\kappa_{2|1}), \tag{149}$$

with, using (145) and (66),

$$\kappa_{2|1} \equiv \left(\frac{\partial^2 \log \psi_1(\tau)}{\partial(i\tau)^2}\right)_{\tau=0} = \frac{\partial^2 \log \Phi_{\bar{N}}(\beta, \bar{V})}{\partial\beta^2} = \overline{(\mathscr{H}_{\bar{N}} - \overline{H}^{(c)}_{\bar{N},\bar{V}})^2}^{(c)}. \tag{150}$$

According to (140) and (141) we have

$$\lim_{\substack{n\to\infty \\ N/n=\bar{N}, V/n=\bar{V}}} \sqrt{n} \exp\left\{-\beta\left(\sqrt{n}\xi - n\frac{\partial \log \Phi_{\bar{N}}(\beta, \bar{V})}{\partial\beta}\right)\right\} \cdot$$

$$\cdot {}^{(n)}\Omega_N^\dagger\left(\sqrt{n}\xi - n\frac{\partial \log \Phi_{\bar{N}}(\beta, \bar{V})}{\partial\beta}, V\right) \Big/ {}^{(n)}\Phi_N^\dagger(\beta, V) =$$

$$= \lim_{n\to\infty} \Delta_n\left(\xi + \frac{1}{\sqrt{n}}\left(\frac{\partial \log \Phi_N^\dagger(\beta, \bar{V})}{\partial\beta} - \frac{\partial \log \Phi_{\bar{N}}(\beta, \bar{V})}{\partial\beta}\right)\right). \tag{151}$$

Since the limit (108) is established to be uniform in ξ, the right-hand side of (151) is equal to the limit of Δ_n when evaluated for ξ, (the difference in ξ-values tending to zero for $n \to \infty$). This limit is again the right-hand side of (149), so that we obtain, using also (131), (139) and (141),

$$\lim_{\substack{n\to\infty \\ N/n=\bar{N},\, V/n=\bar{V}}} \frac{1}{n} \, {}^{(n)}\overset{-(\mathrm{m})}{A}_{N,V} \left(\sqrt{n}\xi - n \frac{\partial \log \Phi_{\bar{N}}(\beta, \bar{V})}{\partial \beta} \right) \Big/ \overset{-(\mathrm{c})}{A}_{\bar{N},\bar{V}}(\beta) = 1. \quad (152)$$

Here we may in conclusion choose ξ equal to zero, which yields Khinchin's[5]) second asymptotic result

$$\lim_{n\to\infty} \frac{1}{n} \, {}^{(n)}\overset{-(\mathrm{m})}{A}_{n\bar{N},n\bar{V}}(n\overset{-(\mathrm{c})}{H}_{\bar{N},\bar{V}}(\beta)) = \overset{-(\mathrm{c})}{A}_{\bar{N},\bar{V}}(\beta) \equiv \frac{1}{n} \, {}^{(n)}\overset{-(\mathrm{c})}{A}_{n\bar{N},n\bar{V}}(\beta), \quad (153)$$

expressing (*cf.* (81)) the asymptotic equivalence for $n \to \infty(\bar{N}$ and $\bar{V}$ constant) of the microcanonical and the canonical phase averages, for a separable system, of the sum function of any phase function with a finite lower bound to its microcanonical phase average (for then the function decreased by this bound has the property (137)).

Examples of phase functions for which (153) holds are: $\mathscr{A}_N = \mathscr{H}_N$, $\mathscr{A}_N = \mathscr{G}_N$ and $\mathscr{A}_N = \mathscr{S}_N$ (or $\mathscr{T}_N$), and consequently also $\mathscr{A}_N = \mathscr{U}_N$ and $\mathscr{A}_N = \mathscr{V}_N$. For $\mathscr{H}_N$ we have

$$\mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N) \geqslant E_N^{(0)}(V), \quad (154)$$

and hence $\overset{-(\mathrm{m})}{H}_{N,V} \geqslant E_N^{(0)}$; the result (153), however, is in this case nothing but an identity. According to (77) we have $\overset{-(\mathrm{m})}{G}_{N,V} \geqslant 0$. The function $\mathscr{S}_N$ has the property that its sum function is again the same phase function; with (74) and (75), (153) yields in this case

$$\lim_{n\to\infty} \frac{{}^{(n)}\Sigma_{n\bar{N}}(n\overset{-(\mathrm{c})}{H}_{\bar{N}}(\beta, \bar{V}), n\bar{V})}{{}^{(n)}\Omega_{n\bar{N}}(n\overset{-(\mathrm{c})}{H}_{\bar{N}}(\beta, \bar{V}), n\bar{V})} = \frac{1}{\beta}. \quad (155)$$

As regards $\mathscr{G}_N$, we are also interested in the asymptotic evaluation for $n \to \infty(\bar{N}$ and $\bar{V}$ constant) of the frequency function (61) determining the distribution of the values of ${}^{(n)}\mathscr{G}_N$ on the hypersurface ${}^{(n)}\mathscr{H}_{N,V} = E$,

$${}^{(n)}\Delta_{N,V}^{(\mathrm{m})}(E; G) = {}^{(n)}Y_N(E, G, V)/{}^{(n)}\Omega_N(E, V), \quad (156)$$

where

$${}^{(n)}Y_N(E, G, V) = \frac{1}{(\bar{N}!)^n} \iint \mathrm{d}\boldsymbol{p}^N \, \mathrm{d}\boldsymbol{r}^N \delta\{E - {}^{(n)}\mathscr{H}_{N,V}(\boldsymbol{p}^N, \boldsymbol{r}^N)\} \cdot$$
$$\cdot \delta\{G - {}^{(n)}\mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\}. \quad (157)$$

The asymptotic form of ${}^{(n)}\Omega_N$ we already derived in (149), and ${}^{(n)}Y_N$ may be considered as a "two-dimensional" analogue of ${}^{(n)}\Omega_N$. Hence we seek to apply the two-dimensional central limit theorem on the basis of distributions determined by a frequency function of the form (*cf.* (136))

$$\Delta(\xi, \eta) = \exp\{-\beta(\xi + \overset{-(c)}{H}_{N,V})\}\, Y_N(\xi + \overset{-(c)}{H}_{N,V}, \eta + \overset{-(c)}{G}_{N,V}, V)/\Phi_N(\beta, V), \quad (158)$$

where

$$Y_N(E, G, V) = \frac{1}{N!}\int\int \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N \delta\{E - \mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\}\, \delta\{G - \mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\}. \quad (159)$$

The corresponding characteristic function is

$$\psi(\tau, v) = \exp(-i\tau \overset{-(c)}{H}_{N,V} - iv\overset{-(c)}{G}_{N,V})\, \Phi_N(\beta - i\tau, v, V)/\Phi_N(\beta, V), \quad (160)$$

where, for complex s and real v,

$$\Phi_N(s, v, V) = \frac{1}{N!}\int\int \mathrm{d}\boldsymbol{p}^N\, \mathrm{d}\boldsymbol{r}^N \exp\{-s\mathscr{H}_N(\boldsymbol{p}^N, \boldsymbol{r}^N) + iv\mathscr{G}_N(\boldsymbol{p}^N, \boldsymbol{r}^N)\} =$$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}E\, \mathrm{d}G\, \mathrm{e}^{-sE + ivG}\, Y_N(E, G, V), \quad (161)$$

(in absolute value smaller than when evaluated for the real part of s and vanishing v, and hence finite for Re $s > 0$ and all v). Using the fact that $\mathscr{H}_N = \mathscr{T}_N + \mathscr{U}_N$ and $\mathscr{G}_N = \mathscr{S}_N + \mathscr{V}_N$, we find that (*cf.* (146))

$$\Phi_N(s, v, V) =$$

$$= \frac{1}{N!}\left(\frac{2\pi m}{s}\right)^N \left(\frac{2\pi m}{s - 2iv}\right)^{\frac{1}{2}N} \int \mathrm{d}\boldsymbol{r}^N \exp\{-s\mathscr{U}_N(\boldsymbol{r}^N) + iv\mathscr{V}_N(\boldsymbol{r}^N)\}, \quad (162)$$

so that, according to (160),

$$|\psi(\tau, v)| \leqslant \left(\frac{\beta}{|\beta - i\tau|}\right)^N \left(\frac{\beta}{|\beta - i\tau - 2iv|}\right)^{\frac{1}{2}N}, \quad (163)$$

and, furthermore,

$$|\psi_n(\tau, v)| = \left|\psi_1\left(\frac{\tau}{\sqrt{n}}, \frac{v}{\sqrt{n}}\right)\right|^n \leqslant \frac{1}{1 + \beta^{-2}\tau^2}\, \frac{1}{1 + \beta^{-2}(\tau + 2v)^2} \quad \text{for } n \geqslant 2. \quad (164)$$

Now, since $(1 + x^2)^{-2}$ integrated for $-\infty \leqslant x \leqslant \infty$ yields a constant (π), (164) ascertains that $|\psi_n|$ has the properties mentioned at the end of section

4, and the central limit theorem (126) may be applied, giving

$$\lim_{\substack{n\to\infty\\ N/n=\bar N,\, V/n=\bar V}} n \exp\{-\beta(\sqrt{n}\xi + n\overset{-(c)}{H}_{\bar N,\bar V})\}\cdot$$

$$\cdot {}^{(n)}Y_N(\sqrt{n}\xi + n\overset{-(c)}{H}_{\bar N,\bar V}, \sqrt{n}\eta + n\overset{-(c)}{G}_{\bar N,\bar V}, V)/\{\Phi_{\bar N}(\beta, \bar V)\}^n =$$

$$= (2\pi B)^{-1} \exp\{-\tfrac{1}{2}(\kappa_{0,2|1}\xi^2 - 2\kappa_{1,1|1}\xi\eta + \kappa_{2,0|1}\eta^2)/B^2\},$$

$$B = (\kappa_{2,0|1}\kappa_{0,2|1} - \kappa^2_{1,1|1})^{\frac{1}{2}}, \tag{165}$$

with

$$\kappa_{2,0|1} = \overline{(\mathscr{H}_{\bar N} - \overset{-(c)}{H}_{\bar N,\bar V})^2}^{(c)} = \kappa_{2|1}, \quad \kappa_{1,1|1} = \overline{(\mathscr{H}_{\bar N} - \overset{-(c)}{H}_{\bar N,\bar V})(\mathscr{G}_{\bar N} - \overset{-(c)}{G}_{\bar N,\bar V})}^{(c)},$$

$$\kappa_{0,2|1} = \overline{(\mathscr{G}_{\bar N} - \overset{-(c)}{G}_{\bar N,\bar V})^2}^{(c)}. \tag{166}$$

Combining the results (149) and (165) for $\xi = 0$, we obtain for (156) the asymptotic evaluation

$$\lim_{n\to\infty} \sqrt{n}\,{}^{(n)}\Delta^{(m)}_{n\bar N,n\bar V}(n\overset{-(c)}{H}_{\bar N,\bar V}; \sqrt{n}\eta + n\overset{-(c)}{G}_{\bar N,\bar V}) = \left(2\pi\frac{B^2}{\kappa_{2|1}}\right)^{-\frac{1}{2}} \exp\left(-\tfrac{1}{2}\eta^2 \Big/ \frac{B^2}{\kappa_{2|1}}\right), \tag{167}$$

i.e. the limit distribution is Gaussian in the variable $(G - n\overset{-(c)}{G}_{\bar N,\bar V})/\sqrt{n}$, with variance $\kappa_{0,2|1} - \kappa^2_{1,1|1}/\kappa_{2|1}$. Now let us consider the consequences of the assumption that this conclusion is also true from the description by the corresponding sets of moments (the reverse of the problem treated in section 4). For the first moment this means that

$$\lim_{n\to\infty} \frac{1}{\sqrt{n}} \{{}^{(n)}\overset{-(m)}{G}_{n\bar N,n\bar V}(n\overset{-(c)}{H}_{\bar N,\bar V}(\beta)) - n\overset{-(c)}{G}_{\bar N,\bar V}(\beta)\} = 0, \tag{168}$$

which result implies (153) for $\mathscr{A}_N = \mathscr{G}_N$ (but is stronger). For the second moment we obtain in this way that (still for $E = n\overset{-(c)}{H}_{\bar N,\bar V}$)

$$\lim_{n\to\infty} \frac{1}{n} \overline{({}^{(n)}\mathscr{G}_{n\bar N} - n\overset{-(c)}{G}_{\bar N,\bar V})^2}^{(m)} = \lim_{n\to\infty} \frac{1}{n} \overline{({}^{(n)}\mathscr{G}_{n\bar N} - {}^{(n)}\overset{-(m)}{G}_{n\bar N,n\bar V})^2}^{(m)} =$$

$$= \overline{(\mathscr{G}_{\bar N} - \overset{-(c)}{G}_{\bar N,\bar V})^2}^{(c)} - \left\{\overline{(\mathscr{H}_{\bar N} - \overset{-(c)}{H}_{\bar N,\bar V})(\mathscr{G}_{\bar N} - \overset{-(c)}{G}_{\bar N,\bar V})}^{(c)}\right\}^2 \Big/ \overline{(\mathscr{H}_{\bar N} - \overset{-(c)}{H}_{\bar N,\bar V})^2}^{(c)}, \tag{169}$$

where also (168) has been used. We see that

$$\lim_{n\to\infty} \frac{\overline{({}^{(n)}\mathscr{G}_{n\bar N} - {}^{(n)}\overset{-(m)}{G}_{n\bar N,n\bar V})^2}^{(m)}}{({}^{(n)}\overset{-(m)}{G}_{n\bar N,n\bar V})^2} = 0, \tag{170}$$

indicating that the frequency function (61) is, for a separable system of a large number n of components, indeed very sharply peaked. On the basis of a more detailed version of (149), giving also the order of the remainder, Khinchin[5]) actually proved (168) and (169) for an arbitrary sum function in a direct, but very laborious way (the remainder for both limits being of the order $n^{-\frac{1}{2}}$).

§ 6. *Stability of the pair potential*[10]). Suppose that we have a real function φ of a real positive variable r, which is finite for all r. Then we may write

$$\sum_{\substack{i,j=1\\i<j}}^{N} \varphi(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \equiv \tfrac{1}{2} \sum_{i,j=1}^{N} \varphi(|\boldsymbol{r}_i - \boldsymbol{r}_j|) - \tfrac{1}{2}N\varphi(0) \equiv$$

$$\equiv \tfrac{1}{2}\int\int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'\varphi(|\boldsymbol{r} - \boldsymbol{r}'|)\, \nu_N(\boldsymbol{r}, \boldsymbol{r}^N)\, \nu_N(\boldsymbol{r}', \boldsymbol{r}^N) - \tfrac{1}{2}N\varphi(0), \tag{171}$$

where

$$\nu_N(\boldsymbol{r}, \boldsymbol{r}^N) = \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i). \tag{172}$$

Introducing the 3-dimensional Fourier transforms of φ and ν,

$$\hat{\varphi}(\boldsymbol{t}) = \int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-i\boldsymbol{t}\cdot\boldsymbol{r}}\, \varphi(|\boldsymbol{r}|), \tag{173}$$

$$\hat{\nu}_N(\boldsymbol{t}, \boldsymbol{r}^N) = \int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-i\boldsymbol{t}\cdot\boldsymbol{r}}\, \nu_N(\boldsymbol{r}, \boldsymbol{r}^N), \tag{174}$$

we have

$$\int\int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'\varphi(|\boldsymbol{r} - \boldsymbol{r}'|)\, \nu_N(\boldsymbol{r}, \boldsymbol{r}^N)\, \nu_N(\boldsymbol{r}', \boldsymbol{r}^N) =$$

$$= \frac{1}{(2\pi)^3} \int \mathrm{d}\boldsymbol{t}\hat{\varphi}(\boldsymbol{t})\, \hat{\nu}_N(\boldsymbol{t}, \boldsymbol{r}^N)\, \hat{\nu}_N(-\boldsymbol{t}, \boldsymbol{r}^N). \tag{175}$$

It follows from (173) that

$$\hat{\varphi}(\boldsymbol{t}) = 2\pi \int_0^\infty\int_0^\pi \mathrm{d}r\, \mathrm{d}\theta\, r^2 \sin\theta\, \mathrm{e}^{-i|\boldsymbol{t}|r\cos\theta}\, \varphi(r) = \frac{4\pi}{|\boldsymbol{t}|} \int_0^\infty \mathrm{d}r\, r \sin|\boldsymbol{t}|\, r\, .\, \varphi(r), \tag{176}$$

which expression implies that $\hat{\varphi}$ is a real function $\hat{\varphi}_1$ of $|\boldsymbol{t}|$. Furthermore we conclude from (172) and (174) that

$$\hat{\nu}_N(\boldsymbol{t}, \boldsymbol{r}^N) = \sum_{i=1}^{N} \mathrm{e}^{-i\boldsymbol{t}\cdot\boldsymbol{r}_i} = \hat{\nu}_N^*(-\boldsymbol{t}, \boldsymbol{r}^N), \tag{177}$$

(the star denoting complex conjugate). Now it is a consequence of (171), (175) and (177) that

$$\sum_{\substack{i,j=1\\i<j}}^{N} \varphi(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \geqslant -\tfrac{1}{2}N\varphi(0), \tag{178}$$

whenever

$$\hat{\varphi}_1(t) \geqslant 0 \quad \text{for all } t \quad (\geqslant 0). \tag{179}$$

Hence, if such a φ has also the property that

$$\varphi(r) \leqslant u(r) \quad \text{for all } r, \tag{180}$$

then the pair potential u is stable:

$$\sum_{\substack{i,j=1\\i<j}}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \geqslant - Nu_0 \quad \text{with} \quad u_0 = \tfrac{1}{2}\varphi(0). \tag{181}$$

It is possible to prove in this way that the Lennard-Jones type potential

$$u(r) \geqslant C_1 r^{-n} \quad \text{for} \quad r < a, \quad u(r) \geqslant -C_2 r^{-n} \quad \text{for} \quad r \geqslant a, \tag{182}$$

for certain positive constants C_1, C_2, n and a, is stable if $n > 3$. Consider

$$\varphi(r) = C_1(r^2 + \alpha^2)^{-n/2} - (C_1 + C_2)\, 2^{n/2}(r^2 + a^2)^{-n/2}, \tag{183}$$

where α is an arbitrary positive number. We have (since $r^2 + \alpha^2 > r^2$)

$$\varphi(r) < C_1 r^{-n} \quad \text{for all } r, \tag{184}$$

and (with $r^2 + a^2 \leqslant 2r^2$, or $r \geqslant a$)

$$\varphi(r) < C_1 r^{-n} - (C_1 + C_2)\, r^{-n} = -C_2 r^{-n} \quad \text{for} \quad r \geqslant a, \tag{185}$$

so that (180) is satisfied. For (176) we get

$$\hat{\varphi}_1(t) = C_1 \alpha^{3-n}\, G(\alpha t) - (C_1 + C_2)\, 2^{n/2}\, a^{3-n}\, G(at), \tag{186}$$

where (for $p \geqslant 0$)

$$G(p) = \frac{4\pi}{p} \int_0^\infty \mathrm{d}r\, r \sin pr \cdot (r^2 + 1)^{-\frac{1}{2}n} = \frac{2\pi}{\frac{1}{2}n - 1} \int_0^\infty \mathrm{d}r \cos pr \cdot (r^2 + 1)^{-\frac{1}{2}n+1}. \tag{187}$$

Using the expression (valid for $n > 2$)

$$\Gamma(\tfrac{1}{2}n - 1) = \int_0^\infty \mathrm{d}x\, \mathrm{e}^{-x}\, x^{\frac{1}{2}n-2}, \tag{188}$$

we find by means of Poisson's transformation [11]) that

$$G(p)\, \frac{\Gamma(\frac{1}{2}n)}{2\pi} = \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}x \cos pr \cdot (r^2 + 1)^{-\frac{1}{2}n+1}\, \mathrm{e}^{-x}\, x^{\frac{1}{2}n-2} =$$

$$= \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}y \cos pr \cdot \mathrm{e}^{-y(r^2+1)}\, y^{\frac{1}{2}n-2} = \tfrac{1}{2}\sqrt{\pi} \int_0^\infty \mathrm{d}y \exp\left\{-\frac{1}{4}\frac{p^2}{y} - y\right\} \cdot y^{\frac{1}{2}(n-5)}, \tag{189}$$

by writing $x = y(r^2 + 1)$, and changing the order of the integrations. We see that G is a positive and decreasing function of p, so that from (186) we conclude that also (179) is satisfied:

$$\hat{\varphi}_1(t) \geqslant \{C_1 \alpha^{3-n} - (C_1 + C_2)\, 2^{n/2}\, a^{3-n}\}\, G(at) \geqslant 0, \tag{190}$$

provided that we choose (with $n > 3$)

$$\alpha \leqslant \left\{ \frac{C_1}{(C_1 + C_2)\, 2^{n/2}} \right\}^{1/(n-3)} a, \tag{191}$$

(implying that $\alpha < a$). Hence we obtain from (182) the result (181) with

$$u_0 = \tfrac{1}{2} a^{-n}\, C_1 \left[\left\{ \frac{(C_1 + C_2)\, 2^{n/2}}{C_1} \right\}^{1+(3/n-3)} - \frac{(C_1 + C_2)\, 2^{n/2}}{C_1} \right] > 0. \tag{192}$$

Writing the stability property (181) as

$$\sum_{i=1}^{N} \{ \sum_{\substack{j=1\\ j\neq i}}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\} \geqslant -2Nu_0, \tag{193}$$

we see that, for each configuration $\boldsymbol{r}^N$,

$$\sum_{\substack{j=1\\ j\neq i}}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \geqslant -2u_0 \quad \text{for at least one index } i\,^{*)}. \tag{194}$$

On the basis of this consequence, Ruelle[10) 13)] has derived the thermodynamic limit behaviour (for all-sided expansion of a spherical volume V) of the grand canonical correlation functions $\rho^{(g)}_{M,V}(M = 1, 2, \ldots)$, using the Kirkwood-Salsburg integral equation for these functions, and the theory of linear operators. The functions $\rho^{(g)}_{M,V}$ are defined by

$$\rho^{(g)}_{M,V}(\beta, \mu; \boldsymbol{r}^M) = \frac{1}{\Xi_V(\beta, \mu)} \sum_{N=0}^{\infty} \frac{e^{-\mu(M+N)}}{N!} \int \mathrm{d}\boldsymbol{r}^{(N)} \exp\{-\beta \mathscr{U}_{M+N}(\boldsymbol{r}^{M+N})\}, \tag{195}$$

where $\boldsymbol{r}^{(N)} \equiv (\boldsymbol{r}_{M+1}, \ldots, \boldsymbol{r}_{M+N})$, and Ξ_V is given by (87) with (85) and (67). It follows that

$$\int \mathrm{d}\boldsymbol{r}_1\, \rho^{(g)}_{1,V}(\beta, \mu; \boldsymbol{r}_1) = -\frac{\partial \log \Xi_V(\beta, \mu)}{\partial \mu}, \tag{196}$$

---

*) Penrose[12)] has shown for a hard core potential (a special case of (182)): $u(r) = \infty$ for $r < a$, $u(r) \geqslant -C_2 r^{-n}$ for $r \geqslant a$, with $n > 3$, that there exists a constant u_0' such that

$$\sum_{\substack{j=1\\ j\neq i}}^{N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \geqslant -2u_0' \text{ if } \sum_{\substack{j,k=1\\ j\neq k\neq i}}^{N} u(|\boldsymbol{r}_j - \boldsymbol{r}_k|) < \infty.$$

and consequently Ruelle[13]) has also been able to prove in this context that $-V^{-1}\,\partial \log \Xi_V/\partial\mu$ tends uniformly to a limit for $V \to \infty$ and $\mu > 2\beta u_0 + 1 + \log C$, where

$$C(\beta) \equiv \int \mathrm{d}\boldsymbol{r}\,|\mathrm{e}^{-\beta u(|\boldsymbol{r}|)} - 1|. \tag{197}$$

(According to Ruelle[10]), C is finite for a stable and strongly tempered potential, *i.e.* with

$$u(r) \leqslant 0 \quad \text{for} \quad r \geqslant r_0, \tag{198}$$

in addition to (181)). Two other conclusions may be drawn from this result: for $\mu > 2\beta u_0 + 1 + \log C$ there are no first order phase transitions and (integrating with respect to μ) $V^{-1} \log \Xi_V$ tends for $V \to \infty$ uniformly to a limit:

$$\lim_{V\to\infty} \frac{1}{V} \log \Xi_V(\beta, \mu) = p^{(\mathrm{g})}(\beta, \mu). \tag{199}$$

The latter limit, however, can be established directly from (181) and (198) for all μ, by means of the limit theorem for subadditive functions (see Ch. I section 3; Ruelle[10]) gives a derivation for all-sided expansion of a cubical volume V). Then it is interesting to investigate whether both sides of (199) may again be differentiated with respect to μ:

$$\lim_{V\to\infty} \frac{1}{V} \frac{\partial^p \log \Xi_V(\beta, \mu)}{\partial\mu^p} = \frac{\partial^p p^{(\mathrm{g})}(\beta, \mu)}{\partial\mu^p} \quad \text{for} \quad p \geqslant 1. \tag{200}$$

There exist two different approaches to this problem, both confirming (200), except at phase transition points: one, due to Griffiths[14]), concerns the case $p = 1$ and excludes only first order transitions, the other, due to Yang and Lee[15]) and improved by Lewis and Siegert[16]) and Penrose[12]), establishes (200) for all p outside transitions of any order. The application of Griffiths' theorem (the proof of which is reproduced in the Appendix) is based on the fact that (*cf.* (150))

$$\frac{\partial^2 \log \Xi_V(\beta,\mu)}{\partial\mu^2} = \overline{(N - \overline{N_V}^{(\mathrm{g})})^2}^{(\mathrm{g})} > 0, \tag{201}$$

and is quite straightforward. According to the ideas of Yang and Lee, we must study the intricate properties of the function

$$\Xi_V(\beta, \mu - \log(1 + w\,\mathrm{e}^{\mu})) = \sum_{N=0}^{\infty} (\mathrm{e}^{-\mu} + w)^N\, \Phi_N(\beta, V) \tag{202}$$

for complex w, using the fact that it is an entire function of w*).

*) In fact Yang and Lee[15]) considered the case of a hard-core potential, for which $\Phi_N = 0$ for N larger than a certain value $N_V^{(0)}$ satisfying $N_V^{(0)} < V/(4\pi/3)\,(\frac{1}{2}a)^3$.
Then (202) is a polynomial in w, and can be treated in a more simple way than in the general case.

Since we have, with (181),

$$|\Xi_V(\beta, \mu - \log(1 + w\,e^{\mu}))| \leqslant \exp\left\{\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} V(e^{-\mu} + |w|)\,e^{\beta u_0}\right\}, \tag{203}$$

the order of the entire function (202) is smaller than or equal to one. (According to Ruelle[17]) the order is actually zero for potentials to which a function φ may be found satisfying (180), and (179) with in particular $\hat{\varphi}_1(0) > 0$. This is indeed the case for the Lennard-Jones type potential (182) with (183)). The partial derivative of the function (202) with respect to w at $w = 0$ is found to be equal to $\exp \mu$ times the function $-\partial \log \Xi_V/\partial\mu$, which is negative and, noting (201), decreasing in μ. Hence, choosing a value $\mu' > \mu$ in the region where, according to the result stated above, (200) always holds for $p = 1$, we may write for some $\varepsilon > 0$ and V large enough, that

$$0 > \left(\frac{\partial \log \Xi_V(\beta, \mu - \log(1 + w\,e^{\mu}))}{\partial w}\right)_{w=0} > -e^{\mu}\frac{\partial \log \Xi_V(\beta, \mu')}{\partial \mu'} >$$

$$> -e^{\mu} V\left(\frac{\partial p^{(g)}(\beta, \mu')}{\partial \mu'} + \varepsilon\right). \tag{204}$$

Now we will prove in the appendix a theorem to the effect that, if we consider a point μ with the property that a positive number R may be found such that

$$\Xi_V(\beta, \mu - \log(1 + w\,e^{\mu})) \neq 0 \text{ for } |w| \leqslant R(\beta, \mu) \quad \text{and all } V, \tag{205}$$

then we may conclude, on the basis of (199) and the inequalities $\Xi_V \geqslant 1$ for $w = 0$, (203) and (204), that

$$\lim_{V\to\infty} \frac{1}{V} \log \Xi_V(\beta, \mu - \log(1 + w\,e^{\mu})) = p^{(g)}(\beta, \mu - \log(1 + w\,e^{\mu}))$$

$$\text{for } |w| < R(\beta, \mu), \tag{206}$$

uniformly in w. This result implies that (200) holds for all p in such a point μ. Note that the points μ with the property (205) are apparently not phase transition points of any (finite) order, but on the other hand it is not excluded that points where $p^{(g)}$ is indefinitely differentiable with respect to μ, yet do not have this property (205) (we should call this possibility transitions of infinite order). Whereas we know from the convexity of $p^{(g)}$ in μ that the first order transition points are only countable (*i.e.* finite or denumerable) in number, nothing of this kind is known for the higher order transitions of a real system.

When a sequence of real convex functions $\varphi_n(x)(n \to \infty, x$ real) tends to a limit

$$\lim_{n\to\infty} \varphi_n(x) = \varphi(x), \tag{A 1}$$

then the limit function $\varphi(x)$ is also convex, or, in other words, the first derivatives $\varphi_n'(x)(n \to \infty)$ and $\varphi'(x)$ are all increasing, each one with at most a countable number of jump discontinuities. Moreover, as will be shown here, we have

$$\lim_{n\to\infty} \varphi_n'(x) = \varphi'(x) \tag{A 2}$$

at every point where $\varphi'(x)$ is continuous (Griffiths' theorem[14]); the discreteness of the variable n in this appendix is not essential, it may be made continuous without any restrictions).

Proof: Suppose that $\varphi'(x)$ is continuous for $x = x_0$, but that (A 2) does not hold at this point: in particular, assume that there is a number $\varepsilon > 0$ such that

$$\varphi'(x_0) - \varphi_n'(x_0) > \varepsilon \tag{A 3}$$

for arbitrarily large values of n. This assumption will appear to contradict (A 1), Since $\varphi'(x)$ is continuous at x_0, we may find a number $\delta > 0$ such that

$$|\varphi'(x) - \varphi'(x_0)| \leqslant \tfrac{1}{2}\varepsilon \quad \text{if} \quad |x - x_0| \leqslant \delta(\varepsilon). \tag{A 4}$$

Now, as $\varphi_n'(x)$ is increasing, (A 3) and (A 4) imply that

$$\varphi'(x) - \varphi_n'(x) > \varphi'(x) - \varphi_n'(x_0) \geqslant \tfrac{1}{2}\varepsilon \quad \text{for} \quad x_0 - \delta(\varepsilon) \leqslant x \leqslant x_0. \tag{A 5}$$

Integration of both sides of this inequality from $x_0 - \delta$ to x_0 yields

$$\{\varphi(x_0) - \varphi_n(x_0)\} - \{\varphi_n(x_0 - \delta) - \varphi(x_0 - \delta)\} \geqslant \tfrac{1}{2}\delta(\varepsilon)\,\varepsilon, \tag{A 6}$$

(still for arbitrarily large values of n), so that $\varphi_n(x)$ does not converge to $\varphi(x)$ either at x_0 or at $x_0 - \delta$. In the same way (considering $x_0 \leqslant x \leqslant x_0 + \delta$) the assumption that $\varphi'(x_0) - \varphi_n'(x_0) < -\varepsilon$ for arbitrarily large values of n leads to a contradiction, and we conclude that (A 2) is satisfied for $x = x_0$.

The step from (A 5) to (A 6) uses the fact that a convex function is absolutely continuous and hence equal to the primitive function of its first derivative. A proof which does not invoke this absolute continuity property has been found by Fisher[18]).

Consider next a sequence of complex functions $\varphi_n(w)(n \to \infty, w$ complex) which converges for real values of w. Let $\exp n\varphi_n(w)$ be an entire function of order $\leqslant 1$, to which independent of n a positive constant R may be found such that it does not vanish for $|w| \leqslant R$. From the theory of entire functions[19]) we apply Hadamards' factorization theorem and Jensen's formula. If the order of the entire function $\exp n\varphi_n(w)$ is less than one, its factorization is

$$\exp n\varphi_n(w) = \exp n\varphi_n(0) \cdot \prod_{k=1}^{\infty} (1 - w/w_{k,n}), \tag{A 7}$$

where the $w_{k,n}$ $(k = 1, 2, \ldots)$ are its zeros, with, as assumed,

$$|w_{k,n}| > R > 0 \quad \text{for all } k \text{ and } n. \tag{A 8}$$

Comparing the power series expansion in w for $\varphi_n(w)$ following from (A 7), with the Taylor expansion of $\varphi_n(w)$ around the origin,

$$\varphi_n(w) = \sum_{p=0}^{\infty} w^p \varphi_n^{(p)}(0)/p! \tag{A 9}$$

(which has a radius of convergence at least equal to R), we find that

$$\varphi_n^{(p)}(0)/p! = -\frac{1}{pn} \sum_{k=1}^{\infty} w_{k,n}^{-p}, \qquad p \geqslant 1. \tag{A 10}$$

Using this relation for $p = 1$, (A 7) may also be written as

$$\exp n\varphi_n(w) = \exp n\{\varphi_n(0) + w\varphi_n'(0)\} \cdot \prod_{k=1}^{\infty} (1 - w/w_{k,n}) \exp(w/w_{k,n}), \tag{A 11}$$

in which form it is also the proper factorization if the order is equal to one (and (A 9) is only known to hold for $p \geqslant 2$). From Jensen's formula we derive the inequality

$$\int_R^r \frac{Z_n(r')}{r'} \, \mathrm{d}r' \leqslant \max_{|w|=r} \log |\exp n\{\varphi_n(w) - \varphi_n(0)\}|, \tag{A 12}$$

where $Z_n(r)$ is the number of the zeros $w_{k,n} (k = 1, 2, \ldots)$ with $|w_{k,n}| \leqslant r$ (and hence, according to (A 8), vanishing for r smaller than at least the value R). Now if for positive constants C_1, C_2 and C_3 we have that

$$|\exp n\{\varphi_n(w) - \varphi_n(0)\}| \leqslant \exp n(C_1 + C_2 |w|) \text{ for all } n \text{ and } w \tag{A 13}$$

(a more detailed statement of the fact that $\exp n\varphi_n(w)$ is entire of order $\leqslant 1$) and

$$|\varphi_n'(0)| \leqslant C_3 \quad \text{for all } n, \tag{A 14}$$

then the limit

$$\lim_{n\to\infty} \varphi_n(w) = \varphi(w) \quad \text{for real } w \tag{A 15}$$

may be extended to complex values of w:

$$\lim_{n\to\infty} \varphi_n(w) = \varphi(w) \quad \text{for} \quad |w| < R, \tag{A 16}$$

uniformly.

Proof: From (A 12) and (A 13) it follows, using also the fact that $Z_n(r)$ is positive and increasing in r, that

$$Z_n(r) \equiv Z_n(r) \int_r^{er} \frac{dr'}{r'} \leqslant$$

$$\leqslant \int_r^{er} \frac{Z_n(r')}{r'} dr' \leqslant \int_R^{er} \frac{Z_n(r')}{r'} dr' \leqslant n(C_1 + C_2 \,e\, r). \tag{A 17}$$

For the absolute values of the coefficients in the power series (A 9) we have, according to (A 10), the inequality

$$|\varphi_n^{(p)}(0)/p!| \leqslant \frac{1}{pn} \sum_{k=1}^{\infty} |w_{k,n}|^{-p} \equiv \frac{1}{pn} \int_R^{\infty} r^{-p}\, dZ_n(r). \tag{A 18}$$

Here the Stieltjes integral may be integrated by parts if $p \geqslant 2$ (then the term at the upper boundary vanishes because of (A 17)), and with (A 17) we obtain

$$|\varphi_n^{(p)}(0)/p!| \leqslant \frac{1}{n} \int_R^{\infty} r^{-p-1} Z_n(r)\, dr < \frac{C_1}{pR^p} + \frac{C_2 \,e}{(p-1)\, R^{p-1}}, \quad p \geqslant 2. \tag{A 19}$$

Consequently we have, using also (A 14),

$$|\varphi_n(w) - \varphi_n(0)| \leqslant C_3 |w| + \sum_{p=2}^{\infty} \left\{ \frac{C_1}{p} + \frac{C_2 \,eR}{p-1} \right\} \left(\frac{|w|}{R} \right)^p \quad \text{for} \quad |w| < R, \tag{A 20}$$

or choosing a number ϑ between 0 and 1,

$$|\varphi_n(w) - \varphi_n(0)| \leqslant C_3 \vartheta R + (C_1 + C_2 \,eR) \frac{\vartheta^2}{1-\vartheta} \quad \text{for} \ |w| \leqslant \vartheta R. \tag{A 21}$$

Hence the sequence of functions $\varphi_n(w) - \varphi_n(0) (n \to \infty)$, which according to (A 15) converges to $\varphi(w) - \varphi(0)$ on the part of the real axis contained in the circle $|w| = R$, is also uniformly bounded in the interior of this circle. In these circumstances the Vitali convergence theorem [19]) may be applied, giving

$$\lim_{n\to\infty} \{\varphi_n(w) - \varphi_n(0)\} = \varphi(w) - \varphi(0) \quad \text{for} \quad |w| \leqslant \vartheta R \tag{A 22}$$

uniformly, which result implies (A 16).

The step from (A 15) and (A 21) to (A 22) was performed explicitly in the work of Yang and Lee[15]. Then Lewis and Siegert[16] realized that the Vitali convergence theorem could be applied (their treatment, considering the case of the "pressure" formalism, is, however, unsatisfactory). The use of Jensen's formula we owe to Penrose[12].

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SAMENVATTING

In hoofdstuk I worden een aantal thermodynamische-limietproblemen onderzocht op grond van zeer algemene veronderstellingen omtrent de wisselwerking („stabiliteit" en „sterke afneming"). Hiermee wordt een bijdrage geleverd tot de fundering van de statistische thermodynamica. Na de inleidende paragrafen 1 en 2, volgt in 3 en 4 als belangrijkste onderdeel het aantonen van de gelijkwaardigheid van het microkanonieke, het kanonieke en het grootkanonieke formalisme. De bewijsmethode is een synthese van ideeën van Fisher (gebruikmaking van de limietstelling voor subadditieve functies) en Khinchin (toepassing van het centrale-limiettheorema uit de waarschijnlijkheidstheorie). In gewijzigde vorm wordt deze methode in paragraaf 5 aangewend voor het vaststellen van de asymptotische waarde van de microkanonieke temperatuur. Paragraaf 6 geeft een terugblik op de ontwikkeling van het onderwerp sinds Khinchin's behandeling. In de appendix wordt een hulpstelling bewezen.

In hoofdstuk II komen een aantal onderwerpen aan de orde die verband houden met het in hoofdstuk I behandelde probleem. In paragraaf 1 wordt de benodigde kennis van de thermodynamica uiteengezet. De paragrafen 2 en 3 dienen om het beeld van het vraagstuk omtrent de fundering van de klassieke statistische physica volledig te maken. Paragraaf 4 geeft, op grond van algemene limiettheorema's uit de waarschijnlijkheidstheorie, de wiskundige voorbereiding op de (gedeeltelijk nieuwe) behandeling van Khinchin's asymptotische resultaten voor een separabel systeem, die in paragraaf 5 volgt. In paragraaf 6 en de appendix worden enige resultaten van de recente ontwikkeling op het gebied van thermodynamische-limietproblemen, in min of meer bewerkte vorm weergegeven.

Teneinde te voldoen aan het verzoek van de faculteit der Wiskunde en Natuurwetenschappen, volgt hier een overzicht van mijn studie.

In 1952, na het behalen van het diploma H.B.S.-*B* aan het Groen van Prinsterer Lyceum te Vlaardingen, begon ik mijn studie in de faculteit der Wiskunde en Natuurwetenschappen aan de Rijksuniversiteit te Leiden. In juli 1955 legde ik het candidaatsexamen (richting *a*) af, en in april 1958 slaagde ik voor het doctoraalexamen theoretische natuurkunde. In de periode tussen beide examens deed ik ook praktisch werk, tot januari 1957 op het Kamerlingh Onnes Laboratorium, en daarna op het Instituut-Lorentz. Dit betrof onderzoek op het gebied van, respectievelijk, de paramagnetische relaxatie en de thermodynamica der irreversible processen.

Mijn werkzaamheden op het Instituut-Lorentz als wetenschappelijk medewerker van de Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.-werkgroep M VI), zette ik sedertdien onder leiding van Prof. Dr. P. Mazur voort, met onderzoek omtrent de grondslagen van de statistische physica. De recente resultaten hiervan werden beschreven in dit proefschrift.

Publicaties:

On the canonical distribution in quantum statistical mechanics
J. van der Linden and P. Mazur, Physica 27 (1961) 609.

Asymptotic form of the structure function for real systems
P. Mazur and J. van der Linden, J. math. Phys. 4 (1963) 271.

On the asymptotic problem of statistical thermodynamics for a real system
J. van der Linden, Physica (wordt gepubliceerd).

Teneinde te voldoen aan het verzoek van de faculteit der Wiskunde en Natuurwetenschappen, volgt hier een overzicht van mijn studie.

Na in 1932 na het behalen van het diploma H.B.S. [illegible] aan het [illegible] te Vlaardingen, begon ik mijn studie in de faculteit der Wiskunde en Natuurwetenschappen aan de Rijksuniversiteit te Leiden. In juli 1935 legde ik het candidaatsexamen (richting a) af en in april 1939 slaagde ik voor het doctoraalexamen theoretische natuurkunde. In de tussenliggende tijd [illegible] werk, tot januari 1937 op het Kamerlingh Onnes Laboratorium, te [illegible] op het Instituut-Lorentz. Dit betrof onderzoek op het gebied van [illegible] en de thermodynamica der irreversibele processen.

[illegible]

[illegible]

STELLINGEN

I

De thermodynamische limiet van de mikrokanonieke temperatuur voor een reëel systeem bestaat, en heeft de vereiste eigenschappen.

Dit proefschrift, hoofdstuk I § 5.

II

De gelijkwaardigheid van het mikrokanonieke en het kanonieke phasegemiddelde van een somfunctie voor een separabel systeem, kan eenvoudig aangetoond worden m.b.v. een generalisatie van Khinchin's asymptotische evaluatie van de structuurfunctie van een dergelijk systeem.

A. I. Khinchin, Mathematical Foundations of Statistica Mechanics.
Dit proefschrift, hoofdstuk II § 5.

III

De stelling van Dini voor een monotone rij van functies geldt ook voor een rij $\{\varphi_N(x)\}$ met de eigenschap dat

$$N\varphi_N(x) \geqslant N_1\varphi_{N_1}(x) + (N - N_1)\,\varphi_{N-N_1}(x) \quad \text{als} \quad N \geqslant N_1.$$

Dit proefschrift, hoofdstuk I appendix.

IV

Griffiths' bewijs van de gelijkwaardigheid van het mikrokanonieke en het kanonieke formalisme in de quantumstatistische thermodynamica voor een reëel systeem, is gedeeltelijk onbevredigend. Het bezwaar ertegen kan echter opgeheven worden door gebruik te maken van de voorgaande stelling.

R. B. Griffiths, J. math. Phys. **6** (1965) 1447.

V

De mogelijkheid van een pseudo-klassieke behandeling (m.b.v. Wignerdistributiefuncties) van het asymptotische probleem in de quantumstatistica, zoals verwezenlijkt voor een separabel systeem, komt niet in aanmerking voor een reëel systeem.

J. van der Linden and P. Mazur, Physica **27** (1961) 609.

VI

De bewering van Münster dat de door hem beschouwde statistische functies $\Xi_{l+1}(z)$ voor *alle* waarden van l gehele functies zijn, is onjuist.

A. Münster, Z. Physik **136** (1953) 179; zie ook p. 384 in: S. Flügge, Handbuch der Physik III/2.

VII

Het argument van Landau en Lifshitz, dat in een 1-dimensionaal systeem evenwicht tussen twee verschillende homogene fasen onmogelijk zou zijn, is niet steekhoudend.

L. D. Landau en E. M. Lifshitz, Statistical Physics (p. 482).

VIII

De behandeling die Glarum geeft van de diëlectrische relaxatie in polaire vloeistoffen bevat een verband tussen het in- en het uitwendige macroscopische wisselveld, dat microscopisch gerechtvaardigd moet en kan worden.

S. H. Glarum, J. chem. Phys. **33** (1960) 1371.

IX

Symmetrie-overwegingen en Onsager-relaties sluiten een kruis-effect tussen warmtegeleiding en viscositeit niet uit voor gassen bestaande uit niet-bolvormige molekulen, geplaatst in een magneetveld. Om te zien of dit effect een meetbare orde van grootte heeft, is het van belang het werk van Kagan en Maksimov uit te breiden.

S. R. de Groot and P. Mazur, Non-equilibrium Thermodynamics.
Y. Kagan and L. Maksimov, Soviet Phys. J.E.T.P. **14** (1962) 604.

X

Het door Van Leeuwen gegeven beeld van de wereldgeschiedenis is verwant met de ideeën omtrent de algemene evolutie van Teilhard de Chardin.

A. Th. van Leeuwen, Christianity in World History.
Teilhard de Chardin, Het verschijnsel mens.

VI

De bewering van Münster dat de door hem beschouwde statistische functies $\Sigma_{11}(t)$ voor alle waarden van t gehele functies zijn, is onjuist.

A. Münster, Z. Physik 136 (1953) 179; zie ook p. 204 in S. Flügge, Handbuch der Physik III/2.

VII

Het argument van Landau en Lifshitz, dat in een 1-dimensionaal systeem evenwicht tussen twee verschillende homogene fasen onmogelijk zou zijn, is niet steekhoudend.

L. D. Landau en E. M. Lifshitz, Statistical Physics p. 482.

VIII

De behandeling die Glarum geeft van de dielectrische relaxatie in polaire vloeistoffen bevat een verband tussen het in- en het uitwendige macroscopische veld, dat microscopisch gerechtvaardigd moet en kan worden.

G. H. Glarum, J. Chem. Phys. 33 (1960) 1371.

IX

Symmetrie-overwegingen, als Onsager-relaties, sluiten een kruis-effect tussen warmtegeleiding en viscositeit niet uit voor gassen bestaande uit niet-bolvormige moleculen, geplaatst in een magneetveld. Om te zien of dit effect een meetbare orde van grootte heeft, is het van belang het werk van Kagan en Maksimov uit te breiden.

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