Dynamics and Kinetics – Final Exam

January 19, 2024

Name:

Total 51 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 $n = 0, 1, 2, \ldots$

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

$\cos(2\alpha) = \cos^2(\alpha) - \sin^2(\alpha)$

$\sin(2\alpha) = 2\sin(\alpha)\cos(\alpha)$

$\cos^2\left(\frac{\alpha}{2}\right) = \frac{1+\cos(\alpha)}{2}, \quad \sin^2\left(\frac{\alpha}{2}\right) = \frac{1-\cos(\alpha)}{2}$

$\int \frac{1}{\sqrt{r^2-x^2}}dx = \arcsin\left(\frac{x}{r}\right) + C$

$\arccos(-x) = \pi - \arccos(x)$

$\arcsin(x) = \pi/2 - \arccos(x)$

$\cos(\arcsin(x)) = \sin(\arccos(x)) = \sqrt{1-x^2}$

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

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

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

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

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

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

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

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

1) The gas phase reaction between CO and Cl_2 to form phosgene (Cl_2CO)

$$\mathbf{Cl_2 + CO \xrightarrow{k_{obs}} Cl_2CO}$$

has the rate law

$$\frac{d[\mathrm{Cl_2CO}]}{dt} = k_{obs}\,[\mathrm{Cl_2}]^{3/2}[\mathrm{CO}]$$

(6 points total)

a) Show that the following mechanism is consistent with this rate law.

$$\begin{array}{rcll} \mathrm{Cl_2 + M} & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & \mathrm{2\,Cl + M} & \text{(fast)} \\ \mathrm{Cl + CO + M} & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & \mathrm{ClCO + M} & \text{(fast)} \\ \mathrm{ClCO + Cl_2} & \overset{k_3}{\rightarrow} & \mathrm{Cl_2CO + Cl} & \text{(slow)} \end{array}$$

where M is any gas molecule present in the reaction container. Express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

(3 points)

Assuming a pre-equilibrium in the first two steps, we can write

$$K_1 = \frac{[\mathrm{M}][\mathrm{Cl}]^2}{[\mathrm{Cl_2}][\mathrm{M}]} = \frac{[\mathrm{Cl}]^2}{[\mathrm{Cl_2}]}$$

and

$$K_2 = \frac{[\mathrm{ClCO}][\mathrm{M}]}{[\mathrm{Cl}][\mathrm{CO}][\mathrm{M}]} = \frac{[\mathrm{ClCO}]}{[\mathrm{Cl}][\mathrm{CO}]}$$

so that

$$[\mathrm{Cl}] = K_1^{1/2}[\mathrm{Cl_2}]^{1/2}$$

and

$$[\mathrm{ClCO}] = K_2[\mathrm{Cl}][\mathrm{CO}]$$

For the third reaction step, we obtain the rate law

$$\frac{d[\mathrm{Cl_2CO}]}{dt} = k_3[\mathrm{ClCO}][\mathrm{Cl_2}]$$

We then substitute the expressions for $[\mathrm{Cl}]$ and $[\mathrm{ClCO}]$

$$\begin{aligned}\frac{d[\mathrm{Cl_2CO}]}{dt} &= k_3K_2[\mathrm{Cl}][\mathrm{CO}][\mathrm{Cl_2}] \\ &= k_3K_2K_1^{1/2}[\mathrm{Cl_2}]^{3/2}[\mathrm{CO}]\end{aligned}$$

(2 points)

Using the principle of detailed balance, we find that

$$k_{obs} = \frac{k_3k_2k_1^{1/2}}{k_{-2}k_{-1}^{1/2}}$$

(1 point)

b) An alternative mechanism that has been proposed for this reaction is

$$\mathbf{Cl_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl + M} \qquad \textbf{(fast)}$$

$$\mathbf{Cl + Cl_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cl_3} \qquad \textbf{(fast)}$$

$$\mathbf{Cl_3 + CO \xrightarrow{k_3} Cl_2CO + Cl} \qquad \textbf{(slow)}$$

Show that this mechanism also gives the observed rate law.

(3 points)

For the third reaction step, we obtain the rate law

$$\frac{d[\mathrm{Cl_2CO}]}{dt} = k_3\,[\mathrm{Cl_3}][\mathrm{CO}]$$

Assuming pre-equilibria in the first two steps, we find

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[\mathrm{Cl_3}]}{[\mathrm{Cl}][\mathrm{Cl_2}]}$$

which gives

$$[\mathrm{Cl_3}] = \frac{k_2}{k_{-2}}[\mathrm{Cl}][\mathrm{Cl_2}]$$

as well as

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\mathrm{Cl}]^2[\mathrm{M}]}{[\mathrm{Cl_2}][\mathrm{M}]}$$

which gives

$$[\mathrm{Cl}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{Cl_2}]^{1/2}$$

(2 points)

Substituting this expression for [Cl] gives

$$[\mathrm{Cl_3}] = \frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{Cl_2}]^{3/2}$$

which after substitution into the rate law gives

$$\frac{d[\mathrm{Cl_2CO}]}{dt} = \frac{k_3 k_2 k_1^{1/2}}{k_{-2} k_{-1}^{1/2}}[\mathrm{Cl_2}]^{3/2}[\mathrm{CO}]$$

which corresponds to the observed rate law.

(1 point)

2) Consider the following reaction mechanism.

$$\mathbf{2\,A} \overset{k_1}{\rightarrow} \mathbf{B} \qquad \mathbf{(1)}$$

$$\mathbf{B + C} \overset{k_2}{\rightarrow} \mathbf{A + D} \qquad \mathbf{(2)}$$

Describe an algorithm (no need to write proper code) that uses the stochastic method to simulate the reaction above. (8 points)

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 two reactions has occurred within a time interval Δt is:

$$p_{no\_reaction}(t) = e^{-(k_1 n_A(n_A-1)+k_2 n_B n_C)\Delta t} = e^{-\alpha \Delta t}$$

with

$$\alpha = k_1 n_A(n_A-1) + k_2 n_B n_C$$

and n_A, n_B, and n_C the number of molecules of A, B, and C respectively. Moreover, we will use the variable n_D to describe the number of molecules D. Note that we have taken into account that one molecule of A cannot react with itself.

(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 two reactions has occurred from a second random number r_2 between 0 and 1 as follows.

$$\text{Reaction} \begin{cases} 1 \quad \text{has occured if} \quad r_2 < \frac{k_1 n_\mathrm{A}(n_\mathrm{A}-1)}{\alpha} \\ 2 \quad \text{has occured if} \quad r_2 \geq \frac{k_1 n_\mathrm{A}(n_\mathrm{A}-1)}{\alpha} \end{cases}$$

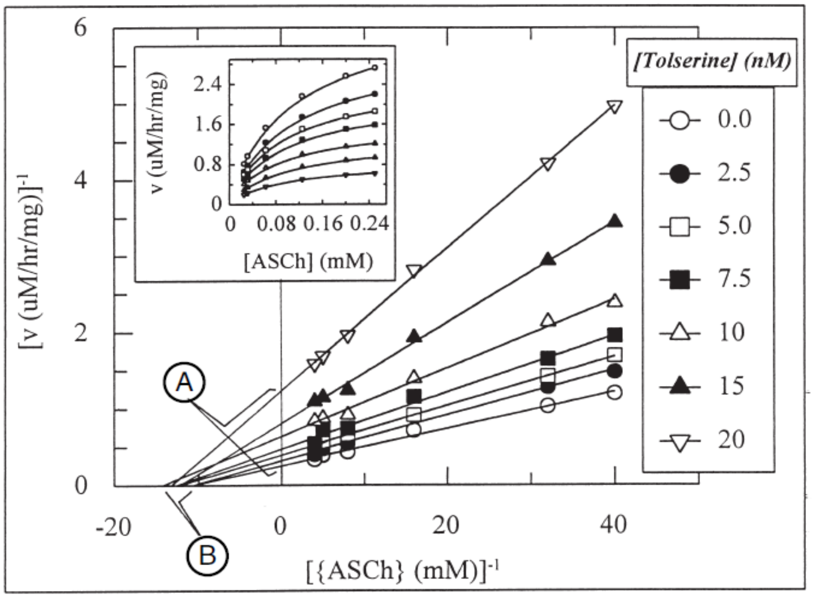
(2 points)

The numbers of molecules n_A, n_B, n_C, and n_D 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_A, n_B, n_C, and n_D as a function of time t.

(1 point)

3) Enzyme kinetics (8 points total)

a) Acetylcholinesterase catalyzes the conversion of acetylthiocholine (ASCh) into thiocholine. Reaction rates v were measured as a function of the substrate concentration in the presence of different concentrations of the inhibitor tolserine.



Which quantities can be obtained from the intercept with the y-axis (A) as well as the intercept with the x-axis (B)? Based on these data, what conclusions can you draw about the type of inhibition?

(2 points)

This plot corresponds to the Lineweaver-Burk plot. Therefore, we can identify the intercept with the y-axis (A) with $\frac{\alpha'}{v_{max}}$, where $\alpha' = 1 + \frac{[\mathrm{I}]}{K_{EI}}$. The intercept with the x-axis (B) corresponds to $-\frac{\alpha'}{\alpha * K_{ES}}$, where $\alpha = 1 + \frac{[\mathrm{I}]}{K_{ESI}}$ and K_{ES} is the Michaelis Menten constant under pre-equilibrium ($k_2 \ll k_{-1}$).

(1 point)

Since both the intercept with the y-axis and the slope change as a function of the inhibitor concentration, we can deduce that mixed (noncompetitive) inhibition occurs.

(1 point)

b) The following mechanism has been proposed for the conversion of acetylthiocholine (S) into thiocholine (P) by the enzyme acetylcholinesterase (E) in the presence of the inhibitor tolserine (I). Note that this is a variant of the mechanisms for inhibition that we have discussed in class.

$$\begin{array}{ccccc}
\mathbf{E + S + I} & \underset{\boldsymbol{k_{-1}}}{\overset{\boldsymbol{k_1}}{\rightleftharpoons}} & \mathbf{ES + I} & \xrightarrow{\boldsymbol{k_2}} & \mathbf{E + P + I} \\
\downharpoonleft\upharpoonright \;\; \boldsymbol{K_{EI}} & & & & \\
\mathbf{EI + S} & \overset{\boldsymbol{K_{ESI}}}{\leftrightarrows} & \mathbf{ESI} & \xrightarrow{\boldsymbol{k_3}} & \mathbf{E + P + I}
\end{array}$$

a) Find an expression for the rate of the reaction in analogy to our treatment of inhibited enzymatic reactions that we have discussed in class. The expression should only depend on the concentrations of the substrate $[S]$, the inhibitor $[\mathrm{I}]$, and the initial enzyme concentration $[\mathrm{E}]_0$. Explain the approximations you have to make in your derivation.

(4 points)

The rate of the reaction is.

$$v = \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] + k_3[\mathrm{ESI}]$$

(1 point)

Furthermore, we assume that k_2 and k_3 are small, so that all other species exist in a pre-equilibrium. We can therefore write down the dissociation constants of the different complexes as follows.

$$K_{ES} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{E}][\mathrm{S}]}{[\mathrm{ES}]}; \quad K_{EI} = \frac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]}; \quad K_{ESI} = \frac{[\mathrm{EI}][\mathrm{S}]}{[\mathrm{ESI}]}$$

(1 point)

In order to substitute the concentration $[\mathrm{ES}]$ in the expression for the rate of the reaction v we write down the mass balance.

$$\begin{aligned}[\mathrm{E}]_0 &= [\mathrm{E}] + [\mathrm{ES}] + [\mathrm{EI}] + [\mathrm{ESI}] \\ &= \frac{K_{ES}[\mathrm{ES}]}{[\mathrm{S}]} + [\mathrm{ES}] + \frac{K_{ES}[\mathrm{ES}][\mathrm{I}]}{K_{EI}[\mathrm{S}]} + \frac{K_{ES}[\mathrm{ES}][\mathrm{S}][\mathrm{I}]}{K_{ESI}[\mathrm{S}]} \\ &= [\mathrm{ES}]\left(1 + \frac{K_{ES}}{[\mathrm{S}]} + \frac{K_{ES}[\mathrm{I}]}{K_{EI}[\mathrm{S}]} + \frac{K_{ES}[\mathrm{I}]}{K_{ESI}}\right)\end{aligned}$$

For the concentration $[\mathrm{ESI}]$, we find

$$[\mathrm{ESI}] = \frac{[\mathrm{EI}][\mathrm{S}]}{K_{ESI}} = \frac{[\mathrm{E}][\mathrm{I}][\mathrm{S}]}{K_{EI}K_{ESI}} = \frac{K_{ES}[\mathrm{I}][ES]}{K_{EI}K_{ESI}}$$

We thus obtain

$$\begin{aligned}v &= k_2[\mathrm{ES}] + k_3[\mathrm{ESI}] \\ &= [\mathrm{ES}]\left(k_2 + k_3\,\frac{K_{ES}[\mathrm{I}]}{K_{EI}K_{ESI}}\right) \\ &= \frac{[\mathrm{E}]_0\left(k_2 + k_3\frac{K_{ES}[\mathrm{I}]}{K_{EI}K_{ESI}}\right)}{1 + \frac{K_{ES}}{[\mathrm{S}]} + \frac{K_{ES}[\mathrm{I}]}{K_{EI}[\mathrm{S}]} + \frac{K_{ES}[\mathrm{I}]}{K_{ESI}}} = \frac{v_{max}}{\alpha' + \alpha\frac{K_{ES}}{[\mathrm{S}]}}\end{aligned}$$

With $v_{max} = [\mathrm{E}]_0\left(k_2 + k_3\,\frac{K_{ES}[\mathrm{I}]}{K_{EI}K_{ESI}}\right)$, $\alpha' = 1 + \frac{K_{ES}[\mathrm{I}]}{K_{ESI}}$, and $\alpha = 1 + \frac{[\mathrm{I}]}{K_{EI}}$.

(2 points)

c) Show how this result changes in the limit of

- **the complex EI binding the substrate only very weakly?**
- **the inhibitor I binding only weakly to the enzyme E?**

What scenario or type of inhibition do you obtain in either case?

(2 points)

In the limit of the complex EI binding the substrate only very weakly, K_{ESI} goes to infinity, and the reaction rate simplifies to the case of competitive inhibition.

$$\lim_{K_{ESI}\to\infty} v = \frac{k_2[\mathrm{E}]_0}{1+\frac{K_{ES}}{[\mathrm{S}]}+\frac{K_{ES}[\mathrm{I}]}{K_{EI}[\mathrm{S}]}} = \frac{k_2[\mathrm{E}]_0}{1+\alpha\frac{K_{ES}}{[\mathrm{S}]}}$$

(1 point)

When the inhibitor binds only very weakly to the enzyme, K_{EI} goes to infinity, and no inhibition occurs. We obtain a rate that resembles the Michaelis Menten equation, with the Michaelis constant $K_M = \frac{k_{-1}+k_2}{k_1}$ replaced by $K_{ES} = \frac{k_{-1}}{k_1}$. This is because our assumption of a pre-equilibrium implies that k_2 is small compared with k_{-1}.

$$\lim_{K_{EI}\to\infty} v = \frac{k_2[\mathrm{E}]_0}{1+\frac{K_{ES}}{[\mathrm{S}]}}$$

(1 point)

This problem has been adapted from the following publication: Kamal, M. A. *et al.* “Kinetics of human acetylcholinesterase inhibition by the novel experimental Alzheimer therapeutic agent, tolserine.” Biochemical pharmacology vol. 60,4 (2000): 561-70.

4) Kinetic theory of gases. (13 points total)

a) Calculate the probability $P(u_{x0})$ that the x-component of the velocity u_x of a molecule lies in the range $-u_{x0} \le u_x \le u_{x0}$. Express the probability $P(u_{x0})$ in terms of the error function $erf(z)$.

$$\boldsymbol{erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} dx}$$

Sketch the probability $P(u_{x0})$.

(4 points)

We calculate the probability by integrating over the one-dimensional velocity distribution.

$$\begin{aligned} P(u_{x0}) &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \int_{-u_{x0}}^{u_{x0}} e^{-\frac{m u_x^2}{2k_B T}} du_x \\ &= 2\left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \int_{0}^{u_{x0}} e^{-\frac{m u_x^2}{2k_B T}} du_x \end{aligned}$$

(1 point)

In order to introduce the error function, we substitute

$$\frac{m u_x^2}{2k_B T} = \omega^2$$

$$du_x = \left(\frac{2k_B T}{m}\right)^{1/2} d\omega$$

with

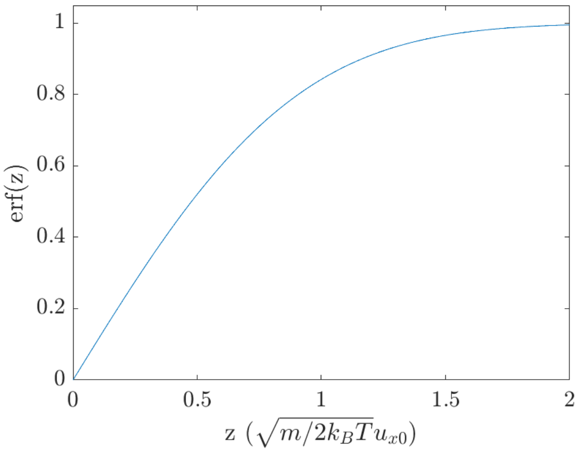
$$\omega_0 = \left(\frac{m}{2k_B T}\right)^{\frac{1}{2}} u_{x0}$$

Therefore,

$$P(u_{x0}) = \frac{2}{\sqrt{\pi}} \int_0^{\omega_0} e^{-\omega^2} d\omega = \mathrm{erf}(\omega_0) = \mathrm{erf}\left(\sqrt{\frac{m}{2k_B T}}\, u_{x0}\right)$$

(2 points)

The probability $P(u_{x0})$ takes the shape of the error function, which is shown below



(1 point)

b) Derive the speed distribution $F(u)du$ of a two-dimensional ideal gas.

Hint: Start from a one-dimensional velocity distribution to derive a two-dimensional distribution of the velocities, and then do a suitable coordinate transformation.

(6 points)

We begin with the one-dimensional distribution of the velocity

$$f(u_j) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m u_j^2}{2k_B T}}$$

which gives us the two-dimensional velocity distribution

$$h(u_x, u_y) du_x du_y = \frac{m}{2\pi k_B T} e^{-\frac{m(u_x^2+u_y^2)}{2k_B T}} du_x du_y$$

(2 points)

We do a coordinate transformation with

$$u^2 = u_x^2 + u_y^2$$
$$u_x = u \cos\phi$$
$$u_y = u \sin\phi$$
$$du_x du_y = u du d\phi$$

(2 points)

and obtain

$$\tilde{h}(u, \phi) du d\phi = \frac{m}{2\pi k_B T} u e^{-\frac{m u^2}{2k_B T}} du d\phi$$

(1 point)

which after integration over all angles becomes

$$F(u)du = \frac{m}{k_B T} u e^{-\frac{m u^2}{2k_B T}} du$$

(1 point)

c) Calculate the most frequent speed with which gas molecules strike a surface. Also calculate the most probable speed of a gas molecule. Finally, calculate the ratio of both.

(3 points)

The most probable speed of a molecule $u_{max,gas}$ can be calculated by setting the derivative of the Maxwell-Boltzmann distribution $F(u)$ to zero.

$$F(u)du \propto u^2 e^{-\frac{mu^2}{2k_BT}} du$$

$$\frac{dF(u)}{du} \overset{!}{=} 0$$

$$\frac{d}{du}\left(u^2 e^{-\frac{mu^2}{2k_BT}}\right) = \left(-\frac{2mu}{2k_BT}u^2 + 2u\right) e^{-\frac{mu^2}{2k_BT}} = 0$$

$$u_{max,gas} = \sqrt{\frac{2k_BT}{m}}$$

(1 point)

In class, we have seen that the frequency with which molecules of speed u collide with a wall is proportional to $uF(u)$. We therefore determine the maximum $u_{max,coll}$ of this function.

$$\frac{d\big(uF(u)\big)}{du} \overset{!}{=} 0$$

$$\frac{d}{du}\left(u^3 e^{-\frac{mu^2}{2k_BT}}\right) = \left(-\frac{2mu}{2k_BT}u^3 + 3u^2\right) e^{-\frac{mu^2}{2k_BT}} = 0$$

$$u_{max,coll} = \sqrt{\frac{3k_BT}{m}}$$

The ratio of both speeds is

$$\frac{u_{max,coll}}{u_{max,gas}} = \sqrt{\frac{3}{2}}$$

(2 points)

5) Reaction dynamics

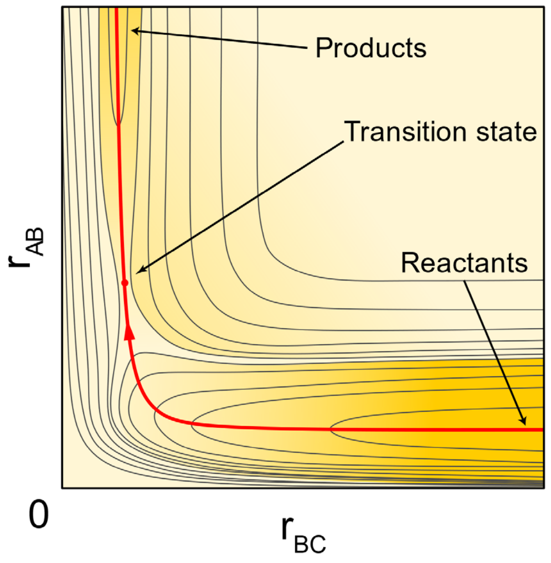
(8 points total)

a) Potential energy surfaces. Sketch the contour plot of a typical potential energy surface of a reaction

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

with the reaction constrained to a linear geometry. Here, A, B, and C are atoms. Assume that the reaction has a so-called "late" transition state, *i.e.* at the transition state, the configuration of the atoms is more similar to the products than the reactants. Draw the minimum energy path of the reaction and indicate where the reactants, the products, and the transition state are located.

(4 points)



Contour plot (2 points)
draw reaction path, indicate reactants, products, and transition state (2 points)

b) Unimolecular reactions. Explain qualitatively how the Hinshelwood rate constant and the RRK rate constant depend on the size of the molecule.

(4 points)

The Hinshelwood rate constant for the activation of a molecule through a collision

$$k_1 = \frac{k_{-1}}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$$

increases with the number of oscillators s since the higher the number of vibrational degrees of freedom, the more energy the molecule stores at thermal equilibrium, so that the probability increases that the total energy of a molecule exceeds the threshold energy E_0.

(2 points)

In contrast, the RRK rate constant

$$k(E) \; = \; \upsilon\left(\frac{E - E_0}{E}\right)^{s-1}$$

decreases with the number of oscillators s since the number of ways to distribute the energy E in the molecule increases. This decreases the probability that the energy stored in the critical mode exceeds the threshold energy E_0.

(2 points)

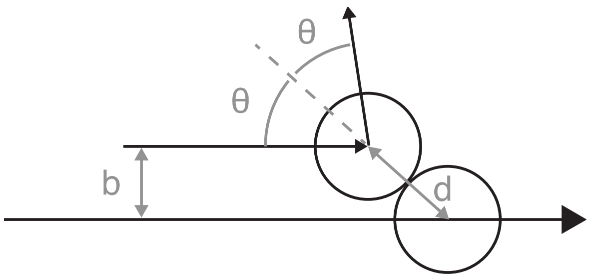
6) Bimolecular collisions

(8 points total)

a) In class, we have derived the deflection function for hard spheres collsions by first deriving an expression for the trajectory of a particle scattered by an arbitrary central potential.

Show that one can also derive this deflection function simply from geometric considerations of the collision geometry. Use the trigonometric identities given on page 1 to arrive at the expression we obtained in class.

(2 points)



From the sketch above we can see that the deflection angle is equal to

$$\chi(b) = \pi - 2\theta$$

(1 point)

with

$$\sin(\theta) = \frac{b}{d}$$

which gives us the final result.

$$\chi(b) = 2 \cdot \left(\frac{\pi}{2} - \arcsin\left(\frac{b}{d}\right)\right) = 2 \cdot \arccos\left(\frac{b}{d}\right)$$

This is the same expression as we derived in class.

(1 point)

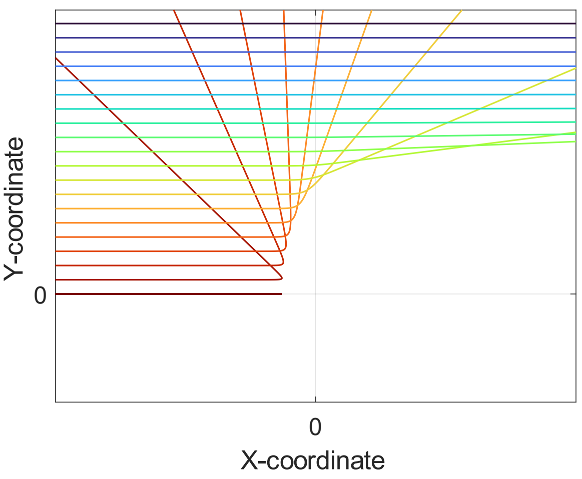
b) Consider bimolecular collisions with a central potential

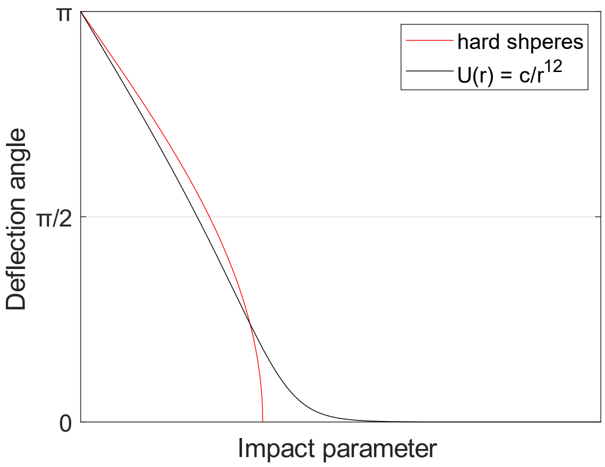
$$\boldsymbol{U(r)=\left(\frac{c}{r}\right)^{12}}$$

where c is a constant and r is the distance between the two particles.

Sketch representative trajectories that illustrate the scattering for small, intermediate, and large impact parameters. Sketch the deflection function together with the deflection function for a hard spheres collision. Explain qualitatively how the differences between these two deflection functions arise.

(3 points)



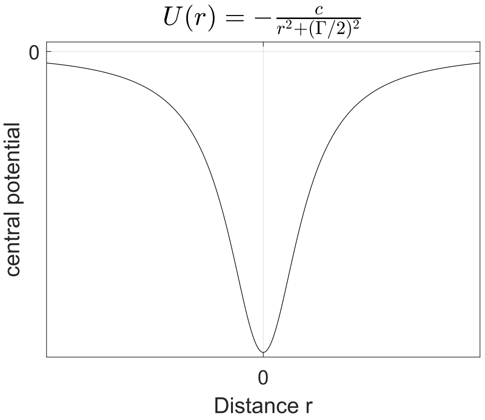


Since $U(r)$ is a steep, repulse potential, the corresponding deflection function is similar to that for hard spheres collisions. At large impact parameters, the deflection function asymptotically approaches zero unlike for the hard spheres potential. This is because $U(r)$ approaches zero more slowly at large impact parameters than the hard spheres potential, which suddenly drops to zero, so that a small deflection occurs even for large impact parameters.

(3 points)

b) Consider bimolecular collisions in a central potential defined by a negative Lorentzian

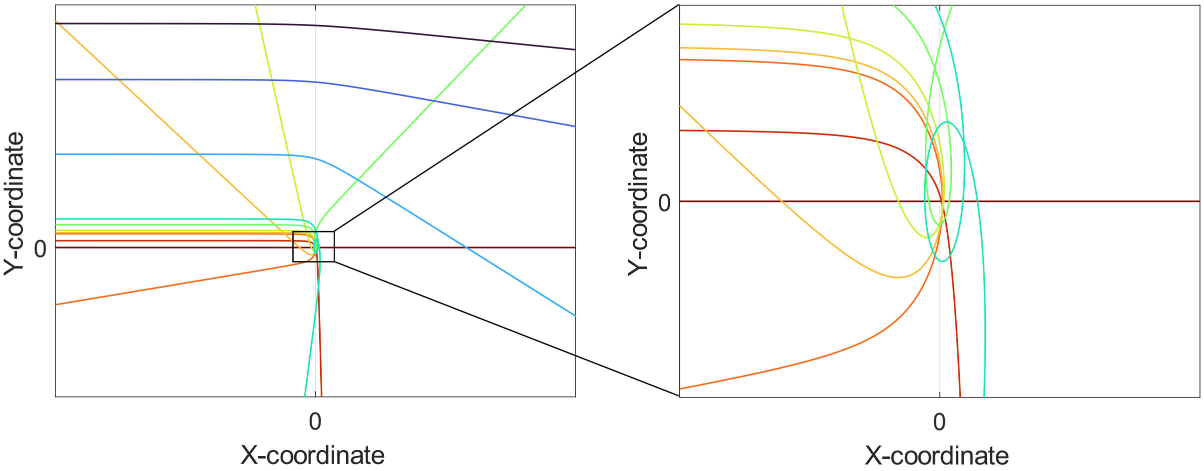
$$U(r) = -\frac{c}{r^2 + \left(\frac{1}{2}\Gamma\right)^2}$$



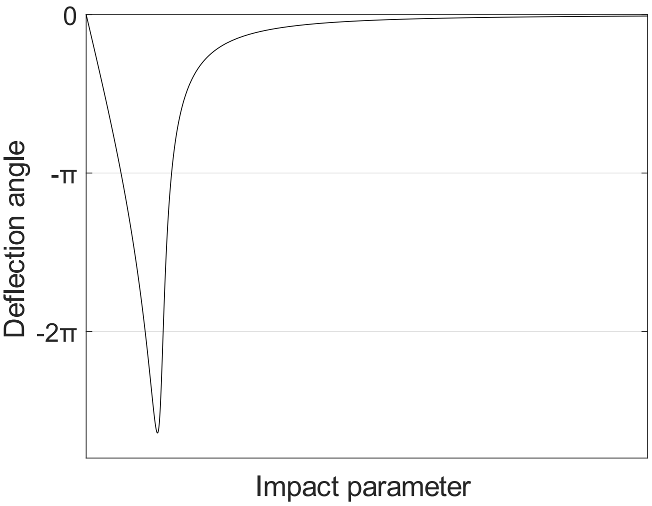
where c is a constant, r is the distance between the two particles, and Γ relates to the width of the Lorentzian.

Sketch representative trajectories that illustrate the scattering for small, intermediate, and large impact parameters. Sketch the deflection function together with the deflection function for a hard spheres collision. Explain qualitatively how the differences between these two deflection functions arise.

(3 points)



Since $U(r)$ is an attractive potential, the corresponding deflection function only shows negative deflection angles — quite in contrast to scattering in a hard spheres potential, which is repulsive and only shows positive deflection angles. This is a consequence of the conservation of angular momentum. In the above sketch, the trajectories can only curve around the origin in the clockwise sense, which leads to negative deflection angles.



The deflection function is zero for large impact parameters. However, as the impact parameter decreases, the trajectories are increasingly deflected towards the origin and even start to spiral around it. This causes the deflection function to drop to more negative values, before it finally goes through a minimum. For very small impact parameters, only small deflections occur, since the acceleration that the particles experience for most of their trajectory are largely parallel to the direction of travel. If the impact parameter is zero, no deflection occurs at all, and the deflection function is zero.

(3 points)