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Stochastic chemical kinetics with energy parameters

Guy Fayolle, Vadim Malyshev, Serguei Pirogov

ABSTRACT: *We introduce new models of energy redistribution in stochastic chemical kinetics with several molecule types and energy parameters. The main results concern the situations when there are product form measures. Using a probabilistic interpretation of the related Boltzmann equation, we find some invariant measures explicitly and we prove convergence to them.*

1 Introduction

Metabolic pathways in molecular biology are chains or networks of chemical reactions providing redistribution of energy, in particular synthesis of ATP molecules, universal energy stocks in cells. Here we elaborate simple models of energy redistribution. According to a classical approximation, the energy of a molecule can be subdivided in two parts: internal (chemical) energy and kinetic energy. The model is the following.

Assume that there are V molecule types $v \in \{1, \dots, V\}$, $n_v(t)$ molecules for each type v at time t . Types v can be interpreted as chemical substances with different formulas, different isomers of the same formula, or even as different energy levels (spectrum) of the same molecule.

The total number of molecules $M = \sum_v n_v(t)$ will be conserved. A molecule may be characterized by a pair (v, T) , $v = 1, \dots, V$, where $T \in R_+$ is the kinetic energy of the molecule. Then each molecule of type v at time t has energy

$$E(t) = I(v) + T(t),$$

where $I(v)$ is the internal (or chemical) energy of any molecule of type v , $T(t)$ being the kinetic energy of a concrete molecule at time t . Thus, for any v, t , $I(v)$ are fixed numbers and $T(t)$ are random.

We use the approach usually referred to as *stochastic chemical kinetics*. It appeared in physical papers, see [5], but was also explored also by mathematicians for many models with small V , (see e.g. the reviews [7, 4]). However these models did not consider any energy parameter. Independently of this, Kac [3] considered a beautiful model with mean field collisions. Deeper results in this model appear even recently, see [1]. However, in Kac's model molecules were characterized only by kinetic energies, that is $V = 1$. Our model can be considered as a mixture of these two: there are molecule types and energy parameter.

The plan of the paper is as follows. In section 2, we introduce our probabilistic microscopic model and provide the corresponding Boltzmann type equation. Proof of the finite microtime scaling limit convergence to this equation uses standard technical tools and will be published elsewhere. In section 3 we get deeper results for the one type case with uniform scattering: find invariant measures and prove convergence of the Boltzmann equation for large macrotime. In section 4 we provide many examples, with similar results for multitype models.

2 Finite time scaling limit

Unless otherwise stated, we consider a system of binary reactions of the form $A+B \rightarrow C+D$. We assume energy conservation and random momentary collisions, that is when a pair of different molecules $(v, T), (v', T')$ collide at time t then a new pair $(v_1, U), (v'_1, U')$ appears at time $t+0$, so that

$$I(v) + T + I(v') + T' = I(v_1) + U + I(v'_1) + U'.$$

Obviously, the reaction is possible only if

$$I(v) + T + I(v') + T' \geq I(v_1) + I(v'_1). \quad (2.1)$$

We define the following continuous time Markov chain. The state is an array of V vectors $((v, T_i), i = 1, \dots, n_v), v \in V$. Thus, their total length $M = \sum_{v=1}^V n_v$ is conserved, but not necessarily n_v . The order of components in each vector $((v, T_i), i = 1, \dots, n_v)$ does not play any role, so that we will consider only functions symmetric in the vector coordinates.

On the time interval $(t, t + dt)$, each pair of molecules $(v, T), (v', T')$ has a collision with probability $\frac{1}{M} \alpha_{vv'}(T, T') dt$. The functions $\alpha_{vv'}(x, y)$ are assumed to be bounded and smooth on R_+^2 . As a result of this collision, some pair $(v_1, U), (v'_1, U')$ appears, provided that condition (2.1) holds for at least one pair (v_1, v'_1) . Otherwise nothing occurs. The distribution of the new pair is defined by the rules listed hereafter. For any v_1, v'_1, v, v', T, T' , the conditional densities

$$P((v_1, U), v'_1 | (v, T), (v', T')) \geq 0$$

are supposed to satisfy the following properties.

1. If

$$I(v) + T + I(v') + T' < I(v_1) + I(v'_1),$$

then

$$P((v_1, U), v'_1 | (v, T), (v', T')) = 0.$$

2. For any v, v', v_1, v'_1, T, T' , the density function

$$f(U) = P((v_1, U), v'_1 | (v, T), (v', T'))$$

is defined on the interval $I = [0, I_v + T + I_{v'} + T' - I(v_1) - I(v'_1)]$ and

$$\sum_{v_1, v'_1} \int_I P((v_1, U), v'_1 | (v, T), (v', T')) dU = 1.$$

Thus the distribution of the triple (v_1, U, v'_1) is entirely defined by

$$P((v_1, U), v'_1 | (v, T), (v', T'))$$

and $U' = I(v) + T + I(v') + T' - (I(v_1) + U + I(v'_1))$.

Hence, for V finite sets $\{T_{v,1}, \dots, T_{v,n_v}\}, v = 1, \dots, V$, we have defined a Markov process on R_+^M , which will be denoted by \mathcal{L}_M . It is worth remarking that, when

the total energy U is fixed, \mathcal{L}_M has a compact state space. Then, under some nondegeneracy conditions on α and P , this Markov chain for fixed M approaches, as $t \rightarrow \infty$, its unique stationary distribution $\pi^{(M)}(U)$. Our goal will be to study, under some conditions, the scaling limit $M \rightarrow \infty$ for fixed t , and also the large time limit $t \rightarrow \infty$.

Let $n_v^{(M)}(A, t)$ denote the number of type v molecules at time t having kinetic energy T in the set $A \subset R_+$. In the limit $M \rightarrow \infty$ we have to impose initial conditions at time zero

$$\lim_{M \rightarrow \infty} \frac{n_v^{(M)}(A, 0)}{M} = \int_A \rho_v(x, 0) dx,$$

for some nonnegative functions $\rho_v(x, 0)$, $\sum_v \int_{R_+} \rho_v(x, 0) dx = 1$, called *concentrations*. Our goal is to prove that, as $M \rightarrow \infty$, the sequence of Markov processes \mathcal{L}_M converges to some deterministic evolution \mathcal{L} of the concentrations. We state now our first result.

Theorem 2.1 *For any A and t , there exist deterministic limits (in probability)*

$$\lim_{M \rightarrow \infty} \frac{n_v^{(M)}(A, t)}{M} = \int_A \rho_v(x, t) dx,$$

where the $\rho_v(x, t)$'s are some non-negative functions satisfying the following Boltzmann type equations

$$\begin{aligned} \frac{\partial \rho_{v_1}(x, t)}{\partial t} = & \sum_{v, v', v'_1} \int_{R_+^2} [\alpha_{vv'}(y, z) P((v_1, x), v'_1 | (v, y), (v', z)) \rho_v(y, t) \rho_{v'}(z, t) \\ & - \alpha_{v_1 v'_1}(x, z) P((v, y), v' | (v_1, x), (v'_1, z)) \rho_{v_1}(x, t) \rho_{v'_1}(z, t)] dy dz, \end{aligned} \quad (2.2)$$

with the initial condition $\rho_v(x, 0)$.

Other reaction types Quite similarly one can consider other types of reactions. For example consider the reaction $A \rightarrow B + C$. In this case on the time interval $(t, t + dt)$ each molecule (v, T) with probability $\alpha_v(T) dt$ is transformed into two molecules (note that the scaling is different here). The distribution of the products $(v_1, U), (v'_1, U')$ is defined by similar kernels $P((v_1, U), v'_1 | (v, T))$ under the condition

$$I_{v_1} + I_{v'_1} \leq I_v + T.$$

3 One type case

3.1 Probabilistic interpretation

We consider in this section the particular situation with only one molecule type v . It will be also assumed that the rates $\alpha(T, T') = \alpha_{vv}(T, T') = \alpha$ and the conditional probabilities $P(U|T, T')$ are uniform on the interval $[0, T + T']$. It turns out

that the limiting stationary distribution can be found explicitly. Indeed, equation (2.2) can be rewritten as

$$\frac{\partial \rho(x, t)}{\partial t} = \alpha \int_x^\infty \frac{ds}{s} \int_0^s \rho(u, t) \rho(s - u, t) du - \alpha \rho(x, t). \quad (3.1)$$

[Similar equations appeared in [2] in a different context]. Now one can guess a fixed point: it is $\rho(x) = \beta e^{-\beta x}$, but it also can be obtained from a very clear probabilistic picture.

Let us consider *finite particle dynamics*, that is the chain \mathcal{L}_M , the states of which are finite subsets of R_+ with M elements.

Take first the case $M = 2$. Define the chains $\mathcal{L}_2(U)$ as the restriction of \mathcal{L}_2 on states with total energy U . Then the chains $\mathcal{L}_2(U)$ are irreducible and nilpotent: that is, already after the first jump we get the stationary distribution $\pi_2(U)$, with T uniformly distributed on $[0, U]$ and $T' = U - T$. Hence, for any initial condition, \mathcal{L}_2 is a mixture of $\mathcal{L}_2(U)$. We see that, for any density $f(U)$, the measure

$$\int_{R_+} \pi_2(U) f(U) dU$$

is an invariant measure for \mathcal{L}_2 . Indeed one of these invariant measures is of greatest interest to us. Let the random vector (ξ_1, ξ_2) on R_+^2 be defined by the measure $\mu_{2, \beta}$, such that the two random variables ξ_1, ξ_2 on R_+ be i.i.d with density $\rho(x) = \beta \exp(-\beta x)$. Consider a new random vector (η_1, η_2) , where η_1 is picked at random on the interval $[0, \xi_1 + \xi_2]$ and $\eta_2 = \xi_1 + \xi_2 - \eta_1$. This defines a transformation of measures $\mu'_{2, \beta} = W \mu_{2, \beta}$. In fact we have the following

Lemma 3.1 *The measure $\mu_{2, \beta}$ is invariant with respect to W , that is*

$$\mu'_{2, \beta} = \mu_{2, \beta}. \quad (3.2)$$

Proof. Immediate, since the density of $\xi = \xi_1 + \xi_2$ is $\beta^2 x \exp(-\beta x)$. Then picking a random point on the interval $[0, x]$ yields $\mu_{2, \beta}$, whence equality (3.2) follows. ■
In addition, (3.2) gives

$$\rho(u) = \int_u^\infty \frac{dx}{x} \int_0^x \rho(y) \rho(x - y) dy,$$

which is exactly the stationary form of equation (3.1).

For $M \geq 3$, the Markov chain \mathcal{L}_M has also irreducible components $\mathcal{L}_M(U)$, consisting of all states (T_1, \dots, T_M) with $T_1 + \dots + T_M = U$. For fixed M and U the invariant measure of the chain $\mathcal{L}_M(U)$ is the uniform measure on the simplex $T_1 + \dots + T_M = U$. An invariant measure on \mathcal{L}_M can be found as follows.

Take M independent particles, having each density $\beta e^{-\beta x}$ on R_+ and let $\mu_{M, \beta}$ denote their joint distribution.

Lemma 3.2 *The measure $\mu_{M, \beta}$ is invariant for \mathcal{L}_M .*

Proof. It follows from the previous lemma, because the generator of \mathcal{L}_M is the sum of generators corresponding to all pairs $(i, j), i, j = 1, \dots, M, i \neq j$. ■

Remark 3.1 *One can show that $\mathcal{L}_M(U)$ is reversible, by using the classical Kolmogorov's reversibility criteria for Markov with transition rates $\lambda_{\alpha\beta}$, namely*

$$\lambda_{\alpha_1 \alpha_2} \lambda_{\alpha_2 \alpha_3} \dots \lambda_{\alpha_k \alpha_1} = \lambda_{\alpha_1 \alpha_k} \lambda_{\alpha_k \alpha_{k-1}} \dots \lambda_{\alpha_2 \alpha_1}.$$

See related questions in [8].

3.2 Convergence for Boltzmann equation

According to the above section, when the total initial energy U satisfies the condition $U = M/\beta$, we have

$$\lim_{M \rightarrow \infty} \lim_{t \rightarrow \infty} \frac{n_v^{(M)}(A, t)}{M} = \int_A \beta e^{-\beta x} dx.$$

We will consider now the quantity $\lim_{t \rightarrow \infty} \lim_{M \rightarrow \infty}$.

Theorem 3.3 For Boltzmann equation (2.2), for any initial condition $\rho(x, 0)$, we have

$$\lim_{t \rightarrow \infty} \rho(x, t) = \beta e^{-\beta x}, \quad x \geq 0 \quad (3.3)$$

Proof. The sketch is the following. First, we prove in the next subsection, under more general assumptions, that any initial distribution converges to some fixed point. Secondly, we will show that there is a unique one-dimensional manifold of fixed points, namely $\beta e^{-\beta x}$, $0 < \beta < \infty$. This will conclude the proof, since β itself is uniquely determined by the initial mean energy

$$T(0) = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M T_i(0) = \frac{1}{\beta}.$$

■

3.3 Local equilibrium condition

We come back here to an arbitrary number of types. We will say that a positive function $f(v, x)$ on $V \times R_+$ with $\sum_v \int f(v, x) dx = C < \infty$, satisfies a *local equilibrium condition* (LE) if, for any γ, γ_1 ,

$$\sum_{\gamma', \gamma'_1} [w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma') f(\gamma'_1) - w(\gamma', \gamma'_1 | \gamma, \gamma_1) f(\gamma) f(\gamma_1)] = 0, \quad (3.4)$$

where we use the notation

$$\gamma = (v, x), \quad \sum_{\gamma} = \sum_v \int dx,$$

and

$$w(\gamma, \gamma_1 | \gamma', \gamma'_1) = \alpha_{v'v'_1}(x', x'_1) P((v, x), v_1 | (v', x'), (v'_1, x'_1)) \delta(x_1 - (x' + x'_1 + I_{v'} + I_{v'_1} - x - I_v - I_{v_1})).$$

One can assume $C = 1$. Then, in the one type case, this is tantamount to saying that \mathcal{L}_2 has the invariant product form distribution $f(x)f(y)$.

The *fixed point condition* (FP)

$$\sum_{\gamma, \gamma', \gamma'_1} [w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma') f(\gamma'_1) - w(\gamma', \gamma'_1 | \gamma, \gamma_1) f(\gamma) f(\gamma_1)] = 0, \quad (3.5)$$

valid for any γ , follows immediately from (3.4).

We shall say that $f(\gamma)$ satisfies a *detailed balance condition* (DB) whenever

$$w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma') f(\gamma'_1) - w(\gamma', \gamma'_1 | \gamma, \gamma_1) f(\gamma) f(\gamma_1) = 0, \quad (3.6)$$

for any $\gamma, \gamma', \gamma_1, \gamma'_1$. In the above one type example, DB condition holds if one chooses

$$f_0 = \beta e^{-\beta x},$$

for any positive β . Note that DB \rightarrow LE \rightarrow FP.

Let us define the *relative entropy* of f with respect to f_0 , assuming both f and f_0 are positive. Farther on, f_0 will be fixed and therefore omitted in the notation, so that

$$H(f) \equiv H(f, f_0) = \sum_{\gamma} f(\gamma) \log \left[\frac{f_0(\gamma)}{f(\gamma)} \right]. \quad (3.7)$$

Theorem 3.4 *Assume that there exists some $f_0(\gamma) > 0$ satisfying the local equilibrium condition. Then for any initial $f(\gamma, 0)$ with $H(f(\cdot, 0))$ finite, the function $f(\gamma) = f(\gamma, t)$, that is the solution of equation (2.2), does satisfy*

$$\frac{dH(f)}{dt} \geq 0.$$

Moreover, as $t \rightarrow \infty$, $f(\gamma, t)$ tends to some fixed point f_{∞} which depends in general on the initial data $f(\gamma, 0)$. LE condition holds for any stationary solution f , that is for any fixed point of (2.2).

Proof. The integrability of $\frac{df(\gamma)}{dt}$ follows from (2.2), so that the following conservation law holds

$$\sum_{\gamma} \frac{df(\gamma)}{dt} = 0. \quad (3.8)$$

Differentiating (3.7) and using (3.8), we get

$$\frac{dH(f)}{dt} = \sum_{\gamma} \frac{df(\gamma)}{dt} \log \left[\frac{f_0(\gamma)}{f(\gamma)} \right].$$

We rewrite condition (3.4) as

$$\sum_{\gamma', \gamma'_1} w(\gamma, \gamma_1 | \gamma', \gamma'_1) \frac{f_0(\gamma') f_0(\gamma'_1)}{f_0(\gamma) f_0(\gamma_1)} = \sum_{\gamma', \gamma'_1} w(\gamma', \gamma'_1 | \gamma, \gamma_1),$$

and set for the sake of shortness $f \equiv \sum_{\gamma, \gamma_1, \gamma', \gamma'_1}$. Then, for any function $f(\gamma)$, we have

$$\int w(\gamma, \gamma_1 | \gamma', \gamma'_1) \frac{f_0(\gamma') f_0(\gamma'_1)}{f_0(\gamma) f_0(\gamma_1)} f(\gamma) f(\gamma_1) = \int w(\gamma', \gamma'_1 | \gamma, \gamma_1) f(\gamma) f(\gamma_1),$$

or, after a change of variables,

$$\int w(\gamma', \gamma'_1 | \gamma, \gamma_1) f(\gamma) f(\gamma_1) = \int w(\gamma', \gamma'_1 | \gamma, \gamma_1) \frac{f_0(\gamma) f_0(\gamma_1)}{f_0(\gamma') f_0(\gamma'_1)} f(\gamma') f(\gamma'_1).$$

Let $\phi(\gamma) = \log \left[\frac{f_0(\gamma)}{f(\gamma)} \right]$. Then

$$\begin{aligned} \frac{dH(f)}{dt} &= \sum_{\gamma} \frac{df(\gamma)}{dt} \phi(\gamma) \\ &= \int \phi(\gamma) [w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma') f(\gamma'_1) - w(\gamma', \gamma'_1 | \gamma, \gamma_1) f(\gamma) f(\gamma_1)] \\ &= \int [\phi(\gamma) - \phi(\gamma')] w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma') f(\gamma'_1) \\ &= \frac{1}{2} \int [\phi(\gamma) + \phi(\gamma_1) - \phi(\gamma') - \phi(\gamma'_1)] w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma') f(\gamma'_1). \end{aligned}$$

Set for a while

$$\begin{cases} \xi = \frac{f_0(\gamma) f_0(\gamma_1) f(\gamma') f(\gamma'_1)}{f(\gamma) f(\gamma_1) f_0(\gamma') f_0(\gamma'_1)}, \\ \alpha = \frac{f_0(\gamma') f_0(\gamma'_1)}{f_0(\gamma) f_0(\gamma_1)}, \end{cases}$$

so that

$$\log \xi = \phi(\gamma) + \phi(\gamma_1) - \phi(\gamma') - \phi(\gamma'_1).$$

Then

$$\frac{dH(f)}{dt} = \frac{1}{2} \int \alpha \xi \log \xi w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma) f(\gamma_1).$$

On the other hand, from the LE condition,

$$\int \alpha \xi w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma) f(\gamma_1) = \int \alpha w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma) f(\gamma_1),$$

which yields

$$\frac{dH(f)}{dt} = \frac{1}{2} \int (\xi \log \xi - \xi + 1) \alpha w(\gamma, \gamma_1 | \gamma', \gamma'_1) f(\gamma) f(\gamma_1) \geq 0,$$

since $\xi \log \xi - \xi + 1 > 0$ if $\xi > 0$, due to the convexity of $\xi \log \xi$.

Assume now that for some $f_0 > 0$ the local equilibrium condition holds. Then it holds also for any other stationary solution f , i.e. satisfying $\frac{df}{dt} = 0$. In fact, note that $\frac{dH(f)}{dt} > 0$ if $f(\gamma) f(\gamma_1) > 0$, $w(\gamma, \gamma_1 | \gamma', \gamma'_1) > 0$ and $\xi \neq 1$. Also, if f is a stationary solution of equation (2.2) then $\frac{df(\gamma)}{dt} = 0$ and hence $\frac{dH(f)}{dt} = 0$. It follows that, for any $\gamma, \gamma_1, \gamma', \gamma'_1$ such that $f(\gamma) f(\gamma_1) > 0$ and $w(\gamma, \gamma_1 | \gamma', \gamma'_1) > 0$, we have $\xi = 1$, that is

$$\frac{f(\gamma') f(\gamma'_1)}{f(\gamma) f(\gamma_1)} = \frac{f_0(\gamma') f_0(\gamma'_1)}{f_0(\gamma) f_0(\gamma_1)}.$$

On the other hand, if $\frac{df(\gamma)}{dt} = 0$, $f(\gamma) = 0$ and $w(\gamma, \gamma_1 | \gamma', \gamma'_1) = 0$, then we get $f(\gamma') f(\gamma'_1) = 0$ as a consequence of equation (2.2). Thus, for any γ, γ_1 , equation (3.4) holds. Any solution $f(t)$ of equation (2.2) as $t \rightarrow \infty$ tends to some stationary solution f_∞ , which depends in general on the initial data $f(0)$. In fact, from the

proof of theorem 2.1, it follows that f is a stationary solution, i.e. $\frac{df}{dt} = 0$, if and only if $\frac{dH(f)}{dt} = 0$ (provided that (2.2) holds). This means that $H(f)$ is a Lyapounov function. Consequently, the expected result follows from the general theory of Lyapounov functions and the proof of the theorem is terminated. ■

3.4 Fixed points and conservation laws

Now we will prove that, for any two fixed points f_0, f , the function $\log \frac{f}{f_0}$ is an additive conservation law. Consider the equation

$$\frac{f(\gamma')f(\gamma'_1)}{f(\gamma)f(\gamma_1)} = \frac{f_0(\gamma')f_0(\gamma'_1)}{f_0(\gamma)f_0(\gamma_1)}. \quad (3.9)$$

For $f_0 = 1$, we have

$$\frac{f(\gamma')f(\gamma'_1)}{f(\gamma)f(\gamma_1)} = 1, \quad (3.10)$$

which shows that $\log f$ is an additive conservation law. Vice versa, if there is a set J of additive conservation laws such that

$$\eta_j(\gamma) + \eta_j(\gamma_1) = \eta_j(\gamma') + \eta_j(\gamma'_1), j \in J,$$

then, for any constants c, c_j ,

$$f(\gamma) = c \prod_{j \in J} \exp(c_j \eta_j(\gamma))$$

is a solution of (3.10). Note that additive conservation laws form a linear space. Thus we have proved that any solution of (3.10) has this form. In the general case (that is if $f_0 \neq 1$), we have

$$\frac{f}{f_0} = c \prod_{j \in J} \exp(c_j \eta_j(\gamma)).$$

It is worth noticing that a nonzero additive conservation law for the chain \mathcal{L}_M is in fact unique, if the chains $\mathcal{L}_M(U)$ are irreducible, for all U .

4 Invariant measures for multitype models

Here we will analyze some cases with $V > 1$, when there exists an invariant measure having a product form.

4.1 Binary reactions without type change

Let for any $v = 1, \dots, V$ a density $\rho_v(x) > 0$ on R_+ be given. Assume only reactions $v, w \rightarrow v, w$ are possible, so that the n_v 's are conserved. Then one can introduce finite particle Markov chains $\mathcal{L}_{n_1, \dots, n_V}$. Suppose in addition that, for any couple of types (v, w) ,

$$\alpha_{vw}(T, T') = \alpha_{vw}(T + T'),$$

which means that the rates depend only on the sum of energies. We need the following definition. Fix a pair (v, w) of types and let ξ_v, ξ_w be independent random variables with joint density $\rho_v(x)\rho_w(y)$. Denote

$$P_{\rho_v\rho_w} = P_{\rho_v\rho_w}(x, y|T) = P(\xi_v = x, \xi_w = y | \xi_v + \xi_w = T)$$

the corresponding conditional distributions, which will be called *canonical kernels* corresponding to the density array (ρ_1, \dots, ρ_V) .

Let $\xi_{v,i}, i = 1, \dots, n_v$, stand for the energy of the i -th particle of type v .

Theorem 4.1 *Fix an array ρ_1, \dots, ρ_V and let a system of $\frac{V(V+1)}{2}$ reactions with canonical kernels $P_{\rho_v\rho_w}$ be given. Then, for any n_1, \dots, n_V , the invariant measures of $\mathcal{L}_{n_1, \dots, n_V}$ are such that the random variables $\xi_{v,i}$ have independent distributions equal to ρ_v . In the thermodynamic limit, for any initial concentrations of types (c_1, \dots, c_V) (here the concentrations of types do not change at all), the invariant energy distribution is unique and given by the independent densities ρ_v . Moreover, for any initial energy distribution, there is convergence to this invariant measure. Also, for any array (ρ_1, \dots, ρ_V) with arbitrary rates $\alpha_{vw}(U)$, there is only one system of kernels for which this array defines an invariant (product form) distribution, these kernels being canonical kernels.*

Proof. Any transition $v, v' \rightarrow v, v'$ conserves U and the related measures. Hence, as for the convergence, the argument is similar to that in the previous section. The other statements follow directly from the definitions. ■

When $\rho_v(x) = \beta e^{-\beta x}$, the kernels are uniform on $[0, T]$, as in the one type case study. Let P^β denote such a kernel. An interesting situation depicted in the next remark arises when

$$\rho_v(x) = \beta_v \exp(-\beta_v x),$$

with different β_v 's.

Remark 4.1 *All other cases can be reduced to the simplest one by the following transformation. Given any density $\rho > 0$ and any $\beta > 0$, introduce the one to one mapping $U = U(\rho, \beta) : R_+ \rightarrow R_+$ such that, for any $x \in R_+$,*

$$\int_0^x \rho(y) dy = \int_0^{U(x)} \beta e^{-\beta y} dy.$$

Then

$$P_{vw} = (U^{-1}(\rho_v, \beta), U^{-1}(\rho_w, \beta)) P^\beta (U(\rho_v, \beta), U(\rho_w, \beta)).$$

4.2 Unary reactions

Now we want to tackle examples in which the n_v 's are not conserved. Then, in general, only

$$\mathcal{L}^M = \bigcup_{n_1 + \dots + n_V = M} \mathcal{L}_{n_1, \dots, n_V}$$

is a Markov chain. In this subsection, we assume that unary reactions

$$v \rightarrow w$$

can take place with rates a_{vw} . Such reactions could be interpreted as isomer to isomer transformations. When $I_v \geq I_w$ the reaction $v \rightarrow w$ always occurs, and the kinetic energy T of the v -particle becomes the kinetic energy $I_v - I_w + T$ of the w -particle. The reaction $w \rightarrow v$ however occurs only if $T - I_v + I_w \geq 0$, in which case the kinetic energy T of the w -particle becomes the kinetic energy $T - I_v + I_w$ of the v -particle.

Consider first the case without binary reactions. Define the following *one-particle* Markov chain: its states are all pairs (v, T) , that is $M = 1$. Moreover, assume that there are only two types. Let $I_1 < I_2$. Consider a pair of densities ρ_1, ρ_2 , and denote by ξ_1, ξ_2 the corresponding random variables. We call this pair *admissible* if the conditional density of $\xi_1 - (I_2 - I_1)$, on the event $\{\xi_1 > I_2 - I_1\}$, is equal to ρ_2 . One example is $\rho_1 = \rho_2 = \beta \exp(-\beta x)$, another being

$$\rho_1(x) = \begin{cases} 0, & \text{for } x < I_2 - I_1; \\ \rho_2(x - I_2 + I_1), & \text{otherwise.} \end{cases}$$

Any invariant measure on $\{1, 2\} \times R_+$ can be written as $\pi_1(1, \rho_1) + \pi_2(2, \rho_2)$ with positive coefficients π_i such that $\pi_1 + \pi_2 = 1$. We have for π_1, π_2 the following equations

$$\pi_1 Y_1 a_{12} = \pi_2 a_{21}, \quad Y_1 = \int_{I_2 - I_1}^{\infty} \rho_1(x) dx.$$

This case exhibits the highest degree of reducibility, each class containing one or two elements: there are plenty of invariant measures – but this is clearly a very unnatural situation. For an arbitrary M with only two types, we have the product of M chains \mathcal{L}^1 , which again leads to a rather unnatural situation.

When there are $V > 2$ types, each class also has a finite number of elements. It is then possible to order the internal energies, assuming for example

$$I_1 \leq I_2 \leq \dots \leq I_V,$$

and also $a_{vw} > 0, \forall v, w$. If the full energy satisfies $I_m < U < I_{m+1}, m = 1, \dots, V$ (putting $I_{m+1} = \infty$) then there are no possible jumps to the types $m + 1, \dots, V$, so that the process evolves as a Markov chain $\mathcal{L}_{1,m}$ with state space $1, \dots, m$ and rates $a_{vw}, v, w = 1, \dots, m$. Hence $\mathcal{L}_{1,m}$ are restrictions of $\mathcal{L}_{1,V}$. For $m = 1$, it becomes a trivial one-point Markov chain. Let $\pi_{m,v}, v = 1, \dots, m$ denote the stationary probability of the state v in $\mathcal{L}_{1,m}$. We have $\pi_{1,1} = 1$.

Note that, if at time 0 the state is $(1, U)$ and U has some density $f(U)$ in $[I_m, I_{m+1}]$, then the stationary distribution is defined by $\pi_{m,v}$ and by the conditional density f of the full energy. Thus everything is defined by the rates a_{vw} and by $f(U)$, that is ρ_1 . Moreover, these quantities can be chosen arbitrarily. Setting for the sake of shortness

$$\pi_v = \pi_{V,v},$$

we propose hereafter some examples.

Shifts In this first example we take $\rho_1(x) = 0$ if $x < I_V - I_1$. Then each ρ_v is just a shift of ρ_1 .

Reversibility Analogously, a system (ρ_1, \dots, ρ_V) of densities will be said *admissible* if the following condition holds: for any v the pair (ρ_v, ρ_{v+1}) is admissible. Then it follows that each pair of densities $(\rho_i, \rho_j), i < j$, is admissible.

Theorem 4.2 *If $I_1 < \dots < I_V$, all $\rho_v(x)$ are strictly positive and the system (ρ_1, \dots, ρ_V) is admissible then \mathcal{L}^M is reversible.*

Proof. Let $f_v(U) = \rho_v(U - I_v)$ for $U \geq I_v$ and $f_v(U) = 0$ for $U < I_v$. We suppose the invariant distribution for the chain \mathcal{L}^M has a product form, each factor being given by $\pi_v f_v(U)$. This means that for each m and for $I_m \leq U < I_{m+1}$

$$\sum_{i=1}^m \pi_i f_i(U) a_{ij} = \pi_j f_j(U) \sum_{i=1}^m a_{ji},$$

for $j = 1, \dots, m$. Then admissibility means

$$f_i(U) = \begin{cases} A_i f_1(U), & \text{for } U \geq I_i, \\ f_i(U) = 0, & \text{otherwise.} \end{cases}$$

Hence

$$\sum_{i=1}^m \pi_i A_i a_{ij} = \pi_j A_j \sum_{i=1}^m a_{ji}, \quad 1 \leq j \leq m.$$

Putting $p_i = \pi_i A_i$, it follows that

$$\sum_{i=1}^m p_i a_{ij} = p_j \sum_{i=1}^m a_{ji}, \quad 1 \leq j \leq m, \quad \forall m = 1, \dots, V.$$

The comparison of these equations for m and $m + 1$ yields

$$p_{m+1} a_{m+1,j} = p_j a_{j,m+1}, \quad \forall j = 1, \dots, m$$

and by induction we get

$$p_i a_{ij} = p_j a_{ji}, \quad \forall i, j,$$

which implies the announced reversibility of \mathcal{L}^M . ■

Exponential In this third example, we also assume the system (ρ_1, \dots, ρ_V) of densities is admissible, and moreover that, for some $\rho(T)$ and all v ,

$$\rho_v = \rho.$$

Theorem 4.3 *Suppose $V \geq 3$, and that the quantities $I_2 - I_1$ and $I_3 - I_2$ are incommensurable. Then*

$$\rho(T) = \beta \exp(-\beta T),$$

for some $\beta > 0$.

Proof. Admissibility implies that

$$\begin{aligned}\rho_2(T) &= A_2\rho_1(T + I_2 - I_1), \\ \rho_3(T) &= A_3\rho_1(T + I_3 - I_1).\end{aligned}$$

If $\rho_1 = \rho_2 = \rho_3 = \rho$ then

$$\rho(T) = A_2\rho(T + x_2) = A_3\rho(T + x_3),$$

where $x_i = I_i - I_1$, $i = 2, 3$ are incommensurable. But these last two equations are compatible only if $A_2^{x_3} = A_3^{x_2}$ and $\rho(T) = \beta \exp(-\beta T)$, with

$$\beta = \frac{\log A_2 - \log A_3}{x_2 - x_3}.$$

■

Energy dependence In the fourth example, the rates $a_{vw} = a_{vw}(T)$ depend on the energy of the input particle v . To construct a model which will be needed later, consider a reversible Markov chain \mathcal{V}_1 on $\{1, \dots, V\}$ with stationary probabilities p_v and rates b_{vw} . Thus

$$p_v b_{vw} = p_w b_{wv}.$$

For reactions $v \rightarrow w$, define the reaction rates as

$$a_{vw}(U) = \begin{cases} 0, & \text{if } U < I_w, \\ (U - I_w)^{\alpha_w} b_{vw}, & \text{otherwise.} \end{cases}$$

Note that these rates are close to zero if the kinetic energy $T_w = U - I_w$ of the w -particle is close to zero. Letting $f_v(U)$ be the density of the full energy of the v -particle, the reversibility condition writes

$$\pi_v f_v(U) a_{vw}(U) = \pi_w f_w(U) a_{wv}(U), \quad (4.1)$$

for $U > \max(I_v, I_w)$. We take as density f the shifted Γ -distribution

$$f_v(U) = \begin{cases} \frac{\beta^{\nu_v}}{\Gamma(\nu_v)} (U - I_v)^{\nu_v - 1} \exp[-\beta(U - I_v)], & \text{if } U > I_v, \\ 0, & \text{otherwise.} \end{cases} \quad (4.2)$$

Here $\nu_v = \alpha_v + 1$. Then equation (4.1) becomes

$$\frac{\pi_v \beta^{\nu_v}}{\Gamma(\nu_v)} e^{\beta I_v} b_{vw} = \frac{\pi_w \beta^{\nu_w}}{\Gamma(\nu_w)} e^{\beta I_w} b_{wv},$$

showing that the stationary probabilities π_v of type v are equal to (up to a common factor)

$$p_v e^{-\beta I_v} \Gamma(\nu_v) \beta^{-\nu_v}, \quad (4.3)$$

and the resulting Markov chain is reversible.

4.3 Binary reactions without energy dependence

Let us suppose that a_{vw} do not depend on energies, so that types evolve independently of the energies. Thus at any time t , we will have probabilities $p_t(n_1, \dots, n_V)$. We will look for cases when there exists an invariant measure on each \mathcal{L}^M , defined by probabilities $p(n_1, \dots, n_V)$, and independent conditional distribution of energies

$$\prod_{v,i} \rho_{v,i},$$

[given n_1, \dots, n_V], defined by densities $\rho_{v,i}(x) = \rho_v(x)$.

Assume all I_v 's are equal, but any reaction $v, w \rightarrow v', w'$ can occur and let now a reaction $v, w \rightarrow v', w'$ be given. We again call

$$P_{\rho_{v'}, \rho_{w'}}(x, y|T)$$

the canonical kernel corresponding to the reaction $v, w \rightarrow v', w'$ and we denote by $\rho_{vw}(T)$ the density of $\xi_v + \xi_w$.

Theorem 4.4 *Suppose an array (ρ_1, \dots, ρ_V) of densities is given, satisfying for any binary reaction $v, w \rightarrow v', w'$ the conditions*

$$\rho_{vw}(T) = \int_{x+y=T} \rho_v(x)\rho_w(y)dx dy = \int_{x+y=T} \rho_{v'}(x)\rho_{w'}(y)dx dy = \rho_{v'w'}(T).$$

Assume also canonical kernels and that, as $t \rightarrow \infty$, the limit of $p_t(n_1, \dots, n_V)$ exists. Then there is an invariant measure having these densities.

4.4 General binary reaction case

Here the I_v 's can be different, but we assume only binary reactions $v, w \rightarrow v', w'$ are possible.

4.4.1 Complete factorization

Denote \hat{i} a pair of types (v, w) . Thus reaction $v, w \rightarrow v', w'$ will be written as $\hat{i} \rightarrow \hat{j}$, where $\hat{i} = (v, w), \hat{j} = (v', w')$. We shall use the analog of the third example with binary reactions. Consider a Markov chain $\mathcal{V}_1 \times \mathcal{V}_1$ on $\{1, \dots, V\} \times \{1, \dots, V\}$ with rates $b_{\hat{i}\hat{j}}$, such that its stationary distribution be a product form $p_{(v,w)} = p_v p_w$ and the chain be reversible. We define, for *vector particles* $\hat{i} = (v, w)$, the energies $I_{\hat{i}} = I_v + I_w$ and

$$f_{\hat{i}}(U) = (f_v * f_w)(U),$$

where f_v, f_w are given in (4.2). Thus $f_{\hat{i}}(U)$ has also a shifted Γ -distribution with parameters $I_{\hat{i}} = I_v + I_w, \nu_{\hat{i}} = \nu_v + \nu_w, \beta$. The reversibility condition, with some unspecified stationary probabilities $\pi_{\hat{i}}$, writes

$$\pi_{\hat{i}} f_{\hat{i}}(U) a_{\hat{i}\hat{j}}(U) = \pi_{\hat{j}} f_{\hat{j}}(U) a_{\hat{j}\hat{i}}(U), \quad (4.4)$$

where $U > \max(I_{\hat{i}}, I_{\hat{j}})$. Letting

$$a_{\hat{i}\hat{j}}(U) = \begin{cases} 0, & \text{if } U < I_{\hat{j}}; \\ (U - I_{\hat{j}})^{\alpha_{\hat{j}}} b_{\hat{i}\hat{j}} & \text{otherwise.} \end{cases}$$

Here

$$\alpha_j = \nu_j - 1 = \nu_{v'} + \nu_{w'} - 1,$$

and the reversibility condition becomes

$$\pi_i \frac{\beta^{\nu_i}}{\Gamma(\nu_i)} e^{\beta I_i} b_{ij} = \pi_j \frac{\beta^{\nu_j}}{\Gamma(\nu_j)} e^{\beta I_j} b_{ji}.$$

We are looking for solutions $\pi_{(v,w)} = \pi_v \pi_w$, since we are primarily interested in factorizable invariant distributions. To this end, we assume in addition that, for any binary reaction $v, w \rightarrow v', w'$, the condition

$$\nu_v + \nu_w = \nu_{v'} + \nu_{w'}$$

is fulfilled. Then

$$\pi_v \pi_w \beta^{\nu_v + \nu_w} e^{\beta I_v} e^{\beta I_w} b_{ij} = \pi_{v'} \pi_{w'} \beta^{\nu_{v'} + \nu_{w'}} e^{\beta I_{v'}} e^{\beta I_{w'}} b_{ji},$$

and up to a common factor, the solution of this system has the form

$$\pi_v = p_v e^{-\beta I_v} \beta^{-\nu_v} \quad (4.5)$$

4.4.2 Unary reactions included

Let $V = \bigcup_{\alpha} V_{\alpha}$ be a disjoint union of sets V_{α} of isomers. Thus, we assume that unary reactions $v \rightarrow w$ are allowed only if v and w belong to the same V_{α} . The energy dependence of unary reactions will be defined in the same way as in section 4.2, but additionally we take ν_v to be constant on each V_{α} , in other words $\nu_v = \nu_w$ for any two isomers $v, w \in V_{\alpha}$.

We consider the same binary reactions as in section 4.4.1, with the assumption that they are concordant with unary reactions in the following sense: $p_{(v,w)} = p_v p_w$ are such that, for any α , the probabilities p_v have the form given in section 4.2 up to a constant factor.

Theorem 4.5 *If the previous conditions are fulfilled, then formula (4.5) gives the factorized reversible invariant distribution, both for binary and unary reactions.*

Proof. It suffices to compare the formulae (4.5) and (4.3), remarking that the factor $\Gamma(\nu_v)$ in (4.3) can be omitted, since ν_v is constant on V_{α} . ■

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