The Entropy of Systems with a Random Number of Particles

R. L. STRATONOVICH
Moscow State University

(Submitted to JETP editor January 19, 1954)
J. Exper. Theoret. Phys. USSR **28**, 409-421 (April, 1955)

The amount of entropy in a volume which contains a random number of particles is found on the basis of entropy and indeterminacy considerations.

THE entropy of a system consisting of a fixed number of particles N (neglecting internal degrees of freedom) is defined by the well-known formula*

$$S = -\int p_N \ln p_N d\Omega + \text{const}, \qquad (1)$$

where p_N is the probability density for a point representing the state of the system in the $6N$-dimensional phase space Ω, However, to the best of my knowledge, the problem of finding the entropy in a volume V which is a part of the whole space accessible to the particles has not yet been solved. A formula like (1) cannot be applied in this case, since the number n of particles in the volume V is itself indeterminate (random). If we set n equal to its mathematical expectation $\bar{n}$ we can evaluate an entropy S_V' in the volume V by a formula analogous to (1). However, S_V' will not be the entropy of the original system, but the entropy of the volume V for some other system, namely a system in which the volume V is surrounded by an impenetrable barrier. To determine correctly the entropy in a volume V of the original system, we need a new formulation, suggested by regarding the entropy as a random quantity.

The subject of the present paper can be approached in another way. The use of a probability density in a $6N$-dimensional space is justified by a consideration of states in thermodynamic equilibrium, because then p_N can be expressed directly by Gibbs' formula. The use of p_N for non-equilibrium states appears purely formal, in view of the impossibility of expressing analytically how p_N changes with time. The solution of a differential equation with a number of independent variables of the order of Avogadro's number is obviously not feasible. To be in a position to carry out calculations (which are perharps tedious, but possible) of non-equilibrium processes, we must return to a consideration of distribution functions. The latter are used, in particular, by Bogoliubov[1]. It is most convenient to deal with distribution functions which characterize local statistical properties as, for example, the functions defined in reference 2. Instead of distribution functions, we can also use a system of correlation functions, which, in their turn, adequately describe the statistical system. The latter functions have the following advantages over distribution functions: In the absence of correlation between the particles, the distribution function becomes a product of lower order distribution functions. In this case the correlation functions become zero. In ordinary physical systems the correlation function is different from zero only when its arguments are sufficiently near one another. The lower order distribution functions and correlation functions are the most important. If a certain accuracy is specified, we can neglect higher order correlations beginning with an order k, depending on the accuracy desired. However, neglecting higher correlations means that the higher order distribution functions factor into products of lower order distribution functions, since the higher the order correlations are set equal to zero. Of course, this considerably simplifies the problem. In the light of what has just been said, there is much more basis for terminating a series made up of correlation functions than of distribution functions. One might say that the transition from distribution functions to correlation functions makes the series converge more rapidly.

Thus, in treating non-equilibrium states it is expedient to consider correlation functions (instead of p_N) and to find out how they change with time. Inasmuch as they completely describe the physical system, we can calculate, in terms of them, all the physical parameters of the system which interest us (density, fluctuations, energy, pressure, entropy, etc.). Accordingly, in view of the application in statistical physics (of non-equilibrium processes)

---

* We shall write the entropy in dimensionless units, omitting Boltzmann's constant.

[1] N. N. Bogoliubov, *Problems of Dynamical Theory in Statistical Physics*, Moscow, 1946

[2] P. I. Kuznetsov, R. L. Stratonovich, and V. I. Tikhonov, Zh. Tekh. Fiz. **24**, 103 (1954)

of a new apparatus, viz. distribution functions and correlation functions, the question arises of how to express the entropy in terms of these functions. This question will be investigated in this paper.

Following Shannon[3] we shall understand entropy to be a measure of the indeterminacy ("neginformation") contained in the given physical process, or, in other words, an index of the amount of its statistical disorder.

We define the entropy of a finite complete set of mutually exclusive events $A_1, \ldots, A_n$ by the formula

$$S = -\sum_{i=1}^{n} P(A_i) \ln \frac{P(A_i)}{Q(A_i)}, \tag{2a}$$

where $P(A_i)$ is the probability of the event A_i and $Q(A_i)$ is its "volume".

The introduction of the "volumes" of events allows us to regard the entropy as a characteristic of an object which can be given a probabilistic description, i.e., as a characteristic of a statistical aggregate. For according to the usual formula

$$S = -\sum_{i=1}^{n} P(A_i) \ln P(A_i)$$

(see reference 3), the entropy depends on which set of mutually exclusive events is chosen, and changes if another complete set of mutually exclusive events is used, even though the object itself and its statistical characteristics have not changed.

The size of the "volumes" of events is derived from the nature of the physical object considered. For example, if a true die is being considered, then the volume of the event consisting of the even throws is three times as large as the volume consisting of a throw of the number one. The reader will become acquainted with another example below, which is not so trivial.

In the general case, including continuous distributions, the entropy is defined by the formula

$$S = -\lim_{Q(A_i)\to \min} \sum_i P(A_i) \ln \frac{P(A_i)}{Q(A_i)}. \tag{2}$$

Here the summation is over mutually exclusive events, the sum of which is an event which is certain to occur; the passage to the limit corresponds to the maximally fine subdivision of events.

If we apply Eq. (2) to a system of particles, the state of which is represented by the random point M in the phase space Ω, we have

$$S = -\int p_N(M) \ln \frac{p_N(M)}{q_N(M)} d\Omega_M. \tag{3}$$

Here p_N is the probability density function for the point M in Ω, q_N is the density of "volume" in the space Ω. Consequently, recalling the third law of thermodynamics and the indeterminacy principle of quantum mechanics, we can conclude (as shown in other work) that in a space of canonically conjugate variables

$$S = -\int p_N \ln (h^{3N} p_N) d\Omega. \tag{4}$$

In the same way, the additive constant in Eq. (1) is determined by Planck's constant.

We shall be interested in how the entropy changes if the number N is increased or decreased without changing the local statistical structure (i.e., with a proportional change in the volume V). For these considerations it is expedient to decompose the entropy (neginformation) into two components, configuration neginformation and exchange neginformation.

$$S = S_c + S_e \tag{5}$$

The exchange neginformation S_e corresponds to the indeterminacy entering the result because of the possibility of exchange between particles at all sets of N points at which particles may be located. Which distribution of the particles on the points (of the $N!$ possible permutations) is actually realized is indeterminate. To each distribution we must ascribe a unique probability and a unique "volume". The probability of each distribution is $1/N!$. Designating the "volume" of each distribution by Q_1, we have, according to Eq. (2),

$$S_e = \ln N! + \ln Q_1.$$

The exchange neginformation must vanish when there is only one particle. From this condition we find

$$Q_1 = 1,$$

whence

$$S_e = \ln N! \tag{6}$$

Corresponding to this fact, the configuration entropy is

$$S_c = -\int p_N \ln (N!\, h^{3N} p_N)\, d\Omega. \tag{7}$$

Let us consider the so-called Gibbs' paradox, consisting in the fact that if we divide a volume (albeit hypothetically) into several parts, the sum of the entropies of the separate volumes does not equal the entropy of the original volume. For example, if we divide the volume V_1 into two volumes $V_2 = V_1/2$, the entropy of the original volume exceeds the sum of the entropies of the

---

[3] *The Theory of Transmission of Electrical Signals in the Presence of Noise,* collection of translations under the editorship of N. A. Zheleznoff, Moscow, 1953

subvolumes by $N_1 \ln 2$, i.e.,

$$S(V_1) - 2S(V_2) = (R/k)\, n_1 \ln 2, \qquad (8)$$

where n_1 is the number of gram-molecules of matter in the volume V_1; $N_1 = (R/k)\, n_1$ is the number of molecules in the same volume.

The solution of this paradox is easily achieved, if we bear in mind that the entropy occurring in Eq. (8) is the sum of an exchange entropy and a configuration entropy. Indeed, using Eq. (6) and applying Stirling's formula, we have

$$S_e(V_1) = \ln N_1! \approx N_1 (\ln N_1 - 1);$$

$$S_e(V_2) = \ln \left(\frac{N_1}{2}\right)! \approx \frac{N_1}{2}\left(\ln \frac{N_1}{2} - 1\right),$$

whence

$$S_e(V_1) - 2S_e(V_2) \approx N_1 \ln 2.$$

Consequently, for the configuration entropy, which describes the statistical structure without individualizing the particles,the Gibbs' paradox does not take place, and

$$S_c(V_1) \approx 2S_c(V_2).$$

According to the quantum mechanical principles the indistinguishability of particles it is impossible to acquire knowledge of the individuality of the particles occupying the given positions (states). Therefore the indeterminacy of the distribution of the particles in different states is actually not a real indeterminacy. The real indeterminacy is the indeterminacy in the position (state) of the non-individualized particles,i.e, the configuration neginformation.

Thus the principle of indistinguishability of particles requires us to restrict our attention to configuration neginformation, which removes Gibbs' paradox. In what follows we shall consider only configuration entropy, but omitting for simplicity the index c. The configuration entropy is in its turn not completely additive, but this non-additivity, which enters because of statistical correlation, is of a completely different nature from the non-additivity of exchange entropy.

Let us return to Eq. (7). We designate by B the event consisting of the Nth particle occupying the element $d\omega_1$ of the six-dimensional canonical variable space, located near the point L_1, at the same time that the second particle lies in the element $d\omega_2$, the third in $d\omega_3$, etc. The probability of the event B is

$$dP_N = p_N(L_1, \ldots, L_N)\, d\omega_1 \ldots d\omega_N. \qquad (9)$$

Since Eqs. (2), (3) have universal validity, the event B has a configuration "volume" equal to

$$dQ_N = q_c d\omega_1 \ldots d\omega_N. \qquad (10)$$

Here, as follows from a comparison of Eqs. (3) and (7)

$$q_c = \frac{1}{N!} h^{-3N} \qquad (11)$$

is the density of configuration "volume".

Summing elementary events of the indicated type, we can calculate the configuration "volume" of the event consisting of just N particles lying in the region W of the space ω. It equals**

$$Q_W(N) = \int_W \ldots \int_W q_c d\omega_1 \ldots d\omega_N = \frac{1}{N!}\left(\frac{W}{h^3}\right)^N \qquad (12)$$

We note that the "volume" of the event consisting of any number of particles lying in the region W is given by the equation

$$Q_W = \sum_{N=0}^{\infty} Q_W(N) = \exp\{W/h^3\}, \qquad (13)$$

whence it follows that when the geometric volumes are added, the abstract "volumes" of the corresponding events are multiplied.

Let us pass from p_N to a consideration of the functions $e_N(L_1,\ldots,L_N)$ ($N = 1,2,\ldots$), which determine the probability

$$dP_N = e_N(L_1, \ldots, L_N)\, d\omega_1, \ldots, d\omega_N \qquad (14)$$

of the event (we designate it by C) consisting of any arbitrary particle lying in the element $d\omega_1$, while at the same time any other particle lies in the element $d\omega_2$, etc., given that, in all, just N particles lie in W. It is easy to convince oneself that the indicated functions can be expressed in terms of the functions appearing in Eq. (9) in the following way:

$$e_N(L_1, \ldots, L_N) = \sum p_N(L_{\alpha_1}, \ldots, L_{\alpha_N}), \qquad (15)$$

where the summation is over all possible ($N!$) permutations of the arguments of the function p_N. When p_N is symmetric, Eq. (15) becomes

$$e_N = N!\, p_N. \qquad (15a)$$

In an analogous fashion we find that the "volume" of the event C is

$$dQ_N = h^{-3N} d\omega_1, \ldots, d\omega_N. \qquad (16)$$

Let us examine how we must sum events of the type C in order to obtain the event A_N, consisting of just N particles lying in W. If we index the particles by the magnitude of any coordinate x (of the six coordinates designated by L), then to obtain

---

** The volume of a region is designated by the same letter as the region.

the event A_N, we must sum events of the type C, subject to the condition $x_1 \leqslant x_2 \leqslant \ldots \leqslant x_N$ (in order to avoid duplication of elementary events). Accordingly

$$P_W(N) = \int\limits_{x_1 \leqslant \ldots \leqslant x_N} \ldots \int e_N(L_1, \ldots, L_N)\, d\omega_1 \ldots d\omega_N.$$

If we remove the ordering in the coordinate x, then, because of the symmetry of the function e_N, we obtain a quantity $N!$ larger. From this it follows that

$$P_W(N) = \frac{1}{N!} \int\limits_W \ldots \int\limits_W e_N(L_1, \ldots, L_N)\, d\omega_1 \ldots d\omega_N, \qquad (17)$$

The equations we have written are valid in the general case when the number of particles in the volume W is random. The events A_N can be represented as a sum of events of the type B or of the type C. In both cases we finally get unique meanings for the probability $P_W(N)$, the "volume" $Q_W(N)$, and the entropy.

According to Eq. (2), to go from the preliminary formula for the entropy

$$S_W = -\sum_N P_W(N) \ln \frac{P_W(N)}{Q_W(N)}$$

to the exact formula, we must pass to the limit in the elementary events (of type B or type C), i.e.,

$$S_W = -\sum_N \int dP_N \ln \frac{dP_N}{dQ_N}.$$

Substituting Eqs. (9), (10), (11) or (14), (16), we obtain

$$S_W = -\sum_{N=0}^{\infty} \int\limits_W \ldots \int\limits_W p_N \times \ln(N! h^{3N} p_N)\, d\omega_1 \ldots d\omega_N \qquad (18)$$

or

$$S_W = -\sum_{N=0}^{\infty} \frac{1}{N!} \int\limits_W \ldots \int\limits_W e_N \times \ln(h^{3N} e_N)\, d\omega_1 \ldots d\omega_N. \qquad (18')$$

The expression just obtained reduces to Eq. (7) when the number N is determinate. In this case only one function p_N or e_N is different from zero.

One is usually interested in the entropy included in a definite region (with volume V) of three-dimensional configuration space (which we designate by ω^*) with coordinates q_1, q_2, q_3. Corresponding to this, the region W will have a projection V on the space ω^* and will extend to infinity in momentum space:

$$-\infty < p_1,\ p_2,\ p_3 < \infty.$$

Let us consider the special case in which the distribution in momenta is statistically independent of the distribution in coordinates, so that

$$e_N = e_N^*(q_1^1, \ldots, q_3^N)\varphi(p_1^1, p_2^1, p_3^1) \ldots \varphi(p_1^N, p_2^N, p_3^N), \qquad (19)$$

where $\phi(p_1, p_2, p_3)$ is the momentum distribution function for one particle; e_N^* is a function having the same meaning as e_N, only pertaining to the three-dimensional space ω^*. So that there may be a complete identity of formulas for the two functions, in particular, so that the probability that just N particles lie in V may be given by the equation

$$P_V^*(N) = \frac{1}{N!} \int\limits_V \ldots \int\limits_V e_N^* d\omega_1^* \ldots d\omega_N^*, = P_W(N), \qquad (20)$$

analogous to Eq. (17), we must normalize $\phi(p_1, \ldots, p_3)$ to unity.

Substituting Eq. (19) in Eq. (18), and using Eq. (20) and the normalization condition, we obtain

$$S_W = S_q + \bar{N} S_1, \qquad (21)$$

where $\bar{N}$ is the mean value of the number N;

$$S_1 = \iiint \varphi(p_1, p_2, p_3) \times \ln[h^3 \varphi(p_1, p_2, p_3)]\, dp_1\, dp_2\, dp_3, \qquad (22)$$

$$S_q = -\sum_{N=0}^{\infty} \frac{1}{N!} \int\limits_V \ldots \int\limits_V e_N^* \ln e_N^*\, d\omega_1^* \ldots d\omega_N^*. \qquad (23)$$

The expression (23) has the same appearance as Eq. (18) (if we disregard an additive constant). We proceed to investigate it, omitting for simplicity the asterisk, and noting that analogous calculations can be carried out immediately for Eq. (18).

The functions e_N are not local characteristics of the particle distribution, since they depend on the choice of the volume V. However, they can be expressed in terms of distribution functions or correlation functions, which express just such local statistical properties. Each distribution function $f_N(M_1, \ldots, M_N)$ (M is a point in the space ω) is defined analogously to Eq. (14) with only this difference, that the condition that just N particles lie in V is abandoned. Following methods applied in reference 2, we can obtain

$$e_N(M_1, \ldots, M_N) = \sum_{s=0}^{\infty} \frac{(-1)^s}{s!} \int\limits_V \ldots \int\limits_V f_{N+s} \times (M_1, \ldots, M_{N+s})\, d\omega_{N+1} \ldots d\omega_{N+s}. \qquad (24)$$

Thus, knowing the distribution functions, which completely describe the statistics of the system of particles, we can calculate from Eqs. (23), (24) the entropy of any region V. As was shown in the introduction, instead of distribution functions it is more convenient to consider correlation functions g_N ($N = 1,2,..$), defined by the equations

$$\sum_{n=0}^{\infty} \frac{1}{n!} \sum_{\alpha_i} f_n(M_{\alpha_1}, \ldots, M_{\alpha_n}) z_{\alpha_1} \ldots z_{\alpha_n} \tag{25}$$

$$= \exp\left\{ \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{\alpha_i} g_n(M_{\alpha_1}, \ldots, M_{\alpha_n}) z_{\alpha_1} \ldots z_{\alpha_n} \right\},$$

where z_α are arbitrary numbers; $f_0 = 1$. From this, assigning the proper values to z_α, we can obtain

$$\sum_{k=0}^{\infty} \frac{1}{k!} \sum_{\alpha_i} e_k(M_{\alpha_1}, \ldots, M_{\alpha_k}) z_{\alpha_1} \ldots z_{\alpha_k} \tag{26}$$

$$= \exp\left\{ \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{\alpha_i} h_k(M_{\alpha_1}, \ldots, M_{\alpha_k}) z_{\alpha_1} \ldots z_{\alpha_k} \right\}.$$

Here

$$h_k(M_1, \ldots, M_k) = \sum_{s=0}^{\infty} \frac{(-1)^s}{s!} \tag{27}$$

$$\times \int_V \cdots \int_V g_{k+s}(M_1, \ldots, M_{k+s})\, d\omega_{k+1} \ldots d\omega_{k+s};$$

the $e_k(M_1, \ldots, M_k)$ are expressed by Eq. (24).

Equation (26) differs in form from (25) only by the presence of the term h_0 in the exponent. Therefore, setting

$$e_k = e_k^0 e^{h_0}, \tag{28}$$

we obtain for the functions e_k^0 and h_k an equation completely analogous to Eq. (25). Such an equation (which is encountered also in the theory of random functions and relates the moment functions with the correlations) always gives the unique relations:

$$e_1^0(M_1) = h_1(M_1);$$

$$e_2^0(M_1, M_2) = h_2(M_1, M_2) + h_1(M_1) h_1(M_2);$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots:$$

$$e_k^0(M_1, \ldots, M_k) \tag{29}$$

$$= \sum_{n_1 + 2n_2 + \ldots = k} \; \underset{\left(\frac{k!}{n_1!\, n_2!\, (2!)^{n_2} \ldots}\right)}{\mathbf{S}} h_1^{(n_1)} h_2^{(n_2)} \ldots,$$

where

$$h_i^{(n)} = \overbrace{h_i h_i \ldots h_i}^{n \text{ times}}.$$

By the symbol S is meant summation over all possible permutations of the arguments (M) of the functions h_i , which do not give identical results The number of such permutations is indicated below in brackets. (To calculate them it is necessary to consider the symmetry of the functions h_i).

If the correlation functions are known, then, by using Eqs. (27), (29) and substituting the latter in the expression

$$S = -h_0 - e^{h_0} \sum_{N=0}^{\infty} \frac{1}{N!} \tag{30}$$

$$\times \int_V \cdots \int_V e_N^0 \ln e_N^0\, d\omega_1 \ldots d\omega_N,$$

which is a consequence of Eqs. (23), (28), we can calculate the entropy of a volume V.

Let us pass to a consideration of the important special case in which there are correlations between the particles only for sufficiently small distances. If the distance between the points considered is much larger than r, a certain correlation distance, then we can assume statistical independence for the occurence of particles at these points. Obviously, just such a state of affairs occurs in physical systems (e.g., in gases), where r is of the order of a radius of action of the intermolecular forces.

We shall make yet another assumption: we shall assume that our system is homogeneous. This assumption is less basic since, if it were not made, the formulas would be only slightly more complicated (provided the inhomogeneities change only slightly over distances r). For the indicated system of particles, the g_n ($M_1, \ldots M_n$) are appreciably different from zero only when all the points $M_1, \ldots, M_n$ are within distances of the order r of each other, i.e., when

$$|M_1 - M_i| \lesssim r \quad (i = 2, \ldots, n).$$

From this it follows that (if g_n vanishes sufficiently rapidly as $|M_i - M_j|$ increases the integral

$$\int_V \cdots \int_V g_n(M_1, \ldots, M_n)\, d\omega_1 \ldots d\omega_n$$

over a volume V, the linear dimensions of which are much larger than r, is approximately proportional to the volume V, i.e.,

$$\int_V \cdots \int_V g_n(M_1, \ldots, M_n)\, d\omega_1 \ldots d\omega_n \tag{31}$$
$$= G_n V\left[1 + O\left(\frac{r}{D}\right)\right],$$

where

$$G_n = \int_V \cdots \int_V g_n(M_1, M_2, \ldots, M_n)\, d\omega_2 \ldots d\omega_n$$

(The point M_1 is fixed, but lies inside V).

At the same time, because of Eqs. (27), (31), we have

$$\int_V \cdots \int_V h_n(M_1, \ldots, M_n)\, d\omega_1 \ldots d\omega_n \approx H_n V. \tag{32}$$

Here

$$H_n = \sum_{s=0}^{\infty} \frac{(-1)^s}{s!} G_{n+s}. \tag{33}$$

Let us examine in turn the terms of the summation with respect to N in the right hand side of Eq. (30). The term corresponding to $N = 0$ equals zero. The second term, which corresponds to $N = 1$, is proportional to V:

$$\int_V e_1^0 \ln e_1^0\, d\omega = R_1 V, \tag{34}$$

where, because of Eq. (29),

$$R_1 = h_1 \ln h_1.$$

Consider the next term. According to Eq. (29) the following equations hold everywhere except in the hyperlayer for which $|M_1 - M_2| \lessapprox r$:

$$e_2^0(M_1, M_2) = h_1(M_1)\, h_1(M_2) = h_1^{(2)};$$
$$\ln e_2^0(M_1, M_2) = \ln h_1(M_1) \tag{35}$$
$$+ \ln h_1(M_2) = (2) \ln h_1;$$
$$e_2^0 \ln e_2^0 = (2)\, h_1^{(2)} \ln h_1 \quad (|M_1 - M_2| \gg r).$$

(Abbreviations like those used here will be used in what follows). Because of the failure of Eqs. (35) in the layer $|M_1 - M_2| \lessapprox r$, the integration of $e_2^0 \ln e_2^0$ leads to the appearance of an additional term [as compared with the integral from Eq. (2) $h_1^{(2)} \ln h_1$] which is proportional to V. Therefore

$$\int_V \int_V e_2^0 \ln e_2^0\, d\omega_1\, d\omega_2 = 2h_1 R_1 V^2 + R_2 V, \tag{36}$$

where by R_2 we designate the corresponding coefficient of proportionality.

Let us consider the term corresponding to $N = 3$. If all three points M_1, M_2, M_3 are far from one another (the number of isolated points $n_1 = 3$), then

$$e_3^0 = e_1^{0\,(3)};$$
$$e_3^0 \ln e_3^0 = (3)\, e_1^{0\,(3)} \ln e_1^0. \tag{37}$$

Accordingly, the integral from $e_3^0 \ln e_3^0$ will contain a term equal to

$$3h_1^2 R_1 V^3.$$

There are the following three hyperlayers: 1) points M_1 and M_2 are near each other and point M_3 is distant from them; 2) M_1 and M_3 near, M_2 distant; 3) M_2 and M_3 near, M_1 distant. These layers are characterized by a number of isolated points $n_1 = 1$, and a number of pairs $n_2 = 1$. For them

$$\epsilon_3^0 = \epsilon_1^0\, {}_2^0;$$
$$\epsilon_3^0 \ln e_3^0 = e_1^0 \epsilon_2^0 \ln e_1^0 + e_1^0 e_2^0 \ln e_2^0. \tag{38}$$

In the indicated layers Eq. (38) exceeds (37) by an amount

$$e_1^0 e_2^0 \ln e_1^0 + e_1^0 e_2^0 \ln e_2^0 - (3)\, e_1^{0\,(3)} \ln e_1^0 \tag{39}$$
$$= e_1^0 \left[e_2^0 - e_1^{0\,(2)}\right] \ln e_1^0 + e_1^0 \left[e_2^0 \ln e_2^0 - e_1^{0\,(2)} \ln e_1^{0\,(2)}\right].$$

But, by Eq. (29),

$$e_2^0 - e_1^{0\,(2)} = h_2;$$

so the excess

$$e_2^0 \ln e_2^0 - e_1^{0\,(2)} \ln e_1^{0\,(2)}$$

is just the excess which gave the increment $R_2 V$ in Eq. (36). Because of this fact and Eq. (32), we find that the integral from Eq. (39) equals

$$(H_2 V)(R_1 V) + (h_1 V)(R_2 V).$$

The expression just found must be multiplied by three, since there are three hyperlayers of the specified type.

Finally, since Eq. (38) is not valid in the hyperlayer in which all three points are near one another ($n_1 = 0$, $n_2 = 0$, and the number of groups of three points, $n_3 = 1$), we must introduce an additional term, proportional to V, with a coefficient which we designate by R_3. In all, we have

$$\iiint e_3^0 \ln e_3^0\, d\omega_1\, d\omega_2\, d\omega_3 \tag{40}$$
$$= 3h_1^2 R_1 V^3 + 3H_2 R_1 V^2 + 3h_1 R_2 V^2 + R_3 V.$$

An analogous method can be applied to the examination of the integral from $e_4^0 \ln e_4^0$ (and higher integrals). If the region in which all points are far from one another introduces a term $4h_1^3 R_1 V^4$ into the integral, then the layers corresponding to points near one another bring contributions proportional to V^3 and V^2. These contributions, being of the same nature as the contributions R_2V, R_3V, can be expressed in terms of the latter. Finally, there remains an additional term R_4V, proportional to the first power of the volume, which cannot be expressed in terms of $R_1, R_2, R_3, h_1, H_2, H_3$.

Let us make a similar examination of the general integral of the indicated type, i.e., the integral from $e_k^0 \ln e_k^0$. We introduce a hyperlayer defined by a set of numbers $n_1, n_2, \ldots$ The latter have the same meaning as above (n_i is the number of groups of i nearby points); therefore $\Sigma i n_i = k$. For this layer

$$e_k^0 = e_1^{0\,(n_1)} e_2^{0\,(n_2)} \ldots e_k^{0(n_k)};$$

$$e_k^0 \ln e_k^0 = (n_1)\, e_1^{0\,(n_1)} e_2^{0\,(n_2)}$$
$$\ldots \ln e_1^0 + (n_2)\, e_1^{0\,(n_1)} e_2^{0\,(n_2)} \ldots \ln e_2^0 + \ldots$$

On evaluating the integral, the following term corresponds to this layer:

$$[n_1 h_1^{n_1-1} H_2^{n_2} \ldots R_1$$
$$+ n_2 h_1^{n_1} H_2^{n_2-1} \ldots R_2 + \ldots]\; V^{n_1+n_2+\ldots}$$

The number of such layers having the same structure (the same set of numbers $n_1, n_2, \ldots$) equals

$$\frac{k!}{n_1!\, n_2!\, (2!)^{n_2} \ldots n_k!\, (k!)^{n_k}}.$$

Consequently, summing over the different layers, we have

$$\int\limits_V \ldots \int\limits_V e_k^0 \ln e_k^0 \, d\omega_1 \ldots d\omega_k \tag{41}$$
$$= \sum_{n_1+2n_2+\ldots=k} \frac{k!\, V^{n_1+n_2+\ldots}}{n_1!\, n_2!\, (2!)^{n_2} \ldots} \sum_j n_j R_j H_j^{n_j-1} \prod_{i\neq j} H_i^{n_i},$$

where $H_1 = h_1$.

If we carry out the summation (41) over $k = 0, 1, 2, \ldots$, then the restriction $n_1 + 2n_2 + \ldots = k$ disappears. Writing

$$\nu_i = \begin{cases} n_i, & i \neq j; \\ n_j - 1, & i = j, \end{cases}$$

we have, changing the order of summation

$$\sum_{k=0}^{\infty} \frac{1}{k!} \int \ldots \int e_k^0 \ln e_k^0 \, d\omega_1 \ldots d\omega_k \tag{42}$$
$$= V \sum_{j=1}^{\infty} \frac{1}{j!} R_j \prod_{i=1}^{\infty} \sum_{\nu_i=0}^{\infty} \frac{1}{\nu_i!} \left(\frac{H_i V}{i!}\right)^{\nu_i}$$
$$= V \left(\sum_{j=1}^{\infty} \frac{1}{j!} R_j\right) \exp\left\{\sum_{i=1}^{\infty} \frac{1}{i!} H_i V\right\}.$$

Substituting this expression in Eq. (30) and bearing in mind that the sum in the exponent vanishes, we find

$$h_0 + V \sum_{i=1}^{\infty} \frac{1}{i!} H_i = V \sum_{i=0}^{\infty} \sum_{s=0}^{\infty} \frac{(-1)^s}{i!\, s!} G_{i+s} = 0.$$

Because of Eq. (27), (33), and the fact that

$$\sum_{i+s=r} \frac{(-1)^s}{i!\, s!} = \frac{1}{(i+s)!} (1-1)^{i+s} = 0,$$

we obtain the result

$$S = -h_0 - V \sum_{j=1}^{\infty} \frac{1}{j!} R_j \tag{43}$$
$$= -V \sum_{j=1}^{\infty} \frac{1}{j!} [R_j + (-1)^j G_j] \quad (G_1 = g_1).$$

This formula, in deriving which, equalities of the type (32) were used, which contains errors of the order r/D, is valid for sufficiently large regions V, when $D \gg r$. Thus, for large volumes, additivity of the entropy holds. If the dimensions of the region are comparable with the correlation distance, then additivity does not hold. Analogously, the energy of a system of mutually interacting particles can be considered additive only for regions, the linear dimensions of which are quite large compared with the radius of action of the intermolecular forces, for, otherwise, the interaction energy between the regions will be significant. The non-additivity of the entropy derives from the presence of correlations between the particles in different regions. When the volumes are large ($D \gg r$), then the correlation, which occurs mainly at the boundaries of the regions, is negligible compared with the general lack of correlation, and to the extent that correlation can be neglected, the entropy is additive and becomes proportional to the volume. The entropy density (which has meaning for sufficiently large volumes) is, according to Eq. (43)

$$s = \frac{S}{V} = -\sum_{j=1}^{\infty} \frac{1}{j!} [R_j + (-1)^j G_j]. \tag{44}$$

The entropy is strictly additive only in the case of the Poisson distribution, corresponding to the absence of all correlations. In this case, if β is the particle density,

$$G_1 = \beta; \quad G_2 = G_3 = \ldots = 0;$$

$$R_1 = \beta \ln \beta; \quad R_2 = R_3 = \ldots = 0;$$

whence, because of Eq. (44)

$$s = \beta(1 - \ln \beta). \tag{45}$$

This formula can be obtained by other means, e.g., by using the expression (23).

The Poisson law corresponds to a complete lack of correlation between the particles and is therefore an extreme case. It gives the maximum entropy density for a given particle density g_1. If the class of admissible distributions is restricted to those with the same energy density, then, of course, the Poisson distribution will not be the maximizing distribution. For non-Poisson distributions the most important correlations are those between pairs, described by the functions $g_2(M_1, M_2)$. As an example, we shall find the expression for the entropy for the case where third-order and higher correlations vanish, i.e., $g_3 = g_4 = \ldots = 0$. In this case, according to Eq. (27)

$$h_1 = g_1 - G_2; \quad h_2 = g_2; \tag{46}$$

$$h_3 = h_4 = \ldots = 0; \quad H_2 = G_2;$$

$$H_3 = \ldots = 0; \quad G_2 = \int_{\omega_2} g_2(M_1, M_2)\, d\omega_2,$$

where the point M_1 is fixed.

The method of calculating the quantities R_1, R_2, R_3, ... follows from their definitions. From Eq. (36), we obtain

$$R_2 = \frac{1}{V} \iint_{VV} \Big[g_2 \ln (h_1^2 + g_2) + h_1^2 \ln \Big(1 + \frac{g_2}{h_1^2}\Big)\Big] d\omega_1 d\omega_2.$$

Having fixed the point M_1, we can decrease the the number of integrations needed to determine R_2;

$$R_2 = \int_{\omega_2} \Big[g_2 \ln (h_1^2 + g_2) + h_1^2 \ln \Big(1 + \frac{g_2}{h_1^2}\Big)\Big] d\omega_2, \tag{47}$$

where $g_2 = g_2(M_1, M_2)$. Corresponding considerations for R_3 lead to the integral

$$R_3 = h_1 \int_{\omega_2}\int_{\omega_3} \Big\{ g_2^{12} \ln \frac{A}{h_1^2 + g_2^{12}} + g_2^{23} \ln \frac{A}{h_1^2 + g_2^{23}} + g_2^{31} \ln \frac{A}{h_1^2 + g_2^{31}} + h_1^2 \ln \frac{h_1^4 A}{(h_1^2 + g_2^{12})(h_1^2 + g_2^{23})(h_1^{23} + g_2^{31})} \Big\} d\omega_2 d\omega_3, \tag{48}$$

where

$$A = h_1^2 + g_2^{12} + g_2^{23} + g_2^{31};$$

$$g_2^{12} = g_2(M_1, M_2); \quad g_2^{23} = g_2(M_2, M_3);$$

$$g_2^{31} = g_2(M_3, M_1).$$

It is easily seen that the integrand vanishes if the condition that all three points be near each other be violated. Indeed, in this case, two of the distances $|M_1 - M_2|$, $|M_2 - M_3|$, $|M_3 - M_1|$ become large (compared with r), so that two of the quantities g_2^{12}, g_2^{23}, g_2^{31} vanish, which leads to the vanishing of the entire integrand and, consequently, to the convergence of the integral. Analogous behavior occurs for R_4, R_5, ...

The entropy density is equal to

$$s = g_1 - \frac{1}{2} G_2 - h_1 \ln h_1 - \frac{1}{2} R_2 - \frac{1}{6} R_3 - \ldots,$$

where the corresponding quantities are defined by Eqs. (46), (47), (48). In special cases there can be relations of smallness between g_1, g_2, and G_2, which can be used to simplify calculations with the indicated formulas.

The results of the present investigation can be extended to cases in which the particles (molecules) have internal degrees of freedom.

Translated by R. Silverman
75