Dynamics and Kinetics – Final Exam

January 19, 2023

Name:

Total 50 points, 3 h to complete the exam

Please note that this is not an open-book exam. You are allowed to use a non-programmable calculator as well as a formula sheet, A5, single-sided, and handwritten. The calculator and formula sheet will be checked during the exam. Computers or are not permitted. Do not write with a pencil or a fountain pen that can be erased. Please have your photo ID ready.

$\int_0^\infty e^{-ax^2}dx = \frac{\sqrt{\pi}}{2\sqrt{a}} \quad (a > 0)$

$\int_0^\infty xe^{-ax^2}dx = \frac{1}{2a} \quad (a > 0)$

$\int_0^\infty x^2e^{-ax^2}dx = \frac{\sqrt{\pi}}{4a^{\frac{3}{2}}} \quad (a > 0)$

$\int_0^\infty x^{2n}e^{-ax^2}dx = \frac{(2n)!\sqrt{\pi}}{2^{2n+1}n!a^{n+\frac{1}{2}}} \quad (a > 0)$

$\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}} \quad (a > 0)$

$\Gamma(z+1) = \int_0^\infty x^z e^{-x}dx$

$\Gamma(z+1) = z\Gamma(z)$, for any real z

$\Gamma(n+1) = n!$, for integer $n = 0, 1, 2, \ldots$

$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

$k_B = 1.38 \cdot 10^{-23}\ \mathrm{J \cdot K^{-1}}$

$R = 8.31\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$

$N_A = 6.02 \cdot 10^{23}\ \mathrm{mol^{-1}}$

$e = 1.60 \cdot 10^{-19}\ \mathrm{C}$

$h = 6.63 \cdot 10^{-34}\ \mathrm{J{\cdot}s}$

$\epsilon_0 = 8.85 \cdot 10^{-12}\ \mathrm{F \cdot m^{-1}}$

$c = 3.00\ \cdot 10^8\ m \cdot s^{-1}$

$1\ amu = 1.66 \cdot 10^{-24}\ g$

1) For the gas-phase reaction of nitric oxide with molecular hydrogen

$$\mathbf{2\ H_2\ (g) + 2\ NO\ (g) \xrightarrow{k_{obs}} N_2\ (g) + 2\ H_2O\ (g)}$$

the observed rate law is

$$\frac{d[\mathrm{N_2}]}{dt} = k_{obs}[\mathrm{H_2}][\mathrm{NO}]^2$$

(8 points total)

a) The following mechanism has been proposed.

$$\mathbf{H_2\ (g) + NO\ (g) + NO\ (g) \xrightarrow{k_1} N_2O\ (g) + H_2O\ (g)}$$

$$\mathbf{H_2\ (g) + N_2O\ (g) \xrightarrow{k_2} N_2\ (g) + H_2O\ (g)}$$

Under which circumstances does this mechanism yield the observed rate law? And which expression do you obtain for k_{obs} under these circumstances? (3 points)

For the rate of production of N_2, we find

$$\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{d}t} = k_2[\mathrm{H_2}][\mathrm{N_2O}]$$

(1 point)

If the second step is much faster than the first, the concentration of N_2O will always be small, so that we can apply the steady-state approximation. This is reasonable assumptions, since N_2O is a reactive species.

$$\frac{\mathrm{d}[\mathrm{N_2O}]}{\mathrm{d}t} = k_1[\mathrm{H_2}][\mathrm{NO}]^2 - k_2[\mathrm{H_2}][\mathrm{N_2O}] = 0$$

so that

$$[\mathrm{N_2O}] = \frac{k_1}{k_2}[\mathrm{NO}]^2$$

(1 points)

and

$$\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{dt}} = k_1[\mathrm{H_2}][\mathrm{NO}]^2$$

which agrees with the observed rate law, with $k_{\mathrm{obs}} = k_1$.

(1 point)

b) A different mechanism has been proposed as well.

$$\mathbf{NO\ (g) + NO\ (g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2\ (g)}$$

$$\mathbf{H_2\ (g) + N_2O_2\ (g) \xrightarrow{k_2} N_2O\ (g) + H_2O\ (g)}$$

$$\mathbf{H_2\ (g) + N_2O\ (g) \xrightarrow{k_3} N_2\ (g) + H_2O\ (g)}$$

Under which circumstances does this mechanism yield the observed rate law? And which expression do you obtain for k_{obs} under these circumstances? (4 points)

For the rate of production of N_2, we find

$$\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{dt}} = k_3[\mathrm{H_2}][\mathrm{N_2O}]$$

(1 point)

If the third step is much faster than the second, the concentration of N_2O will always be small, so that we can apply the steady-state approximation.

$$\frac{\mathrm{d}[\mathrm{N_2O}]}{\mathrm{d}t} = k_2[\mathrm{H_2}][\mathrm{N_2O_2}] \ - \ k_3[\mathrm{H_2}][\mathrm{N_2O}] \ = 0$$

so that

$$[\mathrm{N_2O}] = \frac{k_2}{k_3}[\mathrm{N_2O_2}]$$

After substitution of the concentration of N_2O into the rate of N_2 production, we obtain

$$\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{d}t} = k_2[\mathrm{H_2}][\mathrm{N_2O_2}]$$

(1 point)

If we moreover assume that a pre-equilibrium exists in the first step, we can write

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2}$$

and

$$[\mathrm{N_2O_2}] = \frac{k_1}{k_{-1}}[\mathrm{NO}]^2$$

(1 point)

After substitution of the concentration of N_2O_2 into the rate of N_2 production, we obtain

$$\frac{\mathrm{d}[\mathrm{N_2}]}{\mathrm{d}t} = \frac{k_2 k_1}{k_{-1}}[\mathrm{H_2}][\mathrm{NO}]^2$$

so that the observed rate constant becomes $k_{\mathrm{obs}} = k_2 k_1 / k_{-1}$.

(1 point)

c) Which of the two proposed mechanisms is more likely to be correct? Explain your reasoning. (1 point)

It seems more likely that the mechanism in (b) is correct, since it only involves biomolecular reactions, whereas the mechanism of (a) includes a termolecular reaction, which is unlikely to occur.

(1 point)

2) Describe an algorithm (no need to write proper code) that uses the stochastic method to simulate an enzymatically catalyzed reaction that follows the Michaelis-Menten mechanism. (8 points)

The Michaelis-Menten mechanism involves the following reaction sequence

$$\mathrm{E + S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \overset{k_2}{\rightarrow} \mathrm{E + P}$$

The algorithm consists of two steps, which are repeated for the duration of the simulation.

In the first step, the time interval Δt is determined after which the next reaction occurs.

The probability that none of the three reactions has occurred within a time interval Δt is:

$$p_{no\_reaction}(t) = e^{-(k_1 n_\mathrm{E} n_\mathrm{S} + n_\mathrm{ES}(k_{-1}+k_2))\Delta t} = e^{-\alpha \Delta t}$$

with

$$\alpha = k_1 n_\mathrm{E} n_\mathrm{S} + n_\mathrm{ES}(k_{-1} + k_2)$$

and n_E, n_S, and n_{ES} the number of molecules of E, S, and ES respectively. Moreover, we will use the variable n_P to describe the number of product molecules.

(3 points)

The probability $p_{reaction}(t)dt$ for a reaction to occur in a short time interval $[t, t + dt]$ is therefore equal to the change in the probability of no reaction occurring

$$p_{reaction}(t)dt = -\frac{p_{no\_reaction}(t)}{dt}\, dt = \alpha e^{-\alpha t} dt$$

The cumulative reaction probability (*i.e.,* the probability that any reaction has occurred between 0 and t) is therefore

$$p_r(t) = \int_0^t \alpha e^{-\alpha t} dt = 1 - e^{-\alpha t} = 1 - p_{no\_reaction}(t)$$

(1 point)

We equate this cumulative probability to a random number r_1 between 0 and 1 and solve for Δt in order to determine the time interval Δt after which the next reaction occurs.

$$\Delta t = \frac{1}{\alpha}\ln\left(\frac{1}{1-r_1}\right)$$

which is equivalent to

$$\Delta t = \frac{1}{\alpha}\ln\left(\frac{1}{r_1}\right)$$

(1 point)

In the second step of the algorithm, one determines which of the three reactions has occurred from a second random number r_2 between 0 and 1 as follows.

$$\text{Reaction } \begin{cases} 1 & r_2 < \frac{k_1 n_\mathrm{E} n_\mathrm{S}}{\alpha} \\ -1 & \frac{k_1 n_\mathrm{E} n_\mathrm{S}}{\alpha} \le r_2 < \frac{k_1 n_\mathrm{E} n_\mathrm{S}}{\alpha} + \frac{k_{-1} n_\mathrm{ES}}{\alpha} \\ 2 & r_2 \ge \frac{k_1 n_\mathrm{E} n_\mathrm{S}}{\alpha} + \frac{k_{-1} n_\mathrm{ES}}{\alpha} \end{cases} \text{ has occurred if}$$

(2 points)

The numbers of molecules n_E, n_S, n_ES, and n_P are then updated accordingly, and the time variable t is incremented by Δt. The two steps are then repeated for the duration of the simulation, yielding the numbers of molecules n_E, n_S, n_ES, and n_P as a function of time t.

(1 point)

3) Consider the following reversible reaction:

$$\mathbf{A + X} \underset{\boldsymbol{k_{-1}}}{\overset{\boldsymbol{k_1}}{\rightleftharpoons}} \mathbf{2\ X}$$

(8 points total)

a) Derive an expression for the relative concentrations of A and X at equilibrium. (1 point)

At equilibrium the rates of the forward and backward reactions are equal

$$k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{X}]_{\mathrm{eq}} = k_{-1}[\mathrm{X}]_{\mathrm{eq}}^2$$

so that

$$[\mathrm{X}]_{\mathrm{eq}} = \frac{k_1}{k_{-1}}[\mathrm{A}]_{\mathrm{eq}}$$

(1 point)

b) Assume that for a given set of conditions, the concentration of A barely changes over the course of the reaction, so that it can be treated as constant to good approximation. Using this approximation, calculate the concentration of X as a function of time. (6 points)

For clarity, we denote

$$[\mathrm{X}] = \mathrm{x}$$

and

$$[\mathrm{A}] = [\mathrm{A}]_0 = \mathrm{a}$$

where we have used the approximation that the concentration of A is constant.

The rate equation becomes

$$\frac{\mathrm{dx}}{\mathrm{d}t} = k_1 \mathrm{ax} - k_{-1}\mathrm{x}^2$$

so that

$$\int_{x_0}^{x_t} \frac{dx}{k_1 a x - k_{-1} x^2} = \int_0^t d\tau = t$$

(1 point)

We use the method of partial fractions to integrate the left side.

$$\int_{x_0}^{x_t} \frac{dx}{k_1 a x - k_{-1} x^2} = -\int_{x_0}^{x_t} \frac{A}{(k_{-1} x - k_1 a)} + \frac{B}{x} dx$$

Identifying $A = k_{-1}/k_1 a$ and $B = -1/k_1 a$ gives us the following integral.

$$-\int_{x_0}^{x_t} \frac{k_{-1}}{\left(\frac{k_{-1}}{k_1 a} x - 1\right)} - \frac{1}{k_1 a\, x} dx = \frac{1}{k_1 a}\left[\ln(x) - \ln\left(\frac{k_{-1}}{k_1 a} x - 1\right)\right]_{x_0}^{x_t}$$

$$\frac{-1}{k_1 a}\left[\ln\left(\frac{k_{-1}}{k_1 a} - \frac{1}{x}\right)\right]_{x_0}^{x_t} = \frac{-1}{k_1 a} \ln\left(\frac{k_{-1} - \frac{k_1 a}{x_t}}{k_{-1} - \frac{k_1 a}{x_0}}\right)$$

Alternatively, we can use the following trick.

$$\int_{x_0}^{x_t} \frac{dx}{k_1 a x - k_{-1} x^2} = -\int_{x_0}^{x_t} \frac{dx}{\left(k_{-1} - \frac{k_1 a}{x}\right) x^2}$$

Using the change of variables $u = k_{-1} - \frac{k_1 a}{x}$, $du = \frac{k_1 a}{x^2} dx$ and changing the integration bounds.

$$-\int_{x_0}^{x_t} \frac{dx}{\left(k_{-1} - \frac{k_1 a}{x}\right) x^2} = -\frac{1}{k_1 a}\int_{u_0}^{u_t} \frac{du}{u}$$

$$\frac{-1}{k_1\mathrm{a}}\int_{u_0}^{u_t}\frac{\mathrm{d}u}{u}=\frac{-1}{k_1\mathrm{a}}[ln(u)]_{u_0}^{u_t}=\frac{-1}{k_1\mathrm{a}}ln\left(\frac{u_t}{u_0}\right)$$

Undo substitution,

$$\frac{-1}{k_1\mathrm{a}}ln\left(\frac{u_t}{u_0}\right)=\frac{-1}{k_1\mathrm{a}}ln\left(\frac{k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_t}}}{k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_0}}}\right)$$

(3 points)

Combining the left-hand side with the right-hand side:

$$\frac{1}{k_1\mathrm{a}}ln\left(\frac{k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_t}}}{k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_0}}}\right)=-t$$

$$\frac{k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_t}}}{k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_0}}}=e^{-k_1at}$$

$$k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_t}}=\left(k_{-1}-\frac{k_1\mathrm{a}}{x_0}\right)e^{-k_1\mathrm{a}t}$$

$$x_t=\frac{k_1\mathrm{a}}{k_{-1}-\left(k_{-1}-\frac{k_1\mathrm{a}}{\mathrm{x_0}}\right)e^{-k_1\mathrm{a}t}}$$

(2 points)

c) Under which circumstances is the approximation justified that the concentration of A is constant? (1 point)

The approximation is good if A is provided in large excess and the ratio of the rate constants $\frac{k_1}{k_{-1}}$ is small, so that barely any A is consumed before the reactive mixture reaches equilibrium.

(1 point)

4) Transition State Theory. (11 points total)

a) The contour plot below shows the potential energy surface of the reaction

$$\mathbf{AB + C \rightarrow A + BC}$$

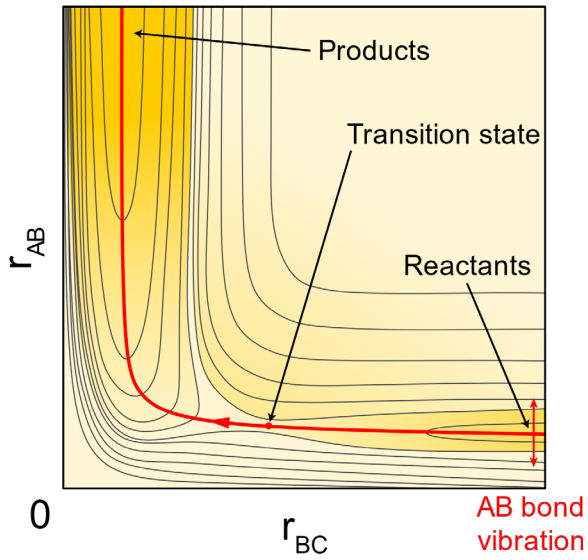
with the reaction constrained to a linear geometry. Here, A, B, and C are atoms, and r_{AB} and r_{BC} are interatomic distances.

Draw the minimum energy path of the reaction and indicate where the reactants and the products are located.

Draw the path on the potential energy surface that the system follows as the reactant AB molecule undergoes bond vibrations (without the distance to the C atom changing).

Indicate the transition state of the reaction and provide a definition of the transition state. At the transition state, what are the relative distances of the three atoms?

(5 points)



minimum energy path with location of reactants and products **(1 point)**

AB bond vibration **(1 point)**

location of transition state **(1 point)**

The transition state is a saddle point, with a maximum along the reaction coordinate (the minimum energy path), and a minimum along all other normal modes. **(1 point)**

The transition state is asymmetric, with the AB distance shorter than the BC distance. **(1 point)**

b) Use the transition state theory to estimate the rate constant of the reaction

$$\mathbf{F + H_2 \rightarrow HF + H}$$

at 300 K.

The activation energy of the reaction is 1.7 kJ/mol. A fluorine atom has a mass of 19 amu, and a hydrogen atom of 1 amu. The H_2 molecule has a rotational constant of B = 61.6 cm^{-1} and a vibrational frequency corresponding to ν = 4395 cm^{-1}. The transition state has a rotational constant of $B^{\ddagger}$ = 2.3 cm^{-1} and vibrational frequencies corresponding to $\nu_{stretch}$ = 4007 cm^{-1}, $\nu_{bend,1}$ = 392 cm^{-1}, and $\nu_{bend,2}$ = 397 cm^{-1}. (6 points)

The TST rate constant is given by

$$k_{TST} = N_A \frac{k_B T}{h} \frac{q_V^{\ddagger}}{q_{V,F}\, q_{V,H_2}} e^{-\frac{E_0}{k_B T}}$$

(1 point)

We calculate the partition functions for the reactants and the transition state.

Reactants.

F : $$q_{V,\mathrm{F}} = q_{V,\mathrm{F},tr} = \frac{1}{h^3}(2\pi\, m_{\mathrm{F}} k_B T)^{3/2} = 8.06 \cdot 10^{31}\ \mathrm{m}^{-3}$$

H_2: $$q_{V,\mathrm{H_2}} = q_{V,\mathrm{H_2},tr} \cdot q_{\mathrm{H_2},rot} \cdot q_{\mathrm{H_2},vib} = 1.21 \cdot 10^{26}\ \mathrm{m}^{-3}$$

$$q_{V,\mathrm{H_2},tr} = \frac{1}{h^3}\left(2\pi\, m_{\mathrm{H_2}} k_B T\right)^{3/2} = 2.75 \cdot 10^{30}\ \mathrm{m}^{-3}$$

$$q_{\mathrm{H_2},rot} = \frac{1}{2}\frac{k_B T}{hcB_{\mathrm{H_2}}} = 1.69$$

$$q_{\mathrm{H}_2,vib} = \frac{e^{-x/2}}{1 - e^{-x}} = 2.60 \cdot 10^{-5}\,, with\ x = \frac{h\,\nu\,c}{k_B T}$$

(2 points)

Transition state.

$$q_V^{\ddagger} = q_{V,tr}^{\ddagger} \cdot q_{rot}^{\ddagger} \cdot q_{vib}^{\ddagger} = 1.17 \cdot 10^{29}\ \mathrm{m}^{-3}$$

$$q_{V,tr}^{\ddagger} = \frac{1}{h^3}(2\pi\, m^{\ddagger} k_B T)^{3/2} = 9.37 \cdot 10^{31}\ \mathrm{m}^{-3}$$

$$q_{rot}^{\ddagger} = \frac{k_B T}{hcB^{\ddagger}} = 90.50$$

$$q_{vib}^{\ddagger} = \frac{e^{-x_1/2} \cdot e^{-x_2/2} \cdot e^{-x_3/2}}{(1-e^{-x_1})(1-e^{-x_2})(1-e^{-x_3})} = 1.37 \cdot 10^{-5}$$

$$\text{with } x_1 = \frac{h\nu_{stretch}c}{k_B T},\ x_2 = \frac{h\nu_{bend,1}c}{k_B T}, and\ x_3 = \frac{h\nu_{bend,2}c}{k_B T}$$

(2 points)

This yields the TST rate constant.

$$k_{TST} = N_A \frac{k_B T}{h} \frac{q_V^{\ddagger}}{q_{V,\mathrm{F}}\, q_{V,\mathrm{H}_2}} e^{-\frac{E_0}{k_B T}}$$

$$= 6.02 \cdot 10^{23}\ \frac{1.38 \cdot 10^{-23} \cdot 300}{6.63 \cdot 10^{-34}} \frac{1.17 \cdot 10^{29}}{8.06 \cdot 10^{31} \cdot 1.21 \cdot 10^{26}} e^{-1700/(8.314 \cdot 300)} m^3 s^{-1} mol^{-1}$$

$$= 2.27 \cdot 10^{7}\ m^3 s^{-1} mol^{-1} = 2.27 \cdot 10^{10}\ M^{-1} s^{-1}$$

(1 point)

5) The reaction cross section of a bimolecular gas-phase reaction has the following dependence on the collision energy E

$$\sigma_R(E) = \begin{cases} 0 & \text{for } E < E^* \\ \pi d^2 p \dfrac{\sqrt{E - E^*}}{E} \sqrt{E^*} & \text{for } E \geq E^* \end{cases}$$

where πd^2 is the hard-spheres collision cross section, p is a steric factor, and E^* is a threshold energy, below which the reaction cross section drops to zero.

Determine the thermal rate coefficient $k(T)$. (7 points)

To obtain the thermal rate coefficient $k(T) = \langle \sigma_R(E) v(E) \rangle$, we average over a thermal population of molecules as given by the Maxwell-Boltzmann distribution $F(v)$ for the relative speed.

$$k(T) = \int_0^\infty \sigma_R(E) v \cdot F(v) dv = \int_0^\infty \sigma_R(E) v \cdot 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{\mu v^2}{2k_B T}} dv$$

(2 points)

We transform the integral with $E = \frac{1}{2}\mu v^2$ and $dv = \frac{dE}{\mu v}$

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi \mu k_B T}\right)^{\frac{1}{2}} \int_0^\infty \sigma_R(E) E e^{-\frac{E}{k_B T}} dE = \frac{1}{k_B T}\left(\frac{8}{\pi \mu k_B T}\right)^{\frac{1}{2}} \int_{E^*}^\infty \pi d^2 p \sqrt{E - E^*} \sqrt{E^*} e^{-\frac{E}{k_B T}} dE$$

where we have adjusted the integral bounds to reflect that the reaction cross section is zero for $E < E^*$.

(2 points)

A change of variables with $\epsilon = E - E^*$ and $dE = d\epsilon$ yields

$$k(T) = \pi d^2 p \frac{1}{k_B T}\left(\frac{8}{\pi \mu k_B T}\right)^{\frac{1}{2}} \sqrt{E^*} e^{-\frac{E^*}{k_B T}} \int_0^\infty \sqrt{\epsilon} e^{-\frac{\epsilon}{k_B T}} d\epsilon$$

We transform the integral with $\epsilon' = \frac{\epsilon}{k_B T}$ and $d\epsilon = k_B T d\epsilon'$

$$\int_0^\infty \sqrt{\epsilon} e^{-\frac{\epsilon}{k_B T}} d\epsilon = (k_B T)^{\frac{3}{2}} \int_0^\infty \sqrt{\epsilon'} e^{-\epsilon'} d\epsilon' = (k_B T)^{\frac{3}{2}} \frac{\sqrt{\pi}}{2}$$

where we have used the gamma function in the last step. We finally obtain the thermal rate constant

$$k(T) = \pi d^2 p \sqrt{\frac{2E^*}{\mu}} e^{-\frac{E^*}{k_B T}}$$

(3 points)

6) Derive the relative speed distribution of two particles in a two-dimensional gas. In order to do so, follow these steps. First write down the combined velocity distribution of two particles, then transform into center of mass coordinates. Integrate out the center-of-mass part to obtain the distribution of the relative velocities. Finally, transform into polar coordinates and integrate out the angular part to obtain the relative speed distribution. (8 points)

Starting with a one-dimensional velocity distribution

$$f(v_i)dv_i = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{mv_i^2}{2k_B T}} dv_i$$

we can write down the two-dimensional distribution for two particles.

$$\begin{aligned} f\left(v_{A,x}, v_{A,y}, v_{B,x}, v_{B,y}\right)dv_{A,x}dv_{A,y}dv_{B,x}dv_{B,y} \\ = f\left(v_{A,x}\right)f\left(v_{A,y}\right)f\left(v_{B,x}\right)f\left(v_{B,y}\right)dv_{A,x}dv_{A,y}dv_{B,x}dv_{B,y} \\ = \frac{m_A m_B}{(2k_B T)^2} e^{-\frac{m_A(v_{A,x}^2+v_{A,y}^2)}{2k_B T}} e^{-\frac{m_B(v_{B,x}^2+v_{B,y}^2)}{2k_B T}} dv_{A,x}dv_{A,y}dv_{B,x}dv_{B,y} \end{aligned}$$

(2 points)

We transform into center of mass coordinates using

$$\begin{cases} \vec{v}_A = \vec{v}_{cm} + \dfrac{\mu \vec{v}_{AB}}{m_A} \\ \vec{v}_B = \vec{v}_{cm} - \dfrac{\mu \vec{v}_{AB}}{m_B} \end{cases}$$

Where $\vec{v}_{cm}$, $\vec{v}_{AB}$, and μ are the velocity of the center of mass, the relative velocity and the reduced mass, respectively.

(1 point)

We transform the differentials

$$d\vec{v}_A d\vec{v}_B = \left| det \begin{vmatrix} \dfrac{\partial \vec{v}_A}{\partial \vec{v}_{cm}} & \dfrac{\partial \vec{v}_A}{\partial \vec{v}_{AB}} \\ \dfrac{\partial \vec{v}_B}{\partial \vec{v}_{cm}} & \dfrac{\partial \vec{v}_B}{\partial \vec{v}_{AB}} \end{vmatrix} \right| d\vec{v}_{cm} d\vec{v}_{AB} = \left| det \begin{vmatrix} 1 & \dfrac{\mu}{m_A} \\ 1 & -\dfrac{\mu}{m_B} \end{vmatrix} \right| d\vec{v}_{cm} d\vec{v}_{AB} = d\vec{v}_{cm} d\vec{v}_{AB}$$

to obtain

$$f(v_{A,x}, v_{A,y}, v_{B,x}, v_{B,y})dv_{A,x}dv_{A,y}dv_{B,x}dv_{B,y} = \frac{m_A m_B}{(2\pi k_B T)^2}\, e^{-\frac{(m_A+m_B)(v_{cm,x}^2+v_{cm,y}^2)+\mu(v_{AB,x}{}^2 + v_{AB,y}^2)}{2k_BT}} dv_{cm,x}dv_{cm,y}dv_{AB,x}dv_{AB,y}$$

(2 points)

We integrate out the center of mass coordinates, realizing that the integral is over a velocity distribution of a particle with mass $m_A + m_B$, where the distribution function has been devided by $m_A + m_B$.

$$\iint_{-\infty}^{\infty} \frac{1}{2\pi k_B T}\, e^{-\frac{(m_A+m_B)(v_{cm,x}^2+v_{cm,y}^2)}{2k_BT}} dv_{cm,x}dv_{cm,y} = \frac{1}{m_A + m_B}$$

(1 point)

We now need to transform the relative velocity distribution to polar coordinates, in order to average over the radial distribution part.

$$\begin{cases} v_{AB,x} = v\cos(\theta) \\ v_{AB,y} = v\sin(\theta) \end{cases}$$

With the change of variables $dv_{AB,x}dv_{AB,y} = v\, dv\, d\theta$, we obtain

$$\frac{\mu}{2\pi k_B T}\, e^{-\frac{\mu(v_{AB,x}^2 + v_{AB,y}^2)}{2k_BT}} dv_{AB,x}dv_{AB,y} = \frac{\mu}{2\pi k_B T}\, e^{-\frac{\mu v^2}{2k_BT}} v dv d\theta$$

Integrating over the radial part yields the relative velocity distribution of a two-dimensional gas

$$\frac{\mu}{2\pi k_B T}\, e^{-\frac{\mu v^2}{2k_BT}} v dv \int_0^{2\pi} d\theta = \frac{\mu}{k_B T}\, e^{-\frac{\mu v^2}{2k_BT}} v dv$$

(2 points)