Is the mean free path the mean of a distribution?

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Abstract

In this note we bring attention to the fact that Maxwell’s mean free path for a dilute hard-sphere gas in thermal equilibrium, \((\sqrt{2}σ_\text{nχ})^{-1}\), is the mean of a probability distribution of free path lengths.
For a gas composed of smooth rigid spheres ("molecules") each molecule affects another’s motion only at collisions ensuring that the molecule travels in a straight line at constant speed between collisions — this is a free path. The mean free path is then the average length of a great many free paths either made by an ensemble of molecules or a single molecule followed for a long time, it being a basic assumption of statistical mechanics that these two types of averages are equivalent. In this note we consider a dilute gas of hard spherical particles of mass \( m \) and radius \( a \) which has attained thermal equilibrium and spatial uniformity. In textbook treatments\(^1\) the mean free path is given as \((\sqrt{2\sigma n\chi})^{-1}\), where \( \sigma = \pi(2a)^2 \) is the total scattering cross section, \( n \) is the average number density throughout the gas, and \( \chi \) may be thought of as a finite-density correction that starts from a value of unity in the extreme dilute limit and increases with increasing density.\(^2\) The value \((\sqrt{2\sigma n\chi})^{-1}\) may be attributed to Maxwell who defined the mean free path \( \lambda_{\text{Maxwell}} \) as the ratio of the mean speed \( \langle v \rangle \), evaluated in the equilibrium velocity distribution \( f(v) \), to the mean collision rate \( \omega \). Working in scaled units where masses are measured in units of \( m \) and velocities are measured in units of \((kT/m)^{1/2}\), the velocity probability density is \( f(v) = (2\pi)^{-d/2} \exp(-v^2/2) \), where \( d \) is the number of spatial dimensions.

The mean collision rate \( \omega \) may be obtained through a standard flux argument that counts the total number of collisions in a given volume during some arbitrary time interval.\(^3\) The condition of molecular chaos is assumed: in the encounter between two spheres their initial velocities are uncorrelated prior to the collision. This assumption allows one to express the collision probability in terms of a product of equilibrium velocity distributions. In considering the effect of finite molecular volume one must grapple with the fact that the average density \( n \) inadequately represents the number of molecular centers in a given volume of space where scattering occurs. A density for the number of molecular centers a given distance from a chosen molecule is discontinuous since no two sphere centers can be closer than a diameter. The appropriate correction to the collision rate appears as a multiplicative factor \( \chi \) evaluated at the point where two spheres collide.\(^4\) One may regard \( n\chi \) as the density just outside the contact surface between the spheres.\(^5\) In a uniform gas \( \chi \) depends only on the dimensionless quantity \( na^3 \). This leads to

\[
\omega = \sigma n\chi \int_0^\infty \int_0^\infty d\mathbf{v}_1 d\mathbf{v}_2 |\mathbf{v}_1 - \mathbf{v}_2| f(\mathbf{v}_1)f(\mathbf{v}_2). \tag{1}
\]

A change of variables from \((\mathbf{v}_1, \mathbf{v}_2)\) to \((\mathbf{v}_1, \mathbf{v}_{\text{rel}} \equiv \mathbf{v}_1 - \mathbf{v}_2)\), the absolute value of the Jacobian...
being unity, and the evenness of the velocity distribution allows us to write

$$\omega = \sigma n \chi \int d v_{\text{rel}} v_{\text{rel}} \int d v_1 f(v_1) f(v_{\text{rel}} - v_1).$$  \hspace{1cm} (2)$$

The inner integral defines the equilibrium probability density for the relative velocity, meaning that the outer integral simply computes the mean relative speed in the gas. Therefore,

$$\lambda_{\text{Maxwell}} \equiv \frac{\langle v \rangle}{\omega} = \frac{\langle v \rangle}{\langle v_{\text{rel}} \rangle} \frac{1}{\sigma n \chi}.$$ \hspace{1cm} (3)$$

A straightforward calculation shows that the ratio $\langle v \rangle / \langle v_{\text{rel}} \rangle = 1 / \sqrt{2}$ for any $d$.

The mean collision frequency $\omega$ is itself the mean of the collision rate $r(v)$ which describes the probability per unit time that a given molecule with speed $v$ undergoes a transition in phase space. In other words, the probability that a given molecule suffers a collision between time $t$ and $t + dt$ is $r(v) dt$. So

$$\omega \equiv \langle r(v) \rangle = \int d v f(v) r(v) \hspace{1cm} (4)$$

and this exposes Maxwell’s mean free path as the ratio of two averages:

$$\lambda_{\text{Maxwell}} = \frac{\langle v \rangle}{\langle r(v) \rangle}.$$ \hspace{1cm} (5)$$

It is not obvious that this ratio is the first moment of any probability distribution for free path lengths. Historically, alternative definitions for the mean free path have been suggested. Tait’s definition takes the distance that a particle of a preselected speed travels from a given instant in time until its next collision and averages over the equilibrium distribution of velocities,\textsuperscript{5}

$$\lambda_{\text{Tait}} \equiv \left\langle \frac{v}{r(v)} \right\rangle.$$ \hspace{1cm} (6)$$

Another definition, which is possible from dimensional considerations, is to first average the inverse collision rate over all velocities and multiply by the mean speed,

$$\lambda_{\text{other}} \equiv \langle v \rangle \left\langle \frac{1}{r(v)} \right\rangle.$$ \hspace{1cm} (7)$$

The detailed form of $r(v)$ is a classic result.\textsuperscript{2} Although it is not needed to understand the claim in this note, in the appendix we present a self-contained derivation for hard sphere molecules in three dimensions that does not require the formalism of scattering theory. This derivation may be of use in an undergraduate thermal physics course. It turns out that
TABLE I. Various mean free paths

| due to | $\lambda(\sigma n \chi)$ |
|--------|---------------------------|
| Maxwell | 0.7071                    |
| Tait    | 0.6775                    |
| other   | 0.7340                    |

definitions (6) and (7) differ from Maxwell’s by about 4%. See Table I. It is worth noting that if the collision rate were independent of speed, then all three definitions of the mean free path would be identical[12].

Our goal is to emphasize a point which has not been stressed in the literature: Eq. (5) can be regarded as the mean of a probability distribution for lengths of free paths. The problem of constructing such a distribution was solved by Visco, van Wijland, and Trizac[7,8]. In addition to studying the distribution analytically they verified their results with numerous computer simulations. We shall now review their construction and see how it leads almost trivially to the claim about Maxwell’s mean free path.

The goal is to find the probability $P(t)dt$ that any given molecule, after surviving a time $t$ since its last collision, suffers a collision in the interval $t$ and $t + dt$. Select a collision at random from the gas and focus attention on one of the molecules involved in that collision. Following Refs. [7] and [8] call this the “tagged” molecule. Prior to the collision the tagged molecule has maintained some constant velocity $v$ for a time $t$. The conditional probability that it has survived for at least time $t$ is $p(t|v) = \exp(-r(v)t)$; one should then multiply this by $r(v)dt$ which yields the probability that the molecule will suffer a collision during a very short time interval succeeding time $t$.

It remains to characterize how likely different velocities $v$ are for the tagged molecule. Since the tagged molecule is obtained by first identifying a collision, the probability distribution must account for the likelihood of finding a velocity in the range $v$ to $v + dv$ in any randomly selected collision. This may be understood by asking the question: In a time interval $T$, with what relative frequency do particles with velocity in the range $v_1$ to $v_1 + dv_1$ collide (with anything) compared to those particles with velocity in the range $v_2$ to $v_2 + dv_2$? The answer is

$$\frac{r(v_1)Tf(v_1)dv_1}{r(v_2)Tf(v_2)dv_2}$$

(8)
Therefore, the tagged molecule’s velocity is obtained from the probability distribution

\[ f_{\text{coll}}(v)dv \equiv \omega^{-1}r(v)f(v)dv. \] (9)

Visco et al. refer to this as the “on-collision velocity distribution.” Note that it is properly normalized. Molecules with larger-than-typical speeds collide more often than those with smaller-than-typical speeds, so in any collision one is more likely to find molecules with larger velocities than the nominal Gaussian distribution would suggest. The distribution is thus a product of a Gaussian and a weight that enhances the relative probability of finding faster particles. For example, in the appendix it is shown that for a three-dimensional hard-sphere gas the corresponding distribution in speeds has a most probable value slightly greater than that for the Maxwell speed distribution.

Sampling velocities from a Gaussian distribution would not be consistent with the requirement that the time \( t \) represents the entire time of free flight of the tagged molecule. Sampling from a Gaussian distribution means that one is choosing a particle at random at any moment in its flight rather than some moment a very short time preceding an encounter with another sphere. In the former case the time \( t \) would exclude the remaining time left on the particle’s linear path to its next collision.

The desired probability distribution for the time \( t \) of a free path is

\[ P(t)dt = \int f_{\text{coll}}(v)dv \, p(t|v) \, r(v)dt. \] (10)

By a similar construction we may obtain the probability distribution for the length \( \ell \) of a free path. \( P(\ell)d\ell \) is formed from a product of three terms: the probability that a molecule of speed \( v \) survives without collision for at least a time equal to \( t = \ell/v \), the subsequent probability to suffer a collision in a short time interval \( d\ell/v \), and the probability density to find a molecule with that speed when selected from a random collision. This must then be integrated over all possible velocities. Therefore,

\[ P(\ell)d\ell = \int f_{\text{coll}}(v)dv \, p(t = \ell/v|v) \, r(v)\frac{d\ell}{v} \]

\[ \Rightarrow P(\ell) = \omega^{-1} \int d\mathbf{v} \frac{r(v)^2}{v} f(v) e^{-r(v)\ell/v}. \] (11)

The expectation value of \( \ell \) in this distribution is easily evaluated by exchanging the order of integration: the \( \ell \)-integral evaluates to \((v/r(v))^2\) and the remaining integral defines the
mean speed in the Gaussian distribution,

\[ \int_0^\infty \ell P(\ell) d\ell = \frac{\langle v \rangle}{\omega}. \tag{12} \]

This is identical to Eq. (5).

**Appendix: Derivation of the collision rate for hard-spheres in 3 dimensions**

The hard sphere gas is a particularly clean system because collisions are instantaneous and it is unnecessary to consider simultaneous collisions of three or more spheres. We consider a gas that has attained steady state and is spatially uniform for which the H-theorem implies that the velocity distribution \( f(v) \) is independent of \( t \) and \( r \). Let our gas consist of \( N \) molecules in a box of volume \( L^3 \) at temperature \( T \). Imagine that a given molecule, labeled 1, has traveled some distance \( \ell \) between collisions. It has been moving with constant velocity \( v_1 \) so that the time spent traveling in a straight line is \( t = \ell/|v_1| \). During that time all \( N - 1 \) other molecules have passed by without making contact. Using reasoning based on excluded volume we will calculate the probability that no other molecule hits 1 during this time. In this framework it is natural to include the lowest order finite-density correction.

When two molecules collide the distance between their centers is \( 2a \). Around each molecule we may draw a concentric “associated sphere” with radius \( 2a \). A collision occurs when the center of a molecule lies on the associated sphere of another molecule. Moreover, that center can never lie within another’s associated sphere. The associated sphere construction is helpful in two respects: 

(i) it shows that the inhabitable volume for the center of molecule 1 is \( L^3 \) less the total volume taken up by the \( N - 1 \) other associated spheres;

(ii) two molecules with overlapping associated spheres shield their common area in such a way that no other molecule’s center can lie on that area.

Since we can only be certain that molecule 1 has maintained a constant velocity during time \( t \), it makes sense to use the rest frame of molecule 1 in which to evaluate the probability that other molecules miss molecule 1. It will be convenient to imagine that the center of molecule 1 occupies a single point, say, the origin of our box. During time \( t \) the associated sphere of molecule 2 sweeps out a piecewise cylindrical volume equal to \( \pi (2a)^2 |v_2 - v_1| t \). The probability that the origin is not in the swept-volume of 2’s associated sphere would
FIG. 1. The “shielding” effect. If a third molecule is sufficiently close to molecule 2, then the surface area of molecule 2’s associated sphere (dashed) which is accessible to molecule 1’s center is reduced by a dome (grayed). For further discussion on this effect see Ref. [3].

appear to be

\[ p_2 = \frac{[L^3 - \frac{4}{3} \pi (2a)^3 (N - 1)] - \sigma |v_2 - v_1| t}{L^3 - \frac{4}{3} \pi (2a)^3 (N - 1)}. \]  \hspace{1cm} (A.1)

However, due to the previously mentioned shielding effect there is a reduced likelihood of molecule 2 colliding with molecule 1 since, at any given moment, only a fraction of the surface area of molecule 2’s associated sphere is available to make contact with molecule 1’s center. See Fig. [1]. That fraction can be found as follows. The probable number of molecular centers within a range \((r, r + dr)\) of the center of any chosen molecule is \(n 4\pi r^2 dr\). Note that for a spatially uniform gas this number is independent of the positions of other molecules. Two overlapping associated spheres whose centers are separated by a distance \(2a < r < 4a\) obstruct, on either sphere, a dome with lateral area \(4\pi a(2a - r/2)\). Therefore, the probable area unavailable to a molecule is

\[ \int_{2a}^{4a} n 4\pi r^2 dr \cdot 4\pi a(2a - r/2) = \frac{11}{3} \pi^2 (2a)^5 n. \]  \hspace{1cm} (A.2)

The available fractional area of molecule 2’s associated sphere which can collide with molecule 1’s center is thus

\[ \frac{4\pi (2a)^2 - \frac{11}{3} \pi^2 (2a)^5 n}{4\pi (2a)^2} = 1 - \frac{11}{12} \pi (2a)^3 n. \]  \hspace{1cm} (A.3)

Expression (A.3) must multiply the swept-volume of molecule 2’s associated sphere. As a check, if expression (A.3) is zero then there is unit probability that the origin lies outside...
the swept-volume. The correct modification of expression (A.1) is therefore

\[
p_2 = \left[ \frac{L^3 - \frac{4}{3} \pi (2a)^3 (N - 1)}{L^3 - \frac{4}{3} \pi (2a)^3 (N - 1)} \right] - \left[ \frac{\sigma |v_2 - v_1| t}{1 - \frac{11}{12} \pi (2a)^3 N} \right]
\]

\[
= 1 - \frac{\sigma n \chi |v_2 - v_1| \ell / |v_1|}{N}, \tag{A.4}
\]

where

\[
\chi \equiv \frac{1 - \frac{11}{12} \pi (2a)^3 n}{1 - \frac{4}{3} \pi (2a)^3 (n - L^{-3})} = 1 + \frac{5}{12} \pi (2a)^3 n + o(n^2). \tag{A.5}
\]

We see that effect (i) tends to increase the probability of collisions whereas effect (ii) tends to decrease it.

A similar argument can be made concerning the probability \( p_3 \) that the swept-volume of molecule 3’s associated sphere does not contain the origin. We assume the probabilities \( p_2, p_3, \) etc. to be independent, however this does not preclude the \( N - 1 \) particles from interacting with each other during time \( t \); their collisions will inevitably “kink” each other’s cylinders. The probability that none of the \( N - 1 \) associated spheres hits molecule 1’s center during this time is given by the product of the individual probabilities:

\[
p(\ell | v_1) = \prod_{i=2}^{N} p_i = \prod_{i=2}^{N} \left[ 1 - \frac{\sigma n \chi |v_i - v_1| / |v_1| \ell}{N} \right]. \tag{A.6}
\]

In this product the values of \( v_i \) are obtained from the equilibrium velocity distribution. One way to estimate this product is to discretize the velocity distribution into a finite number of bins and assign to each \( v_i \) a particular value representative of a bin. In the \( j \)th bin there will be \( N f(v_j) d^3 v_j \) particles. Thus,

\[
p(\ell | v_1) = \prod_{\text{bins}} \left[ 1 - \frac{\sigma n \chi |v_j - v_1| / |v_1| \ell}{N} \right]^{N f(v_j) d^3 v_j}
\]

\[
= \exp \sum_{j} -\sigma n \chi \ell \frac{|v_j - v_1|}{|v_1|} f(v_j) d^3 v_j
\]

\[
= \exp \left[ -\frac{\sigma n \chi \ell}{|v_1|} \int d^3 v f(v) |v - v_1| \right]. \tag{A.7}
\]

In the second step we took the limit of large \( N \) (and large volume so as to keep the concentration fixed and small compared to 1) and in the third step the sum was generalized to a continuous integral over all possible velocities. The collision rate is found by comparing Eq. (A.7) with \( p(t|v_1) = \exp(-r(v_1) \ell / |v_1|) \). We obtain

\[
r(v_1) = \sigma n \chi \int d^3 v f(v) |v - v_1|. \tag{A.8}
\]
The integral can be done by orienting the $z$-axis along $v_1$ so that the length of the difference vector $v - v_1$ may be computed from the law of cosines as $\sqrt{v^2 + v_1^2 - 2vv_1 \cos \theta}$, where $\theta$ is the polar angle. Doing the angular and radial integrations in order produces

$$r(v_1) = \sigma n \chi \sqrt{\frac{2}{\pi}} \int_0^\infty dv' v'^2 e^{-\frac{1}{2}v'^2} \times \begin{cases} v + \frac{v_1^2}{3v} & v > v_1, \\ v_1 + \frac{v_1^2}{3v_1} & v < v_1, \end{cases}$$

$$= \sigma n \chi \left[ \sqrt{\frac{2}{\pi}} \exp\left(\frac{-v_1^2}{2}\right) + (v_1 + v_1^{-1}) \operatorname{erf}\left(\frac{v_1}{\sqrt{2}}\right) \right]. \quad (A.9)$$

The collision rate is finite as $v_1 \to 0$, monotone increasing, and behaves asymptotically as $r(v_1) \sim v_1 + o(1/v_1)$. The mean collision rate is $\omega = \langle r(v) \rangle = \frac{1}{\sqrt{\pi}} \sigma n \chi$.

The distribution in terms of speed, $f_{\text{coll}}(v)4\pi v^2 dv$, is independent of the molecular size and density of the gas. The mean speed is $(3 + \pi)/(2\sqrt{\pi}) \approx 1.7325$ and the most probable speed is found numerically to be 1.5769. These may be contrasted with the corresponding values $\sqrt{8/\pi} \approx 1.5958$ and $\sqrt{2} \approx 1.4142$, respectively, for the Maxwell speed distribution. These two speed distributions are plotted in Fig. 2.

![FIG. 2. Different types of probability density functions for speeds. The dashed curve represents the Maxwellian probability density for randomly picking a molecule with speed $v$ from the gas. It is given by $4\pi v^2 f(v)$. The solid curve represents the probability density for finding a molecule with incoming speed $v$ when a collision is examined at random. It is given by $4\pi v^2 f_{\text{coll}}(v)$.](image)

The free path length distribution given in Eq. (11), when appropriately normalized, may be expressed in terms of a scaling function,

$$\lambda_{\text{Maxwell}} P(\ell/\lambda_{\text{Maxwell}}) = F(\ell/\lambda_{\text{Maxwell}}), \quad (A.10)$$
where

\[ F(x) \equiv \frac{1}{\pi} \int_0^\infty \frac{dv}{v} \psi(v)^2 \exp \left[ -v^2 - \frac{1}{\sqrt{2\pi}} v^{-2} \psi(v)x \right], \quad \psi(v) \equiv ve^{-v^2} + (2v^2 + 1) \int_0^v e^{-t^2} dt. \]

(A.11)

The scaling function \( F \) does not depend on any dimensionless parameters other than its argument which is the ratio of the free path length and the mean free path.\(^{13}\) A plot of \( \ln F \) is shown in Fig. 3. Further discussion of the distribution may be found in the original Refs. \(^7\) and \(^8\).

![Graph showing the scaling function for the free path length density. The solid curve is \( \ln F(x) \). For comparison the dashed curve is a straight line with negative unit slope. The free path length density is not quite exponential.](image)

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1 Frederick Reif, *Fundamentals of Statistical and Thermal Physics* (Waveland, 2008), pp. 463–471.
2 Sydney Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge, 1970), pp. 297–300.
The statistical origin of $\chi$ is the pair distribution function $g$ which encodes the probability of finding a particular arrangement with two particles singled out. In P. M. Chaikin and T. C. Lubensky, *Principles of condensed matter physics* (Cambridge, 1995), pp. 34–38, this function is defined by

$$\langle n(x_1) \rangle g(x_1, x_2) \langle n(x_2) \rangle \equiv \langle \sum_{i \neq j} \delta(x_1 - x_i) \delta(x_2 - x_j) \rangle$$

which represents the probability to simultaneously find a molecular center in a volume element $dx_1$ about $x_1$ and a different molecular center in a volume element $dx_2$ about $x_2$. Here $n(x)$ is the number density operator, the sums go over all particles, and $\langle \ldots \rangle$ is the average over the ensemble of permitted configurations of the spheres. For the hard-sphere model,

$$\langle n(x_1) \rangle g(x_1, x_2) \langle n(x_2) \rangle = \frac{N(N-1) \int dx_3 \ldots dx_N \ e^{-\beta \Phi}}{\int dx_1 \ldots dx_N \ e^{-\beta \Phi}},$$

where the potential energy $\Phi(x_1, \ldots, x_N)$ is infinite if any $|x_i - x_j| < 2a$ and zero otherwise.

For a uniform gas translational and rotational invariance implies that the pair distribution function depends only on the norm of the difference vector $x \equiv x_1 - x_2$. It is shown that $ng(|x|) = \langle \sum_{i \neq 1} \delta(x - x_i) \rangle$ in which it is understood that the first molecule’s center position arbitrarily serves as the origin. From this relation it is clear that $ng(|x|)$ integrated over a thin spherical shell of volume $|x|^{d-1}d|x|d\Omega$ is simply the number of molecular centers lying within that shell. Therefore, $ng(|x|)$ is a local density of molecular centers at radial separation $|x|$. We identify the correction factor $\chi$ with the limit $g(|x|)$ as $|x|$ approaches $2a$ from above. Also note that the assumption of molecular chaos guarantees that the correction factor $\chi$ is independent of velocity.

J. H. Jeans, *The Dynamical Theory of Gases* (Cambridge, 1904), pp. 229–241.

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Paolo Visco, Frédéric van Wijland, and Emmanuel Trizac, “Collisional statistics of the hard-sphere gas,” Phys. Rev. E 77, 041117 (2008).

A similar reasoning is used to obtain the molecular speed distribution of a hot gas effusing through a small hole in an oven. Recall that the Maxwell speed distribution is weighted by an additional factor of the speed reflecting the fact that faster molecules bombard the hole with
greater frequency than slower molecules. That relative frequency is the ratio of their speeds.

This is an approximation based on the observation that the number of overlapping associated spheres in a dilute gas is small compared to the total number of spheres. In order to correct for the possibility of overlap we note that the probable number of molecules close enough to any given molecule for their associated spheres to overlap is proportional to \( n \). Therefore, the probable excluded volume on any molecule scales as \( n \). And there are order \( N \) molecules. Thus, the overlap correction appears at \( o(n^2) \) in the factor \( \chi \).

It is unnecessary to include contributions to the volume from the hemispherical endcaps. This is accounted for when we reduce the amount of inhabitable volume of molecule 1 due to the volumes of the other molecules.

This expression might also be expected to receive finite-density corrections. However, using the expression as written is sufficient to calculate \( \chi \) to \( o(n) \) accuracy.

T. Einwohner and B. J. Alder, “Molecular Dynamics. VI. Free-Path Distributions and Collision Rates for Hard-Sphere and Square-Well Molecules.” J. Chem. Phys. 49, 1458–1473 (1968).