# RELAXATION OF TRANSLATIONAL ENERGY
# IN PERPENDICULAR DIRECTIONS
# FOR RIGID SPHERICAL MOLECULES

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The relaxation time $\tau$ necessary for the equilibration of translational energy in perpendicular directions for the Rigid Spheres Model is shown to be $\tau = \dfrac{3}{8}\dfrac{1}{n\sigma^2}\left(\dfrac{m}{\pi kT}\right)^{\frac{1}{2}}$, where $n$, $m$, $\sigma$, $k$, $T$ denote the number density, the molecular mass and diameter, the Boltzmann constant, and temperature, respectively. The average number of collisions during the relaxation time is $Z = 3/4$. This quantity, which is shown to be a good measure for self-relaxation of translational energy, can be greater for more complicated models; especially $Z$ can be increased even nearly by a factor of two if a simultaneous process of quick rotational relaxation occurs.

## 1. Introduction

In some transport processes in binary mixtures of dilute gases, e.g. the propagation of strong shock waves, four temperatures are introduced (two different temperatures in perpendicular directions for both of the components separately) [1–3]; in this case the analysis of the shock wave structure is more accurate. The process of equilibration of translational energy is so quick that the width of a region in which it takes place is equal to about two mean free paths [4].

The relaxation process of translational equilibration has been already analyzed very extensively, however, only for the equilibration of two components (also electrically charged components [5]) having two temperatures [6–8]. Very simple equations for the relaxation time have been already derived [9, 10].

However, a direct analysis of the process of relaxation of translational kinetic energy in perpendicular directions, which can give an additional explanation for the phenomena

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discussed [1–4], has not so far been performed even for a one component system. The aim of this paper is to perform such an analysis, to determine the relaxation time, and to show how many collisions are necessary for the occurrence of translational equilibration.

## 2. Introductory definitions

We define the relaxation time $\tau$ by the formula

$$\frac{d\langle E_{\parallel}\rangle}{dt} = -\frac{1}{\tau}\langle E_{\parallel} - \tfrac{1}{2}E_{\perp}\rangle, \tag{1}$$

where $t$ is the time, $E_{\parallel}$ and $E_{\perp}$ denote the translational kinetic energies in the perpendicular directions discussed and the brackets are used for the averaging operations described in Section 4. It is also possible to write such an equation for temperatures instead of average energies. However, because it is sufficient to carry out our further derivations for the average energies (which always exist in contrast to various temperatures) we do not discuss temperatures here.

In Eq. (1) the relaxation time does not depend on the values of energies. That is why in order to simplify calculations it is convenient to analyze this equation for the condition in which

$$\langle (E_{\perp})_0 \rangle = 0, \tag{2}$$

where the index 0 is used to denote this condition. We would like to emphasize that from the physical point of view, Eq. (2) can be treated as a very rough approximation because even at the very beginning of the relaxation process discussed, $E_{\perp}$ can be much smaller than $E_{\parallel}$ but it is never equal to zero. This mathematical condition (2) which can be introduced because of the convenient mathematical property of Eq. (1) will be used in further calculations.

From Eqs. (1) and (2) we obtain the expression for the relaxation time

$$\tau = -\frac{\langle (E_{\parallel})_0 \rangle}{\dfrac{d\langle (E_{\parallel})_0 \rangle}{dt}}. \tag{3}$$

We define the collision number $Z$ as the number of collisions during the relaxation time. Then we have

$$Z = \tau \frac{N}{n}, \tag{4}$$

where $n$ is the number density and $N/n$ is the average number of collisions of any one molecule per unit time. In order to calculate $\tau$ and $Z$ we first discuss the collision equations.

## 3. Collision equations

Here, we shall analyze collisions between molecules which are rigid spheres characterized by molecular mass $m$ and the molecular diameter $\sigma$. Figure 1 shows a collision between such molecules. The spheres with the centres $O_1$ and $O_2$ collide at the point P. During
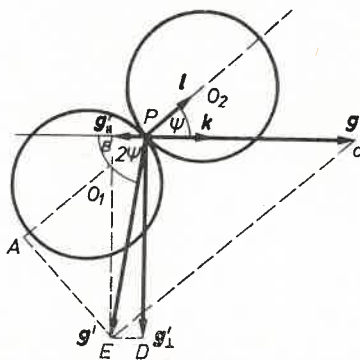


Fig. 1

a collision the velocities of both spheres change from $c_1$ and $c_2$ to $c_1'$ and $c_2'$, respectively. For the spheres which collide as smooth and elastic bodies we have [11]

$$c_1' = c_1 + ll \cdot (c_2 - c_1)$$
$$c_2' = c_2 - ll \cdot (c_2 - c_1), \tag{5}$$

where $l$ is a unit vector in the direction of the line from the centre of molecule 1 to that of molecule 2. For calculating changes in kinetic translational energies of molecules it is convenient to introduce the relative velocities

$$g = c_1 - c_2$$
$$g' = c_1' - c_2'. \tag{6}$$

Then, the collision equation can be simply written as

$$g' = g - 2ll \cdot g. \tag{7}$$

According to the condition (2) the molecules move in one direction before the collision. This direction given by the unit vector $k$ associated with the line $PC$ is denoted by the index $\|$.

From Eq. (7) after taking into consideration that

$$g_\| = kk \cdot g = g$$
$$g_\|' = kk \cdot g' \qquad , \tag{8}$$

we obtain a collision equation for this direction

$$g_\|' = kk \cdot (1 - 2ll) \cdot g, \tag{9}$$

where $\underset{\sim}{1}$ is the unit tensor. From Fig. 1 it can be easily seen that

$$g = g_{\parallel} = \text{PC}; \ g_{\perp} = 0$$
$$g' = \text{PE}; \ g'_{\parallel} = \text{PB}; \ g'_{\perp} = \text{PD}$$
$$-ll \cdot g = \text{PA} = \tfrac{1}{2}(\text{CE}), \tag{10}$$

and

$$k \cdot l = \cos \psi. \tag{11}$$

Thus Eq. (9) can be simply written as

$$g'_{\parallel} = -g \cos 2\psi. \tag{12}$$

This collision equation will be used in the final calculations given in the next section.

### 4. Collision frequency, relaxation time and collision number

In order to use Eq. (3) we write

$$\langle (E_{\parallel})_0 \rangle = \int_{-\infty}^{+\infty} (E_{\parallel})_0 f(c) dc, \tag{13}$$

where $f(c)$ is a distribution function. For the rate of change of the average energy we write

$$\frac{d\langle (E_{\parallel})_0 \rangle}{dt} = \int_{-\infty}^{+\infty} \int_0^{\frac{\pi}{2}} (E'_{\parallel} - (E_{\parallel})_0) \tfrac{1}{2} N(g, \psi) dg d\psi, \tag{14}$$

where $\tfrac{1}{2} N(g, \psi) \, dg \, d\psi$ is the number of collisions for which the relative velocity of molecules $g$ and the angle $\psi$ lie in the ranges $g, dg$ and $\psi, d\psi$, respectively. The energies given in Eqs. (13) and (14) are

$$(E_{\parallel})_0 = \tfrac{1}{2} mc^2, \quad E'_{\parallel} = \tfrac{1}{2} m(c'_{\parallel})^2. \tag{15}$$

After taking into account that the energy differences do not depend on the frame of reference and by using Eq. (12) we have

$$E'_{\parallel} - (E_{\parallel})_0 = \frac{m}{2} [(c'_{\parallel})^2 - c^2] = \frac{m}{2} [(g'_{\parallel})^2 - g^2] = \frac{m}{2} g^2 (\cos^2 2\psi - 1). \tag{16}$$

In order to perform further calculation, it is necessary to make certain assumptions about the distribution function. We assume it to be a Maxwellian one. Then for condition (2) we have the following Maxwellian distribution in the direction $\parallel$ [12]

$$f(c)dc = n \left( \frac{m}{2\pi kT} \right)^{\frac{1}{2}} \exp \left( -\frac{mc^2}{2kT} \right) dc, \tag{17}$$

where $k$ denotes the Boltzmann constant and $T$ temperature. For the sake of simplicity the indices $||$ are omitted here and in some further expressions. Then from integrating of Eqs. (13) and (15) we get simply

$$\langle (E_{||})_0 \rangle = \tfrac{1}{2} nkT. \tag{18}$$

To perform the calculations connected with the collision frequency we have to take into account that [13]

$$N(\boldsymbol{g}, \psi)dgd\psi = \int\limits_{-\infty}^{+\infty} [N(\boldsymbol{G}, \boldsymbol{g}, \psi)dgd\psi]d\boldsymbol{G}, \tag{19}$$

where

$$\boldsymbol{G} = \tfrac{1}{2}(\boldsymbol{c}_1 + \boldsymbol{c}_2) \tag{20}$$

and

$$N(\boldsymbol{G}, \boldsymbol{g}, \psi)d\boldsymbol{G}dgd\psi = N(\boldsymbol{c}_1, \boldsymbol{c}_2, \psi)d\boldsymbol{c}_1 d\boldsymbol{c}_2 d\psi$$

$$= f_1(\boldsymbol{c}_1)f_2(\boldsymbol{c}_2)\boldsymbol{g}\, 2\pi\sigma^2 \sin\psi \cos\psi d\boldsymbol{c}_1 d\boldsymbol{c}_2 d\psi, \tag{21}$$

where the distribution functions of the colliding molecules 1 and 2 are Maxwellian as in Eq. (17). From Eqs. (19), (21), and (17) after taking into consideration that for the transformations (6) and (20) the Jacobian is equal to unity we get

$$N(\boldsymbol{g}, \psi)dgd\psi = \tfrac{1}{2} n^2\sigma^2 \left(\frac{\pi m}{kT}\right)^{\frac{1}{2}} \boldsymbol{g} \exp\left(-\frac{mg^2}{4kT}\right) \sin 2\psi dgd\psi. \tag{22}$$

This quantity is necessary for the final integration of Eq. (14) and it also permits one to calculate $N$ from Eq. (4) because

$$N = 2 \int\limits_{0}^{+\infty} \int\limits_{0}^{\frac{\pi}{2}} N(\boldsymbol{g}, \psi)dgd\psi = 2n^2\sigma^2 \left(\frac{\pi kT}{m}\right)^{\frac{1}{2}}. \tag{23}$$

We have multiplied this integral by two because in the integration of Eq. (22) we have the odd function of $\boldsymbol{g}$ which here gives the same amount of collisions for the negative and positive relative velocities. It should be emphasized that the quantity $N$ calculated in Eq. (23) is connected with the artificial state in which the condition described by Eq. (2) is fulfilled and that $N$ is not equal to the quantity $N_{11}$ usually discussed (cf. Eq. (5.21,1) from Ref. [13]).

The relaxation time can be calculated from Eq. (3), after taking into consideration Eqs. (18) and (14). The integration of Eq. (14) can be easily performed when using Eqs. (16) and (22). Then we get for the relaxation time

$$\tau = \tfrac{3}{8} \frac{1}{n\sigma^2} \left(\frac{m}{\pi kT}\right)^{\frac{1}{2}}. \tag{24}$$

Then from Eqs. (4), (23), and (24) we obtain for the collision number

$$Z = \tfrac{3}{4}. \tag{25}$$

Thus we see that the relaxation time and collision number for the process of equilibration of kinetic translational energy in the perpendicular directions for the molecules described by the model of rigid elastic smooth spheres are rather small quantities.

## 5. Discussion

We see that $Z = 3/4$ is a very small quantity because for the other relaxation processes it is greater. The collision number for vibrational relaxation $Z_{vib}$ can be of an order of magnitude $10^3$–$10^4$ and for rotational relaxation (except $H_2$ at low temperatures where $Z_{rot}$ can be equal to 200) $Z_{rot}$ is in general larger than 2 and its order of magnitude is very often $10^1$ [4, 6].

It is interesting to compare the collision numbers of various relaxation processes with the collision number of the most common processes which appear whenever any temperature fluctuation in the system exist, namely with the self-relaxation of translational energy. The equilibration of translational kinetic energy in the perpendicular direction analyzed here is an example of such a self-relaxation. But when discussing self-relaxation it is necessary to consider also the other process, namely the equilibration of two different translational kinetic energies associated with two gaseous components of a binary mixture, and then to seek for the limiting value of the collision number in the case in which the molecular parameters of both the components are not to be distinguished. It can be easily calculated from the formula given for rigid spheres by Malkin [10] that the collision number for this self-relaxation process is equal to 3/4 too. Thus the collision number $Z = 3/4$ characterizes very well the self-relaxation of rigid spheres for both processes mentioned, i. e. equilibration of energy in the perpendicular directions and equilibration of energy between molecules which have different kinetic energies. The last quantity for molecules which interact with a Maxwellian potential is greater and from the formula of Mc Cormack and Williams [9] it can be calculated to equal 1.

It should be emphasized that all derivations has been performed here for the artificial state (discussed under Eq. (2)) in which the molecules move in one direction. The collision frequency calculated for this artificial state does not correspond to the commonly used quantity describing the motion in three dimentions. It can be seen that of these two quantities the former (cf. Eq. (23)) is not three times but two times smaller than the latter (cf. Eq. (5.21, 1) from Ref. [13]). Otherwise the factor 3/8 in the expression for relaxation time (cf. Eq. (24)) would be replaced by 1/4, however, even then the collision number $Z$ would remain 3/4. The simple derivations for the mentioned state were performed in order to avoid possible errors connected with an introduction of different probabilistic measures in calculations of the collision frequency and the rate of change of average energy in one direction (cf. Eqs. (23) and (14)).

It is interesting to see if the rotational relaxation, for which $Z_{rot}$ is not large, can affect the value of translational energy self-relaxation. We suppose that for the simplest models available such an effect is larger for the model of nearly spherical rotating molecules [14] than for the Bryan-Pidduck model of rough spheres. In the collision equations for both models an additional quantity $j = I/r^2$ (where $I$ is the moment of inertia and $r$, which is the molecular radius, i. e. $\frac{1}{2}\sigma$, in the model of rough spheres, is smaller than $\frac{1}{2}\sigma$ in the modified model [15, 16] and it is even smaller than the radius of gyration in the model of nearly spherical rotating molecules) can be introduced. It plays a similar role for rotation as the molecular mass does for translation [14, 16] and it is also discussed as the effective mass [17]. The influence of $j$ on $Z$ can be simply evaluated from the collision equations for the initial state in which the colliding molecules do not rotate before the collision. Then from Eq. (19) from Ref. [14] it can be seen that the change of energy in such a collision is $[m^{-1}/(m^{-1}+j^{-1})]^2$ times smaller than that in Eq. (16). As the ranges of $m/j$ are $0 < m/j < 0.4$, we see that for $m/j = 0.4$ (for which $Z_{rot} \eqsim 4$) the value of $(1+m/j)^{-2}$ is close to $1/2$. Then $Z$ would be about twice as large as $3/4$. We do not expect such an effect for the model of rough spheres because in the collision equation $j$ appears there only in an additional term describing the exchange of energy (connected with roughness) in the direction perpendicular to the unit vector $l$. But we think that the evaluations for the former model are more important because the model of nearly spherical rotating molecules provides more reasonable results for the transport coefficient than that of the rough spheres.

Just to summarize, we see that the collision number of the relaxation of translational energy in the perpedicular directions for a gas composed of rigid spheres is $Z = 3/4$. This quantity is a good measure of self-relaxation of translational energy for one component systems. It can be larger for other models. It can be even two times larger in a system in which a quick process of rotational relaxation occurs. But in general the discussed translational relaxation is a very quick process always quicker than the process of translational relaxation between two gases which have different temperatures and also faster than the process of rotational relaxation.

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