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Variational principles for entropy production and predictive statistical mechanics

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Abstract. The concepts of the maximum entropy formalism of predictive statistical mechanics are applied to transport processes in the steady state. This yields general arguments, valid in the nonlinear regime, in favour of Kohler's principle and the principle of minimum entropy production.

1. Introduction

In the theory of transport in linear systems there are two well known variational principles concerning the entropy production. We shall term the first the principle of minimum entropy production (PMEP). It can be shown, as a direct consequence of Onsager's reciprocal relations, that if certain thermodynamic forces are allowed to vary, the rate of entropy production in the transport process is at a minimum in the steady state, that is, when the currents or flows conjugate to the free forces are all zero. This is of importance in justifying 'Thomson's hypothesis', applied originally by Lord Kelvin to thermoelectricity and subsequently by a number of authors to other transport phenomena (Denbigh 1951). The second principle was formulated by Kohler to aid in the solution of the semiclassical Boltzmann equation for electrons in metals, but can be given a more general thermodynamic formulation, as discussed in detail by Ziman (1956), and can also be extended to fully quantum-mechanical systems (Jones 1982).

In the following we examine the relationship of these principles to ideas of predictive statistical mechanics (PSM) as developed particularly by Jaynes (1957, 1979, 1980), and in which one proposes to extend ideas developed in equilibrium thermodynamics to constrained equilibrium and irreversible processes. Specifically, we seek to obtain that state, of a given system, which is most likely on the basis of our information, and to do so we maximise the information entropy subject to the constraints implied by the information. If our information is sufficient to determine the actual state, this is also the most likely state. Otherwise PSM gives an average over all cases which are possible on the basis of our information. We should remark that an information-theory approach to statistical mechanics is sometimes resisted on the grounds that our information concerning a system cannot influence its behaviour. This is of course true, but our information *can* influence the nature of our predictions of its behaviour and one convenient way of characterising a system is in terms of what information is required to make these predictions correct, a point we shall return to.

Apart from the interest of connecting the entropy-production theorem with PSM, our considerations involving the latter will not depend on the system being linear and we shall therefore be able to consider what variational principles are possible, on the basis of PSM, in the nonlinear regime. As we shall see, we are also led to an interesting interpretation of the failure of Kohler's principle and the PMEP for non-zero magnetic fields.

2. Variational principle for the most probable state

We define the *extrinsic* entropy production σ_e as the rate of entropy production in terms of the thermodynamic forces X_α and the corresponding fluxes J_α, that is, by the usual macroscopic expression $\sigma_e = \Sigma_\alpha X_\alpha J_\alpha$. The *intrinsic* entropy production σ_i is defined as the rate of entropy production expressed in terms of parameters θ describing the internal state of the system. Thus θ might be a set of microscopic parameters, such as elements of the density matrix, or it might represent the currents in the system.

Suppose now our information is that definite constant thermodynamic forces X_α are applied to a system with entropy production $\sigma_i(\theta)$. From some arbitrary initial state Σ_0 the system would evolve towards the true steady state, attaining it (for all intents and purposes) in some finite time τ. Consider then a possible evolutionary path P starting from Σ_0 and over which the parameters θ change during the time τ, after which they remain constant at a set of values θ' describing a possible steady state. For any possible steady state the intrinsic and extrinsic entropy production must be equal, so that we require $\sigma_i(\theta') = \Sigma_\alpha X_\alpha J'_\alpha$ where $J'_\alpha \equiv J_\alpha(\theta')$, which ensures that the set θ' is consistent with our information. In accordance with the philosophy of PSM we now say that the most probable state (on the basis of the information available) after a time τ is that which maximises the final entropy, and hence the entropy production over the path P. The entropy is a measure of the final number of *a priori* equally probable microstates, and the macroscopic change we predict is therefore that giving the maximum number of these microstates consistent with the information. The microstates, though equally probable *a priori*, may not be equally probable in the circumstances under discussion, but to allocate other probabilities would show a bias which is not warranted by the information available.

If we take t to be very large ($t \gg \tau$) we may neglect the entropy production while θ is changing and take the final entropy change to be just $\sigma_i(\theta')t$. Our conclusion is evidently that the most probable set of parameters θ is that maximising the intrinsic entropy production. On the basis of predictive statistical mechanics, therefore, we may state the general principle: *of all possible steady states satisfying $\sigma_i = \sigma_e$ for given X the most probable steady state on the basis of our information is that for which σ_e is a maximum.*

The information referred to here consists of the X, specifying the external conditions, and the form of $\sigma_i(\theta)$, specifying the system. If this information is complete, by which we mean it is sufficient to determine the steady state, we simply have: *of all possible steady states satisfying $\sigma_i = \sigma_e$ for given X the actual steady state is that for which σ_e is a maximum.*

This is just the general statement of Kohler's principle in thermodynamic terms (Ziman 1956, Jones 1982).

Introducing a Lagrange parameter λ_1, we can see that Kohler's principle implies, for any member θ_α of the set θ,

$$(1-\lambda_1)\partial\sigma_i/\partial\theta_\alpha = -\lambda_1\,\partial\sigma_e/\partial\theta_\alpha \tag{2.1}$$

and

$$(1-\lambda_1)\,\partial^2\sigma_i/\partial\theta_\alpha^2 \leqslant -\lambda_1\,\partial^2\sigma_e/\partial\theta_\alpha^2. \tag{2.2}$$

In a recent discussion of Kohler's principle we emphasised the alternative formulation: of all possible states specified by variables θ' such that $\sigma_e(\theta') = \sigma_e(\theta)$ for given X, the steady state ($\theta' = \theta$) is that which makes $\sigma_i(\theta')$ a minimum. Introducing a Lagrangian parameter λ_2, one sees that this implies

$$\partial\sigma_i/\partial\theta_\alpha = \lambda_2\,\partial\sigma_e/\partial\theta_\alpha \tag{2.3}$$

and

$$\partial^2\sigma_i/\partial\theta_\alpha^2 \geqslant \lambda_2\,\partial^2\sigma_e/\partial\theta_\alpha^2. \tag{2.4}$$

These equations are consistent with (2.1) and (2.2) provided $\partial^2\sigma_e/\partial\theta_\alpha^2 = 0$ and $\lambda_1 > 0$. This will be true if we can choose the J_α to be linear functions of the θ_α, and $\sigma_i(\theta)$ is a homogeneous function of order $n \geqslant 1$.

3. Minimum entropy production

We now consider a particular application of Kohler's principle as given above. Let us examine the condition under which the system in a steady state with currents J_α and thermodynamic forces X can provide a trial function $\sigma_i(\theta)$ for the same system when the thermodynamic forces are X'. To apply the principle we require the intrinsic entropy production for the first state, and since in a steady state this is automatically equal to the extrinsic entropy production, we have

$$\sigma_i(\theta) = \sum_\alpha J_\alpha X_\alpha. \tag{3.1}$$

We also require the extrinsic entropy production the trial state gives with the actual forces X'. This is simply

$$\sigma_e(\theta) = \sum_\alpha J_\alpha X'_\alpha. \tag{3.2}$$

Setting $\sigma_i = \sigma_e$ we see that the first steady state gives a trial state for the second steady state *provided*

$$\sum_\alpha J_\alpha X_\alpha = \sum_\alpha J_\alpha X'_\alpha \tag{3.3}$$

and if this is satisfied then $\sigma_i \leqslant \sigma_e(\theta')$, i.e.

$$\sum_\alpha J_\alpha X_\alpha \leqslant \sum_\alpha J'_\alpha X'_\alpha. \tag{3.4}$$

Equation (3.3) is of course just $\Sigma_\alpha J_\alpha \delta X_\alpha = 0$, and if we require this to be true for arbitrary small variations of δX_γ in those forces which vary from state to state we must set

$$J_\gamma = 0. \tag{3.5}$$

Equation (3.4) now shows that in the steady state the entropy production is at a minimum with respect to arbitrary variations of the free thermodynamic forces (i.e. those conjugate to the currents which are zero).

We note that (3.3) and (3.4) yield

$$\sum_\alpha [J_\alpha(X') - J_\alpha(X)]X'_\alpha \geqslant 0 \tag{3.6}$$

or, if only X_γ varies,

$$\sum_\alpha \frac{\partial J_\alpha}{\partial X_\gamma} X_\alpha \delta X_\gamma + \frac{\partial J_\gamma}{\partial X_\gamma}(\delta X_\gamma)^2 \geqslant 0. \tag{3.7}$$

This implies

$$\sum_\alpha (\partial J_\alpha/\partial X_\gamma) X_\alpha = 0 \tag{3.8}$$

and

$$\partial J_\gamma/\partial X_\gamma \geqslant 0. \tag{3.9}$$

For linear systems we may write

$$J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta \tag{3.10}$$

in which case

$$\partial J_\alpha/\partial X_\gamma = L_{\alpha\gamma} \tag{3.11}$$

so that (3.9) yields

$$L_{\gamma\gamma} \geqslant 0. \tag{3.12}$$

Equations (3.5) and (3.8) respectively imply

$$\sum_\beta L_{\gamma\beta} X_\beta = 0 \tag{3.13}$$

and

$$\sum_\beta L_{\beta\gamma} X_\beta = 0. \tag{3.14}$$

Let only X_α and X_γ be non-zero. These equations are then

$$L_{\gamma\alpha} X_\alpha + L_{\gamma\gamma} X_\gamma = 0 \qquad L_{\alpha\gamma} X_\alpha + L_{\gamma\gamma} X_\gamma = 0 \tag{3.15}$$

i.e.

$$L_{\alpha\gamma} = L_{\gamma\alpha} \tag{3.16}$$

the Onsager relations.

From the above we can see that the PMEP is a formal consequence of Kohler's principle in the nonlinear regime as well as for linear systems.

4. Magnetic fields

For a linear system in the presence of a magnetic field $\boldsymbol{H}$, the intrinsic entropy production is a function of parameters θ which describe both the system Σ and a second system Σ^- the same as the first except that $\boldsymbol{H}$ is reversed (Jones 1982). These parameters do not completely specify the sets of currents J and J^- but only the combination $2\bar{J} = J + J^-$. In that case the θ' consistent with our information are all those values for which $\sigma_i(\theta') = \sigma_i^-(\theta') = \frac{1}{2}(\sigma_e(\theta') + \sigma_e^-(\theta')) = \Sigma\, \bar{J}_\alpha X_\alpha$ and on the basis of PSM one therefore expects the true values of θ to be given by maximising $\sigma_i(\theta')$ subject to $\sigma_i(\theta') = \Sigma\, \bar{J}_\alpha X_\alpha$. This is indeed the correct generalisation of Kohler's principle (Jones 1982), and moreover one finds that the original PMEP is replaced by one for which the entropy production is at a minimum with respect to variations of X_α when $J_\alpha^+ + J_\alpha^- = 0$ (*not* when either Σ or Σ^- is in its steady state).

5. Discussion

We have seen that Kohler's principle and the principle of minimum entropy production follow from the assumptions of predictive statistical mechanics. The argument is of importance in being applicable to nonlinear systems but, as emphasised in § 2, strictly speaking leads to a variational principle for the 'most probable steady-state', not necessarily the actual state of the system. This 'most probable state' is the most unbiased prediction on the basis of our information. We should stress that there is a sense in which we are applying no general principles other than those used in equilibrium statistical mechanics. Given certain macroscopic variables and an expression S for the entropy, one may predict the most probable state on the basis of the information provided. One may now argue that if the state predicted were not the actual state this would be evidence for the existence of microscopic laws not at present known (Jaynes 1957). Similarly, one may argue that if a system subject to thermodynamic forces X does not reach the most probable state then there must be other unknown constraints C on the system. Certainly, if the entropy is at a maximum at equilibrium the C are inoperative at $X \equiv 0$ and we can further see that the C are inoperative in linear systems, since Kohler's principle can be proved independently in this case. From this point of view the testing of Kohler's principle or the PMEP for nonlinear systems would be of fundamental importance in establishing the existence or otherwise of C.

In this connection any counterexample to the PMEP or Kohler's principle must of course be one to which predictive statistical mechanics is relevant. For example, the PMEP is sometimes illustrated by means of a system of parallel resistors (see e.g. Ziman 1956) and the principle breaks down if the resistors are non-ohmic (nonlinear). However, from the present point of view the satisfaction, or otherwise, of the PMEP is simply an accident, for the parallel circuit elements are completely independent for a given voltage—the current in one element is the same irrespective of the presence of any other. The whole point of principles of maximum entropy production is the possibility of discussing complexly interacting systems.

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