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by

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Introduction

This paper describes some problems of asymptotic distribution with relations to physical theory. In section 1, results are given for the asymptotic frequency with which a trigonometric sum passes through a specified value. Section 2 begins with a brief account of the application of these results to determine the rate of unimolecular decomposition of a gas; the section continues by indicating how a refinement of the physical theory poses the more difficult problem of the distribution of the gaps or recurrence times of the trigonometric sum. In section 3 a simpler form of this problem is examined, namely the nature of the gaps between the integers N for which the point with coordinates the fractional parts of $\nu_i N (i = 1, 2 \ldots, n-1)$ lies in a specified region of the unit cube of $(x_1, \ldots, x_{n-1})$ space.

1. The frequency of zeros of a trigonometric sum

Consider the finite trigonometric sum

$$f(t; \psi) = \sum_{i=1}^{n} a_i \cos 2\pi(\nu_i t + \psi_i) \tag{1}$$

where $a_i > 0$, $\nu_i > 0$, $0 \leqq \psi_i < 1$ and ψ denotes the set $\psi_1, \ldots, \psi_n$. This sum may represent a sum of dynamical vibrations, or of alternating currents, with t the time elapsed and a_i, ν_i and ψ_i the amplitude, frequency and "phase" of a component. Alternatively $f(0; \psi)$ is the projection of a random walk of steps a_i on to the direction $\psi_i = 0$. In the former cases there is interest in the average behaviour of $f(t; \psi)$ over a long time-interval. Attention will be confined to the case where $\nu_1, \nu_2, \ldots, \nu_n$ are *linearly independent in the field of rationals*; then the long-time average behaviour of

*) Nijenrode lecture.

$f(t; \psi)$ is the same as that of $f(t; 0)$, and may be represented also by the phase-average, over an equidistribution in $(0, 1)$ of the phases ψ_i, of the behaviour of $f(t; \psi)$ or equally of $f(0; \psi)$. For example, $M(q)$, the asymptotic proportion of time for which $f(t; 0) \leqq q$, is also the probability that the projection $f(0; \psi)$ of a random walk has a value not exceeding q. For this there is the well-known formula

$$dM/dq = \pi^{-1} \int_0^\infty \cos(qx) \prod_{i=1}^{n} J_0(a_i x) dx \tag{2}$$

which may be replaced by a Fourier series [1] which also leads to extensions of Nielsen's identity for Bessel functions [2].

As a more relevant example, let $G_q(T; \psi)$ be the number of up-zeros (that is, zeros with df/dt positive) of $f(t; \psi) - q$ in the range $0 \leqq t < T$. The asymptotic frequency of these up-zeros is

$$L_q = \lim_{T \to \infty} G_q(T; \psi)/T. \tag{3}$$

The ν_i being linearly independent, L_q does not depend on the ψ_i, and equals the phase-averaged frequency for any fixed T, namely

$$T^{-1} \int \ldots \int_0^1 G_q(T; \psi) d\psi_1 \ldots d\psi_n. \tag{4}$$

For this M. Kac found [3])

$$L_q = \pi^{-2} \int\int_0^\infty y^{-2} \cos(xq) \left[\prod_{i=1}^{n} J_0(a_i x) - \prod J_0(a_i z_i) \right] dx dy \tag{5}$$

where $z_i^2 \equiv x^2 + 4\pi^2 \nu_i^2 y^2$. This also may be put as a Fourier series [5].

An approximate formula for (3) had been found [4, 5] for the case where q is near $\sum a_i$. This case will be of interest in a later section, and so will be briefly sketched here. As time-averaging will be used, the phases ψ_i in (1) will be set zero. Let

$$q = \sum_1^n a_i - 2\pi^2 h^2 \tag{6}$$

where h^2 is small. Zeros of $f(t; 0) - q$ then require all the cosines in (1) to be near unity, so that we make here the basic approximation of replacing $\cos 2\pi \nu_i t$ by $1 - 2\pi^2 \{\nu_i t\}^2$, where $\{x\}$ denotes x minus the *nearest* integer, so that $-\frac{1}{2} < \{x\} \leqq \frac{1}{2}$. To this approximation, $f(t; 0) - q$ is positive only when

$$\sum_1^n a_i \{\nu_i t\}^2 < h^2. \tag{7}$$

For convenience let the largest of the ν_i be $\nu_n = 1$; also let $\{t\} = y$, so that $t = N+y$ with N the nearest integer to t. Then where (7) is satisfied the left hand side is

$$a_n y^2 + \sum_1^{n-1} a_i(\{\nu_i N\}+\nu_i y)^2. \tag{8}$$

For given N, the minimum of (8) occurs when $y = -A^{-1}\sum_1^{n-1} a_i\nu_i\{\nu_i N\}$ where $A = \sum_1^n a_i\nu_i^2$; and the minimum is $\phi(\{\nu N\})$ where

$$\phi(x) = \sum_1^{n-1} a_i x_i^2 - A^{-1}\left(\sum_1^{n-1} a_i\nu_i x_i\right)^2 \tag{9}$$

and x, $\{\nu N\}$ are abbreviations for the sets $(x_1, \ldots, x_{n-1})$ and $(\{\nu_1 N\}, \ldots, \{\nu_{n-1}N\})$. To the approximation represented by (7), there is now seen to be one up-zero of $f(t; 0)-q$ near each N for which the point $\{\nu N\}$ lies in the hyperellipsoid

$$\phi(x) = h^2 \tag{10}$$

where (x) are cartesian coordinates in $n-1$ dimensions.

The linear independence of $\nu_1, \ldots, \nu_{n-1}, \nu_n(=1)$ implies that the points $\{\nu N\}$ are asymptotically uniformly distributed in the $(n-1)$-dimensional "cube" $|x_i| \leqq \frac{1}{2}$. Thus the asymptotic proportion of values of N satisfying $\phi(\{\nu N\}) < h^2$ is the content V of the hyperellipsoid (10), which from (9) is

$$V = (A/a_1 a_2 \ldots a_n)^{\frac{1}{2}}\pi^{(n-1)/2}h^{n-1}/\Gamma(\tfrac{1}{2}n+\tfrac{1}{2}). \tag{11}$$

Since each such N is close to one up-zero of $f(t; 0)-q$, the required formula for L_q (approximate because of the cosine approximation in (7)) is

$$L_q = V. \tag{12}$$

The result (12), (11) is formally unaffected by the restriction $\nu_n = 1$.

2. The relation of distribution problems to unimolecular decomposition theories

Formulas (5) and (11), (12) have been used to calculate rates of unimolecular decomposition of gases on classical [6] and quantum mechanical [7] models. It will be a sufficient illustration here to summarize one calculation, namely that of classical high-pressure decomposition, and then to pass to a theory which involves new distribution problems.

A polyatomic molecule is pictured as a vibrating system of atoms which decomposes when some internal coordinate (such as an interatomic stretch) reaches a critically high value q. This internal coordinate behaves to a fair approximation as a sum of "normal-mode" vibrations like $f(t; \psi)$ in (1), so that L_q defined as in (3) or (4) represents the decomposition probability per second, for vibrations of given amplitudes a_i. These amplitudes are of the form

$$a_i = \alpha_i \sqrt{\varepsilon_i} \tag{13}$$

where the α_i are calculable constants and ε_i is the energy in the ith mode of vibration; the molecule is thus capable of decomposition (or "energised") if $f(t; \psi)$ can reach the value q, that is if

$$\sum a_i \equiv \sum \alpha_i \sqrt{\varepsilon_i} \geqq q. \tag{14}$$

At *high* pressures, the proportion of molecules with energy $(\varepsilon_i, \varepsilon_i + d\varepsilon_i)$ in the ith mode has effectively the equilibrium value $\beta \exp(-\beta\varepsilon_i)d\varepsilon_i$, where $1/\beta$ is proportional to the absolute temperature of the gas. Thus the high-pressure rate constant k_∞ (the proportion decomposing per unit time) is

$$k_\infty = \int \cdots \int L_q \exp(-\beta \sum \varepsilon_i)\beta^n d\varepsilon_1 \ldots d\varepsilon_n, \tag{15}$$

the integral being over positive ε_i satisfying (14).

If Kac's formula (5) is used in (15), we find the exact result

$$k_\infty = \nu \exp(-\beta E_0), \tag{16}$$

where $\nu = (\sum \alpha_i^2 \nu_i^2 / \sum \alpha_i^2)^{\frac{1}{2}}$ is a mean frequency, and $E_0 = q^2 / \sum \alpha_i^2$ is the minimum total energy satisfying (14). The approximation (11), (12) has been used to extend this result to lower-pressure rates [8], on the assumption that the decomposition process occurs randomly in time — that is, that the zeros of $f(t; 0) - q$ are randomly spaced.

Further problems. New distribution problems arise in a more careful formulation [9] of low-pressure decomposition rates. Let ω be the number of energy-transferring collisions per molecule per second; ω is proportional to the pressure of the gas. Although at low pressures collisions are not sufficiently frequent to maintain the equilibrium distribution of energised molecules (as used in (15)), it is still reasonable to assume that the proportion of molecules raised by collisions (in unit time) to energized states $(\varepsilon_i, \varepsilon_i + d\varepsilon_i)$ with phases $(\psi_i, \psi_i + d\psi_i)$ is

$$\omega \exp(-\beta \sum \varepsilon_i)\beta^n d\varepsilon_1 \ldots d\varepsilon_n \, d\psi_1 \ldots d\psi_n. \tag{17}$$

A molecule energised at time $t = 0$ will decompose if it suffers no de-energising collision before the time $t = t_1$ of the first up-zero of $f(t; \psi)-q$ (when it is ready to decompose). The probability of no collision in the interval $(0, t_1)$ is $e^{-\omega t_1}$, the incidence of collisions being assumed random. Thus the rate constant k (the proportion decomposing per second) is the integral of $e^{-\omega t_1}$ times the expression (17), over the range (14). This may be written

$$k = \beta^n \int \ldots \int g(\omega) \exp(-\beta \sum \varepsilon_i) d\varepsilon_1 \ldots d\varepsilon_n \tag{18}$$

where

$$g(\omega) = \omega \int \ldots \int_0^1 \exp(-\omega t_1) d\psi_1 \ldots d\psi_n. \tag{19}$$

This phase-average of t_1, the time to the first up-zero of $f(t; \psi)-q$, may be replaced by the asymptotic average of $s(t)$, the time *from* t to the next up-zero of $f(t; 0)-q$, namely

$$g(\omega) = \omega \lim_{T\to\infty} \left[T^{-1} \int_0^T e^{-\omega s(t)} dt \right]. \tag{20}$$

With a slight change of notation, if $t_1, t_2, t_3, \ldots$ are now the up-zeros of $f(t; 0)-q$ then for $t_r \leqq t < t_{r+1}$ we have $s(t) = t_{r+1}-t$; so by dividing the integral in (20) into ranges (t_r, t_{r+1}) we find

$$g(\omega) = L_q[1-\mathrm{av}(e^{-\omega\tau})] \tag{21}$$

where $L_q = \lim_{m\to\infty} (m/t_m)$ is as in (3), and

$$\mathrm{av}(e^{-\omega\tau}) = \lim_{m\to\infty} \left[m^{-1} \sum_{r=1}^{m} \exp(-\omega\tau_r) \right] \tag{22}$$

where $\tau_r = t_{r+1}-t_r$ is a *gap* between successive up-zeros. The averaging in (22) is over gaps, so that similarly

$$\mathrm{av}(\tau) = \lim_{m\to\infty} \left(\sum_1^m \tau_r \right) \Big/ m = 1/L_q. \tag{23}$$

The general decomposition rate is now given by (18) and (21); as $\omega \to \infty$ it tends to the previous formula (15).

The distribution problem posed in (22) is the determination of an asymptotic distribution function $h(\tau)$, namely the proportion of gaps up to length τ. If we assumed the up-zeros occurred "randomly" like collisions in the gas, we should have (compare (23))

$$h(\tau) = 1 - \exp(-L_q \tau) \tag{24}$$

so that in (21) $g(\omega) = L_q\omega/(L_q+\omega)$; this puts the rate (18) in a form like that of standard theories based on "random" decomposition.

A related assumption (again leading to tractable forms of (18)) is that the gaps have a Gamma-type distribution with parameter u, namely

$$dh(\tau) = (L_q u)^u \, \tau^{u-1} \exp(-L_q u\tau) d\tau / \Gamma(u). \tag{25}$$

The case (24) is the extreme, $u = 1$, of (25); the other extreme, namely $u \to \infty$, corresponds to regular (equal) gaps. Some fairly extensive calculations of the zeros of $f(t; 0) - q$ for the case of $n = 7$ vibrations showed distributions well represented by the form (25). It was found, however, that the best-fitting parameter u decreases steadily from a value 6.7 for $q = 0$ to a value near 2 for $q > \frac{1}{2} \sum a_i$; this indicates an increasing "randomness" of gaps with increasing q.

3. Problems of gaps

The preceding general problem of the distribution of gaps between up-zeros of $f(t; 0) - q$ will be examined here in the simpler case where q is as in (6) with h^2 small. Up-zeros t_r are then widely separated, and are very near those integers N for which $\phi(\{\nu N\}) < h^2$ (compare (9): $\{\nu N\}$ again stands for the set $\{\nu_1 N\}, \ldots, \{\nu_{n-1} N\}$ with $\nu_1, \ldots, \nu_{n-1}$ and 1 linearly independent). We therefore replace the problem of the gaps $t_{r+1} - t_r$ by the *problem*: what are the gaps Δ between the successive integers N for which $\{\nu N\}$ lies in the hyperellipsoid (10)? There is some fairly extensive numerical evidence for cases up to $n = 7$. In these cases the calculations show n basic gaps $\Delta = D_1, \ldots, D_n$ and others which can all be expressed in the form

$$\Delta_s = \sum_{u=1}^{n} \lambda_{su} D_u \tag{26}$$

where the λ_{su} are zero or positive integers [9].

General theory. A generalization of the above problem is to seek the gaps Δ between the successive N for which the point $\{\nu N\}$ lies in a closed convex region S within the "unit cube" $|x_i| \leqq \frac{1}{2}$ $(i = 1, 2, \ldots, n-1)$. Some simple notes will be given here on this.

For a given positive δ, there exists an integer N' (depending only

on $\nu_1, \ldots, \nu_{n-1}$ and δ) such that for any point x in the unit cube there is an $N \leqq N'$ making $|\{\nu_i N+x_i\}| < \delta$ for all $i = 1, \ldots, n-1$. This result implies that the gaps Δ (for a given S) are *bounded*; suppose they are (in increasing size) $\Delta_1, \Delta_2, \ldots, \Delta_m$. (The convexity and extent of S affect the Δ's and their relations; for example a gap Δ_s cannot be a multiple $k\Delta_r$ of another unless k is at least of the order $[1/h']$ where h' is the minimum diameter of S for coordinate directions $x_1, \ldots, x_{n-1}$).

We may now subdivide S into distinct subregions S_r corresponding to the Δ_r and such that for x in S_r the point $\{x_i+p\nu_i\}$ is not in S for $p = 1, 2, \ldots, \Delta_r-1$ but is for $p = \Delta_r$; so if $\{\nu N\}$ lies in S_r the next gap is Δ_r. For a large range $N \leqq M$, the numbers of points $\{\nu N\}$ in S and S_r are asymptotic to MV and MV_r, where V and V_r are the contents of S and S_r respectively. Thus the numbers of gaps of lengths $\Delta_1, \ldots, \Delta_m$ are asymptotic to $MV_1, \ldots, MV_m$. The *mean* gap length is $1/V$ ($V = \sum_1^m V_r$), so that

$$\sum_1^m \Delta_r V_r = 1. \tag{27}$$

The case $n = 2$ has been solved in terms of continued fractions [10] but a simpler approach has been indicated by Florek [11]. The problem is of the gaps between N satisfying

$$|\{\nu_1 N\}| < h, \tag{28}$$

where we shall take $h < \frac{1}{4}$. If a and b are the smallest positive integers such that

$$-2h < \{\nu_1 b\} < 0 < \{\nu_1 a\} < 2h, \tag{29}$$

then the *only* gaps are

$$\Delta = a, b, a+b; \tag{30}$$

and these occur with relative frequencies

$$2h-\{\nu_1 a\},\ 2h+\{\nu_1 b\},\ \{\nu_1 a\}-\{\nu_1 b\}-2h \tag{31}$$

respectively. These quantities (31) are the V_r for this one-dimensional S; and here (27) takes the form

$$b\{\nu_1 a\}-a\{\nu_1 b\} = 1. \tag{32}$$

The result (30) is seen to agree with the empirical formula (26).

The result (30) leads in fact by induction to the formula (26) for general n, although this method does not prove that the λ_{su} are all non-negative. Without this condition the theoretical result is of course very weak. It would seem that the "basic" gaps D_u

for (26) should be chosen to be the smallest gaps Δ for which there are identities

$$\sum_{u=1}^{n} \mu_u \{\nu_i D_u\} = 0 \qquad (i = 1, \ldots, n-1) \tag{33}$$

with *all* the $\mu_u > 0$. The corresponding sets λ_{su} in (26) would then be expected to be predominantly positive; the experimental suggestion that they are all positive is open to suspicion.

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