

Statistical Distribution Laws for Rate Processes 2. NonUniform Distributions

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Citation: [The Journal of Chemical Physics](#) **10**, 551 (1942); doi: 10.1063/1.1723763

View online: <http://dx.doi.org/10.1063/1.1723763>

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Statistical Distribution Laws for Rate Processes

2. Non-Uniform Distributions

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(Received May 4, 1942)

The methods developed in the previous paper are used to determine the most general form of statistical distribution law suitable for the treatment of rate processes. The result is particularly applicable to relatively dense systems composed of soft molecules. It is based on the assumptions that each variable whose rate of change is to be measured must be statistically reproducible at all times, and that the molecular motions are not seriously discontinuous. Various special forms of the distribution law result from different ways of expressing the rate variables and experimental conditions. One form is derived for the case in which the rates of change of the average position and kinetic energies of the molecules are to be reproducible. Qualitatively, it agrees with the known frequent behavior of rate experiments, showing frictional dissipation of energy, and the tendency to return to equilibrium. Furthermore, it reduces to the classical distribution law under equilibrium conditions.

IN the previous paper¹ a general method of deriving statistical distribution laws was developed, and was applied to the case of a non-Maxwellian distribution of velocities. In this application, time was not considered explicitly as a variable. In the general study of rate processes, specific attention must be given to the way in which the experimental system changes with time. In so doing, the meaning of a statistical distribution and the form of the resulting distribution law must be somewhat modified.

DISTRIBUTION OF RATE EXPERIMENTS

The statistical method in general is concerned with the distribution of certain statistical elements among several categories. In the study of a rate process, the statistical element is a rate experiment on a single system, in which the significant properties x, y, \dots of the system changed in a particular way with time. The categories among which a series of rate experiments may be distributed are the different possible ways in which the set of properties x, y, \dots of the experimental system may have changed. Thus the statistical treatment of rate processes is concerned with the distribution of a series of repeated rate experiments among various detailed behaviors.

When a particular experiment is said to belong to the detailed behavior i it is implied that the

properties x, y, \dots of the system have changed with time in the way ascribed to this detailed behavior. If the properties of the system have changed in some other way, then the particular rate experiment belongs to a different detailed behavior.

In particular, the variation of the property x with time for the detailed behavior i may be represented by a Taylor's series

$$x_i = \sum_m (d^m x_i / dt^m)_0 (t - t_0)^m / m!, \quad (1)$$

at least up to the time at which the first discontinuity appears in any one of the derivatives. The quantities $(d^m x_i / dt^m)_0$ are values of the various time derivatives of x_i appropriate to the reference time t_0 . Any change in the numerical values of any of these quantities will cause x_i to change in a different way with time. Thus a particular rate experiment belongs to the detailed behavior i if in that experiment all of the quantities $(d^m x / dt^m)_0, (d^m y / dt^m)_0, \dots$ have the values appropriate to this detailed behavior. If any one of them is different from the value required of the detailed behavior i , then the experiment belongs to another detailed behavior.

In classical mechanics, if the coordinates and momenta of all elementary particles in a system are given specified values at the time t_0 , the behavior of the system is completely determined. These coordinates and momenta represent only a limited number of the $(d^m x / dt^m)_0$'s; the rest

¹ B. Longtin, J. Chem. Phys. **10**, 546 (1942).

are not independent variables and hence need not be specified separately. In quantum mechanics a somewhat different situation prevails.

After all of the n repeated rate experiments have been completed and the data recorded, a statistical analysis is in order. At this time the number nw_i of rate experiments belonging to each detailed behavior i is counted. It is at once evident that the value of nw_i is not in any way determined by the length of time elapsed during any portion of an individual experiment, nor does it depend on time in any other way. Nor does the total number n of experiments included in the statistical analysis depend on time. Thus each of the distribution frequencies w_i must be independent of time. Likewise the limit W_i approached by the frequency w_i as the number n is increased² must be independent of time. This constancy of the number of experiments belonging to a particular detailed behavior will be recognized as an analogue of Liouville's theorem.^{3,4}

Average Values

The average value \bar{x} of any property x_i is defined as

$$\bar{x} = \sum_i x_i w_i. \quad (2)$$

If the Taylor series expression given in Eq. 1 is valid, then

$$\begin{aligned} \bar{x} &= \sum_i \sum_{m=0}^{\infty} (d^m x_i / dt^m)_0 w_i (t - t_0)^m / m! \\ &= \sum_{m=0}^{\infty} (t - t_0)^m / m! \sum_i (d^m x_i / dt^m)_0 w_i. \end{aligned} \quad (3)$$

Since neither the w_i 's nor the $(d^m x_i / dt^m)$'s are functions of time, Eq. 3 expresses \bar{x} as a function of time by a Taylor series. Such an expression is valid only up to the first discontinuity. A more general form must be sought when the motion of the system is seriously discontinuous.

One of the important requirements in a series of rate experiments is that each of the properties x, y, \dots whose rate of change is being studied must have a statistically reproducible value at

all times during the progress of the experiment. This implies¹ that at all times

$$D\bar{x} = 0 \quad (4)$$

in the limit as n is increased, where D denotes the change in the quantity operated on, due to passage from the limiting distribution W_1, W_2, \dots to some other distribution w_1, w_2, \dots .

If the Taylor series representation is used,

$$D\bar{x} = \sum_m (t - t_0)^m / m! \sum_i (d^m x_i / dt^m)_0 D w_i, \quad (5)$$

since only w_i is involved in a variation of the distribution. If $D\bar{x}$ is to vanish at all times, the coefficients of each $(t - t_0)^m / m!$ must be zero;

$$\sum_i (d^m x_i / dt^m)_0 D w_i = 0. \quad (6)$$

If Eq. 6 is satisfied for all integral values of m from zero up, then the quantity x will certainly be statistically reproducible at all times up to the first discontinuity.

Distribution Law

A statistical method is meaningless if the limiting frequencies W_i do not exist. In order that they shall exist, it is necessary¹ that

$$D(\log a/w)_{av} = 0 \quad (7)$$

in the limit, $(\log a/w)_{av}$ being the average value of $\log a_i / w_i$, while a_i is the *a priori* probability that the experimental system will exhibit the detailed behavior i . The distribution law appropriate to any particular case is to be found by solving Eq. 7 subject to the experimental restrictions, and the requirement that the average value of 1 be unity.

In the case of rate experiments these restrictions include Eqs. 6. If none of the additional restrictions involves either the w_i 's or W_i 's explicitly, the method of solution used in the previous paper¹ leads to the distribution law

$$\begin{aligned} \log W_i / a_i &= \lambda + \sum_{m=0}^{\infty} [\lambda_{x0}^{(m)} (d^m x_i / dt^m)_0 \\ &\quad + \lambda_{y0}^{(m)} (d^m y_i / dt^m)_0 + \dots]. \end{aligned} \quad (8)$$

The undetermined coefficients $\lambda_{x0}^{(0)}, \lambda_{x0}^{(1)}, \dots, \lambda_{y0}^{(0)}, \lambda_{y0}^{(1)}, \dots$ have values appropriate to the choice of t_0 as the time at which the derivatives $d^m x_i / dt^m$ are to have reproducible values, these

² Here one is comparing a set of statistical analyses each of which includes a different number n of rate experiments.

³ See R. H. Fowler, *Statistical Mechanics* (University Press, Cambridge, 1929), Section 1.5.

⁴ J. W. Gibbs, *The Collected Works* (Longmans, Green and Company, New York, 1928), Vol. 2, Part 1, Chapter 1.

coefficients being the same for all detailed behaviors.

Equation 8 expresses the frequency of occurrence of rate experiments in which the various derivatives $(d^m x_i/dt^m)$ will happen to have any particular set of values $(d^m x_i/dt^m)_0$ at the time t_0 . For example, if the quantities x_i include molecular velocities, Eq. 8 expresses the distribution of velocities, of accelerations, and of higher derivatives of velocity needed at this instant in order that measurement of the quantities x_i shall give statistically reproducible results at all times. If the time t_1 had been chosen as the reference time rather than t_0 , the distribution of velocities, etc., needed at the time t_1 would be given by exactly the same equation,

$$\log W_i/a_i = \lambda + \sum_{m=0}^{\infty} [\lambda_{x1}^{(m)} (d^m x_i/dt^m)_1 + \lambda_{y1}^{(m)} (d^m y_i/dt^m)_1 + \dots], \quad (9)$$

except that the values of $\lambda_x^{(m)}$ and $(d^m x_i/dt^m)$ are now those appropriate to the time t_1 .

If the motion of the experimental system can be expressed by Eq. 1, then each of the derivatives $(d^m x_i/dt^m)_0$ may be expressed in terms of the $(d^m x_i/dt^m)_1$'s by a Taylor series:

$$(d^m x_i/dt^m)_0 = \sum_{r=0}^{\infty} (d^{m+r} x_i/dt^{m+r})_1 (t_0 - t_1)^r / r!. \quad (10)$$

By substituting these values into Eq. 8 and collecting terms containing the same derivative, it is transformed to

$$\log W_i/a_i = \lambda + \sum_x \sum_{m=0}^{\infty} (d^m x_i/dt^m)_1 \times \sum_{s=0}^m \lambda_{x0}^{(s)} (t_0 - t_1)^{m-s} / (m-s)!, \quad (11)$$

where \sum_x implies summation over the different properties x, y, \dots .

Equation 11 expresses the frequency of occurrence of any particular set of values $(d^m x_i/dt^m)$ at the time t , in a series of rate experiments which had been distributed at the time t_0 in the way required by Eq. 8, and then allowed to change in their own natural way. If the distribution law is to be more than a mathematical figment, this result must be the same as that required by Eq. 9. This will be recognized as

analogous to the requirement in the Boltzmann-Enskog-Chapman⁵ treatment of rate processes, that the number of molecules in any particular state of motion be stationary. However, it does not limit the possible applications of the method as severely.

Remembering that the coefficients cannot be functions of the $(d^m x_i/dt^m)$'s, it is evident that the coefficients of like derivatives in Eqs. 9 and 11 must be identical. Hence

$$\lambda_{x1}^{(m)} = \sum_{s=0}^{s=m} \lambda_{x0}^{(s)} (t_0 - t_1)^{m-s} / (m-s)!. \quad (12)$$

Equation 12 appears to express $\lambda_{x1}^{(m)}$ as a function of t_0 as well as of t_1 . However, since neither $\log W_i$ nor the $(d^m x_i/dt^m)_1$'s depend on t_0 , while the $(d^m x_i/dt^m)_1$'s are presumed to be linearly independent in order that Eqs. 6 may all be independent, it is evident that the $\lambda_{x1}^{(m)}$'s can depend only on t_1 and not on t_0 . Hence it must be possible to combine the various terms in Eq. 12 in such a way that t_0 vanishes.

On differentiating Eq. 12 with respect to t_1 it is found that

$$\begin{aligned} \partial \lambda_{x1}^{(m)} / \partial t_1 &= - \sum_{s=0}^{s=m-1} \lambda_{x0}^{(s)} (t_0 - t_1)^{m-1-s} / (m-1-s)! \\ &= - \lambda_{x1}^{(m-1)}, \end{aligned} \quad (13)$$

since $\lambda_{x0}^{(s)}$ is a function only of t_0 and not of t_1 . On differentiating with respect to t_0 and collecting terms containing the same power of $(t_0 - t_1)$, one finds

$$\begin{aligned} \partial \lambda_{x1}^{(m)} / \partial t_0 &= \sum_{s=0}^{s=m} (\lambda_{x0}^{(s-1)} + \partial \lambda_{x0}^{(s)} / \partial t_0) \\ &\quad \times (t_0 - t_1)^{m-s} (m-s)!. \end{aligned} \quad (14)$$

In collecting the terms, two summations over s were combined in one of which the first term was missing; this fact is expressed by defining

$$\lambda_{x0}^{(-1)} \equiv 0. \quad (15)$$

In order that $\lambda_{x1}^{(m)}$ be independent of t_0 , it is necessary that $\partial \lambda_{x1}^{(m)} / \partial t_0$ be zero for all values of t_0 . From Eq. 14 it is evident that this can be true only if

$$\partial \lambda_{x0}^{(s)} / \partial t_0 = - \lambda_{x0}^{(s-1)}. \quad (16)$$

⁵ S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (The University Press, Cambridge, 1939).

Comparison of Eqs. 13 and 16, which are identical in form shows that the requirements that

- (a) the $\lambda_{x0}^{(m)}$'s be independent of t_1 ,
- (b) the $\lambda_{x1}^{(m)}$'s be independent of t_0 ,
- (c) $\log W_i$ be independent of both t_0 and t_1 , and
- (d) that Eqs. 8 and 9 lead to the same result are self-consistent.

From the foregoing it may be concluded that the general distribution law appropriate for any rate process is expressed by Eq. 8, in a form which is independent of the choice of the reference temperature provided the undetermined coefficients satisfy Eqs. 14 and 15. This distribution law is limited only in that it may not apply to processes in which the rate variables show serious discontinuities. For example, it will not apply to any molecular model assuming infinitely hard molecules, but will generally be applicable to any model in which, the molecules are more or less "soft." Thus, while the Chapman-Enskog⁶ method is most suited to the study of rarefied gases, the present method is more suited to the treatment of dense phases.

SPECIAL FORMS

Rate studies in general are concerned with the transport of material and energy, and with chemical reactions which may be expressed mathematically in terms of the change of certain reaction coordinates.⁶ The most detailed conditions of statistical reproducibility which might be needed to handle rate processes would thus require that the average position $\bar{\mathbf{q}}_l$, average momentum $\bar{\mathbf{p}}_l$, and average kinetic energy $(\mathbf{p}_l^2)_{Av}/2m_l$ of each elementary particle l be reproducible at all times. Furthermore, if the experimental system is isolated, the total energy E_i , will be a constant of the motion whose average value must be reproducible.

So long as the momentum \mathbf{p}_{li} is expressible as $m_l d\mathbf{q}_{li}/dt$, the requirement of a reproducible average momentum is implied by the requirement of a reproducible average position, and hence is not an independent restriction. On the other hand, the average kinetic energy is not in general determined by the average momentum

(e.g., $(\mathbf{p}_l^2)_{Av}$ is not equal to $(\mathbf{p}_l)_{Av}^2$, so that the requirement of a reproducible average kinetic energy is independent. Thus the distribution law for this set of restrictions is

$$\log W_i/a_i = \lambda + \lambda_E \{E_i + \sum_l \sum_{m=0}^{\infty} [\mathbf{Q}_l^{(m)} \cdot d^m \mathbf{q}_{li}/dt^m + K_l^{(m)} d^m \mathbf{p}_{li}^2/dt^m]\}, \quad (17)$$

the summation with respect to l extending over all elementary particles.

The coefficients $\lambda_E \mathbf{Q}_l^{(m)}$ and $\lambda_E K_l^{(m)}$ are the λ 's corresponding to the m time derivatives of position and momentum. They must thus satisfy Eqs. 15 and 16 in order that the form of distribution shall be invariant to a change in the reference time. Equation 17 would contain terms in the derivatives $d^m E_i/dt^m$ but for the fact that these derivatives are all zero so long as E_i is a constant of the motion.

Less detailed conditions of reproducibility would require only that the average position, $(\sum_l \mathbf{q}_{li}/N)_{Av}$, average total momentum, $(\sum_l \mathbf{p}_{li})_{Av}$, and average total kinetic energy $(\sum_l \mathbf{p}_{li}^2/m_l)_{Av}$ of a group of N molecules be reproducible. A restriction of this sort leads to the same result, except that $\mathbf{Q}_l^{(m)}$, and likewise $m_l K_l^{(m)}$, has the same value for all molecules of the group.

Closed Form

Equation 17 is not in a form convenient for practical calculations, since it contains an infinite number of terms. It may be reduced to a closed form by assuming that for each of the detailed behaviors, the total momentum and total kinetic energy of each group are changing at a uniform rate. This assumption will not be too severe as a first approximation, provided the number of molecules in each group is very large.

As a result of this assumption, the terms in $d^m \mathbf{p}_{li}^2/dt^m$ can be arranged in groups so that each group vanishes if m is 2 or greater. Similarly the terms in $d^m \mathbf{q}_{li}/dt^m$ may be arranged in groups all of which vanish for any values of m equal to 3 or greater. Equation 17 then reduces to

$$\log W_i/a_i = \lambda + \lambda_E \{E_i + \sum_l [\dot{\mathbf{P}}_l \cdot \mathbf{q}_{li} - \mathbf{P}_l \cdot \mathbf{p}_{li}/m_l + \mathbf{Q}_l \cdot \dot{\mathbf{p}}_{li} - \dot{K}_l \mathbf{p}_{li}^2/2m_l + K_l \mathbf{p}_{li} \cdot \dot{\mathbf{p}}_{li}/m_l]\}. \quad (18)$$

⁶ Cf. Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, New York, 1941).

In this equation it was assumed that the momentum \mathbf{p}_{li} can be expressed as $m_l d\mathbf{q}_l/dt$ where m_l is a generalized mass, while $\dot{\mathbf{p}}_{li}$ is written for $d\mathbf{p}_{li}/dt$. The coefficients $\mathbf{Q}_l^{(0)}$, $\mathbf{Q}_l^{(1)}$, $\mathbf{Q}_l^{(2)}$, $K_l^{(0)}$, and $K_l^{(1)}$ of Eq. 16 have been expressed as $\dot{\mathbf{P}}_l$, $-\mathbf{P}_l$, $m_l \mathbf{Q}_l$, $\dot{K}_l/2m_l$, and $K_l/2m_l$, respectively.

Equations 15 and 16 imply that λ_E is independent of the reference time t_0 . Since they also require that $\lambda_E \mathbf{Q}_l^{(0)}$ be $-\partial \lambda_E \mathbf{Q}_l^{(1)}/\partial t_0$, and that $\lambda_E \mathbf{Q}_l^{(2)}$ be $-\partial \lambda_E \mathbf{Q}_l^{(2)}/\partial t_0$, it is further implied that

$$\mathbf{P}_l = m_l d\mathbf{Q}_l/dt_0, \quad (19)$$

and

$$\dot{\mathbf{P}}_l = d\mathbf{P}_l/dt_0, \quad (20)$$

while

$$d\dot{\mathbf{P}}_l/dt_0 = 0. \quad (21)$$

In the above equations total derivatives are used since in Eqs. 15 and 16 the partial derivatives indicated simply that t_1 was being considered constant; it is not necessary to express this restriction when it is understood that the coefficients do not depend on t_1 in any way. Finally it is implied that

$$\dot{K}_l = dK_l/dt_0, \quad (22)$$

and

$$d\dot{K}_l/dt_0 = 0. \quad (23)$$

The particular form given for Eq. 18 was chosen to emphasize that \mathbf{P}_l must have the dimensions of momentum. Comparison with the results given in the previous paper show that at least in some cases \mathbf{P}_l is just the average particle momentum for the group to which the particle l belongs. In general, due to the appearance of the terms in $\mathbf{p}_{li} \cdot l_i \dot{\mathbf{p}}$, it may be just a little different from the average momentum; for convenience call it the *characteristic* momentum of the group.

Similarly \mathbf{Q}_l must have the dimensions of a coordinate (vector), while $\dot{\mathbf{P}}_l/m_l$ has the dimensions of an acceleration. Equations 19 and 20 show that \mathbf{Q}_l and $\dot{\mathbf{P}}_l/m_l$ are the coordinate and acceleration which correspond to the momentum \mathbf{P}_l . They may thus be referred to as the characteristic coordinate and acceleration of the group, respectively, and will sometimes but not always be equal to the average coordinate and acceleration.

In the classical distribution law λ_E is evaluated⁷ as $-1/kT$ where k is the Boltzmann constant and T the absolute temperature of the system. In the case of the non-homogeneous systems encountered in the study of rate processes, there may be some doubt as to the exact meaning of temperature. It is convenient, however, to write $-1/kT^0$ in place of λ_E , where T^0 is some temperature characterizing the conditions of the experiment, whose exact meaning remains to be discovered in each particular case. The coefficients K_l and \dot{K}_l have no previous analogue; the first has the dimensions of time while the second is dimensionless.

Significance of the Terms

In the distribution of rate experiments among detailed behaviors which is described by Eq. 18, those detailed behaviors will occur most frequently in which each term is large positive or small negative. Since λ_E is $-1/kT^0$, and hence generally negative, each of the bracketed terms will tend toward a minimum value in the most frequent behavior.

At equilibrium only the terms λ and $\lambda_E E_i$ would appear in Eq. 18. Thus the added terms represent a displacement from the equilibrium conditions. Each term $\dot{\mathbf{P}}_l \cdot \mathbf{q}_{li}$ describes a displacement of the molecules from the equilibrium position, which will tend most frequently to make $\dot{\mathbf{P}}_l \cdot \mathbf{q}_{li}$ negative. Thus the most frequent displacement will be in a direction more or less opposite to the characteristic acceleration; the characteristic acceleration is in such a direction as to restore the molecules to their equilibrium position. The terms $\mathbf{Q}_l \cdot \dot{\mathbf{p}}_{li}$ describe the same fact in a different form, namely that the most frequent acceleration is in a direction opposite to the characteristic displacement.

The terms $-\mathbf{P}_l \cdot \mathbf{p}_{li}/m_l$ were introduced and discussed in the previous paper. There it was shown that they represent a non-Maxwellian distribution of velocity in which each group of molecules has a Maxwellian distribution about their characteristic velocity. The terms in $\mathbf{p}_{li}^2/2m_l$ may be combined with the kinetic energy part of E_i , with the result that the kinetic energy of each group is multiplied by $(1 - \dot{K}_l)/kT^0$ instead

⁷ Cf. J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, New York, 1940).

of $1/kT$. In effect, each group of molecules now has a velocity distribution corresponding to a temperature $T^0/(1-\dot{K}_i)$ instead of the temperature T^0 . Thus the terms $-\dot{K}_i \mathbf{p}_i^2/2m_i$ allow for thermal inhomogeneities.

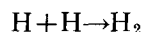
The terms $K_i \mathbf{p}_i \cdot \dot{\mathbf{p}}_i/m_i$ describe the way in which the rate of conversion of potential into kinetic energy (i.e., the rate of production $d\mathbf{p}_i^2/m_i dt$ of kinetic energy) departs from the normal. Thus they describe frictional and collision phenomena where the previous terms described heterogeneity and driving forces. From this standpoint it is perhaps the term most important in determining such properties as viscosity, and diffusional and electric resistances.

Since the term tends as a whole to be negative, the most frequent rate of increase of kinetic energy must be opposite in sign to K_i . When the most frequent value of the kinetic energy is less than the steady state value, it must tend to increase, while if greater it must tend to decrease. Thus the sign of K_i depends on whether the most frequent value of the kinetic energy of the group is greater or less than the steady state value.

Qualitatively, the distribution law described by Eq. 18 appears to agree in major detail with the known most frequent behavior of rate experiments. Quantitatively, it can be expected to be correct only insofar as the assumption of constant rate of change of total momentum and kinetic energy is justified. This assumption is certainly justified at least in the mean for systems in which the rate processes have reached a steady state. A more complete quantitative treatment is best handled in connection with specific problems.

Other Forms

While Eqs. 17 and 18 are adequate to handle the majority of rate processes, they need not always be the most convenient. For example, the simple reaction



may be treated by requiring that the H-H distance have an average value which was initially large and changes reproducibly. Stated in this way, the statistical problem may be handled by means of Eq. 17 or 18. On the other hand it may be more convenient to require that the average number N_2 of molecules of H_2 be initially negligible, and increase with time in a reproducible way. In this case one must return to Eq. 8, including N_2 as one of the variables x_i, y_i, \dots to obtain a distribution law which is an extension of Gibbs' grand canonical ensemble.⁸ The second of above two methods is essentially that used by Eyring⁶ and co-workers in their theory of absolute reaction rates. However, their distribution law does not include terms beyond $m=0$.

At present it would be preferable in any particular problem to start with Eq. 8. A consideration of various possible ways of expressing the experimental restrictions will lead to different forms of the distribution law among which certainly one or two should be conveniently usable.

⁸ See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, 1939), Chapter 6.