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# On the non-equilibrium thermodynamics of some complex dynamical behaviours

D Jou† and J Camacho

Departament de Física (Física Estadística), Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain

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**Abstract.** In many situations of physical interest, the dissipative fluxes may be considered as a sum of an infinite number of terms or an integral. The formalism of extended irreversible thermodynamics (EIT) is generalised to cover these situations. Several kinds of memory functions of special physical interest, such as the stretched exponential or the potential ones, find in the present formulation of EIT a natural place. As simple illustrations, the formal development is applied to charged suspensions, porous media and monatomic ideal gases.

## 1. Introduction

The dynamics of the dissipative fluxes plays a central role in non-equilibrium statistical mechanics, as it is related to the memory functions describing the response of the system to external perturbations. The evolution equations for the dissipative fluxes also form part of the central aims of a non-equilibrium thermodynamic theory, the so-called extended irreversible thermodynamics (EIT) (Casas-Vázquez *et al* 1984, Muller 1985, Jou *et al* 1988, García-Colín 1988). In contrast to the classical theory of non-equilibrium thermodynamics (De Groot and Mazur 1962, Glandsdorff and Prigogine 1971), whose independent variables are those related to the usual balance equations (mass density, barycentric velocity, internal energy, etc), EIT also includes the dissipative fluxes as independent variables (heat flux, bulk and shear viscous pressure, electric current, etc). Then the aim of EIT is to obtain evolution equations for the fluxes themselves considered to be independent variables in their own right. This point of view is of interest for fast phenomena, on the scale of the relaxation time of the fluxes, whereas for slow phenomena the relaxation terms disappear and the fluxes are directly related to the gradient of the classical variables as in the classical theory.

The simplest versions of EIT take the fluxes as single physical quantities. This point of view must be widened in the treatment of more complex systems, as real gases (Nettleton 1960, Jou and Micenmacher 1987, Eu 1980) or polymeric fluids (Lebon *et al* 1987, Camacho and Jou 1990) where different contributions with different dynamical behaviour must be considered in the several fluxes, thus leading to evolution equations for the fluxes which are more complex than the simple exponential decay.

† Also at Institut d'Estudis Catalans, Spain.

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Here we go a step ahead towards a general formulation of EIT, and we address our attention to several kinds of complex dynamical behaviours, such as the stretched exponential decay or the potential decay. In the first case, the decay is of the form

$$\boldsymbol{J}(t) = \boldsymbol{J}(0)[\exp -(t/\tau)^{\beta}] \tag{1}$$

with $\boldsymbol{J}(t)$ a dynamical variable and $\beta$ an exponent $0 < \beta \leq 1$. This kind of dynamical behaviour, known in some contexts as the Kohlrausch law or William–Watts law, has received a wide attention because of its appearance in many different physical systems (Schlesinger 1988, Chamberlin *et al* 1970, Williams and Watts 1970). Decays of the potential kind $t^{-\alpha}$ have also deserved special attention in statistical mechanics, mainly in the context of long time tails (Reichl 1980). Thus it is of interest to consider the thermodynamics associated with this kind of dynamics.

In section 2, we present a general formulation of EIT from a macroscopic point of view, which considers that the dissipative fluxes contain an infinite number of independent contributions. In section 3, we analyse how this formalism is able to cope with some specific kinds of dynamics of the fluxes which are of special interest. Section 4 provides three simple illustrations of the theory, applied to suspensions, porous media and monatomic ideal gases. Section 5 is devoted to some concluding remarks.

## 2. Thermodynamic development

To achieve a maximum simplification we assume a simple system whose equilibrium state is described by means of the internal energy, such as a solid rigid or an incompressible fluid. The extension to more complex situations is straightforward. We assume furthermore a non-equilibrium situation related to a dissipative flux $\boldsymbol{J}$, which could be the heat flux, the electric current, the viscous pressure tensor, the diffusion flux, etc. When $\boldsymbol{J}$ is an electric current the generalised entropy per unit mass $s$ of EIT has the form (Jou *et al* 1988)

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\tau}{2\sigma T}\boldsymbol{J}\cdot\boldsymbol{J} \tag{2}$$

where $\rho$ is the mass density, $\sigma$ the electrical conductivity, $\tau$ the relaxation time of the flux $\boldsymbol{J}$ and T the local equilibrium temperature. For a heat flux $\boldsymbol{q}$ the generalised entropy is

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\tau}{2\lambda T^2}\boldsymbol{q}\cdot\boldsymbol{q} \tag{3}$$

with $\lambda$ the heat conductivity and $\tau$ the relaxation time of $\boldsymbol{q}$. These entropies lead to evolution equations for the fluxes of the relaxational kind

$$\tau\dot{\boldsymbol{J}} + \boldsymbol{J} = \sigma\boldsymbol{E} \tag{4}$$

$\boldsymbol{E}$ being the electric field, and

$$\tau\dot{\boldsymbol{q}} + \boldsymbol{q} = -\lambda\nabla T. \tag{5}$$

When the relaxation terms may be omitted, equations (4) and (5) reduce respectively to Ohm and Fourier laws.

The classical entropy production ($\sigma_s$) for electrical conduction and heat conduction has the form

$$\sigma_s = \frac{1}{T}\boldsymbol{J}\cdot\boldsymbol{E} \tag{6}$$

$$\sigma_s = -\frac{1}{T}\boldsymbol{q}\cdot\nabla T. \tag{7}$$

Note, however, that the entropy production as expressed by (6) and (7) may become negative for evolution equations of the form (4) or (5). Of course, when the relaxation terms may be omitted, Ohm's law and Fourier's law satisfy the positive character of (6) and (7).

Thus, to have a thermodynamic framework consistent with (4) and (5) the entropy is generalised as in (2) and (3). The entropy production related to such generalised entropies is, respectively (Jou *et al* 1988)

$$\sigma_{\mathrm{EIT}} = \frac{1}{T}\boldsymbol{J}\cdot\left(\boldsymbol{E} - \frac{\tau}{\sigma}\dot{\boldsymbol{J}}\right) \tag{8}$$

$$\sigma_{\mathrm{EIT}} = -\frac{1}{T^2}\boldsymbol{q}\cdot\left(\nabla T + \frac{\tau}{\lambda}\dot{\boldsymbol{q}}\right). \tag{9}$$

It is obvious that (4) and (5) satisfy the positive character of (8) and (9). Thus, the compatibility between classical non-equilibrium thermodynamics and the dynamics is not obvious at all, but requires sometimes a modification of very basic quantities, such as the entropy.

To obtain the form of the entropy compatible with a dynamical behaviour of the form (1) we consider that the flux $\boldsymbol{J}$ is the sum of an infinite number of contributions characterised by a continuous parameter $x$, that is to say

$$\boldsymbol{J}(\boldsymbol{r},t) = \int \mathrm{d}x\, f(x)\boldsymbol{J}(x;\boldsymbol{r},t) \tag{10}$$

where $f(x)$ is a weight factor ascribed to the $x$th level and $\boldsymbol{J}(x;\boldsymbol{r},t) \equiv \boldsymbol{J}(x)$ is the value of each contribution to $\boldsymbol{J}$ at the $x$th level. Some specific examples will be dealt below.

For $\boldsymbol{J}$ being the electrical current, we assume that each term $\boldsymbol{J}(x)$ satisfies a relaxational equation of the form (4), i.e.

$$\tau(x)\dot{\boldsymbol{J}}(x) + \boldsymbol{J}(x) = \sigma(x)\boldsymbol{E}. \tag{11}$$

The generalised entropy corresponding to (10) and (11) will be, according to (2)

$$\rho s = \rho s_{\mathrm{eq}} - \frac{1}{2T}\int \frac{f(x)\tau(x)}{\sigma(x)}\boldsymbol{J}(x)\cdot\boldsymbol{J}(x)\,\mathrm{d}x \tag{12}$$

and the entropy production will thus be a simple extension of (8), namely

$$\sigma_{\mathrm{EIT}} = \frac{1}{T}\int \mathrm{d}x\, f(x)\boldsymbol{J}(x)\cdot\left(\boldsymbol{E} - \frac{\tau(x)}{\sigma(x)}\dot{\boldsymbol{J}}(x)\right) \tag{13}$$

which is always positive, as it must be.

Note, finally, that the application of the Einstein formula for the probability of fluctuations

$$Pr \sim \exp\left(\frac{\delta^2 S}{2k}\right) \tag{14}$$

allows us to obtain from (12) the following expression for the second moment fluctuations of the fluxes around an equilibrium state

$$\langle \delta \boldsymbol{J}(x) \delta \boldsymbol{J}(x') \rangle_{\mathrm{eq}} = \frac{kT}{V} \frac{\sigma(x)}{\tau(x)} \frac{1}{f(x)} \delta(x - x'). \tag{15}$$

This is an expression of the fluctuation–dissipation theorem, which relates the dissipative coefficients to the fluctuations of the fluxes. We may use this expression to evaluate the fluctuations of the total flux $\boldsymbol{J}(t)$. From (10) we get

$$\langle \delta \boldsymbol{J}(t) \delta \boldsymbol{J}(0) \rangle = \int \mathrm{d}x \int \mathrm{d}x' \, f(x) f(x') \langle \delta \boldsymbol{J}(x,t) \delta \boldsymbol{J}(x',0) \rangle. \tag{16}$$

Since in equilibrium $\delta \boldsymbol{J}(x,t) = \delta \boldsymbol{J}(x,0) \exp(-t/\tau(x))$, one will have, because of (15)

$$\langle \delta \boldsymbol{J}(t) \delta \boldsymbol{J}(0) \rangle_{\mathrm{eq}} = \frac{kT}{V} \int \mathrm{d}x \, f(x) \frac{\sigma(x)}{\tau(x)} \exp(-t/\tau(x)) \tag{17}$$

and by carrying an integration over the time one recovers the Green–Kubo relations.

This simple and natural generalisation of the previous formalism of EIT will be able to cope with a wide variety of dynamical behaviours for the fluxes, and in particular with some kinds of special interest, as will be shown in the next section.

## 3. Some particular dynamical behaviours

We explore in some detail the consequences of the thermodynamic formalism presented in the previous section. The solution of (11) is

$$\boldsymbol{J}(x,t) = \boldsymbol{J}(x,0) \exp(-t/\tau(x)) + \int_0^t \mathrm{d}t' \, \frac{\sigma(x)}{\tau(x)} \exp\left(-\frac{t-t'}{\tau(x)}\right) \boldsymbol{E}(t'). \tag{18}$$

Here we do not make the usual assumption that the system is in an equilibrium state at $t = 0$, but we allow for the possibility of non-vanishing initial values for $\boldsymbol{J}(x)$.

Two situations deserve special attention: (1) the decay of the flux $\boldsymbol{J}(t)$ starting from a non-equilibrium steady state when the corresponding force $\boldsymbol{E}(t)$ is suddenly switched off; and (2) the memory function describing the response of the system, initially in an equilibrium state, to an external perturbation $\boldsymbol{E}(t)$.

*Case 1. Decay of the flux*
The steady-state value of $\boldsymbol{J}(x)$ is, according to (11),

$$\boldsymbol{J}(x) = \sigma(x)\boldsymbol{E}_0. \tag{19}$$

Thus, when $\boldsymbol{E}_0$ is suddenly turned off in $t = 0$, one has

$$\boldsymbol{J}(t) = \int \mathrm{d}x\, f(x)\boldsymbol{J}(x,t) = \frac{1}{\sigma}\boldsymbol{J}(0)\int \mathrm{d}x\, f(x)\sigma(x)\exp(-t/\tau(x)) \tag{20}$$

with $\boldsymbol{J}(0)$ the initial value of the flux $\boldsymbol{J}$, and $\sigma$ the total electrical conductivity defined as

$$\sigma = \int \mathrm{d}x\, f(x)\sigma(x) \tag{21}$$

*Case 2. Memory functions*
The total value of the flux $\boldsymbol{J}(t)$ at a time $t$ as a response to a perturbation $\boldsymbol{E}(t)$ starting from an equilibrium state may be written in the form of a memory function $\Phi(t-t')$

$$\boldsymbol{J}(t) = \int_0^t \Phi(t-t')\boldsymbol{E}(t')\mathrm{d}t'. \tag{22}$$

According to (18) the memory function will be

$$\Phi(t) = \int \frac{f(x)\sigma(x)}{\tau(x)}\exp(-t/\tau(x))\,\mathrm{d}x. \tag{23}$$

Comparing with (17) one obtains the known relation between the fluctuations and the memory functions (García-Colín *et al* 1984): $\langle\delta\boldsymbol{J}(0)\delta\boldsymbol{J}(t)\rangle = (kT/V)\Phi(t)$.

In (20) and (23) appear integrals of the form

$$\Psi(t) = \int_0^\infty g(x)\exp(-t/\tau(x))\,\mathrm{d}x. \tag{24}$$

Consequently, by choosing different expressions for the $g(x)$ and $\tau(x)$ functions one can obtain a wide variety of dynamical behaviours. We may choose functions of the form

$$\tau(x) = \tau_1 x^s \tag{25}$$

$$g(x) = B\,\mathrm{e}^{-cx} \tag{26}$$

where $\tau_1$,$B$ and $c$ are positive parameters. The dependence of $\tau$ on $x$ in this case is, of course, very simple, but one can consider simple models where this dependence appears quite directly, as in the examples shown below; another interesting example is given by Cohen and Grest (1981) in the study of dense liquids and glasses using percolation theory. Nevertheless, it should be noticed that this model gives arbitrarily small values for $\tau(x)$ as $x$ tends to zero (when $s > 0$) or to infinity (when $s < 0$). This is, from our point of view, physically meaningless since particles need a finite

time to interact and, obviously, no physical magnitude describing the system (such as the dissipative fluxes) can evolve in a time faster than the interaction between the particles. For this reason we must not expect that such a model gives physically meaningful results in the limit of short times. A model with a lower bound for the range of $x$ would be more realistic; if we choose the value of this lower bound as 1 then $\tau_1$ would be the minimum relaxation time. In any case, in this paper we do not analyse the limit of short times so that we can use the model without problems.

For positive $s$, an asymptotic evaluation of integral (24) using (25) and (26) gives, in the long-time limit, a time dependence of the type (Palmer *et al* 1984)

$$\Psi(t) \sim \exp\left[-\left(\frac{t}{\tau}\right)\right]^{1/1+s} \tag{27}$$

where $\tau$ is a time parameter. In this limit, a function of the type $g(x) \sim x^m \exp(-cx^p)$ leads to

$$\Psi(t) \sim \exp\left[-\left(\frac{t}{\tau}\right)\right]^{p/p+s} \tag{28}$$

as can be seen by means of the saddle-point method. Thus in these cases, the exponent turns out to be smaller than 1. It is remarkable that the effect of the potential factor $x^m$ in function $\Psi(t)$ is negligible at long times (see the appendix).

As we have just seen, the stretched-exponential behaviour is obtained in the long-time limit from a wide range of $g(x)$ functions. The problem is that this limit only corresponds to the period of time when the $\Psi(t)$ function has already fallen to a small percentage of its initial value (Palmer *et al* 1985). In any case, notice that according to (20) and (23) the functions $g(x)$ for the cases 1 and 2 only differ in a factor $x^s$, which is irrelevant at the long time limit as it is shown in (28). Therefore, in this limit, the time dependence of the decay function is the same as that of the memory function. (In fact, it can be seen that they differ by factors of order $(t/\tau)^\alpha$, but these are meaningless for long times.)

Some attempts have been made to include the stretched-exponential model in EIT by assuming a time dependent relaxation time (del Castillo and García-Colín 1988). We think that the model proposed in this paper is simpler and more illustrative than the other one, unless one tries to justify this time dependence on some physical grounds such as, for instance, some processes connected in series, as assumed by Palmer *et al*, instead of parallel ones.

However, a numerical evaluation of integral (24) using expressions (25) and (26) shows that it can be well fitted by a stretched-exponential function over long periods of time, including the period of major decay, but with a different exponent $\beta$ (Palmer *et al* 1985). Furthermore, one can find some cases where the stretched exponential behaviour is obtained exactly (in fact we do not need so much, since this behaviour is not experimentally obtained at the very beginning). This is the case when $\tau(x) \sim x^2$ and $g(x) \sim \exp(-cx^2)$, where the exponent $\beta$ takes the value $\frac{1}{2}$. The same exponent is also found, consequently, when $\tau(x) \sim x^p$ and $g(x) \sim x^{p/2-1}\exp(-cx^p)$, as can be directly seen from a simple change of variables. A similar behaviour (but not the same) can be obtained in the case $\tau(x) \sim x^p$ and $g(x) \sim x^{\nu-1}\exp(-cx^p)$, for any $\nu$ and $p$

$$\Psi(t) \sim t^{\nu/2p} K_{\nu/p}(2\sqrt{ct}) \tag{29}$$

where the $K_m$ are the modified Hankel functions. When $\nu/p = \frac{1}{2}$ we recover the previous case.

Another interesting dynamical behaviour, the algebraic decay $\Psi(t) \sim t^{-\beta}$, can be achieved by integral (24) choosing $\tau(x) \sim \exp(cx)$ and $g(x) \sim \exp(-px)$, then $\beta = p/c$. This is the case for the diffusion of particles in a space with a canonical distribution of activation barriers, then $x$ would be its energy and $\boldsymbol{J}$ the flux of particles. This model may be applied to describe the potential decay experimentally found in the activity of some mixtures of radioactive isotopes.

## 4. Simple illustrations

We deal in this section with three simple illustrations clarifying the meaning of the previous section. The two first ones are macroscopic while the second is more related to microscopic quantities.

### *4.1. Suspensions*

Assume a suspension of charged spherical particles of different sizes. The distribution of particles of radius $r$ will be denoted by $f(r)$. The particles are immersed in a simple, viscous, non-polarisable fluid, and the suspension is dilute enough to neglect the effects of interactions between particles. The total electric current will be thus given by

$$\boldsymbol{J}(t) = \int f(r)q(r)\boldsymbol{v}(r,t)\,\mathrm{d}r \tag{30}$$

where $q(r)$ is the charge of particles of radius $r$ and $\boldsymbol{v}(r,t)$ is their velocity at time $t$. Note that $q(r)\boldsymbol{v}(r,t) = \boldsymbol{J}(r,t)$ is the contribution of a particle of radius $r$ to the electric current.

The equation of motion of a particle may be written as

$$m'(r)\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = -\alpha(r)\boldsymbol{v} + q(r)\boldsymbol{E} \tag{31}$$

with $m'(r)$ the effective mass and $\alpha(r)$ a frictional constant. Therefore, the steady-state velocity will be

$$\boldsymbol{v}(r) = \frac{q(r)}{\alpha(r)}\boldsymbol{E} \tag{32}$$

and the relaxation time $\tau(r)$ is

$$\tau(r) = \frac{m'(r)}{\alpha(r)}. \tag{33}$$

We do not consider here long-time tail hydrodynamic effects in the decay of the velocity because, at the present stage, we are aiming only at a simple illustration of the formal framework rather than at a detailed description of charged suspensions.

Since the effective mass is proportional to $r^3$ and the frictional constant is proportional to $r$, it turns out that $\tau(r) \sim r^2$. Furthermore, the electrical conductivity $\sigma(r)$ corresponding to particles of radius $r$ will be

$$\sigma(r) = \frac{q(r)^2}{\alpha(r)}. \tag{34}$$

Therefore, according to the previous section, the electrical flux will decay, for long times, as

$$\boldsymbol{J}(t) = \boldsymbol{J}(0) \exp -(t/\tau)^{1/3} \tag{35}$$

if $f(r)\sigma(r) \sim r^m \exp(-cr)$ or, equivalently, if $f(r) \sim r^n \exp(-cr)$. Of course, a dependence of the type $f(r)\sigma(r) \sim r^m \exp(-cr^p)$ would give an exponent $p/p+2$ instead of $\frac{1}{3}$ for the relaxation (and for the memory function).

Let us consider the thermodynamic aspects of the problem. The generalised entropy (12) may be written explicitly as

$$S = S_{\mathrm{eq}} - \frac{1}{2T} \int f(r) \frac{\tau(r)}{\sigma(r)} q(r)^2 v(r)^2 \, \mathrm{d}r \tag{36}$$

or, according to (33) and (34),

$$S = S_{\mathrm{eq}} - \frac{1}{T} \int \mathrm{d}r \, f(r) \, \tfrac{1}{2} m(r) v(r)^2. \tag{37}$$

Thus, in the situation analysed here, the generalised entropy may be interpreted as the equilibrium entropy minus the contribution of the averaged, systematic microscopic motion of the charged particles, i.e. their kinetic energy divided by the absolute temperature.

### *4.2. Porous media*

Another simple illustration is provided by a porous medium with a fraction $f(r)$ of pores of radius $r$ in parallel. The global equation of motion of the fluid in the cylindrical (but tortuous) pore, denoting by $\boldsymbol{u}$ the average velocity of the fluid in it and by $\Delta p$ the pressure difference between the ends of the pore, would be of the form

$$m(r) \frac{\mathrm{d}\boldsymbol{u}(r)}{\mathrm{d}t} = -\alpha(r)\boldsymbol{u}(r) + \pi r^2 \Delta p \tag{38}$$

with $m(r)$ the mass of the fluid contained in the pore: $m(r) \sim \pi r^2 l(r)\rho$, $\rho$ being the fluid density; and $\alpha(r)$ is of the form $\alpha(r) \sim 2\pi l(r)\eta$, where $l(r)$ is the average length of a pore of radius $r$ and $\eta$ the shear viscosity.

On the other hand the flux $Q(r)$ which corresponds to a pore of radius $r$ is

$$Q(r) = \pi r^2 \boldsymbol{u}(r). \tag{39}$$

If one writes $\boldsymbol{u}(r)$ in terms of $Q(r)$ and substitutes into (38) one obtains

$$m(r) \frac{\mathrm{d}Q(r)}{\mathrm{d}t} = -\alpha(r)Q(r) + \pi^2 r^4 \Delta p. \tag{40}$$

Thus, in the steady state the flux in the pore of radius $r$ would be

$$Q(r) = \frac{\pi^2 r^4}{\alpha(r)} \Delta p \tag{41}$$

whereas the relaxation time will be

$$\tau(r) = \frac{m(r)}{\alpha(r)}. \tag{42}$$

Note that $\tau(r) \sim (r^2 l(r)\rho)/(l(r)\eta) \sim (\rho/\eta) r^2$ so that $\tau(r) \sim r^2$ as in the previous illustration, and $\sigma(r) \sim \pi^2 r^4/\alpha(r)$.

The global flux $Q(t)$ may be written as

$$Q(t) = \int \mathrm{d}r\, f(r) \frac{\pi^2 r^4}{\alpha(r)} \exp(-t/\tau(r)) \Delta p + \int_{-\infty}^{t} \mathrm{d}t'\, K(t-t') \Delta p(t') \tag{43}$$

with the memory function

$$K(t-t') = \int \mathrm{d}r\, f(r) \frac{\pi^2 r^4}{m(r)} \exp\left(-\frac{t-t'}{\tau(r)}\right). \tag{44}$$

Thus, according to (28), if $f(r) \sim r^m \exp(-cr^p)$ the flux would decay with an exponent $p/p+2$, and the same exponent stands for the memory function, both in the long time limit.

The Fourier transform of the memory functions yields a frequency-dependent permeability in a generalised Darcy's law of the form

$$\hat{\boldsymbol{u}}(\omega) = -\mathrm{i}\boldsymbol{k} K(\omega) p(\omega) \tag{45}$$

with $\boldsymbol{k}$ the wavevector. This generalised permeability is of interest in the analysis of waves in porous systems. In the simplest form of Biot's theory, based on the usual Darcy's law, the $K(\omega)$ have the simple form

$$K(\omega) = \frac{K}{1 + \mathrm{i}\omega\tau} \tag{46}$$

where $\tau = \rho_w K/n$, with $n$ the porosity, $\rho_w$ the fluid density and $K$ the low-frequency limit for the permeability. This global definition does not take into account the detailed microstructure of the channels in the porous medium. In contrast, the memory function used in (44) does contain information on the density of channels as a function of the radius.

On the other hand, the entropy of the porous system, according to (12), (39) and substituting $\tau$ and $\sigma$, is

$$\begin{aligned} S - S_{\mathrm{eq}} &= -\frac{1}{2T} \int \mathrm{d}r\, f(r) \frac{\tau(r)}{\sigma(r)} Q(r) Q(r) \\ &= -\frac{1}{T} \int \mathrm{d}r\, f(r) \tfrac{1}{2} m(r) \boldsymbol{u}(r)^2. \end{aligned} \tag{47}$$

The non-equilibrium term is, thus, the kinetic energy of the mean fluid in the pores divided by T.

### 4.3. Heat flux: a microscopic illustration

From a formal point of view the usual version of EIT for an ideal monatomic gas (Jou *et al* 1988) may also be cast in the way proposed in this paper. This allows us to generalise its scope to complicated memory functions. To do this, we work at the level of the velocity distribution function $f(\boldsymbol{r},\boldsymbol{c},t)$, we denote

$$\delta f(\boldsymbol{c},\boldsymbol{r},t) \equiv f(\boldsymbol{c},\boldsymbol{r},t) - f_{\mathrm{eq}}(\boldsymbol{c},\boldsymbol{r},t) \tag{48}$$

with $f_{\mathrm{eq}}$ the local-equilibrium function.

We will assume that the evolution equation for the distribution function $f$ may be written in the absence of external forces as

$$\frac{\partial f}{\partial t} + \boldsymbol{c}\cdot\nabla f = -\frac{1}{\tau(\boldsymbol{c})}\left(f - f_{\mathrm{eq}}\right) \tag{49}$$

with $\tau(\boldsymbol{c})$ a velocity dependent relaxation time.

On the other hand, the macroscopic heat flux $\boldsymbol{q}(\boldsymbol{r},t)$ can be expressed, in terms of the microscopic reduced heat flux $\hat{\boldsymbol{q}}(\boldsymbol{c}) = (\frac{1}{2}mc^2 - \frac{5}{2}kT)\boldsymbol{c}$, as

$$\boldsymbol{q}(\boldsymbol{r},t) = \int \mathrm{d}\boldsymbol{c}\,\hat{\boldsymbol{q}}(\boldsymbol{c})f(\boldsymbol{c},\boldsymbol{r},t) = \int \mathrm{d}\boldsymbol{c}\,\hat{\boldsymbol{q}}(\boldsymbol{c})\delta f(\boldsymbol{c},\boldsymbol{r},t) \tag{50}$$

because the local-equilibrium distribution function $f_{\mathrm{eq}}(\boldsymbol{c},\boldsymbol{r},t)$ does not contribute to $\boldsymbol{q}$. We will write (50) in the form

$$\boldsymbol{q}(\boldsymbol{r},t) = \int \mathrm{d}\boldsymbol{c}\,\hat{Q}(\boldsymbol{c},\boldsymbol{r},t) \tag{51}$$

with $\hat{Q}(\boldsymbol{c},\boldsymbol{r},t) \equiv \hat{\boldsymbol{q}}(\boldsymbol{c})\delta f(\boldsymbol{c},\boldsymbol{r},t)$. An evolution equation for $\hat{Q}(\boldsymbol{c},\boldsymbol{r},t)$ may be obtained from (49). By adding and subtracting $f_{\mathrm{eq}}$ into the left-hand side of (49) one gets

$$\frac{\partial(\delta f)}{\partial t} + \boldsymbol{c}\cdot\nabla(\delta f) = -\frac{1}{\tau(\boldsymbol{c})}\delta f - \boldsymbol{c}\cdot\nabla f_{\mathrm{eq}}. \tag{52}$$

The last term in (52) when one takes for $f_{\mathrm{eq}}$ the local-equilibrium distribution function, and taking into account that the spatial derivative must be evaluated under the condition of uniform pressure in order to avoid convective transport, is

$$\boldsymbol{c}\cdot\nabla f_{\mathrm{eq}} = \frac{1}{kT^2}f_{\mathrm{eq}}\hat{\boldsymbol{q}}(\boldsymbol{c})\cdot\nabla T \tag{53}$$

with $\hat{\boldsymbol{q}}(\boldsymbol{c})$ defined previously. Multiplying (52) by $\hat{\boldsymbol{q}}(\boldsymbol{c})$ one finds

$$\frac{\partial\hat{Q}}{\partial t} + \nabla\cdot[\boldsymbol{c}\hat{Q}] = -\frac{1}{\tau(\boldsymbol{c})}\hat{Q} - \frac{1}{kT^2}f_{\mathrm{eq}}\hat{\boldsymbol{q}}(\boldsymbol{c})\hat{\boldsymbol{q}}(\boldsymbol{c})\cdot\nabla T. \tag{54}$$

We have not included in (52) the term $\frac{5}{2}k\boldsymbol{c}(\delta f)\nabla T$ which comes from the gradient of $\hat{\boldsymbol{q}}(\boldsymbol{c})$ because it is a second-order term in the temperature gradient (notice, moreover, that this term vanishes when integrated over the velocities). The term in $\boldsymbol{c}\hat{Q}$ is the flux of $\hat{Q}$. The influence of the inclusion of such terms in EIT has been studied

elsewhere (Pérez-García and Jou 1986). Here we will neglect its contribution for the sake of simplicity. In this approximation, equation (54) has the form of a Maxwell–Cattaneo law for $\hat{Q}$, as it happened in the previous cases for the magnitude under study. Therefore, according to (54), in a steady state we will have

$$\hat{Q}(\boldsymbol{c},\boldsymbol{r}) = -\frac{\tau(\boldsymbol{c})}{kT^2} f_{\mathrm{eq}}(\boldsymbol{c},\boldsymbol{r})\hat{\boldsymbol{q}}(\boldsymbol{c})\hat{\boldsymbol{q}}(\boldsymbol{c}) \cdot \nabla T \equiv -\lambda(\boldsymbol{c},\boldsymbol{r}) \cdot \nabla T \tag{55}$$

where we have formally denoted $\lambda(\boldsymbol{c},\boldsymbol{r})$ as the tensor relating $\hat{Q}(\boldsymbol{c},\boldsymbol{r})$ with $\nabla T(\boldsymbol{r})$.

Now we turn our attention to the entropy. Applying the well known Boltzmann formula for the entropy

$$\rho s = -k \int \mathrm{d}\boldsymbol{c}\, f \log f \tag{56}$$

to a non-equilibrium state ($f = f_{\mathrm{eq}}[1+\phi]$), one obtains up to second order (Jou *et al* 1988, De Groot and Mazur 1962)

$$\rho s = \rho s_{\mathrm{eq}} - \frac{k}{2} \int \mathrm{d}\boldsymbol{c}\, f_{\mathrm{eq}} \phi^2. \tag{57}$$

In our case $\phi = \delta f / f_{\mathrm{eq}}$, and using that, according to (55), $1/f_{\mathrm{eq}}$ may be written in terms of $\lambda(\boldsymbol{c},\boldsymbol{r})$ and $\hat{\boldsymbol{q}}(\boldsymbol{c})$, expression (55) leads us to

$$\rho s = \rho s_{\mathrm{eq}} - \frac{1}{2} \int \mathrm{d}\boldsymbol{c}\, \frac{\tau(\boldsymbol{c})}{T^2} \lambda^{-1}(\boldsymbol{c},\boldsymbol{r}) : \hat{Q}(\boldsymbol{c},\boldsymbol{r})\hat{Q}(\boldsymbol{c},\boldsymbol{r}) \tag{58}$$

which is precisely the form of the entropy $s$ that should be expected according to section 1.

To produce an expression for the entropy closer to the usual one in EIT one may introduce (55) in (58) to find

$$\rho s = \rho s_{\mathrm{eq}} - \frac{1}{2T^2} \int \mathrm{d}\boldsymbol{c}\, f_{\mathrm{eq}} \frac{\tau(\boldsymbol{c})^2}{kT^2}\, \hat{\boldsymbol{q}}(\boldsymbol{c})\hat{\boldsymbol{q}}(\boldsymbol{c}) : \nabla T \nabla T. \tag{59}$$

When $\tau(\boldsymbol{c}) = \tau_0$ is velocity independent, and taking into account the fluctuation–dissipation result and the isotropy of the system in the equilibrium state

$$\lambda \boldsymbol{U} = \frac{\tau}{kT^2} \int \mathrm{d}\boldsymbol{c}\, f_{\mathrm{eq}} \hat{\boldsymbol{q}}(\boldsymbol{c})\hat{\boldsymbol{q}}(\boldsymbol{c}) \tag{60}$$

with $\lambda$ the thermal conductivity and $\boldsymbol{U}$ the unit tensor, (59) may be written as

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\tau_0 \lambda}{2T^2} \nabla T \cdot \nabla T. \tag{61}$$

Since in the steady state $\boldsymbol{q} = -\lambda \nabla T$, (61) may also be cast as

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\tau}{2\lambda T^2} \boldsymbol{q} \cdot \boldsymbol{q} \tag{62}$$

which is the usual expression for the entropy in EIT.

The present formalism allows us to include in the framework of EIT a wide variety of forms for the time correlation functions for the fluctuations of the heat flux. According to (54) the fluxes $\hat{Q}(\boldsymbol{c},\boldsymbol{r},t)$ relax as

$$\hat{Q}(\boldsymbol{c},\boldsymbol{r},t) = \hat{Q}(\boldsymbol{c},\boldsymbol{r},0)\exp(-t/\tau(\boldsymbol{c})). \tag{63}$$

Therefore, the time correlation function around an equilibrium state

$$\langle\delta\boldsymbol{q}(0)\delta\boldsymbol{q}(t)\rangle = \int\int \mathrm{d}\boldsymbol{c}\,\mathrm{d}\boldsymbol{c}'\,\hat{\boldsymbol{q}}(\boldsymbol{c})\hat{\boldsymbol{q}}(\boldsymbol{c}')\langle\delta f(\boldsymbol{c},0)\delta f(\boldsymbol{c}',t)\rangle_{\mathrm{eq}} \tag{64}$$

taking into account that

$$\langle\delta f(\boldsymbol{c},t)\delta f(\boldsymbol{c}',0)\rangle_{\mathrm{eq}} = \frac{1}{V}f_{\mathrm{eq}}\delta(\boldsymbol{c}-\boldsymbol{c}')\exp(-t/\tau(\boldsymbol{c})) \tag{65}$$

for a sample of volume $V$, with $\delta(\boldsymbol{c}-\boldsymbol{c}')$ the Dirac distribution, will be

$$\langle\delta\boldsymbol{q}(0)\delta\boldsymbol{q}(t)\rangle = \frac{1}{V}\int \mathrm{d}\boldsymbol{c}\,f_{\mathrm{eq}}\hat{\boldsymbol{q}}(\boldsymbol{c})\hat{\boldsymbol{q}}(\boldsymbol{c})\exp(-t/\tau(\boldsymbol{c})). \tag{66}$$

For a velocity independent $\tau(\boldsymbol{c}) \equiv \tau$, this is simply

$$\langle\delta\boldsymbol{q}(0)\delta\boldsymbol{q}(t)\rangle = \exp(-t/\tau)\langle\delta\boldsymbol{q}(0)\delta\boldsymbol{q}(0)\rangle. \tag{67}$$

For other models of $\tau(\boldsymbol{c})$ the temporal behaviour of the time correlation function may be very different from the simple exponential one. To give only an illustration one could consider the simple example in which $\tau(c) \simeq l/c$, with $l$ a constant mean free path. Then (66) could be written as

$$\langle\delta\boldsymbol{q}(0)\delta\boldsymbol{q}(t)\rangle \sim \int_0^\infty \mathrm{d}c\,\left(\tfrac{1}{2}mc^2 - \tfrac{5}{2}kT\right)^2 c^4 \exp\left(-\frac{mc^2}{2kT} - \frac{tc}{l}\right). \tag{68}$$

The integrals may be evaluated taking into account that

$$\int_0^\infty \mathrm{d}x\,x^{n-1}\exp(-\beta x^2 - \gamma x) = (2\beta)^{-n/2}\Gamma(n)\exp\left(\frac{\gamma^2}{8\beta}\right)D_{-n}\left(\frac{\gamma}{\sqrt{2\beta}}\right) \tag{69}$$

with $D_n(z)$ the parabolic cylinder function of order $n$, whose asymptotic behaviour is

$$D_n(z) \sim \exp(-z^2/4)z^n\left(1 - \frac{n(n-1)}{2z^2} + \ldots\right) \tag{70}$$

so that in this case, the long time behaviour of $\langle\delta\boldsymbol{q}(0)\delta\boldsymbol{q}(t)\rangle$ would be of the form $t^{-5}$. If one considered a time dependence of the type $\tau(c) \sim c^{-2}$ the fluctuations would decay with an exponent $\frac{5}{2}$, as can be directly seen. Of course, many other more realistic models for $\tau(\boldsymbol{c})$ could be analysed, and the corresponding non-equilibrium entropy in the steady state could be computed from (59).

## 5. Concluding remarks

The non-equilibrium contributions to the generalised entropy may be justified from a more general perspective than that discussed in the previous sections (Jou *et al* 1988), and which provides a simple interpretation of its physical origin. Note that, according to (8) and (11) the entropy production will be of the form

$$\sigma_s = \int \mathrm{d}x\, f(x) \frac{\boldsymbol{J}(x)\cdot\boldsymbol{J}(x)}{\sigma(x)T}. \tag{71}$$

If one assumes a non-equilibrium steady state with value of $\boldsymbol{J}(x)$ given by $\boldsymbol{J}(x,0)$ one may attribute an entropy to a small volume of the system in the non-equilibrium steady state in the following way: one suddenly isolates the subsystem and lets it reach equilibrium. The final entropy will thus be the local-equilibrium entropy $s_{\mathrm{eq}}$. The initial entropy may be related to the final entropy by integration of the entropy production, namely

$$\rho s_{\mathrm{final}}(\mathrm{eq}) = \rho s_{\mathrm{initial}}(\mathrm{noneq}) + \int_0^\infty \sigma_s\, \mathrm{d}t. \tag{72}$$

Since, according to (11) each $\boldsymbol{J}(x)$ decays exponentially, one has

$$\boldsymbol{J}(x,t) = \boldsymbol{J}(x,0)\exp(-t/\tau(x)) \tag{73}$$

so that

$$\rho s_{\mathrm{neq}} = \rho s_{\mathrm{eq}} - \int_0^\infty \mathrm{d}t \int \mathrm{d}x\, f(x) \frac{\boldsymbol{J}(x,0)\cdot\boldsymbol{J}(x,0)}{\sigma(x)T} \exp(-2t/\tau(x)) \tag{74}$$

and therefore

$$\rho s_{\mathrm{neq}} = \rho s_{\mathrm{eq}} - \frac{1}{2T} \int \mathrm{d}x\, f(x)\tau(x) \frac{\boldsymbol{J}(x,0)\cdot\boldsymbol{J}(x,0)}{\sigma(x)} \tag{75}$$

in agreement with the expression used in (12).

The use of non-equilibrium thermodynamics formalism suggests in a direct way evolution equations more complex than (11). According to non-equilibrium thermodynamics, one should expect a mutual interaction between the several thermodynamic fluxes and forces, in the form

$$-\frac{\tau(x)}{\sigma(x)}\dot{\boldsymbol{J}}(x,t) + \boldsymbol{E} = \mu(x)\boldsymbol{J}(x,t) + \int \mathrm{d}x'\, \mu(x,x')\boldsymbol{J}(x') \tag{76}$$

with $\mu(x,x') = \mu(x',x)$, according to Onsager reciprocity relations. The restrictions of the second law would be in this case not only $\mu(x) \geq 0$ but also

$$\mu(x)\mu(x') \geq \mu(x,x')\mu(x',x) = \mu(x,x')^2. \tag{77}$$

The crossed terms could arise, in the simple models presented in section 4, from the interaction among particles of different radii or velocity, or from crossed connections among the different channels.

As a summary, the usual formalism of EIT has been shown to be able to cope with a wide variety of physical situations, provided it is slightly generalised. The present formulation opens to EIT new perspectives in the analysis of system suspensions, emulsions or porous media, which up to now were not accessible to its standard methods. The stretched-exponential decay, which is found in many complex systems, is included in the present formulation of EIT.

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## Appendix

We evaluate integral (24) for the case $g(x) \simeq x^m \exp(-cx^p)$ and $\tau_x = \tau_1 x^s$ by means of the saddlepoint method and show that for high enough values of time the potential factor $x^m$ is not relevant.

We start from the integral

$$\int \mathrm{d}x\, x^m \exp(-cx^p) \exp\left(-\frac{t}{\tau_1} x^{-s}\right) = \int \mathrm{d}x\, \exp(f(x;t)) \tag{A1}$$

with the function $f(x;t) \equiv -(t/\tau_1)x^{-s} - cx^p + m \log x$. The maximisation of this function occurs for the value $x_0$ satisfying the equation

$$cpx_0^{p+s} - mx_0^s = st/\tau_1 \tag{A2}$$

as it is obtained by simple derivation. It is evident from this equation that $x_0$ must be big at big values of $t$, and since $p > 0$ it is obvious that the first term in the left-hand side becomes more important than the second one in this long time limit.

To calculate integral (A1) by the saddle-point method one approximates $\exp(f(x;t)) \simeq \exp[f(x_0;t) + \frac{1}{2}f''(x_0;t)(x - x_0)^2]$, so that it can be written as

$$\exp(f(x_0;t)) \int \mathrm{d}x\, \exp[\tfrac{1}{2}f''(x_0;t)(x - x_0)^2] \sim \exp(f(x_0;t))(f''(x_0;t))^{-1/2}. \tag{A3}$$

On the other hand, from $cpx_0^{p+s} \simeq s(t/\tau_1)$ one may write $x_0 \sim t^{1/(p+s)}$; thus substituting into the expression for $f(x;t)$ one obtains $\exp(f(x_0;t)) \sim \exp(Mt^{p/(p+s)} + N \log t)$, with $M$ and $N$ some constants. The term in $f''(x_0;t)$ is also of the form $t^\alpha$, so that it contributes with a term of order $\log t$ at the exponent. Since these terms are negligible at long times as compared with the potential one the stretched-exponential behaviour is obtained.

We have thus seen that in the long time limit, when the saddle-point method supplies a stretched-exponential behaviour, the effect of potential terms, $x^m$, in the function $g(x)$ is negligible.

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