

Irreversible thermodynamics of Poisson processes with reaction

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A kinetic model is derived to study the successive movements of particles, described by a Poisson process, as well as their generation. The irreversible thermodynamics of this system is also studied from the kinetic model. This makes it possible to evaluate the differences between thermodynamical quantities computed exactly and up to second-order. Such differences determine the range of validity of the second-order approximation to extended irreversible thermodynamics. [S1063-651X(99)15511-9]

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I. INTRODUCTION

It is widely known that the movements of organisms such as animal migration, cell movements etc., can be modeled by a random walk [1]. However, within the last 30 years several biological experiments have demonstrated the existence of significant correlations in the motions of several types of cells [2]. Their successive movements are not mutually independent [3]. Then, a correlated random walk is appropriate to describe the dynamical evolution of the system. Moreover, it guarantees a finite speed of diffusion. When particle reproduction is also considered, the evolution of the system is described by a hyperbolic reaction-diffusion equation (HRD). These equations have been applied to some fields of biological physics such as human migrations [4], population growth [5], and forest fire models [6]. In this paper we derive a HRD equation from a different point of view. We develop a kinetic description for particle movements by assuming that the changes in the velocity of particles are described by a Poisson process. Irreversible thermodynamics emerges naturally by means of the conventional techniques of the kinetic theory of gases. We derive exact expressions for the entropy, entropy flux, and entropy production and these are compared to the corresponding second-order approximations often used in extended irreversible thermodynamics (EIT) [7].

II. KINETIC DERIVATION

In this section we derive the one-dimensional (1D) reaction-telegraph equation for the particle movement from a kinetic point of view following the ideas by Othmer *et al.* [8]. Although most natural species do not live in one-dimensional environments, the reaction diffusion equation we will derive is the governing equation for dispersal in the limit of 2D interfaces with small curvature and may therefore be viewed as a canonical equation for particle movement. Let $f(x, \mathbf{v}, t)$ be the nonequilibrium distribution function of particles at position x moving with velocity \mathbf{v} at time t . As usual in kinetic theory, the number density of particles at x at time t is

$$n(x, t) = \int f(x, \mathbf{v}, t) d\mathbf{v}, \quad (1)$$

and the particle flux is

$$J(x, t) = \int \mathbf{v} f(x, \mathbf{v}, t) d\mathbf{v}. \quad (2)$$

Let the contribution to the rate of change of f due to reaction or reproduction be given by $r(n)\varphi(\mathbf{v})$, so that new particles with a normalized velocity distribution $\varphi(\mathbf{v})$ appear at a rate depending only on n . Assuming that the velocity changes can be described by a Poisson process of intensity λ , i.e., that the rate at which particles leave a phase space volume centered at (x, \mathbf{v}) is $\lambda f(x, \mathbf{v}, t)$, we have for the net rate at which particles enter the phase space

$$-\lambda f + \lambda \int f(x, \mathbf{v}', t) K(\mathbf{v}' \rightarrow \mathbf{v}) d\mathbf{v}',$$

where the kernel $K(\mathbf{v}' \rightarrow \mathbf{v})$ is the normalized probability of a change of velocity from \mathbf{v}' to \mathbf{v} . Thus, the corresponding Boltzmann equation for the distribution function is given by

$$\frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial x} = Q(f), \quad (3)$$

where $Q(f)$ describes the interaction processes and plays the role of the reactive and elastic collision terms in kinetic theory,

$$Q(f) = r(n)\varphi(\mathbf{v}) - \lambda f + \lambda \int K(\mathbf{v}' \rightarrow \mathbf{v}) f(x, \mathbf{v}', t) d\mathbf{v}'. \quad (4)$$

In order to derive macroscopic transport equations, we proceed in the usual way in kinetic theory. Integration Eq. (3) and use of Eq. (4) yields

$$\frac{\partial n}{\partial t} + \frac{\partial J}{\partial x} = r(n), \quad (5)$$

which is the balance equation for the number density of particles. We assume for simplicity that the speed v_0 of particles is constant and that only direction reversals are allowed. So, the diffusion kernel reads $K(\mathbf{v}' \rightarrow \mathbf{v}) = \delta(\mathbf{v} + \mathbf{v}')$. Multiplying Eq. (3) by \mathbf{v} and integrating we find that

$$\frac{\partial J}{\partial t} + 2\lambda J = r(n)\langle v \rangle - \frac{\partial}{\partial x} \int v^2 f(x, v, t) dv. \quad (6)$$

Assuming the velocities of newborn particles to be $\pm v_0$, with the same probability $1/2$,

$$\varphi(v) = \frac{1}{2} \delta(v + v_0) + \frac{1}{2} \delta(v - v_0), \quad (7)$$

thus the mean value $\langle v \rangle = 0$. Defining

$$f^+ = f(x, +v_0, t), \quad f^- = f(x, -v_0, t),$$

we can rewrite Eq. (1) as $n(x, t) = f^+ + f^-$ and Eq. (2) as $J(x, t) = v_0(f^+ - f^-)$. Therefore, f^+ and f^- may be written in terms of n and J as

$$f^+ = \frac{1}{2} \left(n + \frac{J}{v_0} \right), \quad f^- = \frac{1}{2} \left(n - \frac{J}{v_0} \right). \quad (8)$$

On the other hand, the equation for the particle flux (6) may be written as

$$\frac{\partial J}{\partial t} + 2\lambda J = -v_0^2 \frac{\partial n}{\partial x}, \quad (9)$$

where we have applied that $\int dv v^2 f(x, v, t) = v_0^2(f^+ + f^-) = v_0^2 n$. Equation (9) has the form of a Maxwell-Cattaneo equation for diffusion processes, namely, $\tau(\partial J/\partial t) + J = -D(\partial n/\partial x)$ [7], with a flux relaxation time $\tau = 1/2\lambda$ and a diffusion coefficient $D = v_0^2 \tau$. By combining Eqs. (5) and (9) we obtain a reaction-diffusion equation of the telegrapher's type,

$$\tau \frac{\partial^2 n}{\partial t^2} + [1 - \tau r'(n)] \frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} + r(n). \quad (10)$$

This equation has been also derived in other physical and biophysical contexts such as nonlinear transmission lines (continuum coupled van der Pol oscillators), branching random walks [9], hyperbolic nerve conduction [10], and time-delayed population growth [5,4].

III. IRREVERSIBLE THERMODYNAMICS

The kinetic-theoretical definition for the entropy density is

$$S(x, t) = -k_B \int f(x, v, t) \ln f(x, v, t) dv, \quad (11)$$

where k_B is the Boltzmann constant. The evolution equation for the entropy may be derived by multiplying Eq. (3) by $\ln f$ and integrating over v . In this way we obtain

$$\frac{\partial S}{\partial t} + \frac{\partial J^s}{\partial x} = \sigma[f],$$

with the entropy flux J^s defined as

$$J^s(x, t) = -k_B \int v f(x, v, t) \ln f(x, v, t) dv, \quad (12)$$

and the entropy production $\sigma[f]$ as

$$\begin{aligned} \sigma[f] &= -k_B \int Q(f) \ln f dv \\ &= -k_B \left(\int \frac{\partial f}{\partial t} \ln f dv + \int v \frac{\partial f}{\partial x} \ln f dv \right). \end{aligned}$$

Taking into account Eqs. (7) and (8) we may write

$$S(x, t) = -k_B (f^+ \ln f^+ + f^- \ln f^-), \quad (13)$$

$$J^s(x, t) = -k_B v_0 (f^+ \ln f^+ - f^- \ln f^-), \quad (14)$$

$$\sigma[f] = -k_B r(n) \left[1 + \frac{1}{2} \ln(f^+ f^-) \right] + k_B \lambda (f^+ - f^-) \ln \left(\frac{f^+}{f^-} \right). \quad (15)$$

Equation (13) is the information-theoretic entropy, and its validity in nonequilibrium has been justified [11]. By using Eqs. (13) and (14) together with Eq. (8) one immediately finds that

$$\begin{aligned} S(n, J) &= -\frac{k_B}{2} \left(n + \frac{J}{v_0} \right) \ln \left[\frac{1}{2} \left(n + \frac{J}{v_0} \right) \right] \\ &\quad - \frac{k_B}{2} \left(n - \frac{J}{v_0} \right) \ln \left[\frac{1}{2} \left(n - \frac{J}{v_0} \right) \right], \\ J^s(n, J) &= -\frac{k_B v_0}{2} \left(n + \frac{J}{v_0} \right) \ln \left[\frac{1}{2} \left(n + \frac{J}{v_0} \right) \right] \\ &\quad + \frac{k_B v_0}{2} \left(n - \frac{J}{v_0} \right) \ln \left[\frac{1}{2} \left(n - \frac{J}{v_0} \right) \right]. \end{aligned} \quad (16)$$

The entropy production is, from Eqs. (8) and (15),

$$\begin{aligned} \sigma(n, J) &= \frac{k_B J}{2 v_0 \tau} \ln \left(\frac{n + \frac{J}{v_0}}{n - \frac{J}{v_0}} \right) \\ &\quad - \frac{k_B}{2} r(n) \left\{ 2 + \ln \left[\frac{1}{4} \left(n^2 - \frac{J^2}{v_0^2} \right) \right] \right\}. \end{aligned} \quad (17)$$

The first term in Eq. (17) is the contribution to the entropy production arising from diffusion, whereas the second term is the contribution due to the reactive or reproductive process in the system. Equations (16) may be rewritten as

$$\begin{aligned} S(n, y) &= -k_B n \ln \frac{n}{2} - \frac{n k_B}{2} \sum_{j=1}^{\infty} \frac{y^{2j}}{j(2j-1)}, \\ J^s(n, y) &= -k_B n v_0 \left(1 + \ln \frac{n}{2} \right) y + \frac{n k_B v_0}{2} \sum_{j=1}^{\infty} \frac{y^{2j+1}}{j(2j+1)}, \end{aligned} \quad (18)$$

where $y = J/(n v_0)$. Let us now introduce the density $\rho = nm$, where m is the mass of the particles; the specific volume is $v = 1/\rho$. Then, the specific entropy s is given by $s = S/\rho$ and the specific internal energy u is given by $u = U/\rho$, where U is defined as $U = \int \frac{1}{2} m v^2 f dv = \frac{1}{2} m v_0^2 n$. One can derive an extended Gibbs equation for this system noting from Eq. (18) that the specific entropy is a function of u, v and the flux J , i.e.,

$$ds = \left(\frac{\partial s}{\partial u} \right) du + \left(\frac{\partial s}{\partial v} \right) dv + \left(\frac{\partial s}{\partial J} \right) dJ,$$

where $\partial s / \partial u = (\partial S / \partial v_0) / (nm v_0)$. The temperature T is given by

$$T^{-1} = \left(\frac{\partial s}{\partial u} \right) = \frac{k_B}{m v_0^2} \sum_{j=1}^{\infty} \frac{y^{2j}}{2j-1},$$

where we have made use of Eq. (18). The first term on the right-hand sides of Eqs. (18) gives the local-equilibrium expressions for the entropy and entropy flux, respectively. The last terms are higher-order corrections. Consequently, we have shown in a natural way, without need of any thermodynamical assumption, that the local-equilibrium hypothesis breaks down for the systems under consideration. Moreover, we have obtained expressions for the thermodynamical quantities that hold for any value of the flux J , not only for small ones. On the other hand, the series above are convergent for $y \leq 1$, which corresponds to the constraint $J \leq n v_0$ on the value of the particle flux J in order to have nondivergent expressions for the entropy and the entropy flux. This constraint on J is fulfilled in the kinetic model presented in Sec. II since $J = v_0(f^+ - f^-)$, $n = f^+ + f^-$ and both f^+ and f^- must be positive in order to have physical meaning. The constraint $J \leq n v_0$ also bounds the possible values of the entropy and entropy flux,

$$S(n, J) \geq -k_B n \ln n, \quad J^s(n, y) \leq -k_B J \ln n.$$

The last term in these inequalities corresponds to $y = 1$. In this extreme nonequilibrium state, the entropy is minimum. This corresponds to the state of maximum order (all particles are in the same state), as it was to be expected intuitively. On the other hand, truncating the power series in Eq. (18) up to second order we find for the entropy

$$S(n, J) \approx -nk_B \ln \frac{n}{2} - \frac{k_B J^2}{2n v_0^2}, \quad (19)$$

which is a good approximation for $J \ll n v_0$. Equation (19) is the second-order expression for the entropy of diffusive systems, as usually found in works on extended irreversible thermodynamics (EIT) [7]. The exact and second-order expressions for the corrections to the local-equilibrium entropy are

$$S_{neq}^{ex}(n, y) = -\frac{nk_B}{2} [(1+y) \ln(1+y) + (1-y) \ln(1-y)],$$

$$S_{neq}^{(2)}(n, y) = -\frac{1}{2} nk_B y^2.$$

The relative error ΔS_{neq} may be computed,

$$\Delta S_{neq} = \left| \frac{S_{neq}^{(2)}(n, y) - S_{neq}^{ex}(n, y)}{S_{neq}^{ex}(n, y)} \right|. \quad (20)$$

We have plotted this quantity versus parameter y in Fig. 1, where one may appreciate that it reaches its maximum value in the limit $y \rightarrow 1$. This maximum value may be computed easily to yield $1 - 1/(2 \ln 2)$ or about 28%.

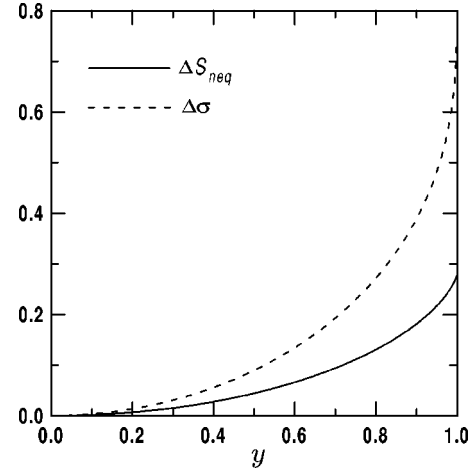


FIG. 1. Comparative plot of the dimensionless relative difference between the second-order and the exact results for the entropy S [solid line, Eq. (20)] and entropy production rate σ [dashed line, Eq. (23)] vs the dimensionless parameter $y = J/(n v_0)$.

A. Reactive process

If we only consider the reactive process, that is if there is no diffusion flux ($J = 0$), the entropy production is due only to particle reaction or reproduction,

$$\sigma_{rep} = \sigma(n, J = 0) = -k_B r(n) \left(1 + \ln \frac{n}{2} \right).$$

This will be negative when the term in brackets becomes positive, that is for $n > 2/e$, provided that for particle generation $r(n) > 0$. This corresponds to the fact that the system composed by the particles is not isolated. Up to this point, we have only taken into account that new particles can appear, but if we want to analyze the entropy production rate of the whole system, we must certainly take into account the source of particles, e.g., the presence of particles of a different species B that may react according to $B + B \rightarrow A + A$, where particles A are those considered up to now. The distribution function f_B of particles B will satisfy an equation identical to Eq. (3), with the only difference that the first term in Eq. (4) will be negative, i.e., $-r(n_A) \varphi(v_A)$, because the removal of a particle of species B implies the appearance of a particle of species A . Here $n_A = n_0 - n_B$, where n_0 is the total number density of particles of the whole system. It is simple to repeat the previous analysis for species B instead of A . This yields the same entropy production rate as above, which has been computed for particles A and is

$$\sigma_A(n, J = 0) = -k_B r(n_A) \left(1 + \ln \frac{n_A}{2} \right),$$

with the only difference that the reaction rate for species B is equal and opposite to that for species A ,

$$\sigma_B(n, J = 0) = +k_B r(n_A) \left(1 + \ln \frac{n_B}{2} \right).$$

By adding both contributions we find out the total entropy

production rate due to the reactive process,

$$\sigma_{react}(n, J=0) = \sigma_A(n, J=0) + \sigma_B(n, J=0) = k_B r(n_A) \ln \frac{n_B}{n_A},$$

and according to the second law $\sigma_{react}(n, J=0) \geq 0$, which implies that $r(n_A) \geq 0$ if, and only if, $n_B > n_A$. This is as it should be, since an isolated reacting system with $n_B > n_A$ will evolve according to $B+B \rightarrow A+A$, i.e., $r(n_A) > 0$, until chemical equilibrium ($n_A = n_B$) is reached, and at this point the direct and reverse reactions will balance each other [$r(n_A) = 0$].

B. Diffusive process

For simplicity, we will here consider a single species [i.e., the first term in Eq. (17)],

$$\sigma_{diff}(n, J) = \frac{k_B J}{2 v_0 \tau} \ln \left(\frac{n + \frac{J}{v_0}}{n - \frac{J}{v_0}} \right) = \frac{n k_B}{\tau} \sum_{j=1}^{\infty} \frac{y^{2j}}{2j-1} \geq 0. \quad (21)$$

The second-order approach ($j=1$) corresponds to

$$\sigma_{diff}^{(2)} = \frac{k_B J^2}{n D}, \quad (22)$$

where we have recalled that $D = v_0^2 \tau$ (see Sec. II). We note that $\sigma_{diff} > \sigma_{diff}^{(2)}$. We are interested now in computing the difference between the exact expression for the entropy production (21) and the second-order approximation (22),

$$\sigma_{diff}^{ex} = \frac{n y k_B}{2 \tau} \ln \left(\frac{1+y}{1-y} \right), \quad \sigma_{diff}^{(2)} = \frac{n k_B}{\tau} y^2,$$

so the relative error is

$$\Delta \sigma = \left| \frac{\sigma_{diff}^{ex} - \sigma_{diff}^{(2)}}{\sigma_{diff}^{ex}} \right|. \quad (23)$$

This magnitude reaches a maximum value equal to 1 in the limit $y \rightarrow 1$, as shown in Fig 1. For sufficiently small values of the particle flux, the second-order approach is reasonably good. For $J = n v_0 / 2$, the error of the second-order result is already of about 10%. The usefulness of any exact model depends, of course, on the situation analyzed. Estimates pre-

dict second-order corrections to be negligible for experimentally accessible values of J [12]. On the other hand, at this moment we think that the simple model presented here has no direct, sensible physical application (note that we have considered particles moving in a 1-dim space). Thus the main interest of our model is conceptual. However, in bio-physical applications our model could be valuable: for example, the diffusion of birds along a coast is essentially a 1D system in which all particles move at about the same speed [13], as assumed here. In these experiments, birds are released from a given space point and the value of the reduced flux is $y \approx 1$ when the first birds reach a point located some distance away [13]. For such a value of y , exact results differ substantially from lower-order approximations (see Fig. 1). Moreover, in the application mentioned the experimental data are inconsistent with classical diffusion, and although it has been noted that the finite velocity of propagation is an important cause behind this disagreement [13], a better model does not seem to have been presented. A detailed application of our model to this problem is the plan of future work. A 2D version of Eq. (10) has been applied to human population expansions, a case for which its predictions agree quite well with observations [4]. We would like to stress that, in contrast to the derivation presented in Ref. [4], Eq. (10) is exact in the simple model here reported.

IV. CONCLUSIONS

From the usual definitions of the entropy and entropy flux in kinetic theory, we have built up a thermodynamical study of a simple nonequilibrium system. Previous work has sometimes focused on second-order approximations [7], although terms up to fourth order have been computed [14]. Here we have been able to develop an exact approach by considering a simple model. Comparison of the exact results to those corresponding to the second-order description has been performed: the exact relative errors for the entropy and entropy production rate have been computed. The results are not at all incompatible with EIT; instead, they are embedded in its framework. They are valid arbitrarily far away from equilibrium.

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