Thermodynamics of Taylor dispersion: Constitutive equations

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This paper shows that the Taylor dispersion flux is a dissipative flux of extended thermodynamics. Every term in the evolution equations for the Taylor flux components is connected to a thermodynamic function and the entropy production is proved to be positive definite. Thermodynamic restrictions on phenomenological coefficients are also satisfied.

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I. INTRODUCTION

Taylor dispersion originally arose in the study of the longitudinal dispersion of a solute suspended in a solvent which flows along a rectilinear tube [1-3]. In 1953, Taylor found the fundamental result that the combined action of a unidirectional velocity field and transverse molecular diffusion leads to a longitudinal diffusion for asymptotic long times. Since then much work has been done trying to generalize his results. These efforts have been addressed in different directions and from very different points of view; besides regarding Taylor dispersion as a hydrodynamic problem [4-9], some authors have stressed its relation to the elimination of fast modes [10,11], or the theory of stochastic processes [12,13]; it has also been applied to a wide variety of physical problems, from contaminant dispersion [14] to the dispersion of polymers in solution [15], to name only two.

There also exists a strong connection between Taylor dispersion and kinetic theory: the problem of finding a closed equation for the averaged concentration starting from the (more detailed) hydrodynamic equations is analogous to the derivation of the latter ones from kinetic theory. Similarly as hydrodynamic equations can also be obtained from a framework which belongs to the same level of description, i.e., the thermodynamics of irreversible processes, we have recently developed a purely onedimensional model for Taylor dispersion valid for all times by using a one-dimensional thermodynamics [16,17]; in this way we have established a link between Taylor dispersion and thermodynamics, a relation which had not been pointed out in the past. To do that, we could not use the classical theory of irreversible processes [18] because it is only able to describe the asymptotic diffusive regime [9]. Thus we set ourselves in the framework of extended irreversible thermodynamics (EIT) [19] and proposed a generalization of the fundamental result by Taylor, namely, the combination of unidirectional velocity fields and transverse molecular diffusion adopts in one dimension the form of a dissipative flux of extended thermodynamics; in the long-time limit these fluxes become diffusive and one recovers Taylor's result. This allowed us to find constitutive equations for the Taylor dispersion flux (more complex than a Fick's law, of course) which were in excellent agreement with numerical simulations for the first moments of the distribution over long time spans (in certain conditions even along all times). This is a very interesting aspect since the extension of asymptotic longitudinal dispersion to shorter times remains an active field of research ([11,7,9,10] among many others).

Our purely one-dimensional model—a feature which distinguishes our approach from previous ones, whose start points are always three-dimensional-provides an evolution equation for the average solute concentration with a few constant (time- and space-independent) coefficients bearing a clear physical meaning. Furthermore, its purely one-dimensional character endows it with a wide generality, so that it furnishes a unifying scheme for a broad variety of physical situations where longitudinal dispersion occurs (for instance, dispersion in porous media or sedimentation of nonspherical particles, to name two systems with interest in engineering sciences). As an example of it, in Ref. [16] we briefly applied the model to the study of tracer dispersion in porous media straightforwardly providing the main features of transient non-Gaussian dispersion shown by experiments [20,21]. For a detailed discussion of the unidimensional approach the reader is referred to Refs. [16,22,17].

Later on, a detailed analysis starting from the tridimensional convection-diffusion equation (i.e., in the tridimensional space) revealed that the Taylor flux, which we had assumed to be simple, was actually made up by an infinite number of contributions; $J_T(x,t) = \sum_{n=1}^{\infty} J_n(x,t)$ (x denotes the coordinate in the flow direction), satisfying the equations [22,17],

$$\dot{J}_{n} + \frac{J_{n}}{\tau_{n}} + \frac{\partial}{\partial x} \sum_{m=1}^{\infty} \gamma_{mn} J_{m} = -\frac{D_{n}}{\tau_{n}} \frac{\partial c(x,t)}{\partial x} + D_{m} \frac{\partial^{2} J_{n}}{\partial x^{2}} ,$$
(1)

where c(x,t) is the averaged concentration, D_m is the molecular diffusivity, the dot indicates material time differentiation, and τ_n , D_n , and γ_{mn} are some coefficients depending on the section geometry and the velocity profile. By performing some kind of renormalization we recovered the constitutive equation found from the purely one-dimensional model, thus getting the analog to the kinetic confirmation of hydrodynamic equations.

The purpose of this paper is to demonstrate the main assumption made in the coarse-grained model, which at

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the same time constitutes its most fundamental result, namely, that the Taylor flux is a dissipative flux of EIT. Notice that the dynamics for the fluxes J_n described by (1) is far from being common in the classical theory of irreversible processes [18], which in the isothermal dispersion under study supplies a simple Fickian law. Meanwhile, Eq. (1) not only contains a diffusive term, but a relaxational one—the first in the left—a term which couples each contribution J_n with the others through the parameters γ_{mn} , and a term that shows a spatial correlation in J_n . Here we prove that all these contributions are perfectly predicted by extended thermodynamics and that, in contrast to classical irreversible thermodynamics [18], the entropy production is positive definite as required by the second law.

The incorporation of Taylor dispersion into the scheme of extended thermodynamics bears also a lot of interest for the followers of EIT. First, from a conceptual point of view, since it means the application of its formalism at a different scale from the usual one in thermodynamics; instead of working in the habitual three-dimensional space, we deal here with a one-dimensional space where the other two spatial coordinates have disappeared in a coarse graining process. Second, because it represents the extension of its range of application to the rich phenomenology of longitudinal dispersion, which includes, for instance, the sedimentation of nonspherical particles or the tracer dispersion in porous media (for a wide list of examples see Ref. [9]). And finally, because these systems are characterized by long relaxation times for the dissipative fluxes so that the consequences of extended thermodynamics are easily accessible to experimentation; we must bear in mind that, in the tridimensional version of EIT, these relaxation times are very short—frequently of the order of the collision times—so that its manifestations usually fall outside the experimental scope.

The paper is organized as follows. In Sec. II, the evolution equations for the Taylor flux components are found from a three-dimensional analysis. In Sec. III, we introduce an entropy and an entropy flux for Taylor dispersion and write the corresponding entropy balance equation; in Sec. IV, the constitutive equations for the contributions J_n are obtained following the usual method in irreversible thermodynamics; and Sec. V is devoted to conclusions.

II. TAYLOR FLUX COMPONENTS

The aim of this section is twofold. On the one hand, it summarizes the procedure followed in Ref. [22] to obtain Eq. (1) from the tridimensional convection-diffusion equation in order for the paper to be self-contained. On the other hand, it extends the stationary-flow study performed there to nonstationary velocity fields.

For the sake of simplicity we restrict ourselves to flows between parallel plates separated by a distance d. This choice presents the advantage of reducing the problem to two dimensions and simplifying the eigenfunctions to mere cosines. The extension to arbitrary geometries is straightforward by using the corresponding eigenfunctions.

For a dilute solution the bidimensional concentration distribution c(x,y,t)—y denoting the coordinate between plates—satisfies the convection-diffusion equation

$$\frac{\partial c}{\partial t} + v'(y, t) \frac{\partial c}{\partial x} = D_m \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right], \tag{2}$$

with v'(y) the velocity profile as seen in an inertial frame; it can be split into two parts, the section-averaged velocity u(t), and the rest: $v'(y,t) \equiv u(t) + v(y,t)$, so that Eq. (2) can be rewritten as

$$\dot{c} + v(y,t) \frac{\partial c}{\partial x} = D_m \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right], \tag{3}$$

where the dot indicates a one-dimensional material time derivative, i.e.,

$$\dot{c} \equiv \frac{dc}{dt} \equiv \frac{\partial c}{\partial t} + u(t)\frac{\partial c}{\partial x} . \tag{4}$$

Since fluid particles in the coarse-grained onedimensional description are slices of width dx along the tube axis, their barycentric velocity—the mean speed of the fluid contained in these volume elements—is the section-averaged speed of the tridimensional fluid particles, i.e, $u(t) \equiv (1/d) \int_0^d dy \ v'(y,t)$; therefore the differential operator in Eq. (4) has indeed the structure of a one-dimensional substantial time derivative.

After introducing the Fourier coefficients for the concentration and velocity,

$$c_n(x,t) = \frac{2}{d} \int_0^d dy \ c(x,y,t) \cos\left[\frac{n\pi y}{d}\right],$$

$$v_n(t) = \frac{2}{d} \int_0^d dy \ v(y,t) \cos\left[\frac{n\pi y}{d}\right],$$
(5)

some direct calculations yield the following equation for the c_n components:

$$\dot{c}_{n} + \frac{1}{2} \frac{\partial}{\partial x} \sum_{m=1}^{\infty} \left[c_{n+m} + c_{|n-m|} \right] v_{m}$$

$$= D_{m} \left[\frac{\partial^{2}}{\partial x^{2}} - n^{2} \frac{\pi^{2}}{d^{2}} \right] c_{n} \quad n = 0, 1, \dots$$
 (6)

For the section-averaged concentration $c(x,t) = 1/2c_0(x,t)$, one has

$$\frac{\partial c(x,t)}{\partial t} + \frac{\partial}{\partial x} \left[c(x,t)u(t) + \sum_{n=1}^{\infty} \frac{1}{2} v_n c_n(x,t) \right]$$

$$= D_m \frac{\partial^2 c(x,t)}{\partial x^2} . \quad (7)$$

It is immediate to read this expression as a mass balance equation which incorporates a convective term $c\left(x,t\right)u\left(t\right)$, a unidimensional molecular diffusion flux $J_{m}=-D_{m}\partial c\left(x,t\right)/\partial x$, and a velocity-dependent spectrum

$$J_n(x,t) = \frac{1}{2}v_n(t)c_n(x,t)$$
, $n = 1, 2, \dots$ (8)

Therefore, J_n is the contribution of the nth

mode to a Taylor flux defined as $J_T(x,t) = (1/d) \int_0^d dy \ c(x,y,t) v(y,t)$, obviously the expression that one should expect for a particle flux related to the velocity field. The purpose of the present work is to demonstrate that this flux, which has a convective character when it is regarded from three dimensions, turns out to be dissipative when seen in one dimension, at the same level of the longitudinal diffusion flux, but of course with several distinguishing features.

If we multiply (6) by $v_n/2$ and manipulate a bit, we obtain a constitutive equation for the fluxes $J_n(x,t)$,

$$\dot{J}_{n} + (\tau_{n}^{-1} - \gamma_{n})J_{n} + \frac{\partial}{\partial x} \sum_{m=1}^{\infty} \gamma_{mn} J_{m} = -\frac{D_{n}}{\tau_{n}} \frac{\partial c(x, t)}{\partial x} + D_{m} \frac{\partial^{2} J_{n}}{\partial x^{2}}, \qquad (9)$$

where we have defined the coefficents

$$\tau_n = \frac{d^2}{D_m n^2 \pi^2} , \quad D_n = \frac{1}{2} v_n^2 \tau_n , \qquad (10)$$

$$\gamma_n = \frac{\dot{v}_n}{v_n}$$
, $\gamma_{mn} = \frac{1}{2} (v_{|m-n|} + v_{m+n}) \frac{v_n}{v_m}$. (11)

In the case of arbitrary (but uniform) section geometries, the results are the same (aside from a normalization factor) except for the time spectrum, which is specific for each geometry. For stationary flows, coefficients, γ_n identically vanish so that we recover Eq. (1).

As mentioned before, these evolution equations are much more complex than the simple Fickian laws coming from classical irreversible thermodynamics. Conversely, they lead to nonpositive entropy productions in this thermodynamic context, as can be straightforwardly seen by introducing Eq. (9) into the classical expression for the entropy production, $\sigma \propto J\partial c(x,t)/\partial x$.

In the following sections we demonstrate that Eq. (9) can be obtained from extended thermodynamics and that coefficients (10) and (11) satisfy the restrictions imposed by this thermodynamic framework.

III. ENTROPY BALANCE

In the study of Taylor dispersion the solution is considered to be so diluted that the barycentric velocity of the mixture coincides with the solvent speed; this fact was used in writing the convection-diffusion equation (2). This way the role of the solvent becomes essentially parametric and consists in imposing the velocity field in which the solute evolves. For this reason, it is not surprising that in the thermodynamic description given here the system is treated as monocomponent.

In extended thermodynamics it is assumed that non-equilibrium states are characterized not only by the classical local-equilibrium variables (such as the specific energy or the specific volume, for a simple system), but also by the dissipative fluxes, which are considered to be independent variables at the same level of the first ones, so that the thermodynamic functions, like the entropy or the entropy flux, depend on all these quantities. Accordingly, we introduce a generalized entropy for Taylor

dispersion which includes, besides the local-equilibrium magnitude c(x,t), the Taylor contributions J_n , and their fluxes $P_n: s(x,t) = s(c,\{J_n\},\{P_n\})$. The incorporation of the second-order tensors P_n allows one to introduce spatial correlations between fluxes, which is a characteristic feature in the dynamics of fluxes J_n as shown in Eq. (9); these terms have been employed in the past, for instance, in the study of phonon hydrodynamics [19] or non-Fickian diffusion in polymers [23].

We thus assume for situations not far from equilibrium a generalized entropy of the form

$$s(x,t) = s_{eq}(x,t) - \sum_{n=1}^{\infty} \frac{1}{2} \alpha_n J_n \cdot J_n - \sum_{n=1}^{\infty} \frac{1}{2} \beta_n P_n : P_n$$
, (12)

with s(x,t) the entropy per unit volume, $s_{\rm eq}(x,t)$ the local-equilibrium term, and the rest are purely nonequilibrium contributions; the symbol ":" indicates tensorial contraction.

This is the simplest expression which makes use of the independent variables under consideration. The positive sign of coefficents α_n and β_n guarantees that the entropy is maximum at equilibrium. These coefficients are independent of J_n and P_n and their form is specific for each particular system. Although they are generally considered as independent of time, in Taylor dispersion they are expected to depend on the velocity profile so that for nonstationary flows they become time dependent.

By differentiating (12) and using the local-equilibrium Gibbs equation, $ds_{eq} = -\mu T^{-1}dc$, with $\mu(x,t)$ the chemical potential of the solute, one finds the following generalized Gibbs equation:

$$ds = -\mu T^{-1} dc - \sum_{n=1}^{\infty} \left[\alpha_n J_n \cdot dJ_n + \frac{1}{2} d\alpha_n J_n^2 + \beta_n P_n \cdot dP_n + \frac{1}{2} d\beta_n P_n \cdot P_n \right] . \quad (13)$$

Contributions in $d\alpha_n$ and $d\beta_n$ are new in the formalism of extended thermodynamics and have their origin in the time dependence of coefficients α_n and β_n commented on above.

For the entropy flux one can distinguish three contributions. Keeping only up to second-order terms in the fluxes, one has the following.

- (i) The classical term linked to the entropic content of the solute particles in solution [18], $-\mu T^{-1}J$, with J(x,t) the total diffusive mass flux, i.e., the sum of the longitudinal molecular diffusion flux $J_m(x,t)$ and the velocity-dependent Taylor flux J_T .
- (ii) A term which accounts for the anisotropy that the velocity field introduces in the dispersion of the solute. This term is assumed to couple each flux with the others: $-\sum_{n.m=1}^{\infty}\alpha_{mn}\cdot(J_mJ_n)/2; \ \alpha_{mn} \ \text{ are vectorial coefficients}$ which point in the flow direction and must necessarily be odd in velocities in order to display this kind of anisotropy, since then the sign of this contribution becomes sensitive to an inversion of the velocity field $(v \rightarrow -v)$.
- (iii) And, finally, the contribution of fluxes P_n . The simplest case is to consider a term like $-\sum_{n=1}^{\infty} \delta_n P_n \cdot J_n$,

with δ_n some coefficients independent of J_n and P_n .

Other terms, like ϕJ_m , $\phi_{mn} \cdot J_m$, or $P_n \cdot \phi_n - \phi$'s being (velocity-dependent) coefficients of proper tensorial order—although mathematically allowed, are forbidden by thermodynamics because they do not lead to positive-definite entropy productions as can be easily proven.

The total entropy flux in a frame which moves with the one-dimensional fluid particles is thus

$$J^{s}(x,t) = -\mu T^{-1} J - \frac{1}{2} \sum_{n,m=1}^{\infty} \alpha_{mn} \cdot (J_{m} J_{n}) - \sum_{n=1}^{\infty} \delta_{n} P_{n} \cdot J_{n}.$$

(14)

In a general frame, there will also be a convective term s(x,t)u(t). We underline that the second term in the right-hand side had not been used so far in extended thermodynamics; we will see that it plays an important role in the case of Taylor dispersion.

After introducing (13), (14), and the mass conservation equation

$$\frac{dc(x,t)}{dt} + \nabla \cdot J(x,t) = 0 \tag{15}$$

 $(\nabla=\partial/\partial x)$ is the gradient operator and d/dt denotes material time differentiation) into the entropy balance equation

$$\frac{ds}{dt} + \nabla \cdot J^s = \sigma_s , \qquad (16)$$

we can write for the entropy production σ_s ,

$$\sigma_{s} = -J_{m} \cdot [T^{-1}\nabla \mu]$$

$$-\sum_{n=1}^{\infty} J_{n} \cdot \left[T^{-1}\nabla \mu + \alpha_{n}\dot{J}_{n} + \frac{1}{2}\dot{\alpha}_{n}J_{n} + \delta_{n}\nabla \cdot P_{n} + \sum_{m=1}^{\infty} \alpha_{mn}\nabla \cdot J_{m}\right]$$

$$-\sum_{n=1}^{\infty} P_{n} : [\beta_{n}\dot{P}_{n} + \frac{1}{2}\dot{\beta}_{n}P_{n} + \delta_{n}\nabla J_{n}].$$
(17)

Use has been made of the fact that coefficients α_{mn} must be symmetric with respect to the interchange of indices m and n, since equality $J_m J_n = J_n J_m$ holds because all vectors J_n point in the same direction. (In fact, vectorial notation has a minor importance in the present problem, which is completely one dimensional; it is taken into account here only to show that all the contributions have the proper tensorial order.)

IV. CONSTITUTIVE EQUATIONS

As usual in irreversible thermodynamics, constitutive equations stem from the second law requirement of positiveness of entropy production. This condition obliges the term inside brackets in expression (17) (thermodynamic forces) to be linked to the dissipative fluxes which precede them. The simplest relation is to consider each force to be proportional to the corresponding conjugate flux.

(i) J_m . For the molecular diffusion flux we define the dissipative coefficient $D_m = (K_m T)^{-1} (\partial \mu / \partial c)_T$, with

 $K_m > 0$, and obtain a Fickian law,

$$J_m = -K_m^{-1} [T^{-1} \nabla \mu] \Longrightarrow J_m = -D_m \nabla c . \tag{18}$$

(ii) P_n . We introduce coefficients K_{2n} (>0) in the equations for P_n ,

$$P_n = -K_{2n}^{-1} \left[\beta_n \dot{P}_n + \frac{1}{2} \dot{\beta}_n P_n + \delta_n \nabla J_n \right] .$$

If coefficients β_n identically vanish, fluxes P_n turn out completely determined by the gradient of J_n ,

$$P_n = -\frac{\delta_n}{K_{2n}} \nabla J_n \ . \tag{19}$$

(iii) J_n . Similarly, fluxes J_n obey relations of the type

$$J_n = -K_{1n}^{-1} \left[T^{-1} \frac{\partial \mu}{\partial c} \middle|_T \nabla c + \alpha_n \dot{J}_n + \frac{1}{2} \dot{\alpha}_n J_n \right]$$

 $+ \delta_n \nabla \cdot P_n + \sum_{m=1}^{\infty} \alpha_{mn} \nabla \cdot J_m ,$

with $K_{1n} > 0$, and substituting (19) one finds an equation of the same form as Eq. (9),

$$\dot{J}_n + \left[\tau_n^{-1} + \frac{\dot{\alpha}_n}{2\alpha_n}\right] J_n + \sum_{m=1}^{\infty} \frac{\alpha_{mn}}{\alpha_n} \nabla \cdot J_m \\
= -\frac{D_n}{\tau_n} \nabla c + \frac{l_n^2}{\tau_n} \nabla^2 J_n , \quad (20)$$

with the identifications

$$D_{n} = \frac{1}{K_{1n}T} \frac{\partial \mu}{\partial c} \bigg|_{T}, \quad \tau_{n} = \alpha_{n} D_{n} T \frac{\partial \mu}{\partial c} \bigg|_{T}^{-1},$$

$$l_{n}^{2} = \frac{\delta_{n}^{2}}{K_{1n}K_{2n}}, \quad (21)$$

$$\gamma_n = -\frac{\dot{\alpha}_n}{2\alpha_n} , \quad \gamma_{mn} = \frac{\alpha_{mn}}{\alpha_n} .$$
 (22)

Extended thermodynamics thus provides a connection between each term in the evolution equation (9) and some thermodynamic functions: the diffusive term is linked as usual to entropy production, the relaxational one is related to the nonequilibrium part of a generalized entropy, the contribution in the divergence is connected to an anisotropic entropy flux, and the term introducing the spatial correlation in fluxes is related to both an entropy flux and an entropy production.

It is important to realize that extended thermodynamics imposes some restrictions on the coefficients appearing in the constitutive equations. These restrictions have to be satisfied for any physical system, and, as we show below, are verified for the present problem.

First of all, notice that not all the coefficients in (20) are independent, as (21) and (22) show. For instance, γ_n 's are determined by α_n 's, i.e., by the quotients τ_n/D_n . By using (21) and (10) we have $\alpha_n \sim v_n^{-2}$, so that $\dot{\alpha}_n/\alpha_n = -2\dot{v}_n/v_n$, and from (22), $\gamma_n = \dot{v}_n/v_n$, in agreement with (11).

From the positiveness of coefficients K_{1n} and K_{2n} as a consequence of the second law, and of α_n and $\partial \mu/\partial c$ be-

cause of stability conditions, it is concluded that coefficients D_n , τ_n , and l_n^2 must be positive. This is in perfect agreement with the results obtained in Sec. II, where D_n , τ_n , and $l_n^2 = D_m \tau_n$ are positive definite.

Furthermore, from (10), (11), and (22), we immediately get

$$\alpha_{mn} = T^{-1} \frac{\partial \mu}{\partial c} \left|_{T} \frac{v_{m+n} + v_{|m-n|}}{v_n v_m} \right|. \tag{23}$$

Note that the condition $\alpha_{mn} = \alpha_{nm}$ predicted by EIT is actually satisfied. It is also noticed that these coefficients are odd in the velocities, as they must be in order to account for the anisotropy introduced by the velocity field.

Since for arbitrary cross sections the expressions for the phenomenological coefficients are the same aside from a normalization factor—excluding the relaxation times, which play no role here—thermodynamic restrictions are corroborated in the general case.

V. CONCLUSIONS

This paper expands on the connection between Taylor dispersion and irreversible thermodynamics that has been recently pointed out. We have proven that every term in the evolution equations for the Taylor flux components is related to a generalized thermodynamic function of extended thermodynamics, and that the corresponding entropy production is positive definite in contrast to what happens in the classical theory of irreversible processes; also the restrictions on the coefficients of the evolution equations imposed by extended thermodynamics are shown to be fulfilled. Therefore we have demonstrated in all generality—arbitrary flows and arbitrary geom-

etries—that these evolution equations are real constitutive equations, and thus the Taylor flux constitutes an actual dissipative flux. This is a considerable extension of the fundamental result by Taylor, which can now be seen as a limiting case for asymptotic long times, when dissipative fluxes of EIT become diffusive.

From the point of view of extended thermodynamics, this paper establishes the extension of its formalism to a different scale (unidimensional) from the usual one in thermodynamics (tridimensional), and opens the possibility of using this thermodynamic approach in the wide variety of physical problems encompassed by longitudinal dispersion. Due to the long relaxation times characterizing dissipative fluxes in these systems, the machinery of the classical theory of irreversible processes is clearly unsuitable; meanwhile, it is the natural place for extended irreversible thermodynamics.

The application to Taylor dispersion has motivated the study of two aspects which had not been considered by EIT in the past: the consequences of the time dependence of the coefficients appearing in the nonequilibrium part of the entropy, and the inclusion of an anisotropic entropy flux. Their consideration leads to some counterparts in the constitutive equations for the fluxes and to new relations among phenomenological coefficients; both are satisfied in the present case.

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