Weakly Nonlocal Non-equilibrium Thermodynamics – Variational Principles and Second Law

Péter Ván

Abstract A general, uniform, rigorous and constructive thermodynamic approach to weakly nonlocal non-equilibrium thermodynamics is reviewed. A method is given to construct and restrict the evolution equations of physical theories according to the Second Law of Thermodynamics and considering weakly nonlocal constitutive state spaces. The evolution equations of internal variables, the classical irreversible thermodynamics and Korteweg fluids are treated.

1 Introduction

Weakly nonlocal, coarse grained, phase field and gradient are attributes of theories from different fields of physics indicating that in contradistinction to the traditional treatments, the governing equations of the theory depend on higher order space derivatives of the state variables. The origin of the idea goes back to the square gradient model of van der Waals for phase interfaces [100], where it is extensively applied [3, 38, 39, 42]. Later applications go far beyond phase boundaries or thermodynamics. Nowadays weakly nonlocal is a nomination in continuum physics dealing with internal structures [10, 27, 46, 50, 61, 66], coarse grained or phase field appears in statistically motivated thermodynamics [1, 3, 5, 34, 80], and gradient is frequently used in mechanics in different context [2, 11, 37, 43, 44, 57, 58, 59, 79, 83, 84, 101].

The simplest way to demonstrate the meaning of weakly nonlocal extensions can be exemplified by the Ginzburg-Landau equation, which is not only a specific equation in superconductivity, as it was introduced originally by Landau and Khalatnikov [45], but a first weakly nonlocal extension of a homogeneous relaxation equation of an internal variable. The traditional derivation of the Ginzburg-Landau equation is
based on a characteristic mixing of variational and thermodynamic considerations. One applies a variational principle for the static part, and the functional derivatives are introduced as thermodynamic forces into a relaxation type equation. A clear variational derivation to obtain a first order differential equation is impossible without any further ado (e.g., without introducing new variables to avoid the first order time derivative, which is not a symmetric operator) [98]. One can apply these kinds of arguments in continuum theories in general, preserving the doubled theoretical framework separating reversible and irreversible parts of the equations [28, 77, 78]. However, there are also other attempts to unify the two parts with different additional hypotheses and to eliminate this inconsistency of the traditional approach [6, 30, 50].

The ultimate aim is to find a unified, general, rigorous and predictive theoretical framework that makes it possible to extend the governing equations of physics with higher order gradients of the continuum fields, beyond the traditional terms. The method should be uniformly applicable from classical systems in local equilibrium up to relativistic systems beyond local equilibrium; should be general to incorporate most of the mentioned classical examples of weakly nonlocal theories without specific assumptions; should reduce the independent additional assumption to a minimum and should be constructive to give calculational methods for systematic higher order extensions of the constitutive space.

This paper is a general tutorial to the mathematical framework of such a theory. In the first section a general methodology of exploiting the Second Law for weakly nonlocal systems is given. The Second Law is considered as a constrained inequality, where the constraints are the evolution equations of the system and their derivatives, depending on the order of the nonlocality. In the third section, evolution equations of internal variables and their different weakly nonlocal extensions are treated. A first order weakly nonlocal theory leads to relaxation type ordinary differential equations, a second order nonlocality leads to the Ginzburg-Landau equation, and a second order nonlocal theory to dual internal variables, unifying the evolution equations of internal variables derived by mechanical methods (by variational principles and dissipation potentials) and by thermodynamics (by heuristic application of the Second Law). In the fourth section we show that classical irreversible thermodynamics can be incorporated naturally in our treatment, a first order weakly nonlocal theory of balance type evolution equations leads to the thermodynamic flux-force relations of classical irreversible thermodynamics with gradients of the intensives as thermodynamic forces. Finally, we demonstrate the applicability of the method to one component heat conducting Korteweg fluids that are first order weakly nonlocal in the energy and in the velocity, and second order weakly nonlocal in the density. In that case nontrivial forms of the pressure tensor ensure the compatibility to the Second Law. As a particular example we derive the constitutive functions of the Schrödinger-Madelung fluids. Finally a summary and discussions follow.