

## Thermodynamic functions for Taylor dispersion

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The link between Taylor dispersion and irreversible thermodynamics pointed out by Camacho [Phys. Rev. E **47**, 1049 (1993)] is substantiated through the study of the thermodynamic functions associated to Taylor dispersion. They are evaluated by two means. First, from the connection between the one-dimensional (1D) thermodynamic functions of extended thermodynamics — entropy, entropy flux, entropy production, and chemical potential — and the constitutive equations describing the dynamics of the Taylor flux components; and second, from a purely thermodynamic analysis in the three-dimensional (3D) space. Both independent procedures are shown to yield the same results, thus confirming the physical entity of the Taylor thermodynamic functions. The different interpretation of the same physical quantities given by 3D and 1D observers is thoroughly discussed.

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### I. INTRODUCTION

The study of Taylor dispersion, originally the longitudinal dispersion of a solute introduced in a solvent flowing through a rectilinear duct, has deserved a great deal of attention since Taylor and Aris published their early works in the 1950s [1–3]. Some authors have generalized its concept in order to apply it to a wide variety of physical situations, as in the generalized Taylor dispersion [4, 5], which confers a unifying structure over transport processes occurring in very different systems [6]. Others have tried to extend the asymptotic Taylor dispersion to shorter times [7–11]; and also pointed out has been its relation to the elimination of fast modes [12, 13] and to the theory of stochastic processes [14, 15].

Recently, we have shown the connection between Taylor dispersion and the thermodynamics of irreversible processes [16, 17]. Using the so-called extended irreversible thermodynamics (EIT) [18], we have proved that the Taylor dispersion flux is an actual dissipative flux of EIT. To that end, we proposed some generalized entropy and entropy flux describing Taylor dispersion, and imposed the positiveness of the entropy production in order to get some constitutive equations for the Taylor flux components. These equations were found to be identical to the equations obtained from a hydrodynamic analysis in the tridimensional space, and the thermodynamic restrictions on the transport coefficients appearing there were also satisfied. Therefore, in Ref. [16] the one-dimensional thermodynamic functions were successfully used as phenomenological tools for the obtaining of the constitutive equations. In contrast, the aim of this work is to find the thermodynamic functions from the comparison of the corresponding quantities in three dimensions, in a similar way to the derivation of macroscopic thermodynamic functions from the mesoscopic description of the kinetic theory of gases (in the latter derivation, the molecular degrees of freedom are integrated to keep only the macroscopic quantities, whereas in the present work

the transversal degrees of freedom are integrated to keep only the longitudinal one). This comparison is not only analytical, but also conceptual, stressing the different interpretation of the thermodynamic functions given by a one-dimensional (1D) observer, for which the transversal coordinates do not exist, and a 3D observer that describes the system in terms of them.

The paper has been organized as follows. In Sec. II, we give a brief summary of the results of Ref. [16] which are needed for the purposes of this paper. In the following sections, the thermodynamic functions for Taylor dispersion are evaluated and contrasted with an analysis of the corresponding quantities in the tridimensional space. Section VII is devoted to some concluding remarks.

### II. THERMODYNAMIC FUNCTIONS FOR TAYLOR DISPERSION

In Ref. [16], we assumed the following generalized entropy function describing Taylor dispersion close enough to equilibrium

$$s(x, t) = s_{\text{eq}}(x, t) - \sum_{n=1}^{\infty} \frac{1}{2} \alpha_n J_n \cdot J_n \quad (1)$$

with  $s(x, t)$  the entropy per unit volume,  $s_{\text{eq}}(x, t)$  the local-equilibrium term, and the latter one a purely nonequilibrium contribution depending on the scalar coefficients  $\alpha_n$  and on the Taylor flux components,  $J_n(x, t)$ , related to the Taylor flux through  $J_T = \sum_{n=1}^{\infty} J_n$ .

For the entropy flux,  $J^s$ , we proposed

$$J^s(x, t) = -\mu T^{-1} J - \frac{1}{2} \sum_{n,m=1}^{\infty} \alpha_{mn} (J_m J_n) - \sum_{n=1}^{\infty} \delta_n P_n \cdot J_n \quad (2)$$

$J = J_m + J_T$  being the total particle flux, namely the sum of the longitudinal molecular flux,  $J_m(x, t)$ , and the Tay-

lor dispersion contribution,  $J_T(x, t)$ ;  $\mu(x, t)$  is the chemical potential of the solute,  $P_n$  denotes the flux of  $J_n$ , and  $\alpha_{mn}$  and  $\delta_n$  are, respectively, vectorial and scalar coefficients independent of the fluxes. The first term reads as the classical contribution to an entropy flux supplied by the usual thermodynamics of irreversible processes [19], but the others are new; they are related with terms in the constitutive equation for  $J_n$  which describe, respectively, anisotropic dispersion and spatial correlations.

The introduction of (1) and (2) into the entropy balance equation leads to a bilinear form for the entropy production where every flux is multiplied by its conjugate thermodynamic force. By imposing the positiveness of the entropy production,  $\sigma_s$ , one obtains

$$\sigma_s(x, t) = K_m J_m^2 + \sum_{n=1}^{\infty} [K_{1n} J_n^2 + K_{2n} P_n^2] \quad (3)$$

(with  $K_i$  some positive phenomenological coefficients) and the constitutive equations [16]

$$J_m = -D_m \frac{\partial c(x, t)}{\partial x}, \quad (4)$$

$$P_n = -\frac{\delta_n}{K_{2n}} \frac{\partial J_n}{\partial x}, \quad (5)$$

$$\begin{aligned} \dot{J}_n + (\tau_n^{-1} - \gamma_n) J_n + \frac{\partial}{\partial x} \sum_{m=1}^{\infty} \gamma_{mn} J_m \\ = -\frac{D_n}{\tau_n} \frac{\partial c(x, t)}{\partial x} + \frac{l_n^2}{\tau_n} \frac{\partial^2 J_n}{\partial x^2}. \end{aligned} \quad (6)$$

$c(x, t)$  denotes the section-averaged concentration, the overdot indicates material time differentiation, and  $D_n, \tau_n, \gamma_n, \gamma_{mn}$ , and  $l_n$  are transport coefficients related to the phenomenological coefficients through the expressions

$$D_m = \frac{1}{K_m T} \left. \frac{\partial \mu}{\partial c} \right|_T, \quad D_n = \frac{1}{K_{1n} T} \left. \frac{\partial \mu}{\partial c} \right|_T, \quad (7)$$

$$\tau_n = \alpha_n D_n T \left. \frac{\partial \mu}{\partial c} \right|_T^{-1},$$

$$l_n^2 = \frac{\delta_n^2}{K_{1n} K_{2n}}, \quad \gamma_n = -\frac{\dot{\alpha}_n}{2\alpha_n}, \quad \gamma_{mn} = \frac{\alpha_{mn}}{\alpha_n}. \quad (8)$$

For unidirectional flows between parallel plates separated by a distance  $d$ , these coefficients take the following values in terms of the Fourier components of the velocity field  $v_n(t)$ , and the molecular diffusivity  $D_m$  [16],

$$\tau_n = \frac{d^2}{D_m n^2 \pi^2}, \quad D_n = \frac{1}{2} v_n^2 \tau_n, \quad l_n^2 = D_m \tau_n, \quad (9)$$

$$\gamma_n = \frac{\dot{v}_n}{v_n}, \quad \gamma_{mn} = (v_{|m-n|} + v_{m+n}) \frac{v_n}{v_m}. \quad (10)$$

In the following sections, we use all these expressions in order to obtain the Taylor thermodynamic functions in terms of the independent variables adopted by extended thermodynamics, namely the local magnitude  $c(x, t)$ , and the dissipative fluxes  $J_m, J_n$ , and  $P_n$ .

### III. ENTROPY

As we have seen, the scheme of extended thermodynamics introduces a generalized entropy for the description of states in the presence of mass fluxes. In this section we analyze this entropy with more detail.

The evaluation of expression (1) for the entropy requires the knowledge of the chemical potential of the solute,  $\mu(x, t)$ , both for the determination of the local equilibrium entropy, and for the estimation of coefficients  $\alpha_n$ , which depend on  $\partial \mu / \partial c|_T$  as (7) shows. Let us note that in the hydrodynamic analysis summarized in Sec. II, the solute particles are considered not to interact among them; this becomes apparent from the fact that the molecular diffusivity  $D_m$  was assumed to be constant, which would not be true for interacting particles since then there exists some dependence of  $D_m$  on the concentration. Therefore, the chemical potential corresponding to the ideal system under study has the same form as for an ideal gas, namely

$$\mu(x, t) = kT \ln c(x, t) + f(T), \quad (11)$$

$k$  being the Boltzmann constant, and  $f(T)$  a functional of the temperature without interest for the present problem, which is completely isothermal, so that we will not consider it from now on.

According to the classical Gibbs equation at constant energy and volume,  $ds = -\mu T^{-1} dc$ , the integration of (11) supplies the local-equilibrium contribution to the entropy

$$s_{\text{eq}}(x, t) = -k c(x, t) [\ln c(x, t) - 1]. \quad (12)$$

On the other hand, from (7), (9), and (11), coefficients  $\alpha_n$  take the values

$$\alpha_n = T^{-1} \left. \frac{\partial \mu}{\partial c} \right|_T \frac{2}{v_n^2} = \frac{k}{c(x, t)} \frac{2}{v_n^2}, \quad (13)$$

so that the entropy function (1) can be written as

$$\begin{aligned} s(c(x, t), \{J_n\}) = & -k c(x, t) (\ln c(x, t) - 1) \\ & - \frac{k}{c(x, t)} \sum_{n=1}^{\infty} \frac{1}{v_n^2} J_n^2. \end{aligned} \quad (14)$$

Let us now analyze the problem from a tridimensional point of view. In 3D (two dimensions for flows between parallel plates), the dispersion of the solute obeys a simple convection-diffusion equation

$$\frac{\partial C(x, y, t)}{\partial t} + v(y, t) \frac{\partial C(x, y, t)}{\partial x} = D_m \nabla^2 C(x, y, t). \quad (15)$$

$C(x, y, t)$  is the solute concentration and  $v(y, t)$  a unidirectional velocity profile; the coordinate  $y$  obviously designates the transverse direction. Equation (15) arises

from a Fickian dependence for the molecular flux, i.e.,  $J_{\text{mol}}(x, y, t) = -D_m \nabla C$ , with  $\nabla$  the bidimensional differential operator. Since this flux is characterized by a vanishing relaxation time, the Gibbs equation describing the system is the local-equilibrium one

$$ds(x, y, t) = -\mu(x, y, t)T^{-1}dC(x, y, t). \quad (16)$$

Similarly as in (11), the chemical potential  $\mu(x, y, t)$  has the form of the chemical potential for an ideal gas, with the only difference that the coordinate space in the present case is wider

$$\mu(x, y, t) = kT \ln C(x, y, t). \quad (17)$$

Again, the integration of (16) leads to

$$s(x, y, t) = -kC(x, y, t) [\ln C(x, y, t) - 1], \quad (18)$$

and integrating over the section, one finds for the entropy per unit volume in the position  $x$

$$s(x, t) = -k \int_0^d \frac{dy}{d} C(x, y, t) [\ln C(x, y, t) - 1]. \quad (19)$$

This is also the expression stemming from information theory [20], where it is interpreted as the ignorance that the knowledge of the function  $C(x, y, t)$  leaves about the transverse distribution of the solute particles.

It is useful to define the quantity  $\phi(x, y, t)$

$$\phi(x, y, t) \equiv \frac{1}{c(x, t)} \sum_{n=1}^{\infty} c_n(x, t) \cos(n\pi y/d), \quad (20)$$

with  $c_n$ , the Fourier components of the concentration  $C(x, y, t)$ , so that  $C \equiv c(x, t) (1 + \phi)$ .

After introducing (20) into (19) and manipulating a bit, one gets

$$s(x, t) = -k c(x, t) [\ln c(x, t) - 1] - k c(x, t) \int_0^d \frac{dy}{d} (1 + \phi) \ln(1 + \phi). \quad (21)$$

The first term coincides with the local-equilibrium contribution of (14). For  $\phi \ll 1$ , that is to say, when transverse inhomogeneities are small as compared to the average value, the expansion of the logarithm:  $\ln(1 + x) \approx x - x^2/2$ , supplies for the nonequilibrium term

$$s(x, t) - s_{\text{eq}}(x, t) = -\frac{1}{2} k c(x, t) \int_0^d \frac{dy}{d} \phi^2. \quad (22)$$

It is interesting to note that this contribution is always negative, as in (14), in agreement with the fact that the entropy is a maximum in equilibrium. Finally, substituting Eq. (20) and using  $J_n = c_n v_n/2$  [16], one obtains

$$s - s_{\text{eq}} = -\frac{1}{4} \frac{k}{c(x, t)} \sum_{n=1}^{\infty} c_n^2 = -\frac{k}{c(x, t)} \sum_{n=1}^{\infty} \frac{1}{v_n^2} J_n^2. \quad (23)$$

We have thus proved that the expressions coming from both procedures, (14) and (23), coincide, although the interpretation of the entropy given in each case is quite different. In the first case, the approach is completely 1D, and the entropy is expressed in terms of one-dimensional

quantities,  $c(x, t)$  and  $J_n(x, t)$ ; nevertheless, in the second one, being tridimensional,  $s(x, t)$  is regarded either as the sum of the entropies of the 3D fluid elements or, in the context of information theory, as a measure of the order of the solute distribution across the section.

#### IV. ENTROPY FLUX

In Sec. II, we employed an expression for the entropy flux which added two new terms to the classical one. The introduction of such terms proved to be useful in obtaining the constitutive equations for  $J_n(x, t)$ . The aim of this section is to establish the connection between these terms and the entropy flux defined in three dimensions. This kinetic comparison bears special interest for the term related to the transient anisotropy because this is the first time that a contribution of this type is included in the formalism of extended thermodynamics.

In order to compare with the tridimensional analysis we evaluate each term separately.

The introduction of the chemical potential (11) in Eq. (2) for the entropy flux gives for the classical contribution simply

$$J_{\text{I}}^s = -k \ln c(x, t) J(x, t). \quad (24)$$

For the term related to the anisotropy of the solute dispersion, expressions (8), (10), and (13) yield

$$J_{\text{II}}^s = -\frac{k}{2c(x, t)} \sum_{m,n=1}^{\infty} \frac{v_{m+n} + v_{m-n}}{v_m v_n} J_m \cdot J_n. \quad (25)$$

The evaluation of the coefficients  $\delta_n$  appearing in the last term of (2), the one associated with the spatial correlation between fluxes, is immediate since they are not independent of the  $\alpha_n$ 's. Since  $P_n$  are the fluxes of  $J_n$ , extended thermodynamics imposes the relation  $\delta_n = \alpha_n$  [18]. Therefore, from (13), we have

$$J_{\text{III}}^s = -\frac{k}{c(x, t)} \sum_{n=1}^{\infty} \frac{2}{v_n^2} P_n \cdot J_n. \quad (26)$$

For further use, we notice another consequence of the relation  $\delta_n = \alpha_n$ . With the help of expressions (8) and (9) for  $l_n^2$ , one finds  $K_{2n} = \alpha_n/D_m$ , so that the constitutive equation for  $P_n$ , Eq. (5), can be written simply as

$$P_n = -D_m \frac{\partial J_n}{\partial x}. \quad (27)$$

On the other hand, in the tridimensional space, the  $x$  component of the entropy flux is written as

$$J_x^s(x, y, t) = s(x, y, t)v(y) - \mu(x, y, t)T^{-1}J_{\text{mol}}^x. \quad (28)$$

When integrated over the section, we thus have an entropy flux linked to molecular diffusion

$$J_{\text{mol}}^s(x, t) = -\int_0^d \frac{dy}{d} \mu(x, y, t)T^{-1}J_{\text{mol}}^x(x, y, t) \quad (29)$$

and the contribution of convection

$$J_T^s = -k \int_0^d \frac{dy}{d} C [\ln C - 1] v(y). \quad (30)$$

(i)  $J_{\text{mol}}^s$ . After introducing (17) into (29), and making use of  $J_{\text{mol}}^s = -D_m \partial C / \partial x$  and  $C = c(1 + \phi)$ , some calculations yield

$$J_{\text{mol}}^s = k \left( \int_0^d \frac{dy}{d} \ln C(x, y, t) \right) D_m \frac{\partial c(x, t)}{\partial x} + k D_m \int_0^d \frac{dy}{d} \ln(1 + \phi) \frac{\partial c(x, t) \phi}{\partial x}. \quad (31)$$

The first term on the right-hand side can be written as  $-\mu(x, t) T^{-1} J_m(x, t)$  if we identify

$$\mu(x, t) \equiv kT \int_0^d \frac{dy}{d} \ln C(x, y, t), \quad (32)$$

which expresses the chemical potential in the reduced coordinate space as the section average of the chemical potential in the complete space. Retaining only up to quadratic terms in nonequilibrium quantities enables one to take the zero-order approximation for  $\mu(x, t)$ :  $\mu(x, t) \simeq kT \ln c(x, t)$  (i.e., the local-equilibrium chemical potential), so that we recover the classical contribution of molecular diffusion to the entropy flux explicit in (24).

With the help of  $J_n = c_n v_n / 2$  and (27), the second term is written up to second order as

$$\frac{k D_m}{2c(x, t)} \sum_{n=1}^{\infty} c_n \frac{\partial c_n}{\partial x} = -\frac{k}{c(x, t)} \sum_{n=1}^{\infty} \frac{2}{v_n^2} J_n \cdot P_n. \quad (33)$$

This is precisely the contribution  $J_{\text{III}}^s$  of Sec. II, Eq. (26).

(ii)  $J_T^s$ . The convective entropy flux, Eq. (30), can be easily manipulated to yield

$$J_T^s = -k \ln c(x, t) J_T - k c(x, t) \int_0^d \frac{dy}{d} [(1 + \phi) \ln(1 + \phi) - \phi] v(y). \quad (34)$$

The first term provides the Taylor contribution to the term  $J_I^s$  described in (24). This is quite remarkable. Similarly as the mass flux in 3D has two contributions — the convective and the dissipative ones — but in 1D the first one is seen as dissipative, with the entropy flux occurs the same, namely, the convective term (30) conspires to give a contribution to  $J^s$  which has the form of a typical entropy flux associated with a dissipative flux, i.e.,  $-\mu(x, t) T^{-1} J(x, t)$ .

On the other hand, for  $\phi \ll 1$ , one can approximate

$$(1 + \phi) \ln(1 + \phi) - \phi \simeq \phi^2 / 2$$

so that the second term in (34) reduces to

$$-\frac{k}{2c(x, t)} \int_0^d \frac{dy}{d} \phi(x, y, t)^2 v(y) = -\frac{k}{2c(x, t)} \sum_{m, n=1}^{\infty} \frac{v_{m+n} + v_{m-n}}{v_m v_n} J_m \cdot J_n \quad (35)$$

which corresponds exactly with  $J_{\text{II}}^s$ , Eq. (25). As expected, the contribution of the entropy flux associated with anisotropic dispersion (as seen from 1D) is related to the convection of the entropy contained in the tridi-

dimensional fluid elements.

We have thus shown that the same expression for the entropy flux is obtained through a classical thermodynamic formalism in three dimensions and extended thermodynamics in one dimension for situations close enough to equilibrium.

## V. ENTROPY PRODUCTION

In Sec. II, we saw that extended thermodynamics provides for Taylor dispersion an entropy production which, besides the dissipation associated with molecular diffusion,  $J_m(x, t)$ , also contains some contributions of  $J_n$  and  $P_n$ . Our present goal is to obtain the tridimensional counterpart of these terms.

The coefficients  $K_m$  and  $K_{1n}$  appearing in (3) are directly obtained with the use of (7) and (9); from the latter section,  $K_{2n} = \alpha_n / D_m$ , so that, with the aid of (13) one finally gets

$$\sigma_s = \frac{k}{c(x, t)} D_m^{-1} J_m^2 + \sum_{n=1}^{\infty} \frac{k}{c(x, t)} \left[ \frac{2}{v_n^2 \tau_n} J_n^2 + \frac{2}{v_n^2 D_m} P_n^2 \right]. \quad (36)$$

On the other hand, from the classical expressions for the entropy and the entropy flux in 3D, Eqs. (18) and (28), it obviously drops a usual entropy production

$$\sigma_s(x, y, t) = \frac{1}{k_m T} J_{\text{mol}}^2(x, y, t), \quad (37)$$

where the dissipative coefficient  $k_m$  is linked to  $D_m$  analogously as  $K_m$  in (7)

$$k_m = \frac{1}{D_m T} \frac{\partial \mu(x, y, t)}{\partial C(x, y, t)} \Big|_T = \frac{1}{D_m T} \frac{1}{C(x, y, t)}. \quad (38)$$

Therefore, one can write  $\sigma_s(x, t)$  as

$$\sigma_s(x, t) = k D_m \int_0^d \frac{dy}{d} \frac{1}{C(x, y, t)} \times \left[ \left( \frac{\partial C(x, y, t)}{\partial x} \right)^2 + \left( \frac{\partial C(x, y, t)}{\partial y} \right)^2 \right]. \quad (39)$$

After introducing  $\phi$  and approximating up to second-order terms, one immediately arrives at

$$\sigma_s(x, t) = \frac{k D_m}{c(x, t)} \int_0^d \frac{dy}{d} \left[ \left( \frac{\partial c(x, t) \phi}{\partial x} \right)^2 + \left( \frac{\partial c(x, t) \phi}{\partial y} \right)^2 \right] + \frac{k D_m}{c(x, t)} \left( \frac{\partial c(x, t)}{\partial x} \right)^2. \quad (40)$$

The last term of this expression coincides with the entropy production related to  $J_m(x, t)$  in (36).

From Eq. (20) for  $\phi$  and Eq. (27) for  $P_n$ , we can

directly evaluate

$$\frac{kD_m}{c(x,t)} \int_0^d \frac{dy}{d} \left( \frac{\partial c(x,t)\phi}{\partial x} \right)^2 = \frac{k}{c(x,t)} \sum_{n=1}^{\infty} \frac{2}{v_n^2} P_n^2. \quad (41)$$

This term coincides with the contribution of  $P_n$  to the entropy production of EIT, Eq. (36). We observe that this term plays the role of a correction to the dissipation embodied in  $[\partial c(x,t)/\partial x]^2$  with the origin in the nonuniformity of the solute distribution along the section.

Finally, the last integral can be easily manipulated to give

$$\frac{kD_m}{c(x,t)} \int_0^d \frac{dy}{d} \left( \frac{\partial c(x,t)\phi}{\partial y} \right)^2 = \frac{k}{c(x,t)} \sum_{n=1}^{\infty} \frac{2}{v_n^2 \tau_n} J_n^2, \quad (42)$$

which is the entropy production related to the Taylor flux components,  $J_n$ . We thus realize that the dissipation vinculated to the Taylor flux proceeds from the transverse molecular diffusion.

## VI. CHEMICAL POTENTIAL

In classical irreversible thermodynamics, according to the local-equilibrium hypothesis, the equations of state in nonequilibrium situations have the same form as in equilibrium. In contrast, extended thermodynamics supplies equations of state containing purely nonequilibrium terms added to the local-equilibrium ones. The present problem, described by one local variable,  $c(x,t)$ , provides only one equation of state

$$-\mu(x,t)T^{-1} = \left. \frac{\partial s(x,t)}{\partial c(x,t)} \right|_{J_n}. \quad (43)$$

The subindex  $J_n$  indicates that in the differentiation the fluxes are kept constant. With the help of (14), this expression yields

$$\mu(c(x,t), \{J_n\}) = \mu(c(x,t)) - \sum_{n=1}^{\infty} \frac{kT}{c(x,t)^2} \frac{1}{v_n^2} J_n^2. \quad (44)$$

The first term is the local-equilibrium contribution (11), and the second one is a purely nonequilibrium term. In Ref. [21], the effects of the nonequilibrium corrections to the chemical potential in the phase diagram of polymer solutions in the presence of shear are analyzed.

On the other hand, during the study of the entropy flux in the three-dimensional space, we obtained expression (32) for the chemical potential. Introducing  $\phi$  and keeping up to second-order terms, one has

$$\mu(x,t) = kT \ln c(x,t) - \frac{kT}{c(x,t)^2} \sum_{n=1}^{\infty} \frac{1}{v_n^2} J_n^2. \quad (45)$$

We observe the same result as in (44), obtained from extended thermodynamics, which can thus be seen as the lowest-order terms of an expansion of the section average of the tridimensional chemical potential.

## VII. CONCLUDING REMARKS

In Ref. [16] we showed that a unidimensional observer could describe exactly the longitudinal dispersion of a solute in a tube along all the time span; this is quite surprising since for such an observer no transversal notion makes any sense, so that the concepts of transverse diffusion and velocity field have no meaning. Therefore, although both the one-dimensional and the three-dimensional observers find the same equations for the dynamics of the fluxes, the concepts and quantities used by each one are quite different. While a 3D researcher expresses the solute dispersion as a combination of molecular diffusion and the convection of the solvent embodied in the velocity field, the 1D scientist talks in terms of dissipative fluxes, one flux related to mere molecular diffusion and the other related to convection; consequently, a mass flux which is seen as convective in 3D is regarded as dissipative in 1D. This dissipative flux, however, is not inserted in the classical thermodynamics of irreversible processes, but is incorporated in extended irreversible thermodynamics.

Similarly as the mass fluxes have different interpretations in one and three dimensions, the thermodynamic functions are regarded differently by 1D and 3D observers. For a 1D researcher these magnitudes are linked to the dynamics of the fluxes, with no reference to transversal coordinates, but for a 3D observer they are averages over the tube section of the corresponding tridimensional quantities. While in 1D, this required the use of extended thermodynamics in order for the entropy production to be positive definite, in 3D the thermodynamic formalism is the classical one, because the molecular diffusion flux is characterized by a vanishing relaxation time at the time scales under study.

For a 1D observer, the contribution of the fluxes to the generalized entropy is connected to a relaxation term in the constitutive equations for the Taylor flux components. For a 3D observer, it designates some ordering of the solute along the section.

With respect to the entropy flux, in 3D it contains two contributions, the diffusive one, related to the molecular diffusion flux, and the convective one. The section average of the first term supplies what in 1D is seen as the diffusive contribution linked to the one-dimensional molecular flux, and the term containing the fluxes  $P_n$ . The convective term, on the other hand, has the remarkable property of providing a term with exactly the same form as the classical expression for an entropy flux, namely  $-\mu T^{-1} J_T$ , with the mass flux being the Taylor flux. From the convective contribution it also drops the anisotropic term of the 1D entropy flux, which turns out quite natural since the anisotropy of the solute dispersion has its origin in the velocity profile.

In three dimensions, the entropy production is given by the molecular diffusion flux; one can distinguish two terms, the one corresponding to the molecular diffusion in the flow direction, and the transverse contribution. In 1D, extended thermodynamics proposes a contribution for each one-dimensional flux  $J_{\text{mol}}$ ,  $J_n$ , and  $P_n$ . The term in  $J_n$  expresses the dissipation related to transverse molecular diffusion, which seems quite natural because the Taylor flux, i.e.  $J_T = \sum_{n=1}^{\infty} J_n$ , originates in the

combination of transverse diffusion and the velocity field. The contributions of  $J_{\text{mol}}$  and  $P_n$  indicate the dissipation linked to the longitudinal component of the 3D molecular flux; the term in  $J_{\text{mol}}$  describes the contribution of the zero-order mode, and the terms in  $P_n$  the ones of the other transverse modes.

In summary, the successful comparison of the Taylor thermodynamic functions with the analysis in the three-dimensional space provides another evidence of the state-

ment given in Ref. [16], namely that the Taylor flux is an actual dissipative flux of extended thermodynamics.

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