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Thermodynamic theory of equilibrium fluctuations

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ABSTRACT

The postulational basis of classical thermodynamics has been expanded to incorporate equilibrium fluctuations. The main additional elements of the proposed thermodynamic theory are the concept of quasi-equilibrium states, a definition of non-equilibrium entropy, a fundamental equation of state in the entropy representation, and a fluctuation postulate describing the probability distribution of macroscopic parameters of an isolated system. Although these elements introduce a statistical component that does not exist in classical thermodynamics, the logical structure of the theory is different from that of statistical mechanics and represents an expanded version of thermodynamics. Based on this theory, we present a regular procedure for calculations of equilibrium fluctuations of extensive parameters, intensive parameters and densities in systems with any number of fluctuating parameters. The proposed fluctuation formalism is demonstrated by four applications: (1) derivation of the complete set of fluctuation relations for a simple fluid in three different ensembles; (2) fluctuations in finite-reservoir systems interpolating between the canonical and micro-canonical ensembles; (3) derivation of fluctuation relations for excess properties of grain boundaries in binary solid solutions, and (4) derivation of the grain boundary width distribution for pre-melted grain boundaries in alloys. The last two applications offer an efficient fluctuation-based approach to calculations of interface excess properties and extraction of the disjoining potential in pre-melted grain boundaries. Possible future extensions of the theory are outlined.

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1. Introduction

1.1. Historical background and goal of the work

Fluctuations of thermodynamic properties play a crucial role in many physical phenomena and diverse applications. Fluctuations are especially important in nanometer-scale systems where they can lead to a large variability of mechanical and functional properties and create noises affecting performance of devices. Fluctuations are unavoidable in molecular dynamics and Monte Carlo simulations of materials, where the system dimensions rarely exceed a few nanometers. In fact, in many atomistic calculations, equilibrium properties of interest are extracted by analyzing statistical fluctuations of other properties [1–3]. Examples include the calculations of elastic coefficients of solid materials from strain and/or stress fluctuations in molecular dynamics [4–7] or Monte Carlo [8,9] simulations; calculation of partial molar properties of solutions from concentration fluctuations [10,11]; and calculation of the interface free energy of solid–liquid [12,13] and solid–solid [14–24] interfaces from capillary fluctuations or fluctuations of the interface width.

Presently, fluctuations are primarily discussed in the statistical–mechanical literature and typically in the context of specific (usually, very simple) models. At the same time, the thermodynamics community traditionally relies on classical thermodynamics [25–29] which, by the macroscopic and equilibrium nature of this discipline, disregards fluctuations and operates solely in terms of static properties. In fact, the very term ''fluctuation'' has a temporal connotation incompatible with the time-independent character of classical thermodynamics.

There is, however, a third direction in thermal physics that pursues a generalized form of thermodynamics that incorporates fluctuations of thermodynamic parameters around equilibrium. By contrast to the statistical–mechanical approach, such theories seek to introduce fluctuations *directly* into the thermodynamic framework via additional assumptions, postulates or similar elements of the logical structure. The goal of such theories is to expand the scope of thermodynamics by introducing statistical elements while preserving the traditional axiomatic approach that distinguishes this discipline. It is this direction in thermal physics that constitutes the subject of the present paper.[1]

The logical foundations of classical thermodynamics have been the subject of research over the past hundred or more years, starting with the works of Carathéodory [30] and Ehrenfest [31] and continuing in modern times [27–29,32–37]. In spite of the fundamental importance of the traditional three laws of thermodynamics, they are essentially a reflection of the historical development of the discipline and do not constitute an autonomous and logically complete structure. The four-postulate structure proposed by Callen [27,28] is detached from the historical context, deeply thought-through, but still far from complete. The most rigorous and complete postulational basis of classical thermodynamics has been formulated by Tisza [29]. His theory, called the Macroscopic Thermodynamics of Equilibrium (MTE), presents an elegant logical structure comprising a set of interconnected definitions, postulates and corollaries. This rigor comes at a price: Tisza's MTE is restricted to a certain class of rather simple thermodynamic systems. Nevertheless, it demonstrates an approach that can be applied for the construction of similar postulational structures for other classes of systems.

Unfortunately, attempts to create a similarly rigorous thermodynamic formalism that would include fluctuations have not been very successful. The thermodynamic fluctuation theory by Greene and Callen [38,39] and Callen's Postulate II′ [27][2] (which generalizes his entropy Postulate II to include fluctuations) turned out to be insufficient. They required additional assumptions, such as the approximation of average values of thermodynamic properties by their most probable values, and relied on the assumption that there is no distinction between the ''canonical thermodynamics'' and

1 Although we do not wish to enter into terminological discussions, we point out that an expanded thermodynamic theory that incorporates statistical elements such as fluctuations could be called statistical thermodynamics. This term would distinguish it from both statistical mechanics and classical thermodynamics. Unfortunately, the term statistical thermodynamics is already used with several different meanings, most notably as a collective reference to statistical mechanics and thermodynamics (which we refer to as thermal physics).

2 Callen's Postulate II′ [27] was abandoned in a later edition of his book [28].