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Modeling the nonequilibrium effects in a nonquasi-equilibrium thermodynamic cycle based on steepest entropy ascent and an isothermal-isobaric ensemble

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ABSTRACT

Conventional first principle approaches for studying nonequilibrium or far-from-equilibrium processes depend on the mechanics of individual particles or quantum states. They also require many details of the mechanical features of a system to arrive at a macroscopic property. In contrast, thermodynamics provides an approach for determining macroscopic property values without going into these details, because the overall effect of particle dynamics results, for example, at stable equilibrium in an invariant pattern of the "Maxwellian distribution", which in turn leads to macroscopic properties. However, such an approach is not generally applicable to a nonequilibrium process except in the near-equilibrium realm. To adequately address these drawbacks, steepest-entropy-ascent quantum thermodynamics (SEAQT) provides a first principle, thermodynamic-ensemble approach applicable to the entire nonequilibrium realm. Based on prior developments by the authors, this paper applies the SEAQT framework to modeling the nonquasi-equilibrium cycle, which a system with variable volume undergoes. Using the concept of hypoequilibrium state and nonequilibrium intensive properties, this framework provides a complete description of the nonequilibrium evolution in state of the system. Results presented here reveal how nonequilibrium effects influence the performance of the cycle.

1. Introduction

Numerous methods for modeling nonequilibrium phenomena exist with each restricted to its own applicable set of spatial and temporal scales. At the macroscopic level, continuum nonequilibrium thermodynamics with the local equilibrium assumption is used but cannot generally be applied at atomistic/mesoscopic levels since the small dimensions of a system result in quantum and for that matter classical effects that the continuum assumption cannot address. Furthermore, nonequilibrium processes in the far-from-equilibrium realm make the application of the continuum formulation of nonequilibrium thermodynamics, i.e., the so-called Onsager formulation (e.g., [1]) questionable due to its underlying assumption of linearity or near-equilibrium behavior. In addition, each method uses a different kinematic and dynamic description of system state and its motion. Thus, a general approach that provides a thermodynamic analysis of nonequilibrium evolution, especially that far-from-equilibrium, across different spatial and temporal scales has been lacking even though general system properties such as the energy and entropy are well defined [2] and their evolutions observable. Steepest-entropy-ascent quantum thermodynamics (SEAQT) [3–11] addresses these issues providing a mathematical framework with a single kinematics and dynamics that crosses all temporal and spatial scales and accounts for both non-continuum quantum and classical effects. At the same time, it is able to provide system property information based on a fundamental as opposed to phenomenological description and thermodynamic system features resulting from nonequilibrium relaxation patterns (in the sense of GENERIC [12,13]), which capture the dynamic balance of detailed and complex microscopic single particle or quantum state evolutions. These patterns represent a reduction of a system's microscopic kinematics, appear to be general, and are independent of the microscopic dynamics, i.e., of the exact form of the micro-mechanical interactions. One of the benefits of this is that the SEAQT framework is able to avoid the computational burdens inherent to existing methods based on mechanics (e.g., the

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Boltzmann equation [14–16] and molecular dynamics [17]) or quantum mechanics (e.g., 'open-system' quantum thermodynamics [18–23], 'closed quantum systems' [24], heat reservoirs mediated by quantum systems [25], quantum nonequilibrium Green's function equations of motion [26–28], and the quantum Boltzmann equation, i.e., the Uehling-Uhlenbeck-Boltzmann equation [29–31]) that require detailed interaction information of the particles or quantum states.

To date, SEAQT has successfully been used to model nonequilibrium processes (even those far-from equilibrium) from the atomistic to the macroscopic level [9–11,32–37] and bases its framework on properties such as energy, particle number, and entropy, which as mentioned before, are well-defined at all scales for equilibrium as well as nonequilibrium states [2]. The non-linear dynamics of state evolution are characterized by the entropy generation, which results from the principle of steepest entropy ascent (or maximum entropy production [38]). This principle forms the basis of the equation of motion that tracks the evolution of energy and entropy in state space. Using the concept of hypoequilibrium state [9] (i.e., a nonequilibrium relaxation pattern), the nonequilibrium trajectory of system state evolution can be fully described across a wide range of initial conditions. In this way, the thermodynamic analysis of nonequilibrium phenomena at different scales, whether classical or quantum, can be studied using a single framework, i.e., a single kinematics and dynamics.

Since an important part of thermodynamics is to study systems for which volume is the only parameter (in the sense of Gyftopolous and Beretta [39,40]), a description of such a system undergoing a cyclic process in the nonequilibrium realm using SEAQT is presented here. Clearly, an important application of thermodynamics is to the study of such processes independent of the exact nature of the microscopic interactions, which take place inside the system. Cyclic processes have been modeled both at the macroscopic level using equilibrium thermodynamics as well as at the quantum level using quantum mechanics [41–43]. The limitation with respect to the former is that the study of a cycle for such a system necessarily assumes that the system (e.g., that of a gas in a piston/cylinder device) is in a stable equilibrium state at any given instant of time and undergoes a quasi-equilibrium process, i.e., the state evolution of the system is very, very slow and the process is reversible. To move the analysis into the practical realm requires the introduction of phenomenological parameters (e.g., experimental polytropic exponents, isentropic efficiencies) to help account for the effects of irreversibilities and, thus, model real engine cycles and guide device design. The limitation with respect to the latter, i.e., approaches based solely on quantum mechanics (e.g., 'open quantum systems' [41,42]), is that the thermodynamic laws appear only to emerge from the results of the quantum master equation of a given approach but are not fundamental to it and are, thus, only used to validate the model set-up [44,8]. Such approaches can provide insight into the mechanical basis of thermodynamics for a limited set of very specific conditions (e.g., weak system-environment interactions or steady state) but predicting all the general effects, which result directly from the laws of thermodynamics is very difficult and may in fact be impossible when, the mechanical interaction details are too complex or simply not available. Thus, the application of such approaches focuses on quantum systems in nonequilibrium but in general cannot be extended to the modeling of classical meso/macroscopic systems in nonequilibrium states, especially those in the far-from-equilibrium realm. In contrast, the SEAQT framework provides a single theoretical model of irreversibility at all temporal and spatial scales based on the laws of thermodynamics, i.e., they are fundamental to the description. The use of the concept of density of states [32,9] with this framework permits tracking the time evolution of all the energy eigenlevels of a system and does so at a relatively small computational expense, enabling the application of this framework to a wide range of systems at the micro/meso/macro levels using energy eigenlevel information developed from experimental measurements or the computational results of quantum chemistry or density functional theory. In addition, using the concept of hypoequilibrium state and rigorous definitions of nonequilibrium intensive properties [9,10], greater physical insight into the influence of nonequilibrium effects on system performance can be revealed.

In the following, unique thermodynamic trajectories for system state evolutions from some initial transient state to steady state are predicted for cyclic processes using the SEAQT equation of motion. This equation is derived from the conservation laws and the principle of steepest-entropy-ascent (or maximum-entropy-production), i.e., from the first and second laws of thermodynamics, and is introduced and discussed in Sections 2.1–2.3 along with the system and state space considered and the quantum and classical system descriptions used. The concepts of hypoequilibrium state, temperature, and pressure for nonequilibrium states are introduced in Section 2.4 and are shown to be closely related to the isothermal-isobaric ensemble of stable equilibrium [45–49]. The definitions of temperature and pressure proposed for nonequilibrium states are fundamental rather than phenomenological and a generalization of these properties from those at stable equilibrium. The SEAQT equation of motion for two interacting systems and for a system interacting with a reservoir are then presented in Section 3 followed in Section 4 by a description of a system undergoing a nonquasi-equilibrium evolution in state. These examples illustrate the inputs and outputs of the model. Finally, in Section 5, results are given for the state time evolution of a system undergoing a transient cyclic process. How nonequilibrium phenomena influence the performance of the cycle is discussed, and a simple case of optimizing the power of the cyclic system relative to the nonequilibrium effects is illustrated.

2. SEAQT equation of motion

2.1. SEAQT equation of motion using a quantum mechanical description

In this section, the system and state description in SEAQT used here is given, and the equation of motion presented. Based on the discussion by Grmela and Öttinger [12,13,50] and Beretta et al. [7,51] the general form of a nonequilibrium framework is a combination of both irreversible relaxation and reversible symplectic dynamics. If written in the generalized form of the Ginzburg-Landau equation [12,51], the equation of motion takes the following form:

$$\frac{d}{dt}\gamma(t) = X^H_{\gamma(t)} + Y^H_{\gamma(t)} \tag{1}$$

where $\gamma(t)$ represents the state evolution trajectory and $X^H_{\gamma(t)}$ and $Y^H_{\gamma(t)}$ are functions of the system state $\gamma(t)$ and represent the reversible symplectic and irreversible relaxation dynamics, respectively. In the SEAQT framework, the system is defined by the Hamiltonian operator $\widehat{H}$, system state is represented by the density operator $\widehat{\rho}$, $X^H_{\gamma(t)}$ follows the Schrödinger equation, and $Y^H_{\gamma(t)}$ is derived from the SEA principle. To describe the evolutionary process, conservation laws are explicitly required in order to construct the equation of motion, which is given in Ref. [52] as

$$\frac{d\widehat{\rho}}{dt} = \frac{1}{i\hbar}\left[\widehat{\rho}, \widehat{H}\right] + \frac{1}{\tau}\widehat{D} \tag{2}$$