Dynamics and Kinetics – Final Exam

January 21, 2022

Name:

Total 48 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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1) In class we discussed two-body classical scattering with a central interaction potential. (9 points total)

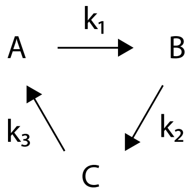
a) Sketch a typical trajectory of a scattering event. Sketch and explain the coordinate system you have chosen. Indicate and explain the masses and velocities involved. Explain the symmetry properties of the trajectory. Mark the impact parameter and deflection angle. (6 points)

- correct trajectory **(1 point)**
- center of mass coordinate system, with the origin coinciding with the origin of the central potential; with r the distance between the particles and polar angles θ and ϕ **(1 point)**
- composite particle with reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and relative velocity $v = v_1 - v_2$ **(1 point)**
- the trajectory is confined to a plane (ϕ does not change) **(1 point)**
- a point of minimum approach (r_c, θ_c) between the particles exists, with the trajectory symmetric with respect to a line through that point and the origin of the coordinate system **(1 point)**
- correct indication of impact parameter and deflection angle **(1 point)**

b) For scattering in a Lennard-Jones potential, sketch a deflection function with the kinetic energy comparable to the well depth. With the help of your sketch, explain the salient features of the deflection function. (3 points)

- correct sketch of the deflection function **(1 point)**
- negative deflection angles and rainbow angle occur because of attractive part of potential, which causes some trajectories to wrap around the scattering center **(1 point)**
- deflection function approaches π for small impact parameters and 0 for large impact parameters **(1 point)**

2) Describe an algorithm (no need to write proper code) to simulate the reaction



with the stochastic method and explain it. (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 three reactions has occurred within a time t is:

$$p_{no\_reaction}(t) = e^{-(k_1 n_A + k_2 n_B + k_3 n_C)t} = e^{-\alpha t}$$

with

$$\alpha = k_1 n_A + k_2 n_B + k_3 n_C$$

and n_A, n_B, and n_C the number of molecules of A, B, and C, respectively.

(2 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. We solve for t in order to determine the time interval Δt after which the next reaction occurs.

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

This is equivalent to

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

(2 points)

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

$$\text{Reaction} \begin{cases} 1 & \\ 2 & \text{has occurred if} \\ 3 & \end{cases} \begin{array}{c} r_2 < \frac{k_1 n_1}{\alpha} \\ \frac{k_1 n_1}{\alpha} \leq r_2 < \frac{k_1 n_1}{\alpha} + \frac{k_2 n_2}{\alpha} \\ r_2 \geq \frac{k_1 n_1}{\alpha} + \frac{k_2 n_2}{\alpha} \end{array}$$

(2 points)

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

(1 point)

3) In class, we have derived the RRK rate constant

$$\boldsymbol{k_2(E) = \nu\left(\frac{E - E_0}{E}\right)^{s-1}}$$

under the assumptions that the s vibrational degrees of freedom can be treated as classical harmonic oscillators. Derive the same expression for s quantized oscillators. (8 points total)

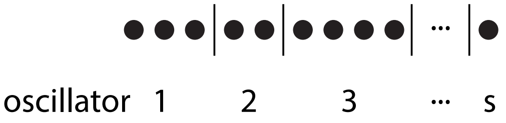
a) Explain the physical meaning of the terms ν and $\left(\frac{E-E_0}{E}\right)^{s-1}$ in the context of the assumptions of the RRK theory. (2 points)

The term ν corresponds to the rate at which a molecule of energy E dissociates (or isomerizes) if the energy stored in the critical mode (eigenfrequency ν) exceeds the threshold energy E (assumption 2 of the RRK theory).

The term $\left(\frac{E-E_0}{E}\right)^{s-1}$ corresponds to the probability that the energy stored in the critical mode exceeds E_0 and is calculated under the assumptions that the activated molecules form a microcanocial ensemble (assumption 1) and continue to do so after some have reacted (assumption 3).

b) Assume that all oscillators have the same eigenfrequency ν and that $E = Nh\nu$. How many possibilities exist to distribute the energy E over the s oscillators? (2 points)

We can visualize the problem as separating a string of N dots (representing the N quanta of vibrational energy) into s sections, where each section represents one oscillator and the number of dots per section represents the number of quanta stored in each oscillator.



There are $s - 1$ separating lines. The total number of ways create such patterns (the dots are indistiguisahble from each other, as are the separating lines) therefore is

$$\frac{(N + s - 1)!}{N!\,(s - 1)!}$$

c) How many possibilities exist to distribute the energy E over the s oscillators if an energy of at least $E_0 = N_0 h\nu$ is stored in the critical oscillator? (2 points)

With only $N - N_0$ quanta left to distribute over the s oscillators, the number of possibilities becomes

$$\frac{(N - N_0 + s - 1)!}{(N - N_0)!\,(s - 1)!}$$

d) With the results from b) and c), derive the RRK rate constant. Which further assumptions do you have to make? (2 points)

The probability of finding at least N_0 quanta in the critical mode is

$$P(E, E_s > E_0) = \frac{(N - N_0 + s - 1)!}{(N - N_0)!\,(s - 1)!} \Big/ \frac{(N + s - 1)!}{N!\,(s - 1)!} = \frac{(N - N_0 + s - 1)!}{(N - N_0)!} \Big/ \frac{(N + s - 1)!}{N!}$$

which for high energies (*i.e.* large N) and a small number of osciallators s, becomes

$$P(E, E_s > E_0) \approx \left(\frac{N - N_0}{N}\right)^{s-1} = \left(\frac{E - E_0}{E}\right)^{s-1}$$

from which we obtain the RRK rate constant.

4) Nitramide (O_2NNH_2) decomposes in water according to the following equation:

$$\mathbf{O_2NNH_2\,(aq) \overset{k}{\rightarrow} N_2O\,(g) + H_2O\,(l)}$$

The experimentally determined rate law is the following:

$$\frac{d[N_2O\,]}{dt} = k_{obs}\frac{[O_2NNH_2]}{[H^+]}$$

The following mechanism has been proposed.

$$\mathbf{O_2NNH_2\,(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^-\,(aq) + H^+\,(aq)} \qquad \textbf{(fast, pre-equilibrium)}$$

$$\mathbf{O_2NNH^-\,(aq) \overset{k_2}{\rightarrow} N_2O\,(g) + OH^-\,(aq)} \qquad \textbf{(slow)}$$

$$\mathbf{H^+\,(aq) + OH^-\,(aq) \overset{k_3}{\rightarrow} H_2O\,(l)} \qquad \textbf{(fast)}$$

(8 points total)

a) Is the proposed mechanism consistent with the rate found experimentally? If so, what is the relationship between observed rate k_{obs} and the rate constants of the elementary steps of the mechanism? (4 points)

The rate of production of NO_2 is given by

$$\frac{d[N_2O]}{dt} = k_2\,[O_2NNH^-]$$

(1 point)

If we assume that a pre-equilibrium exists in the first step, we can write down an equilibrium constant for this step

$$K_c = \frac{[O_2NNH^-][H^+]}{[O_2NNH_2]}$$

(1 point)

so that

$$\frac{d[N_2\mathrm{O}]}{dt} = k_2 K_c \frac{[\mathrm{O_2NNH_2}]}{[\mathrm{H^+}]}$$

(1 point)

This is consistent with the experimentally determined rate law, with

$$k_{obs} = \frac{k_2 k_1}{k_{-1}}$$

(1 point)

b) To analyze the kinetics of this complex reaction, one could consider applying the steady-state approximation to O_2NNH^- (aq). Is this consistent with the rate found experimentally? Under which conditions? (4 points)

Applying the steady state approximation to the concentration of O_2NNH^- (aq) yields

$$\frac{d[\mathrm{O_2NNH^-}]}{dt} = k_1[\mathrm{O_2NNH_2}] - k_{-1}[\mathrm{O_2NNH^-}][\mathrm{H^+}] - k_2[\mathrm{O_2NNH^-}] = 0$$

(1 point)

and

$$[\mathrm{O_2NNH^-}] = \frac{k_1[\mathrm{O_2NNH_2}]}{k_{-1}[\mathrm{H^+}] + k_2}$$

(1 point)

The rate of production of NO_2 therefore becomes

$$\frac{d[N_2\mathrm{O}]}{dt} = \frac{k_2 k_1[\mathrm{O_2NNH_2}]}{k_{-1}[\mathrm{H^+}] + k_2}$$

This results is consistent with the experimentally determined rate law if $k_2 \ll k_{-1}[\mathrm{H^+}]$.

(2 points)

5) The rate of a bimolecular reaction in the gas phase

A + B → products

generally depends on the relative kinetic energy of the collision. Calculate the total frequency of collisions per unit volume between A and B that have a *relative* kinetic energy larger or equal than a threshold energy E_0. (8 points)

The frequency dz_{AB} of collisions per unit volume occurring with a velocity between v and $v + dv$ is

$$dz_{AB} = \sigma_{AB} v_{AB} \rho_A \rho_B F(v_{AB}) dv_{AB}$$

where

$$F(v_{AB}) dv_{AB} = 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v_{AB}^2 e^{-\frac{\mu v_{AB}^2}{2k_B T}} dv_{AB}$$

is a Maxwell-Boltzmann distribution for the relative particle velocity v_{AB} and the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

(2 points)

We carry out a transformation with

$$v_{AB} = \sqrt{\frac{2E}{\mu}}$$

$$dv_{AB} = \frac{dE}{\sqrt{2\mu E}}$$

where E is the relative collision energy, **(1 point)**

so that

$$dz_{AB} = \sigma_{AB} \rho_A \rho_B \left(\frac{1}{k_B T}\right)^{\frac{3}{2}} \left(\frac{8}{\mu\pi}\right)^{\frac{1}{2}} E e^{-\frac{E}{k_B T}} dE$$

(1 point)

The total collision frequency per unit volume for collisions with energy greater than or equal to E_0 is then

$$z_{AB}(E \geq E_0) = \sigma_{AB}\rho_A\rho_B \left(\frac{1}{k_B T}\right)^{\frac{3}{2}} \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \int_{E_0}^{\infty} E e^{-\frac{E}{k_B T}}\, dE$$

(1 point)

We can solve the integral either through partial integration or through suitable transformation and use of the gamma function to obtain

$$\int_{E_0}^{\infty} E e^{-\frac{E}{k_B T}}\, dE = (k_B T)^2 \left(\frac{E_0}{k_B T} + 1\right) e^{-\frac{E_0}{k_B T}}$$

(2 points)

and

$$z_{AB}(E \geq E_0) = \sigma_{AB}\rho_A\rho_B \left(\frac{8 k_B T}{\pi\mu}\right)^{\frac{1}{2}} \left(\frac{E_0}{k_B T} + 1\right) e^{-\frac{E_0}{k_B T}}$$

(1 point)

6) Given is the following reaction.

$$\mathbf{A}\xrightarrow{k_1}\mathbf{B}\xrightarrow{k_2}\mathbf{C}\xrightarrow{k_3}\mathbf{D}\xrightarrow{k_4}\mathbf{E}$$

(7 points total)

a) Determine the concentration of C if the concentrations of B, C, and D are initially zero.

It would certainly be possible to solve this problem sequentially. Instead, use the following approach that is more simple.

In class, we have already integrated the rate equations for the consecutive reaction

$$\mathbf{B}\xrightarrow{k_2}\mathbf{C}\xrightarrow{k_3}\mathbf{D}$$

where the initial concentrations of C and D are zero. For a given initial concentration of B, the time-dependent concentration of C is

$$[\mathbf{C}] = \frac{k_2[\mathbf{B}]_0}{k_3 - k_2}\left(e^{-k_2 t} - e^{-k_3 t}\right)$$

The difference in our problem here is that B does not start out with a fixed initial concentration $[\mathrm{B}]_0$, but is continuously being formed. However, for a very small quantity $d[\mathrm{B}(t')]$ that is formed at a given point in time t', we can calculate how much C will be formed from this amount $d[\mathrm{B}(t')]$ at a later time $t - t'$. Use this idea to solve for the concentration of C. (5 points)

We know that the decay of A is described by

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t'}$$

(1 point)

Therefore, the quantity $d[\mathrm{B}]$ that is being created at any given point in time t' during a time interval dt' is given by

$$d[\mathrm{B}(t')] = -\frac{d[\mathrm{A}(t')]}{dt'}dt' = k_1[\mathrm{A}]_0 e^{-k_1 t'}dt'$$

(1 point)

The quantity of C that is being formed at time t' from this small quantity of B then becomes

$$d[\mathrm{C}(t)] = k_1[\mathrm{A}]_0 e^{-k_1 t'} \frac{k_2}{k_3 - k_2}\left(e^{-k_2(t-t')} - e^{-k_3(t-t')}\right)dt'$$

(1 point)

so that

$$[\mathrm{C(t)}] = \int_0^t k_1[\mathrm{A}]_0 e^{-k_1 t'} \frac{k_2}{k_3 - k_2}\left(e^{-k_2(t-t')} - e^{-k_3(t-t')}\right)dt'$$

(1 point)

$$\begin{aligned}
[\mathrm{C(t)}] &= \frac{k_1 k_2[\mathrm{A}]_0}{k_3 - k_2}\left\{e^{-k_2 t}\int_0^t e^{-(k_1-k_2)t'}dt' - e^{-k_3 t}\int_0^t e^{-(k_1-k_3)t'}dt'\right\} \\
&= \frac{k_1 k_2[\mathrm{A}]_0}{k_3 - k_2}\left\{\frac{e^{-k_1 t} - e^{-k_3 t}}{k_1 - k_3} - \frac{e^{-k_1 t} - e^{-k_2 t}}{k_1 - k_2}\right\}
\end{aligned}$$

(1 point)

b) Based on your result in a), how can you use the same approach to calculate the concentration of D in the following reaction (initial concentrations are all zero except that of A)?

$$\mathbf{A} \xrightarrow{\boldsymbol{k_1}} \mathbf{B} \xrightarrow{\boldsymbol{k_2}} \mathbf{C} \xrightarrow{\boldsymbol{k_3}} \mathbf{D} \xrightarrow{\boldsymbol{k_4}} \mathbf{E}$$

Write down the integral for the concentration of D. There is, however, no need to solve the integral. (2 points)

$$[\mathrm{D(t)}] = \int_0^t k_1[\mathrm{A}]_0 e^{-k_1 t'} \frac{k_2 k_3}{k_4 - k_3}\left\{\frac{e^{-k_2(t-t')} - e^{-k_4(t-t')}}{k_2 - k_4} - \frac{e^{-k_2(t-t')} - e^{-k_3(t-t')}}{k_2 - k_3}\right\}dt'$$