Solution of an apparent inconsistency in the concept of mean free path

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by **Andreas Fröhlich**

Instituto de Física 'Gleb Wataghin', Universidade Estadual de Campinas, Campinas, S.P., Brasil

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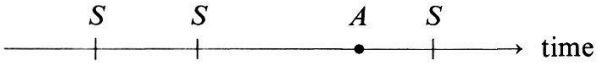
Abstract. The standard procedure starts by defining τ, the mean free flight time of molecules between collisions; but then, after some probability considerations, the mean free flight time appears to be 2τ. This paper develops a more careful application of probability to the question and shows that the two mean values belong to different sample spaces.

Introduction

Some books [1–3] mention a paradoxical result in the theory of mean free path of molecules of a dilute gas. The mean time between collisions, τ, is first defined as the time of a section of the molecule's life divided by the number of collisions that the molecule underwent in this section. Then one makes the assumption and good approximation that at any instant A, regardless of the molecule's past, $\Delta t/\tau$ is the probability that it will collide in the next Δt; this is equivalent to Poisson's law [4], which says that from A onwards the molecule survives without collision for a time t with probability $e^{-t/\tau}$, and with the same probability the last previous collision lies at least a time t back; the expectation values for the time from A to the next and last collisions are thus τ each, which makes 2τ between successive collisions. Especially Sommerfeld [1] considers this to be a serious conceptual difficulty and also treats the analogous problem of throwing dice, which is treated in the second part of this paper. The first part develops a calculation for the original problem, but without the assumption of Poisson's law.

Calculation for collisions in gases and analogous problems (continuous variables)

Representing the probability distributions which yield mean time intervals of τ and 2τ by $W(S)$ and $W(A)$ respectively, we may illustrate the life of a particle on a time line where S represent times at which collisions occur and A is an arbitrary instant of time.



The time interval between consecutive S's shall be referred to as an 'interval'.

$W(S)$ corresponds to the following experiment: Cut up the time-line into its intervals and pack each one into a separate box. Then draw a box at random. The probability that the length of the interval contained in this box lies between T and $T + \Delta T$ shall be called $p(T)\,\Delta T$. Thus $\int_0^\infty dT\,p(T) = 1$. $p(T)\,\Delta T$ also is the probability that from an arbitrary S on, it takes between T and $T + \Delta T$ until to the next S. The mean interval length in $W(S)$ is then

$$\tau \equiv \int_0^\infty dT\,Tp(T).$$

$W(A)$ is the distribution obtained by observing the molecule from an arbitrary instant A onwards, i.e. choosing an A at random on the time-line. A new function $k(t)$ is then defined so that once an A is chosen, $k(t)\,\Delta t$ is the probability that the first S after A lies between t and $t + \Delta t$ after A. $k(t)\,\Delta t$ is also the probability that the last S before A lies between t and $t + \Delta t$ before A.

There is one more function associated with $W(A)$, it shall be called $L(t)$ and means the probability that the time t following A doesn't contain any S, i.e. the next S lies more than t ahead. Obviously

$$L(t) = \int_t^\infty dt'\,k(t').$$

The bridge between $W(S)$ and $W(A)$ is the following: The probability that the arbitrary point A falls into an interval of length between T and $T + \Delta T$ is $[Tp(T)\,\Delta T]/\tau$. One arrives at this result by considering the fraction of the time-axis that is taken up by the intervals of lengths between T and $T + \Delta T$; it must be proportional to $Tp(T)\,\Delta T$. The said fraction is by definition of probability the probability that A lies in a said interval. τ is the normalization constant, such that $\int_0^\infty [Tp(T)\,dT]/\tau = 1$. From $[Tp(T)\,\Delta T]/\tau$, one finds the probability that A lies in a certain section of length Δt within an interval of length between T and $T + \Delta T$ (e.g. in a Δt around the middle of the interval): It is

$$\frac{\Delta t}{T} \cdot \frac{Tp(T)\,\Delta T}{\tau} = \frac{p(T)\,\Delta T\,\Delta t}{\tau}.$$

Examples are:

1. The probability that the time from A to the last S is between t_l and $t_l + \Delta t_l$ and the time from A to the next S between t_n and $t_n + \Delta t_n$ is $[p(t_l + t_n)\,\Delta t_l\,\Delta t_n]/\tau$. From this, all the other distributions of $W(A)$ can be calculated by integration.

2. To obtain $k(t)$ in terms of $p(T)$ we argue that the probability that A lies in an interval of length between T and $T + \Delta T$ and also lies between t and $t + \Delta t$ $(t < T)$ before the end of this interval, is $\tau^{-1}p(T)\,\Delta T\,\Delta t$. Integration over all possible T's $(t < T)$ yields

$$k(t)\,\Delta t = \tau^{-1} \int_t^\infty dT\,p(T)\,\Delta t.$$

Thus $k(t)$ is now expressed in terms of $p(T)$.

In $W(A)$, there are two mean values of importance: One is $\bar{t} \equiv \int_0^\infty dt\,t\,k(t)$, the expectation value of the time from A to the next S. It is also the expectation value of the time from A to the last S. The other is $\bar{T}$, the mean interval length in $W(A)$.

One can write

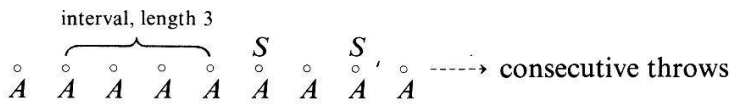
$$\bar{T} = \int_0^\infty T \frac{Tp(T)\,dT}{\tau}, \quad \text{or also} \quad \bar{T} = \iint_0^\infty (t_l + t_n)\tau^{-1}p(t_l + t_n)\,dt_l\,dt_n.$$

t_l and t_n are, as before, the times from A to the last S and the next S. Obviously $T = t_l + t_n$ for any certain A. And, with the bar always meaning 'average of the distribution $W(A)$', $\bar{T} = \overline{(t_l + t_n)}$. But $\overline{(t_l + t_n)} = \bar{t}_l + \bar{t}_n$, and each one of them equals $\bar{t}$. Thus $\bar{T} = 2\bar{t}$, which can also be arrived at by partial integration of $\bar{T} = \tau^{-1} \int_0^\infty dT\, T^2 p(T)$, using $p(T) = -\tau\dot{k}(T)$ and $t^2 k(t) \xrightarrow[t\to\infty]{} 0$.

Each one of these three quantities, $\bar{T}$, $\bar{t}$ and τ, have been regarded as mean free flight times in the literature, but they may all be different. Only $\bar{T} = 2\bar{t}$ always holds. In the case of Poisson's law, one has $L(t) = e^{-t/\tau}$, $k(t) = \tau^{-1} e^{-t/\tau}$, $p(T) = \tau^{-1} e^{-T/\tau}$, with $\tau \equiv \int_0^\infty dT\, Tp(T)$, as before. And thus $\bar{t} = \tau$, $\bar{T} = 2\tau$. It may be due to the sameness of the functional forms of the three functions L, k and p, that their conceptual difference has not been considered sufficiently.

Throwing dice and generalizations (discrete variables)

Throwing dice gives an analogous example [1], with the difference that the continuous variables are now replaced by the natural numbers, 1, 2, 3, ... The die, with its six faces, is thrown an unlimited number of times, a throw and its result being denoted by A. One face is marked, the A's where it appears are also called S's.



The probability for an A to be an S is $\frac{1}{6}$. Thus, at any A, be it an S or not, the probability that to the next S, it takes n more throws, is $l(n) = \frac{1}{6}(\frac{5}{6})^{n-1}$, where $n = 1, 2, 3, \ldots$. By 'length of an interval' shall be meant the number of interspaces between throws that it contains. Then one can say: 'The $W(S)$-probability for an interval to have length n is $l(n)$'. And in $W(S)$, the average length of an interval, denoted by v, becomes $v = \sum_1^\infty nl(n) = 6$. v is analogous to τ. The analog to $\bar{t}$ shall be called $\bar{n}$ and is the expectation value of the number of throws from an arbitrary A on until to the next S. Thus $\bar{n} = \sum_1^\infty nl(n) = 6$. The number of throws (or interspaces between throws) from the arbitrary A backwards to the last S also follows the distribution $l(n)$. However, this time one cannot just add the two $\bar{n}$'s in order to get the mean interval length in $W(A)$. Namely, in the case that the arbitrary A is an S and it is n_l to the last S and n_n to the next S, the number $(n_l + n_n)$ is not the length of an interval, but the length of two intervals. Thus in the case that A is and S, the mean interval length is $\frac{1}{2}\overline{(n_l + n_n)} = \frac{1}{2}(\bar{n}_l + \bar{n}_n) = \frac{1}{2}(\bar{n} + \bar{n}) = \bar{n}$. This case has probability $\frac{1}{6}$, since $\frac{1}{6}$ of the A's are S's. In the example with continuous variables, the set of A's that were S's was of measure zero. To the $\frac{5}{6}$ of A's that are not S's, the mean interval length of $W(A)$ is calculated as follows: An interval of length n contains $(n - 1)$ A's that are not S's, let's call them B's. Thus the probability that an arbitrary B is contained in an interval of length n is $[(n - 1)l(n)]/(v - 1)$. And so, in this case, the mean interval length comes out to be $\sum_1^\infty n[(n - 1)l(n)]/(v - 1)$, which is 12. Adding the two results now with their respective weights of $\frac{1}{6}$ and $\frac{5}{6}$ gives the mean

interval length in $W(A)$, called N. $N = 11$. Thus $N \neq 2\bar{n}$. N can also be calculated in a different way, which is simpler but doesn't exhibit the reason for $N \neq 2\bar{n}$ explicitly: In $W(A)$, the intervals of length n have the relative weight $[np(n)]/v$. Averaging the interval lengths n gives N. Thus $N = \sum_1^\infty n[np(n)/v]$. Again $N = 11$.

Generalizing this example of throwing dice, one can formulate a calculus analogous to the one about t and T, for problems with variables that take on the values 1, 2, 3, ... Just a few parts shall be mentioned here, without deductions. The analog to $p(T)\,\Delta T$ shall be denoted by $p(n)$ and means, among other things, the following: At an arbitrary S, the probability that the next interval is of length n is $p(n)$. The same is true with 'next' replaced by 'last' (or 'next but one', etc.). By 'length of an interval' is meant the number of interspaces between consecutive A's that are contained in the interval. Then there is the analog to τ, $v \equiv \sum_1^\infty np(n)$. v is the mean interval length in $W(S)$, and v^{-1} the fraction of A's that are S's. Then there is a function $k(m) \equiv v^{-1} \sum_{n=m}^\infty p(n)$, which means two useful things: (1) The probability that from an arbitrary A (be it an S or not) to the next (or last) S there are m interspaces. (2) The probability that between an arbitrary interspace and the next (last) S there are $(m - 1)$ interspaces. The quantity $\sum_1^\infty mk(m)$ shall be denoted by $\bar{m}$. Finally, there is N, the mean interval length in $W(A)$. Thus $N = \sum_1^\infty n[np(n)/v]$, and one finds $N = 2\bar{m} - 1$.

Acknowledgements

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[3] F. W. Sears, *Thermodynamics, The Kinetic Theory of Gases, and Statistical Mechanics* (Addison Wesley), section 13-2.
[4] See also H. A. Lorentz, *The Theory of Electrons* (Dover), notes 36 and 57.