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Escape-Rate Formalism, Decay to Steady States, and Divergences in the Entropy-Production Rate

Jürgen Vollmer,[1] László Mátyás,[2] and Tamás Tél[3]

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According to thermodynamics the irreversible entropy production of diffusive relaxation processes diverges at the boundary to the vacuum, i.e., to a state of vanishing particle density. By means of a multibaker map we point out that this divergence is not present in the spatially discrete dynamics, which brings forth the evolution equations of irreversible thermodynamics in the continuum limit. In addition, we show that the irreversible entropy production of relaxation towards a nonempty steady state is proportional to the decay rate of the thermodynamic system subjected to absorbing boundary conditions. This generalizes results of the escape rate formalism.

KEY WORDS: Entropy production; deterministic chaos; absorbing boundary condition; escape-rate formalism; multibaker maps.

1. INTRODUCTION

In summer 1997 we were sitting with Bob Dorfman and a few other friends interested in chaotic systems and transport theory on a terrace close to Oktogon in Budapest. While taking our (decaf) coffee after a very nice Italian meal, we discussed about the logarithmic divergences in the entropy production of systems with absorbing boundary conditions. It was guessed at that time that the problem could be resolved by a careful investigation of

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[1] Max–Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany; e-mail: vollmer@mpip-mainz.mpg.de

[2] Institute for Theoretical Physics, Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary; and Max–Planck-Institute for the Physics of Complex Systems, Nöthnitzer Str. 38, 01187 Dresden, Germany.

[3] Institute for Theoretical Physics, Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary.

the physical interpretation of the absorbing boundary conditions. To our knowledge a thorough analysis of this problem is still missing. We dedicate it hereby to Bob on occasion of his 65th birthday.

The discussion was motivated by our joint interest in the *escape-rate formalism*,(1–4) which identifies transport coefficients based on the asymptotic decay rate of an initial non-stationary density profile towards an empty steady state selected by absorbing boundary conditions, i.e., for systems where eventually all particles disappear. In this formulation the relaxation problem has widely been studied in the context of Markov chains (cf. the sections on *survival probabilities* in ref. 5, and on *absorbing states* in ref. 6), as well as for deterministic chaotic systems.(7–9) However the choice of an empty asymptotic state places severe constrains on the use of absorbing boundary conditions in the calculation of the thermodynamic entropy production. In particular, the thermodynamic entropy production picks up logarithmically diverging boundary contributions when applying the diffusion equation near the boundary. The vanishing of the density leads then to the breakdown of the concept of an entropy-production density in the framework of classical irreversible thermodynamics. Close to a boundary at $x = 0$ the absorbing boundary condition requires a density profile of the form $\rho(x) = \alpha x$. For purely diffusive particle transport, a neighborhood of size Δ gives then rise to the entropy production[4]

$$\Sigma^{(\mathrm{irr})}(\Delta) \equiv \int_0^{0+\Delta} \mathrm{d}x\, D \left(\frac{\partial_x \rho}{\rho} \right)^2 \rho = D\alpha \lim_{\delta \to 0} \ln \frac{\Delta}{\delta}. \tag{1}$$

In the present paper this logarithmic divergence of the thermodynamic entropy production will be discussed from the point of view of spatially extended chaotic systems whose transport properties fully agree with the predictions of irreversible thermodynamics. The microscopic dynamics of the system with absorbing boundaries is physically well behaved, and it gives rise to a mesoscopic description where the thermodynamic densities in small but finite volumes evolve according to master equations. In this setting it is demonstrated that the mesoscopic description does not involve diverging contributions to the (discrete) entropy balance. The divergences only appear in the continuum limit where the master equation is approximated by an advection diffusion equation. Consequently, the diverging terms in the entropy balance reflect the breakdown of the continuum description at locations where the particle density vanishes. We are confident that this picture applies in general. However, to keep the calculations

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[4] The Boltzmann constant is taken to be unity throughout this paper.

as transparent as possible, the discussion is given for isothermal multibaker maps. The possibility for explicit results allows us in that case to also revisit earlier results based on conditionally invariant measures characterizing their chaotic dynamics, and to discuss how the various findings change upon introducing a finite background density.

In Section 2, Eq. (1) is contrasted with the prediction of the irreversible changes in an entropy based on the conditional density characterizing the chaotic saddle forming the backbone of transport in open dynamical systems. This prediction always yields finite values. The isothermal multibaker map is introduced in Section 3, where its entropy balance is also worked out. Section 4 deals with the normal modes of the coarse-grained time evolution. This allows us to address in Section 5 the origin of the logarithmic divergences in the entropy production from the point of view of the multibaker map. The analysis makes use of the eigenvalues of the time-evolution operator,(4, 10) which does not depend on the nature of the asymptotic state. To underline this observation, we also discuss asymptotic states with uniform nonzero densities, and point out that the presence of an arbitrarily small background density in the asymptotic case turns the irreversible entropy production to be finite, but different from the prediction based on the conditional density. In the concluding Section 6 these findings are complemented by a discussion of the behavior of the entropy production in systems relaxing towards a typical steady state of finite density as compared to the case of small (or even vanishing) background densities addressed in the main part.

2. ENTROPY PRODUCTION BASED ON CONDITIONAL INVARIANT MEASURES REVISITED

One of the early studies of irreversible entropy production in deterministic dynamical systems was based on the escape-rate formalism introduced by Gaspard and Nicolis.(1) As a generalization of it, Breymann, Tél and Vollmer(3) considered open dissipative dynamical systems in continuous time. To characterize their irreversible features, they suggested to use the entropy

$$s(t) = -\int \mathrm{d}x\, \psi^{(t)}(x) \ln \psi^{(t)}(x) \tag{2}$$

based on the *normalized conditional phase-space density* $\psi^{(t)}(x)$, describing the probability to find a point which has not yet escaped the system by time t at phase-space coordinate x. Because $\psi^{(t)}(x)$ is a single-particle property, $s(t)$ can be considered as a specific entropy (total entropy per number of particles). The initial condition is selected from an arbitrary *smooth* distribution $\psi^{(0)}(x)$. As time goes on, the phase-space volume of $\psi^{(t)}$ is exponentially shrinking as $\exp[-\varsigma(x)\,t]$, where the local phase-space contraction rate $\varsigma(x)=\sum\lambda_i(x)-\kappa$ is a smooth function of the coordinates.$^{(7)}$ Here, κ is the escape rate from the system, and $\lambda_i(x)$ are the local Lyapunov exponents in the independent directions i in phase space (cf. refs. 7 and 8 for detailed discussions of conditional invariant densities and Lyapunov exponents). On its support the value of the conditional density $\psi^{(t)}(x)$ is exponentially increasing due to its normalization. More precisely, it increases like $\psi^{(t+\mathrm{dt})}(x)=\exp[\varsigma(x)\,\mathrm{dt}]\,\psi^{(t)}(x)\,\chi^{(t+\mathrm{dt})}(x)$, where $\chi^{(t+\mathrm{dt})}$ is the characteristic function of the support at time $t+\mathrm{dt}$. The entropy $s(t+\mathrm{dt})$ at time $t+\mathrm{dt}$ can be determined by inserting this relation into Eq. (2):

$$s(t+\mathrm{dt}) = -\mathrm{dt}\int \mathrm{dx}\,\varsigma(x)\,\psi^{(t)}(x)\,e^{\varsigma(x)\,\mathrm{dt}}\chi^{(t+\mathrm{dt})}(x)$$

$$-\int \mathrm{dx}\,\psi^{(t)}(x)\ln\left[\psi^{(t)}(x)\,\chi^{(t+\mathrm{dt})}(x)\right]e^{\varsigma(x)\,\mathrm{dt}}\chi^{(t+\mathrm{dt})}(x). \tag{3}$$

In both integrals the decrease of the support of ψ is counterbalanced by the factor $\exp[\varsigma(x)\,\mathrm{dt}]$. The first integral is the phase-space average $\bar{\varsigma}$ of $\varsigma(x)$. For $\mathrm{dt}\to 0$ the second one tends to the specific entropy $s(t)$ at time t. Hence, in the long-time limit the time derivative of the entropy

$$\frac{ds}{dt} = -\bar{\varsigma} = \sum_i \bar{\lambda}_i - \kappa, \tag{4}$$

is the difference of the sum of the average Lyapunov exponents $\bar{\lambda}_i$ on the saddle, and the escape rate κ from the saddle. The average is taken with respect to the density $\psi(x)$ of the conditionally-invariant measure. This measure is time independent. Its support is the unstable manifold of the chaotic saddle, i.e., the union of the never escaping orbits in the system. The fact that the time derivative of s approaches a constant reflects the ever refining fractal structures in the density due to the chaoticity of the dynamics.

We now compare $s(t)$ with a coarse-grained entropy $s^{(\mathrm{cg})}(t)$ computed in an analogous way from a coarse-grained conditional density $\psi^{(\mathrm{cg})}(x;t)$, which—in contrast to ψ—converges towards a smooth stationary distribution.

The specific irreversible entropy production (irreversible entropy production per particle) is then obtained as (cf. ref. 3)

$$P^{(\mathrm{irr})} \equiv \frac{d}{dt}\left[s^{(\mathrm{cg})}(t) - s(t)\right] \xrightarrow{\text{long times}} \kappa - \sum_i \bar{\lambda}_i. \tag{5}$$

$P^{(\mathrm{irr})}$ is a specific quantity since s is specific, too. It measures the lack of information on the microscopic state due to the finite resolution of the coarse-grained description.

In systems with a reversible dynamics the phase-space contraction is proportional to the average displacement of particles in the direction of an applied field.(11–16) Consequently, in any open system with reversible dynamics the sum of the average Lyapunov exponents on the chaotic saddle is zero since the average number of steps in the direction of positive phase-space contraction is the same as in the opposite. Therefore, its specific irreversible entropy production amounts to the escape rate,

$$P^{(\mathrm{irr})} = \kappa. \tag{6}$$

In the following we revisit this argument in the light of recent developments(13, 17) dealing with general steady and nonsteady states rather than only the decay to asymptotic states. We work out the irreversible entropy production for an isothermal multibaker map with reversible microscopic dynamics subjected to absorbing boundary conditions.

3. THE ISOTHERMAL MULTIBAKER MAP

Multibaker maps model particle transport in spatially extended systems by a chain of mutually interrelated baker maps.(13, 14, 17–24) They consist of N identical cells of width a and height 1 (the phase-space) in the (x, p) plane. The cells are labeled by the index m (Fig. 1a). After each time unit τ, every cell is divided into three columns (Fig. 1b). Here we consider the case when the right (left) column of width ar (al) is mapped onto a strip of width a and of height l (r) in the right (left) neighboring cell. The middle one, which is of width as, preserves its area, such that its image attains a height s, and $r + l + s = 1$. There are more general parameter settings conceivable, but earlier work(13, 16, 17) showed that the associated macroscopic behavior is then not compatible with irreversible thermodynamics.

The dynamics of the multibaker map models a microscopic dynamics described in the single-particle phase space. It is deterministic, invertible, chaotic, and mixing.(15, 25) To describe irreversible processes one follows the coarse-grained densities ρ_m obtained by averaging over the cells.(13, 14, 17) To

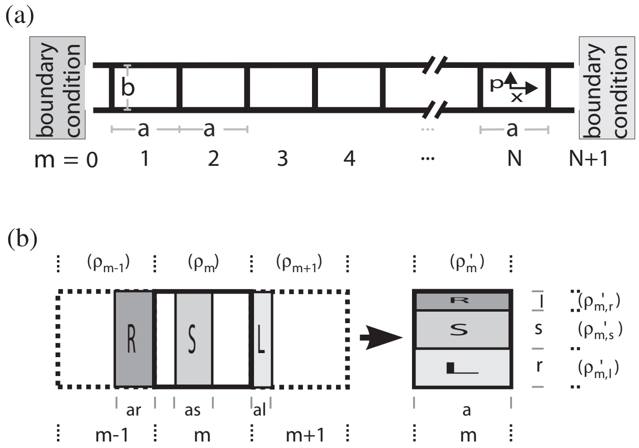

Fig. 1. Graphical illustration of the action of the multibaker map of length $L = aN$ on the phase space (x, p) over a time unit τ. (a) The mapping is defined on a domain of N identical rectangular cells of size $a \times 1$, with boundary condition imposed in two additional cells 0 and $N+1$. (b) The action of the map in any of the cells over time unit τ is illustrated by the deformation of the labels *R*, *S* and *L* in the three branches of the map ending up in cell m. The average value of the density on the cells (strips) [cf. Eq. (7)] is given on the margins.

emphasize the particular choice of coarse-graining over the cells, the coarse-grained densities are also called the *cell densities*. The dynamics of the multibaker map is the same for all cells. There might be inhomogeneities in the cell densities, but the evolution equations are translation invariant.

3.1. Evolution of the Cell Density

In order to find results consistent with non-equilibrium thermodynamics we always consider initial conditions with a uniform density in every cell m. As discussed in refs. 13, 16, 26 this is convenient from a technical point of view, and does not lead to a principal restriction of the domain of validity of the model. Under such conditions the parameters r and l can be considered as transition probabilities from a cell to its right and left neighbor, respectively. After one step of iteration the densities $\rho'_{m,i}$ on the strips $i = R, S, L$ of cell m are (cf. Fig. 1b)

$$\rho'_{m,r} = \frac{r}{l}\, \rho_{m-1}, \qquad \rho'_{m,s} = \rho_m, \qquad \rho'_{m,l} = \frac{l}{r}\, \rho_{m+1}. \tag{7}$$

The factors r/l and l/r give rise to local contraction or expansion of the phase-space volume. One of the factors is larger than unity, and characterizes a local contraction, while the other gives rise to an expansion.

Since in every cell the density remains uniform in the horizontal direction, this update holds at all times such that the coarse-grained density distributions ρ_m and $\rho'_m = r\rho_{m-1} + s\rho_m + l\rho_{m+1}$ at the respective times n and $n+1$ are related by the master equation

$$\rho'_m = (1-r-l)\,\rho_m + r\rho_{m-1} + l\rho_{m+1}. \tag{8}$$

Multiplying the equation by τ^{-1} and introducing the current

$$j_m = \frac{a}{\tau}\,(r\rho_m - l\rho_{m+1}) \tag{9}$$

through the right boundary of cell m, Eq. (8) appears in the form of the continuity equation

$$\frac{\rho'_m - \rho_m}{\tau} = -\frac{j_m - j_{m-1}}{a}. \tag{10}$$

The current through the left boundary of cell m is the same as the current flowing through the right boundary of cell $m-1$.

3.2. Diffusion, Drift, and the Macroscopic Limit

The transition probabilities r and l govern the evolution of the coarse-grained density ρ_m. In view of the master equation (8), the cell-to-cell dynamics of the model is equivalent to the dynamics of an ensemble of random walkers with fixed step length a and local transition probabilities r and l over time unit τ. In terms of the local drift v and diffusion coefficient D the transition probabilities r and l can be expressed as(27)

$$r = \frac{\tau D}{a^2}\left(1 + \frac{av}{2D}\right), \qquad l = \frac{\tau D}{a^2}\left(1 - \frac{av}{2D}\right), \tag{11}$$

such that the current appears in a form very close to its thermodynamic counterpart, viz.

$$j_m = \frac{v}{2}\,(\rho_m + \rho_{m+1}) - D\,\frac{\rho_{m+1} - \rho_m}{a}. \tag{12}$$

The *macroscopic limit* expresses a separation of scales where density gradients inside cells may be neglected, while density differences between the cells and the temporal evolution of the cell densities are only taken into account in leading order. In other words, in this limit $a \ll L = aN$, $\tau \ll L^2/D$, L/v, and upon introducing the quasi-continuous spatial and temporal variables $x \equiv am$ and $t \equiv \tau n$, the current j_m [Eq. (12)] takes the form $j(x; t) = v\,\rho(x; t) - D\,\partial_x \rho(x, t)$, while Eq. (10) becomes $\partial_t \rho(x; t) = -\partial_x j(x; t) = -v\,\partial_x \rho(x; t) + D\,\partial_x^2 \rho(x; t)$. The macroscopic density evolves according to the advection-diffusion equation.

3.3. Local Entropy Balance

The coarse-grained entropy of cell m is defined in terms of the coarse-grained (cell) density ρ_m as

$$S_m = -a\rho_m \ln \frac{\rho_m}{\rho^\star}. \tag{13}$$

In this equation $\rho^\star$ is a constant reference density that is introduced for dimensional reasons. It expresses the free choice of the origin of the entropy scale. The entropy S_m is similar to $s^{(\mathrm{cg})}$ used in Section 2, but it is more general since it is a *local* quantity characterizing cell m, which can be shown to fulfill a local entropy balance in direct analogy to the one of irreversible thermodynamics.(13, 14) Another difference is that the density ρ_m is normalized to the (time-dependent) number $\mathcal{N}$ of particles in the system, in contrast to ψ which is normalized to 1.

To derive the balance equation for (13) one identifies at any given time the difference $S_m - S_m^{(G)}$ of the coarse-grained and the fine-resolved Gibbs entropy $S_m^{(G)}$ as the information on the microscopic state of the system which cannot be resolved in the coarse-grained description. The Gibbs entropy of the multibaker cell is an analogous expression to (13). However, it is evaluated with respect to the non-coarse-grained phase-space density $\rho(x)$, from which it is obtained by integrating $-\rho(x) \ln \rho(x)/\rho^*$ over the coordinate x in the cell. For a coarse-grained initial distributions the Gibbs entropy coincides with the cell entropy initially (i.e., $S_m = S_m^{(G)}$), and after one time step the entropies become (cf. Fig. 1b)

$$S_m^{(G)\prime} = -a\left[s\rho_m \ln \frac{\rho_m}{\rho^\star} + r\rho_{m-1} \ln\left(\frac{r}{l}\,\frac{\rho_{m-1}}{\rho^\star}\right) + l\rho_{m+1} \ln\left(\frac{l}{r}\,\frac{\rho_{m+1}}{\rho^\star}\right)\right] \tag{14}$$

and

$$S'_m = -a\rho'_m \ln \frac{\rho'_m}{\rho^\star}. \tag{15}$$

For the multibaker dynamics the temporal change of the lack of information was identified$^{(3, 4, 13, 23)}$ with the irreversible entropy production $\Delta_i S_m$, and the change $(S_m^{(G)\prime} - S_m^{(G)})$ of the Gibbs entropy with the entropy flux $\Delta_e S_m$. Thus, for every cell one obtains the discrete entropy balance

$$\frac{S'_m - S_m}{\tau} = \frac{\Delta_e S_m}{\tau} + \frac{\Delta_i S_m}{\tau}, \tag{16}$$

where the entropy flux is [cf. (14) and (15)]

$$\begin{aligned}\frac{\Delta_e S_m}{\tau} &= \frac{S_m^{(G)\prime} - S_m^{(G)}}{\tau} \\ &= -\frac{a}{\tau}\left[(\rho'_m - \rho_m) \ln \frac{\rho_m}{\rho^\star} + r\rho_{m-1} \ln\left(\frac{r}{l}\,\frac{\rho_{m-1}}{\rho_m}\right) + l\rho_{m+1} \ln\left(\frac{l}{r}\,\frac{\rho_{m+1}}{\rho_m}\right)\right].\end{aligned} \tag{17}$$

and the entropy production takes the form

$$\begin{aligned}\frac{\Delta_i S_m}{\tau} &= \frac{[S'_m - S_m^{(G)\prime}] - [S_m - S_m^{(G)}]}{\tau} \\ &= \frac{a}{\tau}\left[-\rho'_m \ln \frac{\rho'_m}{\rho_m} + r\rho_{m-1} \ln\left(\frac{r}{l}\,\frac{\rho_{m-1}}{\rho_m}\right) + l\rho_{m+1} \ln\left(\frac{l}{r}\,\frac{\rho_{m+1}}{\rho_m}\right)\right].\end{aligned} \tag{18}$$

The density of irreversible entropy production is $\Delta_i S_m/(a\tau)$. Note that it does not depend on the choice of the reference density $\rho^\star$. In the macroscopic limit all expressions (15)–(18) reduce to the respective predictions of non-equilibrium thermodynamics.$^{(13, 14, 16)}$

3.4. Global Entropy Production

The escape-rate formalism addresses the balance of the global entropy of the chain. The global coarse-grained entropy (the direct analog of $s^{(\mathrm{cg})}$ of Section 2) is

$$S_{\mathrm{tot}} = \sum_{m=1}^{N} S_m = -a \sum_{m=1}^{N} \rho_m \ln \frac{\rho_m}{\rho^\star}. \tag{19}$$

The associated global entropy production rate along the chain is $\Sigma^{(\mathrm{irr})} = \sum_{m=1}^{N} \Delta_i S_m/\tau$, and the total specific irreversible entropy production is obtained as

$$P^{(\mathrm{irr})} = \frac{\Sigma^{(\mathrm{irr})}}{\mathcal{N}} = \frac{\sum_{m=1}^{N} \Delta_i S_m}{\tau \mathcal{N}} \tag{20}$$

where $\mathcal{N} = \sum_{m=1}^{N} a\rho_m$ is the number of particles in the chain at time $n\tau$. The total entropy production can be rearranged to take the form

$$\Sigma^{(\mathrm{irr})} = -\frac{a}{\tau} \sum_{m=1}^{N} \rho'_m \ln \frac{\rho'_m}{\rho_m} + \frac{a}{\tau} \left(r\rho_0 \ln \frac{r\rho_0}{l\rho_1} - l\rho_{N+1} \ln \frac{r\rho_N}{l\rho_{N+1}} \right) + \frac{a}{\tau} \sum_{m=1}^{N-1} (r\rho_m - l\rho_{m+1}) \ln \frac{r\rho_m}{l\rho_{m+1}}, \tag{21}$$

where ρ_0 and ρ_{N+1} are the densities in the boundary cells. The total entropy production can conveniently be split into four terms $\Sigma^{(\mathrm{irr})} = \Sigma_t^{(\mathrm{irr})} + \Sigma_b^{(\mathrm{irr})} + \Sigma_d^{(\mathrm{irr})} + \Sigma_{\mathrm{mix}}^{(\mathrm{irr})}$. The first one

$$\Sigma_t^{(\mathrm{irr})} = -\frac{a}{\tau} \sum_{m=1}^{N} \rho'_m \ln \frac{\rho'_m}{\rho_m} \tag{22}$$

is the contribution from the *temporal* evolution of the density. The contribution proportional to $\ln(r/l)$ of the last term in (21) contains the irreversible entropy production

$$\Sigma_d^{(\mathrm{irr})} = \mathcal{N} \frac{r-l}{\tau} \ln \frac{r}{l} \to \mathcal{N} \frac{v^2}{D} \tag{23}$$

due to the presence of the *drift* v. It does not depend on the particular density distribution so that we can immediately specify its macroscopic limit (indicated by →). By means of (9) and (10) the remaining part can be written as a sum of two terms. One of them,

$$\Sigma_{\mathrm{mix}}^{(\mathrm{irr})} = -\frac{a}{\tau} \sum_{m=1}^{N} (\rho'_m - \rho_m) \ln \frac{\rho_m}{\rho^\star} \tag{24}$$

characterizes the contribution of *mixing* of the neighboring densities. In order to arrive at this form the ratio ρ_m/ρ_{m+1} of the densities appearing at the right hand side of (21) was written as $[(\rho_m/\rho^\star)/(\rho_{m+1}/\rho^\star)]$. The rest

$$\Sigma_b^{(\mathrm{irr})} = \frac{a}{\tau} \left[r\rho_0 \ln \frac{r\rho_0}{l\rho^\star} + l\rho_{N+1} \ln \frac{l\rho_{N+1}}{r\rho^\star} - l\rho_1 \ln \frac{l\rho_1}{r\rho^\star} - r\rho_N \ln \frac{r\rho_N}{l\rho^\star} \right] \tag{25}$$

yields the *boundary* contribution. We shall be interested in the difference between $\Sigma^{(\mathrm{irr})}$ and $\Sigma_d^{(\mathrm{irr})}$, called the irreversible entropy production $\Sigma_{\mathrm{relax}}^{(\mathrm{irr})}$ due to the *relaxation* process,

$$\Sigma_{\mathrm{relax}}^{(\mathrm{irr})} \equiv \Sigma_t^{(\mathrm{irr})} + \Sigma_{\mathrm{mix}}^{(\mathrm{irr})} + \Sigma_b^{(\mathrm{irr})}. \tag{26}$$

4. NORMAL MODES OF THE COARSE-GRAINED TIME EVOLUTION

4.1. Decaying Modes and the Steady State

We are interested in the evolution of the density distributions $\rho_m^{(n)}$ subjected to a fixed constant boundary condition

$$\rho_0^{(n)} = \rho_{N+1}^{(n)} = \rho_B \tag{27}$$

at any time step n. Asymptotically, $\rho_m^{(n)}$ always approaches the uniform density ρ_B. The time evolution of the density can be explored by expanding the deviation $\rho_m^{(0)} - \rho_B$ of the initial distribution $\rho_m^{(0)}$ from the asymptotic state ρ_B in terms of normal modes $\delta_m^{[\nu](n)}$. They vanish at both boundaries, and only change in amplitude but not in their shape,

$$\frac{\delta_m^{[\nu](n+1)}}{\delta_m^{[\nu](n)}} = \exp(-\gamma_\nu \tau). \tag{28}$$

The integer ν labels different modes. There are as many independent modes as the number N of the cells, such that $\nu = 1,\dots, N$. The normal modes take the respective forms

$$\delta_m^{[\nu](n)} \sim \exp\left(-\gamma_\nu n\tau\right) \left(\frac{r}{l}\right)^{m/2} \sin\left(\frac{\pi\nu}{N+1}\, m\right). \tag{29}$$

Substituting the ansatz into Eq. (8) and rearranging the trigonometric terms, one finds the decay rates

$$\gamma_\nu = -\frac{1}{\tau} \ln\left[\, 1-(r+l)+2\sqrt{rl}\, \cos\left(\frac{\pi\nu}{N+1}\right)\right] \to \frac{\pi^2 D}{L^2}\, \nu^2 + \frac{v^2}{4D}. \tag{30}$$

For a general initial condition the *asymptotic* decay is governed by the *slowest* non-vanishing decay rate, γ_1. It coincides with the *escape rate* κ of the transiently chaotic motion(7, 8) inside the chain (i.e., $\kappa \equiv \gamma_1$).(1, 20, 28)

The macroscopic limit of the decay rates has a clear physical content. For vanishing v(1, 2) it states that relaxation is related to the typical diffusive decay rate D/L^2 of structures of size L. The factor π^2 characterizes the geometry of the considered region (a band of width L with straight, parallel walls in our example). More complicated geometries have been studied by Gaspard,(18) and Kaufmann and collaborators.(29, 30)

For a biased motion $v \neq 0$ the drift singles out one side of the system and sweeps out the particles in that direction. This mechanism dominates when the time L/v to cross the system by the biased motion becomes shorter than the typical time scale L^2/D of diffusion, i.e., for

$$\mathrm{Pe} \equiv \left| \frac{vL}{D} \right| \tag{31}$$

much larger than unity. In the context of hydrodynamics, Pe is called Pèclet number.$^{(31)}$ It measures the importance of advection relative to diffusion. Strong diffusive effects are indicated by small Pèclet numbers. For fixed finite v and D, the Pèclet number is always large for a sufficiently large system size L.

4.2. Long-Time Relaxation and the Slowest Mode

For sufficiently long times $n \gg 1$, the coarse-grained density closely approaches the first normal mode. Therefore, the density can be expressed as

$$\rho_m^{(n)} \equiv \rho_B + (\mathcal{N}^{(n)} - \mathcal{N}^{(\infty)})\, \psi_m, \tag{32}$$

where $\mathcal{N}^{(n)} = \sum_{m=1}^{N} a\rho_m^{(n)}$ and $\mathcal{N}^{(\infty)} = \rho_B L$ is the particle number in the background which is also the asymptotic particle number in the system. Moreover,

$$\psi_m = \frac{\mathcal{A}}{L} \left(\frac{r}{l} \right)^{m/2-(N+1)/4} \sin \frac{m\pi}{N+1} \tag{33}$$

is the *coarse-grained* conditionally-invariant density (the analog of $\psi^{(\mathrm{cg})}(x;t)$ used in Section 2). It is normalized to unity ($1 \equiv a \sum_{m=1}^{N} \psi_m$), by virtue of the normalization constant $\mathcal{A}$, which is invariant under the exchange of r and l. Carrying out the summation of the complex geometric series defined by (33) one finds

$$\begin{aligned} \mathcal{A} &= L \frac{1-\exp(-\kappa\tau)}{a\sqrt{rl}} \; \frac{1}{\left(\frac{r}{l}\right)^{(N+1)/4} + \left(\frac{r}{l}\right)^{-(N+1)/4}} \; \frac{1}{\sin \frac{\pi}{N+1}} \\ &\to \frac{\pi}{2} \, \frac{\left(\frac{\mathrm{Pe}}{2\pi}\right)^2 + 1}{\cosh \frac{\mathrm{Pe}}{4}} = \kappa \, \frac{L^2}{2\pi D \cosh \frac{\mathrm{Pe}}{4}}. \end{aligned} \tag{34}$$

Here, the relation $(r/l)^{N/4} = (1+av/D)^{N/4} \to \exp(\mathrm{Pe}/4)$ has been used to evaluate the macroscopic limit. In view of (32) and (34) the macroscopic limit of the asymptotically decaying density (32) takes the form

$$\rho(x,t) = \rho_B + \frac{\mathscr{A}}{L}\,(\mathscr{N}^{(t)} - \mathscr{N}^{(\infty)})\,\exp\left(\mathrm{Pe}\,\frac{2x-L}{4L}\right)\sin\frac{\pi x}{L}. \tag{35}$$

5. BOUNDARY CONTRIBUTIONS TO THE IRREVERSIBLE ENTROPY PRODUCTION

5.1. Absorbing Boundaries

In the case of a long-term relaxation towards an empty state ($\rho_0 = \rho_{N+1} = \rho_B = 0$), Eq. (28) holds for the full density $\rho_m^{(n)}$, and one can write [see Eq. (22)]

$$\Sigma_t^{(\mathrm{irr})} \equiv \kappa\mathscr{N}\,\exp(-\kappa\tau) = \kappa\mathscr{N}' \to \kappa\mathscr{N}, \tag{36a}$$

where $\mathscr{N}'$ is the number of particles at time $(n+1)\,\tau$.

The mixing term (24) can be expressed by means of the total entropy (19) to obtain

$$\Sigma_{\mathrm{mix}}^{(\mathrm{irr})} = \frac{1}{\tau}\,(e^{-\kappa\tau}-1)\,S_{\mathrm{tot}} \to -\kappa S_{\mathrm{tot}}, \tag{36b}$$

and in view of $\rho_0 = \rho_{N+1} = \rho_B = 0$ the boundary contribution (25) becomes

$$\begin{aligned}
\Sigma_b^{(\mathrm{irr})} &= -\frac{a}{\tau}\frac{\mathscr{A}N}{L}\sin\frac{\pi}{N+1}\left\{r\left(\frac{r}{l}\right)^{(N-1)/4}\ln\left[\frac{\mathscr{A}N}{L\rho^*}\left(\frac{r}{l}\right)^{(N+3)/4}\sin\frac{\pi}{N+1}\right]\right.\\
&\quad\left.+l\left(\frac{r}{l}\right)^{-(N-1)/4}\ln\left[\frac{\mathscr{A}\,N}{L\rho^*}\left(\frac{r}{l}\right)^{-(N+3)/4}\sin\frac{\pi}{N+1}\right]\right\}\\
&= -\frac{a}{\tau}\frac{\mathscr{A}\,N}{L}\sin\frac{\pi}{N+1}\left\{\left[r\left(\frac{r}{l}\right)^{(N-1)/4}+l\left(\frac{r}{l}\right)^{-(N-1)/4}\right]\ln\left[\frac{\mathscr{A}\,N}{L\rho^*}\sin\frac{\pi}{N+1}\right]\right.\\
&\quad\left.+\left[r\left(\frac{r}{l}\right)^{(N-1)/4}-l\left(\frac{r}{l}\right)^{-(N-1)/4}\right]\frac{N+3}{4}\log\frac{r}{l}\right\}.
\end{aligned} \tag{36c}$$

Observing that in the macroscopic limit both r and l are in leading order equal to $\tau D/a^2$, and that $\log(r/l) \to av/D$, one obtains for the relaxation contribution to the total irreversible entropy production

$$\Sigma^{(\mathrm{irr})}_{\mathrm{relax}} = \kappa \mathcal{N} \left[1 - \frac{\mathrm{Pe}}{4} \tanh \frac{\mathrm{Pe}}{4} - \ln \left(\frac{\mathcal{N}}{L\rho^\star} \frac{\pi^2}{2} \frac{1 + (\mathrm{Pe}/2\pi)^2}{\cosh(\mathrm{Pe}/4)} \frac{a}{L} \right) \right] - \kappa S_{\mathrm{tot}}. \quad (36\mathrm{d})$$

This expression shows the expected logarithmic divergence since $(a/L) \to 0$ in the macroscopic limit. On the other hand, the result can properly be interpreted only after evaluating S_{tot}. In particular, the reference density $\rho^\star$ has to drop out again in the final result.

In the macroscopic limit the sum over m in the definition of S_{tot} becomes an integral. By using Eqs. (32) one finds

$$\begin{aligned} S_{\mathrm{tot}} = &-\mathscr{A}\, N \int_0^1 \mathrm{dx} \exp\left(-\mathrm{Pe} \frac{2x-1}{4} \right) \sin(\pi x) \\ &\times \ln \left[\frac{\mathscr{A}\, N}{L\rho^\star} \exp\left(-\mathrm{Pe} \frac{2x-1}{4} \right) \sin(\pi x) \right]. \end{aligned} \quad (37)$$

Applying the relation (34), we see that the specific entropy

$$S_{\mathrm{tot}} = \mathcal{N} f \left(\mathrm{Pe}, \frac{\mathcal{N}}{L\rho^\star} \right) \quad (38)$$

is a function of the Pèclet number and of the ratio of $\mathcal{N}/L$ and $\rho^\star$, i.e., of the average density in the system and the reference density respectively. This ratio is another dimensionless number, that involves the parameter $\rho^\star$ selecting the origin of the entropy scale (which, as mentioned earlier, is an arbitrary number in classical physics). The total entropy cannot be evaluated exactly. However, to obtain its behavior in leading order for very large and small Pèclet numbers it is sufficient to approximate the expression under the logarithm by its maximum value. In the two limiting cases one thus finds in leading order in $\mathcal{N}$

$$S_{\mathrm{tot}} = \begin{cases} -\mathcal{N} \ln \left(\mathrm{Pe} \dfrac{\mathcal{N}}{\rho^\star L} \right) & \text{for} \quad \mathrm{Pe} \gg 1, \\ -\mathcal{N} \ln \left(\dfrac{\mathcal{N}}{\rho^\star L} \right) & \text{for} \quad \mathrm{Pe} \ll 1. \end{cases} \quad (39)$$

Based on these forms of the total entropy one can see, that for any finite time it has a finite, nonzero value. In the asymptotic case $t \to \infty$ the total entropy vanishes with the number of particles.

In the limit $a \ll L$, this implies for the total specific entropy production

$$P^{(\mathrm{irr})} = \frac{\Sigma^{(\mathrm{irr})}_{\mathrm{relax}}}{\mathcal{N}} = \begin{cases} \kappa \ln\left(\mathrm{Pe}^{-1}\frac{L}{a}\right) & \text{for} \quad \mathrm{Pe} \gg 1, \\ \kappa \ln \frac{L}{a} & \text{for} \quad \mathrm{Pe} \ll 1. \end{cases} \tag{40}$$

The result shows the expected logarithmic divergence due to the boundary terms. The divergence is an immediate consequence of the vanishing of the particle density at the boundaries, and arises notwithstanding the fact that the associated entropy is finite.[5] The failure of the arguments put forward in Section 2 to cope with this feature should be considered as an example clearly demonstrating the possible pitfalls of efforts to characterize thermodynamic properties by global dynamical-systems related quantities. The reason for the breakdown of the prediction (5) lies in the fact that the argument leading to this result focuses on the shrinking of the support of the measure by assuming the smoothness of the distribution along the unstable manifold. It thus entirely disregards that the density is very inhomogeneously distributed around the absorbing boundaries. It should also be emphasized that the result obtained for the diffusive case $\mathrm{Pe} \ll 1$ is the analog of the thermodynamic expression (1) since in this case $\rho = N\pi/(2L)\sin(x\pi/L)$, such that the parameter α of Eq. (1) takes the value $\alpha = \mathcal{N}\pi/(2L^2)$ and $D\alpha = \mathcal{N}\kappa/2$. The difference by a factor of $1/2$ is due to the fact that Eq. (1) gives the contribution of one end only.

In summary, the divergence of the irreversible entropy production near absorbing boundaries is due to the assumption of zero density and of the validity of the advection-diffusion equation near the boundaries. A way to avoid this divergence is to go *beyond* thermodynamics and to use a microscopic approach. An example of this is the multibaker map in its original form, with *finite* cell size a, where the coarse-grained cell density evolves according to the *discrete* advection-diffusion equation (10, 12).

5.2. Influence of a Small Background Density

We now assume that ρ_B is nonzero but much smaller than ρ_m except for a narrow layer around the boundaries where the sine of (33) approaches

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[5] A straightforward calculation shows that at the boundaries the divergence of the entropy current also involves a diverging term, which drops out with the one in the entropy production in the entropy balance.

zero. In that case Eq. (28) gives an upper bound to the ratio of densities at successive times, that is very accurate in the interior of the system. Consequently, the evaluation of (26) carries over except that the boundary term $\Sigma_b^{(\mathrm{irr})}$ picks up contributions due to the finite density ρ_B in the cells 0 and $N+1$. In the macroscopic limit this term becomes

$$\Sigma_b^{(\mathrm{irr})} \to -\kappa(\mathcal{N} - \mathcal{N}^{(\infty)})\left(1 + \ln \frac{\rho_B}{\rho^\star}\right) \approx -\kappa\mathcal{N}\left(1 + \ln \frac{\rho_B}{\rho^\star}\right). \tag{41}$$

Since the total entropy S_{tot} and the contribution $\Sigma_t^{(\mathrm{irr})}$ to the entropy production do not significantly change for a sufficiently small background density, the full entropy production becomes in the macroscopic limit

$$\Sigma_{\mathrm{relax}}^{(\mathrm{irr})} = -\kappa\mathcal{N} \ln \frac{\rho_B}{\rho^\star} - \kappa S_{\mathrm{tot}}. \tag{42}$$

After substituting S_{tot} from (39), we obtain the specific irreversible entropy production for $\mathcal{N} \gg \mathcal{N}^{(\infty)}$,

$$P^{(\mathrm{irr})} = \begin{cases} \kappa \ln\left(\mathrm{Pe}^{-1} \dfrac{\mathcal{N}}{\mathcal{N}^{(\infty)}}\right) & \text{for} \quad \mathrm{Pe} \gg 1, \\[2ex] \kappa \ln\left(\dfrac{\mathcal{N}}{\mathcal{N}^{(\infty)}}\right) & \text{for} \quad \mathrm{Pe} \ll 1. \end{cases} \tag{43}$$

The result clearly shows that the logarithmic divergences in the entropy production of the previous case are due to the vanishing of a physically indispensable background density ρ_B.

6. DISCUSSION

The result (43) involves only well-behaved macroscopic quantities, and the logarithm of the ratio of the number $\mathcal{N}$ of particles in the system over the number $\mathcal{N}^{(\infty)} = \rho_B L$ of particles approached in the steady state. At intermediate times, where $\mathcal{N}$ is still much larger than $\mathcal{N}^{(\infty)}$, the ratio $\mathcal{N}/\mathcal{N}^{(\infty)}$ decreases to a good approximation exponentially like $\exp(-\kappa t)$ such that the rate of irreversible entropy production starts to decrease linearly like $-\kappa^2 t$. During this time regime the boundary contribution is by a factor of $\log(\mathcal{N}/\mathcal{N}^{(\infty)})$ larger than the bulk contributions accounted for by Eq. (5). Hence, even in the more realistic setting accounting for a finite background density, Eq. (5) only describes a sub-dominant contribution to the entropy-production rate. The reason for its failure is that the contributions arising from the spatial distribution of the particles and the induced inhomogeneous particle currents are not adequately taken into account by an entropy based solely on the conditionally-invariant measure.

In spite of the strong contributions due to the boundary terms, the entropy production remains proportional to the escape rate κ even in more general situations. Besides for the short times, where this follows from Eq. (43), this can be easily illustrated in the long-time regime, where it applies to any thermodynamically relevant system, whose coarse-grained density evolves according to the advection-diffusion equation.

We now derive this assertion in a thermodynamic setting of a density distribution $\rho(x) \equiv \rho_B + \Delta\mathcal{N}\,\psi(x)$, where $\mathcal{N}$ is the instantaneous number of particles, and $\rho(x)$ is close to the background density ρ_B. Since $\rho(x)$ evolves according to the advection diffusion equation with particle current $v\rho(x) - D\,\Delta\mathcal{N}\,\partial_x\psi(x)$ the total entropy production is

$$\begin{aligned}\Sigma^{(\mathrm{irr})} &= \int \mathrm{d}x\,\frac{\rho(x)}{D}\left(v - D\,\frac{\Delta\mathcal{N}\,\partial_x\psi}{\rho(x)}\right)^2\\ &\approx \frac{v^2}{D}\int \mathrm{d}x\,\rho(x) - \frac{(\Delta\mathcal{N})^2}{\rho_B}\,D\int \mathrm{d}x\,\psi(x)\,\partial_x^2\psi(x)\\ &\approx \mathcal{N}\,\frac{v^2}{D} + \kappa\,\frac{(\Delta\mathcal{N})^2}{\mathcal{N}^{(\infty)}}\,g(\mathrm{Pe}) \end{aligned} \tag{44}$$

where $g(\mathrm{Pe}) = \int \mathrm{d}x\,\psi^2(x)$ is a function of Pe only. The corresponding irreversible entropy production due to relaxation is $\Sigma^{(\mathrm{irr})}_{\mathrm{relax}} = \Sigma^{(\mathrm{irr})} - \mathcal{N}\,v^2/D$. In the second line in Eq. (44) the term proportional to $\partial_x\psi$ does not appear since its integral vanishes. Moreover, an integration by parts was used to obtain a second spatial derivative of the density which, according to the advection-diffusion equation, is proportional to its time-derivative, i.e., it amounts to $-\kappa\psi$ for the slowest decaying mode ψ (again we use here that terms proportional to $\partial_x\psi$ and $\psi\,\partial_x\psi$ vanish under the integral). The function $g(\mathrm{Pe})$ depends on the details of the system. Thus, the specific irreversible entropy production taken with respect to $\Delta\mathcal{N}$ is

$$P^{(\mathrm{irr})} = \frac{\Sigma^{(\mathrm{irr})}_{\mathrm{relax}}}{\Delta\mathcal{N}} = \kappa\,\frac{\Delta\mathcal{N}}{\mathcal{N}^{(\infty)}}\,g(\mathrm{Pe}). \tag{45}$$

We emphasize that exactly the same result can explicitly be derived for the multibaker dynamics. After taking the macroscopic limit one then also obtains the particular form of $g(\mathrm{Pe})$.

Equation (45) implies that even in a general thermodynamic setting the relaxational entropy-production is proportional to the escape rate κ, which characterizes the approach towards the stationary state. In contrast to the dynamical-system arguments of Section 2, which based on the escape-rate formalism, the term involves in general a non-trivial function $g(\mathrm{Pe})$ of the Pèclet number, and it has an amplitude $\Delta\mathcal{N}/\mathcal{N}^{(\infty)}$ that is exponentially decaying like $\exp(-\kappa t)$.

It will certainly be interesting to investigate more closely the connection between the escape-rate formalism and the decay to systems supporting non-trivial stationary states. Another step in this direction, which complements the present approach, was taken by Bob Dorfman and his collaborators,(32–34) who recently discussed the approach towards equilibrium in systems with periodic boundary conditions.

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