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Abstract

For the recombination drift-diffusion equations that describe the evolution of charge carriers in scintillating crystals, we obtain the estimates for the energy and solution asymptotic decay. The present results extend those obtained by Fellner and Kniely (2018) for semiconductors with two charge carriers and Shockley-Hall recombination, to the case of $k > 2$ charge carriers and general polynomial recombination term.

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1. Introduction

The generation, recombination, and evolution of charge carriers in scintillating crystals (crystals that convert ionizing radiations into visible light) can be described by the recombination-drift-diffusion (RDD) equation [1], [2]:

$$\begin{aligned} \operatorname{div} MN\nabla\Phi - r(n) = \dot{n}\,, &\qquad \text{in } \Omega\times[0\,,\tau) \\ MN\nabla\Phi\mathbf{m} = 0\,, &\qquad \text{on } \partial\Omega\times[0\,,\tau)\,, \end{aligned} \tag{1}$$

coupled with the Poisson equation

$$\begin{aligned} \epsilon\Delta\varphi = zq\cdot n\,, &\qquad \text{in } \Omega\times[0\,,\tau) \\ [\![\nabla\varphi]\!]\cdot\mathbf{m} = 0\,, &\qquad \text{on } \partial\Omega\times[0\,,\tau)\,. \end{aligned} \tag{2}$$

In (1) and (2) n is the $k-$dimensional array of charge carriers, $N = \operatorname{diag}\{n_1\,,\ldots\,,n_k\}$, $q \in \mathbb{Z}^k$ is the charge vector, M the $k\times k$ mobility matrix, φ the electric potential, z the elementary charge, ϵ the crystal permittivity, $\Omega\subset\mathbb{R}^3$ and $[\![\cdot]\!]$ denotes the jump across the smooth boundary $\partial\Omega$ (outer trace minus the inner trace) whose outward unit normal is $\mathbf{m}$; moreover the quasi-Fermi potential, or scintillation potential, Φ is defined as:

$$\Phi = zq\varphi - \theta\mathfrak{H}'(n)\,, \tag{3}$$

where θ is the absolute temperature and $\mathfrak{H}(n)$ is the entropy, $(\cdot)'$ being the Fréchet derivative. Existence and uniqueness results for the global and weak-strong renormalized solutions of RDD equations, with or without coupling to the Poisson equation, were given in [3]-[8], whereas the asymptotic behavior of solution was studied (for semiconductors and electrochemical drift-diffusion) *e.g.* in [9]-[14].

One of the most important parameters which characterize scintillators is the *decay time* defined as the time for which an experimental measure $\mu(n)$ of charge carriers reduces to $1/e$ of the initial data; from typical experimental data we have that:

$$\mu(n(t)) = A_f\exp(-\frac{t}{\tau_f}) + A_s\exp(-\frac{t}{\tau_s})\,, \tag{4}$$

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where τ_f and τ_s are respectively the *fast* and *slow* decay times.

The decay time is strictly correlated with the asymptotic decay for the solutions of the evolutionary boundary value problem (1), (2) and it is very important, from an applicative point of view, to obtain decay time estimates which depend on the material constitutive parameters that characterize the model.

Such a problem was addressed and successfully solved in [15] (*vid. also* [16], [17]) for semiconductors: there, by using entropic methods and Csiszár-Kullback-Leibler type inequalities, an estimate of the asymptotic decay of the solution which depends explicitly on the material parameters was given. The most important differences between the semiconductors RDD equations and those for scintillators are in the number k of the charge carrier n and in the structure of the recombination term $r(n)$: in general $k > 2$ with at least electron, holes and excitons (loosely bounded electron-hole pairs which travel together) represented in n; moreover, the recombination term is a general cubic polynomial in the components of n which reduces to a quadratic one if we disregard the Auger effect. In the semiconductor model instead $k = 2$ (electrons n_1 and holes n_2), whereas the recombination term has the Shockley-Hall structure $r(n) \approx (n_1 n_2 - 1)$.

In two papers [18], [19] the model of [15] was adapted to scintillators for the case $k = 2$ with n_1 representing both electrons and holes and n_2 representing excitons; in particular in [18] with the available material parameters for four scintillators, we found that the asymptotic estimates for the decay time were very good with a difference of about 3% between the estimates and the experimentally measured decay times.

The results obtained in [18] therefore induced the natural question: can the results of [15] be extended to $k > 2$ and to recombination terms more complex than the Shockley-Hall? In this paper, we take this issue to arrive at a positive answer to the question. To get this result we follow stepwise the procedure given in [15], by adding those technical lemmas, bounds ad additional hypotheses which are necessary to extend their results to the present case. The extension is mostly straightforward, except for some points which requested a little more effort: it is important to remark that no new ideas are present in our work, whose only point of originality is to go a step further toward generalization.

This paper is organized as follows: in §.2 we describe the evolution problem and show that it has a gradient-flow structure: then we define the equilibrium solutions and introduce the notion of relative free energy. We finish the section by putting the equations in an adimensional form which depends on a unique material parameter. In §.3 we extend the two main results of [15]: the energy-dissipation production inequality (Theorem 1) and the convergence to equilibrium (Theorem 2). To achieve these results we needed some new bounds on the equilibrium solutions and, more important, to assume some hypotheses on the recombination processes.

2. The evolution equations for scintillators

2.1. Evolution equations and gradient flows

We represent the charge carrier densities within the scintillation volume Ω with the $k-$dimensional array

$$\Omega \times [0\,,\tau) \ni (x\,,t) \mapsto n(x\,,t) \equiv [n_1(x\,,t)\,,n_2(x\,,t)\,,\dots\,,n_k(x\,,t)]\,, \tag{5}$$

whose associated electric potential $\varphi = \varphi(n)$ is the solution of the Neumann problem

$$\begin{aligned} -\epsilon\Delta\varphi = zq\cdot n\,, &\quad \text{in } \Omega\times[0\,,T)\,, \\ [\![\nabla\varphi]\!]\cdot\mathbf{m} = 0\,, &\quad \text{on } \partial\Omega\times[0\,,T)\,, \end{aligned} \tag{6}$$

here $q \equiv [q_1\,,q_2\,,\dots\,,q_k]$ with $q_j \in \mathbb{Z}$ is the charge vector. We remark that for $n \in L^2(\Omega)$ there exists an unique solution $\varphi \in H^1(\Omega)$ for the Poisson equation (6), provided $\overline{\varphi} = 0$.

The evolution equation for the charge carriers is:

$$\begin{aligned} \operatorname{div}(D[\nabla n] + MNq\otimes\nabla\varphi) - r(n) = \dot{n}\,, &\quad \text{in } \Omega\times[0\,,T)\,, \\ D[\nabla n]\mathbf{m} + MNq(\nabla\varphi^+\cdot\mathbf{m}) = 0\,, &\quad \text{on } \partial\Omega\times[0\,,T)\,, \end{aligned} \tag{7}$$

where M the $k\times k$ constant and positive-semidefinite mobility matrix, which is related to the $k\times k$ diffusivity matrix D by the Einstein-Smoluchowsky relation:

$$D = \frac{\theta k_B}{z}M\,, \tag{8}$$

with θ the absolute temperature, k_B the Boltzmann constant and where the $k \times k$ matrix N is

$$N \equiv \text{diag}\{n_1\,, n_2\,, \dots\,, n_k\}\,; \tag{9}$$

we remark that the present theory is isothermal and then θ is a constant (uniform and time-independent) temperature.

For the equation (7) a gradient flow formulation can be given; here we recall that a gradient flow is a triplet $\{\mathcal{Z}\,, \mathfrak{F}\,, \mathcal{D}\}$ where $\mathcal{Z}$ is a state space, $\mathfrak{F}$ is a driving functional and $\mathcal{D}$ is a dissipation mechanism. In our case the state space is:

$$\mathcal{Z} = L^2_+(\Omega)\,, \tag{10}$$

whereas the driving functional is the Gibbs self free-energy:

$$\mathfrak{F}(n) = \mathfrak{E}(n) - \theta\mathfrak{H}(n)\,; \tag{11}$$

where $\mathfrak{E}(n)$ is the electrostatic self-energy

$$\mathfrak{E}(n) = \frac{1}{2}\int_\Omega \epsilon\|\nabla\varphi(n)\|^2\,, \tag{12}$$

and where the entropic part is given by the Boltzmann-Gibbs entropy

$$\mathfrak{H}(n) = -k_B\int_\Omega \sum_{i=1}^{k} n_i(\log\frac{n_i}{c_i} - 1)\,, \tag{13}$$

with k_B the Boltzmann constant and $c \equiv [c_1\,, c_2\,, \dots\,, c_k]$ an array of normalizing constants. The dissipation mechanism is represented by an operator $\mathcal{K}(n)$ in such a way that the gradient flow is given by

$$\dot{n} = -\mathcal{K}(n)\mathfrak{F}'\,, \tag{14}$$

such that:

$$\mathcal{K}(n)\mathfrak{F}' = \text{div}S\,[\nabla\mathfrak{F}'] - H\mathfrak{F}'\,; \tag{15}$$

here S and H are two positive semi-definite $k \times k$ matrices. The dissipation is provided by the dual (or conjugate) dissipation functional:

$$\Psi^*(n\,, \xi) = \frac{1}{2}\mathcal{K}(n)\xi \cdot \xi = \frac{1}{2}(S\,[\nabla\xi] \cdot \nabla\xi + H\xi \cdot \xi) \geq 0\,. \tag{16}$$

Since

$$\mathfrak{F}' = [zq_1\varphi + \theta k_B \log\frac{n_1}{c_1}\,, zq_2\varphi + \theta k_B \log\frac{n_2}{c_2}\,, \dots\,, zq_k\varphi + \theta k_B \log\frac{n_k}{c_k}] \equiv \Phi \in \mathbb{R}^k\,, \tag{17}$$

with the quasi-Fermi potential Φ representing the *scintillation potential* and provided we set:

$$S = z^{-1}MN\,, \quad H\Phi = r(n)\,, \tag{18}$$

then from (14) and (15) we recover (7); clearly, we restrict our analysis to recombination terms which admit the representation $(18)_2$ and for which, as we shall see in the sequel, a mass-action type kinetic holds.

From the definition (17) we can obtain the components of n in terms of the electric potential φ and of the components Φ_i of the quasi-Fermi scintillation potential (17):

$$n_i = c_i \exp\Big(\frac{\Phi_i - zq_i\varphi}{\theta k_B}\Big)\,, \quad i = 1\,, 2\,, \dots\,, k\,. \tag{19}$$

2.2. Equilibrium solutions

We say that a solution $(n_\infty\,,\varphi_\infty)$ is an equilibrium (stationary) solution when it solves (14) with $\dot{n} = 0$: then by (15) we have:

$$\begin{aligned} \mathrm{div} S\,[\nabla\Phi_\infty] - H\Phi_\infty = 0\,, &\quad \text{in } \Omega\,. \\ S\,[\nabla\Phi_\infty]\mathbf{m} = 0\,, &\quad \text{on } \partial\Omega\,. \end{aligned} \tag{20}$$

together with the Poisson equation (6) for $(n_\infty\,,\varphi_\infty)$ under the same uniqueness conditions.

Since the boundary value problem (20) admits the solution $\Phi_\infty = 0$, then from (19) we arrive at the relation between the components of n_∞ and the stationary electric potential φ_∞:

$$n_i^\infty = c_i \exp(-\frac{z q_i \varphi_\infty}{\theta k_B})\,, \quad i = 1\,,2\,,\ldots\,,k\,, \tag{21}$$

which in turn solves the semilinear Poisson-Boltzmann equation

$$-\epsilon\Delta\varphi_\infty = z\sum_{i=1}^{k} q_i c_i \exp(-\frac{z q_i \varphi_\infty}{\theta k_B})\,, \tag{22}$$

with the Neumann boundary conditions $(6)_2$ for φ_∞.

2.3. Relative free-energy and Power

Let the relative Gibbs self free-energy be defined as

$$\mathfrak{F}(u \mid v) = \mathfrak{F}(u) - \mathfrak{F}(v) - \mathfrak{F}'(v)(u - v)\,, \tag{23}$$

a definition that extends the notion of relative entropy (or Kullback-Leibler divergence) as the measurement of the distance of two probability distributions, where v is the true distribution and u is the approximating distribution we have modeled, and whose properties are:

$$\mathfrak{F}(u \mid v) = \begin{cases} > 0\,, & u \neq v\,, \\ = 0\,, & u = v\,; \end{cases} \tag{24}$$

we notice that in the general case $\mathfrak{F}(u \mid v) \neq \mathfrak{F}(v \mid u)$: however $\mathfrak{F}(u \mid v)$ and $\mathfrak{F}(v \mid u)$ may also coincide for specific $u \neq v$.

From (11) then we get:

$$\mathfrak{F}(n \mid n_\infty) = \frac{1}{2}\int_{\mathbb{R}^3} \epsilon\|\nabla(\varphi - \varphi_\infty)\|^2 + \theta k_B \int_\Omega \sum_{i=1}^{k} n_i \log\frac{n_i}{n_i^\infty} - (n_i - n_i^\infty)\,. \tag{25}$$

We define the power associated with the relative Gibbs free-energy (25) (that we shall also call dissipation or, with abuse of language, entropy production):

$$\mathfrak{D}(n) = -\frac{\mathrm{d}}{\mathrm{d}t}\mathfrak{F}(n \mid n_\infty)\,, \tag{26}$$

which by (6) written for $\varphi - \varphi_\infty$, (14), (15), (16) and since $\Phi_\infty = 0$, leads to:

$$\mathfrak{D}(n) = -\int_\Omega (\Phi - \Phi_\infty)\cdot\dot{n} = -\int_\Omega \Phi\cdot\dot{n} = 2\Psi^*(n\,,\Phi) \geq 0\,. \tag{27}$$

2.4. Adimensional equations

We choose a characteristic length and time pair (L, T) to put the whole problem in a dimensionless formulation on $\Omega^* \times [0, 1)$ with $\text{meas}(\Omega^*) = 1$; then in terms of the adimensional variables

$$u = L^3 n, \quad \psi = \frac{\epsilon L}{z} \varphi, \tag{28}$$

equations $(6)_1$ and $(7)_1$ now read respectively[1]

$$-\Delta\psi = q \cdot u, \quad \text{on } \Omega^* \times [0, 1), \tag{29}$$

and

$$\text{div} M^*(d\nabla u + mUq \otimes \nabla\psi) - hr^*(u) = \dot{u}, \quad \text{on } \Omega^* \times [0, 1), \tag{30}$$

where $U(u) = \text{diag}\{u_1, u_2, \dots u_k\}$, $M^* = \mu^{-1} M$ with $\mu = \sup\{\mu_1, \mu_2, \dots, \mu_k\}$, being μ_i the eigenvalues of M, and where the dimensionless quantities d, m and h are defined by

$$d = \frac{\theta k_B T}{z L^2} \mu, \quad m = \frac{zT}{\epsilon L^3} \mu, \quad h = \rho T L^3, \tag{31}$$

with $r^* = r/h$ and $\rho = 1 + \|r(0)\|_{L^\infty(\Omega)}$.

We choose $T = \rho^{-1}$ as characteristic time and L such that $h = 1$ and $d = m$, in such a way that the adimensional evolution equation depends only on one parameter:

$$m \, \text{div} M^*(\nabla u + Uq \otimes \nabla\psi) - r^*(u) = \dot{u}, \quad \text{on } \Omega^* \times [0, 1). \tag{32}$$

We shall also define the adimensional driving functional $\mathcal{F}(u, \psi)$:

$$\mathcal{F}(u) = \mathfrak{F} \frac{\epsilon L}{z^2} = \frac{1}{2} \int_{\Omega^*} \|\nabla\psi\|^2 + \int_{\Omega^*} \sum_{i=1}^{k} u_i (\log \frac{u_i}{w_i} - 1), \quad w_i = L^3 c_i, \tag{33}$$

and the relative free-energy

$$\mathcal{F}(u \mid u_\infty) = \frac{1}{2} \int_{\Omega^*} \|\nabla(\psi - \psi_\infty)\|^2 + \int_{\Omega^*} \sum_{i=1}^{k} u_i \log \frac{u_i}{u_i^\infty} - (u_i - u_i^\infty). \tag{34}$$

Likewise, we define the dimensionless components Φ_i^* of the quasi-Fermi scintillation potential Φ^*:

$$\Phi_i^* = \Phi_i \frac{\epsilon L}{z^2} = q_i \psi + \log \frac{u_i}{w_i}, \quad i = 1, 2, \dots, k, \tag{35}$$

from which we recover the dimensionless version of (19):

$$u_i = w_i \exp(\Phi_i^* - q_i \psi), \quad i = 1, 2, \dots, k; \tag{36}$$

then, from (36) and the equilibrium condition $\Phi^* = 0$ we have the dimensionless version of (21)

$$u_{i,\infty} = w_i \exp(-q_i \psi_\infty), \quad i = 1, 2, \dots, k. \tag{37}$$

The dimensionless representation $\mathcal{D}$ of the power (27) is given by

$$\mathcal{D} = \int_{\Omega^*} m M^* U \nabla\Phi^* \cdot \nabla\Phi^* + H^* \Phi^* \cdot \Phi^*, \tag{38}$$

[1] Since there will be no confusion in the sequel, we shall use the same symbols for the operators with respect to both the variables (x, t) and $(\hat{x} = x/L, \hat{t} = t/T)$.

where for the recombination term we choose the explicit representation in terms of the $h = 1, 2, \ldots s$ reversible recombination mechanisms with velocities k_h

$$\alpha^h \xrightleftharpoons{k_h} \beta^h\,, \quad h = 1, 2, \ldots s\,, \tag{39}$$

which leads to

$$H^*\Phi^* \cdot \Phi^* = \sum_{h=1}^{s} k_h^* \lambda\Big(\frac{u^{\alpha^h}}{w^{\alpha^h}}, \frac{u^{\beta^h}}{w^{\beta^h}}\Big)\Big(\Phi^* \cdot (\alpha^h - \beta^h)\Big)^2 = \sum_{h=1}^{s} k_h^* \Big(\frac{u^{\alpha^h}}{w^{\alpha^h}} - \frac{u^{\beta^h}}{w^{\beta^h}}\Big)\Big(\log \frac{u^{\alpha^h}}{w^{\alpha^h}} - \log \frac{u^{\beta^h}}{w^{\beta^h}}\Big)\,, \tag{40}$$

where $k_h^* = \rho^{-1} k_h$, the interpolation function $\lambda(x, y)$ is the logarithmic mean

$$\lambda(x, y) = \begin{cases} \dfrac{x - y}{\log x - \log y}\,, & x \neq y\,, \\ x\,, & x = y\,, \end{cases} \tag{41}$$

and to the polynomial of order m representation for the recombination term:

$$r^*(u) = H^*\Phi^* = \sum_{h=1}^{s} k_h^* \Big(\frac{u^{\alpha^h}}{w^{\alpha^h}} - \frac{u^{\beta^h}}{w^{\beta^h}}\Big)(\alpha^h - \beta^h)\,; \tag{42}$$

we remark that the physics of recombination in scintillators is adequately described by a set of recombination mechanisms which from (42) lead to k polynomials of order $m = 3$:

$$r_i^*(u) = a_i + b_{ij}u_j + c_{ijh}u_j u_h + d_{ijhl}u_j u_h u_l\,, \quad i, j, h, l = 1, 2, \ldots, k\,. \tag{43}$$

2.5. Bounds

We establish here some bounds we shall make use of in the sequel.

- Let $K_\infty = \|q\psi_\infty\|_{L^\infty(\Omega^*)}$: then

  $$u_{i,\infty} = w_i \exp(-q_i\psi_\infty) \leq w_i \exp K_\infty\,. \tag{44}$$

  To obtain bounds on the components w_i we consider first the case $k = 2$ and assume that $r_1^*(u) = 0$ is a polynomial of order m and $r_2^*(u) = 0$ is a polynomial of order n. We assume $m = n = 2$ to obtain from (43):

  $$r_\alpha^*(u) = a_\alpha + b_{\alpha\beta}u_\beta + c_{\alpha\beta\gamma}u_\beta u_\gamma\,, \quad \alpha, \beta, \gamma = 1, 2\,. \tag{45}$$

  We eliminate u_1 from (45) to obtain the resultant $\det S = 0$, where the $(m+n)\times(m+n) = 4\times 4$ matrix, Sylvester matrix S is given by:

  $$S \equiv \begin{bmatrix} c_{122} & b_{11} + c_{112}u_2 & a_1 + b_{12}u_2 + c_{122}u_2^2 & 0 \\ 0 & c_{122} & b_{11} + c_{112}u_2 & a_1 + b_{12}u_2 + c_{122}u_2^2 \\ c_{222} & b_{21} + c_{212}u_2 & a_2 + b_{22}u_2 + c_{222}u_2^2 & 0 \\ 0 & c_{222} & b_{21} + c_{212}u_2 & a_2 + b_{22}u_2 + c_{222}u_2^2 \end{bmatrix}; \tag{46}$$

  then the resultant of (45) is a polynomial of degree $mn = m^2 = 4$ in u_2:

  $$p_o u_2^4 + p_1 u_2^3 + p_2 u_2^2 + p_3 u_2 + p_4 = 0\,, \quad p_j = p_j(a_\alpha, b_{\alpha\beta}, c_{\alpha\beta\gamma})\,, \quad j = 0, 1, 2, 3, 4\,. \tag{47}$$

  The Cauchy bound for the roots of (47) is

  $$u_2 \leq \max\left\{\left|\frac{p_o}{p_4}\right|, \left|\frac{p_1}{p_4}\right|, \left|\frac{p_2}{p_4}\right|, \left|\frac{p_3}{p_4}\right|\right\} = W_2(a_\alpha, b_{\alpha\beta}, c_{\alpha\beta\gamma})\,, \tag{48}$$

which by (37) and the definition of K_∞ leads to:

$$w_2 \leq W_2 \exp K_\infty \,. \tag{49}$$

When we eliminate u_2 from (45) we obtain

$$w_1 \leq W_1 \exp K_\infty \,, \tag{50}$$

and hence we arrive at:

$$w_\alpha \leq W \exp K_\infty \,, \quad \alpha = 1, 2 \,, \quad W = \sup\{W_1 \,, W_2\} \,. \tag{51}$$

The whole procedure can be repeated for successive steps when $k > 2$ and for generic, not necessarily equal, m and n to arrive at

$$w_i \leq W \exp K_\infty \,, \quad i = 1, 2 \ldots, k \,, \quad W = \sup\{W_1 \,, W_2 \,, \ldots \,, W_k\} \,, \tag{52}$$

with W depending explicitly on the coefficients of the polynomial $r^*(u) = 0$; then, as a consequence of both (44) and (52), we obtain the bound:

$$u_{i,\infty} \leq W \exp(2K_\infty) \,. \tag{53}$$

- Let us assume that $M^* = \mathrm{diag}\{\mu_1^* \,, \mu_2^* \,, \ldots \mu_k^*\}$: if we denote

$$\mu^* = \inf\{\mu_1^* \,, \mu_2^* \,, \ldots \mu_k^*\} \,, \tag{54}$$

then

$$M^* U \nabla\Phi^* \cdot \nabla\Phi^* \geq \mu^* U \nabla\Phi^* \cdot \nabla\Phi^* \,; \tag{55}$$

let $U_\infty = \mathrm{diag}\{u_{1,\infty} \,, u_{2,\infty} \,, \ldots \,, u_{k.\infty}\}$, then we can write

$$U_\infty U_\infty^{-1} U = U_\infty U^* \,, \quad U^* = U_\infty^{-1} U = \mathrm{diag}\{\frac{u_1}{u_{1,\infty}} \,, \frac{u_2}{u_{2,\infty}} \,, \ldots \,, \frac{u_k}{u_{k,\infty}}\} \,, \tag{56}$$

to arrive at, by (56) and (55)

$$M^* U \nabla\Phi^* \cdot \nabla\Phi^* \geq \mu^* U_\infty U^* \nabla\Phi^* \cdot \nabla\Phi^* \,. \tag{57}$$

- Let

$$k_F = \inf\{k_1^* \,, k_2^* \,, \ldots k_s^*\} \,, \tag{58}$$

then

$$H^* \Phi^* \cdot \Phi^* \geq k_F \sum_{h=1}^{s} (\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \frac{u^{\beta^h}}{u_\infty^{\beta^h}}) \Big(\log \frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \log \frac{u^{\beta^h}}{u_\infty^{\beta^h}} \Big) \,. \tag{59}$$

- As a consequence of (57) and (59) then we can write the following bound for the power (38):

$$\begin{aligned} \mathcal{D} \quad &\geq \quad \int_{\Omega^*} \Big(m\mu^* U_\infty U^* \nabla\Phi^* \cdot \nabla\Phi^* + k_F \sum_{h=1}^{s} (\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \frac{u^{\beta^h}}{u_\infty^{\beta^h}}) \Big(\log \frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \log \frac{u^{\beta^h}}{u_\infty^{\beta^h}} \Big) \Big) \\ &\geq \quad c \int_{\Omega^*} \Big(\frac{1}{2} U^* \nabla\Phi^* \cdot \nabla\Phi^* + \frac{1}{2} \sum_{h=1}^{s} (\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \frac{u^{\beta^h}}{u_\infty^{\beta^h}}) \Big(\log \frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \log \frac{u^{\beta^h}}{u_\infty^{\beta^h}} \Big) \Big) , \end{aligned} \tag{60}$$

where

$$c = \inf \{ \, 2m\mu^* W \exp(2K_\infty) \,, 2k_F \, \} \,. \tag{61}$$

3. Convergence to equilibrium

3.1. Energy-Dissipation production inequality

We are going to obtain an inequality between the Gibbs self free-energy $\mathcal{F}$ and the dissipation $\mathcal{D}$; the proof is given by the means of two propositions which need a preliminary Lemma.

Lemma 1. *Let $a_j \geq 0$, $j = 1, 2, \ldots, k$, then*

$$(\sum_{i=1}^{k} a_k)^2 \leq k \sum_{i=1}^{k} a_k^2 \,. \tag{62}$$

The proof follows directly from the Jensen inequality for convex functions (for this and the other inequalities we shall use in the sequel *vid.* [20]):

$$f\Big(\frac{\Sigma_{i=1}^k a_i}{k}\Big) \leq \frac{\Sigma_{i=1}^k f(a_i)}{k} \,, \tag{63}$$

with $f(\xi) = \xi^2$.

Proposition 1. *There exists an explicit computable constant $K_1 > 0$ such that*

$$\mathcal{F}(n \mid n_\infty) \leq K_1 \int_{\Omega^*} \sum_{i=1}^{k} \frac{(u_i - u_i^\infty)^2}{u_i^\infty} \,, \tag{64}$$

for all $u \in L^2(\Omega^*)$ where $\psi \in H^1(\Omega^*)$ is the unique solution of (29) and with

$$K_1 = 1 + kq^2 \frac{\mathcal{L}(\Omega^*)}{2} W \exp(2K_\infty) \,. \tag{65}$$

The proof is in two steps: the first step is that, since $\log x \leq x - 1$, for $x > 0$, then:

$$\int_{\Omega^*} \sum_{i=1}^{k} u_i \log \frac{u_i}{u_i^\infty} - (u_i - u_i^\infty) \leq \int_{\Omega^*} \sum_{i=1}^{k} u_i (\frac{u_i}{u_i^\infty} - 1) - (u_i - u_i^\infty) = \int_{\Omega^*} \sum_{i=1}^{k} \frac{(u_i - u_i^\infty)^2}{u_i^\infty} \,. \tag{66}$$

For the second step, we consider

$$\int_{\Omega^*} \|\nabla(\psi - \psi_\infty)\|^2 = -\int_{\Omega^*} \Delta(\psi - \psi_\infty) \cdot (\psi - \psi_\infty) = \int_{\Omega^*} (\psi - \psi_\infty) \sum_{i=1}^{k} q_i (u_i - u_i^\infty) \leq \|(\psi - \psi_\infty) \sum_{i=1}^{k} q_i (u_i - u_i^\infty)\|_{L^1} \,, \tag{67}$$

as a consequence of (29) for ψ, ψ_∞ and u, u_∞, and the positivity of the first term. Then by the Hölder inequality and Young *gain-loss* inequality for a constant $\gamma > 0$:

$$\|(\psi - \psi_\infty) \sum_{i=1}^{k} q_i (u_i - u_i^\infty)\|_{L^1} \leq \|\psi - \psi_\infty\|_{L^2} \|\sum_{i=1}^{k} q_i (u_i - u_i^\infty)\|_{L^2} \,, \tag{H}$$

$$\|\psi - \psi_\infty\|_{L^2} \|\sum_{i=1}^{k} q_i (u_i - u_i^\infty)\|_{L^2} \leq \frac{1}{2} (\frac{1}{\gamma} \|\sum_{i=1}^{k} q_i (u_i - u_i^\infty)\|_{L^2}^2 + \gamma \|\psi - \psi_\infty\|_{L^2}^2) \,; \tag{Y}$$

by the Poincaré inequality with $\mathcal{L}(\Omega^*) = \gamma^{-1}$ the Poincaré constant, then we get from (67), (H) and (Y):

$$\int_{\Omega^*} \|\nabla(\psi - \psi_\infty)\|^2 \leq \frac{1}{2} \int_{\Omega^*} \|\nabla(\psi - \psi_\infty)\|^2 + \frac{\mathcal{L}(\Omega^*)}{2} \|\sum_{i=1}^{k} q_i (u_i - u_i^\infty)\|_{L^2}^2 \,. \tag{P}$$

Now, by the Lemma 1 and upon the definition of

$$q = \max_i |q_i| \,, \quad \text{with } \min_i |q_i| \geq 0 \,, \tag{68}$$

then we have

$$\frac{1}{2}\int_{\Omega^*}\|\nabla(\psi-\psi_\infty)\|^2 \le \frac{\mathcal{L}(\Omega^*)}{2}kq^2\int_{\Omega^*}\sum_{i=1}^{k}(u_i-u_i^\infty)^2 = \frac{\mathcal{L}(\Omega^*)}{2}kq^2\int_{\Omega^*}\sum_{i=1}^{k}u_i^\infty\frac{(u_i-u_i^\infty)^2}{u_i^\infty}\,; \tag{69}$$

then, by the estimate (53), we get

$$\frac{1}{2}\int_{\Omega^*}\|\nabla(\psi-\psi_\infty)\|^2 \le \frac{\mathcal{L}(\Omega^*)}{2}kq^2 W\exp(2K_\infty)\int_{\Omega^*}\sum_{i=1}^{k}\frac{(u_i-u_i^\infty)^2}{u_i^\infty}\,, \tag{70}$$

and by (66) and (70) we obtain (64) and (65).

Proposition 2. *There exists an explicit computable constant $K_2>0$ such that*

$$\int_{\Omega^*}\sum_{i=1}^{k}\frac{(u_i-u_i^\infty)^2}{u_i^\infty}\le K_2\mathcal{D}\,, \tag{71}$$

for all $u\in L^2(\Omega^*)$ where $\psi\in H^1(\Omega^*)$ is the unique solution of (29) and with

$$K_2=\frac{k}{\|q\|^2}\sup\{\frac{W\exp(2K_\infty)}{2m\mu^*}\,,\frac{1}{2k_F}\}\,. \tag{72}$$

To prove this, we consider the first term of (60) which, since $\nabla\Phi^*_\infty=0$, can be rewritten as

$$\int_{\Omega^*}U^*\nabla(\Phi^*-\Phi^*_\infty)\cdot\nabla(\Phi^*-\Phi^*_\infty)=\int_{\Omega^*}U^*\nabla(q(\psi-\psi_\infty)+\log\frac{u}{u_\infty})\cdot\nabla(q(\psi-\psi_\infty)+\log\frac{u}{u_\infty})\,, \tag{73}$$

and which, when it is written in components, reads:

$$\begin{aligned}
&\int_{\Omega^*}\sum_{i=1}^{k}\frac{u_i}{u_{i,\infty}}\|\nabla(q_i(\psi-\psi_\infty)+\log\frac{u_i}{u_{i,\infty}})\|^2\\
=\;&\int_{\Omega^*}\sum_{i=1}^{k}\frac{u_i}{u_{i,\infty}}\Big(\|q_i\nabla(\psi-\psi_\infty)\|^2+\|\nabla(\log\frac{u_i}{u_{i,\infty}})\|^2+2q_i\nabla(\psi-\psi_\infty)\cdot\nabla(\log\frac{u_i}{u_{i,\infty}})\Big)\\
\ge\;&2\int_{\Omega^*}\sum_{i=1}^{k}\frac{u_i}{u_{i,\infty}}q_i\nabla(\psi-\psi_\infty)\cdot\nabla(\log\frac{u_i}{u_{i,\infty}})=2\int_{\Omega^*}\sum_{i=1}^{k}q_i\nabla(\psi-\psi_\infty)\cdot\nabla(\frac{u_i}{u_{i,\infty}}-1)\,;
\end{aligned} \tag{74}$$

by the divergence theorem and (29) with the Neumann boundary conditions, from the last term we get

$$\begin{aligned}
&2\int_{\Omega^*}\sum_{i=1}^{k}q_i\nabla(\psi-\psi_\infty)\cdot\nabla(\frac{u_i}{u_{i,\infty}}-1)=2\int_{\Omega^*}\sum_{i,j=1}^{k}q_iq_j\frac{(u_i-u_{i,\infty})(u_j-u_{j,\infty})}{u_{i,\infty}}\\
=\;&2\int_{\Omega^*}\sum_{i=1}^{k}q_i^2\frac{(u_i-u_{i,\infty})^2}{u_{i,\infty}}+2\int_{\Omega^*}\sum_{i\neq j=1}^{k}q_iq_j\frac{(u_i-u_{i,\infty})(u_j-u_{j,\infty})}{u_{i,\infty}}\,,
\end{aligned} \tag{75}$$

and we finally arrive at

$$\frac{1}{2}\int_{\Omega^*}U^*\nabla\Phi^*\cdot\nabla\Phi^*-\int_{\Omega^*}\sum_{i\neq j=1}^{k}q_iq_j\frac{(u_i-u_{i,\infty})(u_j-u_{j,\infty})}{u_{i,\infty}}\ge\frac{q^2}{k}\int_{\Omega^*}\sum_{i=1}^{k}\frac{(u_i-u_{i,\infty})^2}{u_{i,\infty}}\,. \tag{76}$$

It remains now to show that the second term of the left-hand side is bounded above by the recombination term in (60), that is:

$$\int_{\Omega^*}\frac{1}{2}\sum_{h=1}^{s}(\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}}-\frac{u^{\beta^h}}{u_\infty^{\beta^h}})\Big(\log\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}}-\log\frac{u^{\beta^h}}{u_\infty^{\beta^h}}\Big)\ge-\int_{\Omega^*}\sum_{i\neq j=1}^{k}q_iq_j\frac{(u_i-u_{i,\infty})(u_j-u_{j,\infty})}{u_{i,\infty}}\,. \tag{77}$$

Since $(x-y)(\log x - \log y) \geq (\sqrt{x} - \sqrt{y})^2$ then

$$\int_{\Omega^*} \sum_{h=1}^{s} (\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \frac{u^{\beta^h}}{u_\infty^{\beta^h}})\Big(\log \frac{u^{\alpha^h}}{u_\infty^{\alpha^h}} - \log \frac{u^{\beta^h}}{u_\infty^{\beta^h}}\Big) \geq \int_{\Omega^*} \sum_{h=1}^{s} \frac{\Big(\sqrt{u^{\alpha^h} u_\infty^{\beta^h}} - \sqrt{u_\infty^{\alpha^h} u^{\beta^h}}\Big)^2}{u_\infty^{\alpha^h} u_\infty^{\beta^h}}\,, \tag{78}$$

and by the Aczél-Varga's inequality $(a_1 b_1 - a_2 b_2)^2 \geq (a_1^2 - a_2^2)(b_1^2 - b_2^2)$, with $a_1^2 > a_2^2$ and provided we set $a_1 = \sqrt{u^{\alpha^h}}$, $a_2 = \sqrt{u_\infty^{\alpha^h}}$, $b_1 = \sqrt{u_\infty^{\beta^h}}$ and $b_2 = \sqrt{u^{\beta^h}}$, then we have:

$$\Big(\sqrt{u^{\alpha^h} u_\infty^{\beta^h}} - \sqrt{u_\infty^{\alpha^h} u^{\beta^h}}\Big)^2 \geq (u^{\alpha^h} - u_\infty^{\alpha^h})(u_\infty^{\beta^h} - u^{\beta^h})\,, \tag{79}$$

and by (77) and (79) it remains to prove that:

$$\frac{1}{2} \sum_{h=1}^{s} \frac{(u-u_\infty)^{\alpha^h} (u_\infty - u)^{\beta^h}}{u_\infty^{\alpha^h} u_\infty^{\beta^h}} \geq \sum_{i,j=1}^{k} Q_{ij} \frac{(u_i - u_{i,\infty})(u_j - u_{j,\infty})}{u_{i,\infty} u_{j,\infty}} (u_{i,\infty} + u_{j,\infty})\,, \tag{80}$$

where the $k \times k$ matrix Q_{ij} is defined by:

$$Q_{ij} = \begin{cases} |q_i q_j|\,, & \text{if } q_i q_j < 0\,, \quad i \neq j\,; \\ 0\,, & \text{if } q_i q_j > 0\,, \quad i \neq j \\ 0\,, & \text{if } i = j\,. \end{cases} \tag{81}$$

In order to prove (80) we first introduce some additional hypotheses:

- H1 (charge vector): $q_i \in \{-1\,, 0\,, 1\}\,, i = 1\,, 2\,, \ldots\,, k\,;$
- H2 (equilibrium densities): $2(u_{i,\infty} + u_{j,\infty}) \leq 1\,, i \neq j = 1\,, 2\,, \ldots\,, k\,;$
- H3 (recombination processes): each side of the recombination process involves at most two densities, namely $u_i\,, u_j$ with $\alpha_i^h = \alpha_j^h = 1$ and $u_m\,, u_n$ with $\beta_m^h = \beta_n^h = 1\,;$
- H4 (recombination vectors): the recombination processes are of two types
  - with $\beta^h = 0$ for $h = 1\,, \ldots\,, m \leq s$ and $q_i = -q_j = 1$, by H1 and H3;
  - with $\beta_i^r = \alpha_i^p$ for $r, p = 1\,, \ldots\,, s-m\,, i = 1, 2, \ldots k$.

Then , by H3 ad H4 the left-hand side of inequality (80) becomes:

$$\begin{aligned}
&\frac{1}{2}\Big(\sum_{h=1}^{m} \frac{(u_i - u_{i\infty})^{(\alpha_i^h=1)} (u_j - u_{j\infty})^{(\alpha_j^h=1)}}{u_{i\infty}^{(\alpha_i^h=1)} u_{j\infty}^{(\alpha_j^h=1)}} \\
&+ \sum_{r,p=1}^{s-m} \Big(\frac{(u_i - u_{i\infty})^{(\alpha_i^r=1)} (u_j - u_{j\infty})^{(\alpha_j^r=1)} (u_{m\infty} - u_m)^{(\beta_m^r=1)} (u_{n\infty} - u_n)^{(\beta_n^r=1)}}{u_{i\infty}^{(\alpha_i^r=1)} u_{j\infty}^{(\alpha_j^r=1)} u_{m\infty}^{(\beta_m^r=1)} u_{n\infty}^{(\beta_n^r=1)}} \\
&+ \frac{(u_i - u_{i\infty})^{(\alpha_i^p=1)} (u_j - u_{j\infty})^{(\alpha_j^p=1)} (u_{m\infty} - u_m)^{(\beta_m^p=1)} (u_{n\infty} - u_n)^{(\beta_n^p=1)}}{u_{i\infty}^{(\alpha_i^p=1)} u_{j\infty}^{(\alpha_j^p=1)} u_{m\infty}^{(\beta_m^p=1)} u_{n\infty}^{(\beta_n^p=1)}} \Big)\Big) \\
&= \frac{1}{2}\Big(\sum_{h=1}^{m} \frac{(u_i - u_{i\infty})^{(\alpha_i^h=1)} (u_j - u_{j\infty})^{(\alpha_j^h=1)}}{u_{i\infty}^{(\alpha_i^h=1)} u_{j\infty}^{(\alpha_j^h=1)}} \\
&+ \sum_{r,p=1}^{s-m} \Big(\frac{(u_i - u_{i\infty})^{(\alpha_i^r=1)} (u_j - u_{j\infty})^{(\alpha_j^r=1)} (u_{m\infty} - u_m)^{(\alpha_m^p=1)} (u_{n\infty} - u_n)^{(\alpha_n^p=1)}}{u_{i\infty}^{(\alpha_i^r=1)} u_{j\infty}^{(\alpha_j^r=1)} u_{m\infty}^{(\alpha_m^p=1)} u_{n\infty}^{(\alpha_n^p=1)}}
\end{aligned} \tag{82}$$

$$
+\frac{(u_i-u_{i\infty})^{(\alpha_i^p=1)}(u_j-u_{j\infty})^{(\alpha_j^p=1)}(u_{m\infty}-u_m)^{(\alpha_m^r=1)}(u_{n\infty}-u_n)^{(\alpha_n^r=1)}}{u_{i\infty}^{(\alpha_i^p=1)}u_{j\infty}^{(\alpha_j^p=1)}u_{m\infty}^{(\alpha_m^r=1)}u_{n\infty}^{(\alpha_n^r=1)}}\Big)\Big)
$$

$$
=\frac{1}{2}\Big(\sum_{h=1}^{m}\frac{(u_i-u_{i\infty})^{(\alpha_i^h=1)}(u_j-u_{j\infty})^{(\alpha_j^h=1)}}{u_{i\infty}^{(\alpha_i^h=1)}u_{j\infty}^{(\alpha_j^h=1)}}
$$

$$
+2\sum_{r=1}^{s-m}\frac{(u_i-u_{i\infty})^{(\alpha_i^r=1)}(u_j-u_{j\infty})^{(\alpha_j^r=1)}(u_m-u_{m\infty})^{(\alpha_m^p=1)}(u_n-u_{n\infty})^{(\alpha_n^p=1)}}{u_{i\infty}^{(\alpha_i^r=1)}u_{j\infty}^{(\alpha_j^r=1)}u_{m\infty}^{(\alpha_m^p=1)}u_{n\infty}^{(\alpha_n^p=1)}}\Big)
$$

$$
\geq\frac{1}{2}\sum_{h=1}^{m}\frac{(u_i-u_{i\infty})^{(\alpha_i^h=1)}(u_j-u_{j\infty})^{(\alpha_j^h=1)}}{u_{i\infty}^{(\alpha_i^h=1)}u_{j\infty}^{(\alpha_j^h=1)}}\,.
$$

The last term of (82) contains, by H3, only the recombination processes with $q_iq_j=-1$ and hence it can be rewritten in the equivalent form:

$$
\frac{1}{2}\sum_{h=1}^{m}\frac{(u_i-u_{i\infty})^{(\alpha_i^h=1)}(u_j-u_{j\infty})^{(\alpha_j^h=1)}}{u_{i\infty}^{(\alpha_i^h=1)}u_{j\infty}^{(\alpha_j^h=1)}}=\frac{1}{2}\sum_{i,j=1}^{k}Q_{ij}\frac{(u_i-u_{i\infty})(u_j-u_{j\infty})}{u_{i\infty}u_{j\infty}}\,; \tag{83}
$$

accordingly, by (82) and (83) the inequality (80) yields:

$$
\frac{1}{2}\sum_{h=1}^{s}\frac{(u-u_\infty)^{\alpha^h}(u_\infty-u)^{\beta^h}}{u_\infty^{\alpha^h}u_\infty^{\beta^h}}\geq\frac{1}{2}\sum_{i,j=1}^{k}Q_{ij}\frac{(u_i-u_{i\infty})(u_j-u_{j\infty})}{u_{i\infty}u_{j\infty}}\geq\sum_{i,j=1}^{k}Q_{ij}\frac{(u_i-u_{i,\infty})(u_j-u_{j,\infty})}{u_{i,\infty}u_{j,\infty}}(u_{i,\infty}+u_{j,\infty})\,, \tag{84}
$$

which holds true by H2. From (75) ad (76) then we arrive at

$$
\frac{1}{2}\int_{\Omega^*}U^*\nabla\Phi^*\cdot\nabla\Phi^*+\frac{1}{2}\int_{\Omega^*}\sum_{h=1}^{s}\Big(\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}}-\frac{u^{\beta^h}}{u_\infty^{\beta^h}}\Big)\Big(\log\frac{u^{\alpha^h}}{u_\infty^{\alpha^h}}-\log\frac{u^{\beta^h}}{u_\infty^{\beta^h}}\Big)\geq\frac{\|q\|^2}{k}\int_{\Omega^*}\sum_{i=1}^{k}\frac{(u_i-u_{i,\infty})^2}{u_{i,\infty}}\,, \tag{85}
$$

from which we recover in turn (72).

Theorem 1. *Energy-Dissipation production inequality.*
There exists an explicit computable constant $C_{edp}>0$ such that

$$
\mathcal{D}(n)\geq C_{edp}\mathcal{F}(n\mid n_\infty)\,, \tag{86}
$$

with

$$
C_{edp}^{-1}=\frac{k}{\|q\|^2}\sup\{\frac{W\exp(2K_\infty)}{2m\mu^*},\frac{1}{2k_F}\}\Big(1+\frac{\mathcal{L}(\Omega^*)}{2}\|q\|^2W\exp(2K_\infty)\Big)\,. \tag{87}
$$

The proof follows from Proposition 1 and Proposition 2:

$$
\mathcal{F}(n\mid n_\infty)\leq K_1\int_{\Omega^*}\sum_{i=1}^{k}\frac{(u_i-u_i^\infty)^2}{u_i^\infty}\leq K_1K_2\mathcal{D}(n)\,, \tag{88}
$$

with $C_{\rm edp}^{-1}=K_1K_2$.

3.2. Convergence to equilibrium

In this section, we shall assume that there exists a global renormalizable solution for the boundary value problem (29), (30) with Neumann boundary conditions and with initial data

$$
u_o(z)=u(z,0)\,,\quad \psi_o(z)=\psi(z,0)\,, \tag{89}
$$

provided

$$
u_o\in L^2(\Omega^*)\,,\quad \psi_o\in H^1(\Omega^*)\,,\quad \overline{\psi}_o=0\,,\quad q\cdot\overline{u}_o=0\,; \tag{90}
$$

Remark 1. *At the best of our knowledge, no proof of the existence of such a global renormalizable solution exists yet. Indeed in the results provided in [4]-[7] there is no coupling with (29), whereas the only result available for the coupled system (29), (30) deals with the uniqueness of the weak solution [8].*

Remark 2. *The results concerning the existence of a global weak solution obtained e.g. in [23] does not apply because the different form of the recombination term: indeed the result of [7] seems, as far as we know, the most general result available for a generic recombination term $r(n)$. For a detailed review of the available existence results for the scintillator equations vid. also the review [24].*

Lemma 2. *Generalized Csizár-Kullback-Pinsker inequality.*
Let $f, g : \Omega^* \to \mathbb{R}_+ \cup \{0\}$ measurable functions. Then the Kullback-Leibler divergence $\mathcal{H}(f \mid g)$ is bounded by:

$$\mathcal{H}(f \mid g) = \int_{\Omega^*} f \log \frac{f}{g} - (f - g) \geq C^* \Big(\|f - g\|_{L^1(\Omega^*)} \Big)^2 , \quad C^* = \frac{3}{2(\overline{f} + 2\overline{g})} . \tag{91}$$

The proof is given in [16]: this result generalizes the classical result with $C^* = 1/2\overline{f}$ (*vid. e.g.* [21], [22]).

Lemma 3. *Any solution of the boundary value problem (29), (30) with Neumann boundary conditions and with initial data (89), (90) satisfies the bound:*

$$\overline{u}_i \leq M , \quad i = 1 , 2 , \dots , k , \quad M = \frac{5}{2} W \exp(2K_\infty) + \frac{3}{4} \mathcal{F}_o , \tag{92}$$

where $\mathcal{F}_o = \mathcal{F}(u_o)$ denotes the Gibbs free energy corresponding to the initial data.

To prove the bound we write, for any $i = 1 , 2 , \dots , k$ and by the Lemma 2 and Young's inequality we obtain:

$$\overline{u}_i \leq \overline{u}_{i,\infty} + \|u_i - u_{i,\infty}\|_{L^1(\Omega^*)} \leq \overline{u}_{i,\infty} + \Big(\frac{2\overline{u}_i + 4\overline{u}_{i,\infty}}{3} \Big)^{\frac{1}{2}} \Big(\mathcal{H}(u_i \mid u_{i,\infty}) \Big)^{\frac{1}{2}} \leq \overline{u}_{i,\infty} + \frac{1}{3} \overline{u}_i + \frac{2}{3} \overline{u}_{i,\infty} + \frac{1}{2} \mathcal{H}(u_i \mid u_{i,\infty}) , \tag{93}$$

which can be solved for $\overline{u}_i$ to arrive at:

$$\overline{u}_i \leq \frac{5}{2} \overline{u}_{i,\infty} + \frac{3}{4} \mathcal{H}(u_i \mid u_{i,\infty}) . \tag{94}$$

By the bound (53), the identification between the KL-divergence and the Gibbs free-energy and the monotonicity of $\mathcal{F}$ we finally obtain

$$\overline{u}_i \leq \frac{5}{2} \overline{u}_{i,\infty} + \frac{3}{4} \mathcal{F}(u) \leq \frac{5}{2} W \exp(2K_\infty) + \frac{3}{4} \mathcal{F}(u_o) = M . \tag{95}$$

Proposition 3. *For all $u \in L^2(\Omega^*)$ which obeys (92) and $\psi \in H^1(\Omega^*)$ the corresponding solution of (29) with $\overline{\psi} = 0$ and $q \cdot \overline{u} = 0$, the following Csizár-Kullback-Pinsker inequality holds:*

$$\mathcal{F}(u \mid u_\infty) \geq C_{ckp} \sum_{i=1}^{k} \|u_i - u_{i,\infty}\|^2_{L^1(\Omega^*)} , \quad C_{ckp} = \Big(3W \exp(2K_\infty) + \frac{1}{2} \mathcal{F}_o \Big)^{-1} . \tag{96}$$

To proof this proposition we notice that from (34) and the Lemma 3 we have

$$\begin{aligned} \mathcal{F}(u \mid u_\infty) \quad &\geq \quad \int_{\Omega^*} \sum_{i=1}^{k} u_i \log \frac{u_i}{u_i^\infty} - (u_i - u_i^\infty) \geq \sum_{i=1}^{k} \frac{3}{2\overline{u}_i + 4\overline{u}_{i,\infty}} \|u_i - u_{i,\infty}\|^2_{L^1(\Omega^*)} \\ &\geq \quad \frac{3}{2M + 4W \exp(2K_\infty)} \sum_{i=1}^{k} \|u_i - u_{i,\infty}\|^2_{L^1(\Omega^*)} , \end{aligned} \tag{97}$$

which by (92) leads to the thesis.

Theorem 2. *Exponential convergence to equilibrium.*
Let us assume that the weak global solution of the boundary value problem (29), (30) with Neumann boundary conditions and initial data (89), (90) is smooth enough to satisfy the weak Gibbs free-energy production law:

$$\mathcal{F}(u(\cdot\,,t_1)) + \int_{t_0}^{t_1} \mathcal{D}(u(\cdot\,,\tau))\mathrm{d}\tau \leq \mathcal{F}(u(\cdot\,,t_0))\,, \quad \forall\, 0 \leq t_0 \leq t_1 < \infty\,; \tag{98}$$

Then these solutions decay exponentially to the equilibrium $(u_\infty\,,\psi_\infty)$ as a function of $t \geq 0$:

$$\mathcal{F}(u(\cdot\,,t)) \leq \mathcal{F}_o \exp(-C_{edp}t)\,, \tag{99}$$

and

$$\sum_{i=1}^{k} \|u_i - u_{i,\infty}\|^2_{L^1(\Omega^*)} + \|\psi - \psi_\infty\|^2_{H^1(\Omega^*)} \leq \Big(C_2 + 2(1 + \mathcal{L}(\Omega^*))\Big)\mathcal{F}_o \exp(-C_{edp}t) \tag{100}$$

where C_{edp} is given by (87) and $C_2 = (C_{ckp})^{-1}$.

The proof of (99) follows straightforward from Gronwall's lemma: indeed since $\mathcal{D} = -\mathcal{F}'$, then by Theorem 1

$$-\mathcal{F}' \geq C_{\mathrm{edp}}\mathcal{F}\,, \tag{101}$$

and accordingly:

$$\mathcal{F} \leq \mathcal{F}_o \exp(-C_{\mathrm{edp}}t)\,; \tag{102}$$

the proof of (100) follows instead from the Poincaré inequality, proposition 3 applied to (34) and (99).

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