Statistical Foundations of Thermodynamics

II. Equivalence Problem. Stability Conditions

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(Z. Naturforsch. 24 a, 412-417 [1969]; received 19 November 1968)

On the basis of the results obtained in a previous paper it is shown that in the thermodynamic limit the analogues of the Massieu-Planck functions are linked with each other by means of the Legendre transformation. The existence of the limiting function $\varphi_k^{(\infty)}$ implies the existence of the limiting function $\varphi_l^{(\infty)}$ $(l \le k)$ under the same assumptions. Passage to the limit and derivation with respect to all independent variables commute. A statistical derivation of the thermodynamic stability condition in its most general form is given which leads naturally to a statistical interpretation of the concept of thermodynamic stability.

For the microcanonical ensemble the first independent proof of a limit theorem has been given by VAN DER LINDEN¹. The proof is based on the assumption that the potential of the intermolecular forces satisfies the conditions of "stability" and "strong tempering" (for the definition of these concepts which is not needed in what follows we refer to the literature 1-3). It is shown that this limit theorem generates analogous limit theorems for the canonical and the grand canonical ensembles and furthermore that these ensembles, at the thermodynamic limit, are thermodynamically equivalent. In a recent paper³ the method has been improved and generalized to cover all conceivable ensembles of statistical thermodynamics. Moreover, under the stronger assumption of twobody central forces satisfying an additional condition, VAN DER LINDEN⁴ has proved that, for the canonical ensemble, passage to the thermodynamic limit commutes with differentiation with respect to the volume.

Several questions, however, still remain open. First of all it is known⁵ that for the canonical and grand canonical ensembles limit theorems hold under the condition of "weak tempering". It is hardly believable that limit theorems, for the remaining ensembles require stronger assumptions. Secondly the assumption of strong tempering enters explicitly into the proofs of the equivalence whereas, according to the earlier work of MAZUR and VAN DER LIN-

- ² A. MÜNSTER, Statistical Thermodynamics, 2nd ed., Springer Academic Press, New York (in press).
- ³ J. VAN DER LINDEN and P. MAZUR, Physica 36, 491 [1967].
- J. VAN DER LINDEN, Physica 38, 173 [1968].
 M. E. FISHER, Arch. Rat. Mech. Anal. 17, 377 [1964].
- ⁶ P. MAZUR and J. VAN DER LINDEN, J. Math. Phys. 4, 271 [1963].

DEN⁶ and FISHER⁵ we are to expect that on the basis of the limit theorems the equivalence is merely an asymptotic property of the Laplace transformation. Similarly it seems rather improbable that commutability of passage to the limit and differentiation with respect to an extensive parameter (which is needed for a complete statistical foundation of thermodynamics¹) requires stronger assumptions than the limit theorem itself. Finally we note that in reality thermodynamics is always applied to finite systems. Therefore the limits of validity of thermodynamic concepts can be defined only if the asymptotic properties appear as leading terms of asymptotic expansions as yielded e.g. by the Darwin-Fowler method² or by Khinchin's method⁷.

In this paper we shall treat the equivalence problem and related questions without using explicitly assumptions about the intermolecular forces. In other words we shall show that these assumptions enter into the statistical foundation of thermodynamics only via a limit theorem while the thermodynamic formalism itself then follows from the asymptotic properties of the Laplace transformation whatever may be the assumptions made in the proof of the limit theorem. In doing this we shall use the generalisation of Khinchin's method developed in a previous paper⁸ which will enable us to answer the aforementioned questions.

¹ J. VAN DER LINDEN, Physica 32, 642 [1966].

⁷ A. J. KHINCHIN, Mathematical Foundations of Statistical Mechanics, Dover Publ. Inc., New York 1949.

E. STILL, K. HAUBOLD, and A. MÜNSTER, Z. Naturforsch. 24 a, 201 [1969]. In the following this paper will be referred to as paper I. Numbers of sections, theorems and equations will be quoted as, for instance, (I.3).

In § 1 we treat the equivalence problem itself. § 2 is devoted to the study of the derivatives of the Massieu-Planck functions. Finally in § 3 we derive the general form of the thermodynamic stability conditions. It will be shown that the concept of thermodynamic stability is equivalent to a stipulation on fluctuations of extensive parameters.

As shown in paper I the method implies the use of smoothed quantities defined in § I 4. It will be shown in the last section that there is no loss of generality in doing this. For the sake of simplicity, therefore, we shall not introduce a special notation for the smoothed quantities. For the rest we shall use the notation of paper I.

1. Equivalence Problem

Thermodynamic equivalence of various ensembles means that the functions φ_k defined by Eq. (I.1) and (I.11) are Legendre transforms from each other. This cannot be true in general since the corresponding partition functions are Laplace transforms from each other. Hence we prove the following

Theorem 1

a. Under assumption I l – I 3 the limit function $\varphi_l^{(\infty)}$ exists and is linked with $\varphi_k^{(\infty)}$ by means of the Legendre transformation

$$\varphi_k^{(\infty)} = \varphi_l^{(\infty)} - \sum_{i=l+1}^k P_i \, \bar{x}_i \,, \, (k > l) \tag{1}$$

b. $\varphi_l^{(\infty)}$ is a continuous function of all \bar{x}_i the derivatives of which with respect to the \bar{x}_i exist almost every where.

c. For sufficiently large *n* we have

$$\varphi_l^{(n)} = \varphi_k^{(n)} + \sum_{i=l+1}^k P_i \, \bar{x}_i + O(n^{-1} \ln^2 n) \,. \tag{2}$$

Proof

We start from Eq. (I.28) which for $\mathbf{X} = \overline{\mathbf{X}}$ may be rewritten

$$\Phi_{l}^{(n)} = \Phi_{k}^{(n)} + \sum_{i=l+1}^{k} P_{i} \overline{X}_{i} + \ln W^{(n)} [\overline{\boldsymbol{X}}, \boldsymbol{P}(\overline{\boldsymbol{X}})].$$
(3)

From (I.51) we have

$$\ln W^{(n)}(\overline{\mathbf{X}}) = -\frac{1}{2} \ln |B^{(n)}| + \ln [1 + (4)] O(n^{-1} \ln^2 n)] - \frac{1}{2} (k-l) \ln 2 \pi$$

and from assumption I 3

$$|B^{(n)}| = O(n^{k-l}).$$
 (5)

Thus

 $\ln W^{(n)}(\overline{\mathbf{X}}) = O(\ln n).$ (6)

From (3) and (6) Eq. (2) follows immediately.

Taking account of asumption I 1 we can pass to the limit $n \to \infty$ which yields (1) and, at the same time, proves the existence of $\varphi_l^{(\infty)}$ under the assumptions underlying the limit theorem for $\varphi_l^{(\infty)}$.

Finally continuity and existence of the derivatives follow from the corresponding properties of $\varphi_k^{(\infty)}$ and the fact that, if we disregard phase transitions (assumption I 2) and jump discontinuities of the functions $P_i(\bar{x}_i)$ (assumption I 3), we have a oneto-one correspondence between the vectors $\overline{\mathbf{X}}$ and \mathbf{P} .

2. Derivatives of the Function φ_l

Let us now turn to the derivatives of $\varphi_l^{(\infty)}$ with respect to extensive as well as intensive parameters. It will be shown that, within the domain of regularity of $\varphi_k^{(\infty)}$ (assumption I 2), the first and second derivatives exist and that in the thermodynamic limit order of differentiation and passage to the limit may be interchanged. To do this we first prove

$Theorem \ 2$

For sufficiently large n the following relations hold

$$\frac{\partial \varphi_l^{(n)}}{\partial \bar{x}_i} = P_i + O(n^{-1}), \quad (i = l+1, \dots, k)$$
(7)

$$\begin{bmatrix} \frac{\partial^2 \varphi_l^{(n)}}{\partial \bar{x}_i \partial \bar{x}_j} \end{bmatrix} = -\begin{bmatrix} \frac{\partial^2 \varphi_k^{(n)}}{\partial P_i \partial P_j} \end{bmatrix}^{-1} + \begin{bmatrix} O(n^{-1})_{ij} \end{bmatrix}, \quad (8)^{-9}$$
$$(i, j = l+1, \dots, k)$$

$$\frac{\partial \varphi_l^{(n)}}{\partial P_i} = \frac{\partial \varphi_k^{(n)}}{\partial P_i} + O(n^{-1}), \quad (i = 1, \dots, l)$$
(9)

$$\frac{\partial^2 \varphi_l^{(n)}}{\partial P_i \partial P_j} = \frac{\partial^2 \varphi_k^{(n)}}{\partial P_i \partial P_j} + O(n^{-1}), \ (i, j = 1, \dots, l) \ (10)$$

Proof

We start again from Eq. (3). First we note that $\Phi_l^{(n)}$ depends explicitly and through the P_i implicitly on the \overline{X}_i . Thus, taking into account (I 4), we ob-

⁹ Note that (8) is a matrix equation.

tain

$$\frac{\partial \Phi_l^{(n)}}{\partial \overline{X}_i} = P_i + \frac{\partial \ln W^{(n)}}{\partial \overline{X}_i}.$$
 (11)

It follows

$$\frac{\partial^2 \Phi_l^{(n)}}{\partial \overline{X}_i \partial \overline{X}_j} = \frac{\partial P_i}{\partial \overline{X}_j} + \frac{\partial^2 \ln W^{(n)}}{\partial \overline{X}_i \partial \overline{X}_j} \,. \tag{12}$$

This may be rewritten

$$\left[\frac{\partial^2 \Phi_l^{(n)}}{\partial \overline{X}_i \partial \overline{X}_j}\right] = -\left[\frac{\partial^2 \Phi_k^{(n)}}{\partial P_i \partial P_j}\right]^{-1} + \left[\frac{\partial^2 \ln W^{(n)}}{\partial \overline{X}_i \partial \overline{X}_j}\right]$$
(13)

where properties of Jacobians have been used.

Now $W^{(n)}(\overline{X})$ only depends on \overline{X} through P. Therefore, using the principal axes representation ¹⁰, we have

$$\frac{\partial \ln W^{(n)}}{\partial \overline{X}_i} = -\frac{1}{2} |B^{(n)}|^{-1} \sum_{m=l+1}^k \frac{\partial |B^{(n)}|}{\partial \widehat{P}_m} \frac{\partial \widehat{P}_m}{\partial \overline{X}_i} \quad (14)$$
$$+ [1 + O(n^{-1} \ln^2 n)]^{-1} \sum_{m=l+1}^k \frac{\partial O(n^{-1} \ln^2 n)}{\partial \widehat{P}_m} \frac{\partial \widehat{P}_m}{\partial \overline{X}_i}.$$

From the properties of Jacobians we have

$$\begin{bmatrix} \frac{\partial \hat{P}_m}{\partial \overline{X}_i} \end{bmatrix} = \begin{bmatrix} \frac{\partial^2 \Phi_k^{(n)}}{\partial \hat{P}_m^2} \end{bmatrix}^{-1} \cdot \begin{bmatrix} \frac{\partial \overline{\hat{X}}_m}{\partial \overline{X}_i} \end{bmatrix}.$$
 (15)

The tensor components $\partial \overline{\hat{X}} / \partial \hat{X}_i$ represent a rotation in the $\overline{\mathbf{X}}$ -space. Thus

$$\frac{\Im \overline{X}_m}{\Im \overline{X}_i} \leq 1 \tag{16}^{11}$$

Taking account of assumption I 2 we then have

$$\frac{\partial \hat{P}_m}{\partial \bar{X}_i} = O(n^{-1}). \tag{17}$$

In addition we find

$$\frac{\partial |B^{(n)}|}{\partial \hat{P}_m} = O(n^{k-l}).$$
(18)

Finally we have (in the symbolic notation already used above)

$$\sum_{m=l+1}^{k} \frac{\partial O(n^{-1}\ln^2 n)}{\partial \hat{P}_m} \frac{\partial \hat{P}_m}{\partial \overline{X}_i} = O(n^{-2}\ln^2 n).$$
(19)

Here we have used (17). From Eqs. (5) and (14) to (18) we obtain

$$\frac{\partial \ln W^{(n)}}{\partial \overline{X}_i} = O(n^{-1}). \tag{20}$$

¹⁰ Vector components in the principal axes representation will be denoted by ^. In an analogous way we can show that

$$\frac{\partial^2 \ln W^{(n)}}{\partial \overline{X}_i \partial \overline{X}_j} = O(n^{-2}).$$
(21)

Equation (7) follows from (11) and (20), whereas (8) is obtained from (13) and (21). We can derive Eqs. (9) and (10) in an analogous way. This completes the proof of theorem 2.

Now we are ready to study the passage to the limit $n \rightarrow \infty$.

Theorem 3

a. Within the domain of regularity of $\varphi_n^{(n)}$, differentiation of $\varphi_l^{(\infty)}$ with respect to extensive parameters \bar{x}_i $(i = l + 1, \ldots, k)$ and passage to the limit commute.

b. Within the domain of regularity of $\varphi_k^{(\infty)}$, differentiation of $\varphi_l^{(\infty)}$ with respect to intensive parameters P_i $(i = 1, \ldots, l)$ and passage to the limit commute.

Proof

Since according to (1)

$$\frac{\partial \varphi_i^{(\infty)}}{\partial \bar{x}_i} = P_i \tag{22}$$

it follows from Eq. (7) that

$$\lim_{n \to \infty} \frac{\partial \varphi_l^{(n)}}{\partial \bar{x}_i} = \frac{\partial \varphi_l^{(\infty)}}{\partial \bar{x}_i} = \frac{\partial}{\partial \bar{x}_i} \lim_{n \to \infty} \varphi_l^{(n)}.$$
 (23)

Making use of assumption I 2 and Eq. (1), it follows from Eq. (8)

$$\lim_{n \to \infty} \left[\frac{\partial^2 \varphi_l^{(n)}}{\partial \bar{x}_i \partial \bar{x}_j} \right] = - \left[\frac{\partial^2 \varphi_k^{(\infty)}}{\partial P_i \partial P_j} \right]^{-1}$$
(24)
$$= \left[\frac{\partial \bar{x}_j}{\partial P_i} \right]^{-1} - \left[\frac{\partial P_i}{\partial P_i} \right]^{-1}$$

 $\begin{bmatrix} \partial P_i \end{bmatrix} = \begin{bmatrix} \partial \bar{x}_j \end{bmatrix}$

and thus

$$\lim_{n \to \infty} \frac{\partial^2 \varphi_l^{(n)}}{\partial \bar{x}_i \partial \bar{x}_j} = \frac{\partial^2 \varphi_l^{(\infty)}}{\partial \bar{x}_i \partial \bar{x}_j} = \frac{\partial^2}{\partial \bar{x}_i \partial \bar{x}_j} \lim_{n \to \infty} \varphi_l^{(n)}.$$
 (25)

Correspondingly we have from (1)

· (---)

$$\frac{\partial \varphi_l^{(\infty)}}{\partial P_i} = -\bar{x}_i \,. \tag{26}$$

Hence we obtain from (9)

$$\lim_{n \to \infty} \frac{\partial \varphi_i^{(n)}}{\partial P_i} = \frac{\partial \varphi_i^{(\infty)}}{\partial P_i} = \frac{\partial}{\partial P_i} \lim_{n \to \infty} \varphi_i^{(n)}.$$
 (27)

¹¹ In this equation the vertical bars denote the absolute value and not a determinant. Finally we have

$$\lim_{k \to \infty} \frac{\partial^2 \varphi_l^{(n)}}{\partial P_i \partial P_j} = \frac{\partial^2 \varphi_k^{(\infty)}}{\partial P_i \partial P_j} = -\frac{\partial \bar{x}_j}{\partial P_i} \quad (28)$$

 $\lim_{n \to \infty} \frac{1}{n}$ yielding

 $\lim_{n \to \infty} \frac{\partial^2 \varphi_l^{(n)}}{\partial P_i \partial P_j} = \frac{\partial^2 \varphi_l^{(\infty)}}{\partial P_i \partial P_j} = \frac{\partial^2}{\partial P_i \partial P_j} \lim_{n \to \infty} \varphi_l^{(n)}.$ (29) which completes the proof of theorem 3.

If the existence of $\varphi_k^{(\infty)}$ as a piecewise continuous function is taken for granted, some alternative proofs can be given. Equation (27) can be proved by using a theorem on Laplace transforms 12, 13, whereas the proof of Eq. (27) may be based on a theorem due to GRIFFITHS 14, 15.

3. Stability Conditions

It is well-known from classical thermodynamics ¹⁶ that for a system of σ components there exist $\sigma + 1$ independent stability conditions. These may be expressed either in terms of an arbitrarily chosen thermodynamic potential (Massieu-Planck function) or alternatively in terms of the set of $\sigma + 1$ thermodynamic potentials (Massieu-Planck functions). Certain stability conditions are easily obtained in connection with theorems on the existence of Massieu-Planck functions. It is obvious, however, that this procedure does not lead to the complete and general form first given by SCHOTTKY, ULICH and WAG-NER¹⁷. Moreover, no attempt has been made so far to elucidate on this basis the statistical meaning of the concept of thermodynamic stability. Both problems have been treated already by MÜNSTER¹⁸, who used the generalized Gibbs method. In the following we shall derive the same results with the aid of a more rigorous method based on our previous results.

In terms of an arbitrarily chosen Massieu-Planck function φ_k the thermodynamic stability conditions may be written

$$[\varDelta^2 \varphi_k(P_1, \dots, P_k)]_{X_j} > 0, \ (j > k)$$
(30)

 $[\varDelta^2 \varphi_k(x_{k+1}, \dots, x_{r-1})]_{P_i, X_r} < 0, \ (i < k)$ (31)

where Δ^2 is the second order virtual displacement.

- ¹³ A. MÜNSTER, Statistical Thermodynamics, 2nd ed., Vol. I, Springer Academic Press, New York (in press).
- ¹⁴ R. B. GRIFFITHS, J. Math. Phys. 5, 1215 [1964].
- ¹⁵ J. VAN DER LINDEN, Physica 32, 642 [1966].
- ¹⁶ A. MÜNSTER, Classical Thermodynamics, J. Wiley & Sons, New York (in press).

We first recall that the diagonal elements of the dispersion tensor **B** defined by (I.52) are positive for all coordinate representations, from which it follows directly that **B** has a positive definite quadratic form². Then the same must be true for the reciprocal tensor \mathbf{B}^{-1} . If we now pas to the thermodynamic limit, it follows immediately using assumption I 3, that

$$\frac{\partial^2 \varphi_k^{(\infty)}}{\partial \mathbf{P} \partial \mathbf{P}} : \Delta \mathbf{P} \, \Delta \mathbf{P} > 0 \tag{32}$$

in agreement with (30). This inequality holds for any value of k. To derive (31) we use Eq. (8). Since we want to obtain the complete set of stability conditions, i.e. the condition complementary to (32), we have to identify in the left hand member of (8) the index l with k in our present notation, whereas in the right hand member of (8) the index k must be read as r-1-k. Then in an analogous way we obtain

$$\frac{\partial^2 \varphi_k^{(\infty)}}{\partial \overline{\mathbf{x}} \, \partial \overline{\mathbf{x}}} : \varDelta \overline{\mathbf{x}} \, \varDelta \overline{\mathbf{x}} < 0 \tag{33}$$

in agreement with (31). Thus we have formally derived the stability conditions statistically in complete generality.

We still have to deal with the question of how the macroscopic concept of thermodynamic stability is to be understood in the framework of statistical theory. This question is answered by the fact that the tensor **B** determines the fluctuations of the extensive parameters, in particular the variances and covariances. We note first of all that the positive definite character of **B** is a necessary condition for the existence of the variances. Let us now consider the variances and covariances of the relative fluctuations ξ_i , defined by the equation

$$\xi_i = \left(X_i - \overline{X}_i\right) / \overline{X}_i \,. \tag{34}$$

From fluctuation theory 19, 2 we know that for sufficiently large *n* we have

$$\left[\xi_{i}\,\xi_{j}\right]^{(n)} = \left[\frac{1}{\overline{X}_{i}}\left(\frac{1}{\overline{X}_{j}}\,\frac{\partial\overline{X}_{j}}{\partial P_{i}}\right)\right]^{(n)} = \left[O\left(n^{-1}\right)_{ij}\right] (35)$$

provided that the $\overline{X}_i^{-1} \cdot \partial \overline{X}_i / \partial P_i$ are bounded above. Since we can replace \overline{X}_i by X_r in the investigation

- ¹⁷ W. SCHOTTKY, H. ULICH, and C. WAGNER, Thermodynamik, Springer-Verlag, Berlin 1929. ¹⁸ A. MÜNSTER, Z. Phys. **136**, 179 [1953].
- ¹⁹ A. MÜNSTER, Theory of Fluctuations, Rend. Scuol. Intern. Fis. Enrico Fermi, Corso X, Bologna 1960.

¹² A. MÜNSTER, Z. Phys. 136, 179 [1953].

of thet asymptotic behaviour, the condition can be sharpened by stating that (35) holds in every *P*-interval in which $\partial^2 \varphi_k^{(n)} / \partial P_i \partial P_j$ converges uniformly to the limit $\partial^2 \varphi_k^{(\infty)} / \partial P_i \partial P_j$. According to assumption I 2 this happens in every P-interval which contains no phase transition point. This first implies that the tensor $\partial^2 \varphi_k^{(\infty)} / \partial \boldsymbol{P} \partial \boldsymbol{P}$ is positive definite for any value of k, so that the stability condition (32) is fulfilled. Then by the same argument as used above it follows that the tensor $\partial \varphi_k^{(\infty)} / \partial x \partial x$ must be negative definite, so that the stability condition (33) is fulfilled. It is important to note that this conclusion depends explicitly on the validity of (35). Thermodynamic stability is therefore equivalent to the statistical statement that the second relative central moments of the extensive parameters vanish at the thermodynamic limit as $O(X_r^{-1})$. It can be shown² that for the especially important case of the fluctuations of numbers of particles the above formulation is in turn equivalent to the statement that no long range correlation exists between the local density fluctuations. We have thus demonstrated that the "local perturbations" occurring in the thermodynamic definition of stability are identical with statistical fluctuations and that the thermodynamic stability conditions are identical with conditions for the statistical fluctuations.

4. Discussion

We now briefly comment upon our method and results. First, introducing again the index s for the smoothed quantities, we formulate

Theorem 4

a.

(n)

$$\varphi_k^{(n)} - \frac{(n)}{k^s} \quad \text{for all } n. \tag{36}$$

(00)

b. If $\varphi_l^{(\infty)}(\boldsymbol{x}) \equiv \lim \varphi_l^{(n)}(\boldsymbol{x})$ exists as a piecewise continuous function with $\varphi_l^{(n)} \leq A |\mathbf{x}| + B$, (A, B > 0), then

$$\lim_{n \to \infty} \varphi_l^{(n)} = \lim_{n \to \infty} \varphi_{ls}^{(n)} \quad \text{almost everywhere.}$$
(37)

Assertion a. is easily proved by taking the Fourier transform of (I.29) and using the convolution theorem. The proof of assertion b. is given in the appendix. From theorems I 2 and 4 it appears that the smoothing procedure is simply a systematic development of the old idea² that in the foundation of thermodynamics certain features of a truly molecular theory which cannot be detected by any macroscopic measurement may be disregarded. We are not concerned with the question wether a more detailed approach is possible. In this context, however, we recall that the current treatments of the asymptotic problem (e. g. ref. 1, 3-5) for functions, defined originally only on a countable set, a smoothing process is used by introducing a linear interpolation. One may still ask if a more refined approach could possibly lead to results different from ours. This question is answered by theorems I 2, 1 and 4. There are two possibilities. If the "refined approach" vields results which are consistent with thermodynamics then these results cannot be distinguished from ours by any conceivable macroscopic measurement. In the other case we must conclude that a smoothing process (but not necessarily the method of paper I) is a necessary step in foundation of thermodynamics.

On the basis of assumptions I 1 - I 3 we have proved that the thermodynamic equivalence of various ensembles doesn't depend any more on assumptions about the intermolecular forces but is merely an asymptotic property of the Laplace transformation. In particular it follows from theorem 1 that for the microcanonical ensemble a limit theorem holds under the assumption of weak tempering. Similarly, by combining Fisher's limit theorem for the grand canonical ensemble with theorem 1 we can derive a limit theorem for the sequence of functions $\varphi_I^{(n)}(E/V, \mu)$ under the conditions of stability and weak tempering. The exclusion of phase transition points (assumption I 2) doesn't impair the general validity of Eq. (1) since according to assumption (I 1) $\varphi_k^{(\infty)}$ is a continuous function of **P**.

If at the thermodynamic limit a segment of the real P_i-axis would merely consist of transition points of arbitrary orders, then our argument would break down for this segment¹. By means of macroscopic experiment, however, transitions can be detected only up to low finite order (third or perhaps fourth) which form at most a countable set. Hence the concept of transitions of arbitrary orders has no physical meaning within a theory of macroscopic properties and should be disregarded although we have not tried to eliminate it formally.

Finally, we have shown that derivation of a limit function $\varphi_l^{(\infty)}$ with respect to intensive or extensive parameters and passage to the limit commute under the assumption underlying the limit theorem for $\varphi_{\boldsymbol{k}}^{(\infty)}$.

Appendix

Proof of theorem 4 b

Consider the (k-l)-dimensional sphere

$$\Delta(d, \mathbf{x}) = \{\mathbf{x}' \mid |\mathbf{x} - \mathbf{x}'| \leq d\}$$
(38)

for some given value of d. Let us put

X

$$f^{(n)} = \varphi_l^{(n)} - \mathbf{P} \cdot \mathbf{x} \tag{39}$$

and write

$$f_s^{(n)}(\boldsymbol{x}) = \frac{1}{n} \ln \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{x}' \exp\{n f^{(n)}(\boldsymbol{x}')\} \times (40)$$

$$S^{\prime(n)}(\boldsymbol{x}-\boldsymbol{x}^{\prime}) = \frac{1}{n} \ln \left[J_{\mathcal{A}} \left(1 + \frac{J_{CA}}{J_{\mathcal{A}}} \right) \right]$$

with

$$J_{\varDelta(C\varDelta)} = \int_{\varDelta(C\varDelta)} \mathrm{d}\boldsymbol{x}' \exp\{n f^{(n)}(\boldsymbol{x}')\} S^{\prime(n)}(\boldsymbol{x}-\boldsymbol{x}') \quad (41)$$

respectively, $C\Delta$ being the complement of Δ in **x**-space. Making use of the inequality (in *m*-dimensional space)

$$\int_{|\mathbf{x}| \ge d} \exp\{-\mathbf{x} \cdot \mathbf{x}\} d\mathbf{x} = s_m \int_{\varrho=d}^{\infty} \varrho^{m-1} e^{-\varrho^2} d\varrho$$
$$= \frac{1}{2} s_m \int_{d^2}^{\infty} \tilde{\varrho}^{m-3/2} e^{-\tilde{\varrho}} d\tilde{\varrho} \qquad (42)$$
$$= \frac{1}{2} s_m e^{-d^2} \int_{0}^{\infty} (t+d^2)^{m-3/2} e^{-t} dt$$
$$\leq \frac{1}{2} s_m e^{-d^2} P^{(m-1)} (d^2) d^{-1},$$

where s_m is the surface of the unit sphere in m dimensions and $P^{(m-1)}$ a polynomial of degree m-1, we observe that

$$J_{CA} \leq \exp\{n f_{CA\max}^{(n)}\} \frac{1}{2} s_{k-l} \exp\{\left\{-\frac{n^2}{\ln^2 n} d^2\right\} (43) \cdot P^{(k-l-1)}(d^2) d^{-1}$$

where $f_{C\mathcal{A}\max}^{(n)}$ is the maximum of $f^{(n)}$ in $C\mathcal{A}$. On the other hand, we have

$$J_{\Delta} \ge \exp\{n f_{\Delta\min}^{(n)}\} \varepsilon^{(n)}$$
(44)

where $f_{\Delta \min}^{(n)}$ is the minimum of $f^{(n)}$ in Δ and

$$\varepsilon^{(n)} = \int_{\Delta} S'^{(n)}(\boldsymbol{x} - \boldsymbol{x}') \, \mathrm{d}\boldsymbol{x}'_{\overrightarrow{n \to \infty}} \, \mathbf{1} \,. \tag{45}$$

From (43) and (44) it follows

$$\frac{J_{C\mathcal{A}}}{J_{\mathcal{A}}} \leq A P^{(k-l-1)}(d^2) \exp\left\{-\frac{n^2 d^2}{\ln^2 n}\right\}$$
(46)
$$\cdot \exp\left\{n\left(f_{C\mathcal{A}\max}^{(n)} - f_{\mathcal{A}\min}^{(n)}\right)\right\}.$$

Thus $J_{C\Delta}/J_{\Delta}$ is a bounded function whence

$$\frac{1}{n} \ln \left(1 + \frac{J_{CA}}{J_A} \right)_{n \to \vec{\infty}} 0.$$
 (47)

From (44) and similar arguments for the upper bound we have

$$f_{\mathcal{A}\min}^{(n)} + \frac{1}{n}\ln\varepsilon^{(n)} \leq \frac{1}{n}\ln J_{\mathcal{A}} \leq f_{\mathcal{A}\max}^{(n)} + \frac{1}{n}\ln\varepsilon^{(n)}$$
(48)

and thus

$$f_{\mathcal{A}\min}^{(\infty)} \leq f_s^{(\infty)} \left(\boldsymbol{x} \right) \leq f_{\mathcal{A}\max}^{(\infty)} \,. \tag{49}$$

Consider now a point of continuity of $f^{(\infty)}(\boldsymbol{x})$ and take Δ small enough that $f^{(\infty)}(\boldsymbol{x})$ is continuous in Δ . Then

$$f_s^{(\infty)}\left(\boldsymbol{x}\right) = f^{(\infty)}\left(\boldsymbol{x}\right) \tag{50}$$

because if

$$f_s^{(\infty)}(\boldsymbol{x}) = f^{(\infty)}(\boldsymbol{x}') \quad \text{with} \quad \boldsymbol{x} \neq \boldsymbol{x}' \quad (51)$$

we could choose an interval Δ such that $\mathbf{x}' \notin \Delta$ which contradicts (49). This proves assertion b.