IDENTIFYING TEMPERATURE AND RELATED STATISTICS OF NONEQUILIBRIUM STEADY STATES

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by

Puneet Kumar Patra

Under the guidance of

Prof. Baidurya Bhattacharya

ADVANCED TECHNOLOGY DEVELOPMENT CENTER
INDIAN INSTITUTE OF TECHNOLOGY KHARAGPUR
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Abstract

Statistical mechanics, which links the macroscopic properties of a system with the microscopic evolution of its constituents, has been remarkably successful in explaining a varied class of problems ranging from information theory to transportation planning, biological sciences and ecological modelling. However, despite being so powerful the scope of traditional statistical mechanics, like traditional thermodynamics, is limited to systems in equilibrium. Unfortunately, all real processes are irreversible and take place in away-from-equilibrium conditions. These processes involve a continuous flux of matter and energy. Despite significant efforts over the better part of the last century, no unified theoretical formulation has been put forward that can explain these out-of-equilibrium processes completely, and developing such a theory remains an open problem in physics. In absence of a sound theoretical framework, researchers resort to simulations for understanding the physics behind the nonequilibrium processes. One of the most promising simulation tool is nonequilibrium molecular dynamics (NEMD) that aims to provide a quantitative macroscopic description of a system by simulating the microscopic evolution of the atoms that constitute it. A typical NEMD simulation involves driving a system out of equilibrium by means of thermodynamic forces. The extra energy pumped into the system gets dissipated in form of heat and must be removed to attain a steady state, which is often the thermodynamic state of interest in a large class of problems. Usually, synthetic thermostats are employed for this purpose. Over the years, many different thermostatting algorithms have been proposed. The efficacy of these algorithms are usually tested in equilibrium and near-equilibrium conditions. But the existing methods, even for simple problems, like thermal conduction in toy quartic oscillators, reveal that the results are inconsistent with near-equilibrium theory.

This work aims at improving our ability to simulate nonequilibrium phenomena, especially the ones that involve temperature control, and extract meaningful information from the simulated nonequilibrium states. The first part of this thesis uncovers hitherto unknown problems in the existing temperature control algorithms. Our investigations on the ergodicity of the Nosé-Hoover chain thermostat reveals a complicated nature of the dynamics – while the dynamical tests are consistent with the previous finding of ergodicity, the statistical tests indicate nonergodicity with phase-space regions of zero probability. Such complicated dynamics are not found in other ergodic thermostats like the Hoover-Holian thermostat, prompting us to conclude that it is advisable to use the Hoover-Holian thermostat over the chain thermostat. Additionally all synthetic thermostats are supposed to satisfy the Zeroth law in equilibrium. However, we found that the Campisi-Zhan-Talkner-Hänggi (CZTH) thermostat fails to satisfy the Zeroth law, with the situation not improving even when the system is ergodic. Our findings suggest the futility of using the CZTH algorithm to serve as a molecular dynamics thermostat. The third problem we report is about the inconsistency of the most popular algorithms with the local thermodynamic equilibrium hypothesis. Our investigations reveal a substantial difference between the different measures of temperature locally due to the Nosé-Hoover and Braga-Travis thermostats, a situation which is far from being ideal in local thermodynamic equilibrium conditions.

Three new temperature control algorithms have been proposed in this work to improve the shortcomings in the state of the art: (i) the Patra-Bhattacharya (PB) thermostat, as it has been christened in literature, which simultaneously controls the kinetic and configurational temperatures, (ii) the $C_{1,2}$ thermostat which simultaneously controls the

first two orders of configurational temperatures, and (iii) the $C_1K_{1,2}$ thermostat which controls three different measures of temperatures. The PB thermostat resolves the inconsistencies in the near-equilibrium conditions and unlike the CZTH thermostat, satisfies the Zeroth law despite being nonergodic. The $C_{1,2}$ thermostat improves the ergodic characteristics of the nonergodic Braga-Travis thermostat, and the $C_1K_{1,2}$ thermostat resolves the nonergodicity of the PB thermostat. Unlike the Nosé-Hoover chains, these thermostats are ergodic from both statistical and dynamical sense. It is interesting to note that the PB algorithm is able to simultaneously and arbitrarily thermostat the kinetic and the configurational variables at a pair of equal or unequal values. This unique ability can be used to develop what we call a differential thermal conduction model, where in there exists a temperature difference amongst the kinetic and configurational variables within a thermostatted region. An exhaustive numerical study on the differential thermal conduction model reveals several interesting features like its ability to serve as a heat pump and answering the long open question of the importance of configurational variables in thermal conduction. However, existing experimental techniques are still at a nascent stage to control the kinetic and configurational variables at different values, and therefore, the utility of the differential thermal conduction remains theoretical so far.

Development of these better algorithms renders it possible to mimic experiments more realistically on computers, a boon for researchers studying nonequilibrium processes. Unfortunately, such costly and time consuming protocol driven numerical experiments still need to be performed for large number of cases to understand the nonequilibrium landscape. Thus, effective techniques, that can extract useful information from limited data, are needed. For this purpose, (i) a fast and an accurate method of reconstructing nonequilibrium distribution functions (MaxRent), and (ii) a new fluctuation theorem have been proposed (GCFT). MaxRent utilizes the information about previously known states and limited information about the current state within the framework of principle of maximum relative entropy to construct the entire spectra of nonequilibrium distribution. The proposed GCFT generalizes the Crooks fluctuation theorem and removes the necessity of performing repeated samplings if the temperature at which the desired free-energy difference is to be calculated changes. The generalized fluctuation theorem can be used to obtain the generalized Jarzynski's equality and other important thermodynamic relations.

Keywords: Nonequilibrium statistical mechanics, nonequilibrium molecular dynamics, fluctuation relations, maximum relative entropy