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# A More Sophisticated Treatment of Collisions

Carl W. David

*University of Connecticut*, [Carl.David@uconn.edu](mailto:Carl.David@uconn.edu)

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# A More Sophisticated Treatment of Collisions

C. W. David

*Department of Chemistry  
University of Connecticut  
Storrs, Connecticut 06269-3060*

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## I. FRACTION OF MOLECULES CAPABLE OF COLLIDING

For A-type molecules, we have the fraction of molecules whose velocity components are between  $v_x$  and  $v_x + dv_x$ , etc., as

$$\frac{dN_A}{N_A} = \left(\frac{m_A}{2\pi kT}\right)^{\frac{3}{2}} e^{-m_A(v_x^2+v_y^2+v_z^2)/(2kT)} dv_x dv_y dv_z \quad (1.1)$$

and for B-type molecules, we have

$$\frac{dN_B}{N_B} = \left(\frac{m_B}{2\pi kT}\right)^{\frac{3}{2}} e^{-m_B(v_u^2+v_v^2+v_w^2)/(2kT)} dv_u dv_v dv_w \quad (1.2)$$

and the number of collisions between A-type and B-type molecules in these velocity ranges per unit time is:

$$dZ_{AB} = \frac{dN_A dN_B}{V^2} \pi d_{AB}^2 c_{AB} \quad (1.3)$$

where

$$c_{AB} = \sqrt{(v_x - v_u)^2 + (v_y - v_v)^2 + (v_z - v_w)^2}$$

Adding up all the collisions over all velocity ranges gives:

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$$\int dZ_{AB} = \pi d_{AB}^2 \frac{N_A N_B}{V^2} \left(\frac{m_B}{2\pi kT}\right)^{3/2} \left(\frac{m_B}{2\pi kT}\right)^{3/2} \int dv_x \int dv_y \int dv_z \int dv_u \int dv_v \int dv_w \left\{ e^{-m_A(v_x^2+v_y^2+v_z^2)/(2kT) - m_B(v_u^2+v_v^2+v_w^2)/(2kT)} \sqrt{(v_x - v_u)^2 + (v_y - v_v)^2 + (v_z - v_w)^2} \right\}$$


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To proceed with the integration, it is convenient to convert to the center of mass coordinate system where

$$\dot{X}_{c.of.m.} = \frac{m_A v_x + m_B v_u}{m_A + m_B} = \delta$$

$$\dot{Y}_{c.of.m.} = \frac{m_A v_y + m_B v_v}{m_A + m_B} = \zeta$$

$$\dot{Z}_{c.of.m.} = \frac{m_A v_z + m_B v_w}{m_A + m_B} = \eta$$

and

$$\dot{x}_{AB} = v_x - v_u \equiv \alpha$$

$$\dot{y}_{AB} = v_y - v_v \equiv \beta$$

$$\dot{z}_{AB} = v_z - v_w \equiv \gamma$$

we can get the new differential volume element using the Jacobian (see Appendix), i.e.,

$$dv_x dv_y dv_z dv_u dv_v dv_w = J(\alpha, \delta) J(\beta, \zeta) J(\gamma, \eta) d\alpha d\beta d\gamma d\delta d\zeta d\eta$$

where each Jacobian looks like the first, i.e.,

$$J(\alpha, \delta) = \begin{vmatrix} \frac{\partial \alpha}{\partial v_x} & \frac{\partial \delta}{\partial v_x} \\ \frac{\partial \alpha}{\partial v_u} & \frac{\partial \delta}{\partial v_u} \end{vmatrix} = \begin{vmatrix} 1 & \frac{m_A}{m_A + m_B} \\ -1 & \frac{m_B}{m_A + m_B} \end{vmatrix} = 1$$

so

$$\int dZ_{AB} = \pi d_{AB}^2 \frac{N_A N_B}{V^2} \left(\frac{m_B}{2\pi kT}\right)^{3/2} \left(\frac{m_B}{2\pi kT}\right)^{3/2} \int d\alpha \int d\beta \int d\gamma \int d\delta \int d\zeta \int d\eta e^{-\mu(\alpha^2+\beta^2+\gamma^2)/(2kT) - (m_A+m_B)(\delta^2+\zeta^2+\eta^2)/(2kT)} \sqrt{\alpha^2 + \beta^2 + \gamma^2}$$

$$\int dZ_{AB} = \pi d_{AB}^2 \frac{N_A N_B}{V^2} \left(\frac{m_B}{2\pi kT}\right)^{3/2} \left(\frac{m_B}{2\pi kT}\right)^{3/2} \int d\alpha \int d\beta \int d\gamma \sqrt{\alpha^2 + \beta^2 + \gamma^2} e^{-\mu(\alpha^2+\beta^2+\gamma^2)/(2kT)} \int d\delta \int d\zeta \int d\eta e^{-(m_A+m_B)(\delta^2+\zeta^2+\eta^2)/(2kT)}$$

where all integrals are over the range  $-\infty \rightarrow +\infty$ .

We then have, since they are all standard integrals

$$\int dZ_{AB} = Z_{AB} = \pi d_{AB}^2 \frac{N_A}{V} \frac{N_B}{V} \left( \frac{m_A}{2\pi kT} \right)^{3/2} \left( \frac{m_B}{2\pi kT} \right)^{3/2} \left( \left( \frac{2\pi kT}{m_A + m_B} \right)^{1/2} \right)^3 8\pi \left( \frac{kT}{\mu} \right)^2$$

and employing

$$\frac{1}{m_A} + \frac{1}{m_B} = \frac{1}{\mu}$$

one obtains ( $\rho$  is the number density!)

$$Z_{AB} = \pi d_{AB}^2 \rho_A \rho_B \left( \frac{\sqrt{\mu}}{2\pi kT} \right)^3 8\pi \left( \frac{kT}{\mu} \right)^2 \quad (1.4)$$

which is

$$Z_{AB} = \pi d_{AB}^2 \rho_A \rho_B \sqrt{\frac{8kT}{\pi\mu}} \quad (1.5)$$

For a pure A system,  $\mu = m_A/2$  and  $\rho_A = \rho_B = \rho$ , and dividing by two to avoid the double count, one has

$$Z_{AA} = \frac{\pi d^2 \rho \sqrt{2}}{2} \sqrt{\frac{8kT}{\pi m_A}} \quad (1.6)$$

## II. MOLECULES COLLIDING WITH A WALL

The volume of the cylinder constructed in the figure is

$$cdt \cos \vartheta dS$$

and the number of molecules in that volume is

$$\rho cdt \cos \vartheta dS$$

where  $\rho$  is the number density. The fraction of those molecules which have the correct (appropriate) angle, and speed to actually strike the differential element of surface area on the wall,  $dS$ , in time  $dt$  is

$$\rho cdt \cos \vartheta SK e^{-mc^2/(2kT)} c^2 dc \sin \vartheta d\vartheta d\varphi$$

where  $K$  is the normalization constant.

$$dN = [\rho(c \cos \vartheta)] K e^{-mc^2/(2kT)} c^2 dc \times \sin \vartheta d\vartheta d\varphi (dSdt)$$

i.e.,

$$\int \frac{dN}{dSdt} = \rho K \int_0^{2\pi} d\varphi \int_0^{\pi/2} \cos \vartheta \sin \vartheta d\vartheta \int_0^\infty e^{-mc^2/(2kT)} c^3 dc$$

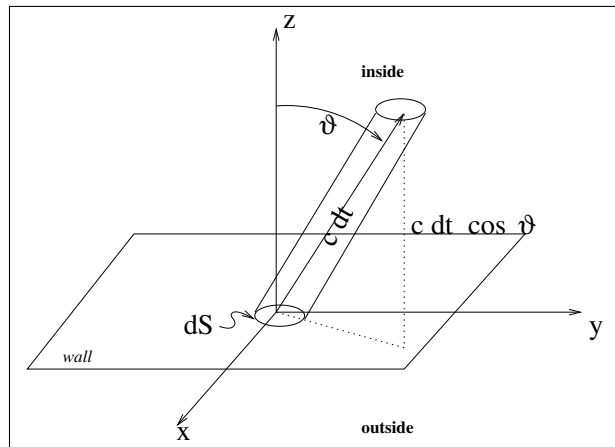


FIG. 1: Cylinder containing molecules which will collide with  $dS$  in time  $dt$

Since

$$\int_0^{\pi/2} \cos \vartheta \sin \vartheta d\vartheta = -\frac{\cos^2 \vartheta}{2} \Big|_0^{\pi/2} = \frac{1}{2}$$

and

$$\int_0^{2\pi} d\varphi = 2\pi$$

we have

$$\frac{dN}{dSdt} = \frac{1}{4\pi} \frac{1}{2} \bar{c} (2\pi) = \frac{\rho \bar{c}}{4}$$

## III. APPENDIX

From elementary calculus, as example, the Jacobian connecting Cartesian to polar coordinates (in the plane) proceed from the definitions:

$$x = r \cos \varphi$$

and

$$y = r \sin \varphi$$

so

$$\frac{\partial(x, y)}{\partial(r, \varphi)} = J = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \varphi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \varphi} \end{vmatrix} = \begin{vmatrix} \cos \varphi & -r \sin \varphi \\ \sin \varphi & r \cos \varphi \end{vmatrix} = r$$

so  $dx dy = r dr d\varphi$ .