

Cross sections, rate constants, microscopic reversibility, detailed balance, and the master equation in inelastic and reactive kinetics

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I. INTRODUCTION

II. STATE-TO-STATE RATE CONSTANTS

A. Inelastic collisions with a structureless atom

For simplicity, we restrict ourselves to the situation where we have a molecule in state $|i\rangle$ with rotational degeneracy $(2j_i + 1)$ and internal energy ε_i which collides with a structureless particle and undergoes a transition to state $|f\rangle$ with rotational degeneracy $(2j_f + 1)$ and internal energy ε_f . The collision between the molecule and the structureless particle can be characterized by the initial velocity and the impact parameter b , as shown in Fig. 1.

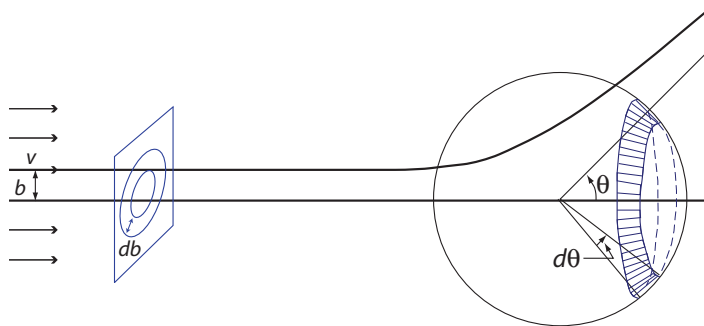


FIG. 1. Scattering of an incident beam of particles by a target (taken from fig. 3.1 of H. Goldstein, *Classical Mechanics*).

At each impact parameter, there is a probability $P_{if}(b)$ that an inelastic transition will take place from state $|i\rangle$ to state $|f\rangle$. The overall probability, integrated over all impact parameters, is then

$$\int_0^{\infty} 2\pi b P_{if}(b) db.$$

The weighting by $2\pi b$ occurs because collisions at impact parameter b can occur anywhere on the circumference of a circle of radius b .

This integral, which has the dimensions of area, is called the inelastic “cross section”. Before the collision, the angular momentum associated with the relative motion of the molecule and the target is $\vec{l} = \vec{b} \times \vec{p} = \mu v b$, where μ is the collision reduced mass. In quantum mechanics, this relation becomes $J + 1/2 = \mu v b / \hbar$, where J is restricted to integer values. Thus,

the cross section, in quantum mechanics, is

$$\sigma_{i \rightarrow f}(v) = \frac{2\pi\hbar^2}{(\mu v)^2} \sum_{J=0}^{\infty} (J + 1/2) P_{if}^J(v) = \frac{\pi}{k_i^2} \sum_{J=0}^{\infty} (2J + 1) P_{if}^J(v) \quad (1)$$

Here k_i , the wavevector in the initial state, is

$$k_i^2 = \frac{2\mu E_x}{\hbar^2} = \frac{2\mu(\mathcal{E} - \varepsilon_i)}{\hbar^2}$$

where E_c is the initial translational energy, \mathcal{E} is the total energy, and ε_i is the internal energy in state $|i\rangle$, with $\mathcal{E} = E_c + \varepsilon_i$. Note that the continuously variable transition probability $P_{if}(b)$ is here replaced by a discrete transition probability which depends on the particular value of the angular momentum. Now, suppose the initial and final levels are characterized by degeneracies $(2j_i + 1)$ and $(2j_f + 1)$. Then, the cross section, summed over the rotational degeneracy of the product state and averaged over the rotational degeneracy of the initial state, is

$$\begin{aligned} \sigma_{i \rightarrow f}(\mathcal{E}) &= \frac{\pi}{(2j_i + 1)k_i^2} \sum_J \sum_{m_i, m_f} (2J + 1) P_{j_i m_i, j_f m_f}^J(\mathcal{E}) \\ &= \frac{\pi}{(2j_i + 1)k_i^2} \sum_J \sum_{m_i, m_f} (2J + 1) \left| T_{j_i m_i, j_f m_f}^J(\mathcal{E}) \right|^2 \end{aligned} \quad (2)$$

Here, T designates an T -matrix element, the square of which is the transition probability; and m_i and m_f are the space-frame projection quantum number of the initial and final rotation levels of the molecule. In Eq. (2) the independent variable is now the total energy rather than the initial translational velocity. Note that we refer here to the cross section at total energy \mathcal{E} , whereas in Eq. (1) the cross section is written as a function of the collision velocity. There is a one-to-one correspondence between the two independent variables, since

$$v = (2\mu E_c)^{1/2} = [2\mu(\mathcal{E} - \varepsilon_i)]^{1/2}$$

Now, the T matrix is symmetric – which is a consequence of time reversibility – so that the transition probabilities satisfy *microscopic reversibility*

$$P_{j_i m_i, j_f m_f}^J(\mathcal{E}) = P_{j_f m_f, j_i m_i}^J(\mathcal{E})$$

Note that this relation applies to the transition probabilities at the same total energy. Because of this symmetry, we can relate the $i \rightarrow f$ cross section given by Eq. (2) to the equivalent equation for the $f \rightarrow i$ cross section, obtaining

$$(2j_i + 1)k_i^2\sigma_{i \rightarrow f}(\mathcal{E}) = (2j_f + 1)k_f^2\sigma_{f \rightarrow i}(\mathcal{E})$$

or

$$(2j_i + 1)(\mathcal{E} - \varepsilon_i)\sigma_{i \rightarrow f}(\mathcal{E}) = (2j_f + 1)(\mathcal{E} - \varepsilon_f)\sigma_{f \rightarrow i}(\mathcal{E}) \quad (3)$$

This equality applies to the $i \rightarrow f$ and $f \rightarrow i$ cross sections at the same total energy but not at the same collision energy.

The rate of collision induced transitions is equal to the cross section times the incoming flux (number of particles impinging on the target per unit time per unit area). By elementary kinetic theory, the flux is just equal to the relative velocity times the number density of particles (ρ). Thus the bimolecular rate is

$$\frac{dn_{i \rightarrow f}}{dt} = \rho k_{i \rightarrow f}(v) = \rho v \sigma_{i \rightarrow f}(v)$$

where $k_{i \rightarrow f}(v)$ is the ‘‘rate constant’’ (some people call this the rate ‘‘coefficient’’) at relative velocity v , and ρ is the number density of the collision partner. The thermal rate constant is given by the average of $k(v)$ over a Maxwell distribution of relative velocities

$$k(T) = \int_0^\infty k(v) f(v) dV$$

where

$$f(v) = \sqrt{\frac{2}{\pi}} \left(\frac{\mu}{k_B T} \right)^3 v^2 \exp(-\mu v^2 / 2k_B T)$$

and k_B is Boltzmann’s constant.

We can convert this integration to extend over collision energy E_c , rather than collision velocity, using the relations $E_c = \mu v^2 / 2$, $v = (2E_c / \mu)^{1/2}$, and $dv \sqrt{2/\mu} E_c^{-1/2} dE_c$. We obtain

$$k_{i \rightarrow f}(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_0^\infty \sigma_{i \rightarrow f}(\mathcal{E}) E_c \exp(-E_c / k_B T) dE_c \quad (4)$$

We can then convert the integration variable from collision energy to total energy, obtaining

$$\begin{aligned} k_{i \rightarrow f}(T) &= \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_{\varepsilon_i}^{\infty} \sigma_{i \rightarrow f}(\mathcal{E})(\mathcal{E} - \varepsilon_i) \exp[-(\mathcal{E} - \varepsilon_i)/k_B T] d\mathcal{E} \\ &= \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \exp(\varepsilon_i/k_B T) \int_0^{\infty} \sigma_{i \rightarrow f}(\mathcal{E})(\mathcal{E} - \varepsilon_i) \exp(-\mathcal{E}/k_B T) d\mathcal{E} \end{aligned} \quad (5)$$

Because the cross section vanishes unless the total energy \mathcal{E} is greater than the larger of ε_i and ε_f , the range of integration can be set to $\{0, \infty\}$ without any loss of generality (as we have done in the 2nd line of the previous equation). By switching the indices i and f in the last equation we obtain an equivalent relation for the $f \rightarrow i$ rate constant:

$$k_{f \rightarrow i}(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \exp(\varepsilon_f/k_B T) \int_0^{\infty} \sigma_{f \rightarrow i}(\mathcal{E})(\mathcal{E} - \varepsilon_f) \exp(-\mathcal{E}/k_B T) d\mathcal{E} \quad (6)$$

Substituting Eq. (3) into the last equation, we obtain

$$k_{f \rightarrow i}(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \left[\frac{2j_i + 1}{2j_f + 1} \right] \exp(\varepsilon_f/k_B T) \int \sigma_{i \rightarrow f}(\mathcal{E})(\mathcal{E} - \varepsilon_i) \exp(-\mathcal{E}/k_B T) d\mathcal{E}$$

Relating this equation to Eq. (5), we can show that

$$(2j_f + 1) \exp(-\varepsilon_f/k_B T) k_{f \rightarrow i}(T) = (2j_i + 1) \exp(-\varepsilon_i/k_B T) k_{i \rightarrow f}(T) \quad (7)$$

which is the fundamental detailed balance relation. This can be written, equivalently, as

$$\frac{k_{f \rightarrow i}(T)}{k_{i \rightarrow f}(T)} = \frac{(2j_i + 1)}{(2j_f + 1)} \exp(\Delta E/k_B T) \quad (8)$$

where

$$\Delta E = \varepsilon_f - \varepsilon_i \quad (9)$$

1. *High- and low-temperature limits*

It is worthwhile examining the low- and high-temperature limiting cases. At high temperature where $k_B T \gg \Delta E$ and $\lim_{T \rightarrow \infty} \exp(\Delta E/k_B T) = 1$ we obtain

$$\lim_{T \rightarrow \infty} \frac{k_{f \rightarrow i}(T)}{k_{i \rightarrow f}(T)} = \frac{(2j_i + 1)}{(2j_f + 1)}$$

Thus, at high temperature the ratio of the backward to forward rate constants is just the inverse of the ratio of the rotational degeneracies. Imagine that all $m \rightarrow m'$ transitions are equally probable. Then the larger rate will occur for transitions into the state with the largest number of m projection states.

At low temperature $\Delta E \gg k_B T$, so that the rate for collisional de-excitation ($\varepsilon_f < \varepsilon_i$) will become much larger than the rate for collisional excitation. Again, this is reasonable: At low temperature, where the average translational energy is small, it will be much harder to go uphill than downhill.

We remember that the Boltzmann probability for population of level j is

$$p_j(T) = Z_r(T)^{-1} (2j + 1) \exp(-\varepsilon_j/k_B T)$$

with the rotational partition function defined by

$$Z_r(T) = \sum_j (2j + 1) \exp(-\varepsilon_j/k_B T)$$

Thus, Eq. (7) is equivalent to

$$p_f k_{f \rightarrow i}(T) = p_i k_{i \rightarrow f}(T) \tag{10}$$

which is perhaps the simplest expression: The forward and reverse rates, weighted by the fractional Boltzmann populations of the two states at temperature T , are equal.

B. Overall inelastic collisional depletion and infill rates

Consider a situation a particular initial rotational level i of a given vibrational manifold is populated (as, for example, by laser excitation from a lower state) and where one subsequently monitors the population of this initially populated level. If none of the other

neighboring rotationally levels is populated at $t = 0$, then the time rate of change of the initially populated level is

$$\frac{dn_i}{dt} = -\rho n_i \sum_{f \neq i} k_{i \rightarrow f} \equiv -\rho n_i k_i^{(L)} \quad (11)$$

where $k_i^{(L)}(T)$ is the rate constant for loss of population out of this initial level.

In this experiment the population in level i follows first-order decay kinetics and initially decreases exponentially with time. At longer time, as the populations in the other levels becomes significant, the kinetic equations must be modified to include back reactions. Eventually, the evolution of the level populations must reflect the thermalization of the rotational populations in the vibrational level of interest.

Now, consider a situation where all the rotational levels are in thermal equilibrium and where we initially deplete level i and monitor the collisional refilling of this level. The time rate of change of the population of the initially depleted level is

$$\frac{dn_i}{dt} = \rho \sum_{f \neq i} n_f k_{f \rightarrow i} \quad (12)$$

(we can initially ignore back reaction out of the depleted level).

If the rotational states are at thermal equilibrium at temperature T , then

$$n_f = p_f(T)n$$

where n is the total population of the vibrational manifold under consideration. Thus, we can transform Eq. (12) to

$$\frac{dn_i}{dt} = \rho n \sum_{f \neq i} p_f k_{f \rightarrow i} \quad (13)$$

We can use the detailed balance relation [Eq. (10)] to rewrite the preceding equation as

$$\frac{dn_i}{dt} = \rho n \sum_{f \neq i} p_i k_{i \rightarrow f} = \rho n_i \sum_{f \neq i} k_{i \rightarrow f} = \rho n_i k_i^{(L)} \quad (14)$$

Thus, the refilling rate constant is equal in magnitude (and opposite in sign) to the loss rate that one would measure in a more typical depletion experiment.

C. Reactive collisions

In the case of a reactive collision, Eq. (2) still remains valid, but because the collision reduced mass differs from reactants to products, since (for an $A+BC \rightarrow AB+C$ reaction)

$$\mu_{reactant} = \frac{M_A(M_B + M_C)}{M_A + M_B + M_C}$$

and

$$\mu_{product} = \frac{M_C(M_A + M_B)}{M_A + M_B + M_C}$$

the equation for microscopic reversibility [Eq. (3)] becomes (replacing the indices i and f by r and p)

$$(2j_{re} + 1)\mu_r (\mathcal{E} - \varepsilon_r) \sigma_{r \rightarrow p}(\mathcal{E}) = (2j_p + 1)\mu_p (\mathcal{E} - \varepsilon_p) \sigma_{p \rightarrow r}(\mathcal{E}) \quad (15)$$

Note that this equation is a just a statement of conservation Equations (4), (5), and (6) still remain valid, except that for the occurrence of the two different reduced masses. After a little algebra, one obtains a detailed balance relation similar to Eq. (8)

$$\begin{aligned} \frac{k_{j' \rightarrow j}^{(b)}(T)}{k_{j \rightarrow j'}^{(f)}(T)} &= \left[\frac{\mu_r}{\mu_p} \right]^{3/2} \frac{(2j + 1)}{(2j' + 1)} \exp(\Delta E_{j \rightarrow j'} / k_B T) \\ &= \left[\frac{M_A(M_B + M_C)}{M_C(M_A + M_B)} \right]^{3/2} \frac{(2j + 1)}{(2j' + 1)} \exp(\Delta E_{j \rightarrow j'} / k_B T) \end{aligned} \quad (16)$$

This relation applies to reaction from a particular $j_r = j$ rotational level of the reactants to a particular $j_p = j'$ rotational level of the products. For simplicity the superscript index f (forward) implies reaction from reactant to products while the superscript b (backward) refers to reaction of the products to yield reactants. The exoergicity, defined in the case of an inelastic collision by Eq. (9), has to be modified here to

$$\Delta E_{j \rightarrow j'} = \Delta E_{rxn} + \varepsilon_{j'} - \varepsilon_j$$

where ΔE_{rxn} is the reaction (endo/exo)ergicity (the energy of reaction). Note that ΔE_{rxn} is negative for an exoergic reaction. Thus

$$\exp(\Delta E_{j \rightarrow j'} / k_B T) = \exp(\Delta E_{rxn} / k_B T) \exp(\varepsilon_{j'} / k_B T) \exp(-\varepsilon_j / k_B T) \quad (17)$$

Here ε_j is the rotational energy of level j *with the zero of energy taken as the ground rotational level*.

Thus, Eq. (16) can be rewritten as

$$k_{j' \rightarrow j}^{(b)}(T) = k_{j \rightarrow j'}^{(f)}(T) \left[\frac{\mu_r}{\mu_p} \right]^{3/2} \frac{(2j+1) \exp(-\varepsilon_j/k_B T)}{(2j'+1) \exp(-\varepsilon_{j'}/k_B T)} \exp(\Delta E_{rxn}/k_B T) \quad (18)$$

Now, the Boltzmann probability that rotational level j is occupied at temperature T is

$$p_j(T) = \frac{(2j+1) \exp(-\varepsilon_j/k_B T)}{\sum_j (2j+1) \exp(-\varepsilon_j/k_B T)} = \frac{(2j+1) \exp(-\varepsilon_j/k_B T)}{Z_r(T)}$$

where $Z_r(T)$ is the rotational partition function. In other words

$$(2j+1) \exp(-\varepsilon_j/k_B T) = p_j(T) Z_r(T) \quad (19)$$

If you introduce this equation and Eq. (17) into Eq. (16), you obtain

$$p_{j'}(T) Z_r^{(p)}(T) k_{j' \rightarrow j}^{(b)}(T) = \left[\frac{\mu_r}{\mu_p} \right]^{3/2} \exp(\Delta E_{rxn}/k_B T) p_j(T) Z_r^{(r)}(T) k_{j \rightarrow j'}^{(f)}(T) \quad (20)$$

Now, let us define a thermally-averaged total rate constant which is the sum, over all accessible final rotational levels, and the average, over all populated initial rotational levels, of the state-to-state rate constant. The average over the initial states is just the sum over the rate out of each initial state weighted by the probability that the initial rotational level is populated, namely $p_j(T)$. For the forward (reactant \rightarrow product) direction this thermally-averaged rate constant is

$$k^f(T) = \sum_j \sum_{j'} p_j(T) k_{j \rightarrow j'}^{(f)}(T)$$

and, for the backward (product \rightarrow reactant) direction

$$k^b(T) = \sum_j \sum_{j'} p_{j'}(T) k_{j' \rightarrow j}^{(b)}(T)$$

Since the masses, the rotational partition functions, and the $\exp(\Delta E_{rxn}/k_B T)$ term in Eq. (20) do not depend on j and j' , we can carry out these sums directly, just by summing

Eq. (20) over j and j' . We obtain

$$Z_r^{(p)}(T) \sum_{\tilde{j}, \tilde{j}'} p_{\tilde{j}'}(T) k_{\tilde{j}' \rightarrow \tilde{j}}^{(b)}(T) = \left[\frac{\mu_r}{\mu_p} \right]^{3/2} \exp(\Delta E_{rxn}/k_B T) Z_r^{(r)}(T) \sum_{\tilde{j}, \tilde{j}'} p_{\tilde{j}}(T) k_{\tilde{j} \rightarrow \tilde{j}'}^{(f)}(T)$$

We identify the terms under the double summation on both the left and right-hand sides as the thermally-averaged total rate constants, so that we can simplify this equation to give

$$k^{(b)}(T) = \left[\frac{\mu_r}{\mu_p} \right]^{3/2} \frac{Z_r^{(r)}(T)}{Z_r^{(p)}(T)} \exp(\Delta E_{rxn}/k_B T) k^{(f)}(T) \quad (21)$$

This is, I believe, the correct detailed balance relation for the overall reaction rate constants.

Exercise

Exercise #1 Generalize the preceding development to a reacting system which has denumerable rotational and vibrational levels, to obtain an a detailed balance relation which is an extension of Eq. (21, namely

$$k^{(b)}(T) = \left[\frac{\mu_r}{\mu_p} \right]^{3/2} \frac{Z^{(r)}(T)}{Z^{(p)}(T)} \exp(\Delta E_{rxn}/k_B T) k^{(f)}(T) \quad (22)$$

where the partition functions are the sums over all vibration-rotation states of the reactants and/or products, weighted by their degeneracies.

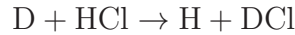
D. Limiting behavior This subsection is not yet finished

It is worthwhile to examine the limiting behavior of Eq. (22). First, for exoergic reactions, ΔE_{rxn} is negative, and usually much larger than $k_B T$. Thus the factor $\exp(\Delta E_{rxn}/k_B T)$ will be small, implying that the backward reaction, which is uphill, will have a rate constant which is significantly smaller than that for the forward reaction, which is downhill.

Now, suppose that the reaction is nearly thermoneutral, so that $\Delta E_{rxn} \approx 0$. In this case the ratio of the partition functions will govern the relative size of the forward and backward

reactions. In a statistical limit, reaction from any reactant state to any product state will be equally probable. Thus, if there are far more reactant states than product states, the backward reaction will be favored. The partition functions are sums over all the available states, weighted by their Boltzmann factors, and thus are the effective number of available states at a given temperature T . We see from Eq. (22) that, for a thermoneutral reaction, reaction will favor the side with the higher density of states.

An interesting special case is an isotopic exchange reaction, for example,



Here, the heat of reaction is just the difference between the zero-point energies of DCl and HCl, namely

$$\Delta E_{rxn} \approx \frac{1}{2} [\omega_e(\text{DCl}) - \omega_e(\text{HCl})]$$

III. RELAXATION KINETICS

A. Master equation: generalities

Consider a system of N levels at temperature T . The rate of change of the population in level i is equal to an overall loss rate plus an infill rate due to transfer from all other levels. These rates are proportional to the rate constants multiplied by the number density of the collision partner, ρ . In other words

$$dn_i/dt = \rho \left[-k_{ii}n_i + \sum_{f \neq i} n_f k_{f \rightarrow i}(T) \right] \quad (23)$$

or, explicitly

$$\begin{aligned} dn_1/dt &= \rho [-n_1 k_{11}(T) + n_2 k_{21}(T) + n_3 k_{31}(T) + \dots + n_N k_{N1}(T)] \\ dn_2/dt &= \rho [+n_1 k_{21}(T) - n_2 k_{22}(T) + n_3 k_{32}(T) + \dots + n_N k_{N2}(T)] \\ dn_3/dt &= \rho [+n_1 k_{31}(T) + n_2 k_{23}(T) - n_3 k_{33}(T) + \dots + n_N k_{N3}(T)] \\ &\vdots = \vdots \\ dn_N/dt &= \rho [+n_1 k_{N1}(T) + n_2 k_{2N}(T) + n_3 k_{3N}(T) + \dots - n_N k_{NN}(T)] \end{aligned} \quad (24)$$

We can write these coupled first-order differential equations in matrix notation as

$$dn/dt = \rho \mathbf{K} \mathbf{n} \quad (25)$$

where n is the column vector of populations in states $\{1\dots N\}$ and \mathbf{K} is the matrix of rate constants. This set of coupled first-order differential equations is called a [master equation](#). The if^{th} off-diagonal matrix element of \mathbf{K} is the $f \rightarrow i$ rate constant and the diagonal matrix element K_{ii} is equal to the negative of the total loss rate of level i . This reversed notation (the if^{th} element of the \mathbf{K} matrix is the rate constant for the transition from level f to level i) is also referred to as [Einstein notation](#).

In addition the off-diagonal matrix elements of the \mathbf{K} matrix are related by the detailed balance relation [Eq. (8)], which we rewrite here as

$$\frac{k_{fi}(T)}{k_{if}(T)} = \frac{(2j_i + 1)}{(2j_f + 1)} \exp(\Delta E/k_B T)$$

or, more generally

$$\frac{k_{fi}(T)}{k_{if}(T)} = \frac{g_i}{g_f} \exp(\Delta E/k_B T)$$

where g_f and g_i are the degeneracies of levels f and i .

The rate of change in time of the total population $n = \sum_i n_i$ is then given by summing Eqs. (24), we obtain

$$\begin{aligned} dn/dt &= \sum_i dn_i/dt \\ &= n_1 \left[-k_{11} + \sum_{f \neq 1} k_{f1}(T) \right] + n_2 \left[-k_{22} + \sum_{f \neq 2} k_{f2}(T) \right] + \dots + n_N \left[-k_{NN} + \sum_{f \neq N} k_{fN}(T) \right] \end{aligned}$$

In general, dn/dt has to be equal to zero, for all choices of n_i . Thus, the terms multiplying each n_i in the preceding equation must vanish, separately, so that

$$k_{ii} = \sum_{f \neq i} k_{fi} \quad (26)$$

Inserting this result into Eq. (23) gives the expected relation

$$dn_i/dt = \rho \left[- \sum_{f \neq i} k_{i \rightarrow f}(T) n_i + \sum_{f \neq i} n_f k_{f \rightarrow i}(T) \right] = \rho \left[- \sum_{f \neq i} [-n_i k_{i \rightarrow f} + n_f k_{f \rightarrow i}(T)] \right] \quad (27)$$

As we will demonstrate in the Appendix, all the eigenvalues of the rate-constant matrix \mathbf{K} are ≤ 0 and, specifically, one eigenvalue is equal to zero.

B. Master equation: analytic solution

Now, let us construct the diagonal matrix $\mathbf{\Pi}$, whose diagonal elements are the Boltzmann populations, namely

$$\Pi_{ij} = \delta_{ij} g_i \exp(-E_i/kT) ,$$

and the square root of this matrix $\mathbf{\Pi}^{1/2}$ where

$$\Pi_{ij}^{1/2} = \delta_{ij} [g_i \exp(-E_i/kT)]^{1/2} ,$$

and

$$\mathbf{\Pi}^{1/2} \times \mathbf{\Pi}^{1/2} = \mathbf{\Pi}$$

We can recast Eq. (25) as

$$d\mathbf{n}/dt = \rho \mathbf{\Pi}^{1/2} \left[\left(\mathbf{\Pi}^{1/2} \right)^{-1} \mathbf{K} \mathbf{\Pi}^{1/2} \right] \left(\mathbf{\Pi}^{1/2} \right)^{-1} \mathbf{n}$$

or

$$d\tilde{\mathbf{n}}/dt = \rho \left[\left(\mathbf{\Pi}^{1/2} \right)^{-1} \mathbf{K} \mathbf{\Pi}^{1/2} \right] \tilde{\mathbf{n}} = \rho \tilde{\mathbf{K}} \tilde{\mathbf{n}} \quad (28)$$

where

$$\tilde{\mathbf{K}} = \left(\mathbf{\Pi}^{1/2} \right)^{-1} \mathbf{K} \mathbf{\Pi}^{1/2}$$

Here, the new population vector $\tilde{\mathbf{n}}$ is equal to the populations \mathbf{n} by

$$\tilde{\mathbf{n}} = \left(\mathbf{\Pi}^{1/2} \right)^{-1} \mathbf{n} \quad (29)$$

or

$$\tilde{n}_i(t) = n_i(t) / [g_i \exp(-E_i/kT)]^{1/2}$$

The $\tilde{\mathbf{K}}$ matrix is symmetric, so that it can be diagonalized by an orthogonal transformation \mathbf{D}

$$\mathbf{D}^T \tilde{\mathbf{K}} \mathbf{D} = \tilde{\mathbf{\Lambda}}$$

where $\tilde{\mathbf{\Lambda}}$ is a diagonal matrix of real eigenvalues and where

$$\mathbf{D}^T \mathbf{D} = \mathbf{D} \mathbf{D}^T = \mathbf{I}$$

The columns of \mathbf{D} are the eigenvectors of $\tilde{\mathbf{K}}$.

We can then simplify Eq. (28) as

$$d\tilde{\mathbf{n}}/dt = \rho \tilde{\mathbf{K}} \tilde{\mathbf{n}} = \rho \mathbf{D} \mathbf{D}^T \tilde{\mathbf{K}} \mathbf{D} \mathbf{D}^T \tilde{\mathbf{n}} = \rho \mathbf{D} \tilde{\mathbf{\Lambda}} \mathbf{D}^T \tilde{\mathbf{n}}$$

or, after premultiplying by \mathbf{D}^T ,

$$d\mathcal{N}/dt = \rho \tilde{\mathbf{\Lambda}} \mathcal{N}$$

where

$$\mathcal{N} = \mathbf{D}^T \tilde{\mathbf{n}} = \mathbf{D}^T (\mathbf{\Pi}^{1/2})^{-1} \mathbf{n} \quad (30)$$

Thus, each component of the population vector \mathcal{N} relaxes exponentially (and independently), namely

$$\mathcal{N}_i(t) = \mathcal{N}_i(0) \exp(\rho \tilde{\Lambda}_i t)$$

Exercise

Exercise #2. Show that the eigenvalues of $\tilde{\mathbf{K}}$ are identical to the eigenvalues of \mathbf{K} .

Because of the identity you've just demonstrated in the preceding exercise, the eigenvalues of $\tilde{\mathbf{K}}$ are negative semi-definite. Since one eigenvalue of \mathbf{K} is zero, one eigenvalue of $\tilde{\mathbf{K}}$ will also be zero. The eigenvector which corresponds to this eigenvalue – let's call it \mathcal{N}_∞ – corresponds to the equilibrium population distribution, since at long time all the other

eigenvectors, which correspond to negative eigenvalues, will decay to zero. Now the \mathcal{N} eigenvectors (the columns of the D matrix), are expansions in the $\tilde{\mathbf{n}}$ basis, which are the populations divided by the square root of the Boltzmann weights. To transform the \mathcal{N} eigenvectors into the populations we need to invert Eq. (29), obtaining

$$\mathbf{n}_\infty = \mathbf{\Pi}^{1/2} \mathbf{D}$$

This should, of course, be the Boltzmann population, namely

$$(\mathbf{n}_\infty)_i = \frac{1}{Z(T)} g_i \exp(-E_i/kT)$$

where

$$Z(T) = \sum_i g_i \exp(-E_i/kT)$$

C. Relaxation of an initial population

Suppose we have an initial population \mathbf{n}_0 . In terms of the $\tilde{\mathbf{n}}$ basis, the initial population is [from Eq. (29)] $\tilde{\mathbf{n}}_0 = (\mathbf{\Pi}^{1/2})^{-1} \mathbf{n}_0$. We can expand this distribution in terms of the eigenvectors of $\tilde{\mathbf{K}}$, to get

$$\mathcal{N}_0 = \mathbf{D}^T \tilde{\mathbf{n}}_0 = \mathbf{D}^T (\mathbf{\Pi}^{1/2})^{-1} \mathbf{n}_0$$

The individual components of the vector \mathcal{N}_0 are the initial magnitudes of the individual eigenvectors of $\tilde{\mathbf{K}}$. As time goes on, these magnitudes decay exponentially, so that at any later time, the populations in the various n_i levels are

$$\mathbf{n}(t) = \sum_i \mathbf{\Pi}^{1/2} \mathbf{D} \mathcal{N}_0 \exp(\rho \mathbf{\Lambda} t)$$

Note that here $\mathcal{N}_0 \exp(\rho \mathbf{\Lambda} t)$ is a column vector, with elements $\mathcal{N}_i(t=0) \exp(\rho \Lambda_i t)$.

D. Master equation: numerical solution

Another method of solving the master equation is based on the finite difference approximation to the derivative

$$\left. \frac{df}{dt} \right|_{t+\delta t} \approx \frac{f(t+\delta t) - f(t)}{\delta t}$$

so that

$$\mathbf{n}(t + \delta t) \approx \rho (\mathbf{K}\delta t + \mathbf{I}) \mathbf{n}(t)$$

If we start at $t = 0$ and repeat this propagation m times, we obtain

$$\mathbf{n}(m\delta t) \approx \rho (\mathbf{K}\delta t + \mathbf{I})^m \mathbf{n}(t = 0)$$

E. Matlab-based simulation

To illustrate the details of population relaxation, I have attached a Matlab script ([master_equation.m](#)) which solves, following the diagonalization procedure presented above, the master equation for the relaxation of M coupled rotational levels, ranging from $j = 0$ to $j = M - 1$, with degeneracies $2j + 1$ and energies $\varepsilon_j = Bj(j + 1)$, where B is the rotational constant. The rate matrix is modelled by an exponential gap approximation in which the lower triangle of the rate matrix is given by

$$k_{ij}(T) = k_{max} \exp[\alpha(\varepsilon_j - \varepsilon_i)/k_B T], \quad i > j$$

where k_{max} and α are two parameters. The upper triangle of the rate matrix is given by detailed balance

$$k_{ij}(T) = \frac{g_j}{g_i} \exp[(\varepsilon_i - \varepsilon_j)/k_B T], \quad i < j$$

This model is applied in the script [master_equation.m](#) to a system defined by the values given in [Table I on the following page](#).

The script determines the relative populations of each j level as a function of time, ranging from $t = 0$ to $t = 5$ ps in steps of 10 fs for two different initial conditions: (1) when only the $j = 6$ level is populated and (2) when all the levels are thermally populated and then the $j = 6$ level initially bleached. [Figure 2](#) shows two results from the first simulation. In the

TABLE I. Parameters used in simulation of the solution of the master equation, contained in the Matlab script `master_equation.m`.

parameter	value
M	15
B	10 cm^{-1}
k_{max}	$5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
α	2
T	1000 K
ρ	$3.2 \cdot 10^{22} \text{ molecule cm}^{-3}$

right panel we plot the time evolution of the average rotational energy

$$E_{av}(t) = \frac{\sum_{j=0}^{M-1} \varepsilon_j n_j(t)}{\sum_{j=0}^{M-1} n_j(t)}$$

where $\varepsilon_j = Bj(j+1)$.

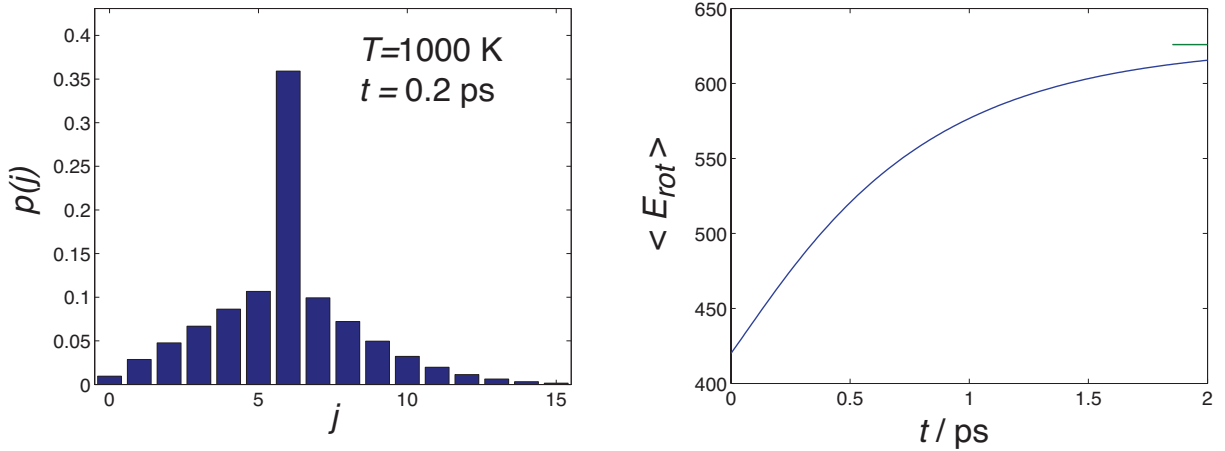


FIG. 2. Results of simulations run by the Matlab script `master_equation.m`. Left panel: Relative populations after initially populating just the $j = 6$ rotational level after an elapsed time of 0.2 ps. Right panel: Relaxation of the average rotational energy. The green line marks the long-time (Boltzmann) limit.

Exercise

Exercise #2. The plot presented in Fig. 2 shows that in the case of initial population in just the $j = 6$ level, the average rotational energy grows from $\varepsilon_{j=6}$ at $t = 0$ up to the Boltzmann limit at $T = 1000$, namely

$$E_{rot}(T) = \frac{\sum_{j=0}^{M-1} (2j+1)\varepsilon_j \exp(-\varepsilon_j/k_B T)}{\sum_{j=0}^{M-1} (2j+1) \exp(-\varepsilon_j/k_B T)}$$

If the average rotational energy were to relax exponentially, we would have

$$E_{av}(t) = A + B \exp(-\kappa t) \quad (31)$$

where A and B are constants. How are these constants related to $\varepsilon_{j=6}$ and $E_{rot}(T)$?

Exercise #3. By fitting the data from the matlab script [master_equation.m](#), obtain an estimate of the relaxation rate κ . If you were to measure κ , what inferences could you make about the elements in the rate matrix \mathbf{K} ? Suppose you limited yourself just to short time. What relation is there between the observed relaxation rate and the elements of \mathbf{K} ?

Exercise #4. The matlab script [master_equation.m](#) also allows you to simulate an experiment in which the population in the $j = 6$ level of an initially thermal population is depleted, and then is filled in by collisions. For this scenario, come up with a simple expression for the time-dependence of the rotational energy similar to Eq. (31) and then fit the computed values of the average rotational energy as a function of time to obtain an estimate of the relaxation rate κ . Here also, if you were to measure κ , what inferences could you make about the elements in the rate matrix \mathbf{K} ?

IV. APPENDIX: PROPERTIES OF THE EIGENVALUES OF THE RATE MATRIX

We can show that all the eigenvalues of the \mathbf{K} matrix are negative by making use of the [Gershgorin circle theorem](#). This theorem states that for any complex $N \times N$ matrix all eigenvalues lies within at least one of the N so-called Gershgorin disks. The i^{th} disk is a closed circle centered at the diagonal matrix element A_{ii} with radius R_i equal to $\sum_{j \neq i} |A_{ji}|$. Because all the offdiagonal elements of the \mathbf{K} matrix are positive, this implies

that $R_i = \sum_{j \neq i} A_{ji}$. Now, in the \mathbf{K} matrix each diagonal element is equal to the sum of the off-diagonal diagonal elements in column i . Thus, $R_i = |A_{ii}|$. Consequently, each Gershgorin disk is centered at $-A_{ii}$ and is large enough to touch the origin from below. This then shows that all the eigenvalues of the \mathbf{K} matrix are negative semi-definite.

In other words, if we diagonalize \mathbf{K} by the similarity transformation \mathbf{C}

$$\mathbf{K} \mathbf{C} = \mathbf{C} \mathbf{\Lambda}$$

or

$$\mathbf{C}^{-1} \mathbf{K} \mathbf{C} = \mathbf{\Lambda}$$

where $\mathbf{\Lambda}$ is a diagonal matrix, then $\Lambda_i \leq 0, \forall_i$. In addition, because of Eq. (26), the rows of the \mathbf{K} matrix are not linearly independent, so that the matrix is singular, and has at least one zero eigenvalue.

As an example, we consider a 3×3 rate constant matrix, obtained by using the Matlab script [master.equation.m](#) with the parameters of Table I *except* $N = 2$ and $T = 100K$. The \mathbf{K} matrix is

$$\mathbf{K} = 10^{-11} \begin{bmatrix} -3.7015 & 1.2499 & 0.4218 \\ 2.8121 & -2.8314 & 1.6872 \\ 0.8895 & 1.5815 & -2.1090 \end{bmatrix} \quad (32)$$

This matrix does satisfy detailed balance. The matrix of eigenvalues is

$$\mathbf{\Lambda} = 10^{-11} \begin{bmatrix} 0 & 0 & 0 \\ 0 & -5.3061 & 0 \\ 0 & 0 & -3.3358 \end{bmatrix}$$

Figure 3 on the next page shows the three Gershgorin disks, centered on the three diagonal elements of matrix (32), as well as the location of the three eigenvalues.

[1] The authors are also grateful to [Gregory Hall](#), [Christopher Jarzynski](#), [Harris Silverstone](#) and [Dianne O'Leary](#) for helpful comments and suggestions.

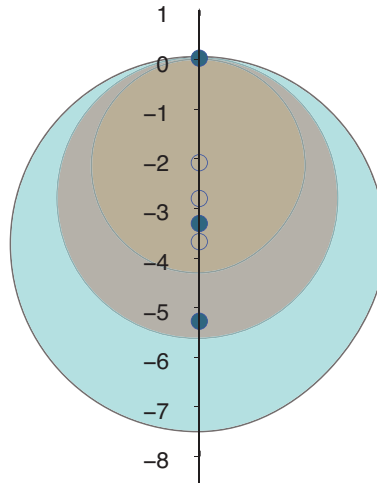


FIG. 3. Location of the three Gershgorin disks for matrix (32). The centers of the disks, indicated by the small open circles, correspond to the three diagonal elements of (32). The three filled circles indicate the eigenvalues of the sample \mathbf{K} matrix given in (32).