

Thermostats, Non-Equilibrium Temperature, and Entropy Production in Non-Equilibrium Molecular Dynamics Simulations

Peter Daivis^{C,S}

RMIT University, School of Applied Sciences, Melbourne, Victoria, Australia

peter.daivis@rmit.edu.au

It is often assumed for the sake of convenience that consistent values of the transport properties of fluids can be computed by steady-state non-equilibrium molecular dynamics simulations if the system is thermostatted to a fixed value of the kinetic temperature. The kinetic temperature is well-defined and unique at equilibrium, but it is well-known that the x y and z directional kinetic temperatures may differ from each other in strongly sheared steady states, introducing ambiguity into the identity of the thermodynamic temperature. Indeed, there are many other possible choices of temperature, such as the configurational and normal temperatures in addition to the kinetic temperatures. There is strong evidence that non-linear properties, such as the zero shear rate limit of the first normal stress coefficient, are quite sensitive to the choice of temperature that we thermostat, unlike linear properties like the zero-shear rate viscosity. Consequently, much more sophisticated ideas about temperature, thermal equilibrium and entropy production are required. In this paper, we discuss the issue of temperature and thermostats for non-equilibrium molecular dynamics from a thermodynamic point of view and show that for steady states that are far from equilibrium (such that the local equilibrium approximation is violated), we must allow for temperature inhomogeneity between different degrees of freedom. We also propose an expanded thermodynamic treatment of shearing steady states, along with concrete thermodynamic relationships that can be used to test the new treatment.