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Irreversible thermodynamic analysis of two-layer systems

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A thermodynamic study of two-layer systems is developed. The generalized entropy, entropy flux, and entropy production for these systems are evaluated exactly as functionals of the concentration $P(x,t)$ and the particle flux $J(x,t)$. In contrast to what happens in local-equilibrium irreversible thermodynamics, the entropy production is shown to be positive definite for plausible stochastic models of particle exchange between layers. A nonequilibrium temperature is also introduced in this context, and its physical interpretation is discussed.

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The two-layer model is a simple model for diffusion processes which has been rediscovered in several contexts of the physical sciences. In its most intuitive form, it consists of a system whose particles jump at random times between two states, say 1 and 2, each of them having associated a velocity along the x axis (v_1 and v_2). Denoting with $P_i(x,t)$, $i = 1,2$, the probability density of finding a particle in the i state at position x and time t, the general problem is to obtain the solute distribution $P(x,t) = P_1 + P_2$, and the net particle flux, $J(x,t) = P_1 v_1 + P_2 v_2$ for given initial and boundary conditions.

There exists a wide variety of situations where this model applies. Among them, maybe the most direct one is chromatography, where one can distinguish a mobile state ($v_1 = v$), and an adsorbed state ($v = 0$) [1, 2]. It has also been studied as the simplest model for Taylor dispersion, i.e., the study of the longitudinal dispersion of a solute dropped in a solvent which flows through a tube [3]; the essence of this problem resides in the coupling between transverse molecular diffusion and the velocity profile inside the tube; obviously, the two-layer model captures its basic ingredients: the velocity field is reduced to its simplest form, two layers, and molecular diffusion is modelized through the random jumps between them. Aside from its fundamental interest in Taylor dispersion, the model has been used in the study of solute dispersion in rivers [4].

The two-layer model is also in the heart of the so-called persistent random walk [5,6]; this is a random walk where a particle jumps from a site to the contiguous one of a discrete unidimensional lattice with the feature that the next jump is more probable to be in the sense of the last one; that is to say, if the last step of the random walker was to the right, the next one is more likely to be to the right also. Then one can talk of two different functions, the probability for a particle to move to the right at x and t, $P_1(x,t)$, or to the left, $P_2(x,t)$. This random process has been employed as a stochastic model for quantum diffusion in one-dimension (1D) to recover the Landauer equation for the diffusion of electrons at 0 K [7].

There exist other systems where the model applies, such as electrophoresis [8] or nuclear magnetic resonance [9], for a review of them see Ref. [1]. In all these cases, however, the interest is focused on the knowledge of the total probability (or concentration) $P(x,t)$, i.e., in the dynamics of the two-layer systems. The purpose of this work is to analyze its thermodynamic aspects, a point of view that has not been dealt with in the past. We will see that, similarly as this model provides a very useful simplification of the dynamics of the physical problems while keeping its essence, it also serves as a clarifying illustration of the thermodynamic description in nonequilibrium situations.

The existence of an entropy function for nonequilibrium states is a question open to discussion. The so-called extended irreversible thermodynamics (EIT) proposes a generalization of the local-equilibrium entropy, only depending on the equilibrium variables, through the inclusion of the dissipative fluxes as independent variables in a generalized entropy. This theory has been confirmed by the kinetic theory of ideal and real gases, of polymeric solutions, by projector operator methods or information theory [10]. Nevertheless, in all the cases, the confirmation is limited to the second order in the fluxes. In this example, in contrast, we will obtain the exact dependence of these functionals with the flux and concentration, and show that the dynamics of the fluxes obtained from the theory of stochastic processes leads to a positive entropy production beyond the second order in the fluxes.

The paper is organized as follows. We first find the equations governing the time evolution of the solute distribution, $P(x,t)$, and the net particle flux, $J(x,t)$, from the stochastic nature of the model. Second, after showing that the constitutive equations for J thus obtained do not satisfy the positiveness of the local-equilibrium entropy production, the generalized entropy, entropy flux and entropy production are evaluated and the positiveness of the latter is proved for the flux dynamics found at the stochastic level of description. Later on, we introduce a nonequilibrium temperature in this context and discuss its interpretation. We end with some concluding remarks.

Let us first write the equations for the probability densities, $P_i(x,t)$ (for the sake of simplicity, it is taken $v_1 = v$, $v_2 = -v$). One has

$$\dot{P}_1 + v\frac{\partial P_1}{\partial x} = -m, \tag{1}$$

$$\dot{P}_2 - v\frac{\partial P_2}{\partial x} = m, \tag{2}$$

where the dot indicates partial time differentiation, and m the rate of particle exchange between both states.

By adding (1) and (2) one obtains the particle conservation equation

$$\dot{P} + \frac{\partial J}{\partial x} = 0, \tag{3}$$

and subtracting (2) from (1) the equation for the particle flux, $J(x,t) = (P_1 - P_2)v$,

$$\dot{J} + v^2\frac{\partial P}{\partial x} = -2mv. \tag{4}$$

In the simplest situation, it is assumed that the rate at which particles leave state i is proportional to P_i, so that m takes the form $m = r(P_1 - P_2)$, with $r\,dt$ the probability for a particle to go from one state to the other during the time interval dt; this is the so-called Goldstein-McKean model, whose connection with kinetic theory and generalized hydrodynamics has been extensively studied since it supplies the simplest example of a nonhomogeneus transport equation [11]. Equation (4) then adopts a Maxwell-Cattaneo form

$$\tau\dot{J} + J = -D\frac{\partial P}{\partial x}, \tag{5}$$

$\tau \equiv 1/2r$ and $D \equiv v^2\tau$ being positive constant parameters. The combination of (3) and (5) yields the well-known telegrapher's equation

$$\tau\,\ddot{P} + \dot{P} = D\frac{\partial^2 P}{\partial x^2}. \tag{6}$$

Other cases, however, could be considered for m, such as a quadratic rate, $m = r(P_1^2 - P_2^2)$, or cubic, $m = r(P_1^3 - P_2^3)$. In all of them the resulting equation for $J(x,t)$ has the form (5) but with nonconstant parameters, so that the dynamics of J—and of $P(x,t)$—also becomes nonlinear. For instance, it is easy to obtain for the quadratic dynamics, $\tau^{-1} = 2rP$, and for the cubic, $\tau^{-1} = r(3P^2 + J^2)/2$.

Let us note that the constitutive equation (5) is not compatible with the positiveness of the local-equilibrium entropy production. Indeed, in classical irreversible thermodynamics [12], the entropy production is proportional to $-J\partial P/\partial x$. If we substitute (5) in this expression we find two terms, one proportional to $(\partial P/\partial x)^2$, which is always positive, and another in $\dot{J}\partial P/\partial x$, with no definite sign, so that the positivity of σ is not guaranteed, contrary to the local version of the second law of thermodynamics.

Extended thermodynamics, however, overcomes this difficulty. First, we are evaluating the entropy function $s(P,J)$ for a two-layer system. In terms of the probability densities, $P_i(x,t)$, the standard expression for the entropy density is

$$s(x,t) = -kP_1\ln P_1 - kP_2\ln P_2, \tag{7}$$

k being the Boltzmann constant. On the other hand, from the definitions of P and J it is immediate to write (7) as

$$\begin{aligned} s(P,J) = &-\frac{k}{2}\left(P + \frac{J}{v}\right)\ln\left[\left(P + \frac{J}{v}\right)\Big/2\right] \\ &-\frac{k}{2}\left(P - \frac{J}{v}\right)\ln\left[\left(P - \frac{J}{v}\right)\Big/2\right]. \end{aligned} \tag{8}$$

In contrast to what is usually found in extended thermodynamics, this expression gives the entropy functional for any value of J, and not only for small ones. Let us also notice that, from its definition, $J \leq Pv$, i.e., there exists a maximum value for the particle flux, for which the entropy tends to $-kP\ln P$, corresponding to the case where all the particles are in the same layer; the existence of a maximum flux is a prediction of EIT from stability arguments in nonequilibrium steady states [10] as well as a suitable condition to preserve the positiveness of the solutions of the telegrapher's equation [13].

For $J \ll Pv$, Eq. (8) gives

$$s = -kP\ln(P/2) - \frac{k}{2}\frac{J^2}{Pv^2}. \tag{9}$$

The first term describes the local-equilibrium part, and the second one provides the first correction in purely nonequilibrium contributions; this term turns to be quadratic in the fluxes as usual in EIT. An expression like (9), with a coefficient of J^2 in P^{-1} has already been found in the past as an extension of the Boltzmann H function in order to establish a H theorem for generalized telegrapher type equations [14], and also in Taylor dispersion [15].

Similarly, for the entropy flux one has

$$\begin{aligned} J^s(x,t) &= (-P_1\ln P_1 + P_2\ln P_2)\,kv \\ &= -\frac{kv}{2}\left(P + \frac{J}{v}\right)\ln\left[\left(P + \frac{J}{v}\right)\Big/2\right] \\ &\quad+\frac{kv}{2}\left(P - \frac{J}{v}\right)\ln\left[\left(P - \frac{J}{v}\right)\Big/2\right]. \end{aligned} \tag{10}$$

In the limit $J \ll Pv$, expression (10) yields

$$J^s = -k\left(\ln\frac{P}{2} - 1\right)J = -\mu_0 T^{-1}J, \tag{11}$$

where $\mu_0 T^{-1} = (\partial s/\partial P)_{J=0}$ is the local-equilibrium chemical potential computed with (9). Thus we see that, close to equilibrium, the entropy flux has the form of a typical dissipative flux (something similar occurs in Taylor dispersion [15]).

Introducing (8) and (10) into the entropy balance equation the entropy production σ is obtained. With the help of the particle conservation equation (3), one easily gets

$$\sigma = \dot{s} + \frac{\partial J^s}{\partial x} = -\frac{k}{2v}\left[\dot{J} + v^2\frac{\partial P}{\partial x}\right]\ln\left[\frac{P + J/v}{P - J/v}\right]. \tag{12}$$

Again, we stress that, contrary to what is usually done in EIT, this entropy production is valid for all J, and not only for small fluxes. In this limit, the logarithm can be expanded to give

$$\sigma = -\frac{k}{Pv^2} J \left[\dot{J} + v^2 \frac{\partial P}{\partial x} \right] , \tag{13}$$

which has the standard form in extended thermodynamics as a bilinear expression of fluxes and forces, the latter not only containing the concentration gradients but also the time derivative of the fluxes.

The question that we must now study is whether the evolution equations for $J(x,t)$ found from particular dynamics for the exchange between states lead to a positive value of σ. In order to prove so, let us realize that Eq. (4) contains the term inside brackets of (12), and that for jump dynamics supplying a source rate of the type $m = r(P_1^l - P_2^l)$, with l an integer—as in the three cases considered above—, m can be writen as $m = AJ$, with $A = r\sum_{i=1}^{l} P_1^{l-i} P_2^{i-1}$ a positive quantity; then we have

$$\sigma = \frac{kA}{2v} J \ln \left[\frac{P + J/v}{P - J/v} \right] . \tag{14}$$

Finally, using the mathematic property

$$(x - y)\ln(x/y) \geq 0 \tag{15}$$

for any x and y, it is concluded that σ keeps always positive values, except at equilibrium, where $J = 0$ and $\sigma = 0$.

Conversely, we could use the condition of positive entropy production to obtain the possible evolution equations for $J(x,t)$. Bearing in mind (15), this implies

$$\dot{J} + v^2 \frac{\partial P}{\partial x} = -f(P,J)J,$$

$f(P,J)$ being a positive function, in agreement with (5).

We may stress that, until now the positiveness of the generalized entropy production of EIT for Maxwell-Cattaneo dynamics for the fluxes had been proved keeping in the entropy production only up to second order terms [Eq. (13)]. This is quite reasonable since the Maxwell–Cattaneo (MC) equation (or the telegrapher's equation) is expected to work for small values of J, while for higher J's one expects a nonlinear behavior. In the present example, however, for the case $m = r(P_1 - P_2)$, we obtain that the MC equation describes the evolution of J even for high values of J, so that the demonstration of positivity of the exact entropy production was in order. In this work, furthermore, the positiveness of the entropy production has been proved not only for linear dynamics for the jumps between layers, but also for some nonlinear cases.

Let us remark that up to now most of the analyses of a flux-dependent nonequilibrium entropy were based on kinetic theory and limited to second-order terms in the fluxes. Only a few number of papers had been devoted to a general analysis of the thermodynamic quantities: on the basis of information theoretical analyses of energy transport in a closed ring formed by a harmonic chain [16], in which case the entropy per particle is

$$s = k\left[1 + \ln\epsilon + \ln\left(1 - x^2\right)\right] , \tag{16}$$

ϵ being the energy per particle and $x \equiv q/v\epsilon$, with q the heat flux and v the speed of phonons; or in the study of energy transport in electromagnetic radiation, which yields [17]

$$s = au^{3/4} \frac{\left[\sqrt{4 - 3x^2} - 1\right]^{1/4}}{\left[2 - \sqrt{4 - 3x^2}\right]^{1/2}} x, \tag{17}$$

with $a = \frac{2}{\sqrt{3}}[\frac{8\pi^5 k^4}{15h^3c^3}]^{1/4}$ and $x \equiv q/cu$, c being the speed of light and u the energy density.

Therefore, our expression (8) adds to the very reduced number of papers about a nonequilibrium entropy dependent on the flux, but not limited to the quadratic terms in the fluxes. Besides this, our analysis has the advantage of providing a very simple and direct approach to such a generalized entropy.

Our purpose now is the introduction of thermal effects in the context of two-layer systems. One way to do it would be to consider two layers with different energies, let us say ϵ and 0, in which particles can move with velocities $\pm v$. In this case, the stochastic description contains four probability densities, namely, P_1^+, P_1^-, corresponding to particles of energy ϵ moving to the right or to the left, respectively, and P_2^+, P_2^- standing for particles of 0 energy; in order to simplify notation, in some cases we will denote these densities simply by $P_i, i = 1,2,3,4$, respectively.

Instead of them, one can describe the system using the hydrodynamic quantities P, J, u, and q (u being the internal energy and q the heat flux), related to the latter ones through

$$\begin{aligned} P &= P_1^+ + P_1^- + P_2^+ + P_2^- , \\ J &= (P_1^+ - P_1^- + P_2^+ - P_2^-)v, \\ u &= (P_1^+ + P_1^-)\epsilon, \\ q &= (P_1^+ - P_1^-)v\epsilon. \end{aligned} \tag{18}$$

The equations for these magnitudes depend, of course, on the specific dynamics chosen for the jumps of the particles. For a simple dynamics, it is direct to obtain Maxwell-Cattaneo like equations for both fluxes, J and q, by following the procedure of the previous example. Nevertheless, the point that deserves special attention in the present analysis is the thermodynamic temperature. The physical interpretation of a nonequilibrium temperature is a question open to debate; for an update discussion of the subject see Ref. [18] and the references therein. In the present example, we are seeing below that the nonequilibrium temperature of extended irreversible thermodynamics can be interpreted as an extension of the equilibrium statistical-mechanic concept of temperature.

Similarly to Eqs. (7) and (8), we can write a generalized entropy density depending not only in the classical variables P and u but also in the fluxes J and q:

$$s(P,J,u,q) = -k\sum_{i=1}^{4} P_i \ln P_i, \tag{19}$$

where $P_i = P_i(P,u,J,q)$ are the expressions for P_i in terms of the hydrodynamic quantities as obtained from (18). On the other hand, the generalized temperature is introduced in extended thermodynamics as a direct generalization of the equilibrium temperature, namely,

$$T^{-1} = \left.\frac{\partial s}{\partial u}\right|_{P,J,q} = -k\sum_{i=1}^{4}(\ln P_i + 1)\left.\frac{\partial P_i}{\partial u}\right|_{P,J,q} = \frac{k}{2\epsilon}\ln\left[\frac{P_2^+ P_2^-}{P_1^+ P_1^-}\right]. \tag{20}$$

The last equality coming from the relations $\partial P_1^{\pm}/\partial u = 1/2\epsilon$ and $\partial P_2^{\pm}/\partial u = -1/2\epsilon$, as can be easily seen from (18). Finally, by substituting the expressions for P_i, one obtains the generalized temperature as a function of the state variables:

$$T^{-1}(P,u,J,q) = \frac{k}{2\epsilon}\ln\frac{[(P+J/v)\epsilon-(u+q/v)]\,[(P-J/v)\epsilon-(u-q/v)]}{(u+q/v)(u-q/v)}. \tag{21}$$

Let us emphasize once again that, in constrast to the local-equilibrium temperature, only dependent on the local-equilibrium variables P and u, expression (21) also contains the mass and heat fluxes.

On the other hand, from Eq. (20), we have

$$\left(\frac{P_2^+ P_2^-}{P_1^+ P_1^-}\right)^{1/2} = e^{-\frac{\epsilon}{kT}}. \tag{22}$$

This expression provides an interpretation of the generalized temperature as a quantity that basically supplies the quotient between the populations of two microscopic states that differ an energy ϵ in nonequilibrium situations, similarly to the interpretation of the absolute temperature in equilibrium statistical mechanics. More precisely, the exponential term gives the ratio between the geometric averages of the number of particles moving to the right and to the left in both states. In equilibrium, the fluxes J and q vanish, so that $P_j^+ = P_j^-$ from (18), $T = T_{eq}$ and expression (22) reduces to the result of equilibrium statistical mechanics. Therefore, we have seen that, for this simple example, the generalized nonequilibrium temperature of extended thermodynamics has a statistic counterpart as a generalization of the equilibrium statistical mechanic concept of temperature.

Finally, some comments on the relation of this work with a previous one by Jiu-li *et al.* are in order [19]. In the latter paper, mainly devoted to the analysis of the role of fluctuations in macroscopic stability, the authors develop a thermodynamic treatment of Markovian processes by studying the master equation. An entropy production is obtained with a form analogous to the classical entropy production for a set of chemical reactions, affinities, and reaction rates being some functions of the transition rates between states, W_ρ. The present work, in contrast, focuses on the study of transport processes. Furthermore, instead of writing the thermodynamic functions, such as the entropy, the entropy flux or the entropy production, in terms of stochastic quantities—the transition rates, W_ρ, and the probabilities P_i—, we express the thermodynamic functions in terms only of thermodynamic state variables in the scheme of extended thermodynamics, namely the total concentration and energy, P and u, and the mass and heat fluxes, J and q. Thus, contrary to the previous work, our treatment is completely thermodynamic; this allows us to introduce other thermodynamic variables which are absent in Ref. [19], like the chemical potential and the temperature. Furthermore, we have seen that there exists a complete agreement between our macroscopic description and the stochastic one. For instance, the dynamics for the dissipative fluxes obtained at the stochastic level satisfy the positivity of the entropy production or, conversely, they have the form predicted from this thermodynamic requirement both in the linear and the nonlinear case. In paper [19], on the contrary, the stochastic model is compared with local-equilibrium thermodynamics and the agreement only takes place in the linear regime.

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