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Statistical Distribution Laws for Rate Processes

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A re-examination of the fundamental hypotheses of statistical mechanics shows that the principle of the most probable distribution may be interpreted in such a way as to be applicable as well to systems which are not at equilibrium. The general method of deriving distribution laws for systems not at equilibrium is outlined. The use of this method is illustrated by deriving a general distribution law for systems in which the velocities are required to be non-Maxwellian. The distribution of velocities of molecules in any group having a specified average velocity is Maxwellian relative to the group average velocity. The average total energy of such a system is shown to be the sum of the kinetic energies of mass motion of the several groups of molecules plus the Maxwellian average energy corresponding to the given volume and temperature.

G ROSS physical properties of a system of molecules may be calculated from the molecular constants either by kinetic theory methods or by those of statistical mechanics. The kinetic theory method as applied by Enskog,[1] Chapman,[2,3] and others consists in solving the Maxwell-Boltzmann integro-differential equation by successive approximations. The zeroth approximation is Maxwell's law[4] of velocity distribution. The second and third approximations have been obtained only with difficulty,[3] and little work has been done on higher approximations. The method at present is further limited to gases at low pressures.

The method of statistical mechanics, whether based on the canonical ensemble of Gibbs[5] or the principle of maximum probability[6] is more direct, giving the form of the statistical distribution function free of approximations. However, this method has been developed only for systems at equilibrium. The limitation to systems at equilibrium is not necessary, and may be removed by re-examining the fundamental hypotheses.

In developing a statistical mechanics which is applicable to rate processes, it is desirable to insure at the same time that it will apply as well to condensed systems. For this reason, the method of Jeans,[6] in which the element of the statistical ensemble is the whole system of molecules, will be followed. The language used is that of classical mechanics; however, only minor changes are required by the substitution of relativistic and wave mechanics.

GENERALIZED STATISTICAL MECHANICS

Definitions

In establishing a law connecting the gross physical properties of a system, a series of connected measurements are made on the same system. The procedure is then repeated on the same or another practically identical system under comparable conditions. The number of repetitions is increased until the experimenter is confident that further repetitions will not materially alter the average values of the measured properties.

The requirement of *comparable conditions* implies that certain gross parameters g_1, g_2, $\cdots$ of the system are the same in each repetition of the series of measurements. This specification is inadequate, as evidenced by the different values of the properties x, y, $\cdots$ obtained in the several sets of measurements. A complete specification would describe the system as existing in the state i whose properties are precisely x_i, y_i, $\cdots$. The inadequate specification leaves the system to assume any one of the detailed states 1, 2, $\cdots$, i, $\cdots$ by chance.

The system may happen to assume the i state in a number nw_i out of n repetitions. This defini-

[1] D. Enskog, *Kinetische Theorie der Vorgänge in mässig verdünnten Gasen* (Dissertation, Upsala, 1917).

[2] S. Chapman, Phil. Trans. Roy. Soc. **A211**, 433 (1912); **216**, 279 (1916); **217**, 115 (1917).

[3] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, 1939).

[4] J. C. Maxwell, Phil. Trans. Roy. Soc. **157**, 49 (1867).

[5] J. Willard Gibbs, *The Collected Works* (Longmans, Green and Company, New York, 1938), Vol. 2.

[6] J. H. Jeans, Phil. Mag. [6] **5**, 597 (1903).

tion of the relative frequencies w_i is such that

$$\sum_i w_i = 1, \tag{1}$$

while the average value of the property x_i for this particular set of repetitions is

$$\bar{x} = \sum_i x_i w_i. \tag{2}$$

If the property x is constant over the states i, then $x_i = x_j = \cdots = \bar{x}$; the average value is the same as that for each state. In particular, $\sum_i w_i$ is the average value, $\bar{1}$, of unity.

As the number n of repetitions is increased, w_i may approach a limit denoted by W_i if the limit exists. Then since x_i depends only on the definition of the state i, the average value $\bar{x}$ will approach a limit X given by Eq. 2 when W_i is substituted for w_i. Let the operator D denote the value of the quantity operated on minus its limiting value. Thus $Dw_i = w_i - W_i$, $D\bar{x} = \bar{x} - X$, etc. By applying this operator to Eqs. 1 and 2, one finds

$$\sum_i Dw_i = D1 = 0, \tag{3}$$

and

$$D\bar{x} = \sum_i x_i Dw_i. \tag{4}$$

In the limit of large n, the operator D must be interpreted as denoting the change in the value operated on due to a trial variation in the values of the W_i's.

Fundamental Hypothesis

In order to give any meaning to statistical methods, it is necessary to make some assumption which in effect requires that

the set of limiting frequencies W_i exists and is determined by the conditions imposed on the set of repeated experiments.

The relation between the values W_i and the experimental conditions constitutes the statistical distribution law by means of which the limiting average values X, Y, $\cdots$ of various physical properties may be calculated.

Let a_i denote the *a priori* probability that in a single experiment the system will assume the particular detailed state i. In general this quantity is to be interpreted as the quantum weight of the state i, although other interpretations may be necessary in some cases. Further let $\mathbf{W}_n(w_1,$ $w_2, \cdots)$ denote the probability that out of a series of n experiments the state 1 was assumed exactly nw_1 times, the state 2 in nw_2 times, etc. If the performance of n repeated experiments constitutes a series of unrelated events, then

$$\mathbf{W}_n(w_1, w_2 \cdots) = n! \prod_i (a_i{}^{nw_i}/nw_i!). \tag{5}$$

Using Stirling's approximation, if the number n of experiments is very large, Eq. 5 may be written in the form

$$\log \mathbf{W}_n = n(\log a/w)_{Av}, \tag{6}$$

where $(\log a/w)_{Av}$ represents

$$\sum_i w_i \log a_i/w_i.$$

The hypothesis of a limiting distribution implies that in the limit of a very large number of experiments, the distribution $w_1 = W_1$, $w_2 = W_2$, $\cdots$ becomes very much (i.e., infinitely) more probable than any other distribution. For this to be true it is necessary that $(\log a/w)_{Av}$ have a value for this distribution which is at least infinitesimally greater than that for any other distribution. If $(\log a/w)_{Av}$ is a continuous function of the w_i's, then its value for the limiting distribution is a true maximum, and its variation

$$\sum_i (\log a_i/W_i - 1)Dw_i = 0 \tag{7}$$

for all small values of the Dw_i's which are consistent with the experimental conditions. Actually, $(\log a/w)_{Av}$ is defined only for integral values of the numbers nw_i, and may be considered a continuous function only in the limit of very large values of n.

Equation 7 is analogous to the usual principle of maximum probability,[6,7] but must be interpreted somewhat differently. In the usual treatment the distribution law concerns the number of independent molecules out of a very large total number which are to be found in a particular quantum state at equilibrium. The distribution implied by Eq. 7 is not concerned with numbers of molecules, but rather with the number of experiments out of a large number n, in which the system as a whole is observed to as-

[7] See, for example, E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, New York, 1938), Section 199.

sume a particular detailed state. The statistics of independent molecules may be considered as a special case in which the experimental system consists of only a single molecule. Furthermore, no assumption has been made which in any way limits the result to equilibrium states.

Distribution Law

To obtain the distribution law appropriate to any particular set of experimental conditions, Eq. 7 is to be solved subject to these conditions. The form of the resulting distribution law will depend on the nature of the restrictions which the system must satisfy.

In obtaining the solution, it is only necessary to consider a set of independent restrictions. If one of the restrictions implies a second, only the first need be included; the second will necessarily be satisfied. By using this principle extensively, calculation of the distribution law is greatly simplified.

The major features of the resulting distribution law are determined by equations which contain either the w_i's or the W_i's explicitly. Of these Eq. 7 is the only one which has been found to be generally true for systems at equilibrium. Any other such restriction involving the w_i's or W_i's explicitly can therefore be valid only under special conditions which are imposed by the experimenter.

The arbitrary restrictions imposed by the experimenter may often be expressed in the form

$$\sum_i x_i D w_i = 0, \tag{8}$$

where the property x_i depends only on the state of the system and not explicitly on the frequencies w_i or W_i. For example, the rejection of data for which the average value $\bar{x}$ does not tend toward a definite limit leaves a set of data for which $D\bar{x} = 0$ in the limit; Eq. 8 is satisfied. This is simply the requirement that the property x_i have a statistically reproducible value.

As a working hypothesis it will be assumed that no arbitrary restriction containing the w_i's or W_i's explicitly need be considered which cannot be expressed in the form of Eq. 8. In all cases so far investigated, of the various possible ways of expressing a particular experimental condition, the one most closely representing the phys-

ical facts has been in the form of Eq. 8. Since in practice such arbitrary restrictions can be executed only by rejecting data until the number of experiments falling in each detailed state has the specified value, it would also appear that any form other than Eq. 8 implies an unduly biased selection of data. The possible occurrence of such restrictions will therefore be left to be treated as special cases.

The remaining restrictions do not involve the W_i's or w_i's explicitly. Hence the required solution of Eq. 7 may be obtained by first eliminating the Dw_i's from an independent set of restrictions of the form of Eq. 8, together with Eq. 7. The resulting equation is then to be solved simultaneously with the remaining restrictions.

The result obtained in the first step by the method of Lagrange multipliers[6, 8, 9] is

$$\log W_i / a_i = \lambda_x x_i + \lambda_y y_i + \cdots + \lambda_1, \tag{9}$$

in which each coefficient λ must have the same value for all states of the system, but is otherwise as yet unrestricted. These coefficients may therefore prove to be functions of the parameters g_j whose values are independent of the detailed states of the system. The term λ_1 enters in order to insure that Eq. 3 can be satisfied. Each of the other terms corresponds to one of the independent equations, there being one term for each equation.

Of the remaining restrictions, those which contain x_i, $y_i \cdots$ explicitly impose certain conditions on these variables. The others, which do not contain these variables, can enter only through the λ's. It is usually convenient to leave the distribution law in the form of Eq. 9, remembering that additional restrictions remain to be satisfied.

Systems at Equilibrium

When the only experimental restriction is that the total energy E_i of the system have a statistically reproducible value (i.e., $D\bar{E} = 0$ in the limit), then Eq. 9 reduces to

$$\log W_i / a_i = \lambda_E E_i + \lambda_1. \tag{10}$$

Equation 10 represents the Gibbs[5] canonical en-

[8] See, for example, R. B. Lindsay, *Introduction to Physical Statistics* (John Wiley and Sons, New York, 1941), p. 54.
[9] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, New York, 1940), Chapters 3 to 5.

semble, in which the coefficient λ_E has the experimental value[9] $-1/kT$, while λ_1 has the value A/kT, where A is the Helmholtz free energy, k the Boltzmann constant, and T the thermodynamic temperature.

In applying Eq. 10 it is assumed that the number of molecules N_{Bi} of each component B has a definite value. If instead it is only assumed that the value is statistically reproducible, then $D\bar{N}_B = 0$ in the limit for each component. In this case, Eq. 10 also contains a term $\lambda_B N_{Bi}$ for each component so restricted, and then represents the grand canonical ensemble[5,10] in which each λ_B is $(1/kT)$ times the partial molal free energy (i.e., chemical potential) of the component. Other restrictions lead to other important forms of the ensemble.[10]

NON-MAXWELLIAN VELOCITY DISTRIBUTIONS

The most general problem of velocity distributions is that in which it is required that each molecule l have a different statistically reproducible average momentum $\bar{\mathbf{p}}_l$; the restriction $D\bar{\mathbf{p}}_l = 0$ is satisfied by each molecule in the limit. Since these restrictions are independent of the requirement $D\bar{E} = 0$, Eq. 10 must now contain an additional term $\boldsymbol{\lambda}_l \cdot \mathbf{p}_l$ for each molecule. By the classical method it may be shown that the coefficient λ_E still has the value $1/kT$. Expressing E_i as the sum of a potential energy V_i and the kinetic energy, the distribution law is found to be

$$\log W_i/a_i = -\frac{1}{kT}(V_i + \sum_l \mathbf{p}_{li}{}^2/2m_l) + \sum_l \boldsymbol{\lambda}_l \cdot \mathbf{p}_{li} + \lambda_1, \quad (11)$$

where m_l is the mass of molecule l.

By writing $\boldsymbol{\mu}_l$ in place of $m_l kT \boldsymbol{\lambda}_l$, Eq. 11 may be expressed in the form

$$\log W_i/a_i = -V_i/kT - \sum_l (\mathbf{p}_{li} - \boldsymbol{\mu}_l)^2/2m_l kT + (\lambda_1 - \sum_l \boldsymbol{\mu}_l{}^2/2m_l kT). \quad (12)$$

The last term contains only parameters which are independent of the states i, and hence is a new arbitrary constant

$$\lambda_0 = \lambda_1 - \sum_l \boldsymbol{\mu}_l{}^2/2m_l kT. \quad (13)$$

[10] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, 1939), Section 611.

It is thus seen that $\log W_i/a_i$ is the same function of the $(\mathbf{p}_{li} - \boldsymbol{\mu}_l)$'s and λ_0 for the non-Maxwellian distribution velocities that it would be of the $\mathbf{p}_{li}$'s and λ_1 for a Maxwellian distribution at the same temperature.

The summation over states of any function f_i which contains the momenta and the constants $\boldsymbol{\mu}_l$ only in the differences $(\mathbf{p}_{li} - \boldsymbol{\mu}_l)$ will be invariant to a change of the $\boldsymbol{\mu}_l$'s, provided only that the array of detailed states i is always transformed into itself by any shift of the origin of momenta in phase space. This requirement is satisfied *a fortiori* when the spectrum of permissible velocities forms an unlimited continuum.

In particular, from Eq. 1 it is seen that

$$\exp(-\lambda_0) = \sum_i a_i$$

$$\times \exp\left[(-1/kT)(V_i + \sum_l (\mathbf{p}_{li} - \boldsymbol{\mu}_l)^2/2m_l)\right], \quad (14)$$

which is such a summation. Since $\exp(-\lambda_0)$ must therefore be invariant to a change in the $\boldsymbol{\mu}_l$'s, its value can be obtained by setting all of the $\boldsymbol{\mu}_l$'s equal to zero. It is then seen that λ_0 is equal to A_0/kT, where A_0 is the value of the Helmholtz free energy for the system at the given temperature and in the specified volume, for a Maxwellian distribution of velocities.

Similarly, the value of $(\mathbf{p}_{li} - \boldsymbol{\mu}_l)_{Av}$ must be invariant to a change of the $\boldsymbol{\mu}_l$'s and hence equal to its Maxwellian value. This value is zero since $(\mathbf{p}_{li} - \boldsymbol{\mu}_l)_{Av}$ is then the Maxwellian average momentum. In general $(\mathbf{p}_{li} - \boldsymbol{\mu}_l)_{Av}$ may be expanded as $\bar{\mathbf{p}}_{li} - \boldsymbol{\mu}_l$, since $\boldsymbol{\mu}_l$ is constant over the states i. Hence it has been shown that

$$\bar{\mathbf{p}}_{li} = \boldsymbol{\mu}_l; \quad (15)$$

the constants $\boldsymbol{\mu}_l$ must be equal to the specified average momentum.

The distribution law may now be expressed in the complete form

$$\log W_i/a_i = \frac{1}{kT}[A_0 - V_i - \sum_l (\mathbf{p}_{li} - \bar{\mathbf{p}}_l)^2/2m_l]. \quad (16)$$

It is interesting to note that essentially Eq. 16 was obtained by Maxwell,[3,4] but for some reason the constant $\bar{\mathbf{p}}_l$ has always been interpreted as

$m_l\mathbf{v}_0$, where $\mathbf{v}_0$ is the velocity of a system of reference coordinates. For this reason the terms in $\bar{\mathbf{p}}_l$ have always been dropped. From the present derivation it is obvious that such a narrow interpretation was unwarranted.

In any particular velocity distribution problem the requirements will probably take the form that the total momentum of molecules of a particular group should have a statistically reproducible value. A detailed treatment of this case shows that the appropriate distribution law is obtained from Eq. 16 by setting each $\bar{\mathbf{p}}_l$ equal to the group average molecular momentum. Thus Eq. 16 represents the general distribution law for all problems of non-Maxwellian distribution of momenta, provided the array of detailed states i possesses the requisite transformation property.

Several important features of this distribution law may be observed. First it is noted that the distribution of velocities of molecules about the specified group average velocity is Maxwellian. In particular, if all molecules in the system are to have the same group average velocity, the law represents a mass of molecules moving with this velocity whose distribution of velocities relative to the center of gravity of the mass is Maxwellian. Furthermore, in general the distribution law is invariant to any change in velocity of the reference coordinates.

One application of this distribution law is illustrated by calculating the average energy of a system in which the velocity distribution is non-Maxwellian. Following the same procedure used to evaluate the $\mathbf{u}_l$'s, one may define a quantity $[V_i + \sum_l (\mathbf{p}_{li} - \bar{\mathbf{p}}_l)^2/2m_l]_\text{Av}$ which is invariant to a change in the $\mathbf{p}_l$'s, and whose value is $\bar{E}_0$, the Maxwellian average total energy of the system for the same temperature and volume. By expanding the separate terms of this average, the result,

$$[\bar{V}_i + \sum_l (\mathbf{p}_{li}^2/2m_l)]_\text{Av}$$

$$- \sum_l (\mathbf{p}_{li}\cdot\bar{\mathbf{p}}_l/m_l)_\text{Av} + \sum_l (\bar{\mathbf{p}}_l^2/2m_l)_\text{Av} = \bar{E}_0 \quad (17)$$

is obtained. The first term is the required average energy $\bar{E}$ while the second has the value $-\sum_l \bar{\mathbf{p}}_l^2/m_l$, and the third the value $\sum_l \bar{\mathbf{p}}_l^2/2m_l$. Making these substitutions, the average energy

$\bar{E}$ is found to have the value

$$\bar{E} = \bar{E}_0 + \sum_l \bar{\mathbf{p}}_l^2/2m_l. \quad (18)$$

Equation 18 expresses the average total energy of the system as the sum of the Maxwellian total energy, which consists of potential and thermal energy, plus the kinetic energy of mass motion of groups of molecules. The correctness of this result may be seen from considering the special case of, for example, a planetary system, in which the total energy of the system consists of the Maxwellian total energies of the individual planets plus the kinetic energy of mass motion of each planet.

This result is to be compared with the second approximation in the method of Enskog and Chapman,[3,7] which gives $W_i^0(1 + \sum_l \mathbf{b}_l\cdot\mathbf{p}_{li})$ for the distribution function. Here W_i^0 is the Maxwellian distribution function, and $\mathbf{b}_l$ is a small arbitrary constant. Although this form agrees with Eq. 16 to this degree of approximation, it requires $\bar{E} = \bar{E}_0$ which cannot be generally true. It is only with the inclusion of the third and higher approximations that the expression for the average energy begins to take the proper form.

CONCLUSIONS

The method of deriving statistical distribution laws by solving Eq. 7 subject to the expressed independent experimental restrictions is a simple extension of the method used for systems at equilibrium. It is, however, in no way limited to equilibrium conditions. While the application of this method has been illustrated only by the derivation of a distribution law for systems in which the velocities are required to be non-Maxwellian, it may also be used to solve other statistical problems encountered in the study of rate processes.

It is of course recognized that the true test of this as well as of any theory is whether it agrees satisfactorily with experimental results, particularly when extended into new fields. At present this test has been applied only qualitatively, but with promising results. Consequently the author has no illusions that the distribution law for rate processes has been found in its ultimate form, but only hopes that a step has been taken in the right direction.