Entropy production in diffusion-reaction systems: The reactive random Lorentz gas

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We report the study of a random Lorentz gas with a reaction of isomerization $A \rightleftharpoons B$ between two colors of moving particles elastically bouncing on hard disks. The reaction occurs when the moving particles collide on catalytic disks, which constitute a fraction of all the disks. Under dilute-gas conditions, the reaction-diffusion process is ruled by two coupled Boltzmann-Lorentz equations for the distribution functions of the colors. The macroscopic reaction-diffusion equations with cross-diffusion terms induced by the chemical reaction are derived from the kinetic equations. We use an H theorem of the kinetic theory in order to derive a macroscopic entropy depending on the gradients of color densities and which has a non-negative entropy production in agreement with the second law of thermodynamics.

I. INTRODUCTION

During recent decades, irreversibility and transport properties have been intensively studied in low-dimensional dynamical systems [1–16]. It has been shown that the macroscopic transport coefficients can be related to the characteristic quantities of the microscopic dynamics [4]. Moreover, results have also been obtained for the entropy balance in dynamical systems sustaining transport processes of diffusion [4,11–14], electric conduction [6], cross effects [8,9], and shear viscosity [10]. For these processes, the irreversible entropy production of nonequilibrium thermodynamics could be derived from the underlying microscopic dynamics.

In addition to transport, reaction processes have also been investigated from the viewpoint of dynamical systems theory. Reaction-diffusion processes play a crucial role in physicochemical systems far from thermodynamic equilibrium and they have been much studied at the macroscopic level of description on the basis of phenomenological nonequilibrium thermodynamics [17].

Recently, several microscopic models of reaction-diffusion processes have been introduced and analyzed in order to understand the foundations of the phenomenological assumptions. The simplest reactions are isomerizations $A \rightleftharpoons B$ where the two species A and B may be considered as colors or spins carried by the moving particles and changing or flipping upon reactive events [18]. Models of reaction-diffusion processes can be obtained by coupling the isomerization to the deterministic diffusion of multibaker or Lorentz gas dynamical systems [19–23]. In the early version of Refs. [19,20], the isomerization $A \rightleftharpoons B$ was supposed to happen with unit probability upon the passage of the particle to a catalytic site where the reaction occurs. In Ref. [21], a spatially periodic reactive Lorentz gas was introduced in which the isomerization $A \rightleftharpoons B$ occurs with a probability $0 \leqslant p_0 \leqslant 1$ when the particle collides on catalytic disks. The catalytic disks are few among the disks which compose the Lorentz gas. Spatially periodic Lorentz gas and multibaker models with reaction $A \rightleftharpoons B$ have been studied in detail and their diffusive and reactive modes were constructed together

with their dispersion relations [21–23]. In this way, the macroscopic reaction-diffusion equations could be derived in a systematic way from the underlying dynamics. The analysis revealed the existence of cross-diffusion effects induced by the reaction. Such cross diffusion is typically overlooked in the phenomenological approach [24,25].

The purpose of the present paper is to address the problem of entropy production in such reaction-diffusion systems with cross diffusion. As shown here below, it turns out that the entropy production of the standard phenomenological entropy may be negative because of the cross-diffusion effects. Although this problem only happens for extreme particle densities it nevertheless sheds some doubts on the phenomenological assumptions. In order to clarify this issue, we here consider a *random* Lorentz gas with a fraction of catalytic disks where the isomerization $A \rightleftharpoons B$ occurs with a given probability p_0. The color A or B carried by the moving particle may correspond to the spin of the particle, in which case the catalytic disks model some spin-flipping impurities in the system. For dilute Lorentz gases, we can use kinetic theory and linear Boltzmann-Lorentz equations [26,27]. Thanks to such master equations, we can derive an H theorem which allows us to obtain an expression for the entropy. We prove that the corresponding entropy production is non-negative with respect to the time evolution induced by the macroscopic reaction-diffusion equations.
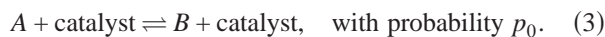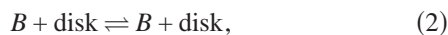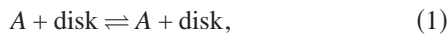
The plan of the paper is the following. The kinetic equations of the reactive Lorentz gas are introduced in Sec. II where we prove the H theorem. The macroscopic reaction-diffusion equations are derived in Sec. III. The entropy balance is obtained and discussed in Sec. IV. Conclusions are drawn in Sec. V.

II. THE REACTIVE LORENTZ GAS

In the random Lorentz gas, fixed circular scatterers correspond to heavy particles and moving point particles to light ones. The system is defined by the density of the scatterers n, their radius a, and the velocity of the light particles $\vec{v} = v(\cos\varphi, \sin\varphi)$, the system being two dimensional. Because

the magnitude of the velocities is fixed, the velocity vector can be characterized solely by the angle φ. Here, we consider a random distribution of the disks with low density $n \ll a^{-2}$.

The reactive Lorentz gas [21] consists of two different types of light particles A and B that have a free flight between the collisions. Some of the fixed scatterers act as catalysts, i.e., if an A particle collides with such a scatterer it becomes a B with the probability p_0, and vice versa. The catalysts have a density n_r. The reaction scheme is

$$A + \text{disk} \rightleftharpoons A + \text{disk}, \tag{1}$$

$$B + \text{disk} \rightleftharpoons B + \text{disk}, \tag{2}$$

$$A + \text{catalyst} \rightleftharpoons B + \text{catalyst}, \quad \text{with probability } p_0. \tag{3}$$

The colors can be considered as the two components of spin one-half carried by the moving particles. The evolution of the system can be characterized by the two distribution functions of the two components $f_A(\vec{r}, \vec{v})$ and $f_B(\vec{r}, \vec{v})$. The integral over the velocities of these functions gives the number density at point $\vec{r}$ of each component A or B. Having in mind that the time evolution of the distribution function f_A (f_B) is also influenced by the presence of the other component B (A) which may collide with a catalyst, we obtain the system of equations

$$\partial_t f_A + \vec{v} \cdot \vec{\nabla} f_A = \frac{av(n - p_0 n_r)}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right| [f_A(\vec{r}, \varphi')$$

$$- f_A(\vec{r}, \varphi)] + \frac{av p_0 n_r}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right|$$

$$\times [f_B(\vec{r}, \varphi') - f_A(\vec{r}, \varphi)], \tag{4}$$

$$\partial_t f_B + \vec{v} \cdot \vec{\nabla} f_B = \frac{av(n - p_0 n_r)}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right| [f_B(\vec{r}, \varphi')$$

$$- f_B(\vec{r}, \varphi)] + \frac{av p_0 n_r}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right|$$

$$\times [f_A(\vec{r}, \varphi') - f_B(\vec{r}, \varphi)]. \tag{5}$$

One can observe that the total system of moving particles A and B follows a diffusive process that can be characterized by the the sum of the distribution functions,

$$f \equiv f_A + f_B. \tag{6}$$

The time evolution of f is given by a linear Boltzmann equation, also known as the Boltzmann-Lorentz equation [26,27]:

$$\partial_t f + \vec{v} \cdot \vec{\nabla} f = \frac{avn}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right| [f(\vec{r}, \varphi') - f(\vec{r}, \varphi)]. \tag{7}$$

This equation rules the so-called *diffusion sector*. In order to have the time evolution of both distribution functions, we need a further equation in addition to Eq. (7).

If we introduce the quantity

$$g \equiv f_A - f_B, \tag{8}$$

and take the difference of Eqs. (4) and (5), we obtain the equation

$$\partial_t g + \vec{v} \cdot \vec{\nabla} g = \frac{av(n - 2p_0 n_r)}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right| [g(\vec{r}, \varphi')$$

$$- g(\vec{r}, \varphi)] - 4av p_0 n_r g(\vec{r}, \varphi), \tag{9}$$

which rules the *reaction sector*. One can notice that the last equation describes a decay in time of the function g that can be separated from the rest of the solution,

$$g(\vec{r}, \varphi, t) = e^{-4av p_0 n_r t} h(\vec{r}, \varphi). \tag{10}$$

The equation for h reads

$$\partial_t h + \vec{v} \cdot \vec{\nabla} h = \frac{av(n - 2p_0 n_r)}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right|$$

$$\times [h(\vec{r}, \varphi') - h(\vec{r}, \varphi)], \tag{11}$$

which has the same form as Eq. (7).

A. *H* theorem

The Boltzmann entropy of the system of Eqs. (4) and (5) is given by the sum of the entropies of the two components:

$$s = \int d\varphi \left(f_A \ln \frac{f^0}{f_A} + f_B \ln \frac{f^0}{f_B} \right), \tag{12}$$

where Boltzmann's constant is taken equal to unity, $k_B = 1$.

Inserting into the integral on the right-hand side the time evolution Eqs. (4) and (5), we get for the variation of the entropy

$$\partial_t s = \int d\varphi \left\{ \ln \frac{f^0}{e f_A} [-\vec{v} \cdot \vec{\nabla} f_A + C(f_A, f_B)] \right.$$

$$\left. + \ln \frac{f^0}{e f_B} [-\vec{v} \cdot \vec{\nabla} f_B + C(f_B, f_A)] \right\}, \tag{13}$$

where the collision integral $C(f_A, f_B)$ has the form

$$C(f_A, f_B) = \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right| \left[\frac{av(n - p_0 n_r)}{2} (f_A' - f_A) \right.$$

$$\left. + \frac{av p_0 n_r}{2} (f_B' - f_A) \right], \tag{14}$$

with the notations

$$f_A = f_A(\vec{r}, \varphi, t), \tag{15}$$

$$f_A' = f_A(\vec{r}, \varphi', t), \tag{16}$$

$$f_B = f_B(\vec{r}, \varphi, t), \tag{17}$$

$$f_B' = f_B(\vec{r}, \varphi', t). \tag{18}$$

This relation can be written in the form of a balance equation

$$\partial_t s = -\vec{\nabla} \cdot \vec{J}_s + \sigma_s, \tag{19}$$

where

$$\vec{J}_s = \int d\varphi \, \vec{v} \left(f_A \ln \frac{f^0}{f_A} + f_B \ln \frac{f^0}{f_B} \right) \tag{20}$$

is the entropy current and

$$\sigma_s = \frac{av}{4} \int d\varphi \, d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right| \left\{ (n - p_0 n_r) \left[(f_A' - f_A) \ln \frac{f_A'}{f_A} \right. \right.$$
$$\left. + (f_B' - f_B) \ln \frac{f_B'}{f_B} \right] + p_0 n_r \left[(f_B' - f_A) \ln \frac{f_B'}{f_A} \right.$$
$$\left. \left. + (f_A' - f_B) \ln \frac{f_A'}{f_B} \right] \right\}$$
$$\geq 0 \tag{21}$$

is the entropy production [24]. One can see in this general form of the entropy production that it is non-negative under the consistency condition that

$$0 \leq p_0 n_r \leq n. \tag{22}$$

Therefore, the second law of thermodynamics is satisfied for the entropy (12) during the reaction-diffusion process described by the Boltzmann-Lorentz equations (4) and (5).

III. DERIVATION OF THE MACROSCOPIC REACTION-DIFFUSION EQUATIONS

In order to understand the time evolution of the system and, in particular, of the macroscopic densities of particles A and B, we have to solve the coupled Boltzmann-Lorentz equations (4) and (5). Since these equations are linear, they yield an eigenvalue problem and their solutions can be decomposed in terms of eigenfunctions. The time evolution can then be determined by the spectrum of the associated eigenvalues.

A convenient way to find the solution of Eqs. (7) and (11)

$$\partial_t X + \vec{v} \cdot \vec{\nabla} X = \frac{c}{2} \int_{-\pi}^{+\pi} d\varphi' \left| \sin \frac{\varphi - \varphi'}{2} \right| [X(\vec{r}, \varphi') - X(\vec{r}, \varphi)] \tag{23}$$

is by writing the distribution functions $X = f$ or h as a Fourier series in the velocity angle φ,

$$X(\vec{r}, \varphi, t) = \sum_{l=-\infty}^{+\infty} X_l(\vec{r}, t) e^{il\varphi}. \tag{24}$$

As a consequence of Eq. (7) or (11), the Fourier components X_l satisfy the following coupled differential equations:

$$\partial_t X_l + v \frac{\partial_x - i\partial_y}{2} X_{l-1} + v \frac{\partial_x + i\partial_y}{2} X_{l+1} = \frac{8l^2 c}{1 - 4l^2} X_l \tag{25}$$

with

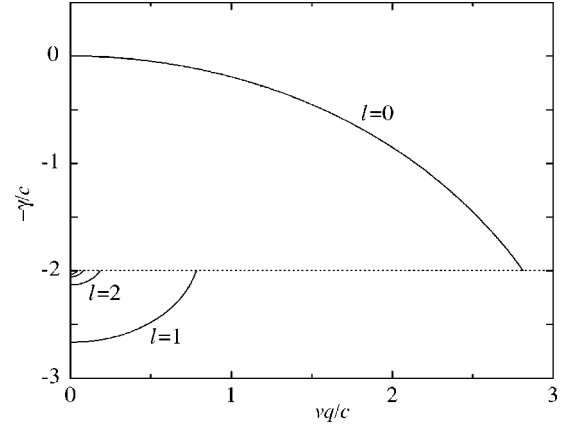$$c = avn \quad \text{for } X = f \tag{26}$$

and

FIG. 1. The dimensionless eigenvalues $-\gamma/c$ of Eq. (29) versus the dimensionless wave number vq/c with $q = \sqrt{q_x^2 + q_y^2}$.

$$c = av(n - 2p_0 n_r) \quad \text{for } X = h. \tag{27}$$

The distribution function X being a real function, the Fourier coefficients with negative index are the complex conjugates of their positive index counterparts: $X_{-l} = X_l^*$ for any l. If we take solutions in the form

$$X_l(\vec{r}, t) = U_l \exp(-\gamma t) \exp(i\vec{q} \cdot \vec{r}), \tag{28}$$

we obtain the eigenvalue equations

$$-\gamma U_l + iv \frac{q_x - iq_y}{2} U_{l-1} + iv \frac{q_x + iq_y}{2} U_{l+1} = \frac{8l^2 c}{1 - 4l^2} U_l, \tag{29}$$

for $l \in \mathbb{Z}$. Expanding in powers of the wave number $\vec{q}$, the decay rates are given by

$$\gamma = \frac{8l^2 c}{4l^2 - 1} - \frac{3(4l^2 - 1)v^2}{16c} q^2 + O(q^4), \tag{30}$$

with $l = 0, 1, 2, \ldots$ and $q = \sqrt{q_x^2 + q_y^2}$. Figure 1 shows the spectrum obtained by solving numerically the eigenvalue equations (29) for $c > 0$. We observe that the branch for $l = 0$ has a convexity which is opposite to the one of the other branches for $l = 1, 2, \ldots$. Moreover, all the branches terminate on the line $\gamma = 2c$, which fixes the maximum value of the wave number for each branch. This feature prevents the eigenvalues from becoming of opposite sign, hence avoiding instability in agreement with the stability provided by the H theorem. For the diffusion sector, the constant c is always positive. However, the sign of the constant c may change in the reaction sector and we must treat separately the cases $c > 0$ and $c \leq 0$.

A. The case $0 < p_0 n_r < n/2$

In this case, we have that $c > 0$ in both the diffusion and reaction sectors.

The previous spectral analysis shows that, after a relaxation time of the order of $(avn)^{-1}$, the dynamics is dominated by the first Fourier components X_0, X_{+1}, and X_{-1}:

$$X \simeq X_0 + X_{+1} e^{+i\varphi} + X_{-1} e^{-i\varphi}. \tag{31}$$

In order to obtain a macroscopic description, we introduce the densities

$$\rho_+ \equiv \rho_A + \rho_B = \int_{-\pi}^{+\pi} f(\vec{r}, \varphi)d\varphi = 2\pi f_0, \tag{32}$$

$$\rho_- \equiv \rho_A - \rho_B = \int_{-\pi}^{+\pi} g(\vec{r}, \varphi)d\varphi = 2\pi g_0 \tag{33}$$

and the currents

$$\vec{J}_+ \equiv \vec{J}_A + \vec{J}_B = \int_{-\pi}^{+\pi} \vec{v} f(\vec{r}, \varphi)d\varphi, \tag{34}$$

$$\vec{J}_- \equiv \vec{J}_A - \vec{J}_B = \int_{-\pi}^{+\pi} \vec{v} g(\vec{r}, \varphi)d\varphi. \tag{35}$$

We observe that the zeroth-order Fourier component f_0 of the distribution function f in the expansion (24) is related to the total density $\rho_+ = \rho_A + \rho_B$ according to Eq. (32). Similarly, Eq. (33) shows that the zeroth-order component g_0 of the distribution function g gives the difference of densities $\rho_- = \rho_A - \rho_B$. On the other hand, the first-order Fourier components X_{+1} and X_{-1} are related to the currents. As a consequence, we obtain the distribution functions f and g in terms of the corresponding densities and currents

$$f \simeq \frac{1}{2\pi}\left(\rho_+ + \frac{2}{v^2}\vec{v} \cdot \vec{J}_+\right), \tag{36}$$

$$g \simeq \frac{1}{2\pi}\left(\rho_- + \frac{2}{v^2}\vec{v} \cdot \vec{J}_-\right). \tag{37}$$

The distribution functions for the species A and B are thus given by

$$f_A \simeq \frac{1}{2\pi}\left(\rho_A + \frac{2}{v^2}\vec{v} \cdot \vec{J}_A\right), \tag{38}$$

$$f_B \simeq \frac{1}{2\pi}\left(\rho_B + \frac{2}{v^2}\vec{v} \cdot \vec{J}_B\right). \tag{39}$$

Equations (25) for $l=0$ and ± 1 then lead to the coupled equations

$$\partial_t \rho_+ = -\vec{\nabla} \cdot \vec{J}_+, \tag{40}$$

$$\partial_t \vec{J}_+ = -\frac{8av}{3}n\vec{J}_+ - \frac{v^2}{2}\vec{\nabla}\rho_+, \tag{41}$$

and

$$\partial_t \rho_- = -\vec{\nabla} \cdot \vec{J}_- - 4avp_0 n_r \rho_-, \tag{42}$$

$$\partial_t \vec{J}_- = -\frac{8av}{3}\left(n - \frac{p_0 n_r}{2}\right)\vec{J}_- - \frac{v^2}{2}\vec{\nabla}\rho_-. \tag{43}$$

We notice that the currents relax on a fast time scale so that we can assume that they quickly adjust to their values in a quasistationary state as

$$\vec{J}_+ = -D\vec{\nabla}\rho_+ \quad \text{for } t \gg \frac{3}{8avn}, \tag{44}$$

$$\vec{J}_- = -D^{(r)}\vec{\nabla}\rho_- \quad \text{for } t \gg \frac{3}{8av(n - p_0 n_r/2)}, \tag{45}$$

with the diffusion coefficient

$$D = \frac{3v}{16an}, \tag{46}$$

and the reactive diffusion coefficient

$$D^{(r)} = \frac{3v}{16a(n - p_0 n_r/2)}. \tag{47}$$

Equation (44) is the expression of Fick's law for the particles while Eq. (45) is its reactive analog. Substituting Eqs. (44) and (45) into Eqs. (40) and (42) for the densities, we obtain the diffusion equation

$$\partial_t \rho_+ = D\nabla^2 \rho_+, \tag{48}$$

as well as the reaction-diffusion equation

$$\partial_t \rho_- = D^{(r)}\nabla^2 \rho_- - 2\kappa\rho_-, \tag{49}$$

with the reaction rate constant

$$\kappa = 2avp_0 n_r. \tag{50}$$

This result shows that the reaction rate constant is the product of the speed v with the cross section $2a$ of the disks, multiplied by the density n_r of the catalytic scatterers and weighted by the probability of reaction p_0. The two equations (48) and (49) show the existence of two slow modes in the system corresponding to the decay rate (30) with $l=0$, namely, the *diffusive mode* of the dispersion relation,

$$\Gamma = Dq^2 + O(q^4), \quad \text{diffusive mode,} \tag{51}$$

and the *reactive mode* of the dispersion relation,

$$\Gamma = 2\kappa + D^{(r)}q^2 + O(q^4), \quad \text{reactive mode.} \tag{52}$$

The equations of motion (48) and (49) determines the time evolution of the densities $\rho_A = (\rho_+ + \rho_-)/2$ and $\rho_B = (\rho_+ - \rho_-)/2$ according to the coupled reaction-diffusion equations

$$\partial_t \rho_A = D_{AA}\nabla^2 \rho_A + D_{AB}\nabla^2 \rho_B - \kappa(\rho_A - \rho_B), \tag{53}$$

$$\partial_t \rho_B = D_{BA}\nabla^2 \rho_A + D_{BB}\nabla^2 \rho_B + \kappa(\rho_A - \rho_B), \tag{54}$$

where the transport coefficients can be identified as

$$D_{AA} = D_{BB} = \frac{D + D^{(r)}}{2}, \tag{55}$$

$$D_{AB} = D_{BA} = \frac{D - D^{(r)}}{2}. \tag{56}$$

The important conclusion is here that there appears a phenomenon of cross diffusion which is induced by the reaction. This phenomenon has been previously found and analyzed in reaction-diffusion models based on the periodic Lorentz gas
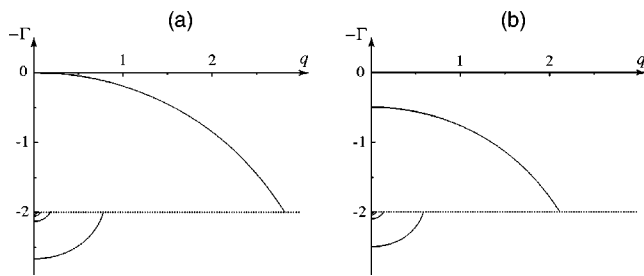
FIG. 2. Eigenvalues $-\Gamma$ versus the wave number $q=\sqrt{q_x^2+q_y^2}$ in the regime $0<p_0 n_r<n/2$ where $c>0$: spectrum of (a) the diffusion sector; (b) the reaction sector. The parameter values are $v=1$, $an=1$, and $p_0 n_r=0.125n$. The spectra are similar up to rescalings of the axes [and a vertical translation in the reaction sector (b)] for the other values of the parameters as long as $0<p_0 n_r<n/2$.

and the multibaker map in Refs. [19–23] where the coupled reaction-diffusion equations (53) and (54) have been obtained by other methods. In the random Lorentz gas, we can use the kinetic theory in order to derive these macroscopic equations and the value of the cross-diffusion coefficients

$$D_{AB}=D_{BA}=-\frac{3vp_0 n_r}{64an(n-p_0 n_r/2)}. \tag{57}$$

We notice that these coefficients vanish with the reaction probability p_0 and the density of catalysts n_r. Accordingly, in the absence of reaction, the cross-diffusion terms vanish with the reaction term and we recover two uncoupled diffusion equations for A and B particles.

The coupled reaction-diffusion equations (53) and (54) can be rewritten as

$$\partial_t \rho_A=-\vec{\nabla}\cdot\vec{J}_A-\kappa(\rho_A-\rho_B), \tag{58}$$

$$\partial_t \rho_B=-\vec{\nabla}\cdot\vec{J}_B+\kappa(\rho_A-\rho_B), \tag{59}$$

in terms of the currents

$$\vec{J}_A=-\frac{D+D^{(r)}}{2}\vec{\nabla}\rho_A-\frac{D-D^{(r)}}{2}\vec{\nabla}\rho_B, \tag{60}$$

$$\vec{J}_B=-\frac{D+D^{(r)}}{2}\vec{\nabla}\rho_B-\frac{D-D^{(r)}}{2}\vec{\nabla}\rho_A, \tag{61}$$

which shows that the current of one species is influenced by the gradient of the other species because of the chemical reaction.

In addition to the diffusive and reactive slowest modes, we also find faster modes often referred to as kinetic modes. All these modes exist in both the diffusion sector ruled by Eq. (23) for $X=f$ and in the reaction sector ruled by Eq. (23) for $X=h$. All these modes are characterized by dispersion relations which form a whole spectrum. Figure 2 depicts the whole spectra of the diffusion and reaction sectors in the case $0<p_0 n_r<n/2$.

B. The case $p_0 n_r=n/2$

In this case, we remark that Eq. (23) for $X=h$ has a vanishing coefficient $c=0$ in the reaction sector so that the equation for $X=h$ is purely advective,

$$\partial_t h+\vec{v}\cdot\vec{\nabla}h=0. \tag{62}$$

Its solutions are given by $h=h(\vec{r}-\vec{v}t)$, and $g=e^{-2\kappa t}h(\vec{r}-\vec{v}t)$ obeys

$$\partial_t g+\vec{v}\cdot\vec{\nabla}g=-2\kappa g. \tag{63}$$

In this case, there is no reactive diffusion coefficient that characterizes the reactive process.

C. The case $n/2<p_0 n_r<n$

As we noticed before, $p_0 n_r$ cannot exceed the value n for consistency. In this case, we have that Eq. (23) for $X=f$ still has a coefficient $c>0$ in the diffusion sector but Eq. (23) for $X=h$ has a negative coefficient $c<0$ in the reaction sector. Accordingly, the spectrum shown in Fig. 1 is upside down in the reaction sector and the slowest reactive mode is no longer the same as before.

Here, we must consider the decay rate (30) with $l=1$. The dispersion relation of the reactive mode is now given by

$$\Gamma=2\kappa'+D^{(r)'}q^2, \tag{64}$$

with the new reaction constant

$$\kappa'=\frac{2av}{3}(2n-p_0 n_r), \tag{65}$$

and the new reactive diffusion coefficient

$$D^{(r)'}=\frac{9v}{16a(2p_0 n_r-n)}. \tag{66}$$

The reaction-diffusion equations (53) and (54) still hold in this case. The coefficients (55) and (56) are still given by the diffusion coefficient D of Eq. (46) but the reaction-diffusion coefficient $D^{(r)}$ should now be replaced by its new value (66). Furthermore, the reaction rate κ should be replaced by the new value (65).

Figure 3 depicts the spectra in the diffusion and reaction sectors in the case $n/2<p_0 n_r<n$. With respect to Fig. 2, the spectrum is unchanged in the diffusion sector but upside down in the reaction sector.

Therefore, a transition occurs at the critical value $p_0 n_r=n/2$ and a different regime exists for high concentrations n_r of catalysts and high values of the reaction probability p_0. In this new regime, the frequency of reactive events becomes of the same order of magnitude as the collision frequency so that the isomerizations $A\rightleftharpoons B$ are nearly as frequent as the elastic collisions. This deeply affects the way the reaction proceeds and, thus, modifies both the reaction rate and the reactive diffusion coefficient. We can no longer speak of diffusion-controlled reaction as in the case $0<p_0 n_r<n/2$ of Sec. III A where diffusive paths composed of many successive elastic collisions on inert disks separate the consecutive encounters with the catalytic disks. In contrast, in the case
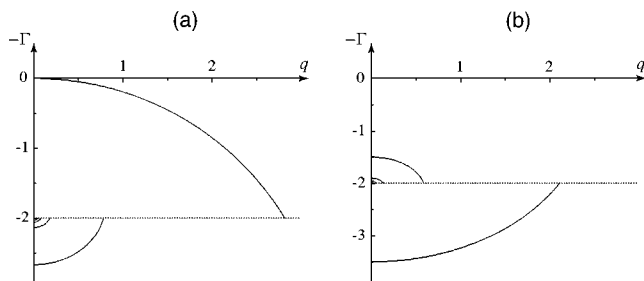
FIG. 3. Eigenvalues $-\Gamma$ versus the wave number $q=\sqrt{q_x^2+q_y^2}$ in the regime $n/2<p_0 n_r<n$ where $c>0$: spectrum of (a) the diffusion sector; (b) the reaction sector. The parameter values are $v=1$, $an=1$, and $p_0 n_r=0.875n$. The spectra are similar up to rescalings of the axes [and a vertical translation in the reaction sector (b)] for the other values of the parameters as long as $n/2<p_0 n_r<n$.

$n/2<p_0 n_r<n$ of the present subsection, the catalytic disks are more numerous than the inert disks so that the moving particle can very often have a ballistic flight between two consecutive encounters with catalytic disks. As a consequence, the reaction is controlled by the local dynamics between next-neighboring disks. This dynamics is supposed to be described by the eigenvalues of the Boltzmann-Lorentz equation which have the largest rates and correspond to the shortest time scales. These eigenvalues are found at the bottom of the spectrum of the diffusion sector in Fig. 3(a). Since the dynamics on short time scales controls the reaction, we thus find these eigenvalues at the top of the spectrum of the reaction sector in Fig. 3(b). This explains that the spectrum in Fig. 3(b) looks upside down with respect to the one in Fig. 3(a). The preceding reasoning also suggests that corrections beyond the approximation given by the coupled Boltzmann-Lorentz equations (4) and (5) could become important as $p_0 n_r \rightarrow n$.

In the following, we shall focus on the case $0<p_0 n_r<n/2$ where the catalysts are dilute enough.

IV. THE ENTROPY BALANCE

In this section, we derive the equation for the balance of entropy from the H theorem in two approximations for the entropy density. In kinetic theory, we have a well-defined expression for the entropy which guarantees that the entropy production is always non-negative. However, at the level of the macroscopic description given by the reaction-diffusion equations (53) and (54), the entropy is given as an approximation of the expression (12) of kinetic theory and we must verify the domain of validity where the corresponding entropy production is non-negative.

The first approximation we consider is based on the standard phenomenological entropy defined in irreversible thermodynamics of reaction processes [24,25]. We show that the corresponding entropy production is non-negative in a broad range of values for the densities ρ_A and ρ_B including the thermodynamic equilibrium state but there is a small domain where the entropy production corresponding to this approximation fails to remain non-negative.

Therefore, we consider a second approximation which includes extra terms involving the gradient of the densities. We

show that the corresponding entropy production always remains non-negative.

A. Entropy without gradients

Supposing that the system is sufficiently dilute, the phenomenological irreversible thermodynamics supposes that the entropy density has the following expression:

$$s = \rho_A \ln \frac{\rho^0}{\rho_A} + \rho_B \ln \frac{\rho^0}{\rho_B}. \tag{67}$$

This entropy density is obtained from the entropy (12) of kinetic theory by using the expansions (38) and (39) of the distribution functions and by keeping the terms in the densities themselves and discarding terms in the gradients. The reference density is thus given by $\rho^0=2\pi f^0$, which amounts to supposing equality of the masses of the particles A and B.

The variation of the entropy density s in time is given by the balance equation

$$\partial_t s = -\vec{\nabla} \cdot \vec{J}_s + \sigma_s, \tag{68}$$

here calculated by using the coupled reaction-diffusion equations (58) and (59). The entropy current density is obtained in terms of the currents (60) and (61) of particles A and B as

$$\vec{J}_s = \vec{J}_A \ln \frac{\rho^0}{e\rho_A} + \vec{J}_B \ln \frac{\rho^0}{e\rho_B}, \tag{69}$$

while the entropy production takes the form

$$\sigma_s = \kappa(\rho_A - \rho_B)\ln \frac{\rho_A}{\rho_B} - \vec{J}_A \cdot \frac{\vec{\nabla}\rho_A}{\rho_A} - \vec{J}_B \cdot \frac{\vec{\nabla}\rho_B}{\rho_B}. \tag{70}$$

In order to obtain an expression that is quadratic in the currents, we invert Eqs. (60) and (61) and obtain the gradients in terms of the currents as

$$\vec{\nabla}\rho_A = -\frac{\vec{J}_A}{D} + \frac{2\kappa}{3v^2}(\vec{J}_A - \vec{J}_B), \tag{71}$$

$$\vec{\nabla}\rho_B = -\frac{\vec{J}_B}{D} - \frac{2\kappa}{3v^2}(\vec{J}_A - \vec{J}_B). \tag{72}$$

Substituting in the entropy production (70), we get

$$\sigma_s = \kappa(\rho_A - \rho_B)\ln \frac{\rho_A}{\rho_B} + \alpha\vec{J}_A^2 + 2\beta\vec{J}_A \cdot \vec{J}_B + \gamma\vec{J}_B^2, \tag{73}$$

with the coefficients

$$\alpha = \frac{1}{\rho_A}\left(\frac{1}{D} - \frac{2\kappa}{3v^2}\right), \tag{74}$$

$$\beta = \frac{\kappa}{3v^2}\left(\frac{1}{\rho_A} + \frac{1}{\rho_B}\right), \tag{75}$$

$$\gamma = \frac{1}{\rho_B}\left(\frac{1}{D} - \frac{2\kappa}{3v^2}\right). \tag{76}$$

The first term in the entropy production (73) is always non-negative because $(x-y)\ln(x/y) \geq 0$ for all positive values of the real numbers x and y. On the other hand, the last terms constitute a quadratic form which is non-negative under the conditions that $\beta^2 - \alpha\gamma < 0$ with $\alpha > 0$ and $\gamma > 0$. With the diffusion coefficient (46) and the reaction rate (50), we can check that

$$\alpha = \frac{4a}{3v\rho_A}(4n - p_0 n_r) > 0, \qquad (77)$$

$$\gamma = \frac{4a}{3v\rho_B}(4n - p_0 n_r) > 0, \qquad (78)$$

because of the consistency condition (22). Next, the condition $\beta^2 - \alpha\gamma < 0$ is given by

$$\xi^2 + 2\left[1 - 2\left(\frac{2}{y} - 1\right)^2\right]\xi + 1 < 0, \qquad (79)$$

in terms of the density ratio

$$\xi \equiv \frac{\rho_B}{\rho_A} \qquad (80)$$

and the parameter

$$y \equiv \frac{p_0 n_r}{2n} = \frac{4\kappa D}{3v^2}. \qquad (81)$$

The roots $\xi_\pm$ of Eq. (79) satisfy $\xi_+ = 1/\xi_-$. If $\xi_+ \geq \xi_-$, the entropy production is thus non-negative in the domain

$$\xi_+ \rho_A \geq \rho_B \geq \xi_- \rho_A. \qquad (82)$$

It turns out that the sum of the roots

$$\xi_+ + \xi_- = 2\left[2\left(\frac{2}{y} - 1\right)^2 - 1\right] \qquad (83)$$

is always positive in the interval $0 < y < \frac{1}{2}$ where the condition of consistency (22) is verified. (The sum $\xi_+ + \xi_-$ is negative only in the interval $4 - 2\sqrt{2} = 1.1715\ldots < y < 4 + 2\sqrt{2} = 6.8284\ldots$ outside the domain of consistency.) Since ξ_+ and ξ_- have the same sign, they both are positive in the consistency domain $0 < y < \frac{1}{2}$, which means that there exists a domain of the quadrant $(\rho_A \geq 0, \rho_B \geq 0)$ where the entropy production (73) can be negative. This domain is composed of $\xi_- \rho_A > \rho_B \geq 0$ and $\xi_- \rho_B > \rho_A \geq 0$. Another way of saying it is that the domain (82) where the entropy production is non-negative is smaller than the quadrant $(\rho_A \geq 0, \rho_B \geq 0)$ of all the possible densities ρ_A and ρ_B. The domain of non-negativity extends to

$$1441.9\ldots \rho_A \geq \rho_B \geq 0.000\,693\,48\ldots\rho_A \quad \text{for } y = 0.1, \qquad (84)$$

to

$$321.99\ldots \rho_A \geq \rho_B \geq 0.003\,105\,6\ldots\rho_A \quad \text{for } y = 0.2, \qquad (85)$$

and to

$$33.970\ldots \rho_A \geq \rho_B \geq 0.029\,437\ldots\rho_A \quad \text{for } y = 0.5. \qquad (86)$$

It is only in the limit $y=0$ without chemical reaction that the domain of non-negativity coincides with the quadrant $(\rho_A \geq 0, \rho_B \geq 0)$. In the presence of the chemical reaction, the situation is unsatisfactory because the scheme is not consistent with the second law of thermodynamics even if the domain of negative entropy production is small and only concerns color densities that are very far from the thermodynamic equilibrium. If the reaction-diffusion equations (53) and (54) had no cross-diffusion terms, this problem would not happen and the standard entropy would have a non-negative production. However, the cross-diffusion terms are well established by the kinetic theory in Sec. III and by previous work [19–23]. Moreover, the H theorem proved in Sec. II A shows that there is no problem with entropy production at the level of kinetic theory. This suggests that the phenomenological entropy (67) has shortcomings and that a better approximation should be obtained from the full entropy (12) of kinetic theory.

B. Entropy with gradients

To cure the problem reported above, we thus choose to expand the entropy (12) of kinetic theory to include terms with the gradients of the densities. For this purpose, we substitute the expansions (38) and (39) of the distribution functions in the entropy (12) and we truncate up to the terms that are quadratic in the currents to get

$$s = \rho_A \ln\frac{\rho^0}{\rho_A} + \rho_B \ln\frac{\rho^0}{\rho_B} - \frac{1}{v^2}\left(\frac{\vec{J}_A^2}{\rho_A} + \frac{\vec{J}_B^2}{\rho_B}\right), \qquad (87)$$

where the particle currents are given in terms of the density gradients according to Eqs. (60) and (61). Accordingly, the entropy (87) is quadratic in the density gradients.

Here again, we calculate the time variation of the entropy density s by using the coupled reaction-diffusion equations (58) and (59). The balance equation for entropy is here also given by

$$\partial_t s = -\vec{\nabla} \cdot \vec{J}_s + \sigma_s, \qquad (88)$$

with an entropy current similar to Eq. (69),

$$\vec{J}_s = \vec{J}_A \ln\frac{\rho^0}{e\rho_A} + \vec{J}_B \ln\frac{\rho^0}{e\rho_B} + O(3), \qquad (89)$$

up to the terms $O(3)$ of third order in the gradients. However, the entropy production now takes the more complicated form

$$\sigma_s = \kappa(\rho_A - \rho_B)\ln\frac{\rho_A}{\rho_B} - \vec{J}_A \cdot \frac{\vec{\nabla}\rho_A}{\rho_A} - \vec{J}_B \cdot \frac{\vec{\nabla}\rho_B}{\rho_B} + \frac{2\kappa}{v^2}(\vec{J}_A - \vec{J}_B) \cdot \left(\frac{\vec{J}_A}{\rho_A} - \frac{\vec{J}_B}{\rho_B}\right) - \frac{\kappa}{v^2}(\rho_A - \rho_B)\left(\frac{\vec{J}_A^2}{\rho_A^2} - \frac{\vec{J}_B^2}{\rho_B^2}\right) + O(4), \qquad (90)$$

where $O(4)$ denotes terms of fourth order in the gradients.

Replacing the gradients by the currents with Eqs. (71) and (72), we obtain

$$\sigma_s = \kappa(\rho_A - \rho_B)\ln\frac{\rho_A}{\rho_B} + \frac{1}{D}\left(\frac{\vec{J}_A^2}{\rho_A} + \frac{\vec{J}_B^2}{\rho_B}\right) + \frac{4\kappa}{3v^2}(\vec{J}_A - \vec{J}_B)$$

$$\cdot\left(\frac{\vec{J}_A}{\rho_A} - \frac{\vec{J}_B}{\rho_B}\right) - \frac{\kappa}{v^2}(\rho_A - \rho_B)\left(\frac{\vec{J}_A^2}{\rho_A^2} - \frac{\vec{J}_B^2}{\rho_B^2}\right) + O(4), \quad (91)$$

or equivalently

$$\sigma_s = \kappa(\rho_A - \rho_B)\ln\frac{\rho_A}{\rho_B} + \alpha\vec{J}_A^2 + 2\beta\vec{J}_A \cdot \vec{J}_B + \gamma\vec{J}_B^2 + O(4), \quad (92)$$

with the coefficients

$$\alpha = \frac{1}{\rho_A}\left(\frac{1}{D} + \frac{\kappa}{3v^2} + \frac{\kappa\rho_B}{v^2\rho_A}\right), \quad (93)$$

$$\beta = -\frac{2\kappa}{3v^2}\left(\frac{1}{\rho_A} + \frac{1}{\rho_B}\right), \quad (94)$$

$$\gamma = \frac{1}{\rho_B}\left(\frac{1}{D} + \frac{\kappa}{3v^2} + \frac{\kappa\rho_A}{v^2\rho_B}\right). \quad (95)$$

The coefficients α and γ are always positive, while the condition $\beta^2 - \alpha\gamma < 0$ of non-negativity of the quadratic form is here given by

$$\xi^2 + 2\frac{(y+2)^2+4}{y(12-y)}\xi + 1 > 0, \quad (96)$$

with the ratio ξ defined by Eq. (80) and the parameter $0 < y < \frac{1}{2}$ by Eq. (81). The opposite inequality is obtained compared to Eq. (79) because the dependence on the ratio ξ is here more complicated but still simple enough to lead to the quadratic equation (96). In the physical domain $0 < y < \frac{1}{2}$, the roots ξ_+ and $\xi_- = 1/\xi_+$ of Eq. (96) are real and negative because

$$\xi_+ + \xi_- = -2\frac{(y+2)^2+4}{y(12-y)} < 0. \quad (97)$$

Accordingly, Eq. (96) holds for any $\xi > 0$ where $\xi = \rho_B/\rho_A$. As a consequence, the quadratic part of the entropy production (92) is non-negative in the quadrant of all the physically allowed densities where $\rho_A \geq 0$ and $\rho_B \geq 0$. If the gradients of densities are small enough so that the corrections of fourth order in Eq. (92) are negligible, the whole entropy production (92) is also non-negative.

We have thus proved that the inclusion of the gradient terms in the entropy avoids the aforementioned problem and guarantees that the entropy production remains non-negative for all the values of the color densities if the gradients are sufficiently small.

C. Interpretation of the gradient terms in the entropy

The entropy density given by Eq. (87) can be expressed as follows in terms of the gradients of the particle densities by using Eqs. (60) and (61):

$$s = \rho_A \ln\frac{\rho^0}{\rho_A} + \rho_B \ln\frac{\rho^0}{\rho_B} - \frac{K_{AA}}{2}(\vec{\nabla}\rho_A)^2 - K_{AB}\vec{\nabla}\rho_A \cdot \vec{\nabla}\rho_B$$

$$- \frac{K_{BB}}{2}(\vec{\nabla}\rho_B)^2, \quad (98)$$

with the coefficients

$$K_{AA} = \frac{(D+D^{(r)})^2}{2v^2\rho_A} + \frac{(D-D^{(r)})^2}{2v^2\rho_B}, \quad (99)$$

$$K_{BB} = \frac{(D+D^{(r)})^2}{2v^2\rho_B} + \frac{(D-D^{(r)})^2}{2v^2\rho_A}, \quad (100)$$

$$K_{AB} = \frac{(D+D^{(r)})(D-D^{(r)})}{2v^2}\left(\frac{1}{\rho_A} + \frac{1}{\rho_B}\right), \quad (101)$$

which are independent of the velocity v.

The gradient terms are of the same kind as those appearing in the Ginzburg-Landau free energy. Here, they appear in the entropy with the opposite sign in agreement with the required thermodynamic stability of the equilibrium state [28,29]. Indeed, the entropy must be maximal in a stable equilibrium state. This is the case since the quadratic form in Eq. (87) or (98) is negative. Accordingly, the entropy reaches a maximum at the equilibrium state where the gradients and the currents vanish.

The gradient terms are responsible for statistical correlations between the particles. Indeed, the entropy density (98) can be used to define the entropy functional

$$S[\rho_A, \rho_B] = \int s \, d\vec{r}, \quad (102)$$

and the probability distribution for statistical average given by the functional integrals

$$\langle\mathcal{O}\rangle_{eq} = \frac{\displaystyle\int \mathcal{D}\rho_A \mathcal{D}\rho_B \mathcal{O} \exp\{(1/k_B)S[\rho_A,\rho_B]\}}{\displaystyle\int \mathcal{D}\rho_A \mathcal{D}\rho_B \exp\{(1/k_B)S[\rho_A,\rho_B]\}} \quad (103)$$

for an observable $\mathcal{O}$. This allows us to calculate the correlation functions of the particle densities at the thermodynamic equilibrium. We consider the correlation functions of the densities (32) and (33):

$$C_{++}(\vec{r}) \equiv \langle\rho_+(\vec{r})\rho_+(0)\rangle_{eq} - \langle\rho_+\rangle_{eq}^2, \quad (104)$$

$$C_{--}(\vec{r}) \equiv \langle\rho_-(\vec{r})\rho_-(0)\rangle_{eq} - \langle\rho_-\rangle_{eq}^2, \quad (105)$$

$$C_{+-}(\vec{r}) \equiv \langle\rho_+(\vec{r})\rho_-(0)\rangle_{eq} - \langle\rho_+\rangle_{eq}\langle\rho_-\rangle_{eq}, \quad (106)$$

where $\langle\rho_+\rangle_{eq} = \rho_{eq} = (2/e)\rho^0$ and $\langle\rho_-\rangle_{eq} = 0$. Partial differential equations can be obtained for these correlation functions by the variational principle $\delta S = 0$ based on the entropy functional (98) evaluated around the thermodynamic equilibrium

$$s \simeq s_{\text{eq}} - \frac{(\rho_+ - \rho_{\text{eq}})^2 + \rho_-^2}{2\rho_{\text{eq}}} - \frac{K_{++,\text{eq}}}{2}(\vec{\nabla}\rho_+)^2 - \frac{K_{--,\text{eq}}}{2}(\vec{\nabla}\rho_-)^2.$$

(107)

The coefficients are given by $s_{\text{eq}} = \rho_{\text{eq}}$ and

$$K_{++,\text{eq}} = \frac{1}{4}(K_{AA} + K_{BB} + 2K_{AB})_{\text{eq}} = \frac{2D^2}{v^2\rho_{\text{eq}}}, \qquad (108)$$

$$K_{--,\text{eq}} = \frac{1}{4}(K_{AA} + K_{BB} - 2K_{AB})_{\text{eq}} = \frac{2D^{(\text{r})2}}{v^2\rho_{\text{eq}}}, \qquad (109)$$

$$K_{+-,\text{eq}} = \frac{1}{4}(K_{AA} - K_{BB})_{\text{eq}} = 0. \qquad (110)$$

We notice that the vanishing of the coefficient (110) implies that there is no cross term in the gradients of $\rho_\pm$ in Eq. (107). The fluctuations described by Eq. (103) are Gaussian around the equilibrium since the entropy density (107) is quadratic. As a consequence, the correlation functions obey the equations

$$\left(\nabla^2 - \frac{1}{\ell_+^2}\right)C_{++}(\vec{r}) = 0, \qquad (111)$$

$$\left(\nabla^2 - \frac{1}{\ell_-^2}\right)C_{--}(\vec{r}) = 0 \qquad (112)$$

for $\vec{r} \neq \vec{0}$ and with the correlation lengths

$$\ell_+ \equiv \sqrt{\rho_{\text{eq}}K_{++,\text{eq}}} = \frac{3\sqrt{2}}{16an}, \qquad (113)$$

$$\ell_- \equiv \sqrt{\rho_{\text{eq}}K_{--,\text{eq}}} = \frac{3\sqrt{2}}{16a(n - p_0 n_r/2)}, \qquad (114)$$

and $C_{+-}(\vec{r}) = 0$. These correlation lengths are of the order of the mean free path of the particles between the scatterers of radius a and density n. The correlation functions are given by Bessel functions of zeroth order and they behave at long distance as

$$C_{\pm\pm}(\vec{r}) \sim \frac{1}{\sqrt{r}} \exp\left(-\frac{r}{\ell_\pm}\right), \qquad (115)$$

with $r = \sqrt{x^2 + y^2}$. The difference between these correlation functions characterizes the statistical correlations between the densities of particles A and B. The fact that the correlation lengths take different values, $\ell_+ \neq \ell_-$, means that the statistical correlations between the species A and B are nontrivial. A definition of entropy consistent with the second law of thermodynamics should thus take into account the effects of such statistical correlations in the phenomenon of cross diffusion induced by the chemical reaction.

V. CONCLUSIONS

In this paper, we have studied a reactive random Lorentz gas in which a point particle carrying a color A or B (or a

spin one-half) bounces among randomly distributed disk scatterers. Some of these disks are catalytic in the sense that the reaction $A \rightleftharpoons B$ occurs with a given probability p_0 upon collision with these catalytic disks. In the case of a particle with a spin, the catalytic disks correspond to impurities flipping the spin. Under dilute-gas conditions, the time evolution of the distribution functions of finding the particle with a given color or spin at some position $\vec{r}$ with some velocity $\vec{v}$ are ruled by two coupled Boltzmann-Lorentz kinetic equations which satisfy an H theorem. The H quantity defines the entropy at the kinetic level of description.

The time evolution separates into a diffusion sector for the total distribution function and a reaction sector for the difference of the distribution functions of the colors. The spectrum of eigenmodes of both sectors can be constructed in detail. The diffusive (reactive) modes are the slowest modes among all the modes of the diffusion (reaction) sector, which provides us with the diffusion coefficient of the diffusive mode, as well as the reaction rate constant and the reactive diffusion coefficient of the reactive mode. This analysis and the knowledge of these coefficients allow us to obtain the macroscopic reaction-diffusion equations. These equations present cross-diffusion terms which are induced by the reaction if the reaction probability p_0 is not vanishing, as in previous studies of the reactive periodic Lorentz gas and multibaker models [19–23]. In the reactive random Lorentz gas, our analysis shows that a transition happens in the reaction sector between a regime at low concentrations of catalytic disks and reaction probabilities and another one at high concentrations and probabilities.

Using the derivation of the macroscopic reaction-diffusion equations, we have studied the problem of the entropy production on the basis of the entropy defined in kinetic theory in terms of the distribution functions and the associated H theorem. The entropy of kinetic theory can be expanded in powers of the gradients of the densities of both colors A and B. At the lowest order of this expansion, the entropy density is simply a function of the color densities themselves and coincides with the expression of the phenomenological nonequilibrium thermodynamics [24,25]. The balance equation of this entropy without gradient can be derived from the macroscopic reaction-diffusion equations. Because of the cross-diffusion effects induced by the reaction, the resulting entropy production may become negative for extreme values of the ratio between the color densities. This is certainly a problem of principle for the phenomenological approach. In order to solve this problem, we have considered the entropy density at the next order of the expansion in the gradients of color densities. At this next order, the entropy density contains terms that are quadratic in the gradients in addition to the contribution of the phenomenological entropy. The balance equation of this entropy with gradients turns out to have an entropy production that is non-negative for all the color densities and for small enough gradients of color densities, in consistency with the second law of thermodynamics.

The entropy density with gradients is interpreted as the entropic version of the Ginzburg-Landau free energy. The addition of gradient terms is shown to be responsible for statistical correlations in the densities of the colors A and B

over spatial scales of the order of the mean free path of the particle. The consideration of these spatial correlations appears to be necessary to get a non-negative entropy production in the presence of chemically induced cross diffusion. The inclusion of these gradients in the entropy is justified by the kinetic theory and by the consistency so obtained with the second law of thermodynamics. Such an entropy functional with gradients is also justifed by analogy with the Ginzburg-Landau free energy [28,29]. The inclusion of gradients in the entropy requires a departure from the classical Onsager-Prigogine nonequilibrium thermodynamics [24,25]. This classical nonequilibrium thermodynamics neglects the possible interplay between the diffusion and the reaction, such as the cross diffusion induced by the chemical reaction. This effect is expected in systems with a high reaction probability and high concentrations of reactants with respect to the inert species which do not participate in the reaction. We think that the present work clearly shows that this chemically induced cross diffusion is compatible with kinetic theory and the second law of thermodynamics and should be an experimentally observable effect.

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