

Monodimensional oscillator chains consist of particles moving monodimensionally and interacting with the nearest neighbor only, which makes it numerically possible to compute the state equation in equilibrium using statistical mechanics. In nonequilibrium steady states, monodimensional chains often violate the locality condition required by the local thermodynamics equilibrium, because correlations can persist over long distances and times. This can result in anomalous thermodynamical properties.

This PhD study focuses on the relations that connect the average length, fluctuation, force, and kinetic energy of monodimensional chains. The work proceeds along the following main directions:

- Deriving the equilibrium state equation and fluctuation expressions under both fixed-length and fixed-force boundary conditions;
- Proving the equivalence of these two boundary conditions in the thermodynamic limit;
- Generalising the equilibrium expressions to nonequilibrium single-oscillator relations by assuming a factorised nonequilibrium distribution;
- Verifying all conclusions through molecular dynamics simulations of Lennard-Jones chains;
- Extending the framework to coupled-chain models that combine Lennard-Jones with harmonic interactions.

Firstly, the state equation of Lennard-Jones chains under fixed-force boundary condition at equilibrium is derived through statistical mechanics, which is analytically approximated by the microscopic equivalent for the van der Waals and Tonks equations. The validity of these equations is analysed across different thermodynamic regimes. It is shown that the microscopic van der Waals equation provides a good description at elevated temperatures and that, in the high-temperature limit, it is asymptotically reduced to the microscopic Tonks equation, which has a linear form. Although different boundary conditions lead to more complicated forms of the the

state equation, it is rigorously proved that various boundary conditions become equivalent in the thermodynamic limit.

Secondly, a factorised nonequilibrium distribution is introduced. Based on this ansatz, single-oscillator relations are constructed that express the average length and length fluctuation of each oscillator as functions of its average kinetic energy and average force, which are naturally interpreted as microscopic temperature and pressure, respectively. Molecular dynamics simulations demonstrate that these single-oscillator relations hold accurately when the number of particles in the chain is sufficiently large. The minimum number required depends on the decay of correlations among single-particle quantities—namely length, speed, and energy. High temperature, low pressure, and the use of Langevin thermostats are found to accelerate correlation decay, thereby enabling the single-oscillator relations to be realised even for chains of small number of particles.

Furthermore, the same framework is applied to analyse the equilibrium state equations, fluctuation expression, and nonequilibrium relations of coupled chain models that bind a Lennard-Jones chain with an harmonic chain. By partitioning the coupled model into repeated cells, the statistical-mechanical expressions for the equilibrium state equation and fluctuations are derived and analytically approximated in both the high-temperature and low-temperature limits. The equilibrium expressions are then generalised into nonequilibrium single-cell relations, which remain valid as long as correlations among different cells decay sufficiently fast. Compared with the single Lennard-Jones chain, the single-cell relations for coupled chains are more robust, owing to faster-decaying correlations. One possible explanation is that the more complex interactions in the coupled model facilitate better thermalisation. Related work on this topic is currently ongoing.