

Reaction dynamics in the low pressure regime: The Kramers model and collisional models of molecules with many degrees of freedom^{a)}

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The escape rate constant out of a metastable well for an impulsive collisional (BGK) model and the Fokker–Planck frictional (Kramers) model is evaluated analytically for arbitrary potentials and any number of degrees of freedom in the low collision or low friction limit. Completely statistical behavior of the collisionless dynamical system is assumed. The rate constants increase dramatically with the number of degrees of freedom. The result of the weak collision Kramers model allows us to evaluate the collision efficiency β_c without adjustable parameters. It is argued that some reactions could be described by a non-Markovian Kramers model with an appropriate number of degrees of freedom.

INTRODUCTION

Since Kramers landmark paper¹ the escape rate of a Brownian particle from a metastable well has been the subject of numerous studies.² Consideration of this problem for multidimensional systems was initiated by Landauer³ and Langer⁴ and only recently Matkowski and Schuss^{5,6} developed powerful general techniques to attack such problems.^{7–9} The original one dimensional Kramers model has been extended to non-Markovian situations.^{10–13} Such modifications have been applied to explain the viscosity dependence of isomerisation reaction rate constants with varying success.^{13–17}

On the other hand, over the past several decades there have been many studies of unimolecular reactions in the gas phase.^{18–20} In the past, theoretical approaches in this field have been formulated in the strong collision approximation where each collision is assumed to completely randomize the energy of the decomposing molecule. Experiments¹⁸ showed that for certain bath molecules the rate constant can be much smaller than the “strong collision” model would predict. Models that incorporate such “weak collision” behavior were developed but these models involve adjustable parameters like the average energy transferred per collision $\langle \Delta E \rangle$ which is determined from experiment.

That the Kramers model in the low friction limit is a special case of the weak collision limit in unimolecular rate theory has been appreciated.^{21–23} In this paper this is explored in more detail. In the main part of the paper explicit expressions are derived for the dissociation rate constants in the BGK model^{21–25} and the Kramers model for any potential and for an arbitrary number of degrees of freedom in the low collision or low friction limit—using techniques borrowed from unimolecular rate theory.

These results are a natural extension of the results for one degree of freedom.^{1,24} The rate constants are found to increase strongly with increasing number of degrees of freedom. Lastly solution of the Kramers problem allows us to obtain explicit relations for the collision efficiency β_c in the weak collision limit.

GENERAL BACKGROUND

Consider a polyatomic molecule with fixed center of mass and orientation. Suppose that the remaining n degrees of freedom can be described by a classical Hamiltonian

$$H(\Gamma) = \sum_{i=1}^n \frac{p_i^2}{2m_i} + V(\mathbf{x}), \quad (1)$$

which exhibits completely chaotic motion. Then its total energy E is the only constant of motion. The potential energy $V(\mathbf{x})$ is chosen to have a single metastable well whose minimum and its single saddle point are separated by an energy barrier Q . We divide the phase space Γ into a *reactant* and a *product* region according to the position vector \mathbf{x} with a suitably chosen boundary which includes the saddle point. The metastable well lies completely in the reactant region. If this molecule suffers infrequent collisions, its total energy E will be the only slowly relaxing variable. Let us denote the probability of the system having an energy between E and $E + dE$ and being in the reactant region by $P(E, t)dE$. Because of the random nature of the collisions the evolution of the probability density $P(E, t)$ can be described by a Markovian Master equation¹⁸

$$\begin{aligned} \frac{\partial}{\partial t} P(E, t) = & \int_0^\infty dE' [K(E, E')P(E', t) \\ & - K(E', E)P(E, t)] - k_{\text{RRKM}}(E)P(E, t). \end{aligned} \quad (2)$$

The collision kernel $K(E', E)$ which satisfies detailed balance is the transition probability for a change in energy

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from E to E' per unit time. In the low pressure limit $K(E', E)$ is the product of the collision frequency α and the conditional transition probability density of the energy after the collision E' given the energy E prior to the collision. The dissociation into products is determined by the RRKM-rate constant $k_{\text{RRKM}}(E)$. The over all dissociation rate constant k can be obtained by solving Eq. (2) for the *normalized* steady state distribution $P_{ss}(E)$ which gives the total flux into the product region¹⁸

$$k = \int_Q^\infty dE k_{\text{RRKM}}(E) P_{ss}(E). \quad (3)$$

Given $K(E', E)$ and $k_{\text{RRKM}}(E)$ this method provides a general framework for evaluation of dissociation rate constants at low enough pressures.

If the collisions are frequent enough, the steady state distribution is well approximated by the equilibrium distribution

$$P_{\text{eq}}(E) = \frac{1}{Z(\beta)} \Omega(E) e^{-\beta E}, \quad (4)$$

where

$$\Omega(E) = \int d\Gamma \delta(E - H(\Gamma)) \quad (5)$$

is the density of states,

$$Z(\beta) = \int_0^\infty dE e^{-\beta E} \Omega(E) \quad (6)$$

is the partition function and $\beta = 1/k_B T$. Note that all integrations over the phase space are restricted to the reactant region only. In this case of frequent collisions Eq. (3) is just the definition of the transition state rate constant.

On the other hand, in the low collision limit the dissociation is so effective in removing particles above threshold that it acts as a perfect sink. So we have the boundary condition

$$P_{ss}(E) = 0 \quad \text{for } E > Q. \quad (7)$$

In the low collision limit two limiting cases are of interest. The first case is the strong collision limit where the transition kernel allows large energy changes. The second one is the weak collision limit in which only small displacements are allowed. We treat these two cases in the next two sections separately.

STRONG COLLISION LIMIT

In this limit one collision allows large energy transfer. Then the steady state distribution is well approximated by the equilibrium distribution below the threshold energy. To satisfy the boundary condition Eq. (7) we need to introduce a proper normalization factor. Then substituting Eq. (2) in the steady state ($\partial P/\partial t = 0$) into Eq. (3) we obtain the rate constant^{18,21}

$$k = \left[\int_0^Q dE P_{\text{eq}}(E) \right]^{-1} \int_Q^\infty dE' \int_0^Q dE K(E', E) P_{\text{eq}}(E). \quad (8)$$

The simplest collisional model is the *strong collision approximation*¹⁹ where

$$K(E', E) = \alpha P_{\text{eq}}(E') \quad (9)$$

and α is the collision frequency. The rate constant Eq. (8) becomes

$$k = \alpha \int_Q^\infty dE P_{\text{eq}}(E) \quad (10)$$

as shown in many standard texts.^{19,20} The ratio of the rate constant of a given collisional model to the strong collision rate constant Eq. (10) is called the collision efficiency β_c . For $n - 1$ harmonic oscillators and one deep ($\beta Q \gg 1$) piecewise harmonic well the strong collision rate constant can be shown to be²⁶

$$k \sim \alpha \frac{(\beta Q)^{n-1}}{(n-1)!} e^{-\beta Q}. \quad (11)$$

Of course this holds only if the motion near threshold is completely irregular—an assumption which is not satisfied for a collection of truly harmonic modes. Nevertheless it indicates the general trends of the result. The same restriction applies to later examples where we evaluate rate constants for harmonic oscillators.

Often collision kernels are defined in phase space Γ and the energy collision kernel is obtained from^{21,22}

$$K(E', E) = \left\langle \int d\Gamma' \delta(E' - H(\Gamma')) K(\Gamma', \Gamma) \right\rangle_E, \quad (12)$$

where we have introduced the microcanonical average

$$\langle \dots \rangle_E = \frac{1}{\Omega(E)} \int d\Gamma \delta(E - H(\Gamma)) \dots \quad (13)$$

The other more realistic strong collision kernel is the *BGK-model*²¹⁻²⁵

$$K(\Gamma', \Gamma) = \alpha \delta(\mathbf{x}' - \mathbf{x}) P_{\text{eq}}(\mathbf{p}'), \quad (14)$$

where only the momenta \mathbf{p} are randomized according to a Maxwell-Boltzmann distribution after a collision. Using Eq. (12) the rate constant Eq. (8) can be evaluated as

$$k = \alpha \frac{\langle \theta(Q - V(\mathbf{x})) h(\mathbf{x}) (1 - h(\mathbf{x})) \rangle}{\langle \theta(Q - V(\mathbf{x})) h(\mathbf{x}) \rangle}, \quad (15)$$

where $\theta(x)$ is the Heaviside step function and the canonical configurational average $\langle \dots \rangle$ is restricted to the reactant region. We have introduced the abbreviation

$$h(\mathbf{x}) = \frac{\gamma(n/2, \beta Q - \beta V(\mathbf{x}))}{\Gamma(n/2)} \quad (16)$$

using the notation from Abramowitz and Stegun²⁷ for the Γ function and the incomplete γ function. One can see that Eq. (15) agrees with the result by Skinner and Wolynes for one degree of freedom²⁴ up to a negligible term of order $e^{-\beta Q}$. Analysis of this expression for n harmonic oscillators with one truncated at energy Q gives for deep wells ($\beta Q \gg 1$) the same asymptotic result as the strong collision approximation [namely Eq. (11)]. For a realistic potential Eq. (14) can be evaluated most easily by a Monte Carlo procedure. Usually we can expect that

the collision efficiency $\beta_c \simeq 1$ and is independent of temperature for the BGK model.

WEAK COLLISION—KRAMERS LIMIT

In this case the transition kernel allows only small energy changes compared to $k_B T$ and is therefore sharply peaked at $E = E'$. This limit includes the Fokker–Planck operator of the original Kramers treatment. In this case we can perform a Kramers–Moyal expansion of the integral operators in Eq. (2) taking detailed balance into account. The standard steps presented by Carrier and Keck²⁸ for example lead to the energy diffusion equation

$$\frac{\partial}{\partial t} P(E, t) = -\frac{\partial j_E}{\partial E} - k_{RRKM}(E)P(E, t), \quad (17)$$

where the energy flux is

$$j_E = -D(E) \left[\frac{\partial}{\partial E} P(E, t) - P(E, t) \frac{d \log P_{eq}(E)}{dE} \right]. \quad (18)$$

The energy diffusion coefficient turns out to be the second moment of the transition kernel²⁸

$$D(E) = \frac{1}{2} \int dE' K(E', E) (E' - E)^2. \quad (19)$$

The escape rate constant is found by solving Eq. (17) for the steady state distribution. The two integration constants are determined from Eq. (7) and the normalization condition. Using Eq. (17) in the steady state the rate constant Eq. (3) becomes the inverse of the familiar mean first passage time formula²

$$k = \left[\int_0^Q dE \frac{1}{P_{eq}(E) D(E)} \int_0^E dE' P_{eq}(E') \right]^{-1}. \quad (20)$$

To solve the Kramers problem for any number of degrees of freedom in the low friction limit we only have to evaluate the energy diffusion coefficient $D(E)$. Before specializing to Fokker–Planck collision dynamics let us analyze the impulsive collision kernel

$$K(\Gamma', \Gamma) = \delta(\mathbf{x}' - \mathbf{x}) K(\mathbf{p}'; \mathbf{x}, \mathbf{p}). \quad (21)$$

Using Eqs. (12) and (21), Eq. (19) becomes

$$D(E) = \frac{1}{2} \left\langle \int d\mathbf{p}' K(\mathbf{p}'; \mathbf{x}, \mathbf{p}) [H(\mathbf{p}', \mathbf{x}) - E]^2 \right\rangle_E \quad (22)$$

which can be simplified by substituting

$$H(\mathbf{p}', \mathbf{x}) - E$$

$$= H(\mathbf{p}', \mathbf{x}) - H(\mathbf{p}, \mathbf{x})$$

$$= \sum_{i=1}^n \frac{1}{m_i} p_i (p'_i - p_i)$$

$$+ \sum_{i=1}^n \frac{1}{2m_i} (p'_i - p_i)^2 \quad (23)$$

resulting in

$$D(E) = \sum_{i,j} \frac{1}{m_i m_j} \langle K_{ij}^{(2)}(\Gamma) p_i p_j \rangle_E + O(K^{(3)}), \quad (24)$$

where we introduced the second moment of the collision kernel

$$K_{ij}^{(2)}(\Gamma) = \frac{1}{2} \int d\mathbf{p}' (p'_i - p_i)(p'_j - p_j) K(\mathbf{p}'; \mathbf{x}, \mathbf{p}) \quad (25)$$

and $O(K^{(3)})$ symbolizes contributions from higher moments. By performing Kramers–Moyal expansion of the kernel Eq. (21) as indicated by Skinner and Wolynes²¹ one can readily identify the second moments Eq. (25) from the multidimensional version of the Fokker–Planck equation²⁹ to be $kT \zeta_{ij}(\mathbf{x})$ and that $O(K^{(3)}) \rightarrow 0$. Because of hydrodynamic interaction the friction tensor $\zeta_{ij}(\mathbf{x})$ can depend on the mutual configuration of the particles. At this point the energy diffusion coefficient becomes

$$D(E) = \sum_{i,j} \frac{k_B T}{m_i m_j} \langle \zeta_{ij}(\mathbf{x}) p_i p_j \rangle_E. \quad (26)$$

If the friction tensor is independent of the configuration, this expression can be further simplified by evaluating the average $\langle p_i p_j \rangle_E$. In the canonical ensemble this average is

$$\frac{1}{Z(\beta)} \int_0^\infty dE e^{-\beta E} \Omega(E) \langle p_i p_j \rangle_E = \frac{m_i}{\beta} \delta_{ij}. \quad (27)$$

Since $Z(\beta)$ is the Laplace transform of $\Omega(E)$ [cf. Eq. (6)] inverting Eq. (27) gives³⁰

$$\langle p_i p_j \rangle_E = \delta_{ij} \frac{m_i}{\Omega(E)} \int_0^E dE' \Omega(E'), \quad (28)$$

which together with Eq. (26) yields the final expression for the energy diffusion coefficient in the Kramers problem

$$D(E) = k_B T f \frac{1}{\Omega(E)} \int_0^E dE' \Omega(E'), \quad (29)$$

where $\Omega(E)$ is the density of states defined in Eq. (5) and

$$f \equiv \sum_{i=1}^n \frac{\zeta_{ii}}{m_i} \quad (30)$$

is the trace of the mass weighted friction tensor.

Kramers¹ solved this problem for one degree of freedom in action space which leads to an energy diffusion coefficient

$$D(E) = \frac{\zeta}{m} k_B T \nu(E) J(E), \quad (31)$$

where $\nu(E)$ is the frequency and $J(E)$ the action. Using the fact that the density of states for one degree of freedom is the inverse frequency and that $dE/dJ = \nu$ we readily verify that our result Eq. (29) reduces to Eq. (31) for one degree of freedom.

The expression for the energy diffusion coefficient Eq. (29) allows us to evaluate the rate constant for any particular potential using Eq. (20). Consider n harmonic oscillators with one truncated at energy Q for example. In this case $\Omega(E) \propto E^{n-1}$ for $E < Q$ and the rate constant becomes for deep wells ($\beta Q \gg 1$)

$$k \sim f \frac{(\beta Q)^n}{n!} e^{-\beta Q}. \quad (32)$$

If this is specialized to isotropic friction, the result derived by Matkowsky and Schuss⁷ is recovered. If we consider arbitrary potential whose minimum has nonvanishing normal mode frequencies it can be shown that for deep wells ($\beta Q \gg 1$) Eq. (32) still holds up to some multiplicative factor of order of unity. To evaluate the rate constants exactly it is necessary to determine the density of states $\Omega(E)$ for the potential energy in question and integrate Eq. (20) numerically.

Evaluating the ratio of the rate constants Eq. (32) and Eq. (11) we obtain the collision efficiency for the Kramers model for deep harmonic wells

$$\beta_c \sim \frac{f}{\alpha n} \beta Q. \quad (33)$$

Evaluating the same expressions for arbitrary deep wells ($\beta Q \gg 1$) one similarly finds that $\beta_c \propto T^{-1}$. To obtain this relation a result from Enskog theory of hard sphere gases has been used, namely that the collision frequency α and the friction constant f have the same temperature dependence at low densities.

CONCLUSION

In this paper we have evaluated the rate constants for the BGK model [cf. Eq. (15)] and the Kramers model [cf. Eq. (20) and (29)] all in the low collision limit for any number of degrees of freedom and arbitrary potentials. In accord with unimolecular rate theory our models predict rate constants which increase dramatically with increasing number of degrees of freedom. The BGK model is a strong collision model and has a collision efficiency $\beta_c \simeq 1$ independent of temperature. The strong collision models differ substantially from the weak collision models like the Kramers model which allow only small energy transfer per collision. This behavior can be described as diffusion in energy space provided that $\beta^2 D(E) \ll \alpha$ for all $E < Q$ which means that $\beta_c \ll 1$ for any weak collision model.^{18,32} Therefore, the rate constant in the Kramers model is much *smaller* than in a strong collision model at equal collision frequency. The choice of the Kramers model as a particular weak collisional model allows us to derive an explicit expression for the collision efficiency β_c [cf. Eq. (33) for a harmonic well] and we find that $\beta_c \propto T^{-1}$. Previous discussions of β_c which have been based on assumed behavior of adjustable parameters as $\langle \Delta E \rangle$ also suggest the same temperature dependence.¹⁸

We should clarify a possibly puzzling fact that the collision efficiency for the Kramers model Eq. (33) is indeed small despite the large βQ factor. Let us take $n = 1$ for simplicity. The weak collision limit is achieved only if $f\beta Q \ll \alpha$ is satisfied, otherwise the Kramers model is *not* valid. From the Enskog theory of hard sphere gases we can estimate α and f (the latter from the diffusion coefficient). We find that we must choose a sufficiently

small solvent to solute mass ratio (which is essentially f/α) to satisfy $f\beta Q \ll \alpha$ for a given βQ . Note that although the asymptotic Eq. (33) is exact for $\beta Q \gg 1$, it is also an excellent approximation to the exact result [Eqs. (10), (20), and (29)] for most temperatures of interest. Only for unusually high temperatures (in practice $\beta Q \lesssim 5$) Eq. (33) is no longer appropriate: With increasing temperature the exact result goes through a minimum and shows a final increase in accord with a related study.³¹

In our treatment we focus on the strong collision and weak collision limits only. Extensive studies³² of the transition between these two limits based on model collision kernels in energy space showed that the behaviour of the collision efficiency is quite insensitive to the details of the particular collision kernel. We believe that a simple Pade approximant as used by Skinner and Wolynes²¹ can interpolate between these two limits very well and in this way one might be able to avoid the cumbersome exact analysis.

The assumptions in deriving our results are identical with those of statistical rate theories, i.e., the system is completely irregular and the total energy is the only conserved variable in the absence of coupling. However in real molecules the question of non-RRKM behavior must be considered.^{20,26,33} Such effects could be described by replacement of the RRKM-rate constant by the true rate constant³³ and if the system is non-ergodic the collision kernel can be replaced by an appropriate set of collision kernels acting in the irregular and regular regions of the phase space. Extreme non-RRKM behavior could probably also be treated by a model in which the strongly coupled degrees of freedom only feel an effective friction (or collision kernel) renormalized by the weakly coupled degrees of freedom.³⁴ Such non-RRKM behavior was implicitly assumed by Carmeli and Nitzan in their study of two coupled degrees of freedom.³⁵ In real systems there are further conserved quantities beside the total energy and we must incorporate them into the theory. The center of mass momentum can be eliminated by the procedure used by Bak and Lebowitz²² for example. The problem of angular momentum was discussed in the strong collision approximation^{19,20} and for more general collision kernels.³² The most important extension would be the treatment of realistic soft collisions and non-Markovian friction kernels. Similarly, double well problems could be treated within an analogous formalism. However, judging from studies in one dimension^{13,21} the rate constants of the double well problem will usually differ by a factor of order unity from the corresponding single well problem. Furthermore one can also address the average energies transferred per collision $\langle \Delta E \rangle$ in this framework. In agreement with recent experiments³⁶ both models considered here predict temperature independent $\langle \Delta E \rangle$ at high energies. We hope to discuss such questions in the future and compare the results with experimental data.

Deviations from the low collision regime were extensively studied for model collision kernels in energy space.³⁷

For the BGK model we are unaware of any such treatment. However the results will probably resemble the strong collision approximation. In the case of energy diffusion one can also follow the approximate treatment of Landauer.^{38,39} In higher dimensions however the actual dependence of the rate constant on the friction constant will be different because one cannot approximate $\Omega(E)k_{\text{RRKM}}(E)$ by a constant near threshold as was done for one degree of freedom.³⁸ However as emphasized by Troe³⁷ a plot of $\log k$ vs $\log \alpha$ is quite insensitive to the details of the collisional models and simple interpolation formulas can probably provide sufficient accuracy.

Recently a one dimensional non-Markovian Kramers model (Langevin model) has been used to explain the viscosity dependence of isomerization reactions in liquids.¹³⁻¹⁷ We believe that such a model is adequate over a wide range of densities if at least the following two conditions are satisfied. First the reaction must be in the weak collision regime for low pressures. This restriction follows from the fact that the low friction limit of any Langevin model is a special case of the weak collision limit of unimolecular rate theory. Second we have to incorporate the correct number of strongly coupled degrees of freedom into the model. This observation springs from the fact that the low pressure rate constant increases strongly with increasing number of degrees of freedom. Therefore the low-pressure falloff region shifts rapidly towards lower pressures as the complexity of the decomposing molecule increases and therefore becomes increasingly difficult to observe.¹⁸ This is one possible explanation for Fleming's inability to observe the low pressure falloff.¹⁷ In liquids as opposed to gases however it is possible that a portion of the overdamped regime of a multidimensional Langevin model or a BGK model can be well approximated by an effective one dimensional Langevin model. For the case of harmonic saddle points reduction of the multidimensional problem to one dimension was performed by Hynes and co-workers.⁴⁰ This rationalizes the success of such models in some cases.¹⁴⁻¹⁶ However a one dimensional model will fail to predict the position of the maximum and the low pressure falloff.

The experimental tests of such Langevin models of chemical reactions in the liquid phase have been based on varying the viscosity by changing the solvent.¹⁵⁻¹⁷ In our view much more conclusive tests could be obtained by studying the change of the rate constant at fixed temperatures in one (preferably simple) solvent by varying the density (i.e., pressure) from the low density gas phase to the high density liquid phase. This type of approach was already suggested by Troe.⁴¹ Recently Jonas has made a very interesting study in high pressure liquids.⁴² It would be very useful to augment this work by studying the low pressure falloff of the rate constant. Subsequent experiments⁴³ along these lines are difficult to compare with the original work of Jonas without the availability of the raw data.

In conclusion we would like to summarize our results. With the assumption of molecular chaos we derive

analytic results for the decomposition rate constants for the BGK model and the Kramers model in the low collision or low friction limit for an arbitrary number of degrees of freedom. The explicit evaluation of the simple formulas involves in the BGK model an equilibrium average and in the Kramers model the density of states. In accord with unimolecular rate theory and experimental data the rate constants obtained increase strongly with increasing number of degrees of freedom. Roughly speaking the BGK model has a collision efficiency $\beta_c \approx 1$ and the Kramers model with a much smaller rate constant gives $\beta_c \propto T^{-1}$ and $\beta_c \ll 1$. The explicit result for the collision efficiency of the weak collision Kramers model does not contain any adjustable parameters. We expect that only unimolecular reactions which lie in the weak collision limit at low pressures could be described over a wide range of densities by a non-Markovian version of a Kramers model with an appropriate number of degrees of freedom.

Note added in proof: After we submitted our manuscript we became aware of analogous studies of the non-Markovian Langevin model.⁴⁴ Their results reduce to ours in the Markovian Kramers limit. Naturally this model is also in the weak collision limit and applies only if $\beta^2 D(E) \ll \alpha$ for all $E < Q$. This will be satisfied at lower temperatures than for the Kramers model since the friction is reduced by non-Markovian effects.

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