On the Formalism of Thermodynamic Fluctuation Theory*

RICHARD F. GREENE† AND HERBERT B. CALLEN
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania
(Received March 16, 1951)

From the statistical mechanical occupation probability of microstates Einstein has inferred a distribution function for the macroscopic states of a canonical ensemble. The conventional theory of thermodynamic fluctuations proceeds by making certain series expansions in the Einstein function and by dropping all cubic and higher order terms. In this paper we establish that: (*a*) The correlation moments for the extensive thermodynamic parameter fluctuations may be computed directly from the distribution function for the microstates, without introducing an intermediate macroscopic distribution function. (*b*) These same moments can be evaluated from the Einstein function without making series expansions or invoking approximations. (*c*) All moments computed by methods (*a*) or (*b*) agree exactly. (This may be taken as an alternative derivation of the Einstein function.) (*d*) The second moments computed by the conventional method are correct, but all higher moments are incorrect.

I. INTRODUCTION

STATISTICAL mechanics predicts both the average values of the thermodynamic variables of a system in equilibrium and the characteristics of the fluctuations of these variables about their average values.[1] In this paper we discuss and, to some degree, extend the theory of the fluctuations of the extensive thermodynamic parameters.[2] In particular we investigate the Einstein method[3] which, by introducing macroscopic concepts at the fundamental level of the distribution function, affords great insight into macroscopic fluctuation phenomena.

The general subject of fluctuations is of interest for a number of reasons. Recent developments in cryogenics have led to the increasing application of thermodynamics at low temperatures. Problems of thermodynamic stability, of critical points,[4] and of phase transitions[5] have also received extensive recent attention. In each of these cases the fluctuations play a fundamental role, as they do in all "marginal" applications of thermodynamics. Finally, in a recent paper[6] by Welton and one of us, it has been conjectured that a logical approach to a theory of linear irreversible processes lies through the analysis of equilibrium fluctuations, and it is in connection with this program that the present investigation of fluctuation theory is undertaken.

II. THE DISTRIBUTION FUNCTION FOR MICROSTATES

In order to introduce a convenient notation we briefly restate the results of statistical mechanics in giving the occupation probabilities of the microstates in a canonical ensemble.

For the set of extensive parameters $x_0, x_1, x_2, \cdots$ which determines the macroscopic state of a thermodynamic system, we adopt the convention that x_0 shall represent the internal energy, whereas $x_1, x_2, x_3, \cdots$ are parameters such as the volume, mole numbers, etc. The expectation values of these parameters in an equilibrium state will be denoted by $X_0, X_1, X_2, \cdots$.

The entropy may be considered as a single-valued first-order homogeneous function of the extensive parameters, $S(X_0, X_1, X_2, \cdots)$; the inverse function, $X_0(S, X_1, X_2, \cdots)$, being similarly single-valued, first-ordered, and homogeneous. Whereas the latter functional form is the more convenient for the conventional development of thermodynamics, we shall find the former form to be considerably more convenient in the analysis of fluctuations. Indeed much of the awkwardness of fluctuation formalisms has arisen from the habitual maintenance of the second form as fundamental.

The intensive parameters are conventionally defined by the equations,

$$T\equiv \partial X_0/\partial S,\quad P_k\equiv \partial X_0/\partial X_k;\quad k=1, 2, 3,\cdots. \tag{1}$$

Alternatively, we shall find it convenient to define a set of intensive parameters by the equations,

$$F_k\equiv \partial S/\partial X_k;\quad k=0, 1, 2, \cdots, \tag{2}$$

whence

$$F_0=1/T,\quad F_k=-P_k/T;\quad k=1, 2, 3, \cdots. \tag{3}$$

By Euler's theorem on homogeneous functions we have

$$X_0=TS+\textstyle\sum_1 P_kX_k \tag{4}$$

and

$$S=\textstyle\sum_0 F_kX_k. \tag{5}$$

A set of partial Legendre transforms of the energy (the so-called generalized Gibbs' functions) may be defined by the equations,

$$X_0[T, P_1, P_2, \cdots, P_r]\equiv X_0-TS-\sum_1^r P_kX_k. \tag{6}$$

* This work was supported in part by the ONR. It is taken from a Ph.D. thesis submitted to the University of Pennsylvania by one of the authors (RFG).
† John F. Frazer Fellow.
[1] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, England, 1938).
[2] A theory of fluctuations of intensive thermodynamic parameters will be given in a subsequent paper.
[3] A. Einstein, Ann. phys. **33**, 1275 (1910).
[4] M. J. Klein and L. Tisza, Phys. Rev. **76**, 1861 (1949).
[5] L. Tisza, Technical Report No. 127, Research Lab. of Electronics, M.I.T. (1949) (unpublished).
[6] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

The possibility of considering these transforms as functions of the parameters T, P_1, P_2, $\cdots$, P_r, X_{r+1}, X_{r+2}, $\cdots$, instead of parameters S, X_1, $\cdots$, X_r, X_{r+1}, X_{r+2}, $\cdots$, is determined by the nonvanishing of the jacobian of this transformation. This jacobian is identical with the discriminant of the quadratic forms determining the stability of the system,[5] and thus vanishes only at critical points. One thus obtains the relations,

$$\left.\begin{aligned}(\partial/\partial T)X_0[T, P_1, \cdots, P_r] &= -S,\\ (\partial/\partial P_k)X_0[T, P_1, \cdots, P_r] &= -X_k;\\ k &= 1, 2, \cdots, r.\end{aligned}\right\} \quad (7)$$

A set of analogous Legendre transforms of the entropy (which we shall call the generalized Massieu[7] functions) may be defined by the equations,

$$S[F_0, F_1, \cdots, F_r] \equiv S - \sum_0^r F_k X_k. \quad (8)$$

Except at critical points the generalized Massieu functions may be considered as functions of the parameters, F_0, F_1, $\cdots$, F_r, X_{r+1}, X_{r+2}, $\cdots$, and satisfy the equations,

$$(\partial/\partial F_k)S[F_0, \cdots, F_r] = -X_k; \quad k = 0, 1, 2, \cdots, r. \quad (9)$$

We now consider a macroscopic system and its environment in equilibrium. The system parameters x_{r+1}, x_{r+2}, $\cdots$ are assumed to be fixed:

$$x_{r+k} = X_{r+k}; \quad k = 1, 2, 3, \cdots, \quad (10)$$

but we assume the interaction with the environment to be such that the parameters, x_0, x_1, x_2, $\cdots$, x_r, are able to fluctuate about their equilibrium values; i.e., we consider a system "canonical with respect to x_0, x_1, $\cdots$, x_r and microcanonical with respect to x_{r+1}, x_{r+2}, $\cdots$."[8]

The distribution function for the occupation probability of the microstates is then

$$f_n = \exp[(X_0[T, P_1, \cdots, P_r] - x_0^n + \sum_1^r P_k x_k^n)/kT] \quad (11)$$

or

$$f_n = \exp[-(S[F_0, \cdots, F_r] + \sum_0^r F_k x_k^n)/k], \quad (12)$$

where f_n is the occupation probability for the n^{th} microstate and x_k^n is the expectation value of x_k in the n^{th} microstate.

[7] E. A. Guggenheim, *Thermodynamics* (North Holland Publishing Company, Amsterdam, 1949).

[8] Implicit in the canonical formalism is the assumption that the environment is so large that its "capacity" places no bounds upon the variation of x_0, x_1, $\cdots$, x_r. Except in the region of critical points, the fluctuations are generally sufficiently small so that the effect of finite environmental "capacity" is negligible.

III. CORRELATION MOMENTS FROM THE MICRODISTRIBUTION FUNCTION

We now show that the correlation moments of the fluctuating extensive parameters can be computed directly from the distribution function for the microstates [Eq. (12)]; i.e., if δx_k denotes the deviation of x_k from its equilibrium value: $\delta x_k \equiv (x_k - X_k)$, and if $\langle b \rangle$ denotes the expectation value, or ensemble average, of any quantity b, then a typical moment which we may wish to calculate is (taking i, j, $k \leqslant r$) the third moment

$$\langle (x_i^n - X_i)(x_j^n - X_j)(x_k^n - X_k) \rangle \equiv \langle \delta x_i \delta x_j \delta x_k \rangle.$$

If ω_n is the degeneracy of the n^{th} microstate, the ensemble average can be written more explicitly as

$$\langle \delta x_i \delta x_j \delta x_K \rangle = \sum_n \omega_n f_n (x_i^n - X_i)(x_j^n - X_j)(x_k^n - X_k). \quad (13)$$

However it follows from the form of f_n that

$$\begin{aligned}\partial f_n/\partial F_k &= -((\partial/\partial F_k)S[F_0, \cdots, F_r] + x_k^n) f_n/k\\ &= -(x_k^n - X_k) f_n/k, \quad (14)\end{aligned}$$

whence

$$\begin{aligned}&\langle \delta x_i \delta x_j \delta x_k \rangle\\ &\quad = -k \sum_n \omega_n (\partial f_n/\partial F_i)(x_j^n - X_j)(x_k^n - X_k)\\ &\quad = -k(\partial/\partial F_i)[\sum_n \omega_n f_n (x_j^n - X_j)(x_k^n - X_k)]\\ &\qquad + k \sum_n \omega_n f_n [(x_j^n - X_j)(\partial/\partial F_i)(x_k^n - X_k)\\ &\qquad + (x_k^n - X_k)(\partial/\partial F_i)(x_j^n - X_j)],\end{aligned}$$

$$\langle \delta x_i \delta x_j \delta x_k \rangle = -k(\partial/\partial F_i)\langle \delta x_j \delta x_k \rangle - k\langle \delta x_k \rangle \partial X_j/\partial F_i - k\langle \delta x_k \rangle \partial X_j/\partial F_i.$$

However,

$$\langle \delta x_j \rangle = 0 = \langle \delta x_k \rangle$$

and we obtain

$$\langle \delta x_i \delta x_j \delta x_k \rangle = -k(\partial/\partial F_i)\langle \partial x_i \delta x_j \delta_k \rangle. \quad (15)$$

The form of this equation is clearly maintained for moments of any order higher than the third, so that we have, for instance;

$$\begin{aligned}&\langle \delta x_i \delta x_j \delta x_k \delta x_l \rangle\\ &\quad = -k(\partial/\partial F_l)\langle \delta x_i \delta x_j \delta x_k \rangle - k(\partial X_i/\partial F_l)\langle \delta x_j \delta x_k \rangle\\ &\qquad - k(\partial X_j/\partial F_l)\langle \delta x_i \delta x_k \rangle - k(\partial X_k/\partial F_l)\langle \delta x_i \delta x_j \rangle. \quad (16)\end{aligned}$$

The second moments must be considered separately. We have

$$\begin{aligned}\langle \delta x_i \delta x_j \rangle &= \sum_n \omega_n f_n (x_i^n - X_i)(x_j^n - X_j)\\ &= -k \sum_n \omega_n (x_j^n - X_j) \partial f_n/\partial F_i\\ &= -k(\partial/\partial F_i)[\sum_n \omega_n f_n (x_j^n - X_j)]\\ &\qquad + k \sum_n \omega_n f_n (\partial/\partial F_i)(x_j^n - X_j)\\ &= -k\partial \langle \delta x_j \rangle/\partial F_i - k(\partial X_j/\partial F_i)\sum_n \omega_n f_n\\ &= -k\partial X_j/\partial F_i. \quad (17)\end{aligned}$$

Equations (15), (16), and (17) form a set of iteration equations from which we immediately obtain

$$\langle \delta x_i \delta x_j \delta x_k \rangle = k^2 \partial^2 X_k / \partial F_i \partial F_j \tag{18}$$

and

$$\begin{aligned}\langle \delta x_i \delta x_j \delta x_k \delta x_l \rangle &= -k^3 \partial^3 X_i / \partial F_j \partial F_k \partial F_l + k^2 (\partial X_i/\partial F_l)(\partial X_j / \partial F_k) \\ &\quad + k^2 (\partial X_j / \partial F_l)(\partial X_i / \partial F_k) \\ &\quad + k^2 (\partial X_k / \partial F_l)(\partial X_i / \partial F_j). \end{aligned} \tag{19}$$

Equations (17), (18), and (19) are then the fundamental equations for the correlation moments of the thermodynamic extensive parameters. It is, of course, clear that the indices appearing on the right sides of these equations may be freely permuted. It should also be noted that in performing the differentiations indicated, the fundamental set of independent parameters is to be considered to be $F_0, \cdots, F_r, X_{r+1}, X_{r+2}, \cdots$.

IV. THE MACROSCOPIC DISTRIBUTION FUNCTION

We shall now briefly review the logic whereby the distribution for the microstates may be transformed into a distribution function for macroscopic states.[6] It follows immediately from Eq. (12) that the probability $W dx_0 \cdots dx_r$ of finding a system, canonical with respect to $x_0, x_1, \cdots, x_r$ with parameters instantaneously in the ranges $dx_0, dx_1, \cdots, dx_r$ is

$$W dx_0 \cdots dx_r = \Omega dx_0 \cdots dx_r \times \exp(-(S[F_0, \cdots, F_r] + \sum_0^r F_k x_k)/k) \tag{20}$$

where $\Omega dx_0 \cdots dx_r$ is the total number of microstates, each state being weighted with its degeneracy, in the range $dx_0, dx_1, \cdots, dx_r$.

We now let Ω_0 denote the value of Ω corresponding to unit density of states in the space of $x_0, x_1, \cdots, x_r$ and recall that the entropy in a *microcanonical* ensemble having parameters in the range $dx_0, dx_1, \cdots, dx_r$ is defined[9] as

$$s \equiv k \ln(\Omega/\Omega_0) \tag{21}$$

whence

$$W = \Omega_0 \exp[-(S[F_0, \cdots, F_r] - s + \sum_0^r F_k x_k)/k] \tag{22}$$

or

$$W = \Omega_0 \exp[-\{S - s + \sum_0^r F_k (x_k - X_k)\}/k]. \tag{23}$$

The essential point of the argument is to now note that although S is the entropy of a *canonical* ensemble with parameters $X_0, X_1, \cdots, X_r$ and s is the entropy of a *microcanonical* ensemble with parameters $x_0, x_1, \cdots, x_r$, nevertheless s is the same function of its parameters as S is of its parameters. This fact is a fundamental theorem of statistical mechanics, rooted in the enormously high dimensionality of the phase spaces (speaking classically) of thermodynamic systems, and responsible for the fact that there is a single general thermodynamics, rather than a "microcanonical thermodynamics" and a separate "canonical thermodynamics." Thus we may now simply say that s is the entropy of a system in equilibrium, with parameters $x_0, x_1, \cdots, x_r$.

To recapitulate, the probability of finding a system with deviations from equilibrium between $\delta x_0 = (x_0 - X_0)$ and $\delta x_0 + d\delta x_0 = [(x_0 + dx_0) - X_0]$, and between $\delta x_1 = (x_1 - X_1)$ and $\delta x_1 + d\delta x_1 = [(x_1 + dx_1) - X_1]$, and

. . . . ,

between $\delta x_r = (x_r - X_r)$ and $\delta x_r + d\delta x_r = [(x_r + dx_r) - X_r]$ is

$$W dx_0 \cdots dx_r = \Omega_0 dx_0 \cdots dx_r \times \exp[-(S - s + \sum_0^r F_k \delta x_k)/k], \tag{24}$$

where S and s are the entropies of systems in equilibrium with parameters $X_0, X_1, \cdots, X_r$ and $x_0, x_1, \cdots, x_r$, respectively.

Although we shall adopt Eq. (24) as the fundamental macroscopic distribution function and shall show that all quantities of interest can be computed directly from it, the conventional procedure at this point has been to expand either $(s-S)$ or $(x_0 - X_0)$ in a Taylor series and to drop the cubic and higher order terms in the expansion. Of these two procedures, the expansion of $(x_0 - X_0)$ is the more awkward, but has nevertheless been the more common. We shall illustrate the more reasonable, but still unnecessary procedure of expanding $(s-S)$. We obtain

$$s - S = \sum_0^r F_k \delta x_k + \tfrac{1}{2} \sum_{j,k=0}^r S_{jk} \delta x_j \delta x_k + (1/3!) \sum_{i,j,k=0}^r S_{ijk} \delta x_i \delta x_j \delta x_k + \cdots, \tag{25}$$

where

$$S_{jK} = S_{kj} = \partial^2 S / \partial X_j \partial X_k = \partial^2 s / \partial x_j \partial x_k \tag{26}$$

(the latter evaluated at $X_0, X_1, \cdots, X_r$), and similarly for $S_{ijk}, S_{ijkl}, \cdots$. Dropping the cubic the cubic and higher order terms, we obtain

$$W \simeq A \exp(\sum_{j,k=0}^r S_{jk} \delta x_j \delta x_k / 2k), \tag{27}$$

where A is a renormalization constant. We shall refer to Eq. (25) as the "approximate macroscopic distribution function," as distinguished from the true macroscopic distribution function of Eq. (24).

V. CORRELATION MOMENTS FROM THE MACROSCOPIC DISTRIBUTION FUNCTION

We shall now show that the correlation moments of the fluctuating extensive parameters can be computed directly from the true macroscopic distribution function, (23), without invoking approximations, such as cutting off a series expansion. We shall also find that all the correlation moments so computed are identical

[9] A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover Publications, New York, 1949).

with those obtained from the microdistribution function, so that the two distribution functions are completely equivalent. The calculation of this section may therefore be considered as constituting an alternate derivation of the macroscopic distribution function.

Consider a typical third moment,

$$\langle\delta x_i\delta x_j\delta x_k\rangle=\Omega_0\int\cdots\int dx_0\cdots dx_r\delta x_i\delta x_j\delta x_k \times\exp[-(S-s+\sum^r F_t\delta x_t)/k]. \quad (28)$$

As in Eq. (14) we now have

$$\partial W/\partial F_k=-W(x_k-X_k)/k. \quad (29)$$

The procedure following Eq. (14) may now be repeated, with sums replaced by integrations, and one easily obtains the iteration Eqs. (15) and (16). Again the second moments must be considered separately, and we easily obtain Eqs. (17), (18), and (19). We thus see that the macroscopic distribution function may be directly used as the basis of calculation and yields the correct results in all cases.

VI. AN ALTERNATE FORM FOR THE SECOND MOMENTS

We have seen that the correct second correlation moments are given by

$$\langle\delta x_j\delta x_k\rangle=-k\partial X_j/\partial F_k$$

where, in the partial differentiation, the independent variables are to be taken as $F_0, \cdots, F_r, X_{r+1}, X_{r+2}, \cdots$. We now develop an alternative, and more familiar, form for these second moments, which is of interest in the theory of critical fluctuations,[10] and which bears on the calculation which proceeds from the approximate macroscopic distribution function. Let the inverse matrix to the $(r+1)$ by $(r+1)$ matrix S_{jk} have the elements,

$$\mathcal{S}_{jk}\equiv(\text{cofactor } S_{jk})/\|S_{jk}\|\equiv\mathcal{S}_{kj}. \quad (30)$$

Then we shall show that

$$\langle\delta x_j\delta x_k\rangle=-k\mathcal{S}_{jk}. \quad (31)$$

Consider the quantity $\partial X_j/\partial F_k$. Recalling the independent variables implied therein, and employing jacobian notation, we have

$$\begin{aligned}\frac{\partial X_j}{\partial F_k}&=\frac{\partial(X_j, F_0, \cdots, F_{k-1}, F_{k+1}, \cdots, F_r)}{\partial(F_k, F_0, \cdots, F_{k-1}, F_{k+1}, \cdots, F_r)}\\&=\frac{\partial(F_0, \cdots, F_{k-1}, X_j, F_{k+1}, \cdots, F_r)}{\partial(F_0, \cdots, F_{k-1}, F_k, F_{k+1}, \cdots, F_r)}\\&=\frac{\partial(X_0, \cdots, X_r)}{\partial(F_0, \cdots, F_r)}\cdot\frac{\partial(F_0, \cdots, F_{k-1}, X_j, F_{k+1}, \cdots, F_r)}{\partial(X_0, \cdots, X_r)}. \quad (32)\end{aligned}$$

[10] M. J. Klein and L. Tisza, Phys. Rev. 76, 1861 (1949).

Consider the first of the two jacobians in this equation:

$$\begin{aligned}\frac{\partial(X_0, \cdots, X_r)}{\partial(F_0, \cdots, F_r)}&=\left(\frac{\partial(F_0, \cdots, F_r)}{\partial(X_0, \cdots, X_r)}\right)^{-1}\\&=\left(\frac{\partial[(\partial S/\partial X_0), \cdots, (\partial S/\partial X_r)]}{\partial(X_0, \cdots, X_r)}\right)^{-1}\\&=\|S_{jk}\|^{-1}. \quad (33)\end{aligned}$$

The second jacobian in Eq. (32) is identical with the determinant of the matrix, except that the elements of column k are $\partial X_j/\partial X_0$, $\partial X_j/\partial X_1$, $\cdots$, $\partial X_j/\partial X_r$. Thus column k has a unity in position j and zeros elsewhere. Making a laplace expansion of the determinant according to the elements of column k we thus obtain

$$\frac{\partial(F_0, \cdots, F_{k-1}, X_j, F_{k+1}, \cdots, F_r)}{\partial(X_0, \cdots, X_r)}=(\text{cofactor } S_{jk}) \quad (34)$$

which, together with Eqs. (32) and (33) establishes our result, Eq. (31).

VII. APPROXIMATE CORRELATION MOMENTS

Having now obtained the correct correlation moment by direct calculation based on the true distribution functions, without recourse to approximations, we shall examine the validity of the results obtained by the conventional methods, based on the approximate macroscopic distribution function of Eq. (25).

We shall find it convenient to define

$$(\delta f_k)=k(\partial/\partial\delta x_k)\cdot\log_e W \quad (35)$$

and we shall see in a subsequent paper that this function plays a fundamental role in the theory of fluctuations of *intensive* parameters. With

$$W=A\exp(\sum_{j,k=0}^{r} S_{jk}\delta x_j\delta x_k/2k)$$

we find that

$$(\delta f_k)=\sum_{j=0}^{r} S_{jk}\delta x_j \quad (36)$$

which, except at critical points, may be inverted:

$$\delta x_j=\sum_{k=0}^{r}\mathcal{S}_{kj}(\delta f_k). \quad (37)$$

Now let ϕ be a function of the form,

$$\phi\equiv(\delta x_0)^{n_0}(\delta x_1)^{n_1}\cdots(\delta x_r)^{n_r}, \quad (38)$$

where the n_j are non-negative integers, and consider the quantity

$$\langle\phi(\delta f_m)\rangle=\int\cdots\int d(\delta x_0)\cdots d(\delta x_r)W\phi(\delta f_m)$$
$$=k\int\cdots\int d(\delta x_0)\cdots d(\delta x_r)\phi\partial W/\partial\delta x_m$$
$$=k\int\cdots\int d(\delta x_0)\cdots d(\delta x_r)$$
$$\times[\partial(\phi W)/\partial\delta x_m-W\partial\phi/\partial\delta x_m]. \quad (39)$$

Integrating the first term with respect to δx_m we see that this term vanishes because of the vanishing of ϕW at the limits of integration. Thus

$$\langle\phi(\delta f_m)\rangle=-k\langle\partial\phi/\partial\delta x_m\rangle=-kn_m\langle\phi/\delta x_m\rangle. \quad (40)$$

Using Eq. (37) we can now put

$$\langle\phi\delta x_k\rangle=\sum_{m=0}^{r}\mathcal{S}_{mk}\langle\phi(\delta f_m)\rangle=-k\sum_{m=0}^{r}\mathcal{S}_{mk}n_m\langle\phi/\delta x_m\rangle. \quad (41)$$

This equation furnishes us with an iteration equation for the approximate correlation moments, the moments on the right being two orders lower than the moment on the left. If we take $\phi=1$ so that $n_m=0$ for all m we obtain $\langle\delta x_k\rangle=0$ as is to be expected. If we put $\phi=\delta x_j$ we have $n_m=\delta_{mj}$ (where δ_{mj} is the Kronecker delta) and

$$\langle\delta x_j\delta x_k\rangle=-k\mathcal{S}_{jk} \quad (42)$$

which is identical with (32). This result shows that all the second moments computed with approximate macroscopic distribution function are exact. It has heretofore been considered, on the contrary, that the dropping of the higher terms in the exponent of W must cause small but nonzero errors in the results (42) for the second moments, and that these errors might conceivably become significant near critical points.

It is also easy to see that all the third, fifth, seventh, . . . moments are given as zero in the aforementioned approximate scheme, since our iteration procedure reduces them all to a linear combination of first moments, which latter must vanish. Furthermore all the fourth, sixth, eighth, . . . moments are also incorrectly given by the approximate macroscopic distribution function: For consider a fourth moment

$$\langle\delta x_i\delta x_j\delta x_k\delta x_l\rangle=-k(\mathcal{S}_{il}\langle\delta x_j\delta x_k\rangle+\mathcal{S}_{jl}\langle\delta x_i\delta x_k\rangle+\mathcal{S}_{kl}\langle\delta x_i\delta x_j\rangle)$$
$$=k^2(\mathcal{S}_{il}\mathcal{S}_{jk}+\mathcal{S}_{jl}\mathcal{S}_{ik}+\mathcal{S}_{kl}\mathcal{S}_{ij}). \quad (43)$$

If we compare the right-hand members of Eqs. (43) and (19) we note that each contains certain purely thermodynamic quantities and different powers of Boltzmann's constant; but transformations among purely thermodynamic quantities cannot involve Boltzmann's constant, so that Eqs. (43) and (19) cannot be identical. Therefore we see that the approximate macroscopic distribution function yields all the second moments of the thermodynamic extensive parameter fluctuations exactly, but that all the higher moments are incorrectly given.

VIII. CONCLUSION

In considering the various fluctuation moments of thermodynamic extensive parameters, we may either take a microscopic point of view and proceed directly from the distribution function for the microstates in the canonical ensemble, or we may take a completely macroscopic viewpoint and proceed from the Einstein function which gives the probability of each instantaneous macroscopic fluctuation. In both cases we may proceed entirely without approximation, and the results of both methods agree completely. The macroscopic point of view provides insight into various phenomena, such as irreversibility and the fluctuations in the intensive parameters, which is not so directly afforded by the microscopic point of view.