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Using the Second Law to Develop Non-equilibrium Thermodynamics and Absence of Entropy Loss in a Phase Space Confinement PURU GUJRATI, The University of Akron — We start from the second law of thermodynamics applied to an isolated system consisting of the system surrounded by an extremely large medium, and formulate a general non-equilibrium thermodynamic description of the system when it is out of thermal and mechanical equilibrium with the medium. Our approach allows us to identify the correct form of the non-equilibrium entropy, Gibbs free energy and enthalpy of the system under all conditions including possible ergodicity braking due to phase space confinement. We find that there is never any loss of entropy. We also obtain an extension of the classical non-equilibrium thermodynamics due to de Donder in which one normally assumes thermal and mechanical equilibrium with the medium. We find that the temperature and pressure differences between the system and the medium act as thermodynamic forces, which are normally neglected in the classical non-equilibrium thermodynamics. These forces play an important role in relaxation processes in addition to other internal order parameters. We apply our approach to study the general trend during structural relaxation in glasses and establish the phenomenology behind the concept of the fictive temperature on firmer theoretical foundation.

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