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On the Establishment of Grand Canonical Distributions

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It is shown, in accordance with the accepted principles of statistical mechanics, that the establishment of a grand canonical distribution is to be expected in an ensemble which represents the attainment of equilibrium in an "open" system, connected with appropriate reservoirs for supplying the various kinds of molecules involved, and in thermal contact with a large heat bath at a given temperature. This finding is of assistance, in placing on a sound and understandable basis the use which has been made of grand canonical ensembles, for the representation of thermodynamic equilibrium in "open" systems.

§1. INTRODUCTION

IT is the task of the science of statistical mechanics to give satisfactory treatment to the properties and behavior of mechanical systems in situations where the condition of the system of interest is not sufficiently well determined to provide a complete specification of its precise mechanical state.[1] This task is performed by correlating the properties and behavior, to be expected for the system of interest itself, with the average properties and behavior for the members of a representative ensemble of systems of similar structure, which are appropriately distributed over different possible precise states. To obtain such an appropriate distribution, the members of the representative ensemble, in accordance with the fundamental postulate of statistical mechanics as to *a priori* probabilities and phases, are to be distributed with equal probabilities and random phases among the different possible precise states which agree equally well with the actual condition of the system of interest, insofar as that is determined.

In the case of systems, which from a microscopic point of view are composed of many separate molecules in molecular states that may be rapidly changing, but which from a macroscopic point of view are in a steady condition of equilibrium, three different kinds of representative ensemble have proved of special importance. These three kinds of ensemble are given the same names—microcanonical, canonical, and grand canonical—in a modern *quantum-mechanical* treatment, as were originally given to the analogous ensembles in the *classical* development of statistical mechanics by Gibbs.[2] Any ensemble of these three kinds can itself be shown to be in a condition of statistical equilibrium, and hence is thus in any case made suitable for representing a system of interest which for its part is in a condition of macroscopic equilibrium. The three kinds of ensemble differ from each other, however, with regard to the energies and compositions assigned to their component members, and are thus made suitable for representing systems of interest which have achieved equilibrium under different conditions of contact or connection with their surroundings.

In a *microcanonical ensemble*, each member of the ensemble is taken as having the same values for its external coordinates such as total volume, and for the numbers of constituent molecules of the various independent kinds present, as prevail in the system of interest itself; and the members are distributed over their different possible energy eigenstates, with random phases and with probabilities satisfying

$$\begin{aligned} P_i &= \text{const.} \qquad (E_i \text{ in range } E \text{ to } E+\delta E), \\ P_i &= 0 \qquad (E_i \text{ not in range } E \text{ to } E+\delta E), \end{aligned} \tag{1.1}$$

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[1] This holds both for the classical statistical mechanics, where the precise state of a system of f degrees of freedom would be specified by the exact values of $2f$ dynamical variables, and for the quantum-statistical mechanics, where the precise state of a system of f degrees of freedom would be specified by a probability amplitude for f dynamical variables. The treatment of statistical mechanics in this paper will be quantum-mechanical, since we can regard classical mechanics as a special limiting case of quantum mechanics.

[2] For the original classical description of these ensembles see Gibbs, *Elementary Principles of Statistical Mechanics* (New Haven, 1903). For a quantum-mechanical description, see for example, Tolman, *The Principles of Statistical Mechanics* (Oxford, 1938).

where P_i is the probability for finding a member of the ensemble in an eigenstate i corresponding to the energy eigenvalue E_i, and E to $E+\delta E$ denotes a small energy range which has been selected as of interest.

In agreement with the above-described character, a microcanonical ensemble may be regarded as representing a system which has been set up with precisely specified external coordinates such as total volume, with a precisely specified molecular constitution, and with its energy specified in a narrow range, and which has then been allowed to come to equilibrium under conditions of *perfect isolation* from the surroundings such as to preserve its total energy within the narrow range selected.[3] It will be appreciated that these requirements as to energy and isolation are not such as to make a microcanonical ensemble truly appropriate for the representation of thermodynamic equilibrium, since it would then be essential to regard the system as having a specified temperature determined for example by interaction with a heat bath, rather than to regard it as having a specified energy determined by the maintenance of perfect isolation.

In a *canonical ensemble*, each member of the ensemble is again taken as having the same values for its external coordinates and for its molecular constitution as prevail in the system of interest itself; but the members are now taken as distributed over their different possible energy eigenstates, with random phases and with probabilities satisfying

$$P_i = e^{(\psi - E_i)/\theta}, \tag{1.2}$$

where P_i is the probability for finding a member of the ensemble in an eigenstate i corresponding to the energy eigenvalue E_i, and ψ and θ are adjustable parameters having the dimensions of energy.

In agreement with the above-described character, a canonical ensemble may be regarded as representing a system which has been set up with precisely specified external coordinates and molecular constitution, and which has then been allowed to come to equilibrium under conditions of *interaction* with its surroundings such as to justify the probabilities for different energies described by (1.2). As first shown for the classical mechanics by Gibbs,[4] this interaction could be obtained by allowing the system to achieve *thermal equalization* with a large heat bath at temperature $T=\theta/k$, where interchange of energy between the system and bath would provide the fluctuations necessary to correspond to the above probability distribution in energy. Or, as shown more recently by the writer,[5] this interaction could also be obtained by leaving the system in *essential isolation*, where interchange of energy between the system and its containing walls, or other immediate surroundings, would provide the fluctuations necessary to correspond to the above probability distribution in energy, at least over a range in the neighborhood of the mean energy of the members of the ensemble, and where the resulting temperature $T=\theta/k$ would be determined by the mean energy, which in cases of essential isolation is taken as unchanged by the interaction permitted. It will be appreciated, as was first shown for the classical mechanics by Gibbs,[6] that the energy distribution in a canonical ensemble is such as to make it strictly appropriate for representing equilibrium in a "closed" thermodynamic system, where it would be essential to regard the system as having a precisely specified temperature rather than a precisely specified energy.

Finally in a *grand canonical ensemble*, each member of the ensemble is again taken as having the same values for its external coordinates as prevail in the system of interest itself; but the members are now taken as distributed both over different possible molecular constitutions, and over their different possible energy eigenstates, with random phases and with probabilities satisfying

$$P_{n_1, n_2, \cdots n_h, i} = e^{(\Omega+\mu_1 n_1+\mu_2 n_2+\cdots+\mu_h n_h - E_i)/\theta}, \tag{1.3}$$

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[3] For a classical discussion of the process by which the representative ensemble for an isolated system, having a closely specified energy, proceeds in the direction of microcanonical distribution, see Lorentz, *Abhandlungen über theoretische Physik* (Teubner, 1907), §79, p. 289. For a quantum-mechanical discussion, see Tolman, reference 2, §§109 and 110.

[4] Gibbs, reference 2, p. 161. For the quantum-mechanical treatment of the same phenomenon, see Tolman, reference 2, §§111, 112 and 128.

[5] See in particular Tolman, reference 2, §111*d*.

[6] Gibbs, reference 2, Chap. 14. For the corresponding quantum-mechanical discussion, see Tolman, reference 2, Chap. 13.

where $P_{n_1, n_2 \cdots n_h, i}$ is the probability for finding a member of the ensemble with $n_1, n_2 \cdots n_h$ molecules of the h independent kinds present, and in an eigenstate i corresponding to the energy eigenvalue E_i, and where Ω, θ, and $\mu_1 \cdots \mu_h$ are adjustable parameters, having the dimensions of energy or of energy per molecule.

In agreement with the above-described character, a grand canonical ensemble may be regarded as representing a system which has been set up with precisely specified external coordinates such as total volume, and which has then been allowed to come to equilibrium under conditions of *interconnection and interaction* with its surroundings such as to justify the probabilities for different molecular constitutions and for different energies described by (1.3). The nature of the interconnection and interaction which would lead to this result has not hitherto been made the subject of direct investigation.

It is now the purpose of the present article to show that the conditions leading to the establishment of a grand canonical distribution are of such a character that the ensemble can be taken as representing a system of interest which has been allowed to come to equilibrium with its molecular constitution determined by interconnection with suitable reservoirs for providing the different kinds of molecules which it contains, and with its temperature determined by interaction with a suitable heat bath. This result will then be of assistance in placing on a sound and understandable basis the use which has been made of grand canonical ensembles, by Gibbs and others,[7] for the representation of equilibrium in so-called "open" thermodynamic systems.

§2. Distribution in Terms of Sum-Over-States for Reservoirs

In order to carry out the proposed demonstration, we shall wish to consider the equilibrium of a combined system composed of connected parts $S, R_1, R_2, \cdots R_h$. The part S, which may be called the system proper, will itself turn out to be the "open" system of primary interest for which we wish to derive the grand canonical distribution as representing equilibrium. It contains a mixture of all the different independent kinds of substance[8] $1, 2, \cdots h$ that concern us. The parts $R_1, R_2, \cdots R_h$, which may be called reservoirs, are connected with S through semipermeable membranes each of which allows the passage of a single kind of substance $1, 2, \cdots h$, respectively. Each reservoir contains a supply of the substance for which its membrane is permeable. The volumes of the system proper and of the reservoirs are to be taken as having constant values, and for the purposes of the proposed treatment we may assume that external coordinates other than volume are not involved.

Let us now consider the equilibrium which would be reached if the above combination of system proper and reservoirs were allowed to stand in thermal contact with a large heat bath at temperature T. Since the combination as a whole is itself a "closed" thermodynamic system, its condition at equilibrium could be represented by the canonical distribution

$$P_i = e^{(\psi - E_i)/\theta}, \tag{2.1}$$

where P_i is the probability for finding a member of the ensemble in a state i corresponding to an eigenvalue of energy E_i for the combined system, where the parameter ψ has the necessary value so that the total probability for different states is normalized to unity, and where the parameter θ has the value

$$\theta = kT, \tag{2.2}$$

with k as Boltzmann's constant and T the temperature of the bath.

We may assume that the separation between the different parts of the combined system is sufficiently distinct, so that we can distinguish with accuracy between the molecules present in the system proper and those remaining in the reservoirs, and may assume that the interaction between the parts is sufficiently small so that we can regard any energy eigenstate of the whole system as a combination of energy eigenstates for its parts and regard the eigenenergy of the whole as the sum of the eigenenergies of its parts. This will then permit us to rewrite the description

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[7] For the original classical application of grand canonical distributions to this purpose, see Gibbs, reference 2, Chap. 15. For the corresponding quantum-mechanical applications, see Tolman, reference 2, §140.

[8] The different "component substances," in the sense used by Gibbs in his treatise "On the equilibrium of homogeneous substances," Trans. Conn. Acad. III (1875–78).

of the distribution given by (2.1) in the more explicit form

$$P_{n_1,\,n_2,\,\cdots n_h,\,s,\,r_1,\,r_2,\,\cdots r_h} = \exp\left[(\psi - E_s - E_{r_1} - E_{r_2} - \cdots - E_{r_h})/\theta\right], \quad (2.3)$$

where we have replaced P_i by the more explicit symbol $P_{n_1,\,n_2,\cdots n_h}$, s, r_1, r_2, $\cdots r_h$, to denote the probability for a state of the combined system in which the system proper S contains n_1, n_2, $\cdots n_h$ molecules of the h kinds involved and is an eigenstate s, and in which the reservoirs R_1, R_2, $\cdots R_h$ containing the remaining molecules are in eigenstates r_1, r_2, $\cdots r_h$, and where we have replaced E_i by the sum of the eigenenergies E_s, E_{r_1}, E_{r_2}, $\cdots E_{r_h}$ for the parts of the whole system.

By summing the above expression for the probability of a state of the combined system over all states r_1, r_2, $\cdots r_h$ for the reservoirs, which are compatible with their molecular contents, we then obtain

$$\begin{aligned} P_{n_1,\,n_2,\,\cdots n_h,\,s} &= e^{(\psi - E_s)/\theta} \sum_{r_1,\,r_2,\,\cdots r_h} \exp\left[-(E_{r_1} + E_{r_2} + \cdots + E_{r_h})/\theta\right] \\ &= e^{(\psi - E_s)/\theta} \Big(\sum_{r_1} \exp\left[-E_{r_1}/\theta\right]\Big)\Big(\sum_{r_2} \exp\left[-E_{r_2}/\theta\right) \cdots \Big(\sum_{r_h} \exp\left[-E_{r_h}/\theta\right]\Big) \end{aligned} \quad (2.4)$$

as an expression for the probability of a state of the system proper, which is specified by its molecular constitution n_1, n_2, $\cdots n_h$ and by an eigenstate s possible for that constitution. It will be seen that this expression depends on the so-called sum-over-states for the system of reservoirs, and hence on the product of those quantities for the separate reservoirs, where it will be appreciated that the sum-over-states for each reservoir will itself depend, not only on volume and temperature which may be regarded as fixed, but also on the number of molecules in the reservoir, which will vary with the composition of the system proper.

To obtain a notation which indicates that the value for the sum-over-states of each reservoir is dependent on its molecular content, it will be convenient to retain the symbol n_i for the number of molecules of the ith kind, $i = 1, 2, \cdots h$, in the system proper S, and to introduce the new symbols n_i' for the number of molecules of the ith kind in the corresponding reservoir R_i, and n_i^0 for the constant total number in the combined system as a whole. This will give us

$$n_i' = n_i^0 - n_i \quad (2.5)$$

as the value for the number of molecules in the ith reservoir R_i. Ror the sum-over-states of the ith reservoir, we may then introduce the symbol

$$Z_{n_i'} = \sum_{r_i} \exp\left[-E_{r_i}/\theta\right], \quad (2.6)$$

where the subscript to Z indicates that the summation over possible states r_i is to be evaluated when the reservoir contains n_i' molecules.

Substituting symbols of the above form into (2.4), we can now write

$$P_{n_1,\,n_2,\,\cdots n_h,\,s} = e^{(\psi - E_s)/\theta} Z_{n_1'} Z_{n_2'} \cdots Z_{n_h'} \quad (2.7)$$

as our expression for the probability of a state of the system proper of the indicated composition and energy. By studying the dependence of the sums $Z_{n_1'}$, $Z_{n_2'}$, $\cdots Z_{n_h'}$ for the reservoirs on the numbers of molecules n_1', n_2', $\cdots n_h'$ which they contain, and hence in accordance with (2.5) on the numbers of molecules n_1, n_2, $\cdots n_h$ in the system proper, it will then prove possible to obtain the desired information as to the manner in which the probability for a state of an "open" thermodynamic system depends at equilibrium on its composition as well as on its energy.

§3. Lemma on the Dependence of Sum-over-States on Number of Molecules

The precise evaluation of the sum-over-states for a system of interacting molecules is in general a complicated and difficult task which often has to be solved by some method of approximation. It will, however, be possible to obtain the needed information as to the dependence of the sum-over-states of a system on the number of molecules which it contains by making use of the two following known relations. In the first place, when a system of n similar molecules, at a given temperature T, is present in a large enough volume v_0 so that it assumes the properties of a nondegenerate perfect gas, the corresponding sum-over-states can be expressed in the known form[9]

$$Z_{n,\,v_0,\,T}=\frac{1}{n!}\Big(\sum_i \exp\left[-\epsilon_i(v_0)/kT\right]\Big)^n, \tag{3.1}$$

where $\epsilon_i(v_0)$ is an eigenvalue of energy for a single molecule of the kind under consideration in the volume v_0, and we sum over all energy eigenstates i. In the second place, when the system is large enough so that it can be regarded as having a well-defined macroscopic pressure p, the correlation of thermodynamic with statistical-mechanical quantities provided by representing the thermodynamic equilibrium of a "closed" system by a canonical ensemble, shows that the change in sum-over-states with volume, holding composition and temperature constant, can be written in the form[10]

$$\frac{\partial \log Z}{\partial v}=\frac{p}{kT}. \tag{3.2}$$

Combining these two expressions, we may now write

$$\log Z_{n,\,v,\,T}=\log\frac{1}{n!}\left(\sum_i \exp\left[-\frac{\epsilon_i(v_0)}{kT}\right]\right)^n+\frac{1}{kT}\int_{v_0}^{v} p\,dv \tag{3.3}$$

as an expression for the sum-over-states corresponding to a system of n similar molecules at any desired volume v, and temperature T, where v_0 is a large enough volume so that the system then has the properties of a nondegenerate perfect gas.

In applying this expression to the problem outlined in the preceding section, we shall be interested in the value for the sum-over-states of a reservoir when the number of molecules therein is regarded as resulting from a fluctuation Δn away from the mean number of molecules $\bar{n}$ which the reservoir contains at equilibrium. Setting up expressions of the form (3.3) for the two cases when a system, at a given volume v and temperature T, contains $\bar{n}$ and $\bar{n}+\Delta n$ molecules, and subtracting one from the other, we readily obtain

$$\log\frac{Z_{\bar{n}+\Delta n}}{Z_{\bar{n}}}=\log\frac{\bar{n}!}{(\bar{n}+\Delta n)!}+\log\left(\sum_i \exp\left[-\frac{\epsilon_i(v_0)}{kT}\right]\right)^{\Delta n}+\frac{1}{kT}\int_{v_0}^{v} p_{\bar{n}+\Delta n}\,dv-\frac{1}{kT}\int_{v_0}^{v} p_{\bar{n}}\,dv \tag{3.4}$$

as an expression for the ratio of the sum-over-states $Z_{\bar{n}+\Delta n}$ for a system of $\bar{n}+\Delta n$ molecules at a given volume and temperature to the sum-over-states $Z_{\bar{n}}$ for the same system when it contains $\bar{n}$ molecules, where the volume v_0 appearing in the last three terms must be chosen large enough so that the system would behave as a nondegenerate perfect gas when it contains either $\bar{n}+\Delta n$ or $\bar{n}$ molecules in that volume, and where the symbols $p_{\bar{n}+\Delta n}$ and $p_{\bar{n}}$ in the last two terms denote the pressure of the system when it contains $\bar{n}+\Delta n$ or $\bar{n}$ molecules, respectively.

We must now discuss the dependence of the right-hand side of (3.4) on the value of the fluctuation Δn away from the mean molecular content $\bar{n}$, and on the value of the ratio of those two quantities $\Delta n/\bar{n}$. We shall be specially interested in the form of the right-hand side when the ratio $\Delta n/\bar{n}$ approaches zero, and shall wish to carry out the discussion in such a manner as to include not only the possibility of making this ratio small—with any given mean molecular content $\bar{n}$—by restricting attention to cases where the fluctuations Δn are sufficiently small, but also the possibility of making this ratio small—with any given value for the fluctuation Δn—by changing to a larger system (reservoir) with its mean molecular content $\bar{n}$ and its volume v increased in the same ratio.

To examine the dependence of the first term on the right-hand side of (3.4) on the quantities of interest we may rewrite it in the forms

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[9] See for example Tolman, reference 2, Eq. (134.10).

[10] See for example Tolman, reference 2, Eq. (133.3).

$$
\begin{aligned}
\log\frac{\bar{n}!}{(\bar{n}+\Delta n)!}&=\log\frac{1}{(\bar{n}+1)(\bar{n}+2)\cdots(\bar{n}+\Delta n)}\\
&=-\log \bar{n}^{\Delta n}-\log\left(1+\frac{1}{\bar{n}}\right)\left(1+\frac{2}{\bar{n}}\right)\cdots\left(1+\frac{\Delta n}{\bar{n}}\right)\\
&=-\Delta n\log\bar{n}-\left[\frac{1}{\bar{n}}-\frac{1}{2}\left(\frac{1}{\bar{n}}\right)^2+\frac{1}{3}\left(\frac{1}{\bar{n}}\right)^3-\cdots\right]-\left[\frac{2}{\bar{n}}-\frac{1}{2}\left(\frac{2}{\bar{n}}\right)^2+\frac{1}{3}\left(\frac{2}{\bar{n}}\right)^3-\cdots\right]\\
&\qquad-\cdots-\left[\frac{\Delta n}{\bar{n}}-\frac{1}{2}\left(\frac{\Delta n}{\bar{n}}\right)^2+\frac{1}{3}\left(\frac{\Delta n}{\bar{n}}\right)^3-\cdots\right].
\end{aligned}
\tag{3.5}
$$

As $\Delta n/\bar{n}$ goes to zero, either because we restrict our attention to cases where Δn is itself sufficiently small, or because we consider a large enough system to make $\bar{n}$ sufficiently large, this expression goes to

$$
\log\frac{\bar{n}!}{(\bar{n}+\Delta n)!}=-\Delta n\log\bar{n}.
\tag{3.6}
$$

The explicit formulation of (3.5) is made for the case Δn positive, but a similar formulation can be made for the case Δn negative, which leads to the same limiting result (3.6).

The second term on the right-hand side of (3.4) is already expressed in a form which indicates its dependence on the quantities of interest, since it is seen to be the logarithm of a constant raised to the power Δn. It will be appreciated, however, that the value of this constant would be subject to alteration if we changed to a larger reservoir with a larger number of molecules, since we should then in general have to choose a larger volume v_0 to secure the behavior of a nondegenerate perfect gas.

The last two terms on the right-hand side of (3.4) may be re-expressed, in a form to show their dependence on the quantities of interest, by considering a Taylor's expansion for the value of the pressure of the system p as a function of its molecular content n. In doing this we shall assume that the substance in the system obeys an equation of state so that its pressure at a given temperature may be taken as a function of its density. This will let us put

$$
p(n,v)=p(n/v)=p(\rho),
\tag{3.7}
$$

where we introduce the molecular density

$$
\rho=n/v\quad\text{with}\quad \partial\rho/\partial n=1/v.
\tag{3.8}
$$

With the help of (3.7) and (3.8), we may now re-express the last two terms on the right-hand side of (3.4) in the forms

$$
\begin{aligned}
\frac{1}{kT}\int_{v_0}^{v}p_{\bar{n}+\Delta n}dv-\frac{1}{kT}\int_{v_0}^{v}p_{\bar{n}}dv&=\frac{1}{kT}\int_{v_0}^{v}\left[\frac{1}{v}\frac{\partial p}{\partial\rho}\Delta n+\frac{1}{v^2}\frac{\partial^2 p}{\partial\rho^2}\frac{(\Delta n)^2}{2!}+\frac{1}{v^3}\frac{\partial^3 p}{\partial\rho^3}\frac{(\Delta n)^3}{3!}+\cdots\right]dv\\
&=-\frac{\Delta n}{kT}\int_{\rho_0}^{\rho}\left[\frac{1}{\rho}\frac{\partial p}{\partial\rho}+\frac{1}{2}\frac{\partial^2 p}{\partial\rho^2}\frac{\Delta n}{\bar{n}}+\frac{1}{6}\rho\frac{\partial^3 p}{\partial\rho^3}\left(\frac{\Delta n}{\bar{n}}\right)^2+\cdots\right]d\rho,
\end{aligned}
\tag{3.9}
$$

where the derivatives of p with respect to ρ are to be taken when the system has the molecular content $n=\bar{n}$, and where the final form of expression has been obtained with the help of the substitutions $\bar{n}/v=\rho$ and $dv/v=-d\rho/\rho$. The final form of expression in (3.9) has been chosen, in a form depending on integration with respect to the density ρ, in order to make clear the consequences of changing to a larger system (reservoir) with the same proportional increase in molecular content $\bar{n}$

and in volume v. If such a change were made, it will be seen that the lower limit of integration ρ_0 would not need alteration since the properties of the substance could be taken as approaching those of a non-degenerate perfect gas at that given density, and the upper limit of integration and the functions of ρ appearing in the integrand would obviously not be altered. Hence as $\Delta n/\bar{n}$ goes to zero, either because we restrict our attention to cases where Δn is itself sufficiently small, or because we consider a large enough system to make $\bar{n}$ sufficiently large, we see, in accordance with the finite values to be expected for the derivatives of p with respect to ρ that occur in (3.9), that the last two terms on the right-hand side of (3.4) can be taken as going to

$$\frac{1}{kT}\int_{v_0}^{v} p_{\bar{n}+\Delta n}dv-\frac{1}{kT}\int_{v_0}^{v} p_{\bar{n}}dv=-\frac{\Delta n}{kT}\int_{\rho^0}^{\rho}\frac{1}{\rho}\frac{\partial p}{\partial \rho}d\rho. \tag{3.10}$$

Substituting (3.6) and (3.10) in (3.4), we can now write

$$\log\frac{Z_{\bar{n}+\Delta n}}{Z_{\bar{n}}}=-\Delta n\left(\log \bar{n}-\log\sum_i \exp\left[-\frac{\epsilon_i(v_0)}{kT}\right]+\frac{1}{kT}\int_{\rho_0}^{\rho}\frac{1}{\rho}\frac{\partial p}{\partial \rho}d\rho\right), \tag{3.11}$$

or

$$Z_{\bar{n}+\Delta n}=AB^{-\Delta n}, \tag{3.12}$$

where A and B are constants, as expressing in general, for a system of similar molecules at a given volume and temperature, the dependence of sum-over-states on fluctuations Δn in molecular content which are small compared with a particular value $\bar{n}$ for the number of molecules in the system.

§4. DISTRIBUTION IN TERMS OF COMPOSITION OF SYSTEM PROPER

We are now ready to return to our previous expression (2.7) for the probability distribution for states of the system proper S, in terms of expressions for the sum-over-states of each of the reservoirs R_1, R_2, $\cdots R_h$. As a consequence of (3.12), we can now write

$$Z_{n_i'}=A_iB_i^{\bar{n}_i'-n_i'} \tag{4.1}$$

where A_i and B_i are constants, as a correct form of expression for the sum-over-states of the ith reservoir R_i, when it contains any number of molecules n_i' which is near enough the mean number $\bar{n}_1'$ so that the ratio $(n_i'-\bar{n}_i')/\bar{n}_i'$ is small. And by substituting the expression for $n_{i'}$ given by (2.5) this can be rewritten in the form

$$Z_{n_i'}=A_iB_i^{\bar{n}_i'-n_i^0+n_i}, \tag{4.2}$$

where n_i^0 is the total number of molecules of the kind i in the combined system and n_i is the number of that kind in the system proper S.

Substituting expressions of the form (4.2) into our previous expression (2.7) for the probabilities of states of the system proper, we obtain

$$P_{n_1,\, n_2,\, \cdots n_h,\, s}=e^{(\psi-E_s)/\theta}\prod_{i=1}^{h} A_iB_i^{\bar{n}_i'-n_i^0+n_i}. \tag{4.3}$$

And by introducing new symbols defined by

$$e^{\Omega/\theta}=e^{\psi/\theta}\prod_{i=1}^{h} A_iB_i^{\bar{n}_i'-n_i^0} \quad\text{and}\quad e^{\mu_in_i/\theta}=B_i^{n_i}, \tag{4.4}$$

where the quantities Ω and μ_i are constants, we can then finally write

$$P_{n_1,\, n_2,\, \cdots n_h,\, s}=e^{(\Omega+\mu_1n_1+\mu_2n_2+\cdots+\mu_hn_h-E_s)/\theta}, \tag{4.5}$$

as the desired expression for the probability of any state s of the system proper, as determined by its molecular contents n_1, n_2, $\cdots n_h$, and energy E_s, when in that state.

It will be noted that the above dependence on composition and energy is that for a grand canonical distribution. It will be seen, in accordance with the derivation of (4.5), that this distribution can be taken as valid, in the neighborhood of the mean molecular composition of the system proper, for any fluctuation Δn_i in the number of molecules of any kind present therein, which can be regarded as vanishingly small compared with the mean number n_i' present in the corresponding reservoir. It will also be seen, moreover, that the range of validity can be made as wide as desired by taking large enough reservoirs with large enough mean molecular contents $\bar{n}_i'$. Since the change to a larger reservoir may be made by taking the same proportional increase in volume and in mean molecular content, it will be appreciated that such a change need involve no major alteration in the escaping tendency for the molecules in the reservoir or in the character of the equilibrium in the system proper.

The foregoing derivation has been carried out for simplicity for the case when the system proper S is taken as connected through a semipermeable membrane with a separate reservoir for each of the different kinds of molecules involved. Similar derivations can also be carried out, however, for cases when the system is taken as connected through suitable membranes with reservoirs for more than a single substance, or indeed as connected—without any membrane being necessary—with a single reservoir for all the component substances. In treating such cases, the sum-over-states for a reservoir, containing more than a single kind of molecule, can now be obtained by starting with the known expression for sum-over-states when a mixture of molecules is present in a large enough volume to act as a nondegenerate perfect gas, and then adding as before the increase in sum-over-states that occurs on compression to the volume of in-interest. The dependence of the result on molecular constitution can then be investigated, much as before, the main difference lying in the necessity of now introducing a Taylor's expansion, which gives the pressure of the reservoir contents as a function of changes in the numbers of more than a single kind of molecules. The range of validity for the grand canonical distribution is still found in such cases to be limited only by the restriction to fluctuations, around the mean number of molecules of any constituent in the system proper, which are vanishingly small compared with the mean number in the appropriate reservoir. Hence, under such circumstances, we may now take the grand canonical distribution as applying in general to the equilibrium condition for a system proper which is connected with one or more suitable reservoirs for providing its constituent substances.

§5. Concluding Remarks

We may now make some concluding remarks, as to the conditions leading to the establishment of grand canonical distributions, and as to the propriety of using grand canonical ensembles for representing equilibrium in the case of "open" thermodynamic systems.

In accordance with the previously known results of statistical mechanics, we can represent the establishment of equilibrium in a "closed" system of molecules, left in thermal contact with a large heat bath at temperature T, by the establishment of a canonical distribution with $\theta = kT$ in the corresponding representative ensemble, and can then use the canonical ensemble thus arising to represent the condition of equilibrium in the "closed" system of interest. In accordance with the results of the present article, we have found that a canonical distribution in the representative ensemble for a "closed" system, consisting of a system proper connected with a suitable reservoir or reservoirs for furnishing the various kinds of molecules involved, implies a grand canonical distribution, in that part of the ensemble which represents the system proper, for all fluctuations in molecular contents which are vanishingly small compared with the mean contents available in the reservoirs. Hence, introducing the usual term "open" system to denote a system proper which is connected with one or more reservoirs of large enough capacity for the satisfactory accommodation of all fluctuations of interest, we can now represent the establishment of equilibrium, in an "open" system of molecules at temperature T, by the establishment of a grand canonical distribution in the corresponding representative ensemble with $\theta = kT$, and can then use the grand canonical ensemble thus arising to represent the condition of equilibrium in the "open" system under consideration.

In making such use of grand canonical ensembles to represent the condition of equilibrium, in actual situations where a system of interest is connected with one or more reservoirs, cases may arise where the range of validity for the grand canonical distribution is not wide enough to cover all fluctuations in the composition of the system which are of interest. This may occur either because the reservoirs are so small as to make the actual range of validity a very narrow one, or because the character of the system is such as to give a high probability for compositions of the system differing widely from the mean,[11] thus making the range of interest over which we desire accuracy a wide one. In such cases, we have the possibility of giving as accurate a treatment of the probabilities for different compositions of the system as may be necessary, by including higher order terms of the kind $\Delta n/\bar{n}$ in equations such as (3.5) and (3.9). It is to be emphasized, however, in the usual situations where we should wish to apply the grand canonical distribution, that the typical cases which arise are those where the numbers of molecules available in the reservoirs are great enough, and the probabilities for compositions of the system widely different from the mean are small enough, so that the grand canonical ensemble gives an appropriate description of equilibrium.

It should be remarked that the circumstances, which lead to the grand canonical rather than the canonical distribution as the appropriate description of equilibrium, are perhaps more frequently present in nature than is usually appreciated, owing to the frequency with which we are interested in the behavior of a system of molecules which in actuality forms part of, or has been cut off, from a larger system. From a mathematical point of view, this is a fortunate happening, since, in spite of its apparently greater complexity of form, the grand canonical distribution really proves easier to handle than the canonical distribution, owing to the fact that summations over different possible states can be carried out without any limitation on the total number of molecules. Thus in the case of degenerate Einstein-Bose and Fermi-Dirac gases it is found, when the interaction between molecules can be neglected, that the usual expressions for the mean numbers of molecules in different molecular states can be simply and accurately derived for a grand canonical ensemble, although holding only approximately in a canonical ensemble.[12]

In conclusion, it may be emphasized that the foregoing demonstration of an actual tendency toward the establishment of grand canonical distributions in the ensembles by which we represent the establishment of equilibrium in "open" systems, is of assistance in placing on a sound and understandable basis the use which has been made of grand canonical ensembles for the representation of thermodynamic equilibrium in "open" systems. Previous work[7] has shown that this use of grand canonical ensembles provides consistent statistical-mechanical analogs for thermodynamic quantities, in particular analogs for the Gibbs' potentials which give a statistical-mechanical explanation of the known thermodynamic conditions for equilibrium towards the transfer of component substances between systems placed in connection, and an analog for entropy which gives a statistical-mechanical explanation for the thermodynamic principle of the precise additivity of entropies when similar homogeneous systems are combined thus solving the so-called Gibbs paradox. It has not hitherto been apparent, however, that the introduction of grand canonical ensembles to represent the equilibrium of "open" thermodynamic systems is not only suggested by the consistency of the thermodynamic analogies thus provided, but is also dictated by the actual tendency for grand canonical distributions to be established in the ensembles by which we must represent the establishment of equilibrium in "open" systems, if we apply the accepted principles of statistical mechanics.

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[11] A judgment as to the probabilities for compositions differing from the mean can be obtained with the help of the formula for the mean square fluctuations in composition in a grand canonical ensemble, see Gibbs, reference 2, Eq. (541); Tolman, reference 2, Eq. (141.42).

[12] See Pauli, Zeits. f. Physik **41**, 81 (1927); Tolman, reference 2, §114.