

Chemistry 223: Collisions, Reactions, and Transport

© David Ronis
McGill University

1. Effusion, Surface Collisions and Reactions

In the previous section, we found the parameter b by computing the average force exerted on the walls of the container. Suppose, instead, that the rate of collisions (i.e., the number of collisions per unit area per unit time) was desired. This is important for a number of practical considerations; e.g., if a chemical reaction takes place every time a molecule hits the surface, then the rate of the reaction will just be the collision rate.

We obtain the collision rate by repeating the analysis which determined the force on the wall in the previous section. Thus, the number of molecules per unit area with velocity v_x which collide in time interval Δt is

$$n(v_x)|v_x|\Delta t, \quad (1)$$

where we are using the same notation as in the preceding sections. The total number of collisions becomes:

$$Z_{wall}\Delta t = \int_{-\infty}^0 dv_x n_0 \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-mv_x^2/(2k_B T)} |v_x| \Delta t = \left(\frac{k_B T}{2\pi m} \right)^{1/2} n_0 \Delta t \quad (2)$$

Hence, the wall collision rate, Z_{wall} , is given by

$$Z_{wall} = \left(\frac{k_B T}{2\pi m} \right)^{1/2} n_0 = \frac{1}{4} \langle c \rangle n_0, \quad (3)$$

where $\langle c \rangle$ is the average speed, introduced in the preceding section. Aside from the previously mentioned example of chemical reaction on a surface, another application of this expression is in *effusion* through a pinhole. If there is a hole of area A in the surface, the rate that molecules escape the system is just $Z_{wall}A$. Notice that heavier molecules or isotopes will escape more slowly (with a $1/\sqrt{\text{mass}}$ dependence); hence, effusion through a pinhole is a simple way in which to separate different mass species.

The assumption that every collision leads to reaction is not quite right for many reasons (e.g., orientation of the molecule, its internal motion, etc.). The most important of these is easy to understand, namely, the molecule must have enough energy to overcome some sort of activation barrier. For our model this means that the molecule must be moving fast enough when it collides and this is easily incorporated into Eq. (2):

$$Z_{wall}^{reactive} = \int_{-\infty}^{-v_{\min}} dv_x n_0 \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-mv_x^2/(2k_B T)} |v_x| = \frac{1}{4} \langle c \rangle n_0 e^{-E_a/k_B T}, \quad (4)$$

where $E_a \equiv \frac{1}{2} m v_{\min}^2$ is called the activation energy. This is just the well known Arrhenius behavior seen in most reaction rates. Note that plotting $\log(Z_{wall}^{reactive})$ vs $1/T$ would give an approximately straight line, and experimentally this is known as an Arrhenius plot.

2. Gas Phase Collisions and Chemical Reactions

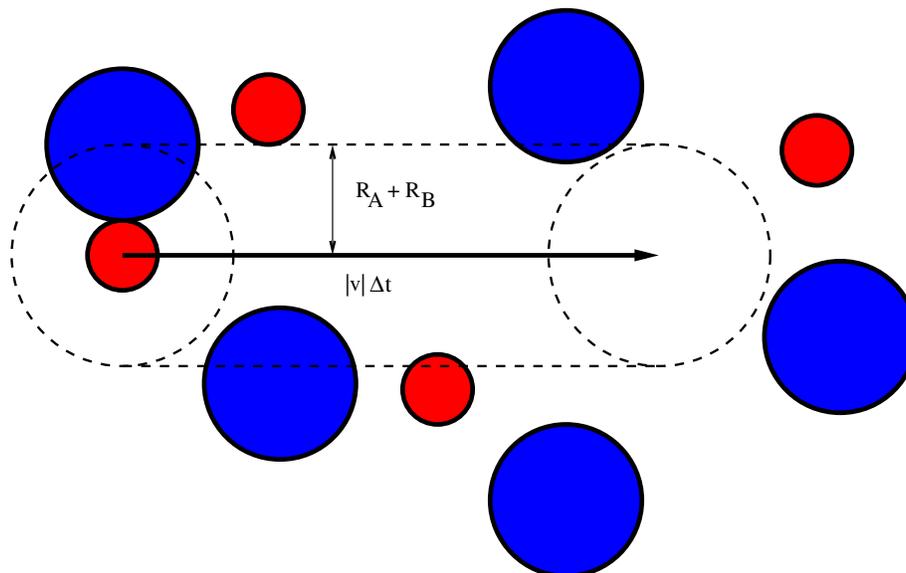


Fig. 1. Any blue molecule contained in the cylinder will collide with our red A molecule in time Δt

Next consider the number of collisions which a molecule of type A makes with those of type B in a gas. We will model the two molecules as hard spheres of radii R_A and R_B , respectively. Moreover, in order to simplify the calculation, we will assume that the B molecules are stationary (this is a good approximation if $m_B \gg m_A$). An A molecule moving with velocity \vec{v} for time Δt will collide with any B molecule in a cylinder of radius $R_A + R_B$ (cf. Fig. 1) and length $|\vec{v}|\Delta t$. Hence, volume swept out will just be

$$|\vec{v}|\Delta t \pi (R_A + R_B)^2, \quad (5)$$

and the actual number of collisions will $n_B \times$ volume swept out. The average A-B collision rate, is obtained by multiplying by the probability density for A molecules with velocity \vec{v} and averaging. Moreover, since only the speed of the molecule is relevant, we may use the molecular speed distribution function obtained in the preceding section to average over the speed of A. Thus, we get

$$Z_{A \text{ with } B's} \Delta t \equiv \int_0^\infty dc \left[4\pi c^2 \left(\frac{m_A}{2\pi k_B T} \right)^{3/2} e^{-m_A c^2 / (2k_B T)} \right] \pi (R_A + R_B)^2 c \Delta t n_B, \quad (6)$$

where note that the quantity in the square brackets is just the speed probability density, $F(c)$. When the integral is evaluated, we find that

$$Z_{A \text{ with } B's} = \pi (R_A + R_B)^2 \langle c_A \rangle n_B, \quad (7)$$

where $\langle c_A \rangle$ is the average molecular speed of A; i.e.,

$$\langle c_A \rangle \equiv \left(\frac{8k_B T}{\pi m_A} \right)^{1/2}. \quad (8)$$

This is the number of collisions *one* A suffers in time Δt . The number of collisions with B's that

all the A molecules in a unit volume suffer per unit time, $Z_{A,B}$, is

$$Z_{A,B} = n_A Z_{A \text{ with } B} = \pi(R_A + R_B)^2 \langle c_A \rangle n_A n_B. \quad (9)$$

As was mentioned at the outset, our expression is correct if the B's are not moving. It turns out that the correction for the motion of B is rather simple (and involves going to what is called the center-of-mass frame, which is not, but which is described in the Appendix); specifically, all we do is replace the m_A in the definition of the mean speed by $\mu_{A,B}$, the *reduced mass* for the A,B pair. The reduced mass is defined as:

$$\mu_{A,B} \equiv \frac{m_A m_B}{m_A + m_B}, \text{ or equivalently, } \frac{1}{\mu_{A,B}} \equiv \frac{1}{m_A} + \frac{1}{m_B}. \quad (10)$$

If $m_B \gg m_A$, $\mu_{A,B} \approx m_A$, i.e., the mass of the lighter species, while if $A = B$, $\mu_{A,A} = m_A/2$.

With this correction, our expression becomes

$$Z_{A,B} = \pi(R_A + R_B)^2 \langle c_{A,B} \rangle n_A n_B, \quad (11)$$

where

$$\langle c_{A,B} \rangle \equiv \left(\frac{8k_B T}{\pi \mu_{A,B}} \right)^{1/2}, \quad (12)$$

is the mean speed of A relative to B. A special case of this expression is the rate of collision of A molecules with themselves. In this case, Eq. (11) becomes

$$Z_{A,A} = \frac{1}{2} \pi \sigma_A^2 \langle c_A \rangle^2 n_A^2, \quad (13)$$

where $\sigma_A = 2R_A$ is the molecular diameter of A and where we have divided by 2 in order to not count each A-A collision twice. Note that we have expressed our result in terms of $\langle c_A \rangle$ and not $\langle c_{A,A} \rangle$, which is the origin of the additional factor of $2^{1/2}$ in Eq. (13).

Equations (11) or (13) give the rate of chemical reaction per unit volume, *assuming zero activation energy* (this is still an upper bound to the rate of reaction). As in the collision with a wall discussion, this is easily generalized by including in the collision rate only those molecules with enough (relative) kinetic energy; i.e.,

$$\text{RATE} = n_A n_B \pi (R_A + R_B)^2 \int_{c_{\min}}^{\infty} dc F(c) c = \pi (R_A + R_B)^2 \langle c_{A,B} \rangle e^{-E_A/k_B T} \left(1 + \frac{E_A}{k_B T} \right) n_A n_B, \quad (14)$$

where $F(c)$ is the (relative) speed distribution and $E_A \equiv \mu_{A,B} c_{\min}^2/2$. When $A=B$ we have to add the additional factor of $1/2$, cf. Eq. (13).

This expression has the correct Arrhenius form except for the extra non-exponential factors containing temperature. However, compared with the exponential factor, these usually do not change very rapidly with temperature and can approximately be treated as constant; recall that we normally show Arrhenius behavior by plotting $\ln(\text{Rate Constant})$ versus $1/T$ to obtain a straight line. The non-exponential terms end up in a logarithm which usually doesn't change much over the range of temperatures studied. Thus, we have derived an approximate expression for the bi-molecular rate constant which has at least some of the qualitative features of those found in gas reactions. Note that in either case we have a second order reaction overall, either first order in A and first order in B or second order in A, cf. Eq. (14) or, ignoring any activation

energy, (13), respectively.

It is important to understand what we mean by 'RATE' in Eq. (14). It is the average number of reactive collisions per unit volume, per unit time. This need not be the rate of disappearance of reactants or appearance of products per unit time per unit volume. To get these we need the stoichiometries in the reaction under consideration. Consider the following reaction



In each reactive collision two A's are consumed, while only one A_2 is produced; thus the rate of disappearance of A is twice the rate of appearance of A_2 , which in turn happens once per event. Hence,

$$\frac{d[A_2]}{dt} = RATE, \quad \text{while} \quad \frac{d[A]}{dt} = -2 \times RATE. \quad (16)$$

Note that Eq. (16) implies that $[A] + 2[A_2]$ is constant. Why should this not be a surprise?

3. Mean Free Path and Transport Phenomena

Next, we will consider how far a molecule can move before it suffers a collision. For simplicity, we will only consider a one component gas. According to Eq. (7), the mean time between collisions is

$$\tau_{collision} \approx \frac{1}{Z_{A \text{ with } A's}} = \frac{1}{2^{1/2} \pi \sigma_A^2 \langle c_A \rangle n_A}, \quad (17)$$

where $\sigma_A = 2R_A$ is the diameter of and A. Hence, the typical distance traveled by a molecule between collisions, λ is approximately $\tau_{collision} \langle c_A \rangle$ or

$$\lambda = \frac{1}{2^{1/2} \pi \sigma_A^2 n_A}. \quad (18)$$

This distance is called the mean free path. Note that it only depends on the number density of the gas and the size of the molecules, but not its mass or the temperature.

We can use these results to obtain an approximate expression for the way in which concentration differences equilibrate in a dilute gas. Consider a gas containing two kinds of molecules in which there is a concentration gradient; i.e., the density of molecules per unit volume, $n_i(z)$ depends on position. One way in which the concentration becomes uniform is via diffusion.

To quantify diffusion, we want to find the net number of molecules of a given type that cross a plane in the gas per unit area per unit time; this is known as the diffusion flux. To see how the diffusion flux depends on molecular parameters, consider the following figure.

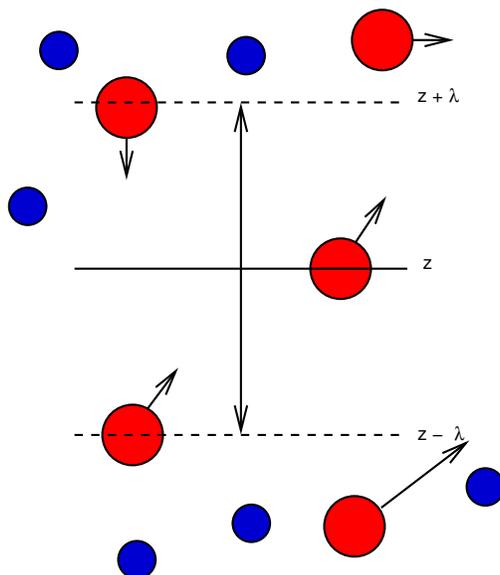


Fig. 2. Any molecule that starts around a mean free path from the mid-plane will not collide with anything and will cross the mid-plane, therefore contributing to the upward or downward flux. The net rate per unit area is just what we considered in our discussion of effusion.

We want the net flux through the plane at z . From our preceding discussion of mean free paths, clearly any molecule that starts roughly from a mean free path above or below z , moving towards z , will not suffer any collisions and will cross. The number that cross the planes at $z \pm \lambda$ per unit area, per unit time is the same as the wall collision rates we calculated above, that is

$$\left(\frac{k_B T}{2\pi m}\right)^{1/2} n(z \pm \lambda) = \frac{1}{4} \langle c_A \rangle n(z \pm \lambda), \quad (19)$$

where we have rewritten Eq. (3) in terms of the average molecular speed, cf. Eq. (8). Since all the molecules that won't collide and will thus cross the plane at z , the net flux (upward) is just

$$J = \frac{1}{4} \langle c_A \rangle n(z - \lambda) - \frac{1}{4} \langle c_A \rangle n(z + \lambda) = -\frac{1}{4} \langle c_A \rangle [n(z + \lambda) - n(z - \lambda)]. \quad (20)$$

Since, for most experiments, the density barely changes on over a distance comparable to the mean free path, we use the Taylor expansion to write

$$n(z \pm \lambda) \approx n(z) \pm \frac{dn(z)}{dz} \lambda + \frac{1}{2} \frac{d^2 n(z)}{dz^2} \lambda^2 + \dots, \quad (21)$$

which, when used in Eq. (20) gives Fick's First Law of diffusion,

$$J = -D \left(\frac{\partial n(z, t)}{\partial z} \right)_t, \quad (22)$$

where we have modified the notation to include the time dependence of the density and where

$$D \equiv \frac{1}{2} \lambda \langle c_A \rangle. \quad (23)$$

D is known as the diffusion constant, is positive, and has units of $length^2/time$.

Clearly there is nothing special about our choice of the z direction in the preceding discussion; it could easily have been in the x or y directions, or all three at once. Under these conditions, the flux, J , becomes a vector, and Fick's First Law of diffusion is

$$\mathbf{J}(\mathbf{r}, t) = -D\nabla n(\mathbf{r}, t),$$

where ∇ is the gradient operator defined as

$$\nabla \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)^T,$$

with T denoting the transpose.

The factor of $1/2$ in our expression for D is not quite right, but the other factors are; e.g., for hard spheres the correct diffusion constant is $3\pi/8 = 1.178\dots$ times larger than the one given above.* Note that only the leading order term was kept in obtaining Eqs. (22) and (23) from Eqs. (20) and (21); the next order one contains $\lambda^3(\partial^3 n(z, t)/\partial z^3)_t$, and in general, only odd powers of λ and numbers of derivatives will appear.

Next consider the total number of molecules inside of some region bounded by planes at z and $z + L$. The length L is small compared to the scales that characterize the concentration nonuniformity, but large compared with the mean free path. Clearly the only way for the total number of molecules in our region, $n(z, t)L$, to change is by fluxes at the surfaces at z and $z + L$. Thus,

$$\frac{\partial n(z, t)L}{\partial t} = -J(z + L, t) + J(z, t) \approx -L \frac{\partial J(z, t)}{\partial z}, \quad (24)$$

where we have again used a Taylor expansion, now for the flux itself. Finally, by using our result for the diffusion flux and canceling the factors of L , we see that

$$\left(\frac{\partial n(z, t)}{\partial t} \right)_z = D \left(\frac{\partial^2 n(z, t)}{\partial z^2} \right)_t, \quad (25)$$

which is a kinetic equation for the relaxation of the concentration and is known as the diffusion equation. Although value of the diffusion constant is quite different, the diffusion equation actually is more general than our derivation might suggest and holds in liquids and solids as well. Finally, note that we have only considered systems where the concentration is only nonuniform in one spatial direction. Should this not be the case, then some simple modifications of our expressions must be introduced; e.g., the diffusive motion in the x and y directions must be included. This is easily done, and Eq. (25) becomes

$$\left(\frac{\partial n(\mathbf{r}, t)}{\partial t} \right)_{\mathbf{r}} = D\nabla^2 n(\mathbf{r}, t), \quad (26)$$

where $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is called the Laplacian operator.

There are standard ways in which to solve diffusion equations, either analytically, for spe-

*See, e.g., Joseph O. Hirschfelder, Charles F. Curtiss, R. Byron Bird, *Molecular Theory of Gases and Liquids* (Wiley-Interscience, 1964), Chapters 7-8. Be warned, the math and physics required is very non-trivial!

cial geometries, or numerically.[†] However, there is one general feature of systems relaxing diffusively. Imagine introducing a small droplet of an impurity into a system. Clearly the droplet will spread in time, and you might naively think that the average droplet size would grow like $\langle c_A \rangle t$. Of course, this ignores collisions and is incorrect. From the diffusion equation dimensional analysis correctly suggests that

$$\frac{1}{t} \approx \frac{D}{R^2} \quad (27)$$

or $R \approx \sqrt{Dt}$, which is much slower than the linear time behavior that would arise in the absence of collisions.[‡] This is what is observed.

An important application of the diffusion equation is to reactions in solution, where the rate determining step is the diffusion of reactants to and product from the reaction place. For example, consider a model where reactions occur on the surface of a spherical colloidal particle of radius R . We assume that once the reactant diffuses to the surface the reaction will occur instantaneously, 100% of the time, implying that $n(R) = 0$. Finally, far from the surface the reactant concentration is n_0 . In steady state, Eq. (26) becomes

$$0 = \nabla^2 n(\mathbf{r}). \quad (28)$$

Given the overall spherical symmetry of the problem, you should expect, correctly, that switching to polar coordinates might be useful. In particular,

$$\nabla^2 n(\mathbf{r}) = \frac{1}{r} \frac{\partial^2 [rn(\mathbf{r})]}{\partial r^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial n(\mathbf{r})}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 n(\mathbf{r})}{\partial \phi^2}, \quad (29)$$

where r , θ and ϕ are the usual polar coordinates and where the last two terms vanish for our geometry. What remains of Eq. (29) is $\partial^2 [rn(r)]/\partial r^2 = 0$ or $n(r) = A + B/r$, where A and B are constants that are determined by applying the boundary conditions, namely, $n(r = \infty) = n_0$ and $n(r = R) = 0$. Thus we see that

$$n(r) = n_0 \left(1 - \frac{R}{r} \right). \quad (30)$$

Finally, the inward diffusion flux according to Fick's Law is

$$J_r \equiv D \frac{\partial n(r)}{\partial r} \Big|_{r=R} = n_0 \frac{D}{R}, \quad (31)$$

which is just the number of reactions per unit area of colloid per unit time. Hence, the total reaction rate per colloid, each having area $4\pi R^2$, is

$$\text{Rate} = 4\pi DRn_0. \quad (32)$$

If the system is a dilute suspension of colloid, with concentration n_C , the total rate per unit time per unit volume becomes

$$\text{Rate} = 4\pi DRn_C n_0, \quad (33)$$

[†] See, e.g., W.H. Press, S.A Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in C: The Art of Scientific Computing*, 2nd ed., (Cambridge University Press, 1992), Ch. 19.

[‡] For a spherical droplet the exact answer is $R = \sqrt{6Dt}$.

which is first order in colloid and in reactant. Note that like in our initial analysis of reactions in the gas phase we have neglected the motion of the colloidal particles a reasonable approximation given the huge size and mass difference between the two species. Should this not be the case, the fix is, alas, not to simply replace the masses by the reduced mass.

Before leaving this topic, note that A. Einstein, in his study of Brownian motion established what is now known as the Stokes-Einstein relation; i.e.,

$$D = \frac{k_B T}{6\pi\eta a}, \quad (34)$$

where η is the solvent dynamic viscosity and a is the size of a reactant molecule. When this is used in Eq. (33) we see that

$$RATE = \frac{2k_B T}{3\eta} \frac{R}{a} n_C n_0. \quad (35)$$

The preceding analysis can be applied to other transport phenomena; in particular to energy or momentum transport. One interesting example is to so-called transport of shear momentum. Consider a flowing system with velocity in the x direction and gradient in the z direction, or

$$\mathbf{v}(\mathbf{r}) = \hat{\mathbf{e}}_x v(z). \quad (36)$$

For linear profiles we have a Couette flow, for parabolic ones a Poiseuille flow, etc. The momentum per unit volume (or momentum density) is just $\hat{\mathbf{e}}_x mnv(z)$. Repeating our analysis of Fig. 2, but now for the flux for the x component of the momentum being transported in the z direction, denoted as $\tau_{x,y}$, gives

$$\tau_{x,y} = -\frac{1}{4} \langle c_A \rangle mn [v(z+\lambda) - v(z-\lambda)] \approx -\frac{\lambda}{2} \langle c_A \rangle mn \left(\frac{\partial v}{\partial z} \right) \equiv -\eta \left(\frac{\partial v}{\partial z} \right), \quad (37)$$

where $\eta \equiv \lambda \langle c_A \rangle mn / 2$ is known as the dynamic viscosity. (Again, like the diffusion coefficient, the factor of 2 isn't quite right, but the rest is.)

If we repeat the steps leading to the diffusion equation, we find that

$$\left(\frac{\partial v_x(z,t)}{\partial t} \right)_z = v \left(\frac{\partial^2 v_x(z,t)}{\partial z^2} \right)_t, \quad (38)$$

where $v \equiv \eta / mn$ is known as the kinematic viscosity and has units of *length*²/*time*. Note that $v = D$ in our treatment, but this is an accidental consequence of our model (the factors of 2 aren't quite right). This last equation is a special case of the Navier-Stokes equations (in particular, we have ignored the role of pressure in directly exerting a force on the molecules, thereby changing the momentum).

4. Appendix: The Center of Mass Frame

Here are the details of the center of mass calculation mentioned in the text. (**You are not responsible for these details**). Consider two particles with masses m_i , at positions \mathbf{r}_i , moving with velocities \mathbf{v}_i , $i = 1, 2$. The center of mass for this system is given by

$$\mathbf{R}_{cm} \equiv \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}. \quad (A.1)$$

Also define the relative coordinate for the pair as

$$\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2. \quad (\text{A.2})$$

Similar definitions hold for the center of mass and relative velocities. A little algebra allows us to express the original coordinates in terms of the center of mass and relative ones; namely,

$$\mathbf{r}_1 = \mathbf{R}_{cm} + \frac{m_2}{m_1 + m_2} \mathbf{r}_{12} \quad (\text{A.3a})$$

and

$$\mathbf{r}_2 = \mathbf{R}_{cm} - \frac{m_1}{m_1 + m_2} \mathbf{r}_{12}, \quad (\text{A.3b})$$

where, again, similar expressions are obtained relating the velocities.

Now consider the probability densities for finding particle 1 at velocity \mathbf{v}_1 and 2 at velocity \mathbf{v}_2 :

$$f(\mathbf{v}_1, \mathbf{v}_2) = \left(\frac{m_1 m_2}{(2\pi k_B T)^2} \right)^{3/2} \exp\left(-\frac{m_1 v_1^2 + m_2 v_2^2}{2k_B T} \right) \quad (\text{A.4a})$$

$$= \left(\frac{(m_1 + m_2)\mu}{(2\pi k_B T)^2} \right)^{3/2} \exp\left(-\frac{(m_1 + m_2)V_{cm}^2 + \mu v_{12}^2}{2k_B T} \right)$$

$$= \left(\frac{(m_1 + m_2)}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{(m_1 + m_2)V_{cm}^2}{2k_B T} \right) \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{\mu v_{12}^2}{2k_B T} \right)$$

$$\equiv f_{cm}(\mathbf{V}_{cm}) \times f_{12}(\mathbf{v}_{12}), \quad (\text{A.4b})$$

where the second equality is obtained by expressing the individual velocities in terms of the center of mass and relative velocities, cf. Eqs. (A.3a) and (A.3b), with μ given by Eq. (10). The third equality is obtained by splitting up the exponentials and the factors in front, and finally, the last equality is obtained by defining the center of mass or relative velocity distributions as usual, but with the masses replaced by the total mass or reduced mass, respectively.

Thus, we've shown that the probability densities for the two particles' center of mass and relative velocities factorize; i.e., they are statistically independent. (Strictly speaking we have to check one more thing, namely, that $d\mathbf{v}_1 d\mathbf{v}_2 = d\mathbf{V}_{cm} d\mathbf{v}_{12}$. This is easily done by showing that the Jacobian for the transformation, cf. Eqs. (A.3a) and (A.3b), is unity, which it is. Jacobians are a Cal III concept). In any event, Eq. (A.4b) shows that any question that only asks about the relative motion of the particles (e.g., as in a collision) can ignore the center of mass part completely, and as was mentioned in the main text, in practice means that we replace the mass by the reduced mass in the distribution.

