

**QUANTITATIVE ESTIMATES FOR THE LARGE TIME  
BEHAVIOR OF A REACTION-DIFFUSION EQUATION  
WITH RATIONAL REACTION TERM**

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We show that the entropy method can be used to prove exponential convergence towards equilibrium with explicit constants when one considers a reaction-diffusion system corresponding to an irreversible mechanism of dissociation/recombination, for which no natural entropy is available.

*Keywords:* Reaction-diffusion equations; Entropy/entropy dissipation method.

## 1. Introduction

We consider a diatomic gas with dissociation/recombination reactions, made up by atoms  $A$  with mass  $m_1$  and molecules  $A_2$  with mass  $m_2 = 2m_1$ . According to a common kinetic model,<sup>1</sup> the gas is described as a mixture of three species, with an additional component, labelled by  $i = 3$ , representing unstable molecules  $A_3 \equiv A_2^*$  (with mass  $m_3 = m_2$ ) and playing the role of a transition state. The mixture is then taken to diffuse in a much denser medium, whose evolution is not affected by the collisions going on, assumed in local thermodynamical equilibrium, namely with distribution function  $f_0 = n_0 M_0$ , where  $M_0$  stands for the normalized Maxwellian with temperature  $T_0$  (constant) and vanishing mass velocity. According to the model, both atoms  $A_1$  and stable molecules  $A_2$  may undergo elastic collisions with other atoms, stable molecules and background particles. Moreover, atoms  $A_1$  may form a stable molecule  $A_2$  passing through the transition state  $A_2^*$ , while, on the other hand, both stable and unstable diatomic molecules may dissociate into two atoms. More precisely, the recombination process occurs in two steps:



where  $P = A, A_2$ , while dissociation occurs via two possible reactions:



All above interactions, modelling the chemical reactions at the kinetic level, have to be understood as irreversible processes. The host medium is assumed here only elastically scattering, and not chemically reacting. A physical situation in which the background is actually involved in chemical processes is extensively discussed in Refs. 2, 3.

Kinetic Boltzmann equations relevant to species  $A_1, A_2, A_2^*$  have been scaled<sup>2</sup> in terms of the typical relaxation times, a small parameter defining the dominant process(es) has been introduced, and the formal asymptotic limit when this parameter vanishes has been consistently investigated. This leads to the derivation of hydrodynamic limiting equations, whose nature varies considerably according to the relative importance of the various processes and to the corresponding pertinent scaling, but which are typically of reaction-diffusion type as long as the scattering with the background plays an important role. We shall deal here with one of the asymptotic limits which seems more realistic in practice, and leads to

$$\partial_t n_i - d_i \Delta_{\mathbf{x}} n_i = \mathcal{Q}_i(n_1, n_2), \quad i = 1, 2, \quad (1)$$

where  $d_i$  are the diffusion coefficients

$$d_1 = \frac{m_1 + m_0}{2m_1 m_0} \frac{T_0}{\bar{\nu}_{10}^s n_0}, \quad d_2 = \frac{2m_1 + m_0}{4m_1 m_0} \frac{T_0}{\bar{\nu}_{20}^s n_0},$$

and  $\mathcal{Q}_i$  are the reaction contributions

$$\mathcal{Q}_2 = \frac{1}{\nu_{31}^t n_1 + \nu_{32}^t n_2} \left[ A(n_1)^3 + B(n_1)^2 n_2 - C n_1 (n_2)^2 - D(n_2)^3 \right] \quad (2)$$

with  $A = \nu_{11}^r \nu_{31}^i > 0$ ,  $B = \nu_{11}^r \nu_{32}^i - \nu_{21}^d \nu_{31}^t$ ,  $C = \nu_{21}^d \nu_{32}^t + \nu_{22}^d \nu_{31}^t > 0$ ,  $D = \nu_{22}^d \nu_{32}^t > 0$ , and  $\mathcal{Q}_1 = -2\mathcal{Q}_2$  (preservation of total number of atoms  $\bar{n}^0$ ).  $\nu_{ij}^k$  are total microscopic collision frequencies, where the superscript  $k$  takes the values  $s, r, i, d$ , corresponding to elastic scattering, recombination  $R$ , inelastic scattering  $I$ , dissociations  $D1, D2$ , respectively, and  $\nu_{3j}^t = \nu_{3j}^i + \nu_{3j}^d$ . Just on the basis of the sign of the coefficients, it can be checked that the cubic function (in the variable  $n_1$ ) into the square brackets in (2) has a positive root  $n_1 = \gamma n_2$  (with  $\gamma > 0$ ), while the other two roots are negative or complex conjugate with negative real part. Therefore

$$\mathcal{Q}_2 = (n_1 - \gamma n_2) \mathcal{P}(n_1, n_2) \quad (3)$$

$$\text{where} \quad \mathcal{P}(n_1, n_2) = \frac{(n_1)^2 + (\alpha + \beta)n_1 n_2 + \alpha \beta (n_2)^2}{\lambda n_1 + \mu n_2} > 0$$

with  $\lambda, \mu > 0$  and  $\alpha, \beta > 0$  or complex conjugate with positive real part. Taking into account conservation of  $\bar{n}^0$ , system (1) with Neumann boundary conditions on a bounded domain of unit measure admits a unique global equilibrium state:

$$n_1^* = \frac{\gamma}{2 + \gamma} \bar{n}^0, \quad n_2^* = \frac{1}{2 + \gamma} \bar{n}^0. \quad (4)$$

## 2. Existence and uniqueness of a strong solution

**Theorem 2.1.** *Let  $d_1, d_2 > 0$  and  $\Omega$  be a bounded regular ( $C^2$ ) open set of  $\mathbb{R}^N$ . We consider initial data in  $C^2(\bar{\Omega})$ , compatible with Neumann boundary conditions, and satisfying the bounds (for some strictly positive constants  $c_1, c_2, \mathcal{C}_1$  and  $\mathcal{C}_2$ ):*

$$0 < c_1 < n_1(0, \mathbf{x}) < \mathcal{C}_1, \quad 0 < c_2 < n_2(0, \mathbf{x}) < \mathcal{C}_2. \quad (5)$$

*Then, there exists a unique (strong) solution  $n_1(t, \mathbf{x}), n_2(t, \mathbf{x})$  in  $C^2(\mathbb{R}^+ \times \bar{\Omega})$  to system (1) with homogeneous Neumann boundary conditions such that, for  $(t, \mathbf{x}) \in \mathbb{R}^+ \times \Omega$ ,*

$$k_1 \leq n_1(t, \mathbf{x}) \leq \mathcal{K}_1, \quad k_2 \leq n_2(t, \mathbf{x}) \leq \mathcal{K}_2, \quad (6)$$

where

$$k_1 = \min \{c_1, \gamma c_2\}, \quad k_2 = \min \{\gamma^{-1} c_1, c_2\}, \quad (7)$$

$$\mathcal{K}_1 = \max \{\mathcal{C}_1, \gamma \mathcal{C}_2\}, \quad \mathcal{K}_2 = \max \{\gamma^{-1} \mathcal{C}_1, \mathcal{C}_2\}. \quad (8)$$

**Proof.** At first we shall prove that the “maximum principle” holds for  $(t, \mathbf{x}) \in [0, T] \times \Omega$ , for each  $T > 0$ , following the same lines as in Ref. 4. Let  $\varepsilon > 0$  be fixed and let us consider the functions

$$n_1^\varepsilon(t, \mathbf{x}) = n_1(t, \mathbf{x}) e^{-\varepsilon t}, \quad n_2^\varepsilon(t, \mathbf{x}) = n_2(t, \mathbf{x}) e^{-\varepsilon t}; \quad (9)$$

we prove that

$$n_1^\varepsilon(t, \mathbf{x}) < \mathcal{K}_1, \quad n_2^\varepsilon(t, \mathbf{x}) < \mathcal{K}_2. \quad (10)$$

From equations (1) it follows that the evolution of  $n_1^\varepsilon, n_2^\varepsilon$  is governed by the system

$$\begin{aligned} \partial_t n_1^\varepsilon - d_1 \Delta_{\mathbf{x}} n_1^\varepsilon &= -2(n_1^\varepsilon - \gamma n_2^\varepsilon) \mathcal{P}(n_1^\varepsilon, n_2^\varepsilon) e^{\varepsilon t} - \varepsilon n_1^\varepsilon, \\ \partial_t n_2^\varepsilon - d_2 \Delta_{\mathbf{x}} n_2^\varepsilon &= (n_1^\varepsilon - \gamma n_2^\varepsilon) \mathcal{P}(n_1^\varepsilon, n_2^\varepsilon) e^{\varepsilon t} - \varepsilon n_2^\varepsilon. \end{aligned} \quad (11)$$

Suppose that inequalities (10) do not hold for all  $(t, \mathbf{x}) \in [0, T] \times \Omega$ , and define the set  $B^\varepsilon = \{\tau > 0 : n_1^\varepsilon(t, \mathbf{x}) < \mathcal{K}_1, n_2^\varepsilon(t, \mathbf{x}) < \mathcal{K}_2 \ \forall (t, \mathbf{x}) \in [0, \tau] \times \Omega\}$ . If we denote  $\tilde{t} = \sup B^\varepsilon$ , there must exist  $\tilde{\mathbf{x}} \in \bar{\Omega}$  such that  $(n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}), n_2^\varepsilon(\tilde{t}, \tilde{\mathbf{x}})) \in \partial B^\varepsilon$ , hence one of the following equalities holds:

$$n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) = \mathcal{K}_1 \quad \text{or} \quad n_2^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) = \mathcal{K}_2.$$

If  $n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) = \mathcal{K}_1$ , by definitions of  $\tilde{t}$  and  $\tilde{\mathbf{x}}$  we have  $n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) \geq n_1^\varepsilon(\tilde{t}, \mathbf{x})$   $\forall \mathbf{x} \in \Omega$ , thus  $d_1 \Delta_{\mathbf{x}} n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) \leq 0$ . Moreover, by evaluating the chemical contributions in the first of (11) at  $(\tilde{t}, \tilde{\mathbf{x}})$  we get

$$-2 \left( n_1^\varepsilon - \gamma n_2^\varepsilon \right) (\tilde{t}, \tilde{\mathbf{x}}) \mathcal{P}(n_1^\varepsilon, n_2^\varepsilon) (\tilde{t}, \tilde{\mathbf{x}}) \leq -2 \left( \mathcal{K}_1 - \gamma \mathcal{K}_2 \right) \mathcal{P}(\mathcal{K}_1, n_2^\varepsilon(\tilde{t}, \tilde{\mathbf{x}})) = 0$$

(the inequality holds since  $n_2^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) \geq \mathcal{K}_2$  and  $\mathcal{P}(n_1^\varepsilon, n_2^\varepsilon) > 0$ , and the last term vanishes since  $\mathcal{K}_1 = \gamma \mathcal{K}_2$ ). Consequently, the equation (11) for  $n_1^\varepsilon$  implies that  $\partial_t n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) \leq -\varepsilon n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) < 0$ , hence  $n_1^\varepsilon(t, \tilde{\mathbf{x}}) > n_1^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) = \mathcal{K}_1$  for  $t < \tilde{t}$ , contradicting the definition of  $\tilde{t}$ . The case  $n_2^\varepsilon(\tilde{t}, \tilde{\mathbf{x}}) = \mathcal{K}_2$  may be treated in a similar way. Consequently, the set  $B^\varepsilon$  is unbounded, hence  $n_1^\varepsilon(t, \mathbf{x}) < \mathcal{K}_1$  and  $n_2^\varepsilon(t, \mathbf{x}) < \mathcal{K}_2$  for all  $\mathbf{x} \in \Omega$  and for all  $t \in [0, T]$ . This means that  $n_1(t, \mathbf{x}) < \mathcal{K}_1 e^{\varepsilon t}$  and  $n_2(t, \mathbf{x}) < \mathcal{K}_2 e^{\varepsilon t}$ , thus, passing to the limit  $\varepsilon \rightarrow 0$ , we have  $n_1(t, \mathbf{x}) \leq \mathcal{K}_1$  and  $n_2(t, \mathbf{x}) \leq \mathcal{K}_2$ .

The ‘‘minimum principle’’ for  $n_1$  and  $n_2$  may be recovered analogously, by studying the evolution of the auxiliary functions  $n_{1,\varepsilon}(t, \mathbf{x}) = n_1(t, \mathbf{x}) e^{\varepsilon t}$  and  $n_{2,\varepsilon}(t, \mathbf{x}) = n_2(t, \mathbf{x}) e^{\varepsilon t}$ .

Boundedness from above of  $n_1$  and  $n_2$  allows to prove existence and uniqueness of a strong solution on  $[0, T]$  to the system (1) (with Neumann boundary conditions) by resorting to a suitable fixed point argument.<sup>5</sup> By sticking together the solutions on  $[0, T]$  (for  $T \in \mathbb{R}^+$ ), we obtain a (unique) solution in  $C^2(\mathbb{R}^+ \times \bar{\Omega})$ .  $\square$

### 3. Entropy functional and convergence to equilibrium

Large time behavior of reaction-diffusion systems has attracted a considerable interest in scientific literature,<sup>6</sup> and we show here that the ‘‘entropy / entropy dissipation method’’, already successfully used in the frame of reversible chemistry,<sup>7</sup> may be extended to the present irreversible situation. A crucial feature of our system (1) is that it admits a unique collision equilibrium  $(n_1^*, n_2^*)$ , given explicitly in (4). Notice that  $\mathcal{Q}_2 \geq 0 \Leftrightarrow n_1 \geq \gamma n_2$ , and conversely for  $\mathcal{Q}_1$ . This suggests that a suitable entropy could be given by the quadratic functional

$$E(n_1, n_2) = \int_{\Omega} \left( \frac{1}{4} (n_1)^2 + \frac{\gamma}{2} (n_2)^2 \right) d\mathbf{x}. \quad (12)$$

**Lemma 3.1 (Relative entropy).** *A direct computation shows that the relative entropy with respect to the equilibrium state  $(n_1^*, n_2^*)$  is related to the  $L^2$ -distance from the equilibrium itself:*

$$E(n_1, n_2) - E(n_1^*, n_2^*) = \frac{1}{4} \|n_1 - n_1^*\|_2^2 + \frac{\gamma}{2} \|n_2 - n_2^*\|_2^2, \quad (13)$$

hence the entropy  $E(n_1, n_2)$  takes its minimum for  $(n_1, n_2) = (n_1^*, n_2^*)$ .

**Lemma 3.2 (Entropy dissipation).** *The entropy dissipation  $D(n_1, n_2) = -\partial_t E(n_1, n_2)$  fulfils the inequality*

$$D(n_1, n_2) \geq \mathcal{C} \left[ E(n_1, n_2) - E(n_1^*, n_2^*) \right], \quad (14)$$

with

$$\mathcal{C} = \min \left\{ \min \left\{ 1, \frac{2+\gamma}{6} \right\} \frac{d_1}{2P(\Omega)}, \min \left\{ \frac{1}{2}, \frac{2+\gamma}{6\gamma} \right\} \frac{d_2}{P(\Omega)}, \frac{2+\gamma}{6} d_3 \right\}, \quad (15)$$

where  $P(\Omega)$  is the Poincaré constant of  $\Omega$ , and  $d_3$  is a positive lower bound for  $\mathcal{P}(n_1, n_2)$ .

**Proof.** By direct computation, the entropy dissipation reads as

$$D(n_1, n_2) = \frac{d_1}{2} \int_{\Omega} |\nabla_{\mathbf{x}} n_1|^2 d\mathbf{x} + d_2 \gamma \int_{\Omega} |\nabla_{\mathbf{x}} n_2|^2 d\mathbf{x} + \int_{\Omega} (n_1 - \gamma n_2)^2 \mathcal{P}(n_1, n_2) d\mathbf{x}.$$

Thanks to Poincaré's inequality and to the lower and upper bounds for  $n_1$  and  $n_2$  given in Theorem 2.1, we have

$$D(n_1, n_2) \geq \frac{d_1}{2P(\Omega)} \|n_1 - \bar{n}_1\|_2^2 + \frac{d_2 \gamma}{P(\Omega)} \|n_2 - \bar{n}_2\|_2^2 + d_3 \|n_1 - \gamma n_2\|_2^2,$$

where  $\bar{n}_i$  denotes the total number of atoms/molecules of species  $i$  in the domain  $\Omega$ . Thanks to the inequality  $|n_i - n_i^*|^2 \leq 2 \left[ |n_i - \bar{n}_i|^2 + |\bar{n}_i - n_i^*|^2 \right]$ , in order to prove Lemma 3.2 it suffices to show that

$$\begin{aligned} I &:= \int_{\Omega} \left[ \frac{d_1}{2P(\Omega)} |n_1 - \bar{n}_1|^2 + \frac{d_2 \gamma}{P(\Omega)} |n_2 - \bar{n}_2|^2 + d_3 |n_1 - \gamma n_2|^2 \right] d\mathbf{x} \\ &\geq \mathcal{C} \int_{\Omega} \left[ \frac{1}{2} |n_1 - \bar{n}_1|^2 + \gamma |n_2 - \bar{n}_2|^2 + \frac{1}{2} |\bar{n}_1 - n_1^*|^2 + \gamma |\bar{n}_2 - n_2^*|^2 \right] d\mathbf{x}. \end{aligned}$$

It obviously holds

$$\frac{1}{2} I \geq \mathcal{C}_1 \int_{\Omega} \left[ \frac{1}{2} |n_1 - \bar{n}_1|^2 + \gamma |n_2 - \bar{n}_2|^2 \right] d\mathbf{x} \quad \text{with} \quad \mathcal{C}_1 = \frac{\min\{d_1, d_2\}}{2P(\Omega)}.$$

It remains to prove that

$$\frac{1}{2} I \geq \mathcal{C}_2 \left[ \frac{1}{2} |\bar{n}_1 - n_1^*|^2 + \gamma |\bar{n}_2 - n_2^*|^2 \right], \quad (16)$$

and to take  $\mathcal{C} = \min\{\mathcal{C}_1, \mathcal{C}_2\}$ . It can be easily checked that  $|\bar{n}_1 - n_1|^2 + |n_1 - \gamma n_2|^2 + \gamma^2 |n_2 - \bar{n}_2|^2 \geq \frac{1}{3} |\bar{n}_1 - \gamma \bar{n}_2|^2$ ; moreover, bearing in mind the expressions of  $(n_1^*, n_2^*)$  together with the fact that  $n_1^* + 2n_2^* = \bar{n}_1 + 2\bar{n}_2 = \bar{n}^0$ , we get

$$\bar{n}_1 - \gamma \bar{n}_2 = \frac{2+\gamma}{2} (\bar{n}_1 - n_1^*) = -(2+\gamma) (\bar{n}_2 - n_2^*).$$

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Therefore (16) becomes

$$|\bar{n}_1 - n_1^*|^2 \geq \frac{6}{2 + \gamma} \frac{1}{\min \left\{ \frac{d_1}{2P(\Omega)}, \frac{d_2}{\gamma P(\Omega)}, d_3 \right\}} \mathcal{C}_2 |\bar{n}_1 - n_1^*|^2,$$

that is true once we put

$$\mathcal{C}_2 = \frac{2 + \gamma}{6} \min \left\{ \frac{d_1}{2P(\Omega)}, \frac{d_2}{\gamma P(\Omega)}, d_3 \right\}.$$

Taking  $\mathcal{C} = \min\{\mathcal{C}_1, \mathcal{C}_2\}$  concludes the proof of Lemma 3.2.  $\square$

**Theorem 3.1 (Exponential convergence to equilibrium).**

Let  $d_1, d_2 > 0$ , and  $\Omega$  be a bounded regular ( $C^2$ ) open set of  $\mathbb{R}^N$ . Let  $(n_1(t, \mathbf{x}), n_2(t, \mathbf{x}))$  be a strong solution (that is, in  $C^2(\mathbb{R}^+ \times \bar{\Omega})$ ) to system (1) with homogeneous Neumann boundary conditions and with initial conditions (5). Then, this solution satisfies the following property of exponential decay towards equilibrium:

$$\frac{1}{4} \|n_1 - n_1^*\|_2^2 + \frac{\gamma}{2} \|n_2 - n_2^*\|_2^2 \leq \left( E(n_1^0, n_2^0) - E(n_1^*, n_2^*) \right) e^{-\mathcal{C}t}, \quad (17)$$

where  $\mathcal{C}$  is given explicitly in (15).

**Proof.** Thanks to Lemma 3.2 we have

$$\partial_t \left[ E(n_1, n_2) - E(n_1^*, n_2^*) \right] \leq -\mathcal{C} \left[ E(n_1, n_2) - E(n_1^*, n_2^*) \right],$$

thus, by applying Gronwall's lemma and bearing in mind the explicit relative entropy (12), we get the sought inequality (17).  $\square$

Unfortunately, in the case of chemically reacting background, the equilibrium state (still unique) is not available in explicit form.<sup>3</sup> However, the strategy presented in this paper, with some additional technicality, allows again explicit estimates on the large time behavior of the relevant solutions.

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