

Statistical Foundations of Thermodynamics

I. Asymptotic Form of the Frequency Functions

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It is shown that, for all conceivable ensembles of statistical thermodynamics, at the thermodynamic limit, the frequency function of the fluctuations of macroscopic extensive parameters equals a Gaussian. The proof is based on a generalisation of Khinchin's method using the concept of "smoothed frequency functions."

It is generally assumed [e. g. ¹⁻⁶] that in the thermodynamic limit (whose exact definition is given below) the frequency functions tend to the Gaussian form. The first rigorous proof of this statement is due to KHINCHIN⁷ who has treated the energy fluctuations of a canonical ensemble composed of systems of non-interacting particles. More recently MAZUR and VAN DER LINDEN⁸ succeeded in extending the proof to the case of interacting particles. In their argument, however, a specific property of the canonical ensemble is used and it is easily shown that the method does not apply to other ensembles. In the following we shall describe a generalisation of Khinchin's method which will enable us to prove the above statement in its most general form.

1. Definitions

It is well-known that any statistical ensemble depending on k intensive parameters generates the analogue of a Massieu-Planck function Φ_k by the equation

$$\Phi_k = \ln \bar{\Xi}_k \quad (1)$$

where $\bar{\Xi}_k$ is the partition function of the ensemble⁹. Now, in the semiclassical approximation¹⁰ the ana-

logues of the Massieu-Planck functions $\Phi_{l+1}(P)$ and $\Phi_l(\bar{X})$ of the intensive parameter $P_{l+1} \equiv P$ and the extensive random variable $X_{l+1} \equiv X$ are related by

$$e^{\Phi_{l+1}(P)} = \int_0^\infty dX e^{-PX + \Phi_l(X)}. \quad (2)$$

For the normalized frequency function we have

$$W(X) = e^{-\Phi_{l+1}(P) - PX + \Phi_l(X)}, \quad (3)$$

$$\bar{X} \equiv \int_0^\infty dX X W(X) = - \frac{\partial \Phi_{l+1}}{\partial P}, \quad (4)$$

$$B \equiv \overline{(\Delta X)^2} \equiv \overline{(X - \bar{X})^2} = \frac{\partial^2 \Phi_{l+1}}{\partial P^2}. \quad (5)$$

In order to investigate the thermodynamic limit, it is convenient to consider the frequency function of the random variable

$$y \equiv \frac{\Delta X}{\sqrt{B}} = \frac{X - \bar{X}}{\sqrt{B}}, \quad (6)$$

$$W(y) = \sqrt{B} \exp\{-\Phi_{l+1}(P) - P[\bar{X} + \sqrt{B}y] + \Phi_l(\bar{X} + \sqrt{B}y)\} \quad (7)$$

the advantage of which is that its dispersion $\bar{y}^2 = 1$.

Finally we introduce the characteristic function

$$\psi(t) = \int_{-\infty}^{\infty} e^{ity} W(y) dy, \quad (8)$$

¹ R. C. TOLMAN, The Principles of Statistical Mechanics, Oxford University Press, Oxford 1938.

² M. J. KLEIN and L. TISZA, Phys. Rev. **76**, 1861 [1949].

³ J. G. KIRKWOOD and R. J. GOLDBERG, J. Chem. Phys. **18**, 54 [1950].

⁴ R. F. GREENE and H. B. CALLEN, Phys. Rev. **83**, 1231 [1951].

⁵ L. D. LANDAU and E. M. LIFSHITZ, Statistical Physics, Pergamon Press, London 1958.

⁶ S. R. DE GROOT and P. MAZUR, Non-Equilibrium Thermodynamics, North Holland Publ. Co., Amsterdam 1962.

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

⁸ P. MAZUR and J. VAN DER LINDEN, J. Math. Phys. **4**, 271 [1963].

⁹ For simplicity we shall always put Boltzmann's constant equal to unity.

¹⁰ We shall confine ourselves to the semi-classical approximation throughout this paper. Our results remain valid, however, in the continuous spectrum approximation of quantum statistics. For the sake of simplicity proofs will be given only for the case of a single random variable. The general case of several random variables can be treated along the same lines.

which may be written as

$$\psi(t) = \exp\left\{-it\left(\frac{\bar{X}}{\sqrt{B}}\right) - \Phi_{l+1}(P) + \Phi_{l+1}(P - it/\sqrt{B})\right\} \tag{9}$$

by virtue of (2) and (7).

2. The Thermodynamic Limit. Assumptions

To investigate the thermodynamic limit, we consider a sequence of systems characterized by the variable

$$X_r^{(n)} = n X_r^{(1)} \tag{10}$$

where $X_r^{(1)}$ is some (fixed) reference value and $n \geq 1$.

On introducing the reduced quantities

$$\varphi_k^{(n)} = \frac{\Phi_k^{(n)}}{n} \quad (k=l, l+1); \quad x = \frac{X}{n} \tag{11}$$

we introduce the thermodynamic limit by $n \rightarrow \infty$ with

$$P = \text{const}, \quad x = \text{const}. \tag{12}$$

To study this limit we base the discussion on the following assumptions:

1. The sequence of functions $\varphi_{l+1}^{(n)}(P)$ converges to a function $\varphi_{l+1}^{(\infty)}(P)$ everywhere finite in a closed interval ΔP of the real axis. The existence of this limit has been show by several authors under different conditions on the intermolecular potential and for different ensembles. For details the reader is referred to the literature ¹¹.

2. There is a finite subspace D in the complex plane $\{s | s = P + iQ\}$ including ΔP such that

$$|\varphi_{l+1}^{(n)}(s)| \leq M < \infty \quad \text{for all } n \text{ and } s \in D. \tag{13}$$

These assumptions exclude phase transition points i. e. we assume that there is an interval of the real axis to which the zeros of $\Xi_{l+1}^{(n)}$ do not come arbit-

Proof:

Statement 2 follows from statement 1. To prove 1 we consider (9). By assumption 2 we may expand $\Phi_{l+1}(P - it/\sqrt{B})$ into a Taylor series at the point $t=0$ if $|t| < d(P)/\sqrt{B}$, where $d(P)$ is the smallest distance from P to the surface points of D . Taking into account (4) and (5)

$$\Phi_{l+1}^{(n)}\left(P - \frac{it}{\sqrt{B}}\right) = \Phi_{l+1}^{(n)}(P) + \frac{i\bar{X}t}{\sqrt{B}} - \frac{1}{2}t^2 + R_3^{(n)}(t, P) \tag{19}$$

with

$$R_3^{(n)}(t, P) = \frac{i}{3!} \left(\frac{\partial^3 \Phi_{l+1}}{\partial s^3}\right)_{s=P-(it/\sqrt{B})} \frac{t^3}{\sqrt{B}^3} \quad (0 < \vartheta < 1) \tag{20}$$

¹¹ A. MÜNSTER, Statistical Thermodynamics, Vol. I, Springer Academic Press, New York (in press).

rarily close for $n \rightarrow \infty$. From Vitali's theorem of convergence ¹² we know that with assumptions 1 and 2

$$\varphi_{l+1}^{(\infty)}(s) = \lim_{n \rightarrow \infty} \varphi_{l+1}^{(n)}(s) \tag{14}$$

is regular in D and

$$\frac{\partial^q \varphi_{l+1}^{(\infty)}(s)}{\partial s^q} = \lim_{n \rightarrow \infty} \frac{\partial^q \varphi_{l+1}^{(n)}(s)}{\partial s^q}. \tag{15}$$

3.

$$b(P) \equiv \frac{\partial^2 \varphi_{l+1}^{(\infty)}(P)}{\partial P^2} = \lim_{n \rightarrow \infty} \frac{\partial^2 \varphi_{l+1}^{(n)}(P)}{\partial P^2} \geq b_0 > 0 \quad \text{for } P \in \Delta P. \tag{16}$$

The possibility of $b_0 = 0$ cannot be excluded in the framework of our considerations. It seems nevertheless highly improbable that this case may occur, for thermodynamic reasons. At any rate, it can be seen from the following that the exclusion of $b_0 = 0$ is a necessary condition to obtain the Gaussian form of the frequency function.

3. Asymptotic Form of the Characteristic Function

On the basis of the preceeding assumptions we shall prove the following

Theorem 1:

1.

$$\psi^{(n)}(t, P) = \exp\left\{-\frac{1}{2}t^2\right\} [1 + O(n^{-1/2}) t^3] \tag{17}$$

for $|t| < \ln n$, $n \geq n(P)$ and $P \in \Delta P$.

2. The sequence $\psi^{(n)}(t, P)$ converges uniformly in any finite t -interval and $P \in \Delta P$ to the Gaussian function

$$\psi^{(\infty)}(t) = \exp\left\{-\frac{1}{2}t^2\right\}. \tag{18}$$

¹² E. C. TITCHMARSH, The Theory of Function, Oxford University Press, Oxford 1939.

Since by the assumptions 1 and 2 $\Phi_{l+1}(s)/n$ converges in D to an analytic function, there is an $n'(P)$ such that for $n > n'(P)$

$$\frac{1}{n} \left| \left(\frac{\partial^3 \Phi_{l+1}}{\partial s^3} \right)_{s=P-(it/\sqrt{B})} \right| \leq K' < \infty \text{ for } |t| < d(P) \sqrt{B}. \tag{21}$$

By assumption 3

$$\sqrt{B} = \sqrt{n b} \geq \sqrt{n b_0}; \quad (b_0 > 0) \quad \text{for } P \in \Delta P. \tag{22}$$

Taking into account (19), (20), (21) and (22) Eq. (9) reads

$$\psi^{(n)}(t, P) = \exp \left\{ \frac{1}{2} t^2 + \frac{1}{\sqrt{n}} g^{(n)}(t, P) t^3 \right\} \tag{23}$$

with

$$|g^{(n)}(t, P)| \leq K < \infty. \tag{24}$$

There is an $n(P) \geq n'(P)$ such that for $n > n(P)$ and $|t| < \ln n$ (23) and (24) yield (17) by expanding the exponential.

From Theorem 1 we may easily derive the following

Corollary

At the thermodynamic limit the moments of the frequency function (7)

$$\mu^{(n)} \equiv \int_{-\infty}^{\infty} y^{(n)} W(y) dy$$

converge to the moments of a Gaussian with dispersion one.

4. Smoothed Frequency Functions

Let us now study the asymptotic behaviour of the frequency function itself.

From Theorem 1 we cannot conclude that the distribution function

$$W^{(n)}(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-ity} \psi^{(n)}(t) \tag{25}$$

converges to the Gaussian distribution, too, since $\psi^{(n)}(t)$ approaches this distribution in any finite interval only.

We may, however, consider a "smoothed" distribution, defined by

$$W_s^{(n)}(y) = \int_{-\infty}^{\infty} dy' W^{(n)}(y') S^{(n)}(y - y') \tag{26}^{13}$$

¹³ Since $W^{(n)}(y)$ has no physical meaning for $y < -\bar{X}/\sqrt{B}$ we may put formally $W^{(n)}(y) = 0$ for $y < -\bar{X}/\sqrt{B}$.

with

$$S^{(n)}(y) = \frac{\sqrt{B}}{\sqrt{2\pi \ln n}} \exp \left\{ -\frac{1}{2} \frac{B}{\ln^2 n} y^2 \right\}. \tag{27}$$

In analogy to (2) we put

$$W_s^{(n)}(X) = \exp \{ -\Phi_{l+1,s}^{(n)}(P) - P \cdot X + \Phi_{l,s}(X) \} \tag{28}$$

where, by use of $\varphi_{k,s}^{(n)} = \Phi_{k,s}^{(n)}/n$ ($k = l + 1, l$), $x = X/n$,

$$\exp \{ n(\varphi_{l,s}^{(n)}(x) - P x) \} = \int_{-\infty}^{\infty} dx \exp \{ n(\varphi_l^{(n)}(x') - P x') \} S'^{(n)}(x - x'), \tag{29}$$

$$S'^{(n)} = \frac{n}{\sqrt{2\pi \ln n}} \exp \left\{ -\frac{1}{2} \left(\frac{n}{\ln n} \right)^2 x^2 \right\}. \tag{30}$$

The smoothing procedure is thus given by convolution with an appropriate smoothing function chosen in such a way that the smoothed frequency function remains normalized and non-negative. This follows directly from the definition of $W_s^{(n)}(y)$ and the fact that

$$\int_{-\infty}^{\infty} S^{(n)}(y) dy = 1. \tag{31}$$

Speaking more physically, the smoothing procedure is nothing else but a local averaging or, what amounts to the same, a damping of the characteristic function for the large values of t .

Obviously the smoothing procedure can be considered to be physically reasonable only if the smoothed frequency function gives, at least for large values of n , a sufficiently accurate picture of the ensemble. This is indeed true as can be seen from the following

Theorem 2:

For any finite closed interval Δ we have

$$\lim_{n \rightarrow \infty} \int_{\Delta} [W^{(n)}(y) - W_s^{(n)}(y)] dy = 0. \tag{32}$$

Proof:

We have

$$\int_{\Delta} dy W_s^{(n)}(y) = \int_{\Delta} dy \int_{-\infty}^{\infty} dy' W^{(n)}(y') S^{(n)}(y - y') = \int_{-\infty}^{\infty} dy' W^{(n)}(y') \int_{\Delta} S^{(n)}(y - y') dy. \tag{33}$$

$S^{(n)}$ approaches the δ -function for n to infinity and thus

$$\lim_{n \rightarrow \infty} \int_{\Delta} dy S^{(n)}(y - y') = \begin{cases} 1 & \text{if } y' \in \Delta, \\ 0 & \text{if } y' \notin \Delta. \end{cases} \tag{34}$$

From (33) and (34) it follows (32).

We are now ready to prove

Theorem 3:

1.

$$W_s^{(n)}(y, P) = \frac{\exp\{-\frac{1}{2}y^2\}}{\sqrt{2\pi}} \left[1 + O\left(\frac{\ln^2 n}{n}\right) + O(n^{-1/2}) y \right] \tag{35}$$

for y finite and $n > n(P)$, $P \in \Delta P$.

2. The sequence of smoothed frequency functions $W_s^{(n)}(y)$ converges uniformly to the Gaussian distribution for $P \in \Delta P$:

$$W_G(y) = \frac{1}{\sqrt{2\pi}} \exp\{-\frac{1}{2}y^2\}. \tag{36}$$

Proof:

Statement 2 follows from statement 1. To prove 1 we consider the characteristic function $\psi_s^{(n)}(t)$ of $W_s^{(n)}(y)$, which may be written by means of (9), (25) and the convolution theorem

$$\psi_s^{(n)}(t) = \psi^{(n)}(t) \tilde{S}^{(n)}(t) \tag{37}$$

where $\tilde{S}^{(n)}(t)$ is the Fourier transform of $S^{(n)}(y)$ [see (26)]:

$$\tilde{S}^{(n)}(t) = \exp\left\{-\frac{1}{2} \frac{\ln^2 n}{B} t^2\right\}. \tag{38}$$

Then

$$W_s^{(n)}(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\{-it y\} \psi^{(n)}(t) \tilde{S}^{(n)}(t). \tag{39}$$

We split the integration into three parts: $|t| \leq \ln n$, $\ln n < |t| \leq \varepsilon\sqrt{n}$ and $\varepsilon\sqrt{n} > |t|$. Taking into account (17) and (23) we get

$$I_1 = \int_{|t| \leq \ln n} dt \exp\{-it y - \frac{1}{2}t^2\} \cdot \left[1 + O(n^{-1/2}) t^3 + O\left(\frac{\ln^2 n}{n}\right) t^2 \right]. \tag{40}$$

In extending the integration over the whole axis, the difference to the value of the integral (40) will be of the order $n^{-c \ln n}$ ($c > 0$) and thus negligible. Furthermore we make use of

$$t^2 \exp\{-\frac{1}{2}t^2\} = \left[\frac{\partial^2}{\partial t^2} + 1 \right] \exp\{-\frac{1}{2}t^2\}, \tag{41}$$

$$t^3 \exp\{-\frac{1}{2}t^2\} = - \left[\frac{\partial^3}{\partial t^3} + 3 \frac{\partial}{\partial t} \right] \exp\{-\frac{1}{2}t^2\}. \tag{42}$$

Then integration by parts yields for finite y

$$I_1 = \sqrt{2\pi} \exp\{-\frac{1}{2}y^2\} \left[1 + O(n^{-1/2}) y + O\left(\frac{\ln^2 n}{n}\right) + O(n^{-c \ln n}); \quad (c > 0). \right] \tag{43}$$

We now estimate I_2 and I_3 . From (23) and (24) it follows the existence of an $\varepsilon > 0$ such that

$$\frac{1}{\sqrt{n}} |g^{(n)}(t, P) t^3| \leq \frac{1}{4} t^2 \quad \text{for } |t| \leq \varepsilon \sqrt{n} \quad \text{and } n > n(P), \tag{44}$$

therefore

$$|I_2| < \int_{|t| > \ln n} dt \exp\{-\frac{1}{4}t^2\} = O(n^{-1/4 \ln n}). \tag{45}$$

We deduce from (9) $|\psi^{(n)}(t)| \leq 1$ for all t and n , thus

$$|I_3| \leq \int_{|t| > \varepsilon \sqrt{n}} dt \tilde{S}^{(n)}(t) = O(n^{-c' \ln n}); \quad (c' > 0). \tag{46}$$

From (43), (45) and (46) follows statement 1.

For $W^{(n)}(X)$ we have with (3) and (6)

$$W^{(n)}(X) = \frac{\exp\{-\frac{1}{2} B^{-1}(X - \bar{X})^2\}}{\sqrt{2\pi B}} \left[1 + O\left(\frac{\ln^2 n}{n}\right) + O(n^{-1})(X - \bar{X}) \right]. \tag{47}$$

With the same arguments we may consider the case of several extensive and intensive variables

$$W^{(n)}(\mathbf{X}) = \exp\{-\Phi_k^{(n)}(\mathbf{P}) - \mathbf{P} \cdot \mathbf{X} + \Phi_l^{(n)}(\mathbf{X})\}, \tag{48}$$

$$\mathbf{P} = (P_{l+1}, \dots, P_k); \quad \mathbf{X} = (X_{l+1}, \dots, X_k), \tag{49}$$

$$\mathbf{P} \cdot \mathbf{X} = \sum_{i=l+1}^k P_i X_i \tag{50}$$

and prove (provided the assumptions 1–3 hold for \mathbf{P})

$$W^{(n)}(\mathbf{X}) = \frac{\exp\{-\frac{1}{2} \mathbf{B}^{-1} : (\mathbf{X} - \bar{\mathbf{X}})^2\}}{\sqrt{(2\pi)^{k-l} |\mathbf{B}|}} \cdot \left[1 + O\left(\frac{\ln^2 n}{n}\right) + O(n^{-1}) \cdot (\mathbf{X} - \bar{\mathbf{X}}) \right], \tag{51}$$

$$\mathbf{B} = \frac{\partial^2 \Phi_k}{\partial \mathbf{P} \partial \mathbf{P}}; \quad |\mathbf{B}| = |B_{ij}|; \quad B_{ij} = \frac{\partial^2 \Phi_k}{\partial P_i \partial P_j}. \tag{52}$$

In the mathematical sense, the assertions of Theorem 3 relate to the smoothed frequency function W_s . From Theorem 2, however, it follows that W_s and W cannot be distinguished by any conceivable macroscopic measurement. Thus if, as usual, the extensive parameters are considered as macroscopic variables, then the asymptotic form of the frequency function is given by Theorem 3 and we may drop the index s from the notation.

5. Concluding Remarks

Using a generalisation of Khinchin's method we have studied the asymptotic behaviour of the fre-

quency function of fluctuations of extensive parameters for the generalized ensemble. It has been shown that, at the thermodynamic limit the characteristic function converges to a Gaussian in finite intervals, that the moments converge to the moments of a Gaussian and finally that the frequency function in the macroscopic sense equals a Gaussian.

The proof is based essentially on two assumptions:

1. Existence of the limit function $\varphi_{l+1}^{(\infty)}(P)$ for real P .
2. Regularity of $\varphi_{l+1}^{(\infty)}$ in a certain domain of the complex plane, i. e. exclusion of phase transitions.

The validity of 1. depends on certain assumptions concerning the intermolecular potentials. We want to stress, however, that these assumptions don't enter explicitly into our proof. Thus the above results would remain valid if, for instance for the pressure ensemble assumption 1. (which has been demonstrated as yet only under the condition of "strong tempering"¹⁴) would be proved under the condition of "weak tempering". Assumption 2. doesn't impair the generality of our results since it can be concluded from general considerations¹⁵, that at a thermodynamic transition point the frequency function cannot be a Gaussian.

The method of "smoothed frequency" functions has been suggested by the work of MASSIGNON¹⁶ and MÜNSTER¹⁷. In our present context it means essentially a mathematical trick which enables us to overcome the difficulties encountered in the generalisation of Khinchin's method. Physical aspects of our procedure will be discussed in a forthcoming paper.

¹⁴ J. VAN DER LINDEN and P. MAZUR, *Physica* **36**, 491 [1967].

¹⁵ A. MÜNSTER, *Statistical Thermodynamics*, 2nd edit. (in press).

¹⁶ D. MASSIGNON, *Mécanique Statistique des Fluides*, Dunod, Paris 1957.

¹⁷ A. MÜNSTER, *Z. phys. Chem. N.F.* **22**, 97 [1959].