



Atomistic long-term simulation of heat and mass transport



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ABSTRACT

We formulate a theory of non-equilibrium statistical thermodynamics for ensembles of atoms or molecules. The theory is an application of Jaynes' *maximum entropy principle*, which allows the statistical treatment of systems away from equilibrium. In particular, neither temperature nor atomic fractions are required to be uniform but instead are allowed to take different values from particle to particle. In addition, following the Coleman–Noll method of continuum thermodynamics we derive a dissipation inequality expressed in terms of discrete thermodynamic fluxes and forces. This discrete dissipation inequality effectively sets the structure for discrete kinetic potentials that couple the microscopic field rates to the corresponding driving forces, thus resulting in a closed set of equations governing the evolution of the system. We complement the general theory with a variational meanfield theory that provides a basis for the formulation of computationally tractable approximations. We present several validation cases, concerned with equilibrium properties of alloys, heat conduction in silicon nanowires and hydrogen desorption from palladium thin films, that demonstrate the range and scope of the method and assess its fidelity and predictiveness. These validation cases are characterized by the need or desirability to account for atomic-level properties while simultaneously entailing time scales much longer than those accessible to direct molecular dynamics. The ability of simple meanfield models and discrete kinetic laws to reproduce equilibrium properties and long-term behavior of complex systems is remarkable.

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1. Introduction

In a number of areas of application, the behavior of systems depends sensitively on properties that pertain to the atomistic scale, i.e., the angstrom and femtosecond scales. Specifically, atomistic details are important where material response is highly non-linear, e.g., at atomistically sharp crack tips and other stress concentrators, near atomic-scale defects such as vacancies and dislocations and at other atomistically sharp features such as free surfaces, grain boundaries and material interfaces (Gil, 2010). However, often the properties and behaviors of interest are macroscopic and take place on the scale of centimeters to meters, and are characterized by slow evolution on the scale of minutes to years. A case in point is degradation in nuclear reactor materials, which results from a combination of heat, irradiation, stress and corrosion

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exposure for extended periods of time (20 or more years, cf., e.g., [Marquis et al., 2009](#) and references therein). This vast disparity of length and time scales poses extraordinary challenges in theoretical and computational material science.

Molecular Dynamics (MD) and Monte Carlo (MC) methods are powerful techniques to study deformation and diffusion mechanisms in systems of particles, but they are limited to relatively small material samples and to time windows of microseconds at best (e.g., [Sutton et al., 1992](#); [Wang et al., 1992](#)). Considerable effort has been devoted to accelerating MD and MC methods and notable successes have been recorded in that direction (cf., e.g., [Voter et al., 2002](#)). However, no computationally tractable atomistically based models appear to be as yet available to study slow phenomena, over time scales of the order of minutes to years, while maintaining a strictly atomistic description of the material.

The present work is concerned primarily with the development of a theory of non-equilibrium statistical thermodynamics for ensembles of atoms or molecules that addresses that theoretical and computational gap. The theory provides a framework for the development of computational models capable of simulating slow thermo-chemo-mechanical processes, such as corrosion or segregation of impurities, that occur over time-windows that are intractable by means of the existing atomistic or atomistically informed models. In particular, the theory effectively accounts for thermal and stoichiometric effects, including heat and mass transport, without the need to track thermal vibrations and individual particle hops explicitly. Given the advantageous properties of numerical methods based on variational formulations, special emphasis is placed in obtaining *variational principles* that characterize the state or evolution in the system.

The proposed theory is an application of Jaynes' *maximum entropy principle* ([Jaynes, 1957a,b](#)) that allows the statistical treatment of systems away from equilibrium. By maximizing a suitable constrained entropy, effective thermodynamic potentials are identified which characterize the instantaneous state of a system and supply driving forces for its evolution. Specifically, we formulate a grand-canonical free entropy that, unlike other conventional thermodynamic potentials such as the free energy, is well-defined away from equilibrium. In addition, the stationarity of the grand-canonical free entropy characterizes the states of thermodynamic equilibrium of the system. In practice, the calculation of the grand-canonical partition function in closed form is generally intractable, which raises the need for approximation theory. Variational meanfield theory is often used to devise computationally tractable approximations to complex thermodynamical systems ([Callen, 1985](#); [Yeomans, 1992](#)). By exploiting the optimality properties of the theory, meanfield models can systematically be developed and Bogoliubov-like variational principles can be proven, even away from equilibrium. In particular, we show that trial meanfield Hamiltonians always lead to guaranteed lower bounds of the grand-canonical free entropy, and that this thermodynamic potential is well defined both in equilibrium and away from it.

The fundamental difference between the present theory and previous approaches based on free-energy minimization (cf., e.g. [Sutton et al., 1992](#); [Wang et al., 1992](#)) is that neither temperature nor atomic fractions are required to be uniform but instead are allowed to take different values from particle to particle. Following [Kulkarni et al. \(2008\)](#), we additionally characterize the evolution of the system, be it towards equilibrium or in response to external driving, by means of kinetic equations of the Onsager type ([Onsager, 1931a,b](#); [De Groot and Mazur, 1962](#)). We develop this discrete kinetic framework by mirroring the classical Coleman–Noll method of continuum thermodynamics ([Coleman and Noll, 1963](#)), with the aim of deriving a dissipation inequality expressed in terms of discrete thermodynamic fluxes and forces. This discrete dissipation inequality effectively identifies the appropriate form of said thermodynamic fluxes and forces and their duality pairings. These pairings in turn set the structure of discrete kinetic potentials that couple the microscopic field rates to the corresponding driving forces, thus resulting in a closed set of equations governing the evolution of the system.

Within the framework just outlined, the discrete kinetic potentials are empirical and subject to modeling, much in the same way as the interatomic potentials used in practice are also empirical and the result of modeling. For instance, [Kulkarni et al. \(2008\)](#) proposed a class of *linear* discrete kinetic equations based on interpolation of the atomistic fields and subsequent use of continuum transport equations such as Fourier's law of heat conduction. The advantage of such discrete models is that they can be calibrated directly against experimentally measured macroscopic transport properties, such as thermal conductivity, while simultaneously affording a measure of atomistic realism. In this work, we develop a general framework for discrete linear kinetics encompassing both heat and mass transport. A general connection between atomistic and macroscopic transport coefficients, such as thermal conductivities and diffusivities, can be forged by means of a standard asymptotic analysis of the long-wavelength limit of the discrete governing equations (cf., e.g., [Askar, 1986](#)). For some simple geometries and sufficiently short-range interactions, this discrete-to-continuum long-wavelength limiting relations suffice to determine all the atomic-level transport constants, thus allowing for a direct experimental calibration of the models.

In addition to formulating the theoretical framework and attendant meanfield approximation theory, we present several validation cases aimed at demonstrating the range and scope of the method and assessing its fidelity and predictiveness. A first concern in this regard is how well simple meanfield models, such as must necessarily be used in practice, approximate thermodynamic driving forces and, in particular, equilibrium properties. We ascertain this question by formulating a simple meanfield model for substitutional alloys and assessing its ability to reproduce equilibrium properties of four alloys, including lattice parameter, linear thermal expansion coefficient, elastic moduli and surface segregation concentration. A second concern is how well empirical discrete kinetic equations can model long-term process in complex systems. Again, we address this question by means of two validation cases: heat conduction in silicon nanowires and hydrogen storage in palladium. The first case tests the ability of the theory to model heat conduction and the second mass transport in applications requiring atomistic resolution while, simultaneously, involving time scales much longer than typically accessible to molecular dynamics. Evidently, heat conduction at the nanoscale and hydrogen storage in metals are

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