NON-NEGATIVE ENTROPY PRODUCTION BY QUASI-LINEAR OR POTENTIAL-BASED FORCE-FLUX RELATIONS[1]

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EXTENDED ABSTRACT

An essential part in modeling out-of-equilibrium dynamics is the formulation of the irreversible dynamics. In the latter, the main modeling task consists in specifying the relations between thermodynamic forces on the one hand and fluxes on the other hand. As a guardrail to ensure that these relations comply with macroscopic observations one uses, among other principles, the second law of thermodynamics. The latter is considered in this contribution as that the local production of entropy is non-negative. Mainly two major directions have been followed in the literature for the specification of force-flux relations. On the one hand, quasi-linear relations are employed, in which so-called transport coefficients occur, that may depend on the forces themselves in which case we call the relation quasi-linear rather than linear. If the (matrix of) transport coefficients is non-negative, the second law is respected. Such relations have a deeper foundation in the physics of fluctuation-dissipation theorems [1; 2]. On the other hand, force-flux relations are also often represented in potential form. In this case, the flux is given by the derivative of a so-called dissipation potential with respect to the force [3]. The second law of thermodynamics is respected by requiring certain properties of the potential, primarily its convexity. In this contribution, we address the question of how these two approaches, quasi-linear and potential-based, are related.

The main outcome of this presentation is that every potential-based force-flux relation can be cast into quasi-linear form, while the reverse statement does not hold true [4]. In other words, the potential-based relations are a subset of those that can be formulated in the quasi-linear setting. While this main result is derived in general terms, it is demonstrated also with the help of three examples: (i) heat conduction in rigid bodies, (ii) homogeneous chemical reactions, and (iii) slippage in complex fluids. In particular, whereas the irreversible processes (i) and (ii) are dissipative, (iii) is not dissipative although it is irreversible. For the models (i) and (ii), conditions for the existence of a dissipation potential are formulated. Conversely, the dissipation potential for model (iii) vanishes since this model is an example of a dissipation-free irreversible process.

It is also shown that the above conclusions about force-flux relations have ramifications for the General Equation for Non-Equilibrium Reversible-Irreversible Coupling (GENERIC: e.g., [5; 6; 7]), which has been formulated in a quasi-linear [6; 7] and a dissipation-potential based [8] form, respectively. Also for the GENERIC it is found that potential-based form is a special case of the quasi-linear approach, as is the case for force-flux relations [4]. It can even be shown that the potential-form of GENERIC exists if and only if one does for the underlying force-flux relations.

While the potential-based forms are subcases of the quasi-linear counterparts, one may still opt for the potential-based form. For example, the potential-based form is necessary to formulate initial-boundary-value problems in variational form. In addition, the differential-geometry perspective on irreversible processes suggests a potential-based formulation [8]. As well, it has recently been suggested [9] that the potential form of GENERIC emerges from an optimization principle. Despite all these arguments, there are convincing arguments in favor of the quasi-linear relations. Firstly, they are more general than the potential-based forms, as shown above. Secondly, the quasi-linear form is the result of systematic coarse-graining using projection-operator techniques [7; 10; 11]. And thirdly, the quasi-linear form is more amenable to experimental determination where one often determines the transport coefficients as the ratio of the flux to the force.

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[1]For the full details of this presentation, the reader is referred to [4].