

STATISTICAL MECHANICS AND PROBABILITY THEORY

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1. Introduction

As pointed out by Khinchin [1], statistical mechanics presents two fundamental classes of problems for mathematics:

- (a) the problems which are closely connected with the ergodic theory, and
- (b) the problems which stem from the fact that the systems considered have many degrees of freedom.

The latter problems are concerned with the creation of an analytic method for the construction of asymptotic formulas.

The present work deals only with the problems of the second class. In order to describe the macroscopic properties of a given mechanical system composed of a very large number of particles with negligible interaction, one often defines the so-called most probable macroscopic state, namely, the distribution of particles (in their different possible states) having the largest probability of realization.

The mathematical expression for the probability of a macroscopic state uses formulas of combinatorial analysis which contain the factorial function, and, in the determination of the most probable state, Stirling's approximation [2] of $N!$. This method is relatively simple but it is not rigorous. Moreover, it is necessary to show in a rigorous way why the most probable state is indeed characteristic of macroscopic properties. The most probable value is not sufficient to determine all the properties of a random variable. However, under rather general conditions, the set of all the moments characterizes the probability distribution. Fowler makes use of the method of steepest descent to determine the values of all moments [3]. However, when he devised his analytical method, the theory of probability was not so developed as it is today. Hence, Fowler did not use certain methods of the theory of probability which, as we shall see, are particularly convenient and efficient. The main problems of statistical mechanics can be reduced to certain fundamental questions of probability theory. This procedure avoids the use of the certainly ingenious but often artificial tools used by Fowler. A number of papers have been published concerning this reduction of statistical mechanics to the theory of probability. A basic point is the following: *the problems of statistical mechanics can be reduced to classical problems of conditional probability*. For instance, it may be necessary to know the statistical properties of a system under the condition that its energy is supposed given.

This paper was prepared with the partial support of the Office of Naval Research.

The comparison of the recent papers on the subject suggests a classification into two broad categories. Khinchin's paper exemplifies the first category, characterized by the use of probability distributions and by the direct application of the central limit theorem in order to obtain asymptotic formulas of statistical mechanics. The second category of papers, exemplified by those of Bartlett [4], of Blanc-Lapierre and Tortrat [5], [6], is characterized by the use of characteristic functions. The essential point in this method of approach is the fact that, under suitable conditions, the product of a large number of characteristic functions is asymptotically equivalent to $e^{-\phi}$, where ϕ is a certain positive definite quadratic form. Although formally different, the two methods are essentially equivalent because both are consequences of the central limit theorem.¹

2. General remarks

We begin by reviewing some classical properties of phase space which are direct consequences of the fundamental principles of dynamics. Let (q, p) denote the coordinates of the point M representing the state of a given system S in its phase space Γ . The letter q will represent the coordinates of position and the letter p those of momentum.

The following results are fundamental for further developments.

(a) If S is an *isolated system*, then its representative point M , or its image, describes, in the phase space, a curve which is entirely contained in the surface Σ_E corresponding to the energy $H(p, q) = E = \text{constant}$.

(b) As time increases, Γ is transformed into itself by a volume-preserving mapping,

$$(2.1) \quad dV = dq \cdot \cdot \cdot dp.$$

(c) It follows from (a) and (b) that, on Σ_E , there exists an integral invariant with respect to time,

$$(2.2) \quad d\phi_E = \frac{d\sigma_E}{|\text{grad } H|_{H=E}},$$

where $d\sigma_E$ is an element of surface on Σ_E , and $\text{grad } H$ is the gradient of the function $H(M)$ on Σ_E .

(d) We suppose that every surface Σ_E is bounded. Then, under certain conditions of metric indecomposability, the probability that M belongs to a given domain $\Delta\Sigma_E$ of Σ_E is proportional to

$$(2.3) \quad \int_{\Delta\Sigma_E} d\phi_E.$$

In order to be more precise, we introduce the function

$$(2.4) \quad \Omega(E) = \int_{\Sigma_E} d\phi_E.$$

Then the probability element becomes

$$(2.5) \quad d\pi_E = \frac{d\phi_E}{\Omega(E)}.$$

¹ We must mention an interesting survey of the subject [8]. Obviously the reader will see in our paper many connections with Gibbs' classical work.

It is important to point out the following remark, previously emphasized by Khinchin. The image M of a given isolated system must remain on the surface Σ_E which corresponds to the value of the initial energy. Then the only probability which has physical significance is the probability which is distributed on this surface Σ_E . There exists no physical necessity to consider a probability distribution on the whole phase space.

The probability distribution on Σ_E is completely characterized by (2.5). This formula emphasizes the role played by the function $\Omega(E)$. We remark that, as a consequence of (2.2) and (2.4), this function can be expressed by

$$(2.6) \quad \Omega(E) = \frac{dV}{dE},$$

where $V(E)$ is the volume inside Σ_E .

Actually, the fundamental problem consists in obtaining an approximation for $\Omega(E)$ for large values of E . Essentially this problem is one of computation of volumes based on the expression for $H(p, q)$. Generally, the system S can be decomposed into components S_1, S_2, S_3, \dots , with negligible interaction among them, so that we can set $H = \sum_j H_j(p_j, q_j)$.

A priori, it is not evident why probability theory is useful to us in obtaining the solution of this problem of computation of volume. As pointed out by Khinchin, it is mainly in the search for the asymptotic properties of a large number of components that some typical methods of probability theory are useful. Hence, the reduction of our problems of statistical mechanics to probability theory results more from the similarity of the mathematical expressions than from the nature itself of the problems.

In order to reduce our problem to classical results of probability theory, it is convenient to consider a *fictitious probability distribution* Π in Γ in such a way that the distribution π_E on Σ_E is the conditional distribution of the *a priori* distribution Π , relative to the fixed value E of the energy. Indeed, only π_E has a physical meaning; there is some freedom in the choice of Π . The only condition on Π is that it reproduce the distribution π_E on Σ_E in the above sense.

What is the advantage of introducing Π ? As we have seen, S can be divided into components S_1, S_2, \dots with negligible interaction so that we have $H = H_1 + H_2 + \dots$. With the j th component S_j , we associate its image M_j in its own phase space Γ_j . Let dV_j be an element of volume in Γ_j . Then obviously

$$(2.7) \quad dV = dV_1 \cdot dV_2 \cdot dV_3 \cdot \dots$$

Consequently, the composition law of the volumes, (2.7), defines the law of composition of the Ω_j associated with the Γ_j of the different S_j . In the simplest case of two components, this law is

$$(2.8) \quad \Omega(E) = \int_0^E \Omega_1(E_1) \Omega_2(E - E_1) dE_1.$$

In the general case of N components, we have

$$(2.9) \quad \Omega(E) = \int \left\{ \prod_{i=1}^{N-1} \Omega_i(E_i) dE_i \right\} \Omega_N \left(E - \sum_{i=1}^{N-1} E_i \right).$$

Because of the conservation of the volume in the phase space Γ , it may be a great temptation to choose dV for the element of probability in the definition of the probability distribution Π ; this is not possible since $\int dV = \infty$; but, let us put this difficulty aside for the present. If dV is the element of probability, $\Omega(E)$ is the probability density of $E(M)$. If we adopt the same definition in each space Γ_i (with dV_i and $\Omega_i(E_i)$), then it is easily seen that (2.7) expresses the independence of the components M_1, M_2, \dots of the random variable M . If we recall that $E = \sum E_i$, we see that (2.9) expresses the independence of the random variables $E_i(M)$. Hence (2.7) and (2.9) show the independence of all the components S_i of S . Of course, we shall have to eliminate the difficulty due to the fact that $\int dV = \infty$.

After these preliminary remarks, we can say that the advantage of the introduction of the *a priori* probability distribution Π is the fact that the independence suggested by (2.7) and (2.9) can be preserved and the conditional distribution on Σ_E will coincide with the distribution π_E as we shall see.

The importance of the choice of Π lies in the simplicity with which formulas of composition can be obtained for systems with a very large number of components.

3. Statement of the principal problems

The principal problems we shall consider can be reduced to the following two types:

Problem 1. Statistical properties of one component or of one set of components. As before, let S be a system and S_1, S_2, \dots be its components with negligible interaction. Let us consider a particular component S_1 or a certain particular set S_c^* of components S_1, S_2, \dots, S_{N_c} . Problem 1 consists in studying the statistical properties of S_1 (or S_c^*) when the value E of the total energy is given. To be more precise, we shall study the statistical properties of M_1 (in Γ_1) or of $M_c = (M_1, M_2, \dots, M_{N_c})$ (in $\Gamma_1 \times \Gamma_2 \times \dots \times \Gamma_{N_c}$) when the value of E is given. It may also be necessary to find the probability distribution of the energy E_1 (or E_c). Problem 1 is exactly the problem studied by Khinchin.

Problem 2. The distribution of the different components among the different possible states. In problem 1 there was no necessity of assuming that all the components are identical. Now we shall make this assumption. Let N denote the number of identical components and let σ_j (energy ϵ_j) denote the different possible quantum states for one component. We shall always assume that the interaction between the different components is so small that each component has its "private" quantum states. We can then describe the situation for the set of N components by giving the numbers N_j of components which are in the different states σ_j . To be more precise, let us consider a particular state σ_1 (or a particular set σ_c^* of states σ_j). Our problem is to study, for given values of $H = E$ and N , the statistical properties of N_1 (or of the set of the N_j which correspond to the σ_j of σ_c^*). Problem 2 is the one studied by Fowler.

Remarks. (a) In problem 1 it is necessary to suppose that the components can be distinguished; in problem 2 this assumption is not necessary.

(b) We shall denote by S the total system and by σ^* the set of all states and, in both problems, we shall use the notation

$$(3.1) \quad S_r^* = S - S_c^*, \quad \sigma_r^* = \sigma^* - \sigma_c^*.$$

4. Reduction of the preceding problems to problems of probability theory. Advantages of exponential weights

Problem 1. We wish the conditional probability distribution associated with Π and with a given value E , to be π_E . If we consider the derivation for the expression of $d\pi_E$ [see (2.2)], we see immediately that, in Π , the density of probability in Γ must be a function of E only. We shall denote this function by $f(E)$. Hence, we have equiprobability near every surface Σ_E . This equiprobability insures that we shall have the correct law for $d\pi_E$. We must now choose $f(E)$ so as to satisfy the obvious condition

$$(4.1) \quad \int f(E)dV = 1 .$$

In addition, if the density of *a priori* probability in every space Γ_i is to have the same properties as in Γ , that is, be a function of E_i only and preserve the independence between the different components, then it is necessary that

$$(4.2) \quad f(E)dV = \prod f_i(E_i)dV_i$$

for $E = E_1 + E_2 + \dots + E_N$ and $dV = \prod_{j=1}^N dV_j$. For that, we must have

$$(4.3) \quad f(E) = \frac{e^{-\alpha E}}{\Phi(\alpha)} \quad \text{and} \quad f_i(E_i) = \frac{e^{-\alpha E_i}}{\Phi_i(\alpha)} ,$$

where α is a positive real number and Φ and Φ_i are normalization factors which are functions of α . The explicit expressions for Φ and for Φ_i are

$$(4.4) \quad \Phi(\alpha) = \int_{\Gamma} e^{-\alpha E} dV \quad \text{and} \quad \Phi_i(\alpha) = \int_{\Gamma_i} e^{-\alpha E_i} dV_i .$$

We shall assume the convergence of the integrals of (4.4) for every α ; it is easy to verify this point in the concrete cases considered.² From (4.2) and (4.3), it follows that

$$(4.5) \quad \Phi(\alpha) = \prod_{j=1}^N \Phi_j(\alpha) .$$

Under this probability distribution in the phase spaces Γ and Γ_j , the M_j are independent random points. Hence, the variables E_j are also independent. With these variables are associated the probability densities

$$(4.6) \quad \gamma_j(E_j) = \Omega_j(E_j) \frac{e^{-\alpha E_j}}{\Phi_j(\alpha)}$$

and we know (because of the independence of the S_j) that the composition law of Ω [see (2.8) and (2.9)], which is a direct consequence of the properties of the phase spaces, is again valid for the $\gamma_j(E_j)$. To summarize, we shall introduce an *a priori* distribution Π of M , defined by the two conditions:

- (a) The S_j components are independent.

² It is easy to see that in concrete cases $\Omega(E)$ increases only as a finite fixed power of E .

(b) In every space Γ_j , M_j is distributed with the probability density

$$(4.7) \quad f_j(E_j; \alpha) = \frac{e^{-\alpha E_j}}{\Phi_j(\alpha)}, \quad \alpha > 0,$$

and the corresponding energy distribution has a density

$$(4.8) \quad \gamma_j(E_j; \alpha) = \frac{\Omega_j(E_j)e^{-\alpha E_j}}{\Phi_j(\alpha)}.$$

The probability distribution for the system of a given energy E is then the conditional law which is derived from Π for the value E . Of course, this result is independent of the chosen value of α .

Therefore, our problem takes the following form:

We consider a certain number, generally large, of independent random multivariables M_1, M_2, \dots and we wish to know the conditional probability distribution of this set of variables, or of a certain subset, when a function of the energies associated with the M_j has a given value. This condition is $\sum E_j(M_j) = E$.

In what follows we shall refer to the above question as the *fundamental problem*. We are especially interested in its solution when the number of variables M_j is very large.

Problem 2. Now what corresponds to π_E ? It is the fundamental postulate of quantum statistics. All the quantum states of the total system S , consistent with the conditions

$$(4.9) \quad E = \sum E_i \quad \text{and} \quad N = \sum N_i,$$

have the same probability (see [2], p. 59). When we say "all the quantum states," we mean "all the possible different quantum states," taking into account the particular physical nature of the N identical systems of which S is composed. If these systems are not distinguishable, all the possible sets (N_1, N_2, \dots) which differ by at least one N_j correspond to distinct states for the total system and are equiprobable. We can attribute to every one a weight

$$(4.10) \quad \mu = 1.$$

If the systems S_j are distinguishable, then we must use

$$(4.11) \quad \mu = \frac{1}{N_1!} \frac{1}{N_2!} \dots$$

In Bose-Einstein's statistics, N_j can take on every value $0, 1, 2, \dots$, whereas in Fermi-Dirac's statistics, N_j is 0 or 1. The *a priori* probability distribution must satisfy the following condition: the quantum states of the total system which are in the same neighborhood as the quantum states defined by (4.9) must be equiprobable. Using the same derivations as in problem 1, we are led to define Π in the following way:

(a) The different variables N_j are independent in the Π distribution.

(b) The probability of having $N_j = k$ is

$$(4.12) \quad p_{j,k} = e^{-\alpha E_j - \beta k} \mu_{j,k} / \Phi_j(\beta, \alpha)$$

where $\mu_{j,k}$ is

- (a) 1 for $k = 0, 1, 2, \dots$ (Bose-Einstein).
- (b) 1 for $k = 0$ or 1, and 0 for $k \geq 2$ (Fermi-Dirac).
- (c) $1/k!$ (classical statistics).

$\Phi_j(\beta, \alpha)$ is a normalization factor so that

$$(4.13) \quad \sum_{k=0}^{\infty} p_{j,k} = 1$$

and α and β are real parameters with the only condition that the series of (4.13) converges. It follows from the relation $E_j = \epsilon_j N_j$ that for $\Phi_j(\alpha, \beta)$ we have

$$(4.14a) \quad \Phi_j = 1 + e^{-(\alpha\epsilon_j + \beta)} \quad (\text{Fermi-Dirac})$$

$$(4.14b) \quad \Phi_j = \frac{1}{1 - e^{-(\alpha\epsilon_j + \beta)}} \quad (\text{Bose-Einstein})$$

$$(4.14c) \quad \Phi_j = e^{-\alpha\epsilon_j + \beta} \quad (\text{classical statistics}).$$

As in problem 1, we introduce

$$(4.15) \quad \Phi(\beta, \alpha) = \prod_{j=0}^{\infty} \Phi_j(\beta, \alpha).$$

The domains of variation of α and β can be limited by the condition of the existence of Φ , so that,

$$(4.16) \quad \log \Phi(\beta, \alpha) = \sum_{j=0}^{\infty} \log \Phi_j(\beta, \alpha).$$

The convergence of the series (4.16) depends on the particular properties of the sequence $\{\epsilon_j\}$. The domain of variation of α is certainly at most equal to the half-axis $\alpha > 0$. If the sequence $\{\epsilon_j\}$ increases fast enough, α can be equal to any arbitrary positive value. For $\alpha = 0$, we have $\Phi = \infty$. In Fermi-Dirac's statistics, β can have any arbitrary value. In Bose-Einstein's statistics, it is necessary that, for every j , $\alpha\epsilon_j + \beta > 0$. If the ϵ_j are ordered so as to increase with j , then the condition is $\beta > -\alpha\epsilon_0$. For $\beta = -\alpha\epsilon_0$ we have $\Phi = \infty$. In the classical theory there are no limitations on β .

Results. Now we wish to emphasize certain results which will be useful for what follows. For problem 1 some of these results can be found in Khinchin's book, but in a different form.

Problem 1. The *a priori* probability density for the energy E is

$$(4.17) \quad \gamma(E; \alpha) = \frac{e^{-\alpha E} \Omega(E)}{\Phi(\alpha)}.$$

(We remarked above that we assume the existence of a positive number A so that $\Omega(E)$ increases no faster than E^A .) From (4.17) it is easily seen that the characteristic function $\phi(v, \alpha)$ of E is

$$(4.18) \quad \phi(v; \alpha) = \Phi(a - iv) / \Phi(\alpha).$$

$\phi(v, \alpha)$ is an analytic function of $z = \alpha - iv$ in the domain $\alpha > 0$, so that ϕ can be expanded in series in a neighborhood of every point of this domain and, particularly, near $v = 0$. Then, we have

$$(4.19a) \quad \Phi(\alpha + \Delta\alpha) = \Phi(\alpha) + \frac{\Delta\alpha}{1!} \Phi^{(1)}(\alpha) + \frac{\Delta\alpha^2}{2!} \Phi^{(2)}(\alpha) + \dots,$$

$$(4.19b) \quad \Phi(\alpha + \Delta\alpha) = \Phi(\alpha) \left\{ 1 + (-1) \frac{\Delta\alpha}{1!} \bar{E} + (-1)^2 \frac{\Delta\alpha^2}{2!} \bar{E}^2 + \dots \right\},$$

$$(4.20) \quad (-1)^n \frac{\Phi^{(n)}(\alpha)}{\Phi(\alpha)} = \bar{E}^n = \int_0^\infty \frac{E^n e^{-\alpha E} \Omega(E) dE}{\Phi(\alpha)}.$$

(The existence of the derivatives $\Phi^{(n)}$ and the convergence of the integrals are always insured.) If (4.19b) is applied to the first moments, then

$$(4.21) \quad \bar{E} = - \frac{d \log \Phi(\alpha)}{d\alpha}, \quad \bar{E}^2 = \frac{1}{\Phi(\alpha)} \frac{d^2 \Phi(\alpha)}{d\alpha^2},$$

$$\overline{E'^2} = \overline{(E - \bar{E})^2} = \frac{d^2 \log \Phi(\alpha)}{d\alpha^2}.$$

Now let us consider

$$(4.22) \quad \Phi_0(\alpha; E_0) = e^{E_0 \alpha} \Phi(\alpha)$$

and

$$(4.23) \quad \phi_0(v, \alpha; E_0) = e^{-ivE_0} \phi(v; \alpha),$$

where $\phi_0(v; \alpha; E_0)$ is the characteristic function of $e_0 = E - E_0$; we have

$$(4.24a) \quad \bar{e}_0 = - \frac{d \log \Phi(\alpha)}{d\alpha} - E_0 = - \frac{d \log \Phi_0(\alpha; E_0)}{d\alpha},$$

$$(4.24b) \quad \overline{(e_0 - \bar{e}_0)^2} = \frac{d^2 \log \Phi(\alpha)}{d\alpha^2}.$$

We remark that Φ_0 is convex and also that it is infinite for $\alpha = 0$ or $\alpha = +\infty$. Hence, Φ always has a unique minimum on $0 < \alpha < +\infty$. For this minimum we have

$$(4.25) \quad \overline{E(\alpha)} = E_0.$$

It is always possible to choose α uniquely so that the mean value $\overline{E(\alpha)}$ in the a priori distribution Π takes on any arbitrary positive value E_0 . This result is true for a particular Φ_j , for a product $\prod \Phi_j$ of an arbitrary number of Φ_j or for Φ which is the product of all the Φ_j .

Problem 2. In an analogous way, the characteristic function of the joint distribution of N_j and E_j in Π is

$$(4.26) \quad \phi_j(u, v; \beta, \alpha) = \Phi_j(\beta - iu; \alpha - iv) / \Phi_j(\beta, \alpha).$$

Now let us consider an arbitrary set s of σ_j quantum states. We shall write

$$(4.27) \quad N_s = \sum_s N_j, \quad E_s = \sum_s E_j, \quad \Phi_s = \prod_s \Phi_j.$$

It is seen that the characteristic function of (N_s, E_s) is

$$(4.28) \quad \phi_s(u, v; \beta, \alpha) = \Phi_s(\beta - iu, \alpha - iv) / \Phi_s(\beta, \alpha).$$

If s contains all the quantum states, then we can remove the symbol s in (4.28). In that case we have

$$(4.29) \quad \phi(u, v; \beta, \alpha) = \Phi(\beta - iu, \alpha - iv) / \Phi(\beta, \alpha).$$

As in problem 1,

$$(4.30) \quad \begin{aligned} \log \phi_s(u, v; \beta, \alpha) &= -iu \frac{\partial \log \Phi_s}{\partial \beta} - iv \frac{\partial \log \Phi_s}{\partial \alpha} \\ &- \frac{1}{2} \left\{ \frac{\partial^2 \log \Phi_s}{\partial \beta^2} u^2 + 2 \frac{\partial^2 \log \Phi_s}{\partial \beta \partial \alpha} uv + \frac{\partial^2 \log \Phi_s}{\partial \alpha^2} v^2 \right\} + \dots \\ &= iu \overline{N}_s + iv \overline{E}_s - \frac{1}{2} \left\{ \overline{N_s'^2} u^2 + 2 \overline{N_s' E_s'} uv + v^2 \overline{E_s'^2} \right\} + \dots, \end{aligned}$$

where

$$(4.31) \quad N_s' = N_s - \overline{N}_s \quad \text{and} \quad E_s' = E_s - \overline{E}_s.$$

We see that

$$(4.32) \quad \overline{N}_s = - \frac{\partial \log \Phi_s}{\partial \beta} \quad \overline{E}_s = - \frac{\partial \log \Phi_s}{\partial \alpha},$$

$$(4.33) \quad \overline{N_s'^2} = \frac{\partial^2 \log \Phi_s}{\partial \beta^2}; \quad \overline{N_s' E_s'} = \frac{\partial^2 \log \Phi_s}{\partial \beta \partial \alpha}; \quad \overline{E_s'^2} = \frac{\partial^2 \log \Phi_s}{\partial \alpha^2}.$$

If s is reduced to a simple element σ_j , then $\epsilon_j N_j' = E_j'$. In this case the correlation coefficient between E_j' and N_j' is 1. If s contains two or more elements, then there is no proportionality relation between N_s' and E_s' and the correlation coefficient is not 1; then,

$$(4.34) \quad \left| \frac{\partial^2 \log \Phi_s}{\partial \beta \partial \alpha} \right|^2 < \frac{\partial^2 \log \Phi_s}{\partial \beta^2} \frac{\partial^2 \log \Phi_s}{\partial \alpha^2}.$$

(The two derivatives in the second member are positive since they are equal to $\overline{N'^2}$ or $\overline{E'^2}$, respectively.) Depending upon the different statistics, we have

$$(4.35) \quad \begin{aligned} \log \Phi_s &= \sum_s \log (1 + e^{-(\alpha \epsilon_j + \beta)}) && \text{(Fermi-Dirac)} \\ \text{or} \quad \log \Phi_s &= - \sum_s \log (1 - e^{-(\alpha \epsilon_j + \beta)}) && \text{(Bose-Einstein)} \\ \text{or} \quad \log \Phi_s &= \sum_s e^{-(\alpha \epsilon_j + \beta)} && \text{(classical statistics).} \end{aligned}$$

The domains of variation for α and β are represented by the following figures.

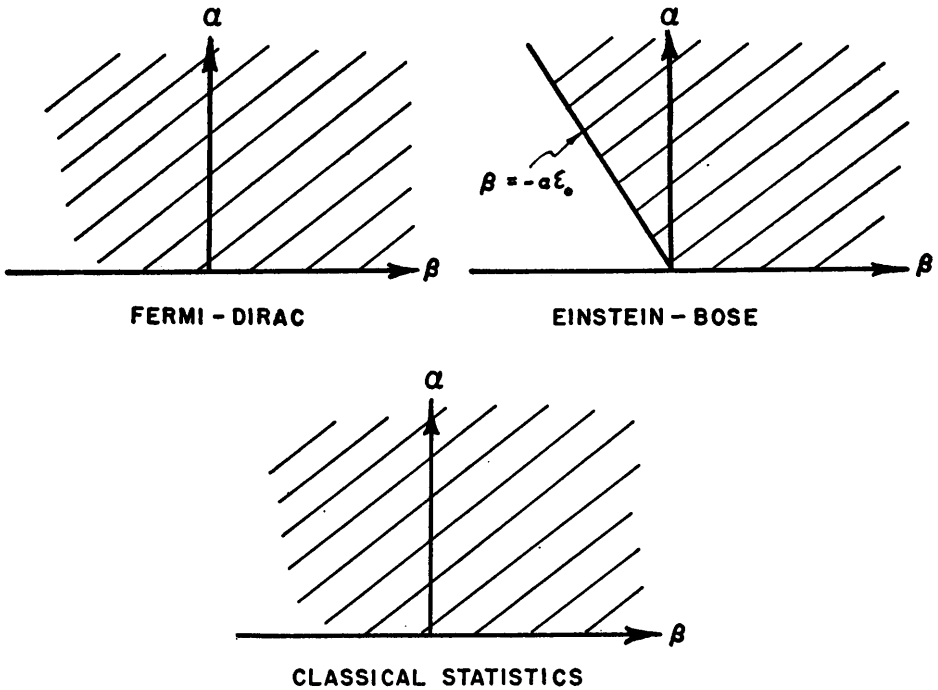


FIGURE 1
Domain of (α, β) for different statistics.

Using the same method of derivation as in problem 1, we introduce

$$(4.36) \quad \Phi_{s,0}(\beta, \alpha; N_0, E_0) = e^{N_0\beta + E_0\alpha} \Phi_s(\beta, \alpha).$$

It is easy to see that, under rather general conditions, $\log \Phi_{s,0}$ is equal to $+\infty$ at all the limits of the variation of α and β . Since $\log \Phi_s$ and $\log \Phi_{s,0}$ are convex, as a consequence of (4.34) and (4.36), $\log \Phi_{s,0}$ has a single minimum. If α_0 and β_0 are the coordinates of this minimum, then

$$(4.37) \quad \overline{N_s(\beta_0, \alpha_0)} = N_0$$

$$(4.38) \quad \overline{E_s(\beta_0, \alpha_0)} = E_0.$$

It is always possible to choose α and β uniquely so that the a priori mean values \bar{N}_s and \bar{E}_s take on two given positive values N_0 and E_0 , respectively.

5. General remarks on the resolution of the fundamental problem

The fundamental problem can be resolved by using either the method of probability density or of characteristic functions. First, we shall demonstrate the two methods in the solution of problem 1.

5.1. *Utilization of probability density.* Let S_c^* be the component (or the set of components) being considered and $(M_c = M_1, M_2, \dots, M_N)$ the image of S_c^* in Γ_c ; we shall denote by $N_c + 1, N_c + 2, \dots, N$ the indices of the remaining components. If E has a given value E_0 , then the multiplication theorem for the probability of compound events immediately gives the probability that M_c be in an element dM_c of Γ_c . This probability is

$$(5.1) \quad f(M_c/E_0) = \frac{\Pr\{M_c \subset dM_c \text{ and } E_0 < E < E_0 + dE\}}{\Pr\{E_0 < E < E_0 + dE\}}.$$

If we take into account the independence of the *a priori* probability distribution of S_r and S_c^* , then

$$(5.2) \quad f(M_c/E_0) = \frac{f(M_c)\gamma_r[E_0 - E_c(M_c)]}{\gamma(E_0)}$$

where $f(M_c)$ is the *a priori* density of M_c , $f(M_c/E_0)$ is the conditional probability density, $\gamma(E_0)$ is the value of the *a priori* probability density of E in Γ for $E = E_0$, and $\gamma_r[E_0 - E_c(M_c)]$ is the value of the *a priori* density of E_r in Γ_r for $E_0 - E_c(M_c)$.

The whole problem is to derive γ and γ_r which are probability densities of certain sums of independent random variables E_j . For this purpose, it is possible to use an approximation, by normal law, as pointed out by Khinchin, if S_c^* contains a large number of components.

Remark. The relation (5.1) gives the probability density relative to the localization of M_c in Γ_c . If we are interested in the value of the energy E_c , we have as a conditional probability density

$$(5.3) \quad \gamma_c(E_c/E_0) = \Omega_c(E_c)f(M_c/E_0)$$

$$(5.4) \quad = \frac{\Omega_c(E_c)\Omega_r(E_0 - E_c)}{\Omega(E_0)}.$$

This relation, which is independent of α , plays an essential role in Khinchin's theory. We shall return to this point later.

5.2. *Utilization of the characteristic functions.*

(a) Localization of M_c in Γ_c . Let Ψ_c be the *a priori* characteristic function of (\vec{M}_c, E_c) , that is to say,

$$(5.5) \quad \Psi_c(\vec{u}_c; v) = e^{\overline{i(\vec{u}_c \cdot \vec{M}_c + vE_c)}} = \int_{\Gamma_c} e^{i(\vec{u}_c \cdot \vec{M}_c + vE_c)} f_c(E_c) dv_c,$$

where \vec{u}_c is a point in a Euclidean space of the same number of dimensions as M_c , and v is the parameter associated with E_c . The characteristic function of $(\vec{M} = \vec{M}_c \times \vec{M}_r, E = \sum E_j)$ is

$$(5.6) \quad \Psi(\vec{u}_c; \vec{u}_r; v; \alpha) = \Psi(\vec{u}_c; v; \alpha)\psi(\vec{u}_r; v; \alpha).$$

It is necessary to derive the characteristic function $\phi(\vec{u}_c, \vec{u}_r/E_0)$ of M when E has a given value E_0 . Through the use of a slight generalization of Bartlett's results [4]

concerning the characteristic function of conditional probabilities, one can easily obtain

$$(5.7) \quad \phi(\tilde{u}_c, \tilde{u}_r/E_0) = \frac{\int e^{-ivE_0}\Psi(\tilde{u}_c; \tilde{u}_r; v, \alpha)dv}{\int e^{-ivE_0}\Psi(0, 0; v, \alpha)dv} .$$

If we are interested in the component S_c^* only, it is enough to set $u_r = 0$. In this case

$$(5.8) \quad \phi(\tilde{u}_c/E_0) = \frac{\int e^{-ivE_0}\Psi(u_c, 0; v, \alpha)dv}{\int e^{-ivE_0}\Psi(0, 0; v, \alpha)dv} .$$

(b) *Distribution of E_c .* If we are interested in E_c , it is necessary to obtain the characteristic function of the *a priori* joint distribution of E_c and E . This characteristic function is $\phi_c(v + v_c; \alpha)\phi_r(v; \alpha)$ and we must replace the formula (5.8) by

$$(5.9) \quad \phi(v_c/E_0) = \frac{\int e^{-ivE_0}\phi_c(v + v_c; \alpha)\phi_r(v; \alpha)dv}{\int e^{-ivE_0}\phi_c(v; \alpha)\phi_r(v; \alpha)dv} .$$

6. Solution of the fundamental problem (problem 1)

6.1. *Hypothesis.* We wish to solve this question using either the method of probability density or that of characteristic functions. Actually we wish to obtain the asymptotic properties of those systems which have a great number of degrees of freedom, or more precisely, of those systems in which the number of degrees of freedom tends to infinity.

It is now necessary to explain exactly what is meant by the expression "the number of degrees of freedom tends to infinity." Indeed, we cannot talk about asymptotic properties if we have not completely defined the way in which our system tends to infinity. In this definition we have to conserve the values associated with the properties which Fowler calls *intensive properties* and whose constancy expresses the stability of the matter of which S is the mechanical image. However, of course, the *extension* of our system increases, that is to say, the quantity of matter increases.

Let us consider the decomposition of the given system S into its components $\{S_i\}$ in which S_c^* is decomposed into the components S_1, S_2, \dots, S_{N_c} and S_r^* into the components $S_{N_c+1}, S_{N_c+2}, \dots, S_{N_r}$. Hence, the total system is decomposed into $N_c + N_r$ components. The component S_c^* which we are studying can remain finite (*small component* interacting with a "heat bath" S_r^*) or tend to infinity (*large component*). We shall always suppose: $N_r \rightarrow \infty$. N_c may be bounded or may tend to infinity. In the latter case, we shall suppose that both ratios N_r/N and N_c/N have limits. When we say: $N_r \rightarrow \infty$, this is not precise enough because we do not necessarily suppose that all the components are identical. We suppose the following three

conditions to hold; they express the stability of the intensive properties of the matter:

$$(6.1) \quad \frac{\sum_r \log \Phi_j(\alpha)}{N_r} \rightarrow a_r(\alpha)$$

$$(6.2a) \quad \frac{\sum_r \frac{d}{d\alpha} \log \Phi_j(\alpha)}{N_r} \rightarrow \frac{da_r}{d\alpha} = -b_r(\alpha)$$

and

$$(6.3a) \quad \frac{\sum_r \frac{d^2}{d\alpha^2} \log \Phi_j(\alpha)}{N_r} \rightarrow \frac{d^2 a_r}{d\alpha^2} = c_r(\alpha) .$$

The relations (6.2a) and (6.3a) are equivalent to the following equations whose meaning is more easily seen:

$$(6.2b) \quad \frac{1}{N_r} \sum_r \bar{E}_j \rightarrow b_r(\alpha)$$

and

$$(6.3b) \quad \frac{1}{N_r} \sum_r \overline{(E_j - \bar{E}_j)^2} \rightarrow c_r(\alpha) .$$

We shall make the natural assumption that $c_r(\alpha) > 0$. In the case of a large component we shall also impose, on the component S_c^* , the conditions analogous to (6.1), (6.2a) and (6.3a) which assure the existence of the limits $a_c(\alpha)$, $b_c(\alpha)$, $c_c(\alpha)$. Our assumptions are also fulfilled by $S = S_c + S_r$ with the limiting values

$$(6.4) \quad \begin{cases} a(\alpha) = k_r a_r + k_c a_c \\ b(\alpha) = k_r b_r + k_c b_c \\ c(\alpha) = k_r c_r + k_c c_c \end{cases}$$

where k_r and k_c represent the limits of $N_r/(N_c + N_r)$ and $N_c/(N_c + N_r)$, respectively.

6.2. *Method of probability densities.* This is essentially the same as the method developed by Khinchin.

(a) Let us first give some simplified and intuitive considerations concerning Khinchin's method. It is easy to see that

$$(6.5) \quad f(M_c/E_0) = \frac{\Omega_r(E_0 - E_c)}{\Omega(E_0)}$$

and, hence, the problem is mainly to determine Ω and Ω_r . In the simple case in which E is a quadratic definite form, the volume $V(E)$ is proportional to the volume of an ellipsoid, given by $(\sqrt{E})^N$ where N is the number of degrees of freedom (see [2] F. Perrin, chapter 3, section 12); in this case, Ω is proportional to $E^{(N/2)-1} = E'$ and it is obvious that

$$(6.6) \quad \frac{\Omega(E_0 + \Delta E)}{\Omega(E_0)} \sim e^{\theta \Delta E} \exp \left[-\frac{(\Delta E)^2}{2\nu/\theta^2} \right]$$

where θ is defined by $1/\theta = E_0/\nu$ and $\Delta E/E_0$ is supposed to be a small quantity. Using heuristic derivation we see that (6.6) leads to a relation which plays an important role in Khinchin's theory. If we set $E_0 + \Delta E = x$ in (6.6), we have

$$(6.7) \quad \frac{\Omega(x)}{\Omega(E_0)} \frac{e^{-\theta x}}{e^{-\theta E_0}} \frac{1}{\sqrt{2\pi} \sigma_\theta} \sim \frac{e^{-(x-E_0)^2/2\sigma_\theta^2}}{\sqrt{2\pi} \sigma_\theta},$$

where $\sigma_\theta^2 = \nu/\theta^2$.

Let us assume that our approximation is correct in an x -domain around E_0 so large as to allow us to integrate both sides of (6.7) from 0 to infinity (actually from $-\infty$ to $+\infty$). Hence, we have

$$(6.8) \quad \int \frac{\Omega(x)e^{-\theta x} dx}{\Omega(E_0)e^{-\theta E_0}} \sim \sqrt{2\pi} \sigma_\theta$$

and using (4.4) and (2.6), we see that

$$(6.9) \quad \Omega(E_0) \sim \frac{e^{\theta E_0} \Phi(\theta)}{\sqrt{2\pi} \sigma_\theta}.$$

By multiplying both sides of (6.7) by x and integrating them from $-\infty$ to $+\infty$, we get

$$(6.10) \quad \int_0^\infty \frac{x \Omega(x) e^{-\theta x}}{\Omega(E_0) e^{-\theta E_0} \sqrt{2\pi} \sigma_\theta} dx \sim E_0.$$

Using (6.9), this integral is approximately equal to

$$(6.11) \quad \int_0^\infty \frac{x \Omega(x) e^{-\theta x}}{\Phi(\theta)} dx = -\frac{d}{d\theta} \log \Phi(\theta)$$

so that we have

$$(6.12) \quad E_0 = -\frac{d}{d\theta} \log \Phi(\theta).$$

We shall now show that Gibbs' law can also be heuristically derived from the above formula (6.6) (case of small component). In the case of a small component we have $N_r \sim N$ and $N_c \ll N_r$. In (6.5) we replace Ω and Ω_r by their approximate expressions following from (6.6) and it is easy to see that we can here use the same value of θ for S and for S_r^* . Thus, we obtain

$$(6.13) \quad f(M_c/E_0) \sim \frac{\Omega_r(E_0)}{\Omega(E_0)} e^{-\theta E_c} \exp \left[-\frac{E_c^2}{2\nu/\theta^2} \right]$$

where $\Omega_r(E_0)/\Omega(E_0) \sim 1/\Phi_c(\theta)$ (as a consequence of (6.9) and of $\Phi = \Phi_r \Phi_c$). Neglecting the second exponential, which must be very close to 1 for a given value of θ and for ν large, we obtain Gibbs' law.

However, it should be noted that we have not shown that the above approxima-

tions are available in a large enough domain, and hence we cannot assert, for instance, that the following integral corresponding to the total probability is unity:

$$(6.14) \quad \int_0^\infty \frac{\Omega_r(E_0)}{\Omega(E_0)} \Omega_c(x) e^{-\theta x} \exp \left[-\frac{x^2}{2\nu/\theta^2} \right] dx .$$

From our point of view, Khinchin's method consists in deriving the above formulas rigorously.

(b) Actual derivation of the conditional distributions. In (5.2) we use the normal approximation for the densities associated with the systems which have a large number of components. In the case of a small component, we use this approximation only for γ_r and γ ; in the case of a large component, we can use this approximation for γ_c , γ_r and γ .

First, we shall present the theorem proved by Khinchin.

THEOREM. *Let x_1, x_2, \dots be a sequence of independent random variables ($\bar{x}_k = 0$); let $U_k(x)$ and $g_k(u)$ denote their probability densities and their characteristic functions, respectively. We assume*

(1) *The derivatives U'_k exist; the integrals of $|U'_k|$ from $-\infty$ to $+\infty$ exist and are bounded uniformly with respect to k .*

(2) *For every random variable, the first five moments exist and it is possible to find two positive numbers λ and μ , independent of k , such that $0 < \lambda < \overline{x_k^2} < \mu$; $|\overline{x_k^3}| < \mu$; $\overline{x_k^4} < \mu$; $|\overline{x_k^5}| < \mu$.*

(3) *There exist positive constants a and b such that $|g_k(u)| > b$, for $|u| < a$.*

(4) *For each interval (c_1, c_2) (with $c_1 c_2 > 0$) there exists a number $\rho(c_1, c_2) < 1$ such that for any u in the interval (c_1, c_2) we have $|g_k(u)| < \rho$ ($k = 1, 2, \dots$).*

If $U_n(x)$ denotes the probability density of the sum of the first n terms in the given sequence of random quantities, then

(a) *for $|x| < 2 \log^2 n$, we have*

$$(6.15a) \quad U_n(x) = \frac{1}{(2\pi B_n)^{1/2}} e^{-x^2/2B_n} + \frac{S_n + T_n x}{B_n^{5/2}} + o\left(\frac{1 + |x|^3}{n^2}\right),$$

(b) *for any arbitrary x , we have*

$$(6.15b) \quad U_n(x) = \frac{1}{(2\pi B_n)^{1/2}} e^{-x^2/2B_n} + o\left(\frac{1}{n}\right),$$

where $B_n = \sum_{k=1}^n \overline{|x_k|^2}$, S_n and T_n are independent of x and do not increase faster than n .

The case of a small component. In this case, N_c is bounded and $N_r \rightarrow \infty$, and it is natural to assume that the total energy E_0 increases proportionally to $N_c + N_r$, that is, as $N \rightarrow \infty$,

$$(6.16) \quad \lim \frac{E_0}{N_c + N_r} = e_0 .$$

Let Φ_c, Φ_r and Φ be the Φ -functions associated with S_c, S_r and S ($\Phi = \Phi_c \Phi_r$), respectively. It follows from (5.2) that

$$(6.17) \quad f(M_c/E_0) = \frac{e^{-\alpha E_c}}{\Phi_c(\alpha)} \left[\frac{d^2 \log \Phi}{d\alpha^2} / \frac{d^2 \log \Phi_r}{d\alpha^2} \right]^{\frac{1}{2}} \cdot \left[\left(\exp A + o\left(\frac{1}{\sqrt{N_r}}\right) \right) / \left(\exp B + o\left(\frac{1}{\sqrt{N}}\right) \right) \right]$$

with

$$(6.18) \quad A = - \left(E_0 - E_c + \frac{d \log \Phi_r}{d\alpha} \right)^2 / 2 \frac{d^2 \log \Phi_r}{d\alpha^2}$$

and

$$(6.19) \quad B = - \left(E_0 + \frac{d \log \Phi}{d\alpha} \right)^2 / 2 \frac{d^2 \log \Phi}{d\alpha^2} .$$

This relation is true for an arbitrary value of α . Actually, we shall see that it has a simple and useful expression for only one value of α which is determined without ambiguity. Indeed, (6.17) is useful only in the case that, at least in the denominator, the term $o(\sqrt{1/N})$ is negligible as compared to the exponential term. In order to realize this condition we proceed in the following manner: for N large but finite, we take for α the single root α_N (see equations 4.25) of

$$(6.20) \quad E_0 = - \frac{d \log \Phi(\alpha; N)}{d\alpha} = \overline{E(\alpha_N)} ,$$

so that the exponential term in the denominator is always equal to 1. For every N , we shall have

$$(6.21) \quad \frac{E_0}{N} = - \frac{1}{N} \frac{d \log \Phi(\alpha; N)}{d\alpha} , \quad (\alpha = \alpha_N) .$$

If $N \rightarrow +\infty$, the first member tends to e_0 and

$$(6.22) \quad \lim_{N \rightarrow \infty} - \frac{1}{N} \frac{d \log \Phi(\alpha, N)}{d\alpha} (\alpha = \alpha_N) = e_0 .$$

Under rather general regularity conditions on the functions $\Phi(\alpha, N)$, $b_r(\alpha)$ and $c_r(\alpha)$ introduced in (6.2) and (6.3), and supposing that $c_r(\alpha) > 0$, which is almost a consequence of the meaning of $c_r(\alpha)$, it is possible to show that:

- (1) As $N \rightarrow \infty$, α_N tends to a unique limit, $\alpha(\infty)$,
- (2) $\alpha(\infty)$ is the single root of

$$(6.23) \quad e_0 = b_r(\alpha(\infty)) .$$

In order to justify this result, it is enough to suppose that the convergences which occur in (6.2a) and (6.3a) are uniform on a segment > 0 surrounding $\alpha(\infty)$. Choosing $\alpha = \alpha_N$, the exponential in the denominator is equal to 1.

Now considering the numerator, we want a good approximation for $f(M_c/E_0)$ in the set of points M_c for which $\Omega_c(E_c(M_c))f(M_c/E_0)$ is not negligible. For such points, the exponential in { } is surely dominant. However, because the exponential

$\exp(-\alpha_N E_c)$ exists in (6.17) and because $\Omega_c(E_c)$ increases only as a finite fixed power of E_c , it is sufficient to consider the values of E_c bounded, for instance, by

$$(6.24) \quad E_c < \frac{1000}{\alpha(\infty)}.$$

If $N \rightarrow \infty$, then using (6.2a), (6.3a) and (6.24), it is seen that

$$(6.25) \quad \lim_{N \rightarrow \infty} \left(\frac{d^2 \log \Phi_r}{d\alpha^2} \right) / \left(\frac{d^2 \log \Phi}{d\alpha^2} \right) = 1$$

$$(6.26) \quad \lim_{N \rightarrow \infty} \left(E_0 - E_c + \frac{d \log \Phi_r}{d\alpha} \right)^2 / \left(\frac{d^2 \log \Phi_r}{d\alpha^2} \right) = 0.$$

Besides, under rather general conditions, if α_N is interior to a certain domain surrounding $\alpha(\infty)$ then the terms $o(1/\sqrt{N})$ in (6.17) can be bounded uniformly with respect to α . Hence, we obtain

$$(6.27) \quad \lim_{N \rightarrow \infty} f(M_c/E_0) = \frac{e^{-\alpha(\infty)E_c}}{\Phi_c[\alpha(\infty)]},$$

which is exactly Gibbs' law.³

THEOREM. *The conditional distribution for a small component S_c^* is equal to the a priori distribution under the condition that α is chosen so that*

$$(6.28) \quad E = \overline{E(\alpha)}$$

where $\overline{E(\alpha)}$ is the a priori mean value of E .

A remark of K. Itô. We are indebted to Professor Itô for a very interesting remark made during the discussion of our paper; this remark leads to the idea that we do not need to use the central limit theorem as we did above to derive the asymptotic expression (6.27). Intuitively speaking, this remark is the following: We wish to derive the asymptotic expression for $f(M_c/E_0)$; such a density of probability is defined by

$$(6.29) \quad f(M_c/E_0)dM_c \sim \frac{p \left\{ M_c \subset dM_c \text{ and } e_0 - \epsilon < \frac{E}{N} < e_0 + \epsilon \right\}}{p \left\{ e_0 - \epsilon < \frac{E}{N} < e_0 + \epsilon \right\}}.$$

Now, let us consider the a priori distribution of the sum $E = E_1 + E_2 + \dots$ where the random variables are independent. Using the law of large numbers we see that, when $N \rightarrow \infty$, we have $\lim[(E - \overline{E(\alpha)})/N] = 0$, that is, $\lim[(E/N) - b_r(\alpha)] = 0$.

Now, let us suppose that we have chosen α so that $b_r(\alpha) = e_0$, that is, $\alpha = \alpha(\infty)$;

³ It is obvious by comparison with (4.4) that the expression defined by (6.27) yields the value 1 for the total probability. If, for N sufficiently large, we assign to α a value $\alpha'_N \neq \alpha_N$ so that the argument of the exponential in the denominator tends to a finite limit $\exp(-\delta^2/2)$, it is easy to see that α'_N also tends to $\alpha(\infty)$ and that, in the limit, both the numerator and the denominator of (6.17) are multiplied by $e^{-\delta^2/2}$ and we obtain the same result as before.

the condition $e_0 - \epsilon < E/N < e_0 + \epsilon$ is automatically fulfilled and we can eliminate it from (6.29). Then we have

$$(6.30) \quad f(M_c/E_0) = f(M_c).$$

For this particular choice of α , the *a priori* density is the same as the conditional density. This derivation is not rigorous but it seems that it would not be very difficult to put in a rigorous form.

The case of a large component. We are interested in the energy of a large component. We begin with the following relation, established above,

$$(6.31) \quad \gamma(E_c/E_0) = \frac{\gamma_c(E_c, \alpha)\gamma_r(E_0 - E_c(M_c))}{\gamma(E_0)}.$$

If we apply Khinchin's theorem to γ_c , γ_r , and γ , we then have

$$(6.32) \quad \gamma(E_c/E_0) = \left[\frac{d^2 \log \Phi}{d\alpha^2} / \frac{d^2 \log \Phi_r}{d\alpha^2} \cdot \frac{d^2 \log \Phi_c}{d\alpha^2} \right]^{\frac{1}{2}} \\ \cdot \frac{1}{\sqrt{2\pi}} \left(\exp A + o\left(\frac{1}{\sqrt{N_r}}\right) \right) \left(\exp C + o\left(\frac{1}{\sqrt{N_c}}\right) \right) / \left(\exp B + o\left(\frac{1}{\sqrt{N}}\right) \right)$$

where A and B are defined in (6.17) and where

$$(6.33) \quad C = - \left[E_c + \frac{d \log \Phi_c}{d\alpha} \right]^2 / 2 \frac{d^2 \log \Phi_c}{d\alpha^2}.$$

We choose α as before, and suppose that

$$(6.34) \quad \lim \frac{E_c}{N_c} = e_c; \quad \lim \frac{E_r}{N_r} = e_r; \quad \lim \frac{N_c}{N} = k.$$

Following Khinchin's notation we set

$$(6.35) \quad B_{c,N_c} = \sum_1^{N_c} \frac{1}{(E_c - \bar{E}_c)^2} \quad B_{r,N_r} = \sum_1^{N_r} \frac{1}{(E_r - \bar{E}_r)^2} \quad B_N = B_{c,N_c} + B_{r,N_r}.$$

In addition we have $\bar{E}_c + \bar{E}_r = E_0$, that is, $E_c - \bar{E}_c = -(E_0 - E_c - \bar{E}_r)$. Setting $A_c = \bar{E}_c = -d \log \Phi_c / d\alpha$, we have, for N_c and $N_r \rightarrow \infty$,

$$(6.36a) \quad \gamma_c(E_c/E_0) \sim \left(\frac{B_N}{2\pi B_{c,N_c} \cdot B_{r,N_r}} \right)^{\frac{1}{2}} \exp \left[- \frac{(E_c - A_c)^2}{2B_{c,N_c}} - \frac{(E_c - A_c)^2}{2B_{r,N_r}} \right]$$

or

$$(6.36b) \quad \gamma_c(E_c/E_0) \sim \frac{1}{(2\pi B)^{\frac{1}{2}}} \exp \left(- \frac{(E_c - A_c)^2}{2B} \right)$$

where

$$(6.37) \quad B = (B_{c,N_c} \cdot B_{r,N_r}) / (B_{c,N_c} + B_{r,N_r}).$$

6.3. Method of characteristic functions.

(a) *Small component.* We use (5.8), where

$$(6.38) \quad \Psi(\vec{u}_c, 0; v, \alpha) = \Psi(\vec{u}_c, v; \alpha) \prod_{(r)} \{ \Phi_j(\alpha - iv) / \Phi_j(\alpha) \} .$$

ϕ_j can be developed in power series of v in the neighborhood of $v = 0$. Let us write the limited development of the third order⁴

$$(6.39) \quad \log \phi_j(v; \alpha) = -iv \frac{d \log \Phi_j}{d\alpha} - \frac{v^2}{2} \frac{d^2 \log \Phi_j}{d\alpha^2} + \frac{iv^3}{3!} (\rho_j + i\rho'_j)$$

where

$$(6.40) \quad \rho_j = \Re \left\{ \frac{d^3 \log \Phi_j}{d\alpha^3} (\alpha - i\theta_j v) \right\} ; \quad \rho'_j = \Im \left\{ \frac{d^3 \log \Phi_j}{d\alpha^3} (\alpha - i\theta'_j v) \right\}$$

($0 < \theta'_j < 1$; $0 < \theta_j < 1$). First, we make the following remarks:

(i) $|\phi_j(v; \alpha)|$ attains its maximum (equal to 1) at $v = 0$. The probability distribution being supposed continuous, $|\phi|$ cannot attain the value 1 for any other value of v . Then, for $|v| \geq \eta$ and η sufficiently small, we have $|\phi_j(v, \alpha)| \leq 1 - \eta'_j = \max$ of $|\phi_j|$ on $|v| \geq \eta$, and also η'_j has the same order as $\frac{1}{2} \eta^2 (d^2 \log \Phi_j / d\alpha^2)$. *A priori*, η may depend on j ; if we can choose a common value of η for all the ϕ_j , we have for $|v| \geq \eta$

$$(6.41) \quad \left| \prod_{(r)} \phi_j \right| \leq \prod |1 - \eta'_j| \\ \sim \left[\exp \left(- \frac{\eta^2}{2} \sum_r \frac{d^2 \log \Phi_j}{d\alpha^2} \right) \right] \sim \exp \left(- \frac{N_r c_r(\alpha) \eta^2}{2} \right) .$$

This bound for the modulus can be used for every positive value of α . Now, let us consider the integrals as in (5.8) and assume that the integral $\int_{-\infty}^{+\infty} |\Psi(u_c, v; \alpha)| dv$ exists.

Thus, it is sufficient that $N_r \eta^2$ should be large enough so that, in the integral of (5.8) relative to v (between $-\infty$ to $+\infty$), only the part of these integrals in the neighborhood $|v| \leq \eta$ of $v = 0$ makes a significant contribution (under the condition that the contribution of this part is not negligible).

(ii) To obtain a simple asymptotic estimate of our integrals it is necessary that the third term of the different developments (6.39) are bounded uniformly in j in a certain neighborhood $|v| \leq \eta$ small enough; for instance, it is sufficient to have

$$(6.42) \quad \left| \frac{d^3 \log \Phi_j(z)}{dz^3} \right| \leq M , \quad \text{with } z = \alpha - iv$$

for all j , for all v such that $|v| \leq \eta$, and for the α values concerned. The sum $iv^3(\rho + i\rho')/3!$ of these terms in the expression of $\log \Pi_{(r)} \phi_j$ is bounded by $v^3 N_r M / 3!$ in modulus and we shall choose η (decreasing with $1/N_r$) so that $N_r \eta^3 \rightarrow 0$ while $N_r \eta^2 \rightarrow \infty$. Then we may neglect these terms in the integration.

Then the integrand in the numerator of (5.8) can be written

$$(6.43) \quad \psi(\vec{u}_c, v, \alpha) \\ \cdot \exp \left[- iv \left(E_0 + \sum_r \frac{d \log \Phi_j}{d\alpha} \right) - \frac{v^2}{2} \sum_r \frac{d^2 \log \Phi_j}{d\alpha^2} + \frac{iv^3}{3!} |\rho + i\rho'| \right] .$$

⁴ We call $\Re(z)$ the real part of the complex number z and $\Im(z)$ its imaginary part so that $z = \Re(z) + i\Im(z)$.

Besides, for estimating the value of the integral on $-\eta, +\eta$, in a simple way it is necessary to eliminate the first oscillating term $\exp \left[-i v \left(E_0 + \sum_r \frac{d \log \Phi_j}{d\alpha} \right) \right]$;

then we put

$$(6.44a) \quad E_0 + \sum_r \frac{d \log \Phi_j}{d\alpha} = 0$$

or, equivalently (s_c being a small component),

$$(6.44b) \quad E_0 + \sum_N \frac{d \log \Phi_j}{d\alpha} = 0 .$$

α_N being chosen in this way, only the parts of the integrals in the neighborhood of $v = 0$ are important; we can take the term $\psi(u_c, v, \alpha)$ out of the integral sign by letting $v = 0$ and $\alpha = \alpha_N$. Then, we obtain the result that if $N \rightarrow \infty$ equation (5.8) tends to

$$(6.45) \quad \phi(\bar{u}_c/E_0) = \Psi_c(\bar{u}_c, 0, \alpha(\infty)) .$$

We again obtain the result of (6.20): The conditional distribution for the small component S_c^* is equal to the *a priori* distribution under the condition that α is chosen so that $E_0 = \bar{E}(\alpha)$, where $\bar{E}(\alpha)$ is the *a priori* mean value of E .

(b) *Large component.* We now use (5.9) with

$$(6.46) \quad \phi_c(v + v_c, \alpha) = \prod_{(c)} \phi_j(v + v_c, \alpha) ; \quad \phi_r(v, \alpha) = \prod_{(r)} \phi_j(v; \alpha) .$$

As in the case of a small component, we use limited developments,

$$(6.47) \quad \log \phi_c(v + v_c, \alpha) \sim -i(v + v_c) \sum_c \frac{d \log \Phi_j}{d\alpha} - \frac{(v + v_c)^2}{2} \sum_c \frac{d^2 \log \Phi_j}{d\alpha^2} + 3\text{rd order},$$

$$\log \phi_r(v, \alpha) \sim -i v \sum_r \frac{d \log \Phi_j}{d\alpha} - \frac{v^2}{2} \sum_r \frac{d^2 \log \Phi_j}{d\alpha^2} + 3\text{rd order}.$$

Under some rather general conditions used in the case of a small component and under some assumptions concerning the decrease of the ϕ_j' functions at infinity, it is easily seen that the integrals of (5.9) depend only on the values of ϕ in the neighborhood of $v = 0$ or of $v = v_c$. In these neighborhoods we use the same uniform bounds for the third derivative that we used in the case of a small component. Then, the effect of the terms of the third order is negligible. Moreover, as before, let us shift the origin as follows:

$$(6.48) \quad E'_c = E_c - \bar{E}_c = E_c - A_c = E_c + \sum_c \frac{d \log \Phi_j}{d\alpha} .$$

Then, in the numerator of (5.9), we have an expression equivalent to

$$(6.49) \quad \left[\exp \left(-i v \left[\sum_N \frac{d \log \Phi}{d\alpha} + E_0 \right] \right) \right] \cdot \exp \left(- \frac{(v + v_c)^2}{2} B_{c.N_c} - \frac{v^2}{2} B_{r.N_r} \right)$$

and, in the denominator, an expression equivalent to

$$(6.50) \quad \left[\exp \left(-i v \left[\sum_N \frac{d \log \Phi_j}{d \alpha} + E_0 \right] \right) \right] \cdot \exp \left(-\frac{v^2}{2} [B_{c,N_c} + B_{r,N_r}] \right).$$

Now, we eliminate the oscillating term by choosing α_N so that

$$(6.51) \quad \sum_N \frac{d \log \Phi_j}{d \alpha} = \frac{d \log \Phi}{d \alpha} = -E_0.$$

Then, we have

$$(6.52) \quad \phi[v_c/E_0] = \frac{\int_{-\infty}^{+\infty} \left[\exp \left(-\frac{(v+v_c)^2}{2} B_{c,N_c} - \frac{v^2}{2} B_{r,N_r} \right) \right] dv}{\int_{-\infty}^{+\infty} \left[\exp \left(-\frac{v^2}{2} [B_{c,N_c} + B_{r,N_r}] \right) \right] dv} \\ = \exp [(-v_c^2 B_{c,N_c} \cdot B_{r,N_r})/2(B_{c,N_c} + B_{r,N_r})] = e^{-v_c^2 B/2}$$

This is exactly the characteristic function relative to E'_c consistent with (6.36b).

6.4. *Comparison.* We have used in parallel ways probability density and characteristic functions to make it clear that these two methods are equivalent to each other. In both cases we obtain the same results:

(a) For a small component the conditional distribution is equal to the *a priori* distribution under the condition that we choose α according to equation (6.20).

(b) For a large component, the energy E is normally distributed and the parameters of this normal distribution can be expressed in a very simple way if α is again chosen according to equation (6.20).

7. Solution of the fundamental problem (problem 2)

The fundamental problem here is to derive the distribution of N_c or of E_c when E and N are given ($E = E_0$ and $N = N_0$).

$$(7.1) \quad N_1 + N_2 + \dots = N_0$$

$$(7.2) \quad \left\{ \begin{array}{l} E_1 + E_2 + \dots = E_0 \\ \text{or} \\ \epsilon_1 N_1 + \epsilon_2 N_2 + \dots = E_0. \end{array} \right.$$

As in Fowler's book, we can assume, with no loss of generality, that the $\{\epsilon_j\}$ are integers.

First, we must solve the fundamental problem in the case of a system S with a finite number of components. We shall later consider the asymptotic problem.

We assume that $\epsilon_l \rightarrow \infty$ if $l \rightarrow \infty$. Then, for sufficiently large l , we shall have

$$(7.3) \quad \epsilon_l > E_0$$

and, indeed, no component is in the quantum states for which (7.3) is fulfilled. Then, in (7.1) and (7.2) we can restrict the summations to be over a finite number of terms, say L . As in Fowler's method we assume that the $\{\epsilon_j\}$ are relatively prime. We shall use here the method of characteristic functions.

The characteristic function of the joint distribution of the random variables $\{N_j\}$ ($j = 1, 2, \dots, L$) is

$$(7.4) \quad \phi(u_1, u_2, \dots, u_L; \beta, \alpha) = \prod_{j=1}^L \phi_j(u_j, 0; \beta, \alpha),$$

and that of $N_1, N_2, \dots, N_L; S_1 = \sum_1^L N_j; S_2 = \sum_1^L \epsilon_j N_j$ is

$$(7.5) \quad \Psi(u_1, \dots, u_L; w, t; \beta, \alpha) = \prod_{j=1}^L \phi_j(u_j + w, t; \beta, \alpha).$$

Let $p(S_1, S_2)$ be the *a priori* probability that S_1 and S_2 have a given pair of values. Then we have

$$(7.6) \quad \Psi = \sum_{S_1, S_2} p(S_1, S_2) e^{i(wS_1 + tS_2)} \phi(u_1, \dots, u_L / S_1, S_2)$$

where $\phi(u_1, \dots, u_L / S_1, S_2)$ is the characteristic function of N_1, \dots, N_L , under the condition that S_1 and S_2 have given values.

By (7.6) it is easy to see that

$$(7.7) \quad \phi(u_1, \dots, u_L / N_0, E_0) = \frac{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} \psi(u_1, \dots, u_L; w, t; \beta, \alpha) e^{-i(wN_0 + tE_0)} dw dt}{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} \psi(0, \dots, 0; w, t; \beta, \alpha) e^{-i(wN_0 + tE_0)} dw dt}.$$

This formula plays the same role in the development as did (5.7) previously. If we are only interested in a particular set of quantum states ($j = 1, 2, \dots, c$), we replace by 0 all u 's corresponding to the other quantum states, and we consider

$$(7.8) \quad \phi(u_1, \dots, u_c; 0, 0, \dots, 0 / N_0, E_0).$$

If we wish to obtain the distribution of $N_1 + N_2 + \dots + N_c$, we put $u_1 = u_2 = \dots = u_c = U$ in (7.8). If we wish to obtain the distribution of $\epsilon_1 N_1 + \dots + \epsilon_c N_c$, we replace in (7.8) u_1, u_2, \dots, u_c by $\epsilon_1 u, \epsilon_2 u, \dots, \epsilon_c u$, respectively.

Now we must study the asymptotic properties and for this purpose we must assume some hypotheses concerning the increase of our system. First, we make some preliminary remarks.

(i) L being defined as before and E_0 being given, we can obviously replace L by any $L' > L$. $\phi(u_1, u_2, \dots, u_{L'} / N_0, E_0)$ does not depend on the u_j for $j > L$. Hence, we can set $L = \infty$ so that it is not necessary to limit the number of the $\{u_j\}$. It is in this sense that we introduce $\phi(u_1, u_2, \dots / N_0, E_0)$.

(ii) Now we shall discuss the assumptions regarding the increase of our system. To do this we must first consider several examples.

Example 1. Let Σ_1 be the system concerned, E_0 and N_0 be the given values for E and N and $\{\sigma_j\}$ be the set of the quantum states for one component. We consider $(n - 1)$ systems $\Sigma_2, \Sigma_3, \dots, \Sigma_n$ identical with Σ_1 (they have the same N_0 and the same E_0). We suppose these systems to be distinct in the space, so that we can dis-

tinguish their quantum states $\{\sigma_j\}$. Now, we assume that $\Sigma_1, \Sigma_2, \dots, \Sigma_n$ can exchange some particles and some energy. Of course, we suppose that the interaction between these systems is so small that the total energy can be considered as the sum of the energies of all the systems. Then we suppose that we are interested in the set σ_c^* ($j = 1, 2, \dots, c$) of Σ_1 and we wish to derive the asymptotic properties of σ_c^* as $n \rightarrow \infty$. To summarize, σ_c^* consists of a particular set of c quantum states of Σ_1 , and σ_r^* consists of all the other quantum states of Σ_1 and all the quantum states of $\Sigma_2, \Sigma_3, \dots, \Sigma_r$; now we shall let n tend to infinity and we assume that the total energy of $\Sigma_1 + \Sigma_2 + \dots + \Sigma_n$ is equal to nE_0 and that the total number of components is equal to nN_0 .

Example 2. This example is analogous to the above one, but now σ_c^* is the set of all the quantum states $j = 1, 2, \dots, c$ corresponding to all the systems $\Sigma_1, \Sigma_2, \dots, \Sigma_n$. Of course, in this case, σ_r^* consists of all the quantum states $j > c$ corresponding to all the systems $\Sigma_1, \dots, \Sigma_n$.

Example 3. Let us consider the gas composed of identical particles in an equipotential box. Let l_1, l_2, l_3 be the lengths of the sides of this box. The eigenvalues of the energy of one particle are

$$(7.9a) \quad \epsilon_{j,k,q} = \frac{h^2}{8m} \left(\frac{j^2}{l_1^2} + \frac{k^2}{l_2^2} + \frac{q^2}{l_3^2} \right)$$

where h is Plank's constant and j, k, q are positive integers. Let N_0 be the number of particles in the box and E_0 the total energy. Now let us consider another box whose sides are $2l_1, 2l_2, 2l_3$ and which contains $8N_0$ particles and having an energy equal to $8E_0$. If we pass from the first box to the second, we extend our system in such a way that it conserves the values associated with the intensive properties. For the second box, the eigenvalues of the energy are

$$(7.9b) \quad \epsilon_{j',k',q'} = \frac{h^2}{8m} \left(\frac{j'^2}{4l_1^2} + \frac{k'^2}{4l_2^2} + \frac{q'^2}{4l_3^2} \right)$$

where j', k', q' are positive integers. If we make the box larger and larger in this way, we see that the sequence of the eigenvalues of the energy becomes more and more dense.

In the definition of σ_c^* we must distinguish two cases: In the first case we are interested in all the quantum states whose energies belong to a certain range of energy ($\epsilon_0 < \epsilon_{j,k,q} < \epsilon_1$). In this case, when the system tends to infinity, the number of quantum states in σ_c^* also tends to infinity. We shall call this case "case (a)." In the second case, we are interested in a constant number of quantum states in the above range. For instance, we are interested in the quantum states that have the smallest energies in the above range. In this case, the number of quantum states in σ_c^* remains constant and equal to c . We shall call this case "case (b)."

The rigorous derivation of the asymptotic properties may be different according to the model chosen but the final results are essentially equivalent.

Moreover, it is necessary to point out that examples 1 and 3 (case b) are related to problems of small components while examples 2 and 3 (case a) concern problems of large components.

(iii) In order to solve the asymptotic problem, we first consider the case of one

small component and we derive the result for example 1. (The general aspects of the derivation are also applicable to example 3 (case b).) Using the equations (4.28), (7.6), (7.7) and (7.8) we have

$$(7.10) \quad \phi(u_1, \dots, u_c; 0, 0, 0 \dots /n, N_0, E_0) = \frac{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} \psi(u_1, \dots, u_c; 0, 0, 0, \dots; w, t; \beta, \alpha) e^{-in(wN_0 + tE_0)} dw dt}{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} \psi(0, \dots, 0; 0, 0, 0 \dots; w, t; \beta, \alpha) e^{-in(wN_0 + tE_0)} dw dt}$$

and

$$(7.11) \quad \psi(u_1, \dots, u_c; 0, 0, \dots; w, t; \beta, \alpha) = \prod_{j=1}^c \phi_j(u_j + w, t; \beta, \alpha) \cdot \prod_{j=c+1}^{\infty} \phi_j(w, t; \beta, \alpha) \cdot \prod_{j=1}^{\infty} \phi_j^{n-1}(w, t; \beta, \alpha).$$

It is possible to proceed in the same way as in section 6.2. However, there is a little difference between these two problems. In section 6.2 the range of variation of v was $(-\infty, +\infty)$. Here the functions considered are periodic with respect to w and t (period 2π). We cannot say that ϕ_j has one, and only one, maximum attained at $w = t = 0$ but we must say, now, that ϕ_j has a maximum at all points $w = 2\pi M_1$ and $t = 2\pi M_2$ (M_1 and M_2 being arbitrary integers). But it has one and only one maximum in the range of integration, and, in the neighborhood of $w = t = 0$, we can use the same method as in section 6.2

$$(7.12) \quad \log \phi_j(u_j, v_j; \beta, \alpha) \sim -i \left(u_j \frac{\partial \log \Phi_j}{\partial \beta} + v_j \frac{\partial \log_j \Phi_j}{\partial \alpha} \right) - \frac{1}{2} \left(\frac{\partial^2 \log \Phi_j}{\partial \beta^2} u_j^2 + 2 \frac{\partial^2 \log \Phi_j}{\partial \beta \partial \alpha} u_j v_j + \frac{\partial^2 \log \Phi_j}{\partial \alpha^2} v_j^2 \right) + \text{terms of the 3rd order.}$$

Then

$$(7.13) \quad \log \prod_1^{\infty} \phi_j^{n-1}(w, t; \beta, \alpha) = -i(n-1) \left[w \sum \frac{\partial \log \Phi_j}{\partial \beta} + t \sum \frac{\partial \log \Phi_j}{\partial \alpha} \right] - \frac{1}{2} (n-1) \left[w^2 \sum \frac{\partial^2 \log \Phi_j}{\partial \beta^2} + 2wt \sum \frac{\partial^2 \log \Phi_j}{\partial \beta \partial \alpha} + t^2 \sum \frac{\partial^2 \log \Phi_j}{\partial \alpha^2} \right] + \text{terms of the 3rd order.}$$

Now we must take the term $\exp | -in(wN_0 + tE_0) |$ into account. In the same manner as we did for section 6.2, we impose the conditions

$$(7.14) \quad nN_0 + (n-1) \frac{\partial \log \Phi}{\partial \beta} = 0, \quad nE_0 + (n-1) \frac{\partial \log \Phi}{\partial \alpha} = 0,$$

where $\Phi = \prod \Phi_j$ as before. If we choose α and β such that (7.14) be fulfilled, only the part of the integrals in the neighborhood of $w = t = 0$ makes a significant

contribution and, in (7.10), we can take the terms related to Σ_1 out from under the integral sign. Finally, we obtain

$$(7.15) \quad \phi(u_1, \dots, u_c; 0, 0 \dots /n, N_0, E_0) \rightarrow \prod_{j=1}^c \phi_j(u_j, t; \beta_\infty, \alpha_\infty) .$$

We have always the same result; the conditional distribution for the small component σ_c^* is equal to the *a priori* distribution under the condition that α and β are chosen according to

$$(7.16) \quad N_0 = \bar{N} \quad \text{and} \quad E_0 = \bar{E}$$

(compare with (7.14) for $n \rightarrow \infty$).

Now, we consider briefly the case of a large component. For instance, we shall study example 2. In the case of a large component we may be interested either in the number N_c or in the energy of the set of components whose quantum state is contained in σ_c^* . Let N_c be this number of components. The formula (7.7) must be modified as follows:

$$(7.17) \quad \phi(u_c, v_c/n, N_0, E_0) = \frac{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} \psi_c(u_c + w, v_c + t; \beta, \alpha) \psi_r(w, t; \beta, \alpha) e^{-in(wN_0 + tE_0)} dw dt}{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} \psi_c(w, t; \beta, \alpha) \psi_r(w, t; \beta, \alpha) e^{-in(wN_0 + tE_0)} dw dt}$$

where

$$(7.18) \quad \begin{cases} \psi_c(u_c + w, v_c + t; \beta, \alpha) = \prod_{j=1}^c \phi_j^n(u_c + w, v_c + t; \beta, \alpha) \\ \psi_r(w, t; \beta, \alpha) = \prod_{j=c+1}^{\infty} \phi_j^n(w, t; \beta, \alpha) . \end{cases}$$

Now we put

$$(7.19) \quad \Phi_c = \prod_{j=1}^c \Phi_j ; \quad \Phi_r = \prod_{j=c+1}^{\infty} \Phi_j ; \quad \Phi = \Phi_c \Phi_r$$

$$(7.20) \quad E'_c = E_c - \bar{E}_c ; \quad N'_c = N_c - \bar{N}_c ;$$

and we choose α and β according to the equations

$$(7.21) \quad E_0 + \frac{\partial \log \Phi}{\partial \alpha} = 0 , \quad N_0 + \frac{\partial \log \Phi}{\partial \beta} = 0 .$$

Let α_0 and β_0 be the solution of this system of two equations. Now we introduce the mean values of the *a priori* joint distribution of (E'_c, N'_c) corresponding to α_0 and β_0

$$(7.22) \quad \begin{aligned} \overline{E'_c} &= n \frac{\partial^2 \log \Phi_c}{\partial \alpha^2} ; & \overline{N'_c} &= n \frac{\partial^2 \log \Phi_c}{\partial \beta^2} ; & \overline{E'_c N'_c} &= n \frac{\partial^2 \log \Phi_c}{\partial \alpha \partial \beta} , \\ \overline{E'_r} &= n \frac{\partial^2 \log \Phi_r}{\partial \alpha^2} ; & \overline{N'_r} &= n \frac{\partial^2 \log \Phi_r}{\partial \beta^2} ; & \overline{E'_r N'_r} &= n \frac{\partial^2 \log \Phi_r}{\partial \alpha \partial \beta} . \end{aligned}$$

Now if we denote by $G_c(w, t; \alpha_0, \beta_0)$ and $G_r(w, t; \alpha_0, \beta_0)$ the characteristic functions of the normal distributions which correspond, asymptotically, to (N'_c, E'_c) and (N'_r, E'_r) , respectively, then, for the conditional joint distribution of (E'_c, N'_c) , we obtain the following expression:

$$(7.23) \quad \phi(u_c, v_c/n, N_0, E_0) \sim \frac{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} G_c(u_c + w, v_c + t) G_r(w, t) dw dt}{\int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} G_c(w, t) G_r(w, t) dw dt}.$$

Indeed, after integration, we obtain for $\phi(u_c, v_c/n = \infty, N_0, E_0)$ the characteristic function of a normal distribution.

8. Conclusion

We have shown that the introduction of *a priori* probability permits us to reduce, in a natural way, several problems of statistical mechanics to some typical questions in the theory of conditional probability. The expressions of the asymptotic properties of systems with many degrees of freedom are always simple if we use the *a priori* distributions for which the average values \bar{E} and \bar{N} are equal to the given values E_0 and N_0 , respectively.

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