

A Brownian Motion Theory of Chemical Reactions

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A theory for the dissociation of a diatomic molecule in weak interaction with a thermostat is proposed. Exact solutions are given for a harmonic oscillator.

In the classical collision theory of chemical reactions in gases it was generally assumed that dissociation of a molecule occurs by direct transitions from low vibrational states to the dissociated state. In recent years⁶ it has however become clear that the energy transfer to the vibrational degrees of freedom during a molecular collision generally is small compared with the dissociation energy. Under these circumstances it is necessary to consider the dissociating molecule as performing a random walk or Brownian motion in "energy space" on its way to the dissociation energy. The small random changes in energy are caused by the collisions between the reacting molecule and the other molecules which act as a thermostat. Although large amounts of translational energy may be transferred during such collisions, only a small part of the collision energy goes into the vibrational degrees of freedom, and we can therefore speak of the reacting molecule as being weakly coupled to a thermostat. For the case of a diatomic molecule imbedded in a crystal lattice it is of course even more so that the molecular oscillator is only loosely coupled to the crystal lattice.

The first one to investigate such an approach to chemical kinetics was Kramers⁵ who in 1940 developed a theory of Brownian motion in a field of force and thus was able to make a diffusion model of chemical reactions as suggested many years before by Christiansen⁴. In this theory one visualizes the chemical reaction as the escape of a particle from a potential minimum due to the shuttling action of the thermostat. If $\Phi(E, t)$ denotes the probability that the particle has the energy E at time t , one finds for the case of weak interaction between the particle and the thermostat ("small viscosity" in the language of Kramers)

$$\frac{\partial \Phi}{\partial t} = \eta \frac{\partial}{\partial J} J \left(1 + kT \frac{\partial}{\partial E} \right) \Phi \quad (1)$$

where $J(E) = \int p dq$ is the action variable, η is the parameter which measures the interaction with the heat bath. In the special case of a parabolic potential minimum this equation reads

$$\frac{\partial \Phi}{\partial t} = \eta \frac{\partial}{\partial x} x \left(1 + \frac{\partial}{\partial x} \right) \Phi \quad (2)$$

where $x = E/kT$.

The coupling parameter (friction coefficient) η is defined by the Langevin equation

$$\dot{p} = -\eta p + K(q) + A(t) \quad (3)$$

in which p is the linear momentum of the particle, $K(q)$ the force whose potential is the potential energy along the reaction coordinate, and $A(t)$ the "random force" which represents the action of the thermostat. It is usually assumed that the friction coefficient is constant (that is, independent of p) but Kramers mentions the possibility that it might be replaced by an arbitrary (even) function of p , although he does not investigate this case further. As we shall see below for the case of Brownian motion in crystals the assumption that η is independent of p is identical with an assumption by Peierls about the interaction between normal modes in a crystal, which can be shown to be valid to the same accuracy as for instance the Debye approximation in the theory of specific heat. It is therefore not inconceivable that one might find physical systems which for their proper description would require a theory in which η is not assumed to be constant.

A quantum mechanical analogue of Kramers' theory was given by Montroll and Shuler⁷ for the case of a particle in a parabolic potential minimum, *i.e.* an harmonic oscillator. Let the classical frequency of the oscillator be ω so that the energy levels are $(n + \frac{1}{2})\hbar\omega$ and let Θ denote $\hbar\omega/kT$. Montroll and Shuler then obtain in their random walk model the following equation

$$\frac{dx_n}{dt} = \kappa \{ n e^{-\Theta} x_{n-1} - [n + (n+1) e^{-\Theta}] x_n + (n+1) x_{n+1} \} \quad (4)$$

where x_n is the probability that the oscillator is in a state with energy $n\hbar\omega$ over the zeropoint energy, and κ is a parameter which measures the interaction with the heat bath. A similar equation has been proposed by Nikitin⁸.

It is not immediately obvious that an equation of this type is a quantum mechanical analogue of the Kramers equation, but assuming $\Theta \ll 1$ so that $e^{-\Theta}$ can be replaced by $1-\Theta$ we can write the equation as

$$\frac{dx_n}{dt} = \Theta \kappa \left\{ n \Theta \frac{x_{n+1} - 2x_n + x_{n-1}}{\Theta^2} + \frac{x_{n+1} - x_n}{\Theta} + n \Theta \frac{x_n - x_{n-1}}{\Theta} + x_n \right\} \quad (5)$$

When we replace $n\Theta$ by x and x_n by Φ and furthermore let $\hbar \rightarrow 0$, we get

$$\frac{\partial \Phi}{\partial t} = \eta [x\Phi'' + (1+x)\Phi' + \Phi] = \eta \frac{\partial}{\partial x} x \left(1 + \frac{\partial}{\partial x} \right) \Phi$$

where η is the limit of $\Theta\kappa$ as $\hbar \rightarrow 0$.

In this way we see that the two approaches lead to corresponding equations and that the equation of Montroll and Shuler therefore is the proper generalization of the Kramers equation.

In both theories one uses transition probabilities or random forces, and this gives rise to the parameter η ($= \Theta\kappa$) which essentially is a non calculable quantity. It is true that, as stated by Montroll and Shuler, η is in principle calculable from the quantum mechanical theory of collisions, but if one tries to do so eqn. (4) will require additional justification, since there is as yet no simple way of getting such a "master equation" directly from quantum mechanics or classical mechanics. If one can justify the use of the master equation, *i.e.*, essentially explain how irreversibility arises in a mechanical system, then within this framework the calculation of η will be immediate, but within the conceptually much simpler framework of the Kramers theory or Montroll and Shuler theory the coupling constant is, to our minds, best considered as an empirical parameter.

To get a theory for chemical reactions one now assumes that the particle under consideration performs a Brownian motion in the potential hole as long as its energy is smaller than E_{act} , and that it is annihilated when its energy exceeds E_{act} . This is evidently a crude model of a particle passing a potential barrier, and since it is possible to solve eqn. (2) exactly for the boundary condition $\Phi(x^*, t) = 0$ (all t), it is possible in this way to estimate how much the distribution in energy space $\Phi(x, t)$ differs from the equilibrium distribution and how much this influences the rate constant.

BROWNIAN MOTION OF A DIATOMIC MOLECULE

Using the explicit assumption that the oscillating molecule is in weak interaction with the thermostat we can write the energy of the system consisting of a molecule plus the thermostat as

$$\mathcal{H} = H_T + H_M + \lambda V$$

where λ is a small dimensionless parameter.

The energy of the thermostat can be considered as a sum of energies of a large number of subsystems without interaction, that is,

$$H_T = \sum_k H_T^{(k)}$$

and we now introduce angle-action variables for the subsystems of the thermostat and for the molecule and make a Fourier expansion of the interaction potential V on the angle variables. For the special case of a harmonic oscillator imbedded in a lattice, which we have considered previously^{1,2,11} we have

$$\mathcal{H} = \sum_{f=1}^N \omega_f J_f + \omega J + \lambda \sum_{\nu} \sum_f \{ V_{\nu f}^+ e^{i(\alpha_f + \nu a)} + V_{\nu f}^- e^{i(-\alpha_f + \nu a)} \}$$

Here f is the wavenumber for the normal modes of the lattice, α and J denote angle-action variables, and $V_{\nu f}^+ = V_f q_{f+}^0 J_{\nu}(fr_0)$, where q_{f+}^0 is the amplitude of the f 'th normal mode, r_0 the amplitude of the molecular oscillator and $J_{\nu}(fr_0)$ denotes the Bessel function of order ν . V_f is assumed to be independent of the energy of the oscillator. For a derivation of this expression for \mathcal{H} see Ref. ¹ or Ref. ²

Using this Hamiltonian the Liouville equation is set up and solved by the perturbation technique used by Brout and Prigogine ³. In the limit $\lambda \rightarrow 0$, $t \rightarrow \infty$, $\lambda^2 t$ finite, $N \rightarrow \infty$ this leads to eqn. (2) after an integration over the frequency spectrum of the lattice, provided the so-called Peierls assumption ⁹

$$\frac{|V_f|^2}{\omega_f^2} = \text{constant}$$

is valid. Since in this derivation of eqn. (2) η is proportional to $|V_f|^2/\omega_f^2$ we see that the assumption that this quantity is independent of f and of the energy of the oscillator is tantamount to the assumption of Kramers, that η is independent of the momentum of the particle. The range of validity of the Peierls approximation has been investigated by Plesner ¹⁰ who has shown that in a one-dimensional lattice with nearest neighbour interaction it has the same range of validity as the Debye approximation for the frequency spectrum of the lattice. Since the assumption of a Debye spectrum is necessary anyway in integrating over the frequency spectrum of the crystal, the Peierls approximation is a reasonable assumption in this case, but it is quite possible that when considering a system where the thermostat is not a crystal one can get an energy dependent friction coefficient.

CHEMICAL REACTION AS ANNIHILATION OF PARTICLES

To use the equation for Φ in a model of chemical reactions we must have an intramolecular potential which allows a dissociation of the molecule, *i. e.*, a potential for which the particle has one or more "bound states" and a "free state" into which it goes or through which it passes from one bound state to another.

So far we have not been able to treat a potential of this type, and we have therefore used the following model of a chemical reaction. A particle which is weakly coupled to a thermostat moves in potential $V = V(q)$ as long as its energy is smaller than E^* , but when its energy reaches E^* , it ceases to exist. For the special case of a harmonic oscillator eqn. (2) will then apply for $x < x^* = E^*/kT$, but for $x > x^*$ we have $\Phi(x, t) = 0$. The solution of this boundary value problem in the range $0 < x < x^*$ is

$$\Phi = \sum_{\alpha} c_{\alpha} e^{-\alpha \eta t} e^{-x} {}_1F_1(-\alpha, 1, x)$$

where the summation over α goes over the roots of

$${}_1F_1(-\alpha, 1, x^*) = 0$$

Table 1.

x^*	α_1	α_2	α_3	α_4	α_5
1.0	10.0000(-1)	71.95819(-1)	18.30293		
1.2	76.97406(-2)	59.41822(-1)	15.19890	28.56591	
1.4	60.82404(-2)	50.50560(-1)	12.98659	24.44412	
1.6	48.96119(-2)	43.86213(-1)	11.33113	21.35661	
1.8	39.96001(-2)	38.72785(-1)	10.04731	18.95957	30.61161
2.0	32.94893(-2)	34.65393(-1)	90.23554(-1)	17.04459	27.53224
2.2	27.38760(-2)	31.34842(-1)	81.88976(-1)	15.48130	25.01535
2.4	22.90635(-2)	28.62121(-1)	74.96262(-1)	14.18098	22.92064
2.6	19.25139(-2)	26.33808(-1)	69.12601(-1)	13.08343	21.15093
2.8	16.24117(-2)	24.40428(-1)	64.14741(-1)	12.14507	19.63642
3.0	13.74233(-2)	22.74995(-1)	59.85461(-1)	11.33406	18.32608
3.2	11.65566(-2)	21.32238(-1)	56.12010(-1)	10.62652	17.18163
3.4	99.02155(-3)	20.08193(-1)	52.84408(-1)	10.00419	16.17379
3.6	84.23423(-3)	18.99773(-1)	49.95132(-1)	94.52907(-1)	15.27981
3.8	71.72192(-3)	18.04421(-1)	47.38103(-1)	89.61433(-1)	14.48182
4.0	61.10610(-3)	17.20256(-1)	45.08492(-1)	85.20806(-1)	13.76510
4.2	52.08030(-3)	16.45650(-1)	43.02396(-1)	81.23801(-1)	13.11836
4.4	44.39394(-3)	15.79309(-1)	41.16610(-1)	77.64445(-1)	12.53196
4.6	37.84039(-3)	15.20119(-1)	39.48498(-1)	74.37784(-1)	11.99804
4.8	32.24797(-3)	14.67208(-1)	37.95862(-1)	71.39850(-1)	11.51003
5.0	27.47317(-3)	14.19805(-1)	36.56844(-1)	68.67103(-1)	11.06244
5.5	18.36738(-3)	13.21352(-1)	33.59200(-1)	62.77588(-1)	10.09137
6.0	12.23186(-3)	12.45678(-1)	31.18660(-1)	57.93720(-1)	92.89385(-1)
6.5	81.09532(-4)	11.87272(-1)	29.22134(-1)	53.91185(-1)	86.17492(-1)
7.0	53.50914(-4)	11.42145(-1)	27.60263(-1)	50.52646(-1)	80.47932(-1)
7.5	35.13758(-4)	11.07323(-1)	26.26165(-1)	47.65390(-1)	75.60263(-1)
8.0	22.96773(-4)	10.80539(-1)	25.14657(-1)	45.19884(-1)	71.39215(-1)
8.5	14.94463(-4)	10.60035(-1)	24.21748(-1)	43.08846(-1)	67.73090(-1)
9.0	96.84116(-5)	10.44433(-1)	23.44301(-1)	41.26605(-1)	64.52799(-1)
9.5	62.51391(-5)	10.32642(-1)	22.79807(-1)	39.68689(-1)	61.71168(-1)
10.0	40.21350(-5)	10.23798(-1)	22.26220(-1)	38.31511(-1)	59.22463(-1)
11.0	16.48616(-5)	10.12366(-1)	21.45267(-1)	36.08260(-1)	55.06124(-1)
12.0	66.87333(-6)	10.06240(-1)	20.90830(-1)	34.39164(-1)	51.75745(-1)
13.0	26.88773(-6)	10.03065(-1)	20.55158(-1)	33.11753(-1)	49.11934(-1)
14.0	10.73105(-6)	10.01469(-1)	20.32486(-1)	32.16846(-1)	47.00818(-1)
15.0	42.56524(-7)	10.00689(-1)	20.18554(-1)	31.47334(-1)	45.32169(-1)
16.0	16.79150(-7)	10.00318(-1)	20.10282(-1)	30.97535(-1)	43.98210(-1)
17.0	65.93358(-8)	10.00144(-1)	20.05540(-1)	30.62793(-1)	42.92842(-1)
18.0	25.78560(-8)	10.00064(-1)	20.02906(-1)	30.39256(-1)	42.11074(-1)
19.0	10.04701(-8)	10.00028(-1)	20.01489(-1)	30.23861(-1)	41.48774(-1)
20.0	39.02197(-9)	10.00012(-1)	20.00747(-1)	30.14040(-1)	41.02246(-1)
∞	0	1	2	3	4

* α_k ($k = 1, 2, 3, 4, 5$) are the zeros of the function ${}_1F_1(-\alpha, 1, x^*)$ considered as a function of α . The numbers in brackets are the powers of ten by which the values given for α_k should be multiplied.

considered as an equation in α . The first five roots of this equation are tabulated in Table 1 for different values of x^* .

It is seen that when $x^* \sim 10$, α_2 (and *a fortiori* $\alpha_3, \alpha_4, \dots$) will be more than a thousand times larger than α_1 , so that to an excellent approximation we can set

$$\Phi = c_1 e^{-\alpha_1 \eta^t} e^{-x} {}_1F_1(-\alpha_1, 1, x)$$

where α_1 is the smallest root in the equation ${}_1F_1(-\alpha_1, 1, x^*) = 0$.

Table 2. The table shows the ratio between the "true" rate constant $k = \eta a_1(x^*)$ and the equilibrium rate constant $k_{\text{eq}} = \eta x^* e^{-x^*}$ as function of x^* .

k/k_{eq}	1.21730	0.83407	0.82245	0.85582	0.88576
x^*	2	4	6	8	10
k/k_{eq}	0.90670	0.92180	0.93257	0.94060	0.94661
x^*	12	14	16	18	20

From this we get immediately that the rate constant for escape from the potential minimum is $a_1 \eta$ and furthermore we see that while the reaction is going on the change in Φ is so that the relative change in Φ is independent of x . In other words, the distribution function in energy space has a quasi-stationary character.

It is easily verified that as $x^* \rightarrow \infty$, a_1 becomes asymptotically equal to $x^* e^{-x^*}$. Since in this limit Φ approaches the equilibrium distribution e^{-x} , we shall denote $k_{\text{eq}} = \eta x^* e^{-x^*}$ the equilibrium rate constant. It is well to bear in mind, though, that in deriving this expression we have nowhere used the assumption about equilibrium as is done, for instance, in the transition state method. Table 2 shows how the exact value of $a_1(x^*)$ compares with the "equilibrium value" of a_1 , and it is seen that for $x^* > 10$ the error is less than 12 %. It is true, therefore, that for reasonable values of the activation energy the equilibrium hypothesis is a good approximation, but only when the equilibrium result is taken to be the limit of the non-equilibrium result, as the barrier height is increased to infinity. To introduce the equilibrium assumption at an earlier stage would not only lead to a quite different result, but it would also lead to a non-consistent theory.

CONCLUSION

Above we have compared the different Brownian motion approaches to chemical kinetics and shown how they lead to the same result in the case of a dissociating harmonic oscillator. In comparison with earlier derivations of the equation for this case our method which is based on the method of Brout and Prigogine may seem unduly complicated. This is due to the fact that we have not made any assumptions about "random interactions", but only used that the thermostat is large (infinitely many degrees of freedom) and that the interaction is weak ($\lambda \rightarrow 0$). Therefore, to our mind, our derivation of the Kramers equation in the weak interaction limit does present some advantage over previous derivations.

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REFERENCES

1. Bak, T. A. *Contributions to the Theory of Chemical Reactions*, Wiley, New York 1959.
2. Bak, T. A., Goche, M. and Henin, F. *Molecular Physics* 2 (1959) 181.
3. Brout, R. and Prigogine, I. *Physica* 22 (1956) 35.
4. Christiansen, J. A. *Z. physik. Chem.* B33 (1936) 145.
5. Kramers, H. A. *Physica* 7 (1940) 284.
6. Mc Coubrey, J. C. and Mc. Grath, W. D. *Quart. Revs. London* 11 (1957) 87.
7. Montroll, E. and Shuler, K. *J. Chem. Phys.* 26 (1957) 454.
8. Nikitin, E. E. *Doklady Akad. Nauk. S.S.S.R.* 121 (1958) 991, translated as *Soviet Phys. Doklady* 3 (1958) 701.
9. Peierls, R. E. *Quantum Theory of Solids*, Oxford University Press 1955, p. 130.
10. Plesner, I. W., Technical Note No. 3, Contract No. AF 61 (052)-133 Air Research and Development Command, United States Air Force.
11. Prigogine, I. and Bak, T. A. *J. Chem. Phys.* 31 (1959) 1368.

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