

A novel derivation of collision theory rate constants for a bimolecular reaction

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Received: 25 January 2011 / Accepted: 9 May 2011 / Published online: 2 June 2011
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Abstract A novel exact derivation for the kinetic constant of a bimolecular reaction according to three well-known models of collision theory is reported. The use of probability density functions, with the introduction of a novel geometry to study the collision process, allows simplifying the derivation to such an extent, that, for a proper statistical background, it is possible to recover the line-of-centers and the angular dependent line-of-centers models in no more than a couple of lectures. Although the derivation is introduced to recover the temperature-dependent kinetic constant, it is shown that the energy-dependent reactive cross section can be recovered as well. A possible confusion in the interpretation of the pre-exponential factor is commented.

Keywords Graduate education · Physical chemistry · Reference textbooks · Kinetic-molecular theory

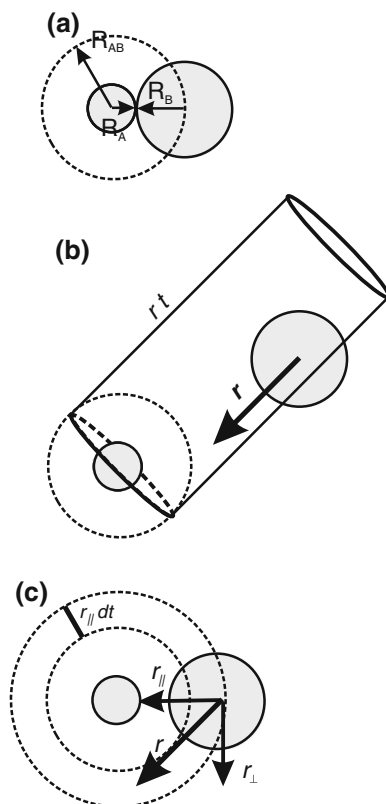
1 Introduction

The interpretation of the kinetic constant of a second order gas phase reaction in terms of collision theory is a fundamental topic in Chemistry. The complete derivation of the kinetic theory results can be found in specialized monographs [1,2], but it is at least partially skipped in standard textbooks in consideration of its length and mathematical difficulty. The line-of-centers (LOC) model is often derived in approximate ways, and the angular-dependent line of centers model (ADLOC) is most often simply skipped. As one can easily come across attempts to get the right results in alternative simpler but approximated ways, we thought it worthwhile to look for a simpler and still exact derivation.

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Fig. 1 Sketches of the geometrical parameters intervening in the collision of a B and an A particle: **a** sketch of the collision sphere of radius $R_{AB} = R_A + R_B$; **b** the collision cylinder and **c** the spherical shell centered on the A particle (the infinitesimal width of the spherical shell has been drawn finite for clarity). Relative velocities are indicated as discussed in the text



2 Notation and background

In the vision of collision theory, a gaseous mixture of compounds A and B with molar mass M_A and M_B in a vessel of volume V kept at temperature T is an ensemble of N_A and N_B rigid spheres of radii R_A and R_B and masses $m_A = M_A/L$ and $m_B = M_B/L$, respectively, where L is Avogadro's constant. The spheres are supposed to move according to Newton's law and to undergo elastic collisions with themselves and with the container. An A–B collision occurs when the distance between the particles lowers to $R_{AB} = R_A + R_B$, a condition which is often stated in terms of an invisible sphere of influence of radius R_{AB} surrounding sphere A (Fig. 1a): if the center of the B particle touches the sphere of influence a collision occurs.¹ The density is assumed low enough that collisions between three particles can be neglected.

¹ Actually, the distance of closest approach for reactants is generally shorter than that allowed for non-reactive collisions and the best radii to be used are not those entering in the description of non reactive collisions [3]. This quantitatively important consideration is irrelevant for the development of the analytical results.

At equilibrium particles are uniformly distributed and their velocities and speeds conform to the Maxwell-Boltzmann distribution, which will be written in one and three dimensions as

$$f(v_i) = \frac{1}{\sqrt{2\pi\xi}} \exp\left(-\frac{v_i^2}{2\xi^2}\right) \quad (1)$$

and

$$w(v) = \frac{4\pi v^2}{(2\pi)^{\frac{3}{2}} \xi^3} \exp\left(-\frac{v^2}{2\xi^2}\right), \quad (2)$$

where v_i is the velocity along axis i , the speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, the variance of velocities is

$$\xi^2 = \frac{1}{\beta m},$$

m is the mass of a particle and $\beta = 1/k_B T$ as usual. Use of the above distributions allows to readily compute the average speed

$$\langle v \rangle = \int_0^{\infty} v w(v) dv = \sqrt{\frac{8}{\pi m \beta}}, \quad (3)$$

and the average of positive velocities along any given axis i

$$\langle v_i \rangle_+ = \int_0^{\infty} v_i f(v_i) dv_i = \sqrt{\frac{1}{2\pi m \beta}}.$$

Notably,

$$\langle v \rangle = 4 \langle v_i \rangle_+.$$

The above distributions are assumed to hold unchanged in the course of the reaction and the probability to find an A particle with velocity in the range $[v_A, v_A + dv_A]$ in a sufficiently large volume V' is

$$dP_A(V', v_A) = \frac{V'}{V} w(v_A) dv_A. \quad (4)$$

3 The novel derivation

In order to get the expressions for the kinetic constants, one can identify three main points:

1. counting the number of collisions happening in unit time in unit volume between molecular pairs with a given relative velocity $\mathbf{r} = \mathbf{v}_B - \mathbf{v}_A$,
2. applying possible criteria for the identification of effective collisions,
3. averaging over all values of the relative velocities.

The novel derivation is based on the distributions for the relative velocities, which will be discussed immediately.

3.1 Distributions of relative velocities

The distribution of relative velocities should be constructed averaging over all $N_{AB} = N_A N_B$ pairs. This can be done with minor effort if one considers *the reproductive property of the Gaussian distribution*, which is the basis of propagation of errors generally thought in laboratories courses. According to that property [4]

if two independent random variables X and Y are normally distributed with means $\langle X \rangle$ and $\langle Y \rangle$, and variances ξ_X^2 and ξ_Y^2 , respectively, the random variable $S = aX \pm bY$ is still normally distributed and has mean $\langle S \rangle = a \langle X \rangle \pm b \langle Y \rangle$ and variance $\xi_S^2 = a^2 \xi_X^2 + b^2 \xi_Y^2$.

Incidentally, it is this property which has allowed a major breakthrough in modern computational chemistry, through the introduction of Gaussian basis sets [5].

Considering thus the reproductive property, for any Cartesian component of the relative velocity $r_i = v_{Bi} - v_{Ai}$, the distribution function will be

$$\bar{f}(r_i) = \frac{1}{(2\pi)^{1/2} \bar{\xi}} \exp\left(-\frac{r_i^2}{2\bar{\xi}^2}\right), \quad (5)$$

which is still a Gaussian distribution with mean

$$\langle r_i \rangle = \langle v_{Bi} \rangle - \langle v_{Ai} \rangle = 0$$

and variance

$$\bar{\xi}^2 = \xi_A^2 + \xi_B^2 = \frac{1}{\beta m_A} + \frac{1}{\beta m_B} = \frac{1}{\beta \mu},$$

where

$$\mu = m_A m_B / (m_A + m_B)$$

is the reduced mass. The functional form of $\bar{f}(r_i)$, (5), is then identical to the corresponding probability density function (PDF) of a single particle, (1), provided that m is replaced by μ (ξ by $\bar{\xi}$). This implies that also the PDF $\bar{w}(r)$, as well as all expressions of averages can be obtained by the results for single particles, but for the change of m with μ . In particular

$$\langle r \rangle = 4 \langle r_i \rangle_+ = \sqrt{\frac{8}{\pi \mu \beta}}. \quad (6)$$

It must be reminded that the computation of $\langle r \rangle$ from the distribution functions $f(v_A)$ and $f(v_B)$ is considerably more involved [1,2] and is reasonably skipped in basic courses. We discovered that a proposal to use the PDF of relative velocity was made many years ago by Blinder [6,7]. Probably the connection with the well-known formula for propagation of statistical errors can give a new chance to adopt this simple and exact argument.

3.2 Counting collisions

The knowledge of the distributions for the relative velocities will enable the computation of the collision frequency density Z_{AB} , i.e. the total number of A–B collisions in unit time and unit volume. In order to simplify successive steps in the demonstration, it will be useful to derive such a quantity using both a cylindrical and a spherical geometry. We are not aware of any introduction of the latter geometry for the matter in question.

3.2.1 Collision cylinders

Consider to sit on the A particle of a colliding A–B pair. If the incoming B particle lies inside a cylinder whose height rt is parallel to the relative velocity and whose basis πR_{AB}^2 bisects the A particle, a collision will occur in time t (Fig. 1b). According to the homogeneity ansatz, the probability that this occurs is the probability to have a pair with relative velocity in the range $[r, r + dr]$ times the probability to have a B particle inside the cylinder:

$$dP_{\text{coll}}(r, t) = \bar{w}(r)dr \times N_B \frac{\pi R_{AB}^2 rt}{V}. \quad (7)$$

The same could be said for all A particles. Therefore

$$\begin{aligned} Z_{AB} &= \frac{N_A \int_0^\infty dP_{\text{coll}}(r, t)}{Vt} \\ &= \frac{N_{AB} \pi R_{AB}^2 \int_0^\infty r \bar{w}(r) dr}{V^2} \\ &= \sigma_0 \langle r \rangle \frac{N_A}{V} \frac{N_B}{V}, \end{aligned} \quad (8)$$

where we have introduced a collision cross section

$$\sigma_0 = \pi R_{AB}^2.$$

3.2.2 Spherical shells

Consider to sit on an A particle and to see a B particle distant $r_{\parallel}t$ from us. We are not granted of a collision in time t . Indeed, in that time t the B particle moving with a relative velocity $\mathbf{r} = \mathbf{r}_{\parallel} + \mathbf{r}_{\perp}$, where \mathbf{r}_{\perp} is the component of relative velocity perpendicular to the line of centers, will move away from the line of centers by $r_{\perp}t$, and this can prevent collision. This limitation is eliminated if we consider an infinitesimal distance $r_{\parallel}dt$. In that case the infinitesimal displacement $r_{\perp}dt$ will be smaller than the finite, albeit small, radius of influence R_{AB} .

The probability that a B particle with relative velocity r_{\parallel} collides with our A particle would be the probability to have a pair with velocity in the range $[r_{\parallel}, r_{\parallel} + dr_{\parallel}]$ times the probability to have a B particle inside the spherical shell of volume $4\pi R_{AB}^2 r_{\parallel} dt$ (Fig. 1c). According to the homogeneity ansatz that probability would amount to

$$dP'_{\text{coll}}(r_{\parallel}, dt) = \bar{f}(r_{\parallel})dr_{\parallel} \times \frac{N_B 4\pi R_{AB}^2 r_{\parallel} dt}{V}. \tag{9}$$

The same could be said for all A particles. Therefore

$$\begin{aligned} Z_{AB} &= \frac{N_A \int_0^{\infty} dP'_{\text{coll}}(r_{\parallel}, dt)}{V dt} \\ &= \frac{N_A N_B 4\pi R_{AB}^2 \int_0^{\infty} r_{\parallel} \bar{f}(r_{\parallel}) dr_{\parallel}}{V^2} \\ &= 4\sigma_0 \langle r_{\parallel} \rangle \frac{N_A}{V} \frac{N_B}{V}, \end{aligned} \tag{10}$$

which is fully consistent with (8) and (6).

3.2.3 First determination of the kinetic constant

Comparison of the definitions of the collision frequency density and the kinetic constant yields to

$$k \left(\frac{N_A}{V} \right) \left(\frac{N_B}{V} \right) = Z_{AB} L,$$

and the introduction of the expression for Z_{AB} , (8) and (10), gives k_0 as the simplest expression of collision theory for the kinetic constant:

$$k_0 = 4 \langle r_{\parallel} \rangle_+ \sigma_0 L \tag{11}$$

$$= \langle r \rangle \sigma_0 L. \tag{12}$$

This estimate generally exceeds the experimental values by several orders of magnitude, which prompts to consider that just a small fraction ϕ of collisions is reactive. A nontrivial model \mathcal{M} of collision theory will give a fraction $\phi_{\mathcal{M}}$ of reactive collisions and thus a kinetic constant

$$k_{\mathcal{M}} = k_0 \phi_{\mathcal{M}}. \quad (13)$$

3.3 The fractions of effective collisions

The analytical forms of the collision frequency density, (7) and (9), enable to define the PDFs $f_c(r_{\parallel})$ and $w_c(r)$, which allow computing the probability of having collisions with relative velocity r or r_{\parallel} in a given interval:

$$w_c(r)dr = \frac{dP_{\text{coll}}(r, t)}{\int dP_{\text{coll}}(r, t)} = \frac{r^3 \exp(-\beta\varepsilon) dr}{\int_0^{\infty} r^3 \exp(-\beta\varepsilon) dr} = \beta^2 \varepsilon \exp(-\beta\varepsilon) d\varepsilon$$

and

$$f_c(r_{\parallel})dr_{\parallel} = \frac{dP'_{\text{coll}}(r_{\parallel}, dt)}{\int dP'_{\text{coll}}(r_{\parallel}, dt)} = \frac{r_{\parallel} \exp(-\beta\varepsilon_{\parallel}) dr_{\parallel}}{\int_0^{\infty} r_{\parallel} \exp(-\beta\varepsilon_{\parallel}) dr_{\parallel}},$$

where we have indicated the relative kinetic energy and the relative kinetic energy along the line-of-centers as $\varepsilon = \frac{1}{2}\mu r^2$ and $\varepsilon_{\parallel} = \frac{1}{2}\mu r_{\parallel}^2$, respectively.

The simplest models of collision theory identify reactive collisions as those having relative speed r or relative velocity along the line of centers r_{\parallel} exceeding a given threshold r_0 . The fractions ϕ_{RS} and ϕ_{LOC} which allow the computation of kinetic constants according to (13) are readily computed as

$$\phi_{\text{RS}} = \int_{r_0}^{\infty} w_c dr \quad (14)$$

$$= \int_{\varepsilon_0}^{\infty} w_c(\varepsilon) d\varepsilon \quad (15)$$

$$= \beta^2 \int_{\varepsilon_0}^{\infty} \varepsilon \exp(-\beta\varepsilon) d\varepsilon$$

$$= (1 + \beta\varepsilon_0) \exp(-\beta\varepsilon_0) \quad (16)$$

$$\phi_{\text{LOC}} = \int_{r_0}^{\infty} f_c(r_{\parallel}) dr_{\parallel} \quad (17)$$

$$= \frac{\int_{\varepsilon_0}^{\infty} \exp(-\beta\varepsilon_{\parallel}) d\varepsilon_{\parallel}}{\int_0^{\infty} \exp(-\beta\varepsilon_{\parallel}) d\varepsilon_{\parallel}} \quad (18)$$

$$= \exp(-\beta\varepsilon_0). \quad (19)$$

3.4 The steric factor

The fractions ϕ_{RS} and ϕ_{LOC} lead to kinetic constants close to the Arrhenius equation $k = A \exp(-E_a/RT)$, which is known to give reasonable good fits of the temperature variations of k in many systems. Indeed the slight temperature dependence of the pre-exponential factor in k_{RS} and k_{LOC} is often overwhelmed by the exponential term. However, in most cases if the energy threshold is obtained from the experimental activation energy, computed kinetic constants k_{LOC} are still considerably higher than experimental ones. This discrepancy is interpreted considering that not only the energy, but also the orientation of the particles must be appropriate for reaction. A steric factor p can be operationally identified by comparison with experiment: $k = pk_{LOC}$. However, rather than recovering a phenomenological p factor from experiments, kinetic theory is asked to provide a model for it. The simplest model considers that one of the reactants is a black and white sphere: colliding B spheres lead to reaction only if they hit the white portion of the A spheres. According to this simple model the steric factor is just the white portion of the surface [8]. This model is unsatisfactory because from experimental data one often obtains values of p in the range 0.1–0.001, which would imply a surprising localization for the orientation of reactive collisions.

More advanced models consider that the threshold energy can be orientation-dependent [3, 9, 10]. In an atom-diatom reaction, $A + BC \rightarrow AB + C$, the threshold energy is expected to change as a function of the attack angle γ : the supplementary to the angle \widehat{ABC} between the three atoms. Calculations on the reaction $H + H_2 \rightarrow H_2 + H$ indicate that the threshold energy can be approximated by

$$\varepsilon_0(\gamma) = \varepsilon_0 + \varepsilon'_0(1 - \cos \gamma), \quad (20)$$

where the smallest value ε_0 corresponds to a collinear attack. The model which considers as effective collisions only those for which $\varepsilon_{\parallel} \geq \varepsilon_0(\gamma)$ is known as angular-dependent line-of-centers (ADLOC) model and predicts a kinetic constant $k_{ADLOC} = k_0\phi_{ADLOC}$. For energies $\varepsilon_{\parallel} > \varepsilon_0 + 2\varepsilon'_0$ every orientation is good for reaction (the sphere is all “white”), for $\varepsilon_{\parallel} < \varepsilon_0$ no orientation will do (the sphere is all “black”) while for $\varepsilon_{\parallel} \in [\varepsilon_0, \varepsilon_0 + 2\varepsilon'_0]$ the “white” sphere will span a fraction of the spherical surface. The fraction of spherical surface limited by a given latitude is

$$P(\gamma_{\max}) = \frac{2\pi \int_0^{\gamma_{\max}} \sin \gamma d\gamma}{4\pi} = \frac{(1 - \cos \gamma_{\max})}{2}.$$

Therefore for $\varepsilon_{\parallel} \in [\varepsilon_0, \varepsilon_0 + 2\varepsilon'_0]$, the limiting reaction condition $\varepsilon_{\parallel} = \varepsilon_0 + \varepsilon'_0(1 - \cos \gamma)$ identifies a fraction of surface given by $P(\gamma_{\max}) = \frac{\varepsilon_{\parallel} - \varepsilon_0}{2\varepsilon'_0}$. Using this fraction, the derivation of the fraction ϕ_{ADLOC} can be made as above using the collision frequency density $f_c(\varepsilon_{\parallel})$:

$$\phi_{\text{ADLOC}} = \frac{\int_{\varepsilon_0}^{\varepsilon_0+2\varepsilon'_0} \frac{\varepsilon_{\parallel}-\varepsilon_0}{2\varepsilon'_0} \exp(-\beta\varepsilon_{\parallel}) d\varepsilon_{\parallel} + \int_{\varepsilon_0+2\varepsilon'_0}^{\infty} \exp(-\beta\varepsilon_{\parallel}) d\varepsilon_{\parallel}}{\int_0^{\infty} \exp(-\beta\varepsilon_{\parallel}) d\varepsilon_{\parallel}} \quad (21)$$

$$= \frac{1}{2\beta\varepsilon'_0} \exp(-\beta\varepsilon_0) [1 - \exp(-2\beta\varepsilon'_0)], \quad (22)$$

which correspond to a steric factor

$$p_{\text{ADLOC}} = \frac{1}{2\beta\varepsilon'_0} [1 - \exp(-2\beta\varepsilon'_0)].$$

Nicely for $\varepsilon'_0 \rightarrow 0$, $p_{\text{ADLOC}} \rightarrow 1$ and $\phi_{\text{ADLOC}} \rightarrow \phi_{\text{LOC}} = \exp(-\beta\varepsilon_0)$. For high values of $\beta\varepsilon'_0$,

$$\phi_{\text{ADLOC}} = \frac{1}{2\beta\varepsilon'_0} \exp(-\beta\varepsilon_0)$$

and

$$p_{\text{ADLOC}} = \frac{1}{2\beta\varepsilon'_0}.$$

(22) was first given in Ref. [10], although its limiting forms at high values of $\beta\varepsilon'_0$ was already given in Ref. [3].² Noticeably derivations based on the w_c distribution are considerably more involved mathematically, and, well understandably, they are skipped even in two excellent specialized monographs [11, 12].

4 Recovering the collision cross sections

Let us now consider that the radius R_{AB} of the sphere of effective collisions not only can differ from that of the sphere of collisions but also can change as a function of relative velocity. In this case the reaction cross section $\sigma = \sigma(r) \neq \sigma_0$ cannot be kept out of the integral sign in (8) and (10). Therefore, in place of (12), we have

$$k = L \int_0^{\infty} \sigma \bar{w}(r) r dr. \quad (23)$$

(23) states that the kinetic constant is an r -weighted average of reaction cross sections. The weighting is due to the fact that in unit time fast particles collide more often than slow particles (they span either longer collision cylinders or larger spherical shells) and thus give a greater contribution to the kinetic constant. Upon changing the integration variable from r to ε , and recalling (6), or—more directly—from (13)

² As pointed out by Levine [J. Phys. Chem. **94**, 8872 (1990)] the ADLOC model has been anticipated by Pelzer and Wigner [Z. Phys. Chem. B **15**, 445 (1932)].

upon changing the energy independent σ_0 into $\sigma(\varepsilon)$ and using the distribution $w_c(\varepsilon)$, the expression of the kinetic constant becomes

$$k = L\langle r \rangle \beta^2 \int_0^{\infty} \sigma(\varepsilon) \exp(-\beta\varepsilon) \varepsilon d\varepsilon. \quad (24)$$

A model \mathcal{M} of kinetic theory is generally obtained starting from the derivations of a $\sigma_{\mathcal{M}}(\varepsilon)$ function. That approach requires an appropriate average over orientation of colliding molecules and, for the simple models discussed here, it is less straightforward than the present one, which uses probability density functions to compute the fraction $\phi_{\mathcal{M}}$. However our discussion seems deficient in that it does not give expressions for the functions $\sigma_{\mathcal{M}}(\varepsilon)$, which can sometimes be compared directly with experiments. This is not the case, because knowledge of the analytical expression $k_{\mathcal{M}} = k_{\mathcal{M}}(\beta)$ is generally sufficient to recover the $\sigma_{\mathcal{M}}(\varepsilon)$ function [10].

To this end, we can rewrite (24) as

$$k_{\mathcal{M}} = L\langle r \rangle \beta^2 \mathcal{L}\{\sigma_{\mathcal{M}}(\varepsilon)\varepsilon\}, \quad (25)$$

where the the symbol \mathcal{L} indicates the Laplace transform.³

Equating (25) with (13), we obtain

$$\frac{\sigma_0 \phi_{\mathcal{M}}}{\beta^2} = \mathcal{L}\{\sigma_{\mathcal{M}}(\varepsilon)\varepsilon\}$$

and then

$$\sigma_{\mathcal{M}}(\varepsilon) = \frac{1}{\varepsilon} \mathcal{L}^{-1} \left\{ \frac{\sigma_0 \phi_{\mathcal{M}}}{\beta^2} \right\}.$$

³ The Laplace transform consists in changing the domain of a function: in our case the $\sigma_{\mathcal{M}}(\varepsilon)\varepsilon$ function is ‘translated’ from the ε domain to the β domain. In general for a function $f(\varepsilon)$ the Laplace transform gives a function:

$$g(\beta) = \int_0^{\infty} f(\varepsilon) \exp(-\beta\varepsilon) d\varepsilon \equiv \mathcal{L}\{f(\varepsilon)\}.$$

Laplace transforms are generally invertible, which means that the original function $f(\varepsilon)$ can be recovered from the function $g(\beta)$ by inverse transformation: $f(\varepsilon) = \mathcal{L}^{-1}\{g(\beta)\}$. Tables of Laplace transforms can easily be found, e.g. <http://mathworld.wolfram.com/LaplaceTransform.html>, <http://www.intmath.com/Laplace-transformation/Intro.php>.

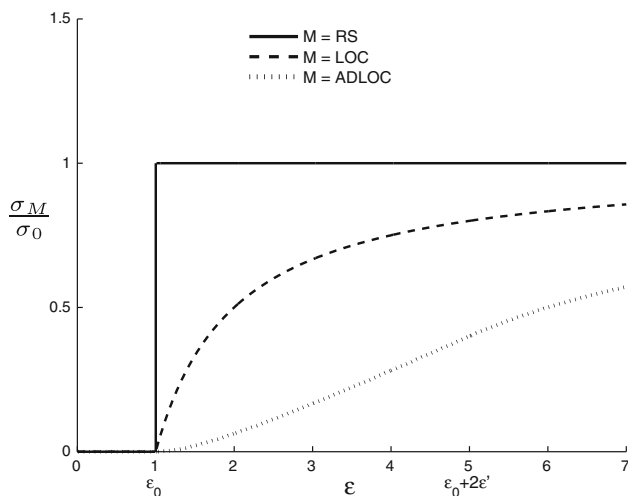


Fig. 2 Reactive cross sections for the three models discussed in the paper: RS is the model with a threshold on relative speed, LOC has a threshold on the line-of-centers component of the relative speed, ADLOC further considers the threshold to depend on the angle of attack γ

Introduction of the fraction of active collisions previously computed, (15), (19) and (22) gives

$$\begin{aligned}\sigma_{\text{RS}}(\varepsilon) &= \sigma_0 H(\varepsilon - \varepsilon_0), \\ \sigma_{\text{LOC}}(\varepsilon) &= \sigma_0 H(\varepsilon - \varepsilon_0) \left(1 - \frac{\varepsilon_0}{\varepsilon}\right), \\ \sigma_{\text{ADLOC}}(\varepsilon) &= \frac{\sigma_0}{4\varepsilon\varepsilon'} \left\{ H(\varepsilon - \varepsilon_0)(\varepsilon - \varepsilon_0)^2 - H(\varepsilon - \varepsilon_0 - 2\varepsilon')(\varepsilon - \varepsilon_0 - 2\varepsilon')^2 \right\},\end{aligned}$$

where $H(x)$ is the Heaviside step function which is null for $x' < x$ and one for $x' > x$.

Figure 2 compares the three cross sections. It can be seen that the ADLOC cross section is lower than the LOC one. Moreover, unlike the other two cross sections, it shows a concave up form for $\varepsilon_0 < \varepsilon < \varepsilon_0 + 2\varepsilon'$, which is considered a great success of this simple model considering that the upward curvature has been obtained in quasi-classical molecular dynamics simulations [12].

5 Further discussion

A further comment deserves the intermediate expression (18) of the fractions of effective collisions. This expression is so deceptively similar to a Boltzmann weight, that it is not uncommon to find the ϕ_{LOC} factor commented as fraction of molecules with enough kinetic energy. This is not the case. Indeed, that fraction can be computed as

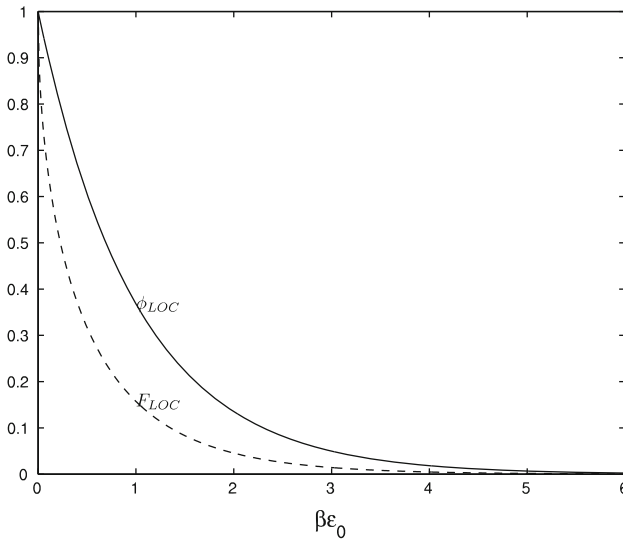


Fig. 3 The fraction of collisions ϕ_{LOC} with kinetic energy along the line-of-centers exceeding a given threshold ϵ_0 is always greater than the fractions of molecular pairs with kinetic energy exceeding the same threshold. $\beta = 1/k_B T$.

$$F_{LOC} = \int_{r_0}^{\infty} \bar{f}(r_{\parallel}) dr_{\parallel} = 1 - \text{erf}(\sqrt{\beta\epsilon_0}).$$

As can be seen in Fig. 3, the fraction F_{LOC} is always smaller than the fraction ϕ_{LOC} , a part from the limiting values $(\beta\epsilon_0)^{\pm 1} = 0$. This is well understandable because fast collisions contribute more to the kinetic constant, as explained above. The distributions $\bar{f}(r_{\parallel})$ and $\bar{w}(r)$ can be used to determine the fraction of molecules with relative velocity in any given interval, but the different distributions $f_c(r_{\parallel})$ and $w_c(r)$ must be used to get the fraction of collisions. Cutting these two distributions above the same value of velocity will thus give a different percentage (Fig. 4). Notably, for a two-dimensional gas model, one gets $F_{LOC}^{2D} = \phi_{LOC}$. Thus, the two-dimensional model of collisions sometimes introduced with the aim of simplifying the mathematics, could lead support to the wrong idea that the pre-exponential factor ϕ_{LOC} is a fraction of molecules with relative velocity exceeding a given threshold, rather than the fraction of collisions with line-of-centers relative velocity exceeding that same threshold.

Herschbach’s Nobel lecture documents that the confusion between the distributions of velocities and that of collisions concerned up to famous Nobel prizes [13]. Indeed, when in 1919 Otto Stern pioneered molecular beams experiments, trying to get an experimental proof of the Maxwell-Boltzmann distribution $w(r)$, he reported a systematic disagreement between experiment and theory. Soon after, he received a letter from Albert Einstein, who pointed out that the disagreement was expected because Stern’s experiment sampled the $w_c(r)$ distribution, rather than $w(r)$.

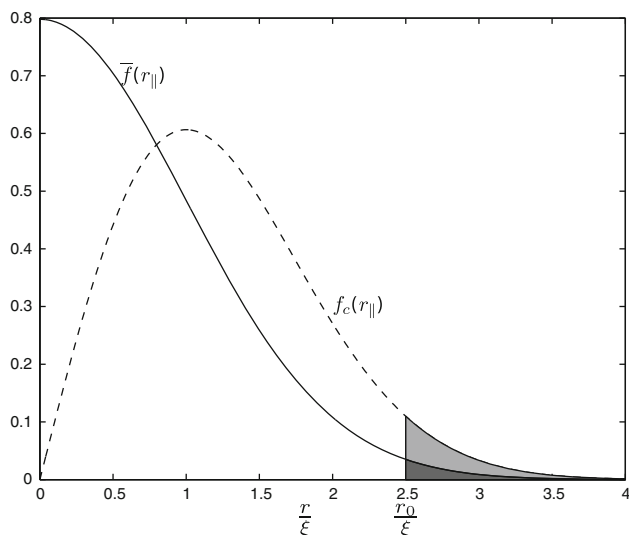


Fig. 4 The different shapes of the probability density functions for relative speeds $\bar{f}(r_{||})$ and for collisions $f_c(r_{||})$ give a graphical justification of the fact that a cut of the distributions above a given threshold leads to the different percentages F_{LOC} (dark shaded area) and ϕ_{LOC} (light shaded area in addition to the dark shaded area). In order to get a universal plot, relative speeds r are normalized to the standard deviation of the relative velocity ξ

6 Conclusions

We have presented a compact and exact derivation of the equations giving the kinetic constant according to the simplest models of collision theory. The demonstration reported has three main novelties.

First, the average relative velocity is derived in a straightforward fashion, thanks to the reproductive property of the Gaussian distribution, which is an ever-present argument in laboratory courses. This exact demonstration is far simpler than the one based on the velocity distributions of the two colliding molecules, and we strongly recommend its introduction in classroom.

Second, the collision frequency density Z is computed by an explicit use of the statistical distributions, using both cylindrical and spherical geometries. The two geometries are equivalent, but the use of the spherical geometry allows utilizing the probability density function of relative velocity, which is advantageous for the development of models of kinetic theory.

Finally, the equations for the kinetic constant according to the three most famous models of collision theory are derived just by using the distribution functions. As for the line-of-centers model, this novel exact approach is of the same complexity of the two-dimensional gas approach, which is sometimes invoked to simplify mathematics. However, the latter approach can engender confusion in the correct interpretation of the pre-exponential factor, which is neither the fraction of molecules with velocity above a threshold nor the fraction of molecular pairs with relative velocity above a threshold, but the fraction of collisions due to molecular pairs with relative veloc-

ity above a given threshold. Moreover the angular-dependent line-of-centers model is derived quite straightforwardly, in a much more compact way than the reported approach based on the impact parameter.

Acknowledgments The author is thankful to Profs. R. Zanasi and A. Peluso for encouragement and discussion. Financial support from the FARB 2010 project is acknowledged.

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