

only the first term in the series in (12), i.e., by taking the average value of potential II into account in region I, and vice versa, we are left with a soluble Schrödinger equation: the potential in I remains spherically symmetric and the extra constant term $1/r_0$ makes for no difficulty in its solution. With this, the approximate potential is $3/r_0$ at point *A* instead of the correct value of $4/r_0$, and at point *B* the approximate potential is $3/r_0$ instead of the correct value of $8/3r_0$. These are the worst cases, in the sense that the approximate potential is much less accurate at these points near the boundary of region I where r_1 is large than it is for r_1 small.

Similarly we still have an exactly soluble problem if

we take into account the average value of the potential in region III, and neglect the tails of the potentials completely in region IV. For if we write the wave function in III as the sum of two wave functions, one in r_1 coordinates and the other in r_2 coordinates, we can always express this wave function in (r, θ) coordinates and match this to the free-space wave function in region IV. One sees from this point of view that although potentials like the Coulomb potential which are slowly varying have the disadvantage that they cannot be solved exactly by the method of the previous section, they have the advantage that they can be well approximated by their average values over appreciable regions of space.

Recurrence Time of a Dynamical System

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 (Received January 21, 1958)

Poincaré cycles of a many-particle system are exemplified by the motion of a linear chain. It is shown that the recurrence time increases in an approximately exponential way with the number of degrees of freedom, and as a power of the sharpness with which the recurrent state is specified. An explicit formula is given which is applicable to other separable dynamical systems as well.

INTRODUCTION

IN an interesting paper by Frisch,¹ the old questions of Poincaré cycles have been reconsidered. Besides Liouville's theorem, with which it is intimately connected, there is probably no other theorem of general dynamics so simple and so well founded as Poincaré's about the recurrence of all bounded mechanical motions. Far from creating a paradox to the mechanical theory of heat—as held by Zermelo in the famous discussion with Boltzmann—it can on the contrary be made a pillar in the foundation of statistical mechanics.

Corresponding recurrence theorems in quantum mechanics were given in a recent paper by Bocchieri and Loinger.² However, as was pointed out by Frisch,¹ very little is known about the actual magnitude of the recurrence times. It is the purpose of the present paper to supply an explicit calculation, albeit for a very special system, *viz.*, a linear chain. To be sure, the linear chain, like any separable mechanical system, is ergodic only in the space of the angle variables, but that does not detract from the meaning of a recurrence. For the calculation one needs only those dynamical features which are common to all separable systems, but for

definiteness we shall write down the formulas appropriate to the linear chain.

1. DYNAMICAL STARTING POINT

Let the chain consist of N equal mass points, harmonically coupled neighbor to neighbor, and consider their longitudinal displacements u_k ($k=0, 1, 2, \dots, N-1$). If we assume the end points of the chain to be free, the normal coordinates,

$$q_j = \sum_k C_{jk} u_k, \quad (j=0, 1, \dots, N-1) \quad (1)$$

are given by

$$C_{jk} = (\epsilon_j/N)^{\frac{1}{2}} \cos[(k + \frac{1}{2})\pi_j/N], \quad \epsilon_j = \begin{cases} 2, & j \neq 0 \\ 1, & j = 0 \end{cases} \quad (2)$$

where the mode $j=0$, representing a free translation of the whole chain, is of no interest for our problem. The corresponding frequencies are

$$\omega_j = \omega_0 \sin(\pi j/2N), \quad (3)$$

where ω_0 is a maximum frequency related to the spring constant and mass of the particles. Compounding momenta and coordinates in the complex vectors

$$Z_j = p_j + im\omega_j q_j, \quad (4)$$

the entire motion is expressed by

$$Z_j = a_j e^{i\omega_j t}, \quad (5)$$

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¹ H. L. Frisch, *Phys. Rev.* **104**, 1 (1956).

² P. Bocchieri and A. Loinger, *Phys. Rev.* **107**, 337 (1957).

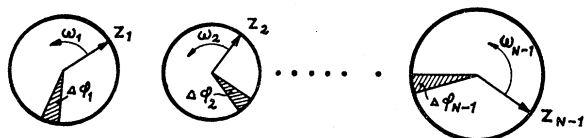


FIG. 1. Motion of the normal coordinates.

where the amplitude constant a_j determines the phase and the (immutable) energy of the j th normal vibration.

2. RECURRENCE

Thus the mechanical state is naturally depicted by a set of vectors $Z_1, Z_2 \dots Z_{N-1}$ rotating with uniform angular velocities $\omega_1 \omega_2 \dots \omega_{N-1}$ (see Fig. 1).

Now in the theory of numbers a famous theorem due to Kronecker³ can be stated as follows: Given such a set of rotating vectors, it is always possible by choice of the time parameter t to restore any situation within finite latitudes:

$$\varphi_j \leq \arg Z_j \leq \varphi_j + \Delta \varphi_j, \quad (j=1, 2, \dots, N-1) \quad (6)$$

provided that the frequencies are rationally independent, that is, that the equation

$$n_1 \omega_1 + n_2 \omega_2 + \dots + n_{N-1} \omega_{N-1} = 0 \quad (7)$$

is insoluble in integers n_j (not all zero).

Clearly, re-entrance into some specified vicinity of the angles $\varphi_j = \omega_j t + \delta_j$ means recurrence of mechanical state within some latitude, whatever are the coordinates used for its description. But it should be noted that although the recurrence time is independent of position in the space of the angles, it is not independent of the state in general. The concept of recurrence is relative to the specification of state. We shall here be concerned only with the simplest type pertaining to the linear chain, *viz.*, the average duration between two consecutive passages through an angular interval $\{\Delta \varphi_1, \Delta \varphi_2, \dots, \Delta \varphi_{N-1}\}$.

Let us define the recurrence time by

$$T_{\text{Rec}} = \lim_{r \rightarrow \infty} (t_r / r), \quad (8)$$

where t_r = time of the r th recurrence. Kronecker's theorem asserts that there will be recurrences. It does not, however, tell us how long one must wait for such an event, and this we are now to determine.

3. LEMMA

Consider two of the vectors (4), Z_1 and Z_2 say, with the periods

$$T_1 = 2\pi / \omega_1 < T_2 = 2\pi / \omega_2, \quad (9)$$

and the times when they pass given initial positions.

³ A proof of the theorem in the form which is suited for our purpose is given by H. Bohr, Proc. Math. Soc. (London) 21, 315 (1923). This proof as well as several others may also be found in *Collected Mathematical Works of Harald Bohr* (Matematisk Forening, Copenhagen, 1952), Vol. 3.

Look especially at the delay: $nT_1 - mT_2$, between the n th passage of Z_1 and the next preceding one of Z_2 , which we denote as the m th. This delay is then certainly $< T_2$:

$$nT_1 - mT_2 = \epsilon T_2, \quad (10)$$

where $0 \leq \epsilon \leq 1$; or, by definition (9),

$$n(\omega_2 / \omega_1) - m = \epsilon. \quad (11)$$

From Eq. (11) it follows that m is the integer part $[n\omega_2 / \omega_1]$ of the number $n\omega_2 / \omega_1$:

$$n\omega_2 / \omega_1 - [n\omega_2 / \omega_1] = \epsilon(n). \quad (12)$$

In the course of n revolutions the angle between Z_1 and Z_2 , when Z_1 is in the specified position, will assume values between 0 and 2π proportional to $\epsilon(n)$. According to a theorem of Weyl,⁴ the remainder $\epsilon(n)$, $n=1, 2, \dots$, will be uniformly distributed in the interval (0,1) if ω_2 / ω_1 is irrational. Under this condition, then, we see that all relative angles, $\varphi_j - \varphi_k$, are equally probable over long times.

The question remains as to whether every two proper frequencies ω_j, ω_k as given by (3) are incommensurable. This is so far already implied by the rational independence (7) which we have assumed. Whether, for a given N , the frequencies given by (3) really are rationally independent is not directly evident. It has been pointed out to us by Professor Ernst Jacobsthal that there are certain, though rare cases, e.g., $N=105$, for which there is indeed dependence. This mathematical question will be analyzed by Professor Jacobsthal in a forthcoming paper in the Proceedings of the *Kongelige Norske Videnskabers Selskab* in Trondheim.

4. RECURRENCE TIME

According to the aforementioned feature of independence and uniform distribution of the angles φ_j , we may now proceed as follows: The probability to find a specified situation at an arbitrary time is

$$\text{Prob} (\dots \arg Z_j \subset \Delta \varphi_j \dots) = \prod_{j=1}^{N-1} \left(\frac{\Delta \varphi_j}{2\pi} \right), \quad (13)$$

and this is again equal to the fraction of a long time during which the vectors Z_j are simultaneously inside their prescribed latitudes $\Delta \varphi_j$, or as we shall say in "coincidence":

$$\text{Prob} = \lim_{t \rightarrow \infty} \left(\frac{\text{time in coincidence}}{\text{total time}} \right). \quad (14)$$

Dividing now numerator and denominator of the right-hand side of (14) by the number r of coincidences and remembering the definition (8), we obtain

$$\frac{T_{\text{coinc}}}{T_{\text{Rec}}} = \prod \left(\frac{\Delta \varphi_j}{2\pi} \right), \quad (15)$$

⁴ H. Weyl, Math. Ann. 77, 313 (1916).

where T_{coinc} is the mean life of the recurrent state. The trick is that it is easier to find T_{coinc} , whereby our problem is solved. It turns out that the reciprocal mean life is equal to the sum of the reciprocal passage times, $1/t_j = \omega_j/\Delta\varphi_j$, of each vector through its interval:

$$\frac{1}{T_{\text{coinc}}} = \frac{1}{t_1} + \frac{1}{t_2} + \dots + \frac{1}{t_{N-1}}. \tag{16}$$

Accordingly we find by (15) and (16) for the recurrence time

$$T_{\text{Rec}} = \prod_{j=1}^{N-1} \left(\frac{2\pi}{\Delta\varphi_j} \right) / \sum_{j=1}^{N-1} \frac{\omega_j}{\Delta\varphi_j}. \tag{17}$$

It was here presumed that all the normal vibrations were excited; if not, the sum and product should only be extended over those modes which are excited in the motion. In the extreme case where only one normal vibration is excited, the formula (17) reduces to

$$T_{\text{Rec}} = 2\pi/\omega_j; \tag{18}$$

the recurrence time degenerates to the period T_j as it must. Likewise if the chain degenerates to a simple oscillator $\nu: N=2$.

Of particular interest is the rate at which the recurrence time increases with the number of degrees of freedom and the sharpness in the definition of the state. Formula (17) illustrates quantitatively what was concluded on general grounds by Frisch,¹ that $T_{\text{Rec}} \sim \Delta\varphi^{-N}$ (more accurately $\sim N^{-1} \cdot \Delta\varphi^{2-N}$). A numerical example will indicate how enormous the recurrence times of this type are, even for quite small systems and a state of relatively broad latitude: For a chain of $N=10$ atoms, a maximum frequency of $\omega_0=10/\text{sec}$, and a common angular latitude $\Delta\varphi = \pi/100$, one finds $T_{\text{Rec}} \sim 10^{10}$ years.

APPENDIX

I. Calculation of the Mean Life of the Recurrent State

Let us first consider the simpler problem of coincidence between only two vectors Z_1 and Z_2 . The times of transit through their intervals are $t_1 = \Delta\varphi_1/\omega_1$ and $t_2 = \Delta\varphi_2/\omega_2$, respectively. We shall then show that the mean duration of a coincidence: $\arg Z_1 \subset \Delta\varphi_1$ and $\arg Z_2 \subset \Delta\varphi_2$, is

$$\bar{t}_{12} = t_1 t_2 / (t_1 + t_2). \tag{19}$$

Assuming that Z_1 passes the midpoint of its interval a time τ before Z_2 passes the midpoint of $\Delta\varphi_2$, coincidence will take place if, and only if

$$-\frac{1}{2}(t_1 + t_2) \leq \tau \leq \frac{1}{2}(t_1 + t_2). \tag{20}$$

In order to determine the coincidence time t_{12} as a function of τ we distinguish the three situations indicated in Fig. 2.

According to the uniform distribution of τ following

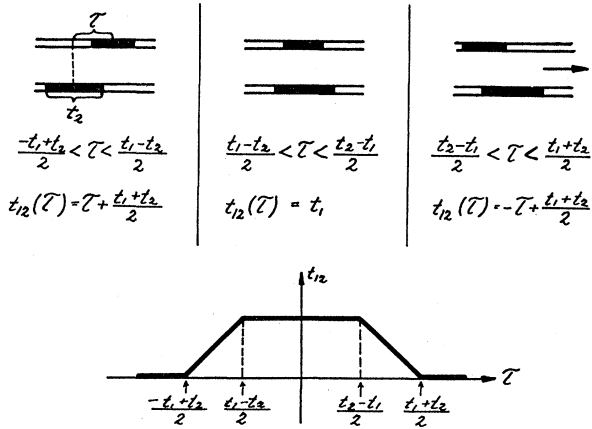


FIG. 2. Lifetime of coincidence t_{12} as function of τ .

from (12), we have then for the mean life of a binary coincidence

$$\bar{t}_{12} = \frac{1}{t_1 + t_2} \int_{-(t_1+t_2)/2}^{(t_1+t_2)/2} t_{12}(\tau) d\tau = \frac{t_1 t_2}{t_1 + t_2}, \tag{21}$$

or

$$\frac{1}{\bar{t}_{12}} = \frac{1}{t_1} + \frac{1}{t_2}.$$

The corresponding procedure is still manageable for the triple coincidences, giving

$$\frac{1}{\bar{t}_{123}} = \frac{1}{t_1} + \frac{1}{t_2} + \frac{1}{t_3}, \tag{22}$$

and indeed the general formula is

$$\frac{1}{\bar{t}_{12\dots n}} = \frac{1}{t_1} + \frac{1}{t_2} + \dots + \frac{1}{t_n}. \tag{23}$$

But a proof by induction does not seem quite easy. It is tempting to argue as follows: The coincidence of $n-1$ vectors is equivalent to a simple event of duration $\bar{t}_{12\dots n-1}$ which is to coincide with vector Z_n being within its interval (passage time t_n). Thus we should have for the n -fold coincidence

$$\frac{1}{\bar{t}_{12\dots n}} = \frac{1}{\bar{t}_{12\dots n-1}} + \frac{1}{t_n}. \tag{24}$$

However, because of the distribution of the times this argument is not complete. We shall therefore prove (23) by two independent methods. The first one of these can even give some information about the distributions instead of just mean values. The second method is more special but has the merit of simplicity.

II. First Proof

The proof desired in the preceding Appendix I is clearly contained in the solution of the following

problem: On a line segment, of length L , we place at random n line segments of lengths $t_1 \leq t_2 \leq t_3 \leq \dots \leq t_n$. By "at random" we mean that the line segments are placed independently, and that all positions of any line segment are equally probable. We shall make L large, but it is convenient to have it finite. We want to calculate the mean length of intersection of all line segments,

$$\bar{t}_{12\dots n} = \int x P(t_1 t_2 \dots t_n; x | t_1 t_2 \dots t_n \text{ intersect}) dx, \quad (25)$$

where $P(t_1 t_2 \dots t_n; x | t_1 t_2 \dots \text{int})$ is the probability that the segments have a common interval of length between x and $x+dx$, given that all of them intersect.

We have then

$$P(t_1 t_2 \dots t_n; x | t_1 t_2 \dots t_n \text{ int}) = \frac{P(t_1 t_2 \dots t_n; x)}{P(t_1 t_2 \dots t_n \text{ int})}. \quad (26)$$

Here $P(t_1 t_2 \dots t_n; x) dx$ = the probability that all the segments overlap over an interval of length between x and $x+dx$ and $P(t_1 t_2 \dots t_n \text{ int})$ = the probability that all n segments intersect. It may be noted that

$$\begin{aligned} P(t_1 \dots t_n; x) &= \int_0^{t_1} P(t_1 \dots t_{n-1}; y_{n-1}) dy_{n-1} P(y_{n-1}, t_n; x) \\ &= \int_0^{t_1} P(t_1 t_2; y_2) dy_2 \int_0^{y_2} P(y_2 t_3; y_3) dy_3 \\ &\quad \times \int_0^{y_3} P(y_3 t_4; y_4) dy_4 \dots \int_0^{y_{n-2}} P(y_{n-2}, t_{n-1}; y_{n-1}) \\ &\quad \times dy_{n-1} P(y_{n-1}, t_n; x). \end{aligned}$$

The upper limits are obtained from the observation that $P(y_n t_{n+1}; y_{n+1}) = 0$ for $y_{n+1} > y_n$. In similar fashion we have

$$\begin{aligned} P(t_1 t_2 \dots t_n \text{ int}) &= \int_0^{t_1} P(t_1 t_2; y_2) dy_2 \int_0^{y_2} P(y_2 t_3; y_3) dy_3 \\ &\quad \times \dots \int_0^{y_{n-2}} P(y_{n-2}, t_{n-1}; y_{n-1}) \\ &\quad \times dy_{n-1} P(y_{n-1}, t_n \text{ int}). \quad (27) \end{aligned}$$

All the probabilities on the right-hand side are now of the form $P(t_1 t_2; x)$ or $P(t_1 t_2 \text{ int})$; and by considering a figure one easily finds ($L \gg t_1 + t_2$)

$$P(t_1 t_2 \text{ int}) = (t_1 + t_2)/L,$$

and

$$P(t_1 t_2; x) = \begin{cases} 2/L, & 0 < x < t_1 \\ (t_2 - t_1)/L, & x = t_1 \\ 0, & x > t_1 \end{cases}$$

or

$$P(t_1 t_2; x) = [2 + (t_2 - t_1)\delta(x - t_1)]/L, \quad x \leq t_1.$$

The δ function is defined so that $\int_0^{t_1} \delta(x - t_1) dx = 1$. With only two segments we find

$$\bar{t}_{12} = \int_0^{t_1} x \frac{P(t_1 t_2; x)}{P(t_1 t_2 \text{ int})} dx = \frac{t_1 t_2}{t_1 + t_2}.$$

The $(n-2)$ -fold integral in (27) is evaluated by induction. Denoting the integral up to an including that over y_{j+1} by I_j , we have

$$\begin{aligned} I_{n-2} &= \frac{1}{L^2} \int_0^{y_{n-2}} (y_{n-1} + t_n) \\ &\quad \times [2 + (t_{n-1} - y_{n-2})\delta(y_{n-2} - y_{n-1})] dy_{n-1} \\ &= \frac{t_n t_{n-1}}{L^2} \left[1 + y_{n-2} \left(\frac{1}{t_n} + \frac{1}{t_{n-1}} \right) \right]. \end{aligned}$$

Assuming

$$I_{n-j} = \frac{t_n t_{n-1} \dots t_{n-j+1}}{L^j} \times \left[1 + y_{n-j} \left(\frac{1}{t_n} + \frac{1}{t_{n-1}} + \dots + \frac{1}{t_{n-j+1}} \right) \right],$$

then

$$\begin{aligned} I_{n-j-1} &= \int_0^{y_{n-j-1}} I_{n-j} \\ &\quad \times [2 + (t_{n-j} - y_{n-j-1})\delta(y_{n-j} - y_{n-j-1})] \frac{dy_{n-j}}{L} \\ &= \frac{t_n t_{n-1} \dots t_{n-j}}{L^{j+1}} \\ &\quad \times \left[1 + y_{n-j-1} \left(\frac{1}{t_n} + \frac{1}{t_{n-1}} + \dots + \frac{1}{t_{n-j}} \right) \right]. \end{aligned}$$

Thus the expression for I_{n-j} is valid in general. Therefore, (with $y_1 = t_1$),

$$\begin{aligned} P(t_1 t_2 \dots t_n \text{ int}) &= I_1 = \frac{t_n t_{n-1} \dots t_2}{L^{n-1}} \left[1 + t_1 \left(\frac{1}{t_n} + \dots + \frac{1}{t_2} \right) \right] \\ &= \frac{t_1 t_2 \dots t_n}{L^{n-1}} \left[\frac{1}{t_1} + \frac{1}{t_2} + \dots + \frac{1}{t_n} \right]. \quad (28) \end{aligned}$$

Finally, to obtain $\bar{t}_{12\dots n}$, we need also

$$\begin{aligned} &\int_0^{t_1} x P(t_1 \dots t_n; x) dx \\ &= \int_0^{t_1} P(t_1 t_2; y_2) dy_2 \int_0^{y_2} P(y_2 t_3; y_3) dy_3 \\ &\quad \times \dots \int_0^{y_{n-2}} P(y_{n-2}, t_{n-1}; y_{n-1}) dy_{n-1} \\ &\quad \times \int_0^{y_{n-1}} x P(y_{n-1}, t_n; x) dx. \end{aligned}$$

The last integral is simply equal to

$$P(y_{n-1}, t_n \text{ int}) \times \bar{t}_{12}(y_{n-1}, t_n).$$

The integral over y_{n-1} is thus exactly of the same form as the integral over x , apart from a constant factor t_n/L , and the same holds for all the remaining integrals, giving

$$\int_0^{t_1} xP(t_1 \dots t_n; x) dx = t_1 t_2 \dots t_n / L^{n-1}. \quad (29)$$

Thus, the combination of this with (26) and (28) gives the desired result

$$\frac{1}{t_{12} \dots t_n} = \frac{1}{t_1} + \frac{1}{t_1} + \dots + \frac{1}{t_n}.$$

By a similar iteration procedure one can also obtain the higher moments of the distribution function.

III. Second Proof

Instead of looking at the $N-1$ vectors Z_j (Fig. 1) separately rotating in their circles, we can map the complete motion $\varphi_1(t) \varphi_2(t) \dots \varphi_{N-1}(t)$ on an N -dimensional sphere. Let N -dimensional polar coordinates be defined by

$$\begin{aligned} x_1 &= r \cos \vartheta_1, \\ x_2 &= r \sin \vartheta_1 \cos \vartheta_2, \\ &\vdots \\ x_{N-1} &= r \sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{N-2} \cos \Phi, \\ x_N &= r \sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{N-2} \sin \Phi. \end{aligned} \quad (30)$$

We have then $\sum x_j^2 = r^2$ and the surface $r = \text{const.}$ is covered once when the angles describe the intervals $0 \leq \vartheta_j < \pi$ and $0 \leq \Phi < 2\pi$. For the line element, one has

$$ds^2 = dr^2 + r^2 [d\vartheta_1^2 + \sin^2 \vartheta_1 d\vartheta_2^2 + \dots + (\sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{N-3})^2 d\vartheta_{N-1}^2 + (\sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{N-2})^2 d\Phi^2], \quad (31)$$

all cross terms cancelling by orthogonality. Accordingly the volume element is the product of the components

$$\begin{aligned} ds_r &= dr, \\ ds_{\vartheta_1} &= r d\vartheta_1, \\ &\vdots \\ ds_{\vartheta_j} &= r \sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{j-1} d\vartheta_j, \\ &\vdots \\ ds_{\Phi} &= r \sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{N-2} d\Phi. \end{aligned} \quad (32)$$

For the present purpose we need only the surface element on the unit sphere,

$$d\Omega = (\sin \vartheta_1)^{N-2} (\sin \vartheta_2)^{N-3} \dots \times \sin \vartheta_{N-2} d\vartheta_1 d\vartheta_2 \dots d\vartheta_{N-2} d\Phi. \quad (33)$$

Identifying now $\vartheta_1, \vartheta_2, \dots, \vartheta_{N-2}, \Phi$ with $\varphi_1/2, \varphi_2/2, \dots, \varphi_{N-2}/2, \varphi_{N-1}/2$, respectively, the polar angles will be defined modulo π when the corresponding angle

variables are defined mod 2π . The situation of the $N-1$ normal coordinates Z_j is thus uniquely specified by a point P on the unit sphere in N dimensions.

The velocity of the point P is the time derivative of the line element. It has the components

$$\begin{aligned} v_1 &= \dot{\vartheta}_1, \\ &\vdots \\ v_j &= \sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{j-1} \dot{\vartheta}_j, \\ &\vdots \\ v_{N-1} &= \sin \vartheta_1 \sin \vartheta_2 \dots \sin \vartheta_{N-2} \dot{\Phi}, \end{aligned} \quad (34)$$

where

$$\dot{\vartheta}_j = \frac{1}{2} \omega_j, \quad \dot{\Phi} = \omega_{N-1}.$$

We have in this way a velocity field (34) over the sphere, which is determined both in direction and magnitude everywhere (except at the poles $\vartheta_j = 0$). The sectors $\Delta \vartheta_j$, corresponding to the latitudes $\Delta \varphi_j = \omega_j \Delta t_j$ of the mechanical state, will delineate a surface element $\Delta \Omega$ on the unit sphere with mutually orthogonal edges:

$$s_j = v_j \Delta t_j \quad (j=1, 2, \dots, N-1).$$

We are now prepared to compute the coincidence time. A coincidence, $\varphi_j \leq \arg Z_j \leq \varphi_j + \Delta \varphi_j$ for every j , is equivalent to the event $P \in \Delta \Omega$, and the mean lifetime of a coincidence is equal to the mean time of transit of P through $\Delta \Omega$. This mean time of transit is equal to the mean segment \bar{l} of the reentrant orbit inside $\Delta \Omega$, divided by the absolute velocity:

$$T_{\text{coinc}} = \bar{l} / |v|, \quad (35)$$

where

$$|v| = (v_1^2 + v_2^2 + \dots + v_{N-1}^2)^{1/2}.$$

Because of the complete symmetry it will now suffice to illustrate the calculation by means of the case $N=2$. Then $\Delta \Omega$ is just the 2-dimensional surface element $\sin \Theta d\Theta d\Phi$ on an ordinary sphere (Fig. 3).

Over long times, all positions Θ, Φ are equally probable and independent according to the auxiliary theorem of Sec. 3. The passages of P 's orbit will therefore fill up $\Delta \Omega$ with uniform density when the number of recurrences gets large. Hence the mean segment \bar{l} must be equal to the area $\Delta \Omega$ divided by the projection of $\Delta \Omega$ in the direction of the velocity upon the $(N-2)$ -dimensional subspace perpendicular to it:

$$\bar{l} = \Delta \Omega / \text{Projection of } \Delta \Omega \text{ along } v. \quad (36)$$

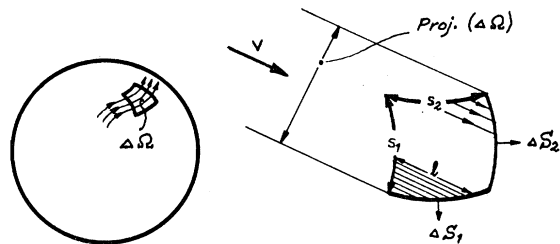


FIG. 3. Passage of orbit through $\Delta \Omega$.

This projection will be (Fig. 3)

$$\text{Proj}(\Delta\Omega) = \frac{v_1}{|v|} \Delta S_1 + \frac{v_2}{|v|} \Delta S_2, \quad (37)$$

where ΔS_j is the surface element whose normal points in the direction of v_j . But because of the orthogonality we have $\Delta\Omega = s_j \Delta S_j$ for any j , so that we may replace ΔS_1 and ΔS_2 in the denominator of (36) by $\Delta\Omega/s_1$ and $\Delta\Omega/s_2$, respectively.

The expression (36) for the mean segment will then take the form

$$l = v / \left(\frac{v_1}{s_1} + \frac{v_2}{s_2} \right), \quad (38)$$

where the denominator is just the sum of the reciprocal passage times $1/t_1 = v_1/s_1$, and $1/t_2 = v_2/s_2$. The extension to more dimensions is now immediate, and so we have generally

$$\frac{1}{T_{\text{coinc}}} = \sum \frac{1}{t_j}, \quad (39)$$

as was to be shown.

ACKNOWLEDGMENT

We would like to thank Dr. H. L. Frisch, whose work¹ instigated this paper, for stimulating correspondence.

Time-Correlation Functions in the Statistical Mechanics of Transport Processes*

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(Received April 8, 1958)

A kinetic equation governing the time dependence of the correlation function of flux is established for dilute gases and is integrated to yield a relation between the correlation time and the transport cross section. The spectrum of the binary collision operator is determined for spherically symmetric forces between molecules, which, for the hard-core model, consists of two discrete values in the classical limit; hence it is shown that the question of validity of approximating the correlation function by an exponential decay depends upon the type of intermolecular force and the temperature of the system. Approximate eigenvalues of the master collision operator are obtained corresponding to the

fluxes of viscosity and thermal conduction, and their relations to the macroscopic transport coefficients are derived. These relations lead to a new approach to the transport properties of dilute gases, which is different from Enskog-Chapman's method, but yields the same results in the classical limit. An expansion formula for the canonical transformation describing the motion of dilute gases is obtained and is employed to clarify the assumption of random *a priori* phases in the momentum representation for spatially uniform gases; this is done by formulating the quantum-mechanical equivalent of Brout's idea in the classical derivation of the master equation.

1. INTRODUCTION

THE typical examples of the molecular theory of transport phenomena, such as the viscosity of dilute gases and the electrical conductivity of metals, are usually based on the Maxwell-Boltzmann integro-differential equation for the velocity distribution function of molecules¹ or its modification. The extension of the kinetic method to the treatment of transport phenomena in dense gases and degenerate quantum gases has not been made in the general case.

On the other hand, according to the recent theories of transport processes,^{2,3} we can obtain molecular expressions for transport coefficients or kinetic coefficients which are valid over the same region as the thermo-

dynamics of irreversible processes.⁴ The most remarkable feature of the theories is the formulation of the transport coefficients in terms of the correlation functions of the equilibrium fluctuations of the corresponding dynamical fluxes F ,

$$\Psi_{F,F}(t) = \frac{1}{2} \langle FF(t) + F(t)F \rangle, \quad (1.1)$$

where the angular brackets mean the average over the canonical ensemble of the system, and $F(t)$ is the value of F after time t and should, in the quantum-mechanical case, be read as the Heisenberg operator. For example, the coefficient of shear viscosity of isotropic fluids can be expressed as^{3,5,6}

$$\eta = (1/VkT) \int_0^\infty dt \Psi_{F,F}(t), \quad (1.2)$$

* This work was supported in part by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research Development Command.

¹ S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, Cambridge, 1939).

² R. Kubo, *J. Phys. Soc. Japan* **12**, 570 (1957).

³ H. Mori, *J. Phys. Soc. Japan* **11**, 1029 (1956).

⁴ S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951).

⁵ M. S. Green, *J. Chem. Phys.* **22**, 398 (1954).

⁶ In the classical limit, Eq. (1.2) agrees with Green's expression⁵ except that the average in (1.1) is made with the canonical ensemble whereas, in his expression, with the micro-canonical ensemble. The latter situation causes a serious difference in the