

Fluctuations far from equilibrium: Hyperbolic transport

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The problem of the statistical properties of fluctuations in systems far from equilibrium is addressed. The discussion is based on a variational approach to hyperbolic transport equations built in a space spanned by the usual thermodynamic properties plus a set of potential functions associated with them. The enlarged space characterizes the far from equilibrium states of the system and fluctuations in the potential functions satisfy the Chapman-Kolmogorov equation. Well known results on processes near equilibrium are recovered in the parabolic transport limit. [S1063-651X(97)05004-6]

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I. INTRODUCTION

Nowadays it is recognized that fluctuations may have an organizing role in nonequilibrium systems as, for instance, in pattern formation, coherence, self-organizing, etc. The schemes developed to study equilibrium or near equilibrium systems have the implicit idea that fluctuations constitute just a noise around the equilibrium state and that in any case they break down the order if they are augmented. The view we assume here is that fluctuations are responsible not only for order, but we consider that fluctuations are the mechanism through which systems transit to ordered states where the final state depends on the initial one and on the dynamics of fluctuations [1].

The description of irreversible processes based on the fluctuations of the thermodynamic properties in a mesoscopic level dates back to Onsager and Machlup [2], who established the connection between these two levels of description for aged systems. These are described in terms of a set of extensive properties with the fluxes taken as the time derivatives of the extensive properties. The formulation led Onsager and Machlup to variational expressions for the transition probability among states whose extremum value is the corresponding maximum probability for the average thermodynamic path of the system. They also derived an expression for the probability for one state which coincides with Einstein's formula for the probability of equilibrium thermodynamic states based on Boltzmann's relation. The statistical properties of the stochastic process associated with fluctuations were completely specified in this way. The scheme introduced by Onsager and Machlup gave as a result the expressions of the transition probabilities in terms of an action functional for the system, with extremum properties while the system is changing through thermodynamic states near equilibrium. Grabert and Green [3] extended the formalism to the case of transport coefficients depending on the extensive thermodynamic properties by using a variational principle for the phenomenological equations. These authors showed that fluctuations in nonlinear systems constitute a Markov process when the phenomenological coefficients depend on the thermodynamic state. Furthermore, their work provided a consistent stochastic interpretation of the terms

appearing in the extremum conditions of the variational principle and made it possible to discuss some relevant statistical properties of fluctuations. Grabert and Green showed that fluctuations in nonlinear systems constitute a Markov process when the phenomenological coefficients depend on the thermodynamic state. Independently, Graham [4] worked out the irreversible processes making use of the method of path integrals in a more mathematical fashion.

Let us remark that the Grabert-Green procedure implies in fact the introduction of an additive stochastic term in the dynamic equations of the system. The physical interpretation of such a term is made in two senses. On the one hand, it is understood as a stochastic thermodynamic force, and on the other, such a force is the momentum in the space of conjugated variables of the system. Once the stochastic modification of the dynamic equations has been made it only remains to find the variational expressions for the transition probability in terms of the Lagrangian function of the variational principle whose stationary conditions are the modified dynamic equations and the time evolution equation of the conjugated momenta.

In this paper we search for the statistical properties of fluctuations in systems far from equilibrium. Following Grabert and Green, we would first ask if a variational approach exists for the time evolution equations of the system. This is not a trivial problem because of the presence in the equations of non-self-adjoint differential operators which do not permit the construction of classical variational principles for them [5,6]. Our first step is then to find a theoretical framework which allows us, on the one hand, to construct a classical variational formulation circumventing the problem of the presence of non-self-adjoint differential operators in the time evolution equations, and on the other, to deal with systems evolving far from equilibrium for time scales comparable to the characteristic relaxation time. Next we would attempt to construct a path integral scheme for far from equilibrium transport process within such a framework by taking advantage of the variational structure of the theory.

Hyperbolic transport equations (derived from first principles by Nettleton [7] and others [8]) have been shown to be a useful tool in the fields of generalized hydrodynamics [9], solid state physics [10], and irreversible thermodynamics

[11,12]. They describe systems beyond the domain of the linear approach of irreversible processes, specifically for a time scale of the order of the relaxation time of the system. The main result of the model is the prediction of a finite velocity for the perturbations giving a description which includes thermal inertial effects. Apart from these merits, hyperbolic transport equations are known to also present limitations [13,14]. Nevertheless, their interest for us arises from the fact that it is possible to construct a classical variational principle for the dynamic equations of the system in terms of a set of new physical fields, the so-called potential functions [15], which together with the thermodynamic properties describes the time evolution of the system for a time scale of the order of the relaxation time. With the introduction of the potential functions associated to each thermodynamic property, we enlarge the thermodynamic space and through a variational principle for the new dynamic equations an equivalent description of the system is obtained [16–18]. Then the variational equations may be reinterpreted as the conditions which give the average path in the conjugated variables space constituted by the potential functions and the thermodynamic properties which have the role of the conjugated momenta. Thus it should be possible to construct a probability field for the thermodynamic transitions and obtain the statistical properties of the fluctuations of the conjugated variables without the introduction of any stochastic term in the transport equations.

We start in Sec. II by establishing the basic equations of hyperbolic transport as derived from the combination of a set of balance and constitutive equations of the Maxwell-Cattaneo-Vernotte type. We proceed then to represent both these equations and the ones arising in parabolic transport (the usual domain of linear irreversible thermodynamics) [19] in a joint variational scheme. Among other results, we show that a unique Lagrangian function, written in terms of the potentials associated with the thermodynamic properties of the system, yields the transport equations as the Euler-Lagrange equations of a Hamilton type variational principle. The next section is then devoted to discussing some aspects of the thermodynamics of hyperbolic transport particularly where, as we will see, the existence of Onsager's reciprocity relations between the transport coefficients is supported from two different points of view. Our scope at this point will be the use of the variational formulation to establish a mesoscopic approach to far from equilibrium transport phenomena. The use of the hyperbolic model for the transport phenomena permits us to extend the study of fluctuations beyond the conditions of local equilibrium. The paper is closed in Sec. V with some comments and final remarks.

II. THE VARIATIONAL APPROACH TO FAR FROM EQUILIBRIUM TRANSPORT EQUATIONS

From a macroscopic point of view, hyperbolic transport equations are obtained by combining a set of balance equations for the thermodynamic densities of the system with Maxwell-Cattaneo-Vernotte equations for the associated fluxes. The hyperbolic equations we consider here may be written as

$$\Gamma_{j,tt} + \frac{1}{\tau_j} \Gamma_{j,t} = \sum_i \frac{L_{ji}}{\tau_j} \Delta \Gamma_i, \quad (1)$$

where the Γ_j ($j=1, \dots, r$) are a set of thermodynamic properties of the system, τ_j is the relaxation time associated to the respective flux \mathbf{J}_j , L_{ji} are the transport coefficients considered here as constants, Δ is the Laplace operator, and a comma denotes partial differentiation.

Mention must be made of some differences between Eq. (1) with respect to equations of the hyperbolic transport problem set up by Nyíri [17] (Eq. 44, p. 50),

$$\sum_k (\alpha_{ik} \Gamma_{k,tt} + \beta_{ik} \Gamma_{k,t} - \gamma_{ik} \Delta \Gamma_k) = 0,$$

where we can observe the coupling between the time change of the thermodynamic properties which arises from adding all the first and second time derivatives of the Γ_i fields on the left hand side of the last equation. In our hyperbolic scheme we have $\alpha_{ik} = \tau_k \delta_{ik}$, $\beta_{ik} = \delta_{ik}$, and $\gamma_{ik} = L_{ik}$ (with δ_{ik} being the Kronecker delta), as may be seen if we start with the Maxwell-Cattaneo-Vernotte equations for the fluxes

$$-\tau_j \frac{\partial \mathbf{J}_j}{\partial t} = \mathbf{J}_j + \sum_i L_{ji} \nabla \Gamma_i, \quad (2)$$

and combine Eqs. (2) with free source balance equations of the form

$$\frac{\partial \Gamma_j}{\partial t} = -\nabla \cdot \mathbf{J}_j. \quad (3)$$

Clearly, from Eqs. (2) and (3) we arrive directly at Eq. (1). We proceed now to expose in some detail the variational scheme for Eq. (1) in order to use it later in the study of the statistics of fluctuations.

The first attempts at the classical variational formulations for irreversible thermodynamics may be found in the extensions of Hamilton's principle to nondissipative fluids, where the internal energy is added to the Lagrangian function. The mass conservation and the condition of reversibility are introduced as subsidiary conditions in the variational principle. These schemes have the energy and momentum equations as the stationary conditions [20].

The inclusion of dissipative effects in the variational formulation depends on the assumed thermodynamic framework [19,21]. There is, however, a common feature in all of these schemes. The initial thermodynamic space is enlarged to include new independent properties of the system. As examples we mention the already exposed cases of the Onsager-Machlup and Grabert-Green variational formulation for near equilibrium systems as well as the Lagrangian formulation of equations for the same kind of systems with second-order time derivatives originally done by Landau and Lifshitz [22]. Noteworthy in this last formulation are the facts that it can also be cast in Hamiltonian form and, what is more relevant to the contents of this paper, that Onsager reciprocity and Lagrangian formulation are intimately related. We will come back to this point later on. The most general classical variational principle for nonequilibrium thermodynamics [23] considers the thermohydrodynamic

space enlarged with the entropy flux. In this case, the subsidiary condition is the mass conservation and the formalism permits one to make use of Nöether's theorem [24] to obtain the conservation equations of the system. In this scheme the closing equations are obtained from an analysis of the entropy production term. Within extended irreversible thermodynamics it has been shown that the time evolution equations have a Hamiltonian structure [25]. Grmela and co-workers [26] defined a Poisson bracket to express the dynamic equations in the form of a general time equation in which the movement generator is a free energy. It has also been shown that the closing time equations for the nonconserved variables may be obtained as the stationary conditions of a variational principle of the restricted type [27]. Mention must be made, however, that this kind of principle loses the extremum property of the functional in the enlarged thermodynamic space, which disqualifies it for use in the description of fluctuations.

The main ideas we use in this section on the potential functions method to find classical variational principles for non-self-adjoint differential equations may be found in previous works [16–18]. The method has its origin in the classical potential theory [28]. In brief, if one considers a differential equation obtained through the subsequent application of linear differential operators on the unknown function u by means of a finite number of steps

$$\mathcal{L}\{u(x)\}=0, \quad (4)$$

with \mathcal{L} the resulting linear differential operator, then the functional

$$L[u]=\int_D F(\mathcal{L}\{u(x)\},x)d\tau \quad (5)$$

defined on the domain D is an extremum if the function

$$S_u(\varepsilon)=L[u(x)+\varepsilon\eta(x)] \quad (6)$$

is an extremum in $\varepsilon=0$ for all the admissible functions $\eta(x)$.

The necessary condition in order for $L[u]$ to be an extremum becomes

$$\tilde{\mathcal{L}}\left\{\frac{\partial F}{\partial \mathcal{L}u}\right\}=0, \quad (7)$$

where we have assumed that the variations at the domain frontier vanish. The operator $\tilde{\mathcal{L}}$ is the adjoint of \mathcal{L} .

The structure of Eq. (7) restricts the type of equations of the form (4) which may be obtained through the variational problem. One may introduce a new function ϕ related to the function u through the operator \mathcal{Q} , as

$$u=\mathcal{Q}\{\phi(x)\}, \quad (8)$$

in such a way that the equation for u is equivalent to an equation of the form (7), which of course may be obtained from a variational principle based on the function ϕ . By virtue of Eq. (8) the function ϕ is called the potential of u .

To specify the operator \mathcal{Q} , let us observe that the variational problem

$$L[\phi]=\int_D F(\tilde{\mathcal{L}}\{\phi\},x)d\tau \quad (9)$$

has the extremum condition

$$\mathcal{L}\left\{\frac{\partial F}{\partial \tilde{\mathcal{L}}\phi}\right\}=\mathbf{0}. \quad (10)$$

The first-order equation

$$\frac{\partial F}{\partial y}=u, \quad (11)$$

with $y=\tilde{\mathcal{L}}\{\phi\}$, yields Eqs. (4) and (10) to be identical. Equation (11) is known as the characteristic equation of Eq. (4) and it determines the dependence of the Lagrangian F with respect to the variable y as well as the relation of u with respect to the potential ϕ .

The method has been applied by Gambár and Márkus [18] to the parabolic transport equations of linear irreversible thermodynamics. Within the irreversible thermodynamic scheme the parabolic equation can be written as [19]

$$\sum_k (L_{ik}\Delta\Gamma_k-\rho S_{ik}^{-1}\Gamma_{k,t})=0, \quad (12)$$

where Γ_k are a set of intensive thermodynamic properties of the system, the coefficients S_{ik}^{-1} and L_{ik} are constants, and $,t$ indicates partial derivation with respect to time. Mention must be made that the sign of the first time derivative in Eq. (12) differs from the sign used by Gambár and Márkus, mainly because we address our effort to describing irreversible processes, where the properties Γ_k are bounded functions for all time.

As we mentioned, the main difficulty in obtaining a classical variational formalism either for parabolic or hyperbolic transport lies in the presence of non-self-adjoint operators, namely, the first time derivative, in the transport equations. In order to deal with fluctuations in nonequilibrium situations within a general formalism, let us separate such a first-order derivative from the self-adjoint part of the transport equations by defining two differential operators as follows:

$$D_{ij}=\begin{cases} L_{ij}\Delta, & \text{parabolic case} \\ \frac{L_{ij}}{\tau_i}\Delta-\delta_{ij}\frac{\partial^2}{\partial t^2}, & \text{hyperbolic case} \end{cases} \quad (13)$$

and

$$K_i=\begin{cases} \rho S_i^{-1}\frac{\partial}{\partial t}, & \text{parabolic case} \\ \frac{1}{\tau_i}\frac{\partial}{\partial t}, & \text{hyperbolic case.} \end{cases} \quad (14)$$

Clearly, the transport equations given by Eqs. (1) and (12) can be rewritten by using these operators in the form

$$(D_{ij}-K_i)\Gamma=0. \quad (15)$$

Note that D_{ij} and K_i are linear and that additionally D_{ij} is self-adjoint as stated above. It must also be noted that the first-order coupling in time of Eq. (12) has been omitted. Then we consider a set of potential functions ϕ_j for the Γ_j fields defined through the relation

$$\Gamma_j = -K_j \phi_j - \sum_i D_{ij} \phi_i. \quad (16)$$

The requirement on the ϕ_j functions in this case is that they must be four times differentiable in their arguments. It is important to emphasize that since we want to present a unified scheme for parabolic and hyperbolic transport, contrary to what happens with the transport equations, we are forced to consider potential functions for the latter which do not reduce to those of parabolic transport in the limit $\tau_j \rightarrow 0$. Let the Lagrangian function

$$L = L(\phi_j, \phi_{j,t}, \phi_{j,tt}, \phi_{j,xx}, \phi_{j,yy}, \phi_{j,zz})$$

be given by the expression

$$L = \frac{1}{2} \sum_j \left[-K_j \phi_j - \sum_i D_{ij} \phi_i \right]^2. \quad (17)$$

The variational problem

$$A = \int \int L \, dV \, dt = \text{extremum}, \quad (18)$$

with the function L given by Eq. (17), has the following Euler-Lagrange conditions for the ϕ_k :

$$\frac{\partial L}{\partial \phi_k} - \frac{\partial}{\partial t} \frac{\partial L}{\partial \phi_{k,t}} + \frac{\partial^2}{\partial t^2} \frac{\partial L}{\partial \phi_{k,tt}} + \Delta \frac{\partial L}{\partial \Delta \phi_k} = 0. \quad (19)$$

If we substitute the expression for the Lagrangian, Eq. (17), we obtain Eq. (15) by virtue of Eq. (16).

One may make the description in terms of the Hamiltonian function H obtained through the Legendre transform

$$H = \sum_j \phi_{j,t} p_j - L, \quad (20)$$

where the conjugated momentum to the potential ϕ_j is given as usual by

$$p_j = \frac{\partial L}{\partial \phi_{j,t}} = \begin{cases} \rho S_i^{-1} \Gamma_j, & \text{parabolic case} \\ -\frac{1}{\tau_j} \Gamma_j, & \text{hyperbolic case.} \end{cases} \quad (21)$$

Let us note that the conjugated momenta p_j have a clear physical meaning and that we have translated the description of the nonequilibrium transport processes to a new physical space whose components are (ϕ_j, p_j) . The potential character of the ϕ_j functions is well exposed by Eq. (16).

In both cases the Hamiltonian of Eq. (20) may be represented by the expression

$$H = \frac{1}{2} \sum_j a_j p_j p_j - \sum_i \sum_j b_j p_j D_{ji} \phi_i, \quad (22)$$

where

$$a_j = \begin{cases} (\rho^{-1} S_j)^2, & \text{parabolic case} \\ \tau_j^2, & \text{hyperbolic case,} \end{cases}$$

$$b_j = \begin{cases} \rho^{-1} S_j L_j, & \text{parabolic case} \\ \tau_j, & \text{hyperbolic case.} \end{cases}$$

It may be shown [18,29] that a Poisson structure exists for the dynamic equations of the conjugated variables for both parabolic and hyperbolic transport. In fact, if we define a Poisson bracket as

$$\{P, Q\} = \sum_j \frac{\delta P}{\delta \phi_j} \frac{\delta Q}{\delta p_j} - \sum_j \frac{\delta Q}{\delta \phi_j} \frac{\delta P}{\delta p_j}, \quad (23)$$

where P and Q depend on the conjugated variables and the functional derivatives $\delta/\delta \phi_j$ and $\delta/\delta p_j$ are given by

$$\frac{\delta}{\delta \phi_j} \equiv \frac{\partial}{\partial \phi_j} - \frac{\partial}{\partial t} \frac{\partial}{\partial \phi_{j,t}} + \frac{\partial^2}{\partial t^2} \frac{\partial}{\partial \phi_{j,tt}} - \nabla \cdot \frac{\partial}{\partial \nabla \phi_j} + \Delta \frac{\partial}{\partial \Delta \phi_j}, \quad (24)$$

$$\frac{\delta}{\delta p_j} \equiv \frac{\partial}{\partial p_j} - \frac{\partial}{\partial t} \frac{\partial}{\partial p_{j,t}} + \frac{\partial^2}{\partial t^2} \frac{\partial}{\partial p_{j,tt}} - \nabla \cdot \frac{\partial}{\partial \nabla p_j} + \Delta \frac{\partial}{\partial \Delta p_j}, \quad (25)$$

the dynamic equations, Eqs. (18) and (19), are particular cases of the general time evolution equation

$$P_{,t} = \{P, H\}, \quad (26)$$

with P a function of the conjugated variables and the Hamiltonian given by Eq. (22).

Particularizing to the hyperbolic case, we can rewrite the dynamic equations, Eqs. (15) and (16), in the Hamiltonian form by considering the modified Hamilton variational principle

$$A = \int \int \left(\sum_j \phi_{j,t} p_j - H \right) dV \, dt = \text{extremum}. \quad (27)$$

By introducing the momenta p_j in the Legendre transform, Eq. (20), and using definition (16) we obtain

$$H = - \sum_j \frac{1}{\tau_j} \phi_{j,t} \Gamma_j - \sum_j \frac{1}{2} \Gamma_j \Gamma_j. \quad (28)$$

Let us observe that

$$\phi_{j,t} = -\tau_j \left(\Gamma_j + \sum_i D_{ij} \phi_i \right), \quad (29)$$

and therefore we may write the Hamiltonian as

$$H = \frac{1}{2} \sum_j \tau_j^2 p_j p_j - \sum_i \sum_j \tau_j p_j D_{ji} \phi_i.$$

Observe that

$$H \equiv H(p_j, \Delta \phi_j, \phi_{j,tt}) \quad (30)$$

while Eq. (27) explicitly becomes

$$\int \int dV dt \left[\sum_j p_j \delta \phi_{j,t} + \sum_j \phi_{j,t} \delta p_j - \sum_j \frac{\partial H}{\partial p_j} \delta p_j - \sum_j \frac{\partial H}{\partial \Delta \phi_j} \delta \Delta \phi_j - \sum_j \frac{\partial H}{\partial \phi_{j,tt}} \delta \phi_{j,tt} \right] = 0,$$

and finally, after a little algebra we arrive at

$$\int \int dV dt \left[\sum_j \left(\phi_{j,t} - \frac{\partial H}{\partial p_j} \right) \delta p_j - \sum_j \left(p_{j,t} + \Delta \frac{\partial H}{\partial \Delta \phi_j} + \frac{\partial^2}{\partial t^2} \frac{\partial H}{\partial \phi_{j,tt}} \right) \delta \phi_j \right] = 0. \quad (31)$$

Since $\delta \phi_j$ and δp_j are independent variations Eq. (31) is satisfied only if

$$\phi_{j,t} = \frac{\partial H}{\partial p_j}, \quad (32)$$

$$p_{j,t} = -\Delta \frac{\partial H}{\partial \Delta \phi_j} - \frac{\partial^2}{\partial t^2} \frac{\partial H}{\partial \phi_{j,tt}}. \quad (33)$$

In order to illustrate the physical content of this kind of formulation we consider the particular example of hyperbolic transport of heat in a rigid conductor solid where the heat is propagating by conduction through waves at finite speeds. The theoretical importance of the problem may be appreciated in the extensive review of Joseph and Preziosi [14]. In this case, we take the temperature as the intensive variable, i.e., $\Gamma = T$, and Eq. (1) takes the form of the telegrapher equation, namely,

$$T_{,tt} + \frac{1}{\tau_q} T_{,t} = c^2 \Delta T, \quad (34)$$

where τ_q is the relaxation time of the heat flux and $c^2 = K/\rho C_v \tau_q$, with K the thermal conductivity and C_v the specific heat.

In the Hamiltonian context the heat conductor is then described by the conjugated field variables ϕ and p as

$$T = -\frac{1}{\tau_q} \phi_{,t} + \phi_{,tt} - c^2 \Delta \phi. \quad (35)$$

$$p = -\frac{1}{\tau_q} T. \quad (36)$$

The dynamic behavior of ϕ and p is given by the extremum conditions of the variational principle Eq. (27) or by the general evolution equations (32) and (33) with the Hamiltonian density H defined as

$$H(p, \phi) = \frac{1}{2} (\tau_q p)^2 - \tau_q p (\phi_{,tt} - c^2 \Delta \phi).$$

These are the Hamiltonian forms of the hyperbolic dynamic equations of the system. In the next section we return

to the general problem and introduce the definition of a function of the conjugated momenta p_j , which may well play the role of a thermodynamic potential. This will allow us to discuss the basis to build the thermodynamics of hyperbolic transport associated with Eqs. (15) and (16).

III. THE THERMODYNAMICS OF HYPERBOLIC TRANSPORT IN THE FRAMEWORK OF POTENTIAL FUNCTIONS

Let us then consider the following function of the space of conjugated variables:

$$P = \sum_j \frac{1}{2} p_j p_j. \quad (37)$$

As we know, its time evolution is given by Eq. (26) with the Hamiltonian given as in Eq. (22).

By substituting the expression for P , Eq. (37), in Eq. (26) we obtain

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \sum_j p_j p_j \right) = \sum_{i,j} L_{ji} (\Delta p_i) p_j - \sum_j \tau_j p_{j,tt} p_j. \quad (38)$$

We can rewrite the first term on the right-hand side of this last equation as

$$L_{ji} (\Delta p_i) p_j = L_{ji} \nabla \cdot [(\nabla p_i) p_j] - L_{ji} \nabla p_i \cdot \nabla p_j, \quad (39)$$

while the second term is written as

$$\tau_j p_{j,tt} p_j = \tau_j \frac{\partial}{\partial t} (p_{j,t} p_j) - \tau_j p_{j,t} p_{j,t}. \quad (40)$$

Introducing Eqs. (39) and (40) in Eq. (38) we arrive at

$$\begin{aligned} \frac{\partial}{\partial t} \left(\frac{1}{2} \sum_j p_j p_j + \sum_j \tau_j p_{j,t} p_j \right) + \nabla \cdot \left[\sum_{i,j} p_j L_{ji} \nabla p_i \right] \\ = \sum_j \tau_j p_{j,t} p_{j,t} - \sum_{i,j} \nabla p_i \cdot L_{ji} \nabla p_j. \end{aligned} \quad (41)$$

Let us note that this equation has the form of a balance equation provided we identify

$$F = \frac{1}{2} \sum_j p_j p_j + \sum_j \tau_j p_{j,t} p_j, \quad (42)$$

$$\mathbf{J}_F = \sum_{i,j} p_j L_{ji} \nabla p_i, \quad (43)$$

$$\sigma_F = \sum_j \tau_j p_{j,t} p_{j,t} - \sum_{i,j} \nabla p_i \cdot L_{ji} \nabla p_j, \quad (44)$$

where \mathbf{J}_F and σ_F are the flux and production of the thermodynamic function F , respectively. As a matter of fact, the structure of the thermodynamic function F reveals that it consists of two different kinds of terms. The first one on the right hand side is related to the near equilibrium entropy as was shown by Márkus and Gambár [18]. The second term is a nonequilibrium contribution which vanishes in principle when τ_j tends to zero.

It is worthwhile to mention that the production term, Eq. (44), is an invariant under global phase transformations if the reciprocity relations between the transport coefficients are satisfied. In fact, if one considers the global phase transformation on the fields ϕ_j [18,30],

$$\phi'_j = \sum_l \delta_{jl} \phi_l - \sum_l \theta^p I(l,) T_{jl}^p \phi_l, \quad (45)$$

where the infinitesimal parameters θ^p do not depend on the spatial coordinates, T_{jl}^p are the transformation generators and the order operator $I(l,)$ is defined as

$$I(l, m) = 1, \quad (46)$$

if the field ϕ'_j is multiplied by the left by the field ϕ'_i [which is assumed to depend on the ϕ_m according to Eq. (45)], and

$$I(l, m) = -1, \quad (47)$$

if the field ϕ'_j is multiplied by the right by the field ϕ'_i [which is assumed to depend on the ϕ_m according to Eq. (45)], then the Lagrangian function transforms as

$$\begin{aligned} L' = \int dV \frac{1}{2} \sum_j \left[\sum_l \delta_{jl} \frac{\partial^2 \phi_l}{\partial t^2} - \sum_{p,l} \theta^p I(l,) T_{jl}^p \frac{\partial^2 \phi_l}{\partial t^2} - \sum_l \frac{1}{\tau_j} \delta_{jl} \frac{\partial \phi_l}{\partial t} + \sum_{p,l} \frac{1}{\tau_j} \theta^p I(l,) T_{jl}^p \frac{\partial \phi_l}{\partial t} \right. \\ \left. - \sum_i L_{ji} \left(\sum_k \delta_{ik} \Delta \phi_k - \sum_{q,k} \theta^q I(k,) T_{ik}^q \Delta \phi_k \right) \right] \left[\sum_m \delta_{jm} \frac{\partial^2 \phi_m}{\partial t^2} - \sum_{r,m} \theta^r I(m,) T_{jm}^r \frac{\partial^2 \phi_m}{\partial t^2} - \sum_m \frac{1}{\tau_j} \delta_{jm} \frac{\partial \phi_m}{\partial t} \right. \\ \left. + \sum_{r,m} \frac{1}{\tau_j} \theta^r I(m,) T_{jm}^r \frac{\partial \phi_m}{\partial t} - \sum_n L_{jn} \left(\sum_g \delta_{ng} \Delta \phi_g - \sum_{s,g} \theta^s I(g,) T_{ng}^s \Delta \phi_g \right) \right]. \quad (48) \end{aligned}$$

We may then show by using the properties of the order operator and taking up to first order in the θ^p parameters that the Lagrangian is invariant under the global phase transformation

$$L' = L. \quad (49)$$

In a similar fashion and after a cumbersome algebra one may show that the production term of the thermodynamic function F is an invariant under global phase transformations, Eq. (45), if the transport coefficients L_{ij} satisfy Onsager's reciprocity relations in the form

$$L_{ij} = L_{ji}. \quad (50)$$

To close this section a fact which reveals another side of the profound role that the Onsager's reciprocity relations have in the domains of irreversible thermodynamics is also mentioned (a review on reciprocity in extended thermodynamics may be found in the work of Nettleton [31]). Let us consider again a system described by the set of thermodynamic properties Γ_j , which has a set of potential functions ϕ_j defined through Eq. (16). The Euler-Lagrange equations of the variational problem, Eq. (18), show the presence of non-self-adjoint differential operators which might be considered a contradiction with the fact that only self-adjoint operators admit a derivation from a variational principle. Some of the non-self-adjoint operators in Eq. (18) are $\phi_{k,tt}$ or $\Delta \phi_{k,t}$. Observe, however, that if Onsager's relations, Eq.

(50), are satisfied and we change $j \rightarrow i$ in the second term within the last bracket on the left-hand side of Eq. (18), we obtain

$$\begin{aligned} \frac{1}{\tau_k} \frac{\partial}{\partial t} \left(-\frac{1}{\tau_k} \phi_{k,t} \right) + \frac{\partial^2}{\partial t^2} \left(\phi_{k,tt} - \frac{L_{ki}}{\tau_i} \Delta \phi_i \right) \\ - \sum_j \frac{L_{jk}}{\tau_k} \Delta \left(\phi_{j,tt} - \frac{L_{ji}}{\tau_i} \Delta \phi_i \right) = 0. \quad (51) \end{aligned}$$

In this last equation for the potential functions ϕ_k all of the differential operators are of the self-adjoint kind. Moreover, we see that the conditions for the existence of variational principles for a set of differential equations as expressed by Finlayson [5], Nyíri [17], and Ichiyangi [32] are equivalent statements [6].

In the next section we develop a mesoscopic description of hyperbolic transport focusing on the probability associated with paths in the phase space within which we have derived the dynamic equations as the Euler-Lagrange conditions of a classical variational principle.

IV. THE PATH INTEGRAL FORMULATION FOR TRANSPORT PHENOMENA FAR FROM EQUILIBRIUM

To simplify we assume a system described by only one thermodynamic property Γ . The dynamical equation for Γ (free of sources) is

$$(D - K)\Gamma = 0. \quad (52)$$

We change the description to a phase space of conjugated variables (ϕ, p) defined through the relation

$$(D+K)\phi = -\Gamma, \quad (53)$$

and Eq. (21).

The dynamical equations for the conjugated variables are written in the Hamiltonian form as

$$\phi_{,t} = \frac{\partial H}{\partial p}, \quad (54)$$

$$p_{,t} = -D \frac{\partial H}{\partial D \phi}, \quad (55)$$

where the Hamiltonian function H is given by Eq. (22) and as before

$$D = \begin{cases} L\Delta, & \text{parabolic case} \\ c^2\Delta - \frac{\partial^2}{\partial t^2}, & \text{hyperbolic case,} \end{cases}$$

with $c^2 = L/\tau_r$ the signal transmission velocity and τ_r the characteristic time constant of the system. Equations (54) and (55) are equivalent to equations

$$(D+K)\phi = bp, \quad (56)$$

$$(D-K)p = 0, \quad (57)$$

where the constant b is

$$b = \begin{cases} \rho^{-1}SL, & \text{parabolic case} \\ \tau_r, & \text{hyperbolic case.} \end{cases}$$

With the above we have translated the description of the system to a space enlarged with the potential ϕ since the conjugated momentum becomes essentially the thermodynamic property Γ . It is well known that the solution of Eq. (56) diverges for $t \rightarrow \infty$. This is physically correct since the description of the equilibrium state is completely defined in terms of Γ , but the nonequilibrium states require a new variable which is the potential function ϕ . Then ϕ must not be defined for the asymptotic limit $t \rightarrow \infty$. In this way, the physical interpretation of ϕ cannot be found in equilibrium. At this point we just know that its partial derivatives are related to the thermodynamic properties of the system through Eq. (56) which is at the same time the grounds for their physical meaning.

To introduce Eqs. (56) and (57) within the context of stochastic processes we consider the potential function ϕ and momentum p as intrinsically fluctuating variables of the system. The origin of this property must be found in the fact that the system is out of equilibrium and therefore uncontrollable inner processes exist which cause random microscopic impacts from internal subsystems. We remark that this assumption does not imply the necessity of new nonequilibrium variables for the system, but its thermodynamic state can still be described through the local equilibrium properties of the conjugated space.

Our problem is then to define the probability field associated with the paths of the system in the conjugated space (ϕ, p) . In order to do this, we consider a collection of replicas of the original system, each one prepared with the same

initial conditions determined in terms of the conjugated variables. This physical ensemble [33] will be described in the ‘‘phase space’’ of the conjugated variables ϕ and p and the definition of the probability field of paths must be in accordance with the fact that the action A must be a maximum for the path obtained as the solution of Eqs. (56) and (57), since it represents the most probable behavior of the system. In what follows we develop the adopted point of view in terms of the physical ensemble to describe the influence of fluctuations in the temporal behavior of the system.

Let us circumvent the question of how to modify the mean dynamic equations to introduce fluctuations and consider then a thermodynamic system described by two conjugated variables ϕ and p which are intrinsically stochastic properties, due to the underlying molecular processes as mentioned above and whose time evolution is described in the average by Eqs. (56) and (57). We ask then for the probability that the system follows a given path between two given thermodynamic states (ϕ, p) and (ϕ', p') . The presence of fluctuations implies that this path is not unique in such a way that we must assign a probability to each admissible path between the same two thermodynamic states separated by a time s . As usual, we divide the interval s in small time intervals τ which are smaller than the hydrodynamic time scale but bigger than the kinetic time scale.

Let us define the transition probability between states as the conditional probability that the system will be in the state ϕ' at time $t = \tau$ given that at time $t = 0$ it was in the state ϕ ,

$$P_\tau(\phi'/\phi) = \frac{\exp[-(1/k)A_\tau(\phi'/\phi)] \partial p / \partial \phi'}{\int dp \exp[-(1/k)A_\tau(\phi, p)]}, \quad (58)$$

where the action has the form

$$\begin{aligned} A_\tau(\phi'/\phi) &= \int_0^\tau dt (p \phi_{,t} - H) \\ &= \int_0^\tau dt \left(p \phi_{,t} - \frac{1}{2} a p^2 + b p D \phi \right), \end{aligned} \quad (59)$$

with

$$a = \begin{cases} (\rho^{-1}S)^2, & \text{parabolic case} \\ \tau_r^2, & \text{hyperbolic case,} \end{cases}$$

and we have to choose ϕ , ϕ' , and τ as independent variables. In this way, $\partial p / \partial \phi'$ from Eq. (58) is the Jacobian of the transformation

$$p = p(\phi, \phi', \tau). \quad (60)$$

Expression (58) is understood as the probability that a fluctuation carries the system from the initial state ϕ at time $t = 0$ to the final state ϕ' during the time interval τ . This probability is normalized through the factor

$$1 / \int dp \exp\left[-\left(\frac{1}{k}\right)A_\tau(\phi, p)\right]$$

in Eq. (58).

In order to compute the transition probability for small time intervals τ we expand the conjugated variables in a Taylor's series

$$\phi(t) = \phi + \phi_{,t}t + \frac{1}{2}\phi_{,tt}t^2 + \dots, \quad (61)$$

$$p(t) = p + p_{,t}t + \frac{1}{2}p_{,tt}t^2 + \dots, \quad (62)$$

where the coefficients are valued at $t_0=0$. We now consider small τ and by using the expansion (61) write the transformation (60) up to the lowest order in τ . We obtain

$$p = \frac{1}{\tau}a^*(\phi' - \phi) + b^*D\phi, \quad (63)$$

where

$$a^* = \begin{cases} (\rho S^{-1})^2, & \text{parabolic case} \\ \frac{1}{\tau_r^2 \tau}, & \text{hyperbolic case,} \end{cases}$$

$$b^* = \begin{cases} -\rho S^{-1}L, & \text{parabolic case} \\ \frac{1}{\tau_r}, & \text{hyperbolic case.} \end{cases}$$

and therefore the Jacobian becomes

$$\frac{\partial p}{\partial \phi'} = \begin{cases} \frac{1}{\tau}(\rho S^{-1})^2, & \text{parabolic case} \\ \frac{1}{\tau_r^2 \tau}, & \text{hyperbolic case.} \end{cases} \quad (64)$$

Since τ is small the system does not appreciably deviate from the mean path and we may then use Eqs. (56) and (63) in the action, Eq. (59). The result is

$$A_\tau(\phi', \phi) = \frac{1}{2}a^*(\phi' - \phi)^2 - b^*D\phi(\phi' - \phi) + \frac{1}{2}c^*\tau(D\phi)^2, \quad (65)$$

with

$$c^* = \begin{cases} -5L^2, & \text{parabolic case} \\ 1, & \text{hyperbolic case.} \end{cases}$$

Finally, the normalization factor is given by

$$N = \sqrt{\frac{a^*}{2k\pi}}.$$

By substituting in the transition probability, Eq. (58), we obtain

$$P_\tau(\phi'/\phi) = \sqrt{\frac{a^*}{2k\pi}} \exp\left\{-\frac{1}{k}\left[\frac{1}{2}a^*(\phi' - \phi)^2 - b^*D\phi(\phi' - \phi) + \frac{1}{2}c^*\tau(D\phi)^2\right]\right\}. \quad (66)$$

It must be noticed from this last result that the transition probability is determined by potential differences and their derivatives. Therefore we assure the existence of this probability field for all times. In this sense the nonbounding property of the potential function does not affect the transition probability. The equilibrium state is then characterized only by the limiting value of the conjugated momentum, since the potential function is not defined for $t \rightarrow \infty$. This is consistent with the fact that the equilibrium state is completely characterized by the thermodynamic property Γ .

We now show that the transition probability, Eq. (66), satisfies the Chapman-Kolmogorov equation [34]. First we approximate this probability as

$$P_\tau(\phi'/\phi) = \sqrt{\frac{a^*}{2k\pi}} \exp\left\{-\frac{1}{2k}c^*\tau(\overline{D\phi})^2\right\} \times \exp\left\{-\frac{a^*}{2k}(\phi' - \phi)^2 + \frac{b^*}{k}\overline{D\phi}(\phi' - \phi)\right\}, \quad (67)$$

where $\overline{D\phi}$ is the value of $D\phi$ at the point $\frac{1}{2}(\phi' + \phi)$. This choice is motivated by our desire to incorporate information on the most probable trajectory. In the absence of any other physical insight as to what to choose this seems to be a reasonable guess.

Explicitly the Chapman-Kolmogorov equation is

$$\int d\phi' P_{\tau''}(\phi''/\phi') P_{\tau'}(\phi'/\phi) = P_\tau(\phi''/\phi). \quad (68)$$

By direct substitution of Eq. (67) in Eq. (68) it may be seen that this last equation is satisfied identically. The algebra is briefly sketched in the Appendix for the hyperbolic case.

For the finite lapse s we may find an expression for the transition probability between the states ϕ and ϕ' by using the Chapman-Kolmogorov equation, Eq. (68). If we divide the interval s in N subintervals τ we have then that

$$P_s(\phi'/\phi) = \int d\phi_1 \cdots d\phi_{N-1} P_\tau(\phi'/\phi_{N-1}) \times P_\tau(\phi_{N-1}/\phi_{N-2}) \cdots P_\tau(\phi_1/\phi), \quad (69)$$

where $\tau = s/N$.

With the above result, we know that either parabolic or hyperbolic transport is a stochastic process which satisfies the Chapman-Kolmogorov equation in the framework of the new physical fields represented by the potential functions associated with the thermodynamic properties of the system.

Is it a Markov process? The answer is not necessarily and we will give some additional comments on this point in the next section.

For the parabolic case we may, however, go on. The transition probability Eq. (67) is written explicitly as

$$P_{\tau}(\phi'/\phi) = \sqrt{\frac{(\rho S^{-1})^2}{2k\pi\tau}} \exp\left[-\frac{5}{2} \frac{\tau L^2}{k} (\Delta\phi)^2\right] \\ \times \exp\left\{-\frac{1}{2k\tau} (\rho S^{-1})^2 (\phi' - \phi)^2 + \frac{\rho S^{-1}}{k} L \Delta\phi (\phi' - \phi)\right\}. \quad (70)$$

The first and second moments of this probability become

$$M_1 = \int d\phi' \Delta\phi P_{\tau}(\phi'/\phi) \\ = -\frac{L\tau}{\rho S^{-1} \Delta\phi} \exp\left[-\frac{2\tau L^2}{k} (\Delta\phi)^2\right], \quad (71)$$

$$M_2 = \int d\phi' (\Delta\phi)^2 P_{\tau}(\phi'/\phi) \\ = \frac{k\tau}{(\rho S^{-1})^2} \exp\left[-\frac{2\tau L^2}{k} (\Delta\phi)^2\right]. \quad (72)$$

The remaining moments vanish at order τ . Therefore we have a Gaussian probability distribution. With moments (71) and (72), the Fokker-Planck equation for the probability is then that of a diffusive process,

$$\frac{\partial P(\phi, t)}{\partial t} = -\frac{\partial}{\partial \phi} (M_1 P) + \frac{1}{2} \frac{\partial^2}{\partial \phi^2} (M_2 P), \quad (73)$$

with positive M_2 . As may be seen, parabolic transport is a stochastic diffusion. The essentials of the results of Onsager and Machlup for near equilibrium systems are therefore recovered here.

In fact, analogous results may be obtained for the hyperbolic case, namely, the first and second moments derived from the probability Eq. (67) are order τ , while higher moments vanish at order τ . So, the statistical properties of the stochastic process associated to the potential ϕ turn out to be identical for both parabolic and hyperbolic transport. However, we have to stress again that, as mentioned in Sec. II, the potential functions themselves are different in each case.

V. DISCUSSION

We have derived a mesoscopic scheme for transport phenomena of intrinsically fluctuating systems based on the existence of a classical variational principle for the dynamical equations which include non-self-adjoint linear differential operators. This scheme involves aged systems as well as processes occurring in times of the order of the relaxation time of the fluxes. This is the main difference of this work with respect to the ones of Onsager and Machlup [2] and Grabert and Green [3] which describe aged homogeneous systems,

where the fluxes are the time derivatives of the thermodynamic properties. The stochastic nature of the systems dealt with by these authors arises from an external stochastic agent which confers the same property to the system.

The virtues of a description for irreversible processes based on path integrals are well known [4]. Among them we remark that it gives a rationale of nonequilibrium thermodynamics and that in the near equilibrium case the Lagrangian is related to the entropy production and the principle of minimum entropy production may be derived from the variational principle. The technique used here to describe the dynamics of nonequilibrium systems is also based on the probability density of a complete path in the space spanned by a new set of thermodynamic properties of the system: the so-called potential functions and the set of local equilibrium properties. The variational scheme is, as has been shown [2–4], the heart of the path integral description of irreversible processes. For the linear case this description is equivalent to that made in terms of the Langevin equation or the Fokker-Planck equation of the works of Onsager and Machlup and Grabert and Green.

The states far from equilibrium require a characterization based on the conserved densities and an additional set of physical fields: the potential functions. It is worthwhile to remark the physical behavior of the potential function ϕ . As was mentioned above, this potential diverges for large times while Γ (and therefore the conjugated momentum p) approaches asymptotically to its equilibrium value. This is not a strange situation in classical field theory. In fact this behavior was considered as a necessary condition for the physical consistency of the formalism. The hyperbolic transport equations contain the first time derivative which is a non-self-adjoint operator. Therefore a classical variational formulation does not exist in principle for them. The potential function method circumvents this difficulty. The point we wish to make is that if one observes the Euler-Lagrange equation for the potential ϕ one still finds some non-self-adjoint differential operators. It has been shown here that by resorting to Onsager's reciprocity relations the terms containing this kind of operators vanish, leaving only those with self-adjoint operators. In connection with this point, it is important to emphasize the role of Onsager's reciprocity which is identical to the one it plays in the original Landau and Lifshitz Lagrangian formulation [22]. It must be stressed, however, that the present formulation is more general than that of Landau and Lifshitz since it allows for the inclusion of spatial inhomogeneities.

The establishment of a mesoscopic approach to hyperbolic transport was also dealt with by Olivares-Robles and García-Colín [35]. The main result of the preceding section concerning hyperbolic transport coincides with that of Olivares-Robles and García-Colín, who, starting from the Chapman-Kolmogorov equation, obtained the hyperbolic equations as the average dynamic equations of the system under the only assumption that the interval τ between events be finite. This interval of time τ has the same meaning for us. The unavoidable question is then if processes with thermodynamic memory may be described with the Chapman-Kolmogorov equation. Some affirmative answers to this question have been given [36], but no doubt this is still an open problem.

The formal aspects of the path integral based formulations for nonequilibrium processes (but still near equilibrium) have recently been surpassed, turning them into an effective computational tool [37]. Our results may well be the grounds for doing the same in the case of processes far from equilibrium.

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APPENDIX

On the left hand side of Eq. (68) we have

$$\begin{aligned} \int d\phi' P_{\tau'}(\phi''/\phi') P_{\tau'}(\phi'/\phi) &= \sqrt{\frac{1}{2k\pi\tau_r^2\tau}} \sqrt{\frac{\tau}{2k\pi\tau_r^2\tau''\tau'}} \exp\left\{-\frac{1}{2k}\tau(\overline{\phi})^2\right\} \\ &\times \int d\phi' \exp\left\{-\frac{1}{2k\tau_r^2\tau''}(\phi''-\phi')^2 + \frac{1}{k\tau_r}\overline{\phi}(\phi''-\phi')\right\} \\ &\times \exp\left\{-\frac{1}{2k\tau_r^2\tau'}(\phi'-\phi)^2 + \frac{1}{k\tau_r}\overline{\phi}(\phi'-\phi)\right\}. \end{aligned}$$

The terms that depend on the intermediate state ϕ' are

$$\begin{aligned} &\exp\left\{-\frac{1}{2k\tau_r^2}\left[\frac{1}{\tau''}\phi''^2 + \frac{1}{\tau'}\phi^2\right]\right\} \int d\phi' \exp\left\{-\frac{1}{2k\tau_r^2}\left[\frac{\tau}{\tau''\tau'}\phi'^2 - 2\left(\frac{1}{\tau''}\phi'' + \frac{1}{\tau'}\phi\right)\phi'\right]\right\} \\ &= \exp\left\{-\frac{1}{2k\tau_r^2}\left[\frac{1}{\tau''}\phi''^2 + \frac{1}{\tau'}\phi^2\right]\right\} \sqrt{\frac{2k\pi\tau_r^2\tau''\tau'}{\tau}} \exp\left\{\frac{\tau''\tau'}{2k\tau_r^2\tau}\left(\frac{1}{\tau''^2}\phi''^2 + \frac{2}{\tau''\tau'}\phi''\phi + \frac{1}{\tau'^2}\phi^2\right)\right\} \\ &= \sqrt{\frac{2k\pi\tau_r^2\tau''\tau'}{\tau}} \exp\left\{\frac{1}{2k\tau_r^2\tau}(\phi''-\phi)^2\right\}. \end{aligned}$$

Then, by substituting this last expression in the above equation we arrive at

$$\int d\phi' P_{\tau'}(\phi''/\phi') P_{\tau'}(\phi'/\phi) = \sqrt{\frac{1}{2k\pi\tau_r^2\tau}} \exp\left\{-\frac{1}{2k}\tau(\overline{\phi})^2\right\} \exp\left\{-\frac{1}{2k\tau_r^2\tau}(\phi''-\phi)^2 + \frac{1}{k\tau_r}\overline{\phi}(\phi''-\phi)\right\} = P_{\tau}(\phi''/\phi').$$

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