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The mean free time and the mean free path: exact expressions for an (approximately) ideal gas

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Abstract The order of magnitudes for the mean free time and the mean free path corresponding to classical (nearly) ideal gases are easy to estimate. The exact values, however, are a little trickier to calculate. To do so, more careful definitions are needed, and one should carefully calculate averages of functions of particle velocities. These are done, and compared with the simpler less-accurate results which are usually used.

1 Introduction

The mean free time τ is the average of the time between two consecutive collisions of a particle. The mean free path λ is the average of the distance traveled by a particle between two consecutive collisions of that particle. In (nearly) ideal gases, the mean free path affects the transport phenomena like diffusion, thermal conductivity, viscosity, electric conductivity, etc, in a simple manner: The corresponding coefficients in all of these are proportional to the mean free path [1–6]. The mean free time and mean free path also appear in the criterion determining whether the wave propagation in a gas is adiabatic or isothermal [7, 8]. The wave propagation is adiabatic (isothermal), if the frequency is much smaller (larger) than the inverse of the mean free time; equivalently, if the wavelength is much larger (smaller) than the mean free path.

The quantities which are expected to determine τ and λ are the number density n, the cross section σ, and a typical velocity w. Based on these, a dimensional analysis can be used to estimate the mean free time and the mean free path:

$$\tau = \frac{c_1}{n\,\sigma\,w}. \tag{1}$$

$$\lambda = \frac{c_2}{n\,\sigma}. \tag{2}$$

c_1 and c_2 are dimensionless constants of order one. It remains to choose (determine) w, and calculate c_1 and c_2. Of course w and c_1 are not independent of each other. One could choose one and calculate the other.

It is easy to calculate the order of these: One takes w equal to $\langle|\boldsymbol{v}|\rangle$ (the average of the length of a particle's velocity), and c_1 and c_2 equal to 1:

$$\tau = \frac{1}{n\,\sigma\,\langle|\boldsymbol{v}|\rangle}. \tag{3}$$

$$\lambda = \frac{1}{n\,\sigma}. \tag{4}$$

This is the result presented in [9] (as an estimation). A more careful study, which distinguishes between the velocity of a particle and the velocity of a particle relative to another particle, with the same value for w results in c_1 and c_2 equal to $(1/\sqrt{2})$:

$$\tau = \frac{1}{\sqrt{2}\,n\,\sigma\,\langle|\boldsymbol{v}|\rangle}. \tag{5}$$

$$\lambda = \frac{1}{\sqrt{2}\,n\,\sigma}. \tag{6}$$

This is done in [10, 11]. These expressions, as shown later, are a result of an approximation of the average of a function with that function of the average. In general, the average of a function is not equal to that function of the average, [12]:

$$\langle f(x)\rangle \neq f(\langle x\rangle). \tag{7}$$

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But sometimes the approximation is a good one.

The coefficients corresponding to the transport phenomena have been extensively studied, both theoretically and experimentally. Diffusion constant has been studied in [13–15], for example. [16–18] are among the references which have investigated thermal conductivity and its coefficient. In [19–21], among others, some topics related to the viscosity and its coefficient are addressed. Some problems regarding electric conductivity are discussed, for example, in [22–24].

Although the mean free path enters the coefficients corresponding to transport phenomena (this coefficients are proportional to the mean free path), its exact expression is rarely studied on its own. It is customary to discuss different transport phenomena separately, as the proportionality constants relating various transport phenomena to the mean free path are not the same. And in such studies, the whole coefficient is obtained directly, without explicitly addressing the mean free path. As a result, producing order-of-magnitude results for the mean free path and mean free time doesn't harm the final exact results for the coefficients corresponding to transport phenomena.

A similar case happens when the Drude model for electric conduction in solids is presented: a simplified approach, in which essentially the average of the square is replaced by the square of the average, results in an expression for the drift velocity which differs from the exact one by a factor of (1/2): the simplified approach leads to

$$v_{\mathrm{D}} = \frac{q\,\tau}{2\,m}\,E. \tag{8}$$

Where q and m are the change and mass of the charge carrier, respectively, while E is the applied electric field. The exact result (given in [25], for example) is

$$v_{\mathrm{D}} = \frac{q\,\tau}{m}\,E. \tag{9}$$

Here too, people usually calculate or measure the drift velocity (or the mobility) directly. So the factor of (1/2) doesn't affect the resulted conductivity. This factor is important, if the above relations are used to obtain the mean free time.

Although the direct approach to calculate or measure the coefficients corresponding to transport phenomena doesn't need exact values for the mean free path or mean free time, these quantities by themselves could be important (interesting). Here the aim is to calculate the mean free path and mean free time for an (approximately) ideal gas, and discuss the effect of simplifications on the dimensionless factors of order one appearing in the relevant expressions.

The scheme of the paper is as follows. In Sect. 2, a general setup is introduced to calculate the mean free time and the mean free path. In Sect. 3, this is applied to a simple model of a particle moving with a constant velocity colliding with particles at rest. In Sect. 4, this model is improved in the sense that the target particles are also assumed to be moving, still with a fixed velocity. In Sect. 5 a realistic model is studied, in which all the particles move, with random velocities, and the exact results are obtained. Section 6 presents a discussion, on the differences of the exact results and the approximate ones (which are still correct, up to order of magnitude), and the origin of such differences.

2 The general framework

During the time t, a particle makes $N(t)$ collisions and moves a distance $L(t)$. $N(t)$ and $L(t)$, are in general random. The mean free time and the mean free path are

$$\tau = \left\langle \frac{t}{N(t)} \right\rangle. \tag{10}$$

$$\lambda = \left\langle \frac{L(t)}{N(t)} \right\rangle. \tag{11}$$

where $\langle X \rangle$ is the average of X.

3 Target particles at rest

Suppose that one particle is moving with the (constant) velocity $\boldsymbol{v}$. Then,

$$L(t) = t\,|\boldsymbol{v}|. \tag{12}$$

Suppose that, in addition, all other particles are at rest. Then, during the time t the particle collides with all particles which are inside a cylinder of height equal to $L(t)$ and the base surface area equal to σ. Hence,

$$N(t) = n\,\sigma\,L(t). \tag{13}$$

In this simplified model, one arrives at

$$\tau = \frac{1}{n\,\sigma\,|\boldsymbol{v}|}. \tag{14}$$

$$\lambda = \frac{1}{n\,\sigma}. \tag{15}$$

In fact, to arrive at these it is sufficient that $|\boldsymbol{v}|$ be constant (and all other particles be at rest). It is seen that in this simplified model,

$$\lambda = |\boldsymbol{v}|\,\tau. \tag{16}$$

4 Moving target particles: fixed velocities

A more realistic model is that the target particles are not at rest. Then a simplified model is that the colliding particle is moving with the constant velocity $\boldsymbol{v}_1$, while the target particles are moving with the constant velocity $\boldsymbol{v}_2$. So the velocity of the colliding particle relative to a target particle is $\boldsymbol{v}_{\mathrm{rel}}$:

$$\boldsymbol{v}_{\mathrm{rel}} = \boldsymbol{v}_1 - \boldsymbol{v}_2. \tag{17}$$

Equation (12) is repeated, with $\boldsymbol{v}_1$ replacing $\boldsymbol{v}$:

$$L(t) = t\,|\boldsymbol{v}_1|. \tag{18}$$

To arrive at the analog of the Eq. (13), one could write things in the rest frame of the target particles. In that frame, the velocity of the colliding particle is $\boldsymbol{v}_{\mathrm{rel}}$. So the analog of the Eq. (13) is the same as (13), with L replaced by L_{rel} (the distance travelled by the colliding particle in the rest frame of the target particles):

$$L_{\mathrm{rel}}(t) = t\,|\boldsymbol{v}_{\mathrm{rel}}|. \tag{19}$$

$$N(t) = n\,\sigma\,L_{\mathrm{rel}}(t). \tag{20}$$

One then arrives at

$$\tau = \frac{1}{n\,\sigma\,|\boldsymbol{v}_{\mathrm{rel}}|}. \tag{21}$$

$$\lambda = \frac{|\boldsymbol{v}_1|}{n\,\sigma\,|\boldsymbol{v}_{\mathrm{rel}}|}. \tag{22}$$

That is,

$$\tau = \frac{1}{n\,\sigma\,|\boldsymbol{v}_1 - \boldsymbol{v}_2|}. \tag{23}$$

$$\lambda = \frac{|\boldsymbol{v}_1|}{n\,\sigma\,|\boldsymbol{v}_1 - \boldsymbol{v}_2|}. \tag{24}$$

It is also seen that

$$\lambda = |\boldsymbol{v}_1|\,\tau. \tag{25}$$

Equations (23) and (24) are to be compared with (14) and (15), respectively. (23) is essentially the same as (14), with $\boldsymbol{v}$ replaced by $\boldsymbol{v}_{\mathrm{rel}}$. But (24) contains two velocities: $\boldsymbol{v}_{\mathrm{rel}}$, which affects the collision frequency; and $\boldsymbol{v}_1$, (the length of) which is the distance rate in the lab frame. These two are in general different, hence they are not canceled in the ratio appearing in the right-hand side of (24); unless, of course, the target particles are at rest, which is the model discussed in the previous section.

5 The realistic model

The model introduced in the above section, still is not realistic. In that, it is assumed that the velocity of the colliding particle is different from that of the target particles. This is not plausible: The identifiers *colliding* and *target* are just labels. It is expected that all particles behave the same. In particular, it is not plausible that the velocity of the colliding particle be different from that of the target particles. But if the velocities are taken to be equal, another problem arises: There would be no collision at all. The mean free time and mean free path become infinite. Moreover, the very assumption that the velocity of a particle is constant, is not realistic. The velocity of a particle changes, as a result of collisions with other particles and container boundaries.

Both of these points are addressed in the realistic model, in which the velocities are not constant, and while the velocities of different particles are not necessarily the same, the velocity distributions for different particles are the same. One still uses Eqs. (17) to (20) to define $L(t)$ and $N(t)$. But these are put in the Eqs. (10) and (11) to obtain the mean free time and mean free path.

$$\tau = \frac{1}{n\,\sigma}\left\langle\frac{1}{|\boldsymbol{v}_{\rm rel}|}\right\rangle. \tag{26}$$

$$\lambda = \frac{1}{n\,\sigma}\left\langle\frac{|\boldsymbol{v}_1|}{|\boldsymbol{v}_{\rm rel}|}\right\rangle. \tag{27}$$

The above averages are time-averages. These are substituted with ensemble averages, or averages over particles. To calculate such averages, the probability distribution for particles' velocities are needed:

$$\langle f(\boldsymbol{v}_1,\boldsymbol{v}_2)\rangle = \int (\mathrm{d}^3\,\boldsymbol{u}_1)\,(\mathrm{d}^3\,\boldsymbol{u}_2)\,\rho_{1\,2}(\boldsymbol{u}_1,\boldsymbol{u}_2)\,f(\boldsymbol{u}_1,\boldsymbol{u}_2). \tag{28}$$

Where $\rho_{1\,2}$ is the probability density for the velocities of the particles 1 and 2. The probability density for the velocity of a particle is the same for all particles, and is denoted by ρ. The velocities of two particles are independent of each other. So the two-particle probability density is related to the one-particle probability density through

$$\rho_{1\,2}(\boldsymbol{u}_1,\boldsymbol{u}_2) = \rho(\boldsymbol{u}_1)\,\rho(\boldsymbol{u}_2). \tag{29}$$

For the one-particle probability density ρ, the Maxwell–Boltzman function is used, [26]:

$$\rho(\boldsymbol{u}) = \left(\frac{m}{2\,\pi\,k_{\rm B}\,T}\right)^{3/2}\exp\left(-\frac{m\,\boldsymbol{u}\cdot\boldsymbol{u}}{2\,k_{\rm B}\,T}\right). \tag{30}$$

where m is the mass of a particle, $k_{\rm B}$ is the Boltzmann constant, and T is the (absolute) temperature.

Putting the probability density in (26) and (27), one arrives at

$$\tau = \frac{1}{\sqrt{\pi}}\,\frac{1}{n\,\sigma}\,\sqrt{\frac{m}{k_{\rm B}\,T}}. \tag{31}$$

$$\lambda = \left(\frac{1}{2}+\frac{1}{\pi}\right)\frac{1}{n\,\sigma}. \tag{32}$$

6 Discussion

The exact results (31) and (32) are, as expected, in the form of (1) and (2); with

$$w = \sqrt{\frac{k_{\rm B}\,T}{m}}. \tag{33}$$

$$c_1 = \frac{1}{\sqrt{\pi}}. \tag{34}$$

$$c_2 = \frac{1}{2}+\frac{1}{\pi}. \tag{35}$$

Of course (33) is only one choice for w, and c_1 depends on this choice. Specifically, the choice (33) is *not* the same as choosing w equal to $\langle|\boldsymbol{v}|\rangle$:

$$\langle|\boldsymbol{v}|\rangle = \sqrt{\frac{8}{\pi}}\,\sqrt{\frac{k_{\rm B}\,T}{m}}. \tag{36}$$

It is usual to use expressions for τ and λ, which are simpler that those used in (26) and (27). Examples are

$$\tilde{\tau} = \frac{1}{n\,\sigma}\,\frac{1}{\langle|\boldsymbol{v}_{\rm rel}|\rangle}. \tag{37}$$

$$\lambda' = \frac{1}{n\,\sigma}\,\langle|\boldsymbol{v}_1|\rangle\left\langle\frac{1}{|\boldsymbol{v}_{\rm rel}|}\right\rangle. \tag{38}$$

$$\tilde{\lambda}' = \frac{1}{n\,\sigma}\,\frac{\langle|\boldsymbol{v}_1|\rangle}{\langle|\boldsymbol{v}_{\rm rel}|\rangle}. \tag{39}$$

These are not equal to the exact values. The reason is that in general the average of a function is not equal to that function of the average:

$$\langle f(\boldsymbol{v}_1,\boldsymbol{v}_2)\rangle \neq f(\langle\boldsymbol{v}_1\rangle,\langle\boldsymbol{v}_2\rangle). \tag{40}$$

The expressions (37) to (39) result in

$$\tilde{\tau} = \frac{\sqrt{\pi}}{4}\,\frac{1}{n\,\sigma}\,\sqrt{\frac{m}{k_{\mathrm{B}}\,T}}. \tag{41}$$

$$\lambda' = \frac{\sqrt{8}}{\pi}\,\frac{1}{n\,\sigma}. \tag{42}$$

$$\tilde{\lambda}' = \frac{1}{\sqrt{2}}\,\frac{1}{n\,\sigma}. \tag{43}$$

An even simpler choice is to use (14) and (15), but with $|\boldsymbol{v}|$ replaced by its average (the average of the length of a particle's velocity):

$$\tau'' = \frac{1}{n\,\sigma}\,\frac{1}{\langle|\boldsymbol{v}|\rangle}. \tag{44}$$

$$\lambda'' = \frac{1}{n\,\sigma}. \tag{45}$$

Equation (44) results in

$$\tau'' = \sqrt{\frac{\pi}{8}}\,\frac{1}{n\,\sigma}\,\sqrt{\frac{m}{k_{\mathrm{B}}\,T}}. \tag{46}$$

All of these, equations (41) to (43), and (45) and (46), are of course in the form of Eqs. (1) and (2); and are of the same order of the exact results (31) and (32): They differ from the exact results only in dimensionless constants of order one. So for order-of-magnitude calculations, one can use these approximate results, even the simplest ones (45) and (46). But for the exact results, taking care of correct averaging is needed, namely (40).

As previously mentioned, these dimensionless factors of order one which enter the exact expressions for the mean free path and mean free time, don't affect the expression obtained for the coefficients corresponding to transport phenomena, as long as these coefficients are obtained directly. But considering the mean free path and mean free time as important quantities by themselves, those dimensionless factors have to be taken into account.

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Data availability Data sharing not applicable to this article as no data sets were generated or analysed during the current study.

Declarations

Conflict of interest The author reports there are no competing interests to declare.

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