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Statistical theory of irreversibly reacting systems

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Abstract. Irreversibly reacting systems have in general a distribution of reaction rates. The interactions continually eliminate possible configurations, or possible bonds, and thus the distribution changes in time. The losses of possible bonds are separated into: *direct* loss of the bond formed; and *correlated* losses which occur via the interaction rule or structural considerations. We distinguish between diffusion- and reaction-limited processes, and pursue only the latter case.

For reaction-limited processes with only direct losses the time dependence of the distribution of reaction rates is governed by an exponential factor. The solution for the case of correlated losses turns out to be closely related to those of the much simpler case of direct losses only. Within a linearized model for the correlation, the particular features of the interactions can be decoupled from the general statistical problem, casting the former into an 'effective time' parameter and thus yielding a general formulation of the statistics.

1. Introduction

Effectively irreversible interactions occur in nature in a variety of situations, as for instance colloidal aggregation [1, 2] where mesoscopic particles stick together by van der Waals forces when they meet; chemical reactions for which the back reaction is negligible as, for example, in polymerization [3], the famous Belousov–Zhabotinski reaction [4] or in predator–prey systems [5] in population dynamics.

All these phenomena are examples of time-dependent stochastic processes which have been investigated as birth–death processes [6], with deterministic rate equations for chemical reactions [7], stochastic models for chemical reactions [8, 9] with emphasis on the formation of structure [10], with stochastic models in population dynamics [11] with respect to self-organization [12], in connection with cellular automata [13], and including the effect of spatial fluctuations on the kinetics [14].

Despite this extensive work on irreversibly interacting systems, less attention has been paid to the fact that if we start with a distribution of different and competing species, fast-reacting species are favourably eliminated from the system, compared with slowly reacting ones; and thus the distribution of species changes continually due to these reactions. The dynamics of this effect is the subject of this work.

In irreversibly reacting systems two variables appear in a natural way. One is the time t , which has a distinct direction due to the irreversibility, and the other is the reaction rate k , defined as the probability per unit time for a irreversible reaction between two individuals. In general not all individuals are equal with respect to their interaction with other individuals and the system has a distribution $\mu(k, t)$ of reaction

rates. The individuals, or particles, continually react and thus a dynamical evolution of the distribution $\mu(k, t)$ is expected. In this paper we discuss the essential features of the dynamical evolution of the distribution of reaction rates for irreversibly interacting systems. Though the theory is applicable to any irreversibly reacting system, for the sake of clarity we present it in terms of particles that collide and stick, as may be encountered in colloidal aggregation [1, 2].

Figure 1 distinguishes different regimes of binary particle interactions to show the context of the present work. The simplest is the hard-core potential, where elastic collisions allow for thermalization and the whole system is well described by equilibrium statistical mechanics. An additional weak attractive potential allows for phase transitions, still well described by equilibrium statistical mechanics.

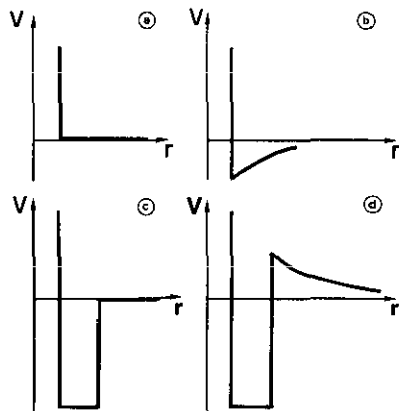


Figure 1. The characteristic forms for the potential $V(r)$ for two-particle interaction as a function of separation r : (a) hard-core potential; (b) weak attractive interaction; (c) irreversible interaction without repulsive barrier; and (d) irreversible interaction with a repulsive barrier.

If the attractive potential exceeds any kinetic energy in the system (figure 1(c)), the interaction (e.g. sticking) is irreversible. For a vanishing potential outside the interaction region, the particles react at first contact and the reaction rate is only determined by the motion of the particles in the host medium. This regime is known as diffusion-limited. If, however, the attractive potential is preceded by a repulsive barrier (figure 1(d)), a particle will, on average, collide with many other particles until it reacts with one of them irreversibly. For a repulsive barrier to be 'sufficiently' high compared with the typical kinetic energy of the particles, the average number of collisions with all other particles before reaction is high and we assume that all two-particle collisions are equally likely. The reaction rate is given by $k \propto \exp(-V_b/k_B T)$, where V_b is the height of the repulsive barrier and T the temperature. The reaction is limited by the probability for reaction during collision and this regime is known as 'reaction-limited'. The height of the repulsive barriers between two particles may in general vary over a wide range due to different sizes, shapes or charge clouds and thus forming a distribution of barrier heights which yields a distribution of reaction rates. The evolution in time of this distribution will be studied in the following.

Assuming that any interaction involves two particles only, it is convenient to work in terms of 'possible bonds' between two particles, instead of terms of particles. We assume that each possible bond is characterized by a fixed reaction rate k , the probability

per unit time of the corresponding reaction occurring during collision. In section 2 we study the simple situation where a reaction of a possible bond eliminates only this particular possibility from the system, i.e. direct losses. An analytic solution for $\mu(k, t)$ can be written down and shows an exponential time dependence. In section 3 we extend our analysis to situations where the reaction of a possible bond eliminates not only this particular possible bond (direct losses) but also correlated bonds (1) that shared one of the two particles forming the particular possible bond and (2) that become sterically inhibited due to structure. The solution for $\mu(k, t)$ shows a striking analogy in form with the solution for the much simpler case of direct losses only. This analogy is further exploited in section 4 by using a linearized model for approximating the correlation. Within this approximation the two situations, direct and correlated losses, are described by the same equations which can only be distinguished by an 'effective time', characteristic for each particular system. In section 5 we give an illustrative example and finally in section 6 we summarize our results.

2. Direct losses only

The simplest situations to study are those where the reaction of a possible bond eliminates only this particular bond. Two examples are represented in figure 2. In figure 2(a) particles react with a wall (e.g. electrode, catalyser, ...) but not with each other. Each particle forms a possible bond with the wall and each possible bond has a reaction rate k . A particle drops out of the system after the reaction and thus does not change the quality of the wall for the following particles. In figure 2(b) particles are distributed on a line and form possible bonds with their nearest neighbours†. The reaction of a possible bond closes only this particular bond.

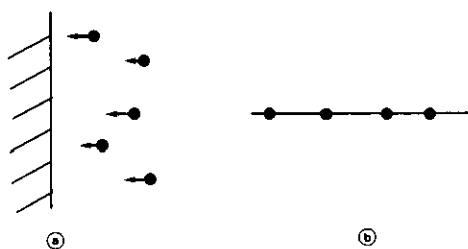


Figure 2. Two examples for irreversibly interacting particles where only direct losses of possible bonds occur: (a) particles react with a wall and not with each other; (b) particles on a line react only with their two nearest neighbours.

Let $B(k, t)$ be the number of possible bonds with reaction rate k at time t and $B_0(t) = \int_0^\infty B(k, t) dk$, the total number of possible bonds at time t . The normalized distribution of reaction rates is defined by

$$\mu(k, t) = \frac{B(k, t)}{B_0(t)}. \quad (1)$$

† Strictly speaking in the one-dimensional case the dilution of particles by reaction should be taken into account by the *ansatz* $dB(k, t)/dt = -kB(k, t)B_0(t)$ which yields the solution $\mu(k, t) = \mu(k, 0) \exp\left(-k \int_0^t B_0(t') dt'\right) \left[\int_0^\infty \mu(k, 0) \exp\left(-k \int_0^t B_0(t') dt'\right) dk\right]^{-1}$, analogous to the solution developed in section 4.

The time evolution is given in terms of $B(k, t)$ by

$$\frac{dB(k, t)}{dt} = -kB(k, t) \quad (2)$$

since k is the probability per unit time of a bond being lost from the population of possible bonds. Substituting $B(k, t)$ from (1) into (2), defining a time-dependent average reaction rate

$$\langle k \rangle(t) = \int_0^\infty k\mu(k, t) dk \quad (3)$$

and eliminating a term, $[B_0(t)]^{-1}[dB_0(t)/dt]$ by integrating over k in (2), yields the following equation for the evolution of the normalized distribution

$$\frac{d\mu(k, t)}{dt} = [\langle k \rangle(t) - k]\mu(k, t). \quad (4)$$

The distribution turns around the pivot $\langle k \rangle(t)$, increasing for $k < \langle k \rangle(t)$ and decreasing for $k > \langle k \rangle(t)$. The solution is

$$\mu(k, t) = \mu(k, 0) \exp \left(\int_0^t [\langle k \rangle(t') - k] dt' \right). \quad (5)$$

Integrating over k and using the fact that $\mu(k, t)$ is normalized to one, we get

$$\langle k \rangle(t) = -\frac{d}{dt} \ln \left(\int_0^\infty \mu(k, 0) e^{-kt} dk \right) \quad (6)$$

$$\mu(k, t) = \frac{\mu(k, 0) e^{-kt}}{\int_0^\infty \mu(k, 0) e^{-kt} dk}. \quad (7)$$

As an explicit example we might think of a system of particles that aggregate on a wall and which have been prepared to have, initially, a uniform distribution of reaction rates up to a maximum value of κ . The aggregation starts at $t = 0$ with the average reaction rate $\kappa/2$ and we find in the long-time limit $\langle k \rangle$ tends to 0 with a $1/t$ time dependence.

3. Direct and correlated losses

A more complex situation occurs if the reaction of a possible bond eliminates not only this particular bond (direct loss) but other bonds as well which are in general correlated to the particular bond. For instance in figure 3(a) each particle forms a possible bond with all other particles. If the particles drop out of the system after the reaction, then the reaction of a possible bond (two particles) eliminates all other bonds that shared one of these two particles as well. Alternatively the reaction may be allowed to continue to lead to a non-trivial structure, as is the case in colloidal aggregation [2] (figure 3(b)): then the sticking of two particles belonging to two different clusters may sterically inhibit other possible bonds, whether both share one of the sticking

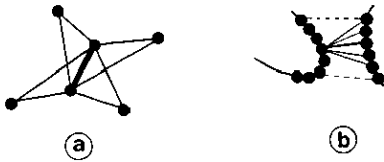


Figure 3. (a) Correlated losses: two irreversibly interacting particles drop out of the system and thus eliminate all possible bonds that were related to these two particles. (b) Correlated and structural losses: two irreversibly interacting particles belonging to two different clusters stick together and thus sterically render other bonds impossible. These structurally inhibited bonds may be those belonging to the two particles (full line) but others (broken line) as well.

particles or not. The correlations may occur via the interaction rule or structural considerations.

We call two possible bonds which may inhibit each other by reaction an incompatible pair of possible bonds. The possible bonds are solely distinguished by the reaction rate k which is determined by the interaction during collision of the particles involved. We assume that due to low reaction rates any spatial fluctuation (e.g. in particle density) have time to equilibrate, so that incompatibility is the sole source of correlation. Let $L(k', k)$ be the number of incompatible pairs of possible bonds with reaction rate k' and k . The reaction of the possible bonds with reaction rate k' eliminates $L(k', k)$ possible bonds with reaction rate k . Thus we find the following ansatz for the change of $B(k, t)$ with time due to reactions

$$\frac{dB(k, t)}{dt} = - \int_0^\infty k' L(k', k) dk' \quad (8)$$

In contrast for fast-reacting systems the assumptions leading to (8) do not hold and only the inclusion of fluctuations can yield the right kinetics [9, 14]. Using the definitions (1) and $l(k', k) = L(k', k)/B_0(t)$, and eliminating a term $[B_0(t)]^{-1} dB_0(t)/dt$ by integrating over k in (8) we get an equation for $\mu(k, t)$

$$\frac{d\mu(k, t)}{dt} = - \int_0^\infty k' l(k', k) dk' + \mu(k, t) \int_0^\infty k' l(k', k) dk' dk. \quad (9)$$

Now $l(k', k)$ can be separated into three classes of pairs of possible bonds, those with no site, one site and two sites in common:

$$l(k', k) = a\alpha_2(k', k) + b\beta_2(k', k) + c\gamma_2(k', k) \quad (10)$$

where a , b and c are the number of incompatible pairs of possible bonds per bond, with respectively no site, one site and two sites in common. For each case the normalized distribution of the reaction rates for a pair of bonds is given respectively by $\alpha_2(k', k)$, $\beta_2(k', k)$ and $\gamma_2(k', k)$. The joint probabilities are conveniently expressed via the conditional probabilities that in a pair of possible bonds one has the reaction rate k' , given that the other has reaction rate k :

$$\alpha_2(k', k) = \mu(k, t)\alpha(k|k') \quad (11a)$$

$$\beta_2(k', k) = \mu(k, t)\beta(k|k') \quad (11b)$$

$$\gamma_2(k', k) = \mu(k, t)\gamma(k|k') = \mu(k, t)\delta(k - k'). \quad (11c)$$

The conditional probability $\alpha(k|k')$ expresses the correlation between two possible bonds with no site in common, which may occur via structural considerations. The correlation between two possible bonds with one site in common is expressed by $\beta(k|k')$. This correlation occurs via the nature of the interaction between two particles. Finally $\gamma(k|k')$ expresses the correlation of a bond with itself. This term is responsible for direct losses.

Substituting (11) and (10) into (9) yields

$$\frac{d\mu(k, t)}{dt} = \mu(k, t)[a(\langle k \rangle - \langle k' \rangle_\alpha) + b(\langle k \rangle - \langle k' \rangle_\beta) + c(\langle k \rangle - k)] \quad (12)$$

where the conditional average reaction rates are

$$\langle k' \rangle_\alpha = \int_0^\infty k' \alpha(k|k') dk' \quad (13a)$$

$$\langle k' \rangle_\beta = \int_0^\infty k' \beta(k|k') dk' \quad (13b)$$

If in a pair of possible bonds with no site and one site in common, the reaction rates were uncorrelated, the $\alpha(k|k')$ and $\beta(k|k')$ would be $\mu(k', t)$ and the average reaction rates would coincide with the conditional ones and the distribution in (12) would change due to direct losses only. Thus for uncorrelated bonds we recover the simple case of direct losses only as described in section 2.

Equation (12) can be integrated to give the solution

$$\mu(k, t) = \mu(k, 0) \exp \left(\int_0^t a(\langle k \rangle - \langle k' \rangle_\alpha) + b(\langle k \rangle - \langle k' \rangle_\beta) + c(\langle k \rangle - k) dt' \right). \quad (14)$$

Integrating over k and using the normalization of $\mu(k, t)$ we get

$$\langle k \rangle(t) = \frac{-d}{(a + b + c)dt} \ln \left[\int_0^\infty \mu(k, 0) \exp \left(- \int_0^t a \langle k' \rangle_\alpha + b \langle k' \rangle_\beta + ck dt' \right) dk \right] \quad (15a)$$

$$\begin{aligned} \mu(k, t) = & \mu(k, 0) \exp \left(- \int_0^t a \langle k' \rangle_\alpha + b \langle k' \rangle_\beta + ck dt' \right) \\ & \times \left[\int_0^\infty \mu(k, 0) \exp \left(- \int_0^t a \langle k' \rangle_\alpha + b \langle k' \rangle_\beta + ck dt' \right) dk \right]^{-1}. \end{aligned} \quad (15b)$$

Though the lack of an explicit expression for $\alpha(k|k')$ and $\beta(k|k')$ inhibits a further analytic exploration of (15), we find the satisfying result that solutions for the situation of correlated losses, (15), are analogous in form to the solutions of the much simpler case of direct losses only ((6) and (7)). This analogy becomes even more obvious in the following approximation.

4. Linear correlation approximation

If the distribution $\mu(k, t)$ is 'not too wide' we may approximate $\langle k' \rangle_\alpha$ and $\langle k' \rangle_\beta$ by its expansion to first order around $\langle k \rangle$:

$$\langle k' \rangle_\alpha = \langle k' \rangle_{\alpha, k=\langle k \rangle} + [k - \langle k \rangle]\zeta \quad (16a)$$

$$\zeta = \left(\frac{d\langle k' \rangle_\alpha}{dk} \right)_{k=\langle k \rangle} \quad (16b)$$

$$\langle k' \rangle_\beta = \langle k' \rangle_{\beta, k=\langle k \rangle} + [k - \langle k \rangle]\eta \quad (16c)$$

$$\eta = \left(\frac{d\langle k' \rangle_\beta}{dk} \right)_{k=\langle k \rangle} \quad (16d)$$

Since $\langle k \rangle = \int_0^\infty \langle k' \rangle_\alpha \mu(k, t) dk$ and analogous for $\langle k' \rangle_\beta$ we find from (16a) and (16c) that $\langle k' \rangle_{\alpha, k=\langle k \rangle} = \langle k \rangle = \langle k' \rangle_{\beta, k=\langle k \rangle}$ and thus

$$\langle k' \rangle_\alpha = \langle k \rangle + [k - \langle k \rangle]\zeta \quad (17)$$

$$\langle k' \rangle_\beta = \langle k \rangle + [k - \langle k \rangle]\eta. \quad (18)$$

Equations (17) and (18) may also be thought of as a model by itself. Substituting (17) and (18) into (14) we get

$$\mu(k, t) = \mu(k, 0) \exp \left(\int_0^t [(k) - k](a\zeta + b\eta + c) dt' \right). \quad (19)$$

Integrating over k and using normalization yields the final result

$$\mu(k, t) = \frac{\mu(k, 0) \exp(-k\Theta)}{\int_0^\infty \mu(k, 0) \exp(-k\Theta) dk} \quad (20a)$$

$$\langle k \rangle = -\frac{d}{d\Theta} \ln \left(\int_0^\infty \mu(k, 0) \exp(-k\Theta) dk \right) \quad (20b)$$

$$\Theta = \int_0^t a\zeta + b\eta + c dt'. \quad (20c)$$

Equations (20a) and (20b) are distinguished from (6) and (7) only by the label of the time variable. All information about the details of the system are condensed in the new 'effective time' Θ . Information about the correlation and number of bonds is given by ζ , η and a , b , respectively. Since Θ depends in an integral form on ζ, η, a and b it contains the history as well. In the case of direct losses only, i.e. no correlation with other bonds, a and b cancel in the derivation and since $c = 1$, the effective time Θ coincides with the real time t .

5. Example

As an instructive example we think of a colloidal aggregate for which the initial distribution has been prepared to be Gaussian:

$$\mu(k, 0) = \frac{1}{\sqrt{2}\sigma F(k_0/\sqrt{2}\sigma)} \exp[-(k - k_0)^2/2\sigma^2] \quad (21)$$

where k_0 is the average reaction rate at $t = 0$ and σ is the width of the distribution. The error function

$$F(x) = \int_{-\infty}^x \exp(-y^2) dy \quad (22)$$

in the normalization factor occurs due to the constraint that $k \geq 0$. Substituting (21) into (20a) and (20b) we get

$$\langle k \rangle(\Theta) = [k_0 - \sigma^2\Theta] + \frac{(\sigma/\sqrt{2}) \exp[-(1/2\sigma^2)(k_0 - \sigma^2\Theta)^2]}{F((1/\sqrt{2}\sigma)(k_0 - \sigma^2\Theta))} \quad (23a)$$

$$\mu(k, \Theta) = \frac{1}{\sqrt{2}\sigma F((1/\sqrt{2}\sigma)(k_0 - \sigma^2\Theta))} \exp\{-(1/2\sigma^2)[k - (k_0 - \sigma^2\Theta)]^2\} \quad (23b)$$

For $\sigma^2\Theta \ll k_0$ the average reaction rate $\langle k \rangle$ decreases linearly in Θ and decreases faster for a broader distribution, whereas in the opposite limit $\sigma^2\Theta \gg k_0$, the average reaction rate tends asymptotically to zero. The distribution remains of Gaussian form with the maximum at $k_0 - \sigma^2\Theta$. Due to the constraint that $k \geq 0$ the maximum does not coincide with the mean value and in particular for $\sigma^2\Theta > k_0$ is located on the negative axis. This explicit expression for the time dependence of the average reaction rate might be particularly useful in the determination of the cluster size distribution via a mean field rate equation [15].

6. Summary

In summary we have studied the time dependence of the reaction rate distribution for irreversibly interacting systems. The problem is formulated in terms of possible bonds between particles. In the reaction-limited regime all possible bonds are equally likely and the reaction is only determined by the reaction rate. The reactions continually eliminate possible bonds from the system. In the case of direct losses only, the distribution has an exponential time dependence. It turns out that the solution for the more complex case of correlated losses is closely related to the simpler case of direct losses only. This analogy is further exploited by approximating the conditional average reaction rate by its expansion to first order. In this approximation we recover the solution of the direct-losses-only case, where the time is replaced by an 'effective time'. This 'effective time' accommodates the details of the interactions and thus decouples them from the general statistical problem. Finally we give an instructive example where the initial distribution is taken to be Gaussian.

Acknowledgments

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